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ELECTRON PARAMAGNETIC RESONANCE

By

S. A. Al'tshuler and B. N. Kozyrev
UNEDITED ROUGH DRAFT TRANSLATION

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BY: S. A. Al'tshuler and B. M. Kozyrev

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NOTE

The electron paramagnetic resonance, discovered in 1944 by the Soviet physicist Ye.K. Zavoyskiy, is now one of the most fruitful physical research methods. Its use has yielded valuable data in the field of solid state physics, magnetism, semiconductor physics, and nuclear physics. In radio, this method has been the basis for the development of a new type of amplifier with exceedingly low internal noise level. Electron paramagnetic resonance is widely used in modern chemistry, and its study in biological objects has also begun.

The book contains a complete survey of research in the field of electron paramagnetic resonance. The most detailed treatment has been given to the theoretical and experimental results pertaining to ionic crystals. It is intended for senior and graduate students as well as for scientists working in physics, radio, chemistry, and biology.
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FOREWORD

Electron paramagnetic resonance, discovered in 1944 by Ye.K. Zavoyskiy, has become one of the most powerful physical research methods. The applications of electron paramagnetic resonance cover a very wide field. In ionic crystals it permits a determination of the magnetic-center energy-level structure, of the minor details of the crystal-lattice structure, and of the parameters characterizing the magnetization kinetics; the study of crystal-lattice imperfections is particularly interesting. In liquid salt solutions, electron paramagnetic resonance makes it possible to investigate the construction of the solvate shells. Interesting data have been obtained on the properties of conduction electrons in metals and semiconductors. For nuclear physics, paramagnetic resonance is a valuable method for the determination of nuclear moments and is one of the most effective means of nuclear polarization.

The paramagnetic resonance method is particularly fruitful in chemistry. It made possible the first detection of free radicals in amounts down to $10^{-10}-10^{-13}$ mole. A promising start toward a study of paramagnetic resonance in biological objects has also been made.

Paramagnetic resonance has recently found a very important application in radio, for the design of a new type of a low-noise amplifier.

All this has made paramagnetic resonance of great interest at present not only to physicists but also to chemists, biologists, and radio engineers.

This book is the first attempt to provide as complete a survey as
possible of the research made in electron paramagnetic resonance. To limit the size of the book the authors had to forego in most cases detailed derivations or detailed descriptions of experimental methods which incidentally have already been described to a considerable extent in the available Russian-language literature. Theoretical and experimental results pertaining to ionic crystals have been dealt with in greatest detail, since such crystals are most thoroughly investigated by paramagnetic resonance methods.

The book covers all the basic literature on electron paramagnetic resonance up to about 1959. The authors have attempted here to summarize all the most important theoretical results and the experimental data that are the most trustworthy.

Chapter I was written by both authors, Chapters II, IV, VII, and §§5.5, 5.7 of Chapter V were written by B.M Kozyrev; Chapters III, VI, VIII, and §§5.1-5.4, 5.6, 5.8, 5.9, and 5.10 of Chapter V were written by S.A. Al'tshuler.

In conclusion, the authors express their deep gratitude to Ye.K. Zavoyskiy for valuable discussions concerning many problems considered in this book. They are also most grateful to R.Sh. Nigmatullin for reviewing the manuscript of Chapter II, to V.B. Shteynshleyger for reviewing the portion of the book devoted to paramagnetic amplifiers, and to N.G. Koloskova for appreciable help in the compilation of the tables.

S.A. Al'tshuler, B.M. Kozyrev

Kazan', 15 July 1959.
PRINCIPAL NOTATION

A - hyperfine magnetic interaction constant;

$\alpha$ - spin-Hamiltonian constant;

$a_0$ - Bohr radius;

B - hyperfine magnetic interaction constant;

$c$ - velocity of light;

D, E - spin-Hamiltonian constants;

e - electron charge;

$e_{\text{eff}}$ - effective charge;

F - spin-Hamiltonian constant;

$g$ - spectroscopic splitting factor;

$g_0$ - Lande factor;

$g_x$, $g_y$, $g_z$ - principal values of g-tensor;

$g_N$ - nuclear g-factor;

g(v) - function of the paramagnetic resonance absorption line shape;

$H_0$ - intensity of static magnetic field;

$H_\tau$ - amplitude of oscillating magnetic field;

$H_{kr}$ - electron energy in the crystal electric field;

$h$ - Planck's constant;

$I$ - nuclear-spin quantum number;

$J$ - electron shell total momentum quantum number;

$J, J_{ik}$ - exchange integral;

$k$ - Boltzmann's constant;

$L$ - electron shell orbital momentum quantum number;

$M$ - momentum projection quantum number;
M_k – kth moment of resonance line;
M – number of ions per unit cell;
M_m – number of magnetically nonequivalent ions per unit cell;
m_e – electron mass;
N_o – number of paramagnetic centers per cubic centimeter;
N_k – number of paramagnetic centers at the k level per cubic centimeter;
n – population difference between two neighboring spin sublevels;
n_0 – population difference between two neighboring spin sublevels in equilibrium state;
P – hyperfine quadrupole interaction constant;
P – radio-frequency field power absorbed per cubic centimeter of the paramagnetic material;
P_{MM}' – probability of system transition from the level M to the level M' under the influence of the oscillating magnetic field;
Q – quality factor;
q – quadrupole moment of the nucleus;
q_{lk} – saturation factor;
R – equilibrium distance from the center to the vertex of the octahedral complex;
S – electron spin quantum number;
S' – effective spin;
T – absolute temperature;
T_1 – longitudinal paramagnetic relaxation time;
T_2 – transverse paramagnetic relaxation time;
T_{21} – cross-relaxation time;
v – average velocity of sound;
Z – nuclear charge;
\beta_0 – Bohr magneton;
$\beta_N$ - nuclear magneton;
$\gamma$ - gyromagnetic ratio;
$\Delta v$ - width of paramagnetic resonance line, in cycles per second;
$\Delta H$ - line width in oersteds;
$\Theta$ - Debye temperature;
$\chi_0$ - static paramagnetic susceptibility;
$\chi$ - complex paramagnetic susceptibility;
$\chi'$ - real part of $\chi$;
$\chi''$ - imaginary part of $\chi$;
$\mu$ - magnetic moment of the particle;
$\nu$ - frequency of oscillating magnetic field;
$\nu_0$ - Larmor precession frequency;
$\rho$ - density of the substance;
$\sigma$ - ultrasonic absorption coefficient;
$\tau$ - spin-lattice relaxation time;
$\tau'$ - spin-spin relaxation time.
Chapter I
INTRODUCTION

§1.1. Elementary Magnetic Resonance

Many modern methods used to investigate properties of particles with nonzero magnetic moments are based on a phenomenon which can be called elementary magnetic resonance. The use of this method has enabled Rabi to propose his well-known method of determining nuclear moments [1], Alvarez and Bloch [2] to measure the magnetic moment of the neutron, Detch [3] to determine the fine structure of the ground level of positronium, Kastler [4] to discover a new optical effect, etc. The same phenomenon serves as the basis for paramagnetic resonance and a few other related effects which occur in substances that contain particles with nonzero magnetic moments.

The nature of elementary magnetic resonance can be explained with the aid of simple classical concepts. Let a particle having a magnetic moment $\mu$ be placed in a magnetic field with intensity $H_0$. Then the moment $\mu$ will precess about $H_0$ with Larmor frequency $\nu_0 = \frac{g_0 e H_0}{\hbar m_0 c}$, where $g_0$ is the Lande factor, which takes on the values 2 and 1 for particles with pure spin and pure orbital electron magnetism, respectively.

Let us assume that a weak magnetic field $H_1$ is applied perpendicular to the field $H_0$ (Fig. 1.1) and rotates about $H_0$ with frequency $\nu$. If $\nu = \nu_0$, then the additional rotating moment produced by the field $H_1$ is always so directed as to make the magnetic moment $\mu$ try to occupy a position in the equatorial plane. The result is a rapid change in the orientation of the moment $\mu$. 

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If the frequencies \( v \) and \( v_0 \) differ noticeably from each other, then the effect of the field \( H_1 \) is negligible, since the motion it induces in the moment \( \vec{I} \) rapidly goes out of phase with its precession. For the same reason, the effect of the field will also be small if \( v = v_0 \), but the direction of rotation of \( H_1 \) is opposed to that of the precession. As a result of the latter fact, the rotating field is replaced in practice by an oscillating one, which can be regarded as the superposition of two fields of equal magnitude but rotating in opposite directions at the same frequency.

It is natural to raise the question of the extent to which the magnitude of the resonance effect depends on the accuracy with which the frequencies \( v \) and \( v_0 \) coincide. The sharpness of the magnetic resonance will be the greater, the smaller the ratio \( H_1/H_0 \).

Let us proceed to analyze the quantum relations in elementary magnetic resonance. Give the particle mechanical and magnetic moments, the maximum components of which in the direction of \( H_0 \) will be denoted by \( J \hbar \) and \( \mu \), respectively. As is well known, \( \mu = g_0 \beta J \), and consequently \( 2J + 1 \) equidistant energy levels* will arise in the magnetic field \( H_0 \), namely:

\[ E_M = g_0 \beta H_0 M, \]

(1.1)

where \( M \) is the magnetic quantum number, \( J \geq M \geq -J \).
An alternating magnetic field $\mathbf{H}_0 \cos 2\pi vt$ can induce magnetic dipole transitions between neighboring energy levels ($\Delta M = \pm 1$), provided this field is perpendicular to $\mathbf{H}_0^*$ and if the following resonance condition is satisfied:

$$E_M - E_{M-1} = g_\beta \beta H_0 = h\nu.$$  \hspace{1cm} (1.2)

This is identical to the classical condition $v = v_0$.

The alternating field will induce transitions from the lower energy levels to the upper ones and vice versa with equal probability. The probabilities of these nonadiabatic transitions were calculated by Guttinger [5], Majorana [6], and Rabi [1].

It can be readily calculated with the aid of (1.2) that the Larmor precession frequency lies within the radio or microwave bands for all the magnetic-field intensities encountered in modern experiments. This is a very important practical fact, for it makes it possible to use the highly sensitive and very convenient radio equipment for experiments based on elementary magnetic resonance.

§1.2. Paramagnetic Resonance

We now proceed from an examination of an isolated magnetic particle to macroscopic bodies, which contain many such particles. We shall call such bodies paramagnetic regardless of the magnitude of the diamagnetic component of the over-all magnetic moment of the substance. The behavior of a paramagnet in a magnetic field depends essentially on the interactions of the paramagnetic particles with one another and with the surrounding diamagnetic particles. These interactions will contribute to the establishment of a thermodynamic equilibrium, if the latter is disturbed for some reason or another. Therefore, in a static magnetic field $\mathbf{H}_0$ in which an equilibrium state has been attained and the distribution laws of classical statistics are applicable, the populations of the individual energy levels are determined by the Boltz-
The populations of the lower energy levels are larger than those of the upper levels, and therefore, if an alternating magnetic field at resonant frequency is turned on, the number of absorption events induced by this field exceeds the number of forced emission events; consequently, the substance will absorb energy from the radio frequency field. Thus, two opposing processes take place in the paramagnet: the radio frequency field equalizes the populations of the different magnetic levels, while the internal interactions tend to restore the Boltzmann distribution, by converting the absorbed radio-frequency field energy into heat.

The ultimate result is a stationary state in which the populations of the magnetic levels stop varying and the radio frequency energy is uniformly absorbed by the paramagnet. If at the same time the intensity of the alternating magnetic field is very large, then the populations of the different magnetic levels will become equalized in the stationary state, after which the absorbed energy will no longer increase with increasing power of the radio frequency field (the so-called saturation sets in).

We see that the effect of resonant paramagnetic absorption is very tightly linked with processes that determine the kinetics of magnetization of paramagnets, or in other words, with paramagnetic relaxation. A very fruitful suggestion in the theory of paramagnetic relaxation was that of Casimir and du Pre [7, 8], namely that the magnetization of the paramagnet be regarded as a two-stage process consisting of the establishment of equilibrium within the "spin system," or the system of magnetic moments of all the paramagnetic particles, followed by energy exchange between the spin system and the "lattice," to which all the remaining degrees of freedom of the paramagnet belong. Of course, this consideration is possible if the interactions inside the
spin system (spin-spin interactions) are much stronger than the interactions between the spin system and the lattice (spin-lattice interactions).

Unless ultra-low temperatures are considered, the lattice temperature can be regarded as invariant, since the specific heat of the lattice greatly exceeds the specific heat of the spin system. The lattice therefore acts like a thermostat in which the spin-system is immersed. The spin system can also be assigned a certain temperature which generally differs from that of the lattice. The establishment of equilibrium between the spin system and the lattice can be regarded as an exchange of energy between these systems, leading to an equalization of their temperatures. The speed of this process can be characterized by the spin-lattice relaxation time, which we denote by \( T \). The spin-lattice relaxation mechanisms of different substances may differ greatly from one another. Therefore the quantity \( T \), in addition to having a strong dependence on the temperature of the paramagnet, is also characterized by variations over a wide range on going from one substance to another.

The rate at which equilibrium is established within the spin system can be characterized by the spin-spin relaxation time \( T' \). Obviously, the very possibility of separating the paramagnet into a spin system and a lattice implies that \( T' \ll T \). Unlike the time \( T \), the value of \( T' \) depends very little on the lattice temperature. We note still another difference between the spin-spin and spin-lattice relaxations. Equilibrium is established within the spin system by energy exchange between different parts of the system, while the total energy of the spin system remains constant. On the contrary, spin-lattice relaxation is connected with a change in the energy of the spin system.

In his phenomenological theory of paramagnetic resonance, Bloch
[9] introduced two relaxation times, longitudinal $T_1$ and transverse $T_2$. Assume that the paramagnet is placed in a static field $\mathbf{H}_0$; then the time $T_1$ characterizes the rate at which equilibrium is established if the magnitude of the field $\mathbf{H}_0$ is instantaneously changed, while its direction is maintained constant; the time $T_2$ determines the relaxation if the direction of the field $\mathbf{H}_0$ is changed instantaneously while its absolute value remains constant. The time $T_1$ characterizes the balancing process associated with the change in the spin-system energy, and can therefore be identified with the spin-lattice relaxation time $\tau$. The time $T_2$ characterizes the speed of a relaxation process in which the spin-system energy is constant; it can be identified with the time $\tau'$. However, the times $\tau$ and $\tau'$ are not always identical with $T_1$ and $T_2$, since the concept of longitudinal and transverse relaxation times $T_1$ and $T_2$ can always be introduced, whereas the times $\tau$ and $\tau'$ are meaningful only when $\tau >> \tau'$. We do not consider here at all whether the two parameters $T_1$ and $T_2$ suffice to describe the complicated process of paramagnetic relaxation. We shall see below that in some cases a large number of parameters must be introduced (see Chapter V).

The internal interactions in the paramagnet not only cause it to absorb energy from the radio frequency field, but also broaden the paramagnetic resonance lines. Whereas for an isolated particle the sharpness of the magnetic resonance depends on the ratio $H_1/H_0$, for a paramagnet the sharpness of resonance and the associated absorption-line width are determined by the spin-spin and spin-lattice interactions, provided there is no saturation. Let us assume that the spin-spin interactions are much stronger than the spin-lattice ones. We take two neighboring magnetic particles. Assuming them isolated, in first approximation, we can ascribe to each particle a system of energy levels (1.1). Let the levels of the two particles have magnetic quantum num-
bers $M_1$ and $M_2$, respectively. The spin-spin interactions give rise to a certain probability $A'$ that the particles will exchange energy after 1 second; if the first particle makes in this case a transition to a level with magnetic quantum number $M_1 + 1$, then the second goes to the level $M_2 - 1$. The spin-spin relaxation time $\tau'$ will have an order of $1/A'$; this time, as we shall show, determines the lifetime of the particles at a definite magnetic energy level, and consequently the width of the absorption line, due to the spin-spin interactions, can be estimated to be $1/\tau'$.

If spin-lattice interactions dominate, then the concept of the time $\tau'$ becomes meaningless, but the spin-lattice relaxation time $\tau$ can be introduced if we consider the probability that an individual paramagnetic particle will go over under the influence of thermal agitation from one magnetic energy level to another. If this probability per second is $A$, then $\tau \sim 1/A$ and the width of the absorption line will have an order of magnitude $1/\tau$. In general, we can estimate the width of the absorption line to be $1/\tau + 1/\tau'$. No rigorous general relation can be given between the width and the relaxation times, since the width depends heavily on the shape of the absorption line.

It follows from what we know concerning the temperature dependence of the relaxation times, that if the resonant paramagnetic absorption line width is determined by spin-lattice interactions, it will decrease rapidly with decrease in temperature; on the other hand, if the decisive role is played by spin-spin interactions, the temperature dependence of the width will be quite weak.

The internal interactions in the paramagnet determine also the position and number of the paramagnetic resonant absorption lines. If the form of the energy spectrum resulting under the action of the field $H_0$ were to be independent of the internal interactions, the sys-
tem of energy levels would be determined as before by Formula (1.1) if in addition the selection rules for transitions between these levels under the influence of the alternating magnetic field were to be conserved, then there would exist only one absorption line, the position of which for a specified intensity \( H_0 \) would be determined by the magnitude of the Lande factor \( g_0 \). Actually, however, whereas in many para-

![Figure 1.2](image1.png)

Fig. 1.2. Plot of paramagnetic resonance absorption in \( \text{CrCl}_3 \) for \( \lambda = 10.87 \text{ cm} \), \( T = 298^\circ \text{K} \) (Ye.K. Zavoyskiy, Sov. phys. 10, 197, 1946). 1) \( H \), oersteds.

![Figure 1.3](image2.png)

Fig. 1.3. Splitting of the ground level of the \( \text{Cr}^{3+} \) ion in a trigonal crystal field and in a magnetic field \( H_0 \) applied parallel to the trigonal axis.

magnets the system of equidistant magnetic energy levels is conserved, the \( g \) factor deviates from its value for the free particle, owing to internal interactions. Figure 1.2 shows a plot of paramagnetic reso-
nance absorption in chromium chloride; the absorption maximum corresponds, as can be readily calculated with the aid of (1.2), to a factor $g \approx 2$, whereas for the ground state $^4F_{3/2}$ of the free $\text{Cr}^{3+}$ ion, the Lande factor has a value $2/5$. The absorption curve of Fig. 1.2 represents the energy absorbed by the paramagnet per second from the radio frequency field, as a function of the intensity $H_0$ of the static magnetic field, for in the overwhelming majority of cases the experiments are carried out at fixed frequency $v$ and variable fields $H_0$.

In condensed media, as pointed out by Kittel [10], the $g$ factor, which determines the splitting of the energy levels in a magnetic field, does not coincide with the factor that yields the gyromagnetic ratio, the latter factor being obtained by measuring the magnetomechanical effects. We shall therefore follow Kittel and call the $g$ factor obtained from experiments on paramagnetic resonance the "spectroscopic splitting factor."

In many paramagnets, particularly those whose magnetism is not purely spin, the system of Zeeman levels ceases to be equidistant. Con-
sequently, several absorption lines arise in place of one, and one ob-
serves, as is customarily stated, the fine structure of the paramag- 
etic resonance spectrum. In single crystals, the form of the spectrum 
can depend strongly on their orientation relative to the field \( H_0 \). By 
way of an example, Fig. 1.3 shows the splitting of the ground level of 
a \( \text{Cr}^{3+} \) ion contained in an \( \text{Al}_2\text{O}_3 \) crystal, as a function of the inten-
sity of the magnetic field \( H_0 \) applied parallel to the trigonal axis of 
the crystal. In this figure \( \epsilon = E_m/D \), \( x = g\beta H_0/D \), and \( 2D \) is the initial 
splitting. Figure 1.4 shows photographs of the fine structure of the 
paramagnetic resonance spectrum for two different crystal orientations, 
with the trigonal axis parallel and perpendicular to the field \( H_0 \).

It is seen from Fig. 1.3 that in the absence of the fields \( H_0 \) the 
splitting of the ground level of the paramagnetic particles lies in 
the radio-frequency region. Thus, resonance absorption of energy from 
a radio frequency field can occur in many cases under the influence of 
magnetic dipole transitions between sublevels that exist in the ab-
sence of a static magnetic field.

We note finally that the internal interactions change the selec-
tion roles. For example, transitions become possible between Zeeman 
levels that are not neighboring, and for a paramagnet in which these 
levels are equidistant this causes the appearance, in addition to the 
principal absorption line corresponding to the Larmor frequency \( \nu_0 \), of 
satellites at frequencies \( 2\nu_0, 3\nu_0 \), etc.

The form of the paramagnetic resonance spectrum depends on the 
presence of magnetic moments in the nuclei of the paramagnetic atoms 
(molecules). The magnetic moments of the nucleus and of the electron 
shell interact with each other and with the static magnetic field \( H_0 \) 
to produce a new system of energy levels for the paramagnet; an im-
portant factor here is whether the field \( H_0 \) is strong enough to break
Fig. 1.5a. Hyperfine structure of the spectrum of Mn$^{2+}$ in an aqueous solution of MnCl$_2$ at $v = 9345$ Mc.

![Hyperfine structure diagram](image)

Fig. 1.5b. Effect of nuclear spin on the spectrum of Mn$^{2+}$ in an aqueous solution of MnCl$_2$ at $v = 147$ Mc. a) $^{55}$Mn$^{2+}$ ($g = 1$); b) free radical ($g = 2$); c) Fe$^{3+}$ impurities in the ampoule glass ($g = 4$).

![Effect of nuclear spin diagram](image)

Fig. 1.6. Fine and hyperfine structures of the spectrum of Mn$^{2+}$ in manganese apatite at $v = 10^{10}$ cps; each of the five fine-structure lines is split into six hyperfine components. (The narrow line in the center of the third group is due to the free radical.)

![Fine and hyperfine structures diagram](image)

the bond between the electron and nuclear moments, or whether the field $H_0$ is so weak that this bond remains unchanged. In the former case,
the position of the paramagnetic resonance absorption lines due to the magnetic moments of the electron shells of the atoms (molecules) is conserved, but a hyperfine structure appears, in that each line breaks up into several components, the number of which depends on the nuclear spin. In the latter case, the picture of the spectrum is completely changed, since the $g$ factors that determine the positions of the absorption lines assume entirely different values.

Figure 1.5a shows the absorption spectrum observed in an aqueous solution of MnCl$_2$ at $v = 9345$ Mc in strong fields $H_0$, ranging from 2900 to 3400 oersteds. The center of the spectrum corresponds to $g = 2.000$; this $g$ factor would determine the position of the absorption line were it not split by the presence of the magnetic moment of the manganese nucleus. Figure 1.5b shows an absorption spectrum consisting of one line and observed in the same solution of MnCl$_2$ at 147 Mc in weak fields $H_0$, ranging from -175 to +175 oersted. The absorption maximum corresponds here to a value of $g$ which is practically exactly equal to 1. Thus, the interaction with the nucleus in weak fields reduces the $g$ factor by one-half in our case. Figure 1.6 shows a typical fine and hyperfine structure of the spectrum of Mn$^{2+}$, observed in an apatite single crystal.

A few other phenomena are closely related with paramagnetic resonance absorption. It is easy to conclude that the effect of an alternating magnetic field on a paramagnet under the conditions of resonance should be to change its magnetization. The result is the appearance of a strong dependence of paramagnetic susceptibility on the frequency $v$; if $v$ is found equal to $v_0$, the dispersion of susceptibility becomes anomalous. The rotation of the plane of polarization of the radio waves and other magnetooptical phenomena also become anomalous, provided that the experimental conditions are such that the magnetic vector of the wave is perpendicular to the applied static magnetic field and that the frequencies $v$ and $v_0$ are close to each other.

We have considered different aspects of the paramagnetic resonance effect, and we can now define it in general terms.
Paramagnetic resonance is an aggregate of phenomena, connected with quantum transitions occurring between energy levels of macroscopic systems under the influence of an alternating magnetic field of resonant frequency.

We refer in this definition to an aggregate of phenomena, for along with paramagnetic resonance absorption, there is observed also paramagnetic resonance dispersion, paramagnetic resonance rotation, etc. In addition, we emphasize here that the phenomena are observed in macroscopic systems, where spin-spin, spin-lattice and similar interactions take place, which distinguishes paramagnetic resonance from the resonance experiments made by Rabi with molecular beams and by Alvarez and Bloch with neutron beams, etc.

Finally, whereas Debye dispersion and absorption of electromagnetic waves in dielectrics occur as a result of electric dipole transitions due to the electric component of the wave, the phenomena which were are studying are due to magnetic dipole transitions, which are excited by an alternating magnetic field.

In the overwhelming majority of cases, paramagnetic resonance is investigated by superimposing on the paramagnet two magnetic fields, a strong static field and a weak alternating one. However, we have seen with Cr\(^{3+}\) as an example that magnetic dipole transitions are possible under the influence of a radio frequency field even in the absence of a static magnetic field. The phenomena connected with transitions of this type are also naturally ascribed to paramagnetic resonance.

The great difference in the magnitude of magnetic moments of the electrons and the nuclei makes it natural to distinguish between electron and nuclear paramagnetic resonance, although both the experimental research methods and the theory of both effects have much in common. One should include in nuclear paramagnetic resonance also nuclear quad-
rupole resonance, a phenomenon due to magnetic dipole transitions occurring in the absence of an external static magnetic field between energy levels arising as a result of interaction between nuclear quadrupole moments and the electric field inside condensed media.

§1.3. Magnitude of the Effect

We proceed to establish certain quantitative relationships. Let the ground level of a magnetic particle be split under the influence of an external magnetic field and internal forces into \( \eta \) sublevels, to which we shall assign the quantum numbers \( M \) and \( M' \). According to the quantum theory of radiation, the probability that the oscillating magnetic field \( H_r \cos 2\eta vt \) will cause a transition within one second from the level \( M \) to the level \( M' \) is

\[
\rho_{MM'} = \frac{8\pi}{\hbar} |\langle M | \mu_x | M' \rangle|^2 \rho_v.
\]

(1.3)

where \( \langle M | \mu_x | M' \rangle \) is the matrix element of the projection of the magnetic moment of the particle along the direction of the alternating magnetic field, and \( \rho_v \) is the mean spectral density of electromagnetic energy, for which we can use in our case the expression

\[
\rho_v = \frac{h}{2\pi} g(v).
\]

(1.4)

We have introduced here a form factor, which takes account of the fact that the absorption line is not infinitesimally narrow but has an appreciable width. The function \( g(v) \) reproduces the absorption line shape and is normalized so that

\[
\int g(v) dv = 1.
\]

(1.5)

If the temperature of the paramagnet is sufficiently high to make \( E_M - E_{M'} = \hbar v \ll kT \), then for a volume of 1 cm\(^3\), containing \( N_0 \) magnetic particles, the difference in the populations of the pair of levels \( M \) and \( M' \) will be

\[
N_M - N_{M'} = \frac{N_0}{v} \frac{h}{kT}.
\]

(1.6)
With the aid of (1.3), (1.4), and (1.6) we obtain the following expression for the power absorbed by a unit volume of the paramagnet in transitions from the level $M$ to the level $M'$:

$$P_{MM'} = (N_M - N_{M'}) P_{MKM'} h \nu = e^2 N \langle M | P_z | M' \rangle | \mu H_{z0} g(\nu) \rangle.$$  \hspace{1cm} (1.7)

To obtain the total power $P$ absorbed as a result of transitions between all the sublevels, it is necessary to sum over all the possible values of $M$ and $M'$. Since the static paramagnetic susceptibility is [11]:

$$\chi = \frac{2N_0}{\mu f} \sum_{M, M'} | \langle M | P_z | M' \rangle |^2,$$  \hspace{1cm} (1.8)

we get

$$P = \frac{e^2}{2} \chi H_{z0}^2 g(\nu).$$  \hspace{1cm} (1.9)

The total power is of interest if the matrix elements $\langle M | P_z | M' \rangle \neq 0$ for those pairs of levels which are spaced by equal intervals, for in this case transitions between different level pairs produce one and the same absorption line.

The $Q$ of the resonant circuit loaded by the paramagnet can be determined from the expression

$$\frac{1}{Q} = \frac{(\frac{P}{\nu})}{2e^2 (H_{z0}^2 \mu)} = 2e^2 \chi H_{z0} g(\nu).$$  \hspace{1cm} (1.10)

Maximum absorption, which occurs at a frequency $\nu = \nu_0$, can be related with the width $\Delta \nu$, for if we write

$$g(\nu) = \frac{q}{\Delta \nu},$$  \hspace{1cm} (1.11)

then we see from (1.5) that $q = 1$. The exact value of $q$ depends on the absorption line shape; if the line has a Gaussian shape, then $q = 0.939$; if it has a Lorentz shape, then $q = 0.636$ (see §1.4).

Formula (1.7) is valid if the field $H_{z0}$ is regarded as being suffi-
ciently small so as not to disturb the equilibrium distribution of the particles over the energy levels. With increasing intensity of the radio frequency radiation, these disturbances can occur and can lead to saturation. Let us establish a quantitative criterion for the existence of this effect. We consider the simplest case of paramagnetic particles, having only two energy sublevels. The population excess in the lower sublevel above that in the upper sublevel will be denoted by \( n \); let \( n = n_0 \) in the equilibrium state. From the definition of the spin-lattice relaxation time we can conclude that in the absence of a radio frequency field the transition to the equilibrium state will be determined by the equation

\[
\frac{dn}{dt} = - \frac{n - n_0}{\tau_0}.
\]  

(1.12)

In the presence of a radio frequency field, the equation for \( n \) becomes

\[
\frac{dn}{dt} = - \frac{n - n_0}{\tau} - 2np_{NM}.
\]  

(1.13)

After the stationary mode is established, we have

\[
\frac{n}{n_0} = \left[1 + 2p_{NM} \right]^{-1}.
\]  

(1.14)

If the energy level in the magnetic field is split into two sublevels, it can always be related to an effective spin \( S' = 1/2 \) and to a spectroscopic splitting factor \( g \), the calculation of which will be described in Chapter III. We can therefore put

\[
\langle M|\mu_x|M'\rangle = - \langle -\frac{1}{2} |g|S_z| + \frac{1}{2} \rangle = g\beta.
\]  

(1.15)

Substituting (1.3) in (1.14) and using (1.4), (1.11), and (1.15) we obtain

\[
\frac{n}{n_0} = \left[1 + \frac{2e g \beta u' \mu_B H}{\mu_B (\mu_0)} \right]^{-1}.
\]  

(1.16)

In the equilibrium state we have \( n/n_0 = 1 \), and this ratio tends to zero as saturation sets in. The quantity \( q_n = n/n_0 \) is called the satu-
tion factor. If the Larmor precession frequency in a field of intensity $H_r$ is designated by $v_r = g\mathcal{E}_r/h$, then the saturation criterion is the following condition:

$$v > \Delta v \frac{1}{2}.$$  \hfill (1.17)

§1.4. Paramagnetic Resonance as a Branch of the Theory of Magnetism

The contemporary state of the theory of paramagnetism is characterized by a changeover from investigation of the magnetic properties of matter under static conditions to phenomena observed in alternating magnetic fields. Modern theory of dynamic paramagnetism is developing along three trends: 1) adiabatic demagnetization; 2) paramagnetic relaxation, and 3) paramagnetic resonance.

The connection between these trends is so close, that some authors [12] believe, for example, paramagnetic resonance to be part of the theory of paramagnetic relaxation, whereas others [13], to the contrary, regard paramagnetic relaxation as paramagnetic resonance due to transitions at zero frequency. This close relation permits a general theoretical analysis of many problems pertaining to all three trends, and acquiring mutually complementary information on different physical constants, such as the magnetic specific heat of substances, relaxation times, etc.

Whereas in the study of the behavior of substances in a constant magnetic field the main characteristic is the static susceptibility $X_0$, on going over to dynamic phenomena the susceptibility is best regarded as a complex quantity, $\chi = \chi' - i\chi''$. The magnetization component that varies in phase with the field is determined by the dynamic susceptibility $\chi'$, while the energy absorbed by the paramagnet from the alternating field is determined by the coefficient $\chi''$. The task of the theory of paramagnetic absorption and dispersion is to establish the
dependence of the coefficients $\chi''$ and $\chi'$ on the frequency of the alternating field and on the intensity of the applied static field. The general connection between the coefficients $\chi'$ and $\chi''$ is given by the Kramers-Kronig relationships [14]

$$
\chi'(\nu) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\nu \chi''(\nu')}{\nu^2 - \nu'^2} d\nu' + \text{const}, \quad \chi''(\nu) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\nu \chi'(\nu')}{\nu^2 - \nu'^2} d\nu',
$$

(1.18)

Dispersion formulas in closed form were obtained only for gases [15]. Naturally, for condensed systems, with their rather complicated internal interactions, a simple solution can hardly be obtained for this problem. It becomes necessary therefore to use approximate formulas. A comparison of (1.18) with $\nu = 0$ with (1.5) gives the connection between $\chi''$ and the line shape function $g(\nu)$:

$$
\chi''(\nu) = \frac{\nu}{2} \nu_0 g(\nu).
$$

(1.19)

In comparisons with experiment, $g(\nu)$ is usually described either by means of a Gaussian function, such as

$$
g(\nu) = \frac{1}{\sqrt{2\pi}\sigma} \left( e^{-\frac{(\nu - \nu_0)^2}{2\sigma^2}} + e^{-\frac{(\nu + \nu_0)^2}{2\sigma^2}} \right) = g_1(\nu) + g_2(\nu),
$$

(1.20)

or by a Lorentz function

$$
g(\nu) = \frac{\Delta \nu}{2\nu_0} \left( \frac{1}{\nu - \nu_0 + \frac{\Delta \nu}{2}} + \frac{1}{\nu + \nu_0 + \frac{\Delta \nu}{2}} \right) = g_1(\nu) + g_2(\nu).
$$

(1.21)

Here $\nu_0 = g\beta H_0 / \hbar$, $\sigma = \Delta \nu / 2 \sqrt{2 \ln 2}$, and $\Delta \nu$ is the absorption line at high frequencies. The second terms in the right members of (1.20) and (1.21) vanish when $\nu \gg \Delta \nu$; the need for introducing these terms is determined by the parity of the absorption effect relative to the field $H_0$ [16].

Experiments on electron paramagnetic resonance are carried out by investigating the dependences of $\chi'$ and $\chi''$ on the magnitude of the
Fig. 1.7. Curves showing paramagnetic resonance absorption and susceptibility dispersion in MnSO$_4$ for $\nu = 9620$ Mc (B.M. Kozyrev, S.G. Salikhov, Yu.Ya. Shamonin, ZhETF 22, 56, 1952).
1) Relative units; 2) H, oersteds.

Fig. 1.8. Curves of paramagnetic resonance rotation in CuSO$_4$·5H$_2$O (N.N. Neprimerov, Izv. AN SSSR, ser. fiz., 18, 368, 1954).
1) $H_0$, oersteds.

Field $H_0$ with $\nu = \text{const}$. Therefore the Kramers-Kronig relations should be modified into [16]:

$$
\chi_s - \chi(H_0) = \frac{i}{\pi} \int_0^\infty \frac{F(H_0 + H) - F(H_0 - H)}{H} dH,
$$

$$
F(H_0) = \frac{i}{\pi} \int_0^\infty \frac{\chi'(H_0 + H) - \chi'(H_0 - H)}{H} dH,
$$

(1.22)

where we put $F(H_0) = \chi''(H_0) - \pi\nu x_0 g_2(\nu)$; $g_2(\nu)$ is a monotonically decreasing function, so that its specific expression is immaterial. Paramagnetic resonance is investigated in most cases by measuring $\chi''(H_0)$.
Paramagnetic dispersion under resonant conditions was first observed by Zavoyskiy [17] in the salt MnSO₄; further measurements of χ'(H₀) are described in references [18]. Figure 1.7 shows typical paramagnetic resonance absorption and dispersion curves.

Paramagnetic resonance can be observed not only by measuring χ' and χ'', but also by studying the rotation of the plane of polarization of microwaves in paramagnets, induced by a static magnetic field. Many workers have considered the theory of this effect [19] and have made suitable measurements [20]. A typical ϕ(H₀) curve is shown in Fig. 1.8.

The angle of rotation ϕ of the plane of polarization and the paramagnetic absorption are related by the simple integral equation [21]

$$\varphi = \frac{4\pi}{\varepsilon} \int \frac{\chi''(H_0 + H) - \chi''(H_0 - H)}{H} dH.$$  (1.23)

Here ϵ is the dielectric constant of the paramagnet.

The integral relations (1.22) and (1.23) enable us to monitor the correctness of the form of the experimentally obtained paramagnetic-resonance curves. Recently, research was initiated also on other analogs of magnetooptical phenomena in the microwave region under magnetic resonance conditions, such as the Cotton-Mouton effect [22].

The aggregate of the results obtained with the aid of paramagnetic resonance provides important characteristics of various substances. It is sufficient to mention the determination of the magnetic and mechanical moments of atoms, molecules, or atomic nuclei, the times of paramagnetic relaxation, etc.

§1.5. Paramagnetic Resonance and Spectroscopy

Paramagnetic resonance is a component part of spectroscopy, since it makes it possible to determine the position of energy levels of magnetic particles. It is of interest to consider the features of para-
magnetic resonance as compared with spectroscopy at optical frequencies.

1. We note first that the range of frequencies used in magnetic-resonance experiments lies between $10^6$ and $10^{11}$ cps. The use of these frequencies, which lie beyond the infrared portion of the spectrum, enables us to investigate with great accuracy energy-level splitting, which is inaccessible or practically inaccessible to optical methods.

2. At radio frequencies the probability of spontaneous transitions is very small, since it is proportional to $v^3$. It is therefore necessary to deal only with forced absorption or emission in the study of paramagnetic resonance.

3. Whereas optical spectra are due in the overwhelming majority of cases to electrical dipole transitions between the energy levels, paramagnetic resonance absorption lines arise exclusively as a result of magnetic dipole transitions. Consequently, the Einstein coefficients for induced absorption and emission are approximately 4 orders of magnitude lower in the case of paramagnetic resonance.

4. In view of the foregoing, the effect of paramagnetic resonance is a very fine one; it can be detected not alone by virtue of the high sensitivity of the radio detection methods employed, but because of the tremendous number of photons that come into play. Thus, 1 milli-watt of power corresponds to $n \approx 10^{20}$ photons of frequency $10^{10}$ cps per second.

5. From the uncertain relations between the numbers of photons and the phase of the electromagnetic wave it follows that in our case, in view of the large value of $n$, the phase will be determined with very great accuracy. A consequence of this is the possibility of considering the electromagnetic field in radio spectroscopy as being a classical quantity.

6. At optical frequencies the line width is always very small com-
pared with the fundamental frequency. In investigations of paramagnetic resonance, the relation between these quantities becomes entirely different, since the interactions that bring about the broadening of the lines can have the same order of magnitude as the energy splittings, which determine the resonant frequencies. Therefore the width of paramagnetic resonance lines is frequently comparable with the fundamental frequency and can be measured with great accuracy. This uncovers great possibilities for the investigation of different types of interactions in paramagnets, by analyzing the shapes and widths of paramagnetic resonance lines and the character of their dependence on different factors.

7. The most important factors that determine the line width are magnetic dipole interactions, exchange forces, local electric fields produced by the surrounding magnetic particles, and finally thermal motion; the natural line width of radio frequency spectra is quite negligible.

8. Unlike conditions prevailing in optical experiments, the radiation used in radio spectroscopy is so monochromatic, that the generated bandwidth turns out to be incomparably narrower than the absorption line width.

9. Paramagnetic resonance spectra are investigated not by measuring the frequency of the incident radiation, but by measuring the natural frequencies of absorbing systems. This measurement is carried out by varying the static magnetic field.

§1.6. History of the Discovery of Paramagnetic Resonance

Paramagnetic resonance was discovered by Ye.K. Zavoyskiy [23] in 1944, in Kazan'; his first experiments pertained to resonant absorption in salts of ions of the iron group. Zavoyskiy's discovery was preceded by certain theoretical assumptions concerning the nature of the
expected effect. Following the well-known experiments by Stern and Gerlach on spatial quantization, Einstein and Ehrenfest [24] advanced several ideas on quantum transitions between magnetic sublevels of atoms under the influence of equilibrium radiation. On the basis of these ideas, Dorfman suggested in 1923 the possibility of resonant absorption of electromagnetic waves by paramagnets, and called this phenomenon the photomagnetic effect [25].

In 1932, I. Waller [26] published at Pauli's suggestion a fundamental paper containing a quantum theory of paramagnetic relaxation in solids. This paper served as the basis for further development of the theory of dynamic phenomena in paramagnets, particularly paramagnetic resonance.

In the middle thirties, Gorter and his co-workers [8] started a systematic study of the absorption and dispersion of radio frequency electromagnetic waves by paramagnets at $10^6\cdot3\cdot10^7$ cps in the presence of static magnetic fields. However, Gorter's attempts at observing paramagnetic resonance were not fruitful [27] in view of shortcomings in the procedure and of the insufficiently high frequencies employed.

Zavoyskiy [23] developed new highly sensitive methods for the investigation of paramagnetic resonance: in place of determining the amount of heat released by the paramagnet, as did Gorter, he started to measure the attenuation of the high-frequency field energy as a result of absorption. To obtain fully resolvable paramagnetic resonance absorption lines, he expanded the range of frequencies employed to $3\cdot10^9$ cps. He not only succeeded in discovering paramagnetic resonance, but investigated many of its regularities, and also greatly extended the region in which paramagnetic relaxation was investigated.

The first theoretical interpretation of Zavoyskiy's experiments was suggested by Ya. I. Frenkel' [28].
A natural continuation of the study of paramagnetic resonance due to magnetic moments of electrons was the discovery of an analogous effect in atomic nuclei, made by Purcell [29] and Bloch [30] and their co-workers two years after the publication of Zavoyskiy's papers. Finally, in 1950, paramagnetic resonance due to transitions between quadrupole energy levels of nuclei in crystals in the absence of an external magnetic field was discovered by Dehmelt and Kruger [31].

A tremendous number of investigations based on this method have been reported in recent years, in connection with the great progress made in microwave techniques, on the one hand, and the observed rather valuable applications of the paramagnetic resonance method to the solution of certain problems in solid state physics, atomic physics, chemistry, and engineering on the other.

REFERENCES TO CHAPTER I

8. Gorter K., Paramagnitnaya relaksatsiya (Paramagnetic relaxation), II (Foreign Literature Press), Moscow, 1949.
- 30 -
If the magnetic moment of the particle has both spin and orbital components, we assume that the field $H_0$ is incapable of disturbing the spin-orbit coupling.

If the magnetic particle is not isolated but is located, for example, in a crystal lattice, then in some cases resonant transitions are possible if the alternating and static magnetic fields are parallel (see Chapter III).
§2.1. Microwave Spectroscopes

Modern procedures for the measurement of paramagnetic resonance are based on the determination of the change in some parameter of an oscillating system containing a paramagnet; these changes may be due to paramagnetic absorption, dispersion of the susceptibility, or rotation of the plane of polarization in the investigated substance.

Methods of this type were first developed by Zavoyskiy both for the frequency range $10^7$-$10^8$ cps [1], and for higher frequencies, on the order of $10^9$ cps [2], approaching the microwave band.

The experiments made prior to the discovery of paramagnetic resonance by Gorter and his school [3], aimed at determining the non-resonant paramagnetic losses at frequencies up to $10^7$ cps, were carried out by calorimetric determination of the heat released in the paramagnet. The heat was determined from the rate at which the specimen was heated by losses occurring in it. This method, in view of its low sensitivity and the difficulty in separating paramagnetic absorption from other types of losses (dielectric losses, losses due to electric conductivity) could not be used to investigate paramagnetic resonance. On the other hand, the procedure of measuring the dynamic susceptibility $\chi'$, used by Gorter, although one of the indirect electrical methods, was suitable only for very low frequencies. Thus, it was Zavoyskiy himself who laid the groundwork for modern methods of magnetic radio spectroscopy.
Different measurement techniques, of course, are used for the microwave band (ν ≈ 10^{10} cps), on the one hand, and for the radio band (ν ≈ 10^6-10^9 cps) on the other. This has caused some authors to distinguish between radio frequency and microwave magnetic spectroscopy. Such a distinction is, however, little justified, since the nature of the investigated phenomena is the same in both cases.

Let us first discuss the methods used in the microwave band. Each microwave magnetic spectroscope consists of the following main parts: 1) a microwave generator with stabilized frequency and stabilized power supply, with provision for monitoring the frequency and the power; 2) an absorbing cell, made in the form of a cylindrical or rectangular resonant cavity; 3) a detector; 4) an amplifying and recording unit, and 5) a source of constant magnetic field. In most cases there is, in addition, 6) a unit for modulating the constant magnetic field (see, for example, Fig. 2.2).

A resonant cavity containing a sample of the investigated substance is placed between the poles of an electromagnet in such a way that the static and microwave magnetic fields acting on the substance are mutually perpendicular. The sample is located in such a place in the cavity, where the microwave magnetic field is maximal and the electric field is minimal (in order to attenuate the nonmagnetic losses). During the course of the measurements, the frequency of the microwave generator exciting the electromagnetic oscillations in the cavity is maintained constant while the intensity of the static magnetic field is varied. This experimental procedure is made necessary by the fact that a study of the dependence of the paramagnetic absorption coefficient on the frequency of the microwave field at H_0 = const would introduce additional experimental difficulties, connected with the change in the generator power with changing frequency of the radiation pro-
duced by the generator.

There are two types of microwave magnetic spectrometers. In the first the paramagnetic resonance absorption is investigated by determining the change in the power passing through the resonant cavity containing the substance (transmitted-wave method), and in the second it is determined from the change in the power reflected from the cavity with the specimen (reflected-wave method).

The transmitted-wave method was first experimentally employed by Cummerow, Holliday, and Moore [4], who showed that the coefficient of paramagnetic absorption can be determined by measuring the power at the output of the cavity resonator.

The second method permits the paramagnetic absorption coefficient to be determined from the coefficient of reflection from the cavity containing the investigated substance. Whitmer, Weidner, Hsiang, and Weiss [5] constructed a microwave magnetic spectroscope operating on the balanced-T bridge method using a dual tee. Measurement of the power $P$ resulting from the unbalancing of the bridge by the paramagnetic losses, makes it possible to determine the reflection coefficient $\gamma$, which is connected with the dynamic susceptibility of the paramagnet:

$$P \sim \gamma = \text{const} (\chi' + \chi'')$$  \hspace{1cm} (2.1)

Both the transmitted-wave and the reflected-wave methods are used in modern spectroscopes.

Before we proceed to consider individual specific installations, which differ essentially in the methods used to indicate the transmitted or reflected power, let us dwell on a few factors that determine the sensitivity of a magnetic spectroscope. By virtue of (1.9) and (1.19), the paramagnet specimen placed in an oscillating magnetic field $H_0 \cos 2\pi vt$ absorbs a power $P = \pi v \chi'' H_0^2$. On the other hand, the power absorbed by the cavity itself can be expressed by $P_0 = (1/Q_0) v H_0^2 V/4$. 
where $Q_0$ is the unloaded $Q$ of the cavity and $V$ is its effective volume. Therefore the ratio of the power absorbed by the investigated specimen to the power dissipated by the cavity itself is

$$\frac{P}{Q} = \frac{4\pi\chi''}{V}. \quad (2.2)$$

We see therefore that the apparatus has maximum sensitivity for the measurement of the coefficient of paramagnetic absorption $\chi''$ when the unloaded $Q$ of the resonant cavity is largest and when the cavity volume is smallest.

Fig. 2.1. Equivalent circuit used in the determination of the sensitivity of a microwave spectroscope.

For a specimen containing paramagnetic particles with spin $S = 1/2$, the absorption coefficient will be $\chi'' = \chi_0 v/\Delta v$, where $\chi_0$ is the static magnetic susceptibility of the specimen, $v$ the frequency of the oscillating magnetic field, and $\Delta v$ the width of the resonance absorption line, expressed in frequency units. When $S = 1/2$ and $g = 2$, the static magnetic susceptibility of one mole of substance is $\chi_0 = 0.38/T$. If the wavelength of the microwave generator is $\lambda \approx 3$ cm, and the width of the paramagnetic resonance line is on the order of 1 oersted,* that is, $\sim 10^{-4}$ cm$^{-1}$, then $\chi''_{\text{mole}} \approx 4$ at room temperature. Consequently, in order for the $Q$ of the cavity to decrease to about one half of the loaded value $Q_0$, we must place in the case of $Q_0 \approx 5000$ approximately $10^{-5}$ mole of our paramagnet in the cavity, if we assume that the effective volume is $V \approx 2-3$ cm$^3$.

To estimate the limiting sensitivity of the spectroscope we can,
following Bleany and Stevens [6], consider an equivalent circuit, in which the resonant cavity is represented by a tuned network with resistance $r$ (Fig. 2.1). The microwave radiation is fed to the tuned network through a self-inductance $M$ from a generator with power $P_1$ and internal resistance $R$. The radiation is detected by a receiver, the resistance of which is also $R$. If the generator has an angular frequency $\omega$ and is exactly tuned to the frequency of the resonant network, then the voltage on the indicator is

$$V_1 = \frac{(r'R')^{1/2}}{r + r'}.$$ 

where $r' = 2\omega^2 M^2 / R$.

Assume that the paramagnetic absorption has changed the quantity $r$ by an amount $\delta r$; then the change in voltage will be

$$\delta V_1 = \frac{r'(RP)^{1/2}}{(r + r')^2}.$$ 

Since $r'$ depends on the coupling with the resonant network, we can tune the latter by changing the coupling (that is, the value of $M$). The sensitivity will be maximal when the voltage $\delta V_2$ reaches a maximum, which occurs when $r = r'$. Let us express $\delta V_2$ in terms of the power $P_2$ entering the receiver. We have $\delta V_2 = \delta r (RP_2)^{1/2} / (r + r')$. This expression shows that the fraction change $\delta V_2 / (RP_2)^{1/2}$ is equal to $\delta r / (r + r')$. Although $P_2$ increases with increasing coupling, on the other hand, $Q$ decreases with the load. At the maximum, the change of the indicator voltage, due to the paramagnetic absorption, will be

$$\delta V_1 = (RP)^{1/4}.$$

If the receiver has a noise figure $N$ and a bandwidth $df$, then the output signal will be equal to the noise at the output, provided the condition $\delta V_2 = (NkTdfR)^{1/2}$ is satisfied.
On the other hand, \( \delta r/r \) is the ratio of the power absorbed by the specimen to the power dissipated by the cavity, which as we have seen is equal to \( 4\pi \chi'' Q_0/\sqrt{V} \); thus, the minimum value of \( \chi'' \) that can be detected by the apparatus satisfies the condition

\[
\chi''_{\text{min}} = \frac{V}{\pi Q_0} \left( \frac{N \pi T \Delta\nu}{P} \right)^{1/4}.
\]  

(2.3)

If we assume as before that \( Q_0 = 5000 \) and \( \lambda = 3 \) cm, then for \( N = 10 \), \( df = 1 \) cps, a generator power of 40 milliwatts, and \( V = 2-3 \) cm\(^3\), the theoretical minimum value \( \chi''_{\text{min}} \) will be \( \sim 10^{-12} \) at room temperature. For an absorption line width \( \sim 10^{-4} \) cm\(^{-1}\), this should correspond to a possibility of detecting a signal against a noise background from about \( 2.5 \times 10^{-13} \) mole of paramagnetic particles with \( S = 1/2 \) (at \( 300^0\)K). The sensitivity actually attained in the apparatus is as a rule much lower than this figure and depends greatly on many factors, particularly on the method used to measure the signal in the apparatus.

Depending on the method used to indicate the microwave paramagnetic resonance spectra, the existing spectroscopes can be subdivided into several groups: 1) direct current indication; 2) detection followed by low-frequency amplification; 3) double modulation; and 4) the superheterodyne method. Very recent papers [7] report the use of the spin-echo method for the investigation of very narrow electron paramagnetic resonance lines; this method was previously used only for nuclear paramagnetic resonance.

The first method is easiest to realize, but in view of its low sensitivity it was used only during the first stages in the development of magnetic radio spectroscopy, when the work was limited to investigations of relatively crude effects, occurring in nondilute paramagnets with broad and intense absorption lines. In this method, the microwave signal was rectified after passing through the measurement
cavity (or after being reflected from it) and was fed through a compensation network to a sensitive galvanometer. The paramagnetic absorption curve was plotted "point by point," with the galvanometer deflections, which were proportional to the power flowing through the detector, being noted for different values of the constant magnetic field intensity $H_0$. For each value of $H_0$ the cavity was first tuned to the generator frequency.

To proceed to an investigation of the narrower and weaker absorption lines, observed in dilute paramagnets, it is necessary to use methods that yield greater sensitivity and permit the spectral pattern to be displayed on an oscilloscope or recorded on a chart.

A method satisfying these requirements employs modulation of the static field $H_0$ by a magnetic field of audio frequency; such modulation was first used by Zavoyskiy [1] in 1944, in work carried out in the radio frequency range. If the amplitude of the modulating field $H$, for a specified intensity of the static magnetic field, encompasses the region of paramagnetic resonance, then a suitable modulation should take place in the power passing through the cavity (or reflected from it). This power modulation can be amplified and fed to an oscilloscope, the horizontal sweep of which is synchronized with the modulation field. During each period of modulation, the field will go through the resonant values of $H_0$ twice; consequently the portion of the spectrum encompassed by the modulation amplitude (or the entire spectrum, if the amplitude is sufficiently large) will be displayed on the oscilloscope screen in the form of a double picture, symmetrical with respect to the center, representing the dependence $\chi''(H_0)$. This method of investigating paramagnetic resonance is essentially convenient for an initial determination of paramagnetic spectra; a study of the details of these spectra is more conveniently carried out by using a modulation
amplitude which is quite small compared with the width of the investigated line. In this case as we gradually pass through $H_0$ in the resonant region, we obtain a curve showing the dependence of the derivative $\frac{d\chi''}{dH_0}$ on $H_0$; it is usually recorded automatically on a chart.

Fig. 2.2. Microwave spectroscope with low-frequency modulation of the magnetic field (transmitted-wave method). 1) Microwave generator; 2) frequency control; 3) power control; 4) attenuator; 5) resonant cavity with the substance; 6) crystal detector; 7) low-frequency amplifier; 8) oscilloscope; 9) phase shifter; 10) modulating coils.

Fig. 2.3. Microwave spectroscope with low-frequency modulation of the magnetic field (reflected-wave method) [8]. 1) Stabilized power supply; 2) klystron oscillator; 3) wave meter; 4) attenuator; 5) phase shifter; 6) hybrid ring; 7) plunger; 8) crystal detector; 9) loop; 10) cavity; 11) specimen; 12) low-frequency amplifier; 13) sweep; 14) electromagnet; 15) oscilloscope; 16) modulating coils. A) cps.
A block diagram of a microwave spectroscope with low-frequency modulation of the magnetic field and with a transmission-type resonant cavity is shown in Fig. 2.2.

Apparatus using the same field modulation but based on the reflected-wave method has been described by Manenkov and Prokhorov [8]. It is shown in Fig. 2.3.

The main factor limiting the sensitivity of spectroscopes of this type is the low-frequency noise of the crystal detector. To avoid this noise and thus increase the sensitivity, Beringer and Castle [9] constructed a spectroscope in which a bolometer was used as a detector. The latter can detect power on the order of a milliwatt without appreciable low-frequency noise. The Beringer and Castle apparatus uses the transmitted-wave method. The microwave generator is frequency stabilized; the narrow-band phase-sensitive amplifier is controlled by a 30 cps frequency, which is used to modulate the field $H_0$. The experimentally estimated sensitivity of this spectroscope does not differ greatly from the theoretically attainable value. A block diagram of the Beringer and Castle spectroscope is shown in Fig. 2.4. This spectroscope was constructed to investigate very weak paramagnetic resonance lines, observed in rarefied gases.

Another method of increasing the sensitivity of radio spectroscopes was first used to measure paramagnetic resonance by Smaller and Jasaytis [10]. It consists of using double modulation of the magnetic field. The Buckmaster and Scovil spectroscope, built on this principle [11], is no less sensitive than a spectroscope with a bolometer. The double modulation principle consists in the following. The spectral density of the crystal-detector noise is inversely proportional to the frequency (at least in the interval $1-24 \times 10^9$ cps). Therefore, if in addition to modulating at an audio frequency $\nu_1$ with high amplitude...
the magnetic field is modulated additionally at a frequency $v_2$, sufficiently high to cause the fraction of the low-frequency noise in excess of the thermal noise in the crystal detector to be negligibly small, and if amplification at frequency $v_2$ is introduced, then the sensitivity (compared with the amplification at the low frequency) should increase greatly. We note that the amplitude of the high-frequency modulation method does not exceed half the width of the investigated spectral line [12].

Buckmaster and Scovil used in their spectroscope a cylindrical cavity, operating in the $H_{III}$ mode; the source of microwave power is a generator operating at $\lambda = 1.2$ cm. The first-modulation frequency is $v_1 = 60$ cps, while that of the second modulation is $v_2 = 462.5$ kcs. A block diagram of this spectroscope is shown in Fig. 2.5. The microwave power is fed from the reflex klystron to a transmission-type cavity to a diode crystal detector. Connected ahead of the cavity are devices to control and monitor the received microwave power and to measure the wavelength. The video signal obtained at the output of the crystal detector passes through an amplifier tuned to 462 kcs with gain $10^6$ and bandwidth 8 kcs; the amplification is to a level at which the signal can be detected linearly. Either an ordinary linear or a phase-sensitive detector can be used, the output of the detector being fed to an oscilloscope. In the former case the oscillogram represents the modulus of the derivative of the line shape, and in the latter the derivative itself. The time sweep voltage of the oscilloscope is obtained from a phase shifter fed by the power source of the low-frequency modulation of the magnetic field (Helmholtz coils). If narrow-band amplification is used, the superposition of a magnetic field of frequency $v_1$ is replaced by a slow and linear variation of the field $H_0$.

The most difficult to attain is the high-frequency modulation,
Fig. 2.4. Microwave spectroscope using a bolometer [9].
1) Microwave stabilized oscillator; 2) cavity; 3) bolometer;
4) DC bridge; 5) 30 cps amplifier with high gain; 6) synchronous amplifier;
7) 30 cps generator; 8) 30 cps power amplifier; 9) galvanometer with large time constant; 10) modulation coils.

Fig. 2.5. Microwave spectroscope with dual field modulation [11].
1) Stabilized oscillator; 2) resonant cavity with substance; 3) detector;
4) amplifier for the frequencies $v_2 + \Delta v$; 5) linear detector;
6) amplifier for $v_1$; 7) oscilloscopes; 8) phase-sensitive detector;
9) phase shifter for $v_2$; 10) modulation coils for $v_2$; 11) modulation coils for $v_1$; 12) phase shifter for $v_1$; 13) frequency control; 14) power control.

For it is necessary for this purpose to introduce a radio frequency magnetic field inside the resonant cavity. For this purpose the reso-
nant cavity is frequently slotted in a plane passing through its axis. If the width of the slot is small compared with the wavelength $\lambda$, then the Q of the cavity is changed little. The radio frequency field can be produced effectively only by modulation current flowing over the internal surface of the cavity. Such a current can be made sufficiently large to ensure a radio frequency magnetic field with amplitude up to 50 oersted at the location of the investigated substance.

An experimental estimate of the sensitivity of the Buckmaster and Scovil spectroscope operating with amplification at 462 kcs and an amplifier bandwidth of 8 kcs has shown that $10^{-11}$ of a mole of free radical with a line width 3.5 oersted at 290$^\circ$K produces a signal/noise ratio of 2/1 for the modulus of the derivative of the line shape. Calculation has shown that using amplification on a very narrow band (1 cps) the maximum sensitivity should be on the order of $10^{-13}$ mole of free radical at 290$^\circ$K.

The dual modulation principle is used also in the microwave magnetic spectroscope of Semenov and Bubnov [13]. The high and low modulation frequencies are 975 kcs and 50 cps, respectively. The depth of the low-frequency modulation is on the order of 300 oersted. The spectrometer is equipped with an automatic frequency control for the klystron oscillator against the operating cavity. A voltage of ~15 mv is fed to the klystron repeller from the automatic frequency control oscillator (630 kcs). This voltage frequency-modulates the microwave oscillations produced by the klystron. If the klystron frequency deviates from that of the cavity, the microwave oscillations are amplitude-modulated. The phase of this "automatic frequency control signal" is determined by the sign of the frequency deviation, and the amplitude is proportional to the magnitude of this deviation. After detection of the microwave oscillations, the control signal is amplified by
a tuned amplifier (630 kcs, gain ~10^5) and is fed to a phase-sensitive 
detector, from which it is applied to the klystron repeller. The end 
result is that the klystron frequency is set at the resonant frequency 
of the cavity containing the investigated substance.

Because of the device just described, the microwave spectroscope 
of Semenov and Bubnov has rather high operating stability. It is there- 
fore most suitable for investigations of the course of chemical reac-
tions. If an oscilloscope is used for registration, its sensitivity 
corresponds to ~4·10^{-10} mole of diphenylpicrylhydrazyl and ~8·10^{-12} 
mole of the same substance if slow chart recording is used. A block 
diagram of the spectroscope is shown in Fig. 2.6.

The superheterodyne measurement method was first used for the 
study of paramagnetic resonance by England and Schneider [14]. It is 
based on the use of a balanced T bridge (or hybrid ring), to which 
power is applied from a measuring klystron of frequency f_1 and from an 
auxiliary klystron of frequency f_2. The frequency difference f_1 - f_2 
is made equal to several times ten megacycles. This is the intermediate 
frequency used to amplify the signal resulting from the unbalance of 
the bridge upon occurrence of paramagnetic absorption. The low-
frequency noise of the crystal detector is thus made negligibly small. 
However, with increasing f_1 - f_2, the noise of the intermediate-
frequency amplifier increases. Taking both factors into account, the 
theoretical optimum of f_1 - f_2 lies close to 30 megacycles [15].

An example of a block diagram of a spectroscope with superhetero-
dyne detection [16] is shown in Fig. 2.7.

If there is no paramagnetic absorption, there should be no signal 
in the fourth arm of the bridge provided the tuning and the balancing 
are exact. Absorption produces an unbalance by changing the reflection 
coefficient and causes the power in klystron 1 to begin to flow in the
fourth arm and to mix in the crystal mixer with the power from the auxiliary klystron, thus producing an intermediate frequency signal which is fed to the amplifier.

It must be borne in mind that the power \( \delta P \) reflected in the fourth arm is not equal to the absorbed power \( \Delta P \), but is only a fraction of the latter; according to Gordy [17]

\[
\frac{\delta P}{\Delta P} = \frac{\Delta P}{P}
\]

where \( P \) is the total power in the cavity.

The different types of microwave magnetic spectrosopes, which we have discussed briefly, make it possible to study with great accuracy the position of the paramagnetic resonance line, and with a somewhat lesser accuracy the line shape.

The accuracy with which the line position is determined depends...
Fig. 2.7. Microwave spectro-
scope operating on the super-
heterodyne principle [16]. 1) Klystron; 2) hybrid ring (or T-bridge; 3) resonant cavity; 4) local heterodyne; 5) mixer; 6) intermediate frequency amplifier; 7) automatic frequency control; 8) video amplifier; 9) oscilloscope; 10) phase shifter; 11) modulation coils; 12) frequency multiplier; 13) receiver; 14) proton flux meter.

Fig. 2.8. Proton flux meter [18]. 1) Coil with specimen in magnetic field; 2) to amplifier and oscilloscope; RFC) radio frequency coils. A) ohm; B) μf; C) kohm; D) RFC; E) 250 v; F) μf.

essentially on the accuracy with which the intensity of the constant magnetic field $H_0$ is measured at resonance, since the measurement of the resonant frequency $\nu$ can frequently be made without large errors.
The determination of the intensity of the magnetic field reduces as a rule likewise to a measurement of a certain frequency, namely the frequency of proton paramagnetic resonance, observed at a given magnetic field. Flux meters constructed on the proton-resonance principle are presently used in all cases where precision measurement of the magnetic field is required. One of the methods of using proton resonance for the determination of the paramagnetic resonance line position is illustrated in Fig. 2.7. The frequency of the proton flux meter is varied until the positions of the maxima of the electron and proton resonances, observed on the screen of a double-beam oscilloscope, occur at one and the same abscissa. One of the possible proton flux meter circuits [18] is shown in Fig. 2.8.

Understandably, the narrower the line and the higher the frequency at which the paramagnetic resonance is measured, the more accurately can the line position be determined. For lines with $\Delta H \approx 1$ oersted and at frequencies corresponding to the millimeter band, the accuracy with which the effective $g$ factor is determined reaches hundredths of a percent. On the other hand, in nondilute paramagnetic salts with broad lines, the effective $g$ factor can be determined only with accuracy not higher than several tenths of a percent, and usually even with lower accuracy.

The study of the paramagnetic resonance line shape is a more difficult problem. Because paramagnetic absorption ($\chi''$) is always accompanied by dispersion of the magnetic susceptibility ($\chi'$), the observed $\chi''(H_0)$ line should generally speaking always be deformed to some degree or another as a result of the $\chi'$ admixture. It is easy to show, however [8], that the influence of the dispersion on the line shape can be neglected provided the following two conditions are satisfied: 1) the natural frequency of the cavity is strictly equal to the frequency...
of the microwave oscillator under the conditions of paramagnetic resonance, and 2) the amount of paramagnetic substance chosen for the measurement is sufficiently small to make the paramagnetic losses in the specimen small compared with the over-all losses in the cavity.

Several special methods were also developed to separate the $\chi''(H_0)$ or $\chi'(H_0)$ effect in pure form [19-21]. These methods are important if condition 2) cannot be satisfied for one reason or another.

A procedure for the measurement of the paramagnetic rotation of the plane of polarization is developed in [22].

For lack of space we shall not stop to describe individual units and parts of the apparatus used in microwave spectroscopes. This description can be found in the books by Gordy, Smith, and Trambarulo [23], Strandberg [24], Ingram [16], and also in the specialized radio literature.

We confine ourselves here merely to a description of devices used in low-temperature and high-temperature measurements of paramagnetic resonance.

The first extensive investigations of paramagnetic resonance spectra at liquid hydrogen or helium temperatures were set up by Bleaney and his co-workers in Oxford [16]. To work at $\lambda = 1.25$ cm and at liquid nitrogen and liquid hydrogen temperatures they used a special type of cylindrical cavity with inside diameter 12 mm and height from 6 to 11 mm, with the input and output coupling apertures made in the upper cover of the cavity, for easier placement of the latter in a Dewar flask. The investigated crystal was mounted on a small platform, covering a third aperture located in the center of the same top cover of the cavity. This platform was secured to a long thin-walled tube made of silver, so that the crystal could be rotated in a chosen plane through any angle relative to the external magnetic field. Wave guides...
supplying microwave power to the cavity were made of thin-wall silver,* with inside dimensions 2.5x6 mm, and filled with distyrene almost to the upper uncooled end, where they gradually taper down. A section through such a cavity is shown in Fig. 2.9. Similar devices are used also for other wavelengths.

Fig. 2.9. Cavity for measurements at low temperatures on a wavelength of 1.25 cm [16].

Fig. 2.10. Cavity with apertures for measurements at low temperatures.

In addition to the foregoing measurement method, others are also used at low temperatures. In particular, the use of a rectangular cavity operating on the $H_{012}$ mode or a cylindrical one on the $H_{011}$ mode offers great advantages. The distribution of the magnetic force lines of the microwave field in such cavities is shown in Fig. 2.10. An aper-
ture is cut in the narrow wall of the cavity (or in the end of the cylinder), and a vessel made of foamed plastic containing the investigated substance is inserted in this aperture [13]. If the required conditions regarding the position and dimensions of the aperture are satisfied, the presence of this aperture does not influence greatly the $Q$ of the cavity, and consequently the sensitivity of the apparatus. Of course, the necessary condition for any measurement with a Dewar flask or with a foamed-plastic vessel, placed inside a cavity, is high stability of the spectroscope, so that the boiling of the cooled liquid does not cause any distortion in the observed spectrum. Such a procedure makes it possible to make measurements at both low and high temperatures [25]. Investigations at high temperatures can also be carried out with the aid of a special heater described in [26].

It must be mentioned that in some cases (for example, in the investigation of relaxation time by the method of paramagnetic resonance line saturation) it becomes necessary to use high amplitudes of the microwave magnetic field. It is customary to use pulse techniques for this purpose [27, 28].

§2.2. Methods of Measurements in the Radio Frequency Band

Two types of methods are used at present to measure $\chi''(H)$ in the radio frequency band: one can be called the method of reaction on the generator, and the other is based on the determination of the change in $Q$ of a resonant circuit (or a cavity) resulting from the paramagnetic losses.

As already mentioned, Gorter's first investigations of nonresonant paramagnetic absorption, observed at low frequencies, were carried out by a direct calorimetric method. The inconvenience of this method, and the fact that it cannot be employed at higher frequencies, have induced Zavoyskiy to go over to indirect electric methods of de-
termining the paramagnetic losses. He developed the method of reaction on the generator [1, 2], which is widely used at present to study both electron and nuclear paramagnetic resonance [29, 30].

When working in the radio frequency band, the investigated substance is usually placed not in a resonant cavity, but in a self-inductance coil, comprising part of the tank circuit of an electronic self-oscillator or inductively coupled to the latter. The Zavoyskiy radio frequency measurement procedure is based on the fact that a change in the active power load $\Delta W$ of the generator producing the electromagnetic oscillations causes, if certain conditions are satisfied, a proportional change in the grid current, $\Delta I_g$, or in the anode current, $\Delta I_a$, of the generator. $\Delta W$ should be proportional to $\Delta I_g$ or $\Delta I_a$ if the power dissipated by the substance as a result of paramagnetic absorption is small compared with the over-all losses in the tank circuit.

Work with magnetic spectrographs in the radio frequency band becomes much more convenient, and their sensitivity is greatly increased, if the constant magnetic field is modulated by a low-frequency field. This modulation, to which we already referred in the preceding section, was first used by Zavoyskiy precisely for the radio frequency band.

The simplest schematic diagram of a setup operating by the Zavoyskiy method is shown in Fig. 2.11.

To measure the absolute values of the paramagnetic absorption in the radio frequency band, a very simple method was used in [31]. This method consisted of determining the change in the $Q$ of the tank-circuit inductance coil with the aid of a somewhat modified $Q$ meter. These changes in the $Q$ are proportional to the value of $\chi''$:

$$\Delta Q = -4\pi \eta \chi'' Q^2,$$

where $\eta$ is the filling factor of the coil. Similar setups were proposed earlier for the measurement of nuclear magnetic resonance [30].
Radio spectroscopes in which the absorbing cell is the tank circuit inductance coil have advantages in that it is more convenient to place the investigated substance in the high frequency field and it is easier to carry out the measurements at either low or high temperatures. However, the low Q of the coils makes such setups not always sufficiently sensitive. Therefore in some cases when particularly high sensitivity is required, the inductance coil of the radio spectroscope is replaced by a high Q cavity. A spectroscope of this type was constructed by Feher and Kip [32] to measure paramagnetic resonance in metals. A block diagram of this spectroscope is shown in Fig. 2.12. The use of a synchronous detector has resulted in this apparatus in a further improvement in the signal/noise ratio.

To conclude this chapter, let us dwell briefly on the sources of constant magnetic field used in the investigation of paramagnetic resonance. In experiments carried out in the microwave band, where the resonant values of $H_0$ usually range from 3000 oersteds upwards the only suitable sources capable of producing such fields are electromagnets. Inasmuch as paramagnetic resonance lines are in the majority of cases...
tens and sometimes even hundreds of oersteds wide, no stringent requirements are imposed on the homogeneity of the magnetic field. In individual cases, however, very narrow lines can also be observed, on the order of tenths of an oersted. For such measurements electromagnets such as employed in nuclear magnetic resonance are used, with suitable stabilization [29].

Fig. 2.12. Block diagram of a radio spectro- scope operating on the principle of measuring $Q$ with a phase-sensitive detector [32].
1) Modulation coils used to produce a sinusoidal magnetic field; 2) modulation coils used to obtain a slowly varying magnetic field; 3) coils used to obtain a constant magnetic field; 4) high-$Q$ cavity ($Q = 1000-1500$); 5) high-frequency generator; 6,7) matching transformers; 8) vacuum tube detector; 9) narrow band amplifier; 10) synchronous detector; 11) amplifier to supply the coils; 12) oscilloscope with DC amplifier; 13) amplifier for automatic recorder; 14) sawtooth voltage generator; 15) generator for sinusoidal reference voltage; 16) automatic recorder; 17) power supply for coils 3.

In measurements of electron paramagnetic resonance at radio frequencies it is possible to produce the constant magnetic field not only with electromagnets but also with Helmholtz coils, since the required field intensity is not large in this case. A determination of the positions of the paramagnetic resonance lines in the radio frequency band is carried out either by measuring the resonant field intensity $H_0$ with a proton flux meter or by means of a standard substance, such as diphenylpicrylhydrazyl, for which the value of the $g$ factor is

- 53 -
known with sufficient accuracy.

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Manuscript Page No. [Footnotes]
35 A line width of this order is usually observed in free radicals.
49 Alloys of low heat conductivity (melchior, stainless steel, etc.) are presently used most frequently for this purpose.
[List of Transliterated Symbols]

Page No.

46  ПЧК = РЧК = radiochastotnyye katushki = radio-frequency coils
52   с = s = setochnyy = grid
52   к = k = kontur = tank circuit
52   cб = sv = [svyazi = coupling]
52   П = P = [not identified]
§3.1. Introduction

The most widely investigated among the various classes of paramagnets are ionic crystals. Paramagnetic properties are possessed by ionic crystals containing transition group elements, for only the atoms of these elements retain unfilled electron shells during the crystal formation process.

To construct a theory for the energy structure of ionic paramagnetic crystals it is necessary first of all to take into account the interactions of the electrons with one another and with the nucleus within each ion, and then take into account the electrostatic, magnetic, and exchange interactions between the different ions, and finally the effect of the external magnetic field. Magnetic and exchange forces produce narrow quasi-continuous energy bands, for these forces are small in substances with not too high a magnetic concentration, and the number of possible orientations of the moments of the magnetic particles of the crystal relative to one another is tremendous. As a result, the magnetic and exchange interactions do not influence as a rule the form of the paramagnetic resonance spectrum* and cause only a broadening of individual lines. We shall therefore dwell on these interactions in Chapter 5, which is devoted to the absorption line shape.

We shall take an approximate account of the electrostatic interaction between free ions by assuming that each ion is in a certain av-
average electric field produced by all the surrounding particles. We shall call this the crystalline field for short. The action of the crystalline field is always weaker than the Coulomb interaction between the electrons in the atom. We can therefore use the self-consistent field method and speak of the configuration of the electrons forming the unfilled shell of the paramagnetic ion. The electron configurations corresponding to various transition groups are $3d^n$ for the iron group (from Ti to Cu), $4d^n$ for the palladium group (from Zr to Ag), $4f^n$ for the rare earth group (from Ce to Yb), $5d^n$ for the platinum group (from Hf to Au), and $6d5f^n$ for the actinides (from U on).

The self-consistent field method does not take full account of the electrostatic interaction between electrons. The calculations, which are usually carried out by the perturbation method, therefore call for a knowledge of the relationship between the unaccounted for part of the electrostatic repulsion between electrons, the magnetic couplings between their spin and orbital moments, and the forces of the crystalline field. Three cases are possible. The crystalline field is called weak if it is unable to break the bond between the orbital and spin moments of the entire unfilled electron shell. The field is assumed average if its action is stronger than the spin-orbit coupling of the electrons, but much weaker than the interaction between individual electrons. Finally, the field is called strong if its action is much stronger than the bond between the electrons of the unfilled shell. The first two cases are realized in hydrated salts of rare-earth elements and the iron-group elements, respectively. A strong field is not encountered in pure form, for if the crystal field becomes considerably stronger than the interaction between individual electrons, then the covalent bond between the paramagnetic atom and its immediate vicinity always begins to assume an appreciable role in
place of the ionic bond. The character of splitting of the energy levels of paramagnetic ions by the crystalline field depends to a great degree on the symmetry of this field. This has enabled Bethe [1] to present a qualitative solution of this problem with the aid of group theory. Tables 3.1 and 3.2 indicate how the electron levels are split for the cases of integral and half-integral momentum quantum number J. The third and following columns show how many energy sublevels are produced in a field of corresponding symmetry, and the numbers in the parentheses denote the degree of degeneracy of these sublevels.

We see from Table 3.2 that in the case of a half-integer spin the energy sublevels always remain at least doubly degenerate. This fact is the consequence of Kramers' general theorem [2], which is of fundamental significance in the theory of paramagnetism. The theorem states that the electric forces are unable to eliminate completely the degeneracy of the energy level of a system containing an odd number of electrons. It follows therefore that paramagnetic resonance can always be observed in paramagnetic ions containing an odd number of electrons, for by eliminating the degeneracy of the ground states, the magnetic field can produce splittings that lie in the radio frequency range. If the number of electrons is even, then all levels may turn out to be simple even in the absence of a magnetic field, and the distance between them may be so large that no practically attainable magnetic fields can bring them close enough together to make resonant absorption of radio frequency radiation possible.

The influence of the crystalline field on the static susceptibility of paramagnetic salts was first considered by Van Vleck [3]. Penney and Schlapp made detailed calculations for several rare-earth salts [4] and iron-group elements [5]. Analogous calculations were made then
TABLE 3.1

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</table>

*See page 93 concerning icosahedral symmetry in ionic crystals.

1) Splitting in a field of; 2) icosahedral symmetry; 3) cubic symmetry; 4) trigonal symmetry; 5) tetragonal symmetry; 6) rhombic symmetry; 7) total splitting; 8) degree of degeneracy of the level of the free atom.

TABLE 3.2

<table>
<thead>
<tr>
<th>J</th>
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</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>3/2</td>
<td>(1)</td>
</tr>
<tr>
<td>5/2</td>
<td>(1)</td>
</tr>
<tr>
<td>7/2</td>
<td>(1)</td>
</tr>
<tr>
<td>9/2</td>
<td>(1)</td>
</tr>
<tr>
<td>11/2</td>
<td>(1)</td>
</tr>
<tr>
<td>13/2</td>
<td>(1)</td>
</tr>
<tr>
<td>15/2</td>
<td>(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>Распределение в поле</th>
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<tbody>
<tr>
<td>1/2</td>
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<tr>
<td>3/2</td>
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<tr>
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<td>(1)</td>
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<tr>
<td>9/2</td>
<td>(1)</td>
</tr>
<tr>
<td>11/2</td>
<td>(1)</td>
</tr>
<tr>
<td>13/2</td>
<td>(1)</td>
</tr>
<tr>
<td>15/2</td>
<td>(1)</td>
</tr>
</tbody>
</table>

1) Degree of degeneracy of the level of the free atom; 2) splitting in a field of; 3) icosahedral symmetry; 4) cubic symmetry; 5) lower symmetry.

by other authors [6], but only after experimental material on paramagnetic resonance in ionic crystals was accumulated did it become possible to construct a consistent theory of energy spectra of paramagnetic ions.

§3.2. Matrix Elements of the Crystalline Field

To calculate the effect of the crystalline field on the energy levels of paramagnetic ions by the perturbation method it is necessary first to calculate the energy matrix elements \( H_{\text{int}} \) of the electrons of...
the unfilled shell in the electric field of the crystal. The energy $H_{\text{ef}}$ can be represented in the form
\[ H_{\text{ef}} = \sum_i -\phi V(x_i, y_i, z_i) \] (3.1)
where $V$ is the potential of the crystalline field and $x_i, y_i, z_i$ are the coordinates of the $i$-th electron of the unfilled shell. Assuming that the electron shells of the paramagnetic atoms and of the particles surrounding it do not overlap and that consequently the potential $V$ satisfies the Laplace equation, we can expand the potential in a series of spherical functions:
\[ V = \sum_{n, m, \ell} A_{nm} Y_{\ell}^m(\theta, \phi) \] (3.2)
This expression can be greatly simplified and only a few terms of the series retained. Only the $d$ and $f$ shells of the paramagnetic atoms can be unfilled in ionic crystals. In calculating the perturbation matrix $H_{\text{ef}}$ with the aid of the $d$-electron wave functions, the spherical functions with $n > 4$ give matrix elements equal to zero [7]. Precisely in the same way, the terms of the series (3.2) with $n > 6$ can be left out in the case of $f$ electrons. It is also necessary to discard the terms of the series with odd $n$, for the matrix elements of odd-order spherical functions vanish by virtue of the invariance of the electron wave functions under the inversion transformation; account is taken here of the fact that all the crystals investigated to date have a symmetry center. The term with $n = 0$ yields an inessential additive constant, which can be set equal to zero. Finally, the fact that $V$ is real leads to $A_{nm} = (A_{nm}^{-1})^*$. Equation (3.2) can be further simplified by taking into account the symmetry of the crystalline field. We notice that the surface spherical function $Y_n^m(\theta, \phi)$ has axial symmetry if $m = 0$, tetragonal symmetry if $m = \pm 4$, trigonal symmetry if $m = \pm 3$, hexagonal sym-
metry if \( m = \pm 6 \), and finally rhombic symmetry if \( m = \pm 2 \). It follows therefore that if we denote \( \mathcal{A}^m_{n^m n^m}(\mathcal{T}, \mathcal{V}) \) by \( \mathcal{U}_n \) and \( \mathcal{A}^m_{n^m n^m}(\mathcal{T}, \mathcal{V}) + \mathcal{A}^m_{n^m n^m}(\mathcal{T}, \mathcal{V}) \) by \( \mathcal{V}_n \), then the potentials of the fields of different symmetries will have the form:

\[
\begin{align*}
V_{\text{tetra}} &= \mathcal{V}_1 + \mathcal{V}_2 + \mathcal{V}_3 + \mathcal{V}_4 \quad \text{(tetragonal)}, \\
V_{\text{trig}} &= \mathcal{V}_1 + \mathcal{V}_2 + \mathcal{V}_3 + \mathcal{V}_4 + \mathcal{V}_5 \quad \text{(trigonal)}, \\
V_{\text{hexa}} &= \mathcal{V}_1 + \mathcal{V}_2 + \mathcal{V}_3 + \mathcal{V}_4 + \mathcal{V}_5 + \mathcal{V}_6 \quad \text{(hexagonal)}, \\
V_{\text{rhom}} &= \mathcal{V}_1 + \mathcal{V}_2 + \mathcal{V}_3 + \mathcal{V}_4 + \mathcal{V}_5 + \mathcal{V}_6 + \mathcal{V}_7 \quad \text{(rhombic)}, \\
V_{\text{triclin}} &= \sum_{m=0}^{2} \mathcal{V}_n \quad \text{(triclinic)}.
\end{align*}
\]

For a field of cubic symmetry, if the polar axis (the Z axis) coincides with the fourfold symmetry axis, the potential assumes the form

\[
V_{\text{cub}} = A_{\text{cub}} \{ \mathcal{V}_1(\theta, \varphi) + \sqrt{\frac{5}{14}} [\mathcal{V}_1(\theta, \varphi) + \mathcal{V}_2(\theta, \varphi)] +
\mathcal{V}_2(\theta, \varphi) - \sqrt{\frac{7}{2}} [\mathcal{V}_1(\theta, \varphi) + \mathcal{V}_2(\theta, \varphi)] \},
\]

On the other hand, if the polar axis is parallel to the volume diagonal of the cube and is therefore a threefold symmetry axis, we have

\[
V_{\text{cub}} = D_{\text{cub}} \{ \mathcal{V}_1(\theta, \varphi) + \sqrt{\frac{15}{7}} [\mathcal{V}_1(\theta, \varphi) + \mathcal{V}_2(\theta, \varphi)] +
\mathcal{V}_2(\theta, \varphi) + \frac{1}{2} \sqrt{\frac{70}{3}} [\mathcal{V}_1(\theta, \varphi) + \mathcal{V}_2(\theta, \varphi)] +
\mathcal{V}_3(\theta, \varphi) \},
\]

The tetragonal field is the sum of an actual field and a cubic field, given by an expression such as (3.4a); in precisely the same manner, a trigonal field can be decomposed into a sum of an actual field and a cubic field given by expression (3.4b).

To continue the calculations it is more convenient to change to Cartesian coordinates. If we denote by \( \mathcal{V}_n \) the following homogeneous polynomials of degree \( n \) in the coordinates \( x, y, \) and \( z \):
\[
V_i = 3z^4 - r^4, \quad V_j = xz, \quad V_k = x^4 - y^4,
\]
\[
V_1 = 35x^4 - 30x^2y^2 + 3r^4, \quad V_2 = (7x^3 - 3r^3) xz,
\]
\[
V_3 = (7z^3 - r^3)(x^3 - y^3), \quad V_4 = (x^3 - 3y^3) xz,
\]
\[
V_5 = x^4 - 8x^4y^4 + y^4, \quad V_6 = 231x^2 - 315x^2z^2 + 105rz^2 - 5z^4,
\]
\[
V_7 = 33x^4 - 30x^2y^2 + 5r^4xz,
\]
\[
V_8 = 16x^2(x^4 - y^4) - 16(x^4 - y^4)x^4 + x^4 + x^4y^4 - y^4x^4 - y^4z^4,
\]
\[
V_9 = (11z^2 - 3r^2)(x^3 - 3y^3)xz, \quad V_{10} = (11z^2 - r^2)(x^3 - 3y^3) xz
\]

then we have \( \mathbf{U}^m_n = \mathbf{E}^m_n \mathbf{V}^m_n \), where

\[
\begin{align*}
B_1 &= \frac{1}{4} \sqrt{\frac{5}{3}} A_1 \quad & B_2 &= \frac{1}{2} \sqrt{\frac{15}{2a}} A_1 \quad & B_3 &= \frac{1}{4} \sqrt{\frac{15}{2a}} A_1 \\
B_4 &= \frac{9}{16} \sqrt{\frac{35}{5}} A_1 \quad & B_5 &= \frac{9}{32} \sqrt{\frac{15}{2a}} A_1 \quad & B_6 &= \frac{1}{32} \sqrt{\frac{15}{2a}} A_1 \\
B_7 &= \frac{3}{4} \sqrt{\frac{35}{2a}} A_1 \quad & B_8 &= \frac{3}{8} \sqrt{\frac{15}{2a}} A_1 \quad & B_9 &= \frac{1}{32} \sqrt{\frac{15}{2a}} A_1 \\
B_{10} &= \frac{1}{8} \sqrt{\frac{13 - 21}{2a}} A_1 \quad & B_{11} &= \frac{1}{32} \sqrt{\frac{13 - 105}{2a}} A_1 \quad & B_{12} &= \frac{1}{32} \sqrt{\frac{13 - 77}{2a}} A_1 \\
B_{13} &= \frac{1}{16} \sqrt{\frac{13 - 105}{2a}} A_1 \quad & B_{14} &= \frac{1}{32} \sqrt{\frac{13 - 105}{2a}} A_1 \quad & B_{15} &= \frac{1}{32} \sqrt{\frac{13 - 77}{2a}} A_1
\end{align*}
\]

The potential of the cubic field (3.4a) has in Cartesian coordinates the form

\[
v_{\text{cubic}} = C_1 (x^4 + y^4 + z^4 - \frac{3}{5} r^4) +
C_2 (2x^4y^4 + z^4) - 15 (x^4y^4 + y^4z^4 +
+ x^4z^4 + x^2z^2 + y^4z^4 - y^4z^4) + 180 x^2 y^2 z^2,
\]

where

\[
C_1 = \frac{15}{4} \sqrt{\frac{2}{5}} A_1 = 20 B_1, \quad C_2 = \frac{1}{4} \sqrt{\frac{13}{2a}} A_1 = 8 B_1.
\]

Now that we have derived analytical expressions for the potential of the crystalline field, let us discuss several general premises concerning the calculation of perturbation matrix elements. Let \( \psi_M(M = J, J - 1, J - 2, \ldots, -J) \) be the wave functions of the ground state of the free atom under the assumption that the only electron interactions considered are those much larger than \( \hbar \omega \). The quantum numbers \( J \) and \( M \) denote the angular momentum and its projection on the Z axis, respectively, which are conserved in this case. It is easy to show that the matrix elements

\[
\langle JM | \Sigma V^m_n | JM' \rangle = \int \psi_M \psi_M \Sigma V^m_n \psi_M \psi_M dx
\]

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vanish if $M \neq m + M'$. In accordance with (3.1), the symbol $\Sigma$ denotes summation over all the electrons of the unfilled shell.

To find the nonvanishing matrix elements that relate states having the same $J$, it is customary to use the method of equivalent operators [8], [9]. The totality of the functions $Y^m_n(m = 0, \pm 1, \pm 2, \ldots, \pm n)$ forms the basis for the irreducible representation of a rotation group of dimensionality $2n + 1$. Each electron coordinate function $\Sigma Y^m_n$ can be set in correspondence with an equivalent operator, that is, with an analogous function of the angular momentum projection operators $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$, which have the same transformation properties. Thus, corresponding to the functions $\Sigma(x^2 - y^2)$ and $\Sigma(3z^2 - r^2)$ are the operators $\hat{J}_x^2 - \hat{J}_y^2$ and $3\hat{J}_z^2 - J(J + 1)$. We note that the determination of the equivalent operators is not complicated by the fact that unlike $\hat{x}$, $\hat{y}$, and $\hat{z}$, the operators $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ do not commute. Therefore to determine the operator equivalent to the expression $x^k y^l z^m$ it becomes necessary to take the arithmetic mean of $(k + l + m)!/k! l! m!$ possible operator permutations $\hat{J}_x \ldots \hat{J}_x \hat{J}_y \ldots \hat{J}_y \hat{J}_z$. For example, the function $\Sigma x y$ corresponds to the operator $1/2(\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x)$.

The matrix elements of the functions $\Sigma Y^m_n$ and of the corresponding equivalent operators coincide, apart from a certain common factor, which is the same for all functions with the same $n$.

Thus, the cumbersome direct calculations of the matrix elements of the crystalline field potential can be replaced by simple calculations of matrix elements of polynomials of the second, fourth, and sixth degree in $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$. Direct calculations are nevertheless necessary to determine the common factors $\alpha$, $\beta$, and $\gamma$, but for this purpose it is sufficient to calculate only one matrix element $\Sigma Y^m_n$ for each electron configuration and for only one potential function with specified $n$. 

- 63 -
### Table 3.3

\[ V_I = \alpha \hat{P} \left[ (3J^2 - J(J+1)) \right]; \]
\[ V_I = \beta \left( J_+J_+ + J_-J_- \right) = \frac{3}{4} \left( J_+ (J_+ + J_+) + (J_+ + J_-) J_- \right); \]
\[ V_I = \frac{3}{2} \left( J_+ + J_- \right); \]
\[ V_I = \frac{5}{J} \left[ (3J^2 - 30J(J+1) + 25J^2 - 6J(J+1) + 3J^2(J+1) \right]; \]
\[ V_I = \frac{5}{4} \left\{ \left[ J_+ - J_+J_+ \right] (J_+ + J_-) + \right. \]
\[ + \left. \left( J_+ + J_- \right) \left[ J_+ - J_+ J_- \right] \right\}; \]
\[ V_I = \frac{5}{4} \left\{ \left[ J_+ - J_+ J_- \right] - \right. \]
\[ - \left. \left( J_+ + J_- \right) \left[ J_+ - J_+ J_- \right] \right\}; \]
\[ V_I = \frac{5}{4} \left\{ J_+ J_- + (J_+ + J_-) J_+ \right\}; \]
\[ V_I = \frac{5}{4} \left( J_+ + J_- \right); \]
\[ V_I = \frac{5}{4} \left( 231J_+ + 315J_+J_+ + 735J_+^2 + 105J_+ J_+ + 925J_+ J_+ + \right. \]
\[ + 294J_+^2 - 5J_+^2 + 40J_+^2 - 60J_+J_+ \right\}; \]
\[ V_I = \frac{5}{4} \left( 33J_+^2 - 30J_+ J_+ + 15J_+ + 5J_+ J_+ J_+ - 10J_+ J_+ J_+ + \right. \]
\[ + 12J_+ J_+ J_+ \left( J_+ + J_+ + J_+ + J_+ \right) \left[ 33J_+^2 - 30J_+ J_+ + 15J_+ + \right. \]
\[ + 5J_+ J_+ J_+ - 10J_+ J_+ J_+ + \left. 10J_+ J_+ J_+ + 12J_+ J_+ J_+ \right\}; \]
\[ V_I = \frac{5}{4} \left( 33J_+^2 - 18J_+ J_+ - 123J_+ + J_+ J_+ + 10J_+ J_+ J_+ + \right. \]
\[ + 10J_+ J_+ J_+ + 102 \right\} \times \]
\[ \times (J_+ J_+ + J_+ J_+) \left[ 33J_+^2 - 18J_+ J_+ - 123J_+ + J_+ J_+ + \right. \]
\[ + 10J_+ J_+ J_+ + \left. \right] \right\}; \]
\[ V_I = \frac{5}{4} \left( 11J_+ - J_+ J_+ \right) - 50J_+ \left( J_+ + J_+ \right) \times \]
\[ \times (11J_+ - 3J_+ J_+ - 50J_+ J_+); \]
\[ V_I = \frac{5}{4} \left( 11J_+ - J_+ J_+ - 38 \right) \left( J_+ + J_+ \right) \times \]
\[ \times (11J_+ - J_+ J_+ - 38); \]
\[ V_I = \frac{5}{4} \left\{ J_+ J_+ + (J_+ + J_+ J_+) \right\}; \]
\[ V_I = \frac{5}{4} \left\{ J_+ + J_+ \right\}; \]

The calculation of the matrix elements relating states with different \( J \) calls for a separate analysis, for in this case the method of

1. Where.

Table 3.3 lists the linearly independent equivalent operators of the polynomials \( V_n^m \) of second, fourth, and sixth degree. The sign of the sum in the expressions for \( \Sigma V_n^m \) has been left out everywhere, and \( \rho \) stands for the distance between the electron and the nucleus.
equivalent operators becomes much more complicated. The results of some calculations are given in §3.6.

In calculating the matrix elements of the functions \( \psi_n^m \) it is useful to bear in mind that
\[
\langle J + h, J - m | V_n^m | J, J \rangle = (-1)^m \langle J + h, m - J | V_n^m | J, J - h \rangle.
\]

(3.8)

§3.3. Iron Group Element Compounds

It is well known from investigations of the static magnetic susceptibility [10] that the effect of the crystalline field is usually much stronger in these substances than the spin-orbit coupling, but is weaker than the forces that determine the principal term of the ion. Consequently the Hamiltonian for the paramagnetic ion of the iron group is best written in the following form:
\[
\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_{ss} + \mathbf{H}_{ls} + \mathbf{H}_{ss} + \mathbf{H}_r
\]
(3.9)

Here \( \mathbf{H}_0 \) is the principal part of the Hamiltonian, which includes all the free-atom interactions that are independent of the spin variables. The remaining terms of the Hamiltonian can be regarded as a perturbation, namely
\[
\mathbf{H}_{ls} = l S \]

is the spin-orbit interaction operator,
\[
\mathbf{H}_{ss} = -\beta \left[ (l S)^2 + \frac{1}{2} (l S) - \frac{1}{3} l (l + 1) S (S + 1) \right]
\]
is the spin-spin interaction operator [11], and
\[
\mathbf{H}_r = \beta (l + 2S) H
\]
is the energy of the electrons in the external magnetic field (the Zeeman energy). The splittings caused by the perturbation forces are of the order of:
\[
\mathbf{H}_{ls} \approx 10^4 \text{ cm}^{-1}, \quad \mathbf{H}_{ss} \approx 10^4 \text{ cm}^{-1}, \quad \mathbf{H}_{ss} \approx 1 \text{ cm}^{-1}, \quad \mathbf{H}_r \approx 1 \text{ cm}^{-1}.
\]

If only the principal Hamiltonian \( \mathbf{H}_0 \) is considered, then the total orbital momentum \( L \) and the spin momentum \( S \) will obviously be conserved.
quantities. We shall assume that the problem of the possible eigenstates of $\hat{A}^0$ has been solved by the self-consistent field method. In calculations by the perturbation method we shall start from the ground state $\hat{A}^0$, characterized by a definite electron configuration and by definite values of $L$ and $S$. The higher-order approximations, which take into account the influence of the excited terms of $\hat{A}^0$ will in most cases be unnecessary. Table 3.4 lists the configurations and terms of the ground states of different ions of the iron-group elements.

The calculation of the effect of the perturbations can be broken up into several stages. A comparison of the magnitudes of the perturbing forces shows that it is possible to calculate first the splitting of the $2L + 1$-fold orbital level under the influence of the crystalline field $H_{Kr}$, setting the remaining interaction aside for the time being.

Since we are dealing with $d$ electrons, expressions (3.3) and (3.4) for the potentials of the crystalline field can be simplified, leaving out the terms $U_n^m$ with $n = 6$. The matrix elements of the potential functions $V_n^m$ can be calculated with the aid of the equivalent operators of Table 3.3. It remains to determine the coefficients $\alpha$ and $\beta$. For this purpose it is sufficient to calculate one matrix element of some potential function $V_n^m$ with $n = 2$ and one with $n = 4$. We choose the functions $V_2^0$ and $V_4^0$, because they have only diagonal matrix elements. For what follows it is necessary to express any one of the wave functions of the principal term of the paramagnetic atom in terms of the one-electron $d$ functions. This is simplest to do by taking a state with maximum projections of the spin and orbital momenta $\{2 1 0 \ldots\}$, which obviously will be characterized by a symmetrical spin function and an antisymmetrical linear combination of the one-electron $d$ functions:
TABLE 3.4

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>Spin Term</th>
<th>$\lambda$, cm$^{-1}$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{2+}$</td>
<td>$d^2$</td>
<td>$^3D$</td>
<td>154</td>
<td>$-\frac{2}{27}$</td>
<td>$\frac{2}{83}$</td>
</tr>
<tr>
<td>V$^{2+}$</td>
<td>$d^4$</td>
<td>$^3P$</td>
<td>104</td>
<td>$-\frac{2}{105}$</td>
<td>$\frac{2}{315}$</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>$d^5$</td>
<td>$^3P$</td>
<td>55</td>
<td>$\frac{2}{105}$</td>
<td>$\frac{2}{315}$</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>$d^4$</td>
<td>$^3P$</td>
<td>87</td>
<td>$\frac{2}{105}$</td>
<td>$\frac{2}{315}$</td>
</tr>
<tr>
<td>Cr$^{2+}$</td>
<td>$d^5$</td>
<td>$^3D$</td>
<td>57</td>
<td>$\frac{2}{21}$</td>
<td>$-\frac{2}{83}$</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>$d^4$</td>
<td>$^3D$</td>
<td>85</td>
<td>$\frac{2}{21}$</td>
<td>$\frac{2}{83}$</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>$d^8$</td>
<td>$^5S$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$d^6$</td>
<td>$^3S$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>$^3D$</td>
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<td>$-\frac{2}{83}$</td>
<td>$\frac{2}{83}$</td>
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<td>$-\frac{2}{105}$</td>
<td>$\frac{2}{315}$</td>
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<td>$^3F$</td>
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<td>$\frac{2}{105}$</td>
<td>$\frac{2}{315}$</td>
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<tr>
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<td>$d^6$</td>
<td>$^3D$</td>
<td>-852</td>
<td>$\frac{2}{21}$</td>
<td>$-\frac{2}{83}$</td>
</tr>
</tbody>
</table>

1) Ion; 2) configuration; 3) principal term; 4) $\lambda$, cm$^{-1}$.

\[ f_m = R(r)Y_2^m(\theta, \phi) \] with $m = 2, 1, \ldots$ Thus, we choose from among the $2L + 1$ different coordinate functions $\psi_M$, corresponding to the ground state $\hat{\mathbf{R}}^0$, the function with the maximum magnetic quantum number $M$. It is easy to verify that if there are less than five $d$ electrons, then

\[ \int \psi_M \sum \psi_M^* \psi_M \, dt = \int f^2 \psi_M^* \psi_M \, dt + \int f^2 \psi_M^* \psi_M \, dt + \ldots \] (3.10)

The number of the integrals in the right half of the equation is equal to the number of $d$ electrons. If their number exceeds five, the calculation is made for the number of electrons lacking to fill the $d$ shell, and the result is taken with the opposite sign. The values of $\alpha$ and $\beta$ calculated in this manner are listed in Table 3.4.

In most of the salts investigated the crystalline field can be resolved into two components: a strong field of cubic symmetry and a
weak field of lower symmetry, for example trigonal or tetragonal. Thus, the energy $\hat{H}_{kr}$ is represented by the sum $\hat{H}_{kr} = \hat{K} + \hat{T}$. The cubic field $\hat{K}$ is produced frequently by the six water molecules located at the vertices of the octahedron whose center is occupied by the paramagnetic ion. This field changes little on going from one element in the iron group to another or even from one salt to another. The apparent reason for this is that the dimensions of the octahedron are determined by the diameter of the paramagnetic atom.

The field $\hat{T}$ has a dual nature: first, it is produced by all the ions of the crystal and has the symmetry of the latter, and second it is due to the deformation of the octahedron resulting from the Jahn-Teller effect. According to the well known theorem of Jahn and Teller [12], the stable state of a nonlinear system of atoms is the one having the least possible degree of degeneracy.

It is necessary to solve first the question of the effect of the cubic field. We see from Table 3.4 that only S, D, and F terms are encountered for the free ions of the iron-group elements. The ions in
the $S$ state will be considered separately. On the other hand, the qualitative picture of the splitting of the $D$ and $F$ terms can be obtained directly from group-theoretical considerations (Table 3.1). The $F$ term splits in a cubic-symmetry field into one singlet and two triplets (Fig. 3.1c and d), while the $D$ term splits into a doublet and a triplet (Fig. 3.1a and b). Calculation by the perturbation method yields the following values of the energies and the corresponding $\psi$ functions [9], calculated for the following two cases:

1) Quantization axis coincides with the trigonal axis of the cube

$$L=2\begin{pmatrix} \psi_1 - \psi_{1.1} \\ 1/\sqrt{2} (\psi_1 + \psi_{1.1}) & \psi_2 \\ 1/\sqrt{2} (\psi_1 - \psi_{1.1}) & \psi_3 \end{pmatrix}$$

2) Quantization axis coincides with the tetragonal axis of the cube

$$L=2\begin{pmatrix} \psi_1 + \psi_{1.1} \\ \psi_2 \\ \psi_3 \\ 1/\sqrt{2} (\psi_1 - \psi_{1.1}) \end{pmatrix}$$

$$\Delta = 6\beta^2 C_4$$

$$L=3\begin{pmatrix} 2/3 \psi_1 + 1/3 \sqrt{5/2} (\psi_2 - \psi_{1.1}) \\ \sqrt{3/8} \psi_1 + \sqrt{5/8} \psi_{1.1} \\ \sqrt{3/8} \psi_1 + \sqrt{5/8} \psi_{1.1} \\ \sqrt{3/8} \psi_1 + \sqrt{5/8} \psi_{1.1} \\ \sqrt{1/\sqrt{2}} (\psi_1 + \psi_{1.1}) \\ \sqrt{5/8} \psi_1 + \sqrt{3/8} \psi_{1.1} \\ \sqrt{5/8} \psi_1 - \sqrt{3/8} \psi_{1.1} \\ 1/\sqrt{2} (\psi_1 + \psi_{1.1}) \\ \sqrt{5/8} \psi_1 - \sqrt{3/8} \psi_{1.1} \\ \sqrt{5/8} \psi_1 + \sqrt{3/8} \psi_{1.1} \\ 1/\sqrt{2} (\psi_1 + \psi_{1.1}) \end{pmatrix}$$

$$\Delta = 54\beta^2 C_4$$

The modulus $\Delta$ denotes total splitting in the cubic field.

Gorter [15] considered the ordering of the energy levels produced under the influence of the field of the water-molecule octahedron, in other words, the question of the sign of $C_4$. It turned out that $C_4 > 0$. 

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It follows therefore that if the ion contains only one electron, then the lower orbital level will be a triplet and the upper a doublet. The electron configuration $d^6$ differs from $d^1$ by an addition of five electrons. Since the term corresponding to the configuration $d^5$ is $6_s$, which is affected by the action of the cubic field only if the higher approximations are taken into account, the same pattern of splitting of the orbital level will occur for both cases, $d^1$ and $d^6$ (Fig. 3.1a). The configuration $d^9$ can be regarded as a filled shell with one hole or with one positive electron. A similar correspondence will exist between the configurations $d^6$ and $d^4$. Consequently the level sequence in the case of $d^9$ and $d^4$ will be reversed (Fig. 3.1b).

For the configurations forming the $F$ terms, it is easy to conclude that in the case of $d^3$ and $d^8$ the lower orbital level will be a singlet (Fig. 3.1d); on the other hand, the configurations $d^7$ and $d^2$ correspond to an inverse sequence of levels, and consequently the lower level is a triplet.

Gorter has also shown that in tetrahedral complexes $C_4 < 0$ for the cubic component of the field. Consequently, the sequence of the sublevels will be the inverse of that indicated for ions with octahedral surroundings.

We now proceed to consider the remaining perturbations, which can be written, in accord with (3.9), in the form

$$\mathcal{H} = \tau + \lambda \mathcal{L} \mathcal{S} - \beta \left[ (\mathcal{L} \mathcal{S})^2 + \frac{\mathcal{L}}{2} (\mathcal{L} \mathcal{S}) - \frac{1}{3} \mathcal{L} (\mathcal{L} + 1) \mathcal{S} (\mathcal{S} + 1) \right] + \beta (\mathcal{L} + 2 \mathcal{S}) H_c \quad (3.12)$$

The experiments are usually made at such temperatures that one can regard as populated those energy levels whose distances from the ground level do not exceed a few hundred cm$^{-1}$. We can therefore be interested only in the lowest orbital level occurring in a cubic field. It is very important to know whether this level is simple or degenerate.
Let us assume that the lower level is simple. If we take into consideration the electron spin, then \((2S + 1)\)-fold degeneracy appears.

The field \(T\), which does not act on the electron spin, can produce only an inessential level shift. In a singlet orbital state, the average momentum \(L\) is zero, and consequently the spin-orbit interaction \(H_{LS}\) also vanishes in the first approximation. Consequently, it is necessary to take the second approximation into consideration, and this yields for the orbital level splitting values of approximately \(\lambda^2/\Delta \approx 1 \text{ cm}^{-1}\), that is, of the same order of magnitude as the Zeeman energy and the spin-spin interaction.

A method for calculating the splittings of the ground state of a magnetic ion was developed in [16, 17] and has found extensive use in experimental investigations of paramagnetic resonance; it is known as the spin-Hamiltonian method. It consists of the following. We go through the usual perturbation theory procedure in two stages. We first calculate the matrix elements \(\hat{H}'\) with the aid of the coordinate wave functions, this being possible by virtue of the fact that the unperturbed Hamiltonian is independent of the spin variables. As a result the perturbation energy turns out to be a function of the spin operator \(\hat{S}\); we shall call this function the spin Hamiltonian.

It is easy to show that the spin Hamiltonian has the form

\[
\mathcal{H}_{\text{spin}} = D_{ij} \hat{S}_i \hat{S}_j + g_{ij} H_e \hat{S}_z,
\]

where the tensors \(D_{ij}\) and \(g_{ij}\) are determined from the formulas

\[
\begin{align*}
D_{ij} &= \frac{L}{\mathcal{L}} \Lambda_{ij} + \lambda_{ij} \Lambda_{ij} + 2 \frac{E_0 - E_n}{E_n} \Lambda_{ij} \\
\Lambda_{ij} &= \sum_{n_k \neq n_i} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0} \\
l_{ij} &= \frac{1}{2} \left\langle 0 | L_i L_j + L_j L_i | 0 \right\rangle - \frac{1}{2} L (L + 1) \delta_{ij},
\end{align*}
\]

(3.13)  (3.14)

Here \(i, j = x, y, z\), and \(E_0\) and \(E_n\) denote the energies of the ground and excited orbital levels, respectively.
If $\mathbf{H}_{kr}$ has tetragonal or trigonal symmetry, then the tensors $D_{ij}$ and $g_{ij}$ are characterized by two principal values, corresponding to two directions: parallel and perpendicular to the symmetry axis. Taking the symmetry axis to be the $Z$ axis, we have

$$\mathcal{H}_{cr} = D \left[ \hat{S}_z - \frac{1}{3} \hat{S}(\hat{S} + 1) \right] + \beta g_{i} \hat{H}_z \hat{S}_z + \beta g_{\perp} (\hat{H}_x \hat{S}_x + \hat{H}_y \hat{S}_y).$$

(3.15)

Deviations from tetragonal symmetry can be taken into account by adding the term $E(\hat{S}_x^2 - \hat{S}_y^2)$ and replacing $g_\parallel$ by the coefficients $g_x$ and $g_y$.

The part of the spin Hamiltonian proportional to $D$ (and to $E$) determines the splitting of the orbital level in the absence of an external magnetic field. The terms proportional to $H_{0x}$, $H_{0y}$, and $H_{0z}$ indicate that the magnetic moment of the atom in the crystal is anisotropic; deviations of the $g$ factor from the value $g = 2$ denote that a small fraction of the momentum connected with the orbital motion is added to the spin momentum of the electrons.

The spin-Hamiltonian method makes it possible to describe the spectrum of paramagnetic resonance by means of a small number of constants: $D$, $E$, $g_{\parallel}$, $g_{\perp}$, ... The determination of these constants from the form of the spectrum constitutes the main task of the experiments in paramagnetic resonance. The theoretical problem is to determine these constants on the basis of a definite model of the crystal.

The theory developed here applies primarily to ions whose lower orbital level in a cubic field is a singlet. These include the ions $\text{Cr}^{3+}$, $\text{V}^{2+}$, and $\text{Ni}^{2+}$. The ions $\text{Cr}^{2+}$, $\text{Mn}^{3+}$, and $\text{Cu}^{2+}$ should also be included in this group, if the field $T$ has a tetragonal symmetry. In the case of these ions $L = 2$ and the lower level resulting from the action of the cubic field is an orbital doublet, on which, in accord with (3.11), the spin-orbit coupling $H_{LS}$ has no influence whatever, while a tetragonal field does split it. Thus, the lower orbital level will
again be simple, and its spin degeneracy will as before be \((2S + 1)\)-fold.

Let us consider a more general case, when the degeneracy of the lower orbital level in a cubic field makes the matrix elements of the spin-orbit coupling \(H_{LS}\) different from zero even in the first approximation. Now the perturbations caused by the spin-orbit coupling \(H_{LS}\) and by the field \(T\) are of the same order of magnitude and should be considered simultaneously. Because of the Jahn-Teller effect, the paramagnetic ion should have minimum degeneracy following the action of these forces. If we apply in addition the Kramers theorem, then we arrive at the following important conclusions: \(H_{LS}\) and the lower-symmetry field \(T\) cause complete splitting of the energy levels of paramagnetic ions with an even number of electrons. Now not only the orbital but also the spin levels will be simple. As a rule, the intervals between these levels exceed \(1\ \text{cm}^{-1}\), and consequently paramagnetic resonance can be observed only with the aid of radio frequency fields in the millimeter band.

If the paramagnetic ion has an odd number of electrons, then the Kramers double degeneracy is retained. In this case the splitting of the energy level in an external magnetic field can be calculated by introducing an effective spin with value \(1/2\). The spin Hamiltonian will have the following simple form:

\[
\mathcal{H}_s = \beta \left( g_x H_x S_x + g_y H_y S_y + g_z H_z S_z \right),
\]

where \(S'_i\) are the Pauli matrices. We shall not stop to discuss the connection between the coefficients \(g_x\), \(g_y\), and \(g_z\) with \(\lambda\) and with the constants of the crystalline field.

Many investigations have been devoted to a detailed theoretical analysis of the paramagnetic resonance spectra of salts of cobalt [18, 19], nickel [20-22], and copper [23-25]. In particular, many theoretical
investigations have been devoted to chrome alums [26-34], which are extensively used in adiabatic demagnetization.

In order to determine the form of the paramagnetic resonance spectrum, it is necessary to know not only the system of the lower energy levels of the paramagnetic ions, but also the probabilities of the magnetic dipole transitions between these levels. The probability of transition between any two levels $M$ and $M'$ is proportional to the square of the nondiagonal matrix element of the projection of the magnetic moment of the electrons on the direction of the alternating magnetic field $|\langle M, \mu_{H_1} M' \rangle|^2$. These matrix elements are particularly easy to calculate if the spin Hamiltonian has been established. If the position of the alternating magnetic field intensity vector is defined in terms of direction cosines $a_1$, $a_2$, and $a_3$, then we can write for the operator of the component of the magnetic moment:

$$\hat{H}_M = a_1 \hat{S}_x + a_2 \hat{S}_y + a_3 \hat{S}_z.$$  \hspace{1cm} (3.17)

It remains to calculate the matrix elements $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ with the aid of the spin wave eigenfunctions of the levels $M$ and $M'$.

§3.4. Paramagnetic Resonance Spectrum of Nickel Ion in an Axial Crystalline Field

We shall examine the general methods used to calculate the paramagnetic spectrum resonance using by way of an example the Ni$^{2+}$ ion in a tetrahedral or trigonal field of a crystal. These calculations pertain, in particular, to the well investigated nickel fluorosilicates, in which the crystalline field has a tetrahedral symmetry. The lower orbital level of Ni$^{2+}$ is a singlet (Fig. 3.1d), and the spectrum can therefore be calculated with the aid of the spin Hamiltonian (3.15), provided that the tetragonal axis is directed along the $Z$ axis.

The nonvanishing matrix elements of the vector $\hat{\mathbf{S}}$ can be calculated from the well known formulas (7):
\[
\begin{align*}
\langle M | S_x | M + 1 \rangle &= \sqrt{3} (S_z + 1) - M (M + 1), \\
\langle M | S_x | M \rangle &= M.
\end{align*}
\] (3.18)

In our case \( S = 1 \), and the nonvanishing elements of \( \mathbb{F} \) assume the following values

\[
\begin{align*}
\langle -1 | S_x | 0 \rangle &= \langle 0 | S_x | 1 \rangle = \frac{1}{\sqrt{2}}; \\
\langle -1 | S_x | 0 \rangle &= \langle 0 | S_x | 1 \rangle = \frac{i}{\sqrt{2}}; \\
\langle -1 | S_x | -1 \rangle &= -1; \langle 1 | S_x | 1 \rangle = 1.
\end{align*}
\] (3.19)

We assume first that the static magnetic field \( H_0 \) is parallel to the tetragonal axis of the crystal. Then the possible values of the spin-level energies \( E_i \) and the corresponding spin wave functions \( \eta_i \) are determined from the equation

\[
\mathbb{H} \eta = E \eta.
\] (3.20)

It is convenient to use the value of \( D \) as the energy unit. We therefore introduce the notation

\[
\begin{align*}
\epsilon_i &= \frac{E_i}{D}, \\
x_{\|} &= \frac{\epsilon_i H_0}{D}, \\
x_{\perp} &= \frac{\epsilon_{i+1} H_0}{D}.
\end{align*}
\] (3.21)

We denote by \( \eta_M \) the eigenfunction \( \hat{S}_z \), corresponding to the eigenvalue \( M \). Since we are using a representation in which the matrix \( \hat{S}_z \) is diagonal, the matrix (3.20) is obviously also diagonal and consequently the eigenvalues of \( \hat{H}_{SD} \) and the corresponding eigenfunctions are

\[
\begin{align*}
\epsilon_0 &= 0, \quad \eta_0 = \eta, \\
\epsilon_\pm &= \frac{1}{2} \epsilon_{\|}, \quad \eta_\pm = \eta_{\|}, \\
\epsilon_\mp &= \frac{1}{2} \epsilon_{\perp}, \quad \eta_\mp = \eta_{\perp}.
\end{align*}
\] (3.22)

With the aid of (3.22), (3.19), and (3.17) we can readily ascertain that the magnetic dipole transitions between the spin levels are possible only under the influence of the alternating magnetic field component perpendicular to the \( Z \) axis. According to (3.19) two absorption lines of equal intensity \( \left( \frac{13}{4} \right)^2 \) should occur, corresponding to the transitions \( 1 \rightarrow 0 \) and \( 0 \rightarrow 1 \).

Let us assume now that the magnetic field \( H_0 \) is perpendicular to the crystal axis. If we assume the field \( H_0 \) to be parallel to the \( X \) axis, then the spin Hamiltonian assumes the form

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With the aid of (3.18) we obtain the following secular equation for the determination of the spin energy levels:

\[
\begin{bmatrix}
1 - \varepsilon & \frac{x_1}{\sqrt{2}} & 0 \\
\frac{x_1}{\sqrt{2}} & -\varepsilon & \frac{x_1}{\sqrt{2}} \\
0 & \frac{x_1}{\sqrt{2}} & 1 - \varepsilon
\end{bmatrix} = 0.
\] (3.24)

The solution of this equation yields the following eigenvalues and eigenfunctions:

\[
\begin{align*}
\varepsilon_a &= \frac{1}{2}(1 - \varepsilon), & \eta_a &= \frac{x_1}{\sqrt{2}} \left( \eta_1 - \frac{1 + \varepsilon}{2x_1} \eta_0 + \eta_n \right), \\
\varepsilon_b &= 1, & \eta_b &= \frac{1}{\sqrt{2}} (\eta_1 - \eta_0), \\
\varepsilon_c &= \frac{1}{2}(1 + \varepsilon), & \eta_c &= \frac{x_1}{\sqrt{2}} \left( \eta_1 - \frac{1 - \varepsilon}{2x_1} \eta_0 + \eta_n \right), \\
\varepsilon_* &= \sqrt{1 + 4x_1^2}.
\end{align*}
\] (3.25)

The matrix elements of the components of the vector \( \vec{S} \), calculated with the aid of the spin functions (3.25) are

\[
\begin{align*}
\langle a | S_x | b \rangle &= \langle b | S_x | c \rangle = 0, & \langle a | S_x | c \rangle &= -\frac{1}{\varepsilon}, \\
\langle a | S_y | b \rangle &= -i \sqrt{\frac{1 + \varepsilon}{2}}, & \langle b | S_y | c \rangle &= i \sqrt{\frac{1 - \varepsilon}{2}}, \\
\langle a | S_y | c \rangle &= 0, \\
\langle a | S_z | b \rangle &= -\frac{\sqrt{2x_1}}{\sqrt{1 + 1/\varepsilon}}, & \langle b | S_z | c \rangle &= -\frac{\sqrt{2x_1}}{\sqrt{1 - 1/\varepsilon}}, \\
\langle a | S_z | c \rangle &= 0.
\end{align*}
\] (3.26)

It is seen from these formulas that in strong magnetic fields, when \( x_1 \gg 1 \), paramagnetic resonance occurs only if the alternating field is perpendicular to the field \( H_0 \). In weak and intermediate magnetic fields, the matrix element is \( \langle a | S_x | c \rangle \neq 0 \) and consequently resonant paramagnetic absorption is possible between the levels \( a \) and \( c \), provided the static and alternating magnetic fields are parallel to each other. A scheme of the energy levels and of the possible transitions is shown in Fig. 3.2.
§3.5. Hyperfine Structure of Paramagnetic Resonance Spectra

The theory of the hyperfine structure of atomic spectra was developed long ago. The novelty in its application to paramagnetic resonance spectra of crystals lies in the need for taking into account the effect of the crystalline field and a few other effects which are of no significance in optical research. The first calculations of the hyperfine structure of paramagnetic resonance spectra, pertaining to copper salts, namely Tutton's salt [35] and the fluorosilicate [36], have disclosed a clear-cut disagreement with the experimental data. The differences between theory and experiment became particularly sharp when, in spite of the theoretical predictions, a hyperfine structure was experimentally established for the paramagnetic absorption lines in the salts of Mn$^{2+}$.

All these contradictions were eliminated with the aid of the "s-configuration interaction" hypothesis [37]. It is well known [38] that the magnetic interaction of the s electrons with the nucleus is much
stronger than that of the electrons with $l \neq 0$. It was assumed that the ground state of the paramagnetic ion contains besides the usually assumed configuration $3d^n$ also a small admixture of configurations containing an unpaired $s$ electron. It is most probable that the hyperfine structure is due to the admixture of the configuration $3s^6d^n4s$ because, first, the transition of the $3s$ electron to the $4s$ orbit calls for a small expenditure of energy; second, in this configuration the total orbital and spin angular momenta can assume the same quantum values $L$ and $S$, resulting from Hund's rule for the ground state of the ion. The $s$ configuration interaction takes place in free atoms and depends little on the crystalline field.

A confirmation of the hypothesis of $s$ configuration interaction can therefore be the isotropy of the hyperfine structure of the paramagnetic resonance spectrum and the fact that the hyperfine splitting constant is approximately the same for all the investigated salts of Mn$^{2+}$. It must be noted that the $s$ configuration effect is particularly important for salts of the iron-group elements, for in these crystals the orbital magnetism is suppressed (the orbital levels are singlets), which greatly reduces the hyperfine splitting.

The general theory of the hyperfine structure of paramagnetic resonance spectra of iron-group element compounds has been developed in [17]. If the paramagnetic atom has a nuclear spin different from zero, then the following expression is added to the Hamiltonian (3.9)

$$
\hat{H}' = \mu \left[ (L^2) + [2L(L+1) - J] S^2 - \frac{3}{2} \right] (\hat{L} \cdot \hat{S}) - \frac{3}{2} \hat{L}^2 + \frac{1}{2} \hat{S}^2 - \mu H_{\text{int}},
$$

where

$$
\rho = \frac{2\mu H_{\text{int}}}{\mu}, \quad q' = \frac{\mu^2 q}{2(2l+1)^2}, \quad \lambda = \frac{(2l+1)-4s}{s(2l-1)(2l+3)(2l-1)},
$$

\[ q = \pm 2s. \]
if \( I \) is the nuclear spin, \( g_N \) is the magnetic moment, and \( \eta \) is the quadrupole moment of the nucleus; \( \eta \) has a plus or minus sign depending on whether the first or second half of the d shell of the atom is filled. The first term in (3.27) takes into account the interaction between the electrons and the magnetic moment of the nucleus, while the second represents the interaction with the quadrupole nuclear moment and the third the energy of the nucleus in the external magnetic field. The coefficient \( k \) is introduced to allow for the influence of the s-configuration interaction. A theoretical calculation of \( k \) is extremely complicated. On the other hand, comparison with the experimental data has disclosed the interesting fact that the coefficient \( k \) is practically the same for all ions of the iron group.

The transition from (3.27) to the spin Hamiltonian can be carried out by the method described in §3.3. We know that it is necessary to distinguish between two cases, depending on whether the atom is in a simple or degenerate state after the action of the cubic field of the crystals. In the former case the spin Hamiltonian, with account of the interaction between the moments of the nucleus and the electron shell and with the external magnetic field has the form

\[
\mathcal{H}_n = A_J \hat{S}_J + P \hat{I}_J - g_N \mu_B \hat{H}_d. \tag{3.28}
\]

If the resultant crystalline field has trigonal or tetragonal symmetry, then

\[
\mathcal{H}_n = A_J \hat{S}_J + B(\hat{S}_x \hat{J}_x + \hat{S}_y \hat{J}_y) + P\left( I^2 - \frac{1}{3} I(I+1) \right) - g_N \mu_B \hat{H}_d. \tag{3.29}
\]

In the second case, the spin Hamiltonian will have the same form but \( \hat{S} \) now stands for the effective spin \( \hat{S}' \). We shall not dwell here on the connection of the coefficients \( A \) and \( B \) with the constants of the crystalline field and the nuclear moments, but it is obvious that the constants of the magnetic hyperfine structure \( A \) and \( B \) are proportional to \( g_N(I/I^3) \), and the quadrupole interaction constant \( P \) is proportional to
The intensity of the individual hyperfine components of the paramagnetic resonance spectrum will be determined as before only by the magnitude of the matrix element of the electron magnetic moment (3.17), since the nuclear magnetic moment is very small. Consequently, in the simplest cases when the component of the nuclear angular momentum $I_z$ is conserved, a selection rule $\Delta m = 0$ exists for the magnetic quantum number.

Most theoretical calculations and experimental researches pertain to strong magnetic fields, the action of which on the unpaired electrons of the paramagnetic atoms exceeds greatly the interactions between the latter and the moments of the nucleus. Calculations of hyperfine splitting in weak magnetic fields are more complicated and have been made only for a few particular cases [39].

In order to verify the hypothesis of the s-configuration interaction, an analysis was made in [37] of the experimental data on the optical spectra of neutral atoms and paramagnetic resonance spectra of the ions of the 3d-transition group elements. This analysis confirmed a premise already stated by Fermi [38] that if there are no s electrons in the ground state of the atom, then an appreciable portion of the hyperfine splitting is frequently determined by the unpaired s electrons of the excited levels. A quantitative estimate of the coefficient $k$ was also made [40] with the aid of the Hartres-Fok functions and yielded a value approximately ten times smaller than that observed. The discrepancy between the theory and experiment can be attributed to the fact that the Hartres-Fok method is not suitable for the calculation of the wave functions near the nucleus.

§3.6. Parameters of the Crystalline Field. The Jahn-Teller Effect

Up to now all the calculations of the energy spectra of the paramagnetic ions in crystals were carried out by the "crystalline field"
method. The parameters of the crystalline field \( A^m_n \) were determined here as a rule by comparing the theoretical results with the experimental data on paramagnetic resonance, on the temperature dependence of the static paramagnetic susceptibility, on the optical absorption spectra, etc. It would be interesting to make a theoretical estimate of the magnitude of the crystalline field and primarily its principal cubic component. Van Vleck [13] and Polder [6] made a numerical calculation under the assumption that the cubic field is made by six point-like charges \( e_{\text{eff}} \) or by six dipoles each with moment \( \mu_e \), located at the vertices of an octahedron at a distance \( R \) from the center. It follows from this model that the parameter \( C_4 \), which was introduced in (3.7), has a value

\[
C_4 = -\frac{35}{4} \frac{r_1^4}{\alpha^4}, \quad \text{or} \quad C_4 = \frac{175}{4} \frac{\mu_e}{R^4}.
\]  

(3.30)

An x-ray structural analysis of alums [41] has shown that \( R = 2.0 \) \( \text{A} \).

To calculate the splitting \( \Delta \) we must also know the value of \( r^7 \) for the 3d electrons. If we use the 3d hydrogen functions, we obtain

\[
r^7 = 126a^7 Z^{-1} = 4.10a^7, \quad \text{or} \quad r^7 = 25.515a^7 Z^{-1} = 31.2a^7.
\]

(3.31)

We have assumed here \( Z = 5.35 \), which follows from the experimental value of 43 ev for the ionization potential of Ti\(^{3+}\). If we assume \( e_{\text{eff}} = -e \) or \( \mu_e = 2.10^{-18} \) CGSE, then the calculated intervals between energy levels in the cubic field are in good agreement with the experimental data. This agreement must nevertheless be regarded as fortuitous, since the model assumed is very crude. Kleiner [42] made more precise calculations for chrome alums, taking into consideration the distribution of the electron cloud in the oxygen ion. The water molecules have their oxygen atoms, which can be regarded as \( O^- \) ions, facing the center of the octahedron. The results of the calculations were in complete contradiction to the experimental data, for even the sign of
the parameter $C_4$ was found to be incorrect. Tanabe and Sugano [43] took account of the covalent bonds between the central ion and the surrounding atoms (see §3.8). Exchange effects cause an inversion of the energy levels and their sequence becomes correct. The absolute value of $C_4$ turns out here to be about $3/2$ times larger than the experimental value.

We have already indicated that only in the first approximation does the crystalline field surrounding a paramagnetic particle have a cubic symmetry in the case of the salts of the iron-group elements. Actually, however, appreciable deviations exist. Superimposed on the strong cubic field is a weak field of lower symmetry, the origin of which is connected with the following three different causes [26].

1. Direct action exerted on the paramagnetic particle by the electric field of the remote particles situated outside the octahedral complex. In alums, for example, this field has a trigonal symmetry and can be represented in the following form:

$$V_{\text{rest}} = (Q + 30Hr^3)(xy + yz + zx) - 35H(x^2y + xy^2 + y^2z + yz^2 + z^2x) + C.$$ \hspace{1cm} (3.32)

Here $x$, $y$, and $z$ are the Cartesian coordinates of the electron and pertain to the principal cubic axes; $G$ and $H$ are constants independent of $r$; $C$ is a polynomial with cubic symmetry and therefore immaterial for our purposes. If we introduce the spherical coordinates $R_i$, $\alpha_i$, and $\beta_i$, which define the position of the charge $e_1$ relative to the paramagnetic center, then we obtain the following expressions for the constants $G$ and $H$:

$$G = -\sum e_i e_R R_i^{-3} \left( \frac{3}{2} \cos^2 \alpha_i \cos \frac{1}{2} \right),$$

$$H = -\frac{1}{63} \sum e_i e_R R_i^{-3} \left[ 35 \cos^4 \alpha_i - 30 \cos^2 \alpha_i - 3 \cos^2 \sin^2 \alpha_i \cos 3\beta_i \right] + 7\sqrt{2} \cos \alpha_i \sin \alpha_i \cos 3\beta_i.$$ \hspace{1cm} (3.33)

Calculations shows that for titanium alums, for example, the splitting of the lower energy level by the field (3.32) is equal to about 350 cm$^{-1}$. 
2. Indirect action of the remote particles. The remote particles cause the octahedral complex to become deformed and distort its cubic field. If we have three pointlike charges $a$, $b$, and $c$, then the direct action of charge $a$ on charge $c$ is stronger than the indirect action due to the motion of charge $b$ under the influence of charge $a$. In our case, however, the indirect action can exceed the direct action, since the electron clouds of the particles forming the paramagnetic octahedral complex overlap one another. One proof of the significance of the indirect action is the well-known fact that the initial splittings of the spin level of iron alums increase when they are magnetically diluted by substituting aluminum ions for the iron ions. In this case the direct effect cannot change appreciably, since the iron and aluminum ions have the same charge, and the radii of these ions are very small compared with the distances between trivalent atoms. On the other hand, the deformation of the octahedron can be greatly influenced by whether the ion at its center is iron or aluminum.

3. The Jahn-Teller effect. This cause of lattice deformation, which leads to a lowering of the symmetry of the crystalline field, is frequently very important. The Jahn-Teller theorem was initially proved for molecules [12] and then extended to include crystals [13, 14]. According to this theorem, the geometrical configuration of nuclei cannot be stable if the electron state of the molecule is degenerate, except in the two following cases: a) the molecule is linear, that is, the nuclei lie on one line; b) the molecule contains an odd number of electrons, and the degeneracy of its electron state is a double Kramers degeneracy, that is, one that cannot be lifted by any change in the electrostatic forces.

The lowering of the symmetry of nuclear configuration, if we exclude the two indicated cases, will lift the degeneracy of the elec-
tron state. It can be proved that the mean energy of different electron states remains constant after the splitting of the energy level. Thus, at least one electron level will lie below the initial one after the deformation of the molecule.

Van Vleck [13] made the transition from the molecule to the crystal by considering the behavior of an octahedral paramagnetic complex in an external trigonal field. The Hamiltonian $\hat{H}$ of the electron state contains as parameters the distances between the centers of the particles (atoms or molecules) forming the complex. An arbitrary displacement of these particles can be described with the aid of 21 normal vibrational coordinates $Q_i$. Expanding the Hamiltonian in powers of $Q_i$ we get

$$\hat{H} = \hat{H}_0 + \hat{V}_{\text{trig}} + \sum_i \hat{V}_i Q_i.$$  (3.34)

Here $\hat{H}_0$ contains all the interactions that are possible inside the regular octahedral complex and are independent of the electron spin of the paramagnetic ion; $\hat{V}_{\text{trig}}$ takes into account the effect of the remote atoms of the crystal lattice. Let $W_0$ be one of the eigenvalues of $\hat{H}_0$. Connected with the energy $W_0$ is one of the set of wave functions given in (3.11). By considering the second and third terms of (3.34) as a perturbation, we can set up and solve a secular equation, the solution of which will give in first approximation the correction to the energy $W_0$. The energy of the entire system is thus a certain function of the displacements $Q_i$. By solving the system of equations

$$\frac{\partial W}{\partial Q_i} = 0 \quad (i=1,2,3,...),$$  (3.35)

we can find such displacements $Q_i^0$ as correspond to a minimum energy $W$, and consequently, to the most stable configuration of the paramagnetic complex. Van Vleck made detailed calculations for titanium, vanadium,
and chrome (excited state) alums. The $Q_1^0$ were found to be of the order of $10^{-9}$ cm. The potential of the low-symmetry crystalline field resulting from the distortion of the octahedral configuration of the water molecules will be a quadratic function of $Q_1^0$. The splittings of the orbital levels due to this field have been calculated to be on the order of $10^2$ cm$^{-1}$. The potential energy of the $f$ electrons of rare-earth atoms in the crystalline field is approximately 100 times smaller than the energy of the $d$ electrons of the iron-group atoms. Consequently $Q_1^0 \approx 10^{-11}$ cm in rare-earth crystals, and consequently the level splitting due to the Jahn-Teller effect can have an approximate value $10^2 \cdot (10^{-2})^2 = 10^{-2}$ cm$^{-1}$. As will be shown below, experiment confirms this conclusion.

The Van Vleck theory was further developed by Pryce and his co-workers [14]. From general considerations, they reached the conclusion that the Jahn-Teller effect pertains not only to degenerate but also to almost-degenerate systems. An interesting example of such almost-degenerate systems are linear triatomic molecules of the type BAB.

In addition, they investigated in detail octahedral complexes which, let us note, are encountered not only in paramagnetic salts, but also in crystals containing F centers, luminescent centers, exciton states, etc. The degeneracy of the electron state of an octahedral paramagnetic complex can be triple or double. If the degeneracy of the energy level is triple, then the deformation of the complex on going to stable nuclear configurations will follow in some cases the (100) axis, and in others the (111) axis. As a result, the complex has either a tetragonal or trigonal symmetry. If the degeneracy is double, the situation is more complicated. The point is that in this case the energy splitting due to the deformation of the complex is proportional to $Q_2^2 + Q_3^2$ if we denote by $Q_2$ and $Q_3$ certain normal vibrational coord-
ordinates of an octahedron of even type. It is convenient to introduce new variables \( \rho \) and \( \alpha \):

\[
Q_x = \rho \sin \alpha, \quad Q_y = \rho \cos \alpha.
\]  

(3.36)

It is clear that the splitting is independent of \( \alpha \). Thus, there exists an infinite set of configurations corresponding to one and the same value of the energy. If we take anharmonic effects into account, then we find that the most stable configuration is obtained by stretching the octahedron along one of the tetragonal axes.

All these results, as indicated by Abragam and Pryce [36] can explain why copper salts, the crystals of which have trigonal symmetry, have an isotropic \( g \) factor and an isotropic and small hyperfine structure constant. In a field of cubic symmetry, the lower orbital level of the copper ion is doubly degenerate and the wave functions belonging to it are, in accord with (3.11), \( \varphi_1 = \psi_0 \) and \( \varphi_2 = (1/2)(\psi_2 + \psi_{-2}) \).

Neither spin-orbit interaction nor a field of trigonal symmetry can lift the degeneracy. The only reason for the splitting of the given orbital level is the Jahn-Teller effect. The following wave functions will belong to the energy sublevels:

\[
\begin{align*}
\psi_1 &= \psi_1 \cos \alpha - \psi_2 \sin \alpha, \\
\psi_2 &= \psi_1 \sin \alpha + \psi_2 \cos \alpha.
\end{align*}
\]  

(3.37)

The principal values of the \( g \) tensor, calculated with the aid of these functions, are

\[
\begin{align*}
\epsilon_x &= 2 - \frac{1}{2} \left( \cos \alpha - \sqrt{3} \sin \alpha \right), \\
\epsilon_y &= 2 + \frac{1}{2} \left( \cos \alpha + \sqrt{3} \sin \alpha \right), \\
\epsilon_z &= 2 - 4 \frac{\lambda}{\Delta} \cos \alpha.
\end{align*}
\]  

(3.38)

If we average over \( \alpha \), we obtain \( \bar{\epsilon}_x = \bar{\epsilon}_y = \bar{\epsilon}_z = 2 - 4(\lambda/\Delta) \). We can explain in similar fashion the isotropy of the hyperfine structure of the paramagnetic resonance spectrum.
§3.7. Salts of Rare-Earth Elements

It is well known that the room-temperature static magnetic susceptibility of rare earth salts can be calculated by assuming that the carriers of the paramagnetism are the three rare earth ions in states determined by Hund's rule [10]. This hypothesis is also confirmed by optical data [44]. We can therefore conclude, first, that deviations from the normal (Russel-Saunders) coupling are small, at least in the ground states, and second, that the action of the crystal field on the paramagnetic ion is weak and not capable of disturbing the spin-orbit coupling. The latter is explained by the following two singularities of rare earth ions.

1. The magnetic properties of the rare earth ions are due to the low-lying 4f-electrons, the mean distance of which to the nucleus is much smaller than that of the 3d electrons. In addition, the external electron shell has a screening effect. The crystalline field therefore causes in the rare earth elements level splittings on the order of 100 cm⁻¹, i.e., about 100 times smaller than in ions of the iron group.

2. Multiple splitting is much larger in rare earth ions than in iron-group ions; it has an order of 10³-10⁴ cm⁻¹.

The spin orbit coupling thus turns out to have a much stronger influence than the crystalline field, and therefore the Hamiltonian for the paramagnetic ion must be written in the form

\[ H = H^0 + H_p + H_x \]  \hspace{1cm} (3.39)

Here \( H^0 \) is the Hamiltonian of the free ion. In the perturbation-method calculations we shall start from the ground state at \( H^0 \), in which the conserved quantities can be taken to be the total angular momentum \( J \) and the orbital and spin momenta \( L \) and \( S \). Sometimes higher approximations, which take into account the influence of the excited levels of \( H^0 \), are of importance; it is usually sufficient to consider the first
excited multiplet level. The intervals between the ground and first-excited levels are known for many elements from optical and magnetic measurements. For the remaining elements, the multiplet-structure constant can be estimated, in accordance with [45], from the following formula:

$$\lambda = 200(Z - 55)c_{1}^{-1}.$$  \hspace{1cm} (3.40)

Table 3.5 lists the ground state of the rare earth ions, and also the data on the first excited energy levels, known from experiment and obtained with the aid of (3.40).

Let us proceed to examine the splittings of the \((2J + 1)\)-fold level of a free ion in a crystalline field \(\hat{K}\). Unlike the hydrated salts of the iron group elements, in which the paramagnetic ion is usually surrounded by an octahedron of water molecules which produces a strong electric field of cubic symmetry, in most salts of rare earth elements the paramagnetic ion surrounding produces a field of trigonal symmetry [47]. The energy levels of ions containing an odd number of electrons therefore splits into \(J + 1/2\) doublets (Table 3.2); on the other hand, if the number of electrons is odd, singlets and doublets are obtained (Table 3.1).

For a quantitative calculation it is first necessary to find an expression for the potential of the crystalline field.* In the case of a \(C_{3v}\) symmetry (formates) the potential is given by formula (3.3b), in which all six coefficients \(A_{n}^m\) differ from zero. For the somewhat higher symmetry \(C_{3h}\) (ethyl sulfates, bromates), we have \(A_{4}^{3} = A_{6}^{3} = 0\). The matrix elements \(H_{kj}\) necessary for the calculations in the first perturbation-theory approximation can be obtained with the aid of the equivalent operators (Table 3.3); the common factors \(\alpha, \beta, \gamma\) for all rare earth ions can be determined with the aid of the \(\psi\) functions corresponding to the states with maximum \(J_{z}\), by changing over from the
TABLE 3.5
Energy Levels of Free Rare Earth Ions

<table>
<thead>
<tr>
<th>Element (X^{2+})</th>
<th>J</th>
<th>2 (Основное состояние)</th>
<th>3 (Возбужденное состояние)</th>
<th>(E_1 - E_2) (теорет.) cm(^{-1})</th>
<th>(E_1 - E_2) (эксперимент.) cm(^{-1})</th>
<th>7 (Ссылка)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce 58</td>
<td>(f^{7+}F_{7/2})</td>
<td>(F_{7/2})</td>
<td>2 100</td>
<td>2 240</td>
<td>[46]</td>
<td></td>
</tr>
<tr>
<td>Pr 59</td>
<td>(f^{7+}H_{9/2})</td>
<td>(H_{9/2})</td>
<td>2 000</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd 60</td>
<td>(f^{7+}H_{11/2})</td>
<td>(H_{11/2})</td>
<td>1 800</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pm 61</td>
<td>(f^{7+}H_{13/2})</td>
<td>(H_{13/2})</td>
<td>1 500</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm 62</td>
<td>(f^{7+}H_{15/2})</td>
<td>(H_{15/2})</td>
<td>980</td>
<td>1 100</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>Eu 63</td>
<td>(f^{7+}F_{7/2})</td>
<td>(F_{7/2})</td>
<td>270</td>
<td>300, 340</td>
<td>[3, 47]</td>
<td></td>
</tr>
<tr>
<td>Gd 64</td>
<td>(f^{7+}S_{9/2})</td>
<td>(S_{9/2})</td>
<td>3 300</td>
<td>-</td>
<td>[46]</td>
<td></td>
</tr>
<tr>
<td>Tb 65</td>
<td>(f^{7+}F_{7/2})</td>
<td>(F_{7/2})</td>
<td>2 000</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy 66</td>
<td>(f^{7+}F_{7/2})</td>
<td>(F_{7/2})</td>
<td>3 300</td>
<td>-</td>
<td>[46]</td>
<td></td>
</tr>
<tr>
<td>Ho 67</td>
<td>(f^{7+}H_{9/2})</td>
<td>(H_{9/2})</td>
<td>5 800</td>
<td>5 050</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>Er 68</td>
<td>(f^{7+}H_{11/2})</td>
<td>(H_{11/2})</td>
<td>6 500</td>
<td>8 000</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>Tm 69</td>
<td>(f^{7+}H_{13/2})</td>
<td>(H_{13/2})</td>
<td>8 400</td>
<td>8 250</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>Yb 70</td>
<td>(f^{7+}F_{7/2})</td>
<td>(F_{7/2})</td>
<td>10 500</td>
<td>10 300</td>
<td>[48]</td>
<td></td>
</tr>
</tbody>
</table>

1) Element; 2) ground state; 3) excited state; 4) theoretical; 5) cm\(^{-1}\); 6) experimental; 7) reference.

\(J, J_z\) representation to the \(L_z, S_z\) representation and then to the \(l_z, s_z\) representation [8].

To calculate the splittings due to \(H_{kr}\) in the second approximation we must know the matrix elements of \(H_{kr}\), relating the ground and first-excited states:

\(\langle J+1, J + m | \mathbf{V}_{m}^k | J, J_z \rangle\).

For this purpose, the following formulas were described in [45, 51]:

\[
\langle J+1, J + m | \mathbf{V}_{m}^k | J, J_z \rangle = i^{-J} \mathbf{V}_m (7J_z^2 - 3J^2 - 6J + 2) \sqrt{(J+1)^{2} - J^2},
\]

\[
\langle J+1, J + m | \mathbf{V}_{m}^k | J, J_z \rangle = \gamma^2 \mathbf{V}_m [33J^2 - 5J_z^2 (6J^2 + 12J + 13) + 5J_z^2 - J_z (20J + 5J_z - 30J^2 + 12)] \sqrt{(J+1)^2 - J_z^2},
\]

\[
\langle J+1, J + m | \mathbf{V}_{m}^k | J, J_z \rangle = - \frac{1}{40} \gamma^2 (4J_z - J + 5) \sqrt{(J+1) + 4J_z (J + 2)},
\]

\[
\langle J+1, J + m | \mathbf{V}_{m}^k | J, J_z \rangle = - \frac{1}{28} \gamma^2 (22J_z^2 - 11J_z (J - 8) - J_z (4J_z + 4J_z^2 - 142J_z + 7J_z - 28)\),
\]

\[
\langle J+1, J + m | \mathbf{V}_{m}^k | J, J_z \rangle = - \frac{1}{14} \gamma^2 \sqrt{(J+1) + 4J_z (J + 2)},
\]

The coefficients \(a, b, \gamma\) and \(a', b', \gamma'\) are listed in Table 3.6.
The values of \( \alpha, \beta, \) and \( \gamma \) can also be calculated with the aid of the Racah coefficients [52].

After solving the secular equation and thus determining the energy levels of the ion in the crystalline field and the corresponding wave functions, it is necessary to proceed to calculate the splittings of these levels by the external magnetic field. We know that \( \hat{H}_{\text{Kr}} \) gives rise either to doublets (ions with odd number of electrons) or to doublets with singlets (ions with even number of electrons). Since the intervals between the energy levels in the crystalline field are somewhat larger than the Zeeman splittings in ordinary magnetic fields, we shall consider the action of the magnetic field on each level separately. Since the spin-lattice interaction in salts of rare earth elements is very strong at room temperature (see §5.3), the experiments must be carried out at temperatures that are so low that only the lowest level is populated in practice.* It is clear that paramagnetic resonance can be observed if this level is not a singlet. The wave functions of the lower doublet are used to calculate the perturbation matrix elements \( \hat{H}_Z = \beta H_0 (\hat{L} + 2\hat{S}) \) by means of the following formulas:

\[
\langle J... | L + 2S | J... \rangle = g_0 \langle J... | J | J... \rangle,
\]

where \( g_0 \) is the Lande effect for the free ion and

\[
\begin{align*}
\langle J+1, J | \hat{L}_z + 2\hat{S}_z | J, J \rangle &= g' \sqrt{(J+1)}^{J-J}, \\
\langle J+1, J | J+1, J \rangle &= \langle J+1, J \pm 1 | J \pm 1 \rangle \\
\pm 1 | J \pm 1 | J \pm 1 \rangle &= g' \sqrt{(J \pm 1)}^{J \pm 1} \\
\end{align*}
\]

where

\[
g' = \left[ \frac{(J+L+S+2)(-J+L+S)(J-L+S+1)(J+L-S+1)}{(J+1)(J+1+S)(J+3)} \right]^{1/2}.
\]

The values of \( g_0 \) and \( g' \) for individual ions are listed in Table 3.6.

The perturbation matrix of second rank has a trace equal to zero and can be represented in the form \( \beta H_0 \mathbf{S}^2 \), where \( \mathbf{S} \) is the Pauli mat-
**TABLE 3.6**

<table>
<thead>
<tr>
<th>Element</th>
<th>( a )</th>
<th>( b )</th>
<th>( r )</th>
<th>( a' )</th>
<th>( \nu )</th>
<th>( r' )</th>
<th>( \epsilon_s )</th>
<th>( \epsilon' )</th>
<th>( N )</th>
<th>( N' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce^{3+}</td>
<td>-2 ( \frac{5}{7} )</td>
<td>2 ( \frac{3}{5}.5.7 )</td>
<td>0</td>
<td>2( \frac{3}{5}.7 )</td>
<td>-2( \frac{6}{7} )</td>
<td>2( \frac{7}{5} )</td>
<td>6</td>
<td>1</td>
<td>( 2.3 )</td>
<td>( \frac{1}{14} )</td>
</tr>
<tr>
<td>Pr^{3+}</td>
<td>-2( \frac{12}{17} )</td>
<td>3( \frac{1}{5}.5.11 )</td>
<td>2( \frac{12}{17} )</td>
<td>2( \frac{12}{17}.14 )</td>
<td>2( \frac{12}{17}.66 )</td>
<td>-1( \frac{7}{17})</td>
<td>6</td>
<td>( \frac{66}{5} )</td>
<td>( 2.3.5 )</td>
<td>-193</td>
</tr>
<tr>
<td>Nd^{3+}</td>
<td>-7</td>
<td>3( \frac{1}{5}.15 )</td>
<td>-5( \frac{1}{7}.19 )</td>
<td>2( \frac{12}{17}.14 )</td>
<td>2( \frac{12}{17}.66 )</td>
<td>2( \frac{12}{17}.66 )</td>
<td>8</td>
<td>( \frac{14}{11} )</td>
<td>( 2.3.17 )</td>
<td>( \frac{14}{11} )</td>
</tr>
<tr>
<td>Pm^{3+}</td>
<td>2( \frac{7}{15} )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>2( \frac{7}{15} )</td>
<td>-1( \frac{7}{15})</td>
<td>3( \frac{1}{5}.15 )</td>
<td>-1( \frac{7}{15})</td>
<td>5</td>
<td>( \frac{7}{15} )</td>
<td>( \frac{7}{15} )</td>
<td>( \frac{1}{14} )</td>
</tr>
<tr>
<td>Sm^{3+}</td>
<td>13</td>
<td>3( \frac{1}{5}.5.7 )</td>
<td>2( \frac{12}{17} )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>2</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
</tr>
<tr>
<td>Tb^{3+}</td>
<td>-1</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
</tr>
<tr>
<td>Dy^{3+}</td>
<td>-2</td>
<td>3( \frac{1}{5}.5.7 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3( \frac{1}{5}.15 )</td>
<td>3</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
</tr>
<tr>
<td>Ho^{3+}</td>
<td>-1</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>3</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
</tr>
<tr>
<td>Er^{3+}</td>
<td>2</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>4</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
</tr>
<tr>
<td>Tm^{3+}</td>
<td>1</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>2( \frac{12}{17}.7 )</td>
<td>5</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
</tr>
<tr>
<td>Yb^{3+}</td>
<td>2</td>
<td>3( \frac{1}{5}.5.7 )</td>
<td>3( \frac{1}{5}.5.7 )</td>
<td>3( \frac{1}{5}.5.7 )</td>
<td>3( \frac{1}{5}.5.7 )</td>
<td>3( \frac{1}{5}.5.7 )</td>
<td>6</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
<td>( \frac{14}{1} )</td>
</tr>
</tbody>
</table>

1. Element.
rix vector and $g$ is a certain tensor with principal values $g_\parallel$, $g_\perp$, $g_\downarrow$. If the wave functions of our doublet, which we symbolically denote by $|+\rangle$ and $|--\rangle$, are so chosen as to make the matrix $L_z + 2S_z$ diagonal, then

$$
\begin{align*}
g_\parallel &= 2\langle +| (\hat{L}_z + 2\hat{S}_z)| +\rangle, \\
g_\perp &= 2\langle +| (\hat{L}_z + 2\hat{S}_z)| --\rangle.
\end{align*}
$$

Thus, the paramagnetic resonance spectrum can be interpreted with the aid of a spin Hamiltonian with effective spin $S' = \frac{1}{2}$:

$$
\mathcal{H}_{\text{en}} = \beta g_\parallel H_0 \hat{S}_z + \beta g_\perp (H_0 \hat{S}_x + H_0 \hat{S}_y).
$$

Ions with an even number of electrons call for a special analysis. In this case it is easy to show that the nondiagonal matrix element is $\langle +| \hat{L}_x + 2\hat{S}_x|--\rangle = 0$. It follows therefore that there should be no paramagnetic resonance effect. Indeed, if the field $H_0$ is parallel to the trigonal axis of the crystal, then the magnetic dipole transitions between magnetic sublevels will be forbidden, but if $H_0$ is perpendicular to the trigonal axis then $g_\perp = 0$.

This effect was nevertheless observed in experiment, for example, in praseodymium salts. An explanation of this effect was found with the aid of the Jahn-Teller theorem [12]: in crystals containing ions having an even number of electrons the symmetry of the electric field is lowered to such an extent that the degeneracy is completely lifted and the doublets are split. These splittings, assumed by Van Vleck [13] are very small in the case of rare-earth ions and do not prevent the observation of paramagnetic resonances under usual magnetic field intensities. The paramagnetic resonance spectrum of ions with an even number of electrons can be calculated with the aid of the spin Hamiltonian

$$
\mathcal{H}_{\text{en}} = \beta g_\parallel H_0 \hat{S}_z + \Delta \hat{S}_x + \Delta \hat{S}_y,
$$

where $\Delta = \sqrt{\Delta_x^2 + \Delta_y^2}$ is the doublet splitting due to the Jahn-Teller ef-
fect in the absence of the magnetic field $H_0$.

Many papers have been devoted to a detailed theoretical analysis of paramagnetic resonance spectra of individual rare earth elements: cerium ethyl sulfate [53, 50], the ethyl sulfates of Nd, Sm, Dy, Er, and Yb [54, 55], to the double nitrates of Ce, Pr, Nd, and Sm [56]. Attempts to interpret the observed paramagnetic resonance spectrum in dysprosium double nitrate have led to an interesting result. It turned out that the crystalline field can be divided into two parts [57]: a strong field of very high symmetry, namely icosahedral, and a weak trigonal field. For the field of icosahedral symmetry

$$A_i = \left( \pm \frac{14}{\sqrt{5}} \right) A_0 \quad A_i = 14A_0 \quad (3.47)$$

and all the remaining $A^m_n$ vanish. To calculate the level splitting in fields of high symmetry it is convenient to use the method proposed in [58].

A large number of field constants $A^m_n$ (up to six) makes difficult a unique interpretation of the observed paramagnetic resonance spectra. It is therefore customary to make use also of optical data, of results obtained by investigating the dependence of the static magnetic susceptibility on the temperature, or of information on the Faraday effect. To be sure, some difficulties arise from the fact that paramagnetic resonance is observed in strongly dilute solid solutions of paramagnetic salts, whereas other experiments are made with concentrated paramagnetic crystals. Dilution changes the electric crystalline field appreciably; in cerium ethyl sulfate these changes cause even the inversion of the two lower neighboring energy levels.

Reference [45] deals also with the general theory of the hyperfine structure of paramagnetic resonance spectra of rare earth ions. Calculation of the hyperfine splitting of the electron energy levels
can be made with the aid of the spin Hamiltonian (3.29) with effective spin $S' = 1/2$. If we denote here the operator of magnetic electron-nucleon interaction by $(\bar{A}/I)\mathbf{N}$, then the hyperfine structure constant will be equal to

$$A = 2\bar{a}\langle +|\hat{N}_z|+\rangle, \quad B = 2\bar{a}\langle +|\hat{N}_z|-\rangle. \quad (3.48)$$

The nonvanishing matrix elements of the operator $\hat{N}$ can be calculated with the aid of the following formulas

$$\begin{align*}
\langle J,...|\hat{N}|J,...\rangle &= N\langle J,...|\hat{J}|J,...\rangle, \\
\langle J+1, J|\hat{N}_z|J, J\rangle &= N'\sqrt{(J+1)} - J. \quad (3.49)
\end{align*}$$

The coefficients $N$ and $N'$ are listed in Table 3.6.

Rare earth ions can be artificially introduced into crystals which produce a field of cubic symmetry around these ions. The splitting of the energy levels in a field of cubic symmetry was considered theoretically in [59], where only part of the potential, proportional to $r^{-1}$, was considered. Bleaney [88] has shown that splitting in a cubic field can be calculated with the aid of a special type of spin Hamiltonian.

We wish to note in conclusion that many papers [4, 6], which in their day have played a major role in the explanation of the magnetic properties of rare earth salts, have lost their importance because of incorrect assumptions made concerning the symmetry of the crystalline field.

§3.8. Ions in the S State

Paramagnetic ions which have electron configurations $3d^5$ and $4f^7$ are in states

$$^4S_{5/2}(\text{Mn}^{2+}, \text{Fe}^{3+}) \text{ and } ^{4}S_{9/2}(\text{Gd}^{3+}, \text{Eu}^{3+}, \text{Cm}^{3+}).$$

The resultant orbital moment of the electrons is zero, and the electric crystalline field should therefore not split the ground levels of these ions. Actually, a small splitting has been ascertained both in experi-
ments on adiabatic demagnetization and from observations of paramagnetic resonance.

The complexity of the processes that bring about the splitting of the energy levels of ions in the $S$ state makes it difficult to attempt direct calculations. It is therefore customary to use the spin Hamiltonian method. In the absence of an external magnetic field, the spin Hamiltonian will be an even polynomial of fourth degree (for $\text{Mn}^{2+}$ and $\text{Fe}^{3+}$) or of sixth degree (for $\text{Gd}^{3+}$, $\text{Eu}^{2+}$, $\text{Cm}^{3+}$) in the projections of the spin momenta $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$. The number of terms of this Hamiltonian is greatly reduced if we take into consideration the symmetry of the crystalline field. Thus, for example, for the $\text{Mn}^{2+}$ or $\text{Fe}^{3+}$ ion we can write the spin Hamiltonian in the form

$$\mathcal{H}_{\text{sp}} = D\left(\hat{S}_1^2 - \frac{33}{12}\right) + E (\hat{S}_2^2 - \hat{S}_3^2) + \frac{a}{6} (\hat{S}_1 + \hat{S}_2 + \hat{S}_3) + \frac{g}{2} \mathbf{H} \cdot \mathbf{S}. \quad (3.50)$$

Here the first term takes into account the effect of the trigonal or tetragonal field with symmetry axes directed along the $Z$ axis; the second term is connected with the small deviations toward the lower symmetries; the third term specifies the action of the cubic-symmetry field, and $S_1$, $S_2$, and $S_3$ are the spin components referred to the cubic axes; the last term takes into account the effect of the external magnetic field. The $g$ factor of ions in the $S$ state is isotropic. Detailed calculations of the positions and intensities of paramagnetic resonance absorption lines were made in [31, 60] for ions with $S = 5/2$ and $S = 7/2$ under the assumption that the crystalline field has a cubic symmetry. Both strong and weak magnetic fields were considered there.

Let us dwell briefly on different mechanisms capable of splitting the ground levels of ions in the $S$ state under the influence of the crystalline field. The origin of the third term in spin Hamiltonian
(3.50) was explained by Van Vleck and Penney [61], who showed that if the effect of a cubic-symmetry electric field and of the spin-orbit interaction are taken into consideration simultaneously, then the ground level of an ion with configuration d⁵ is split in the fifth-order approximation. The constant a can be estimated from the formula

\[ a \approx \frac{Kn}{E_{PS}}. \]  

Here K stands for the matrix element of the potential of the crystalline cubic field \(<3d|V_{\text{cub}}|3d>\), calculated with the aid of the single-electron functions; \( E_{PS} \) is the energy interval between the \(^{4}\text{P}\) and \(^{6}\text{S}\) terms of the free ion. Putting \( K = 10^4 \text{ cm}^{-1} \), \( \lambda = 300 \text{ cm}^{-1} \), and \( E_{PS} = 2.5 \times 10^4 \text{ cm}^{-1} \), we get a \( \approx 10^{-4} \text{ cm}^{-1} \). It is known from experiment that the constant a is approximately one order of magnitude larger for Fe³⁺ than for Mn²⁺. The reason for it is that the ratio \( \lambda/E_{PS} \) is somewhat larger for Fe³⁺ than for Mn²⁺; furthermore, the quantity K is obviously larger for a trivalent ion than for a divalent one.

The origin of the first (and second) term of the spin Hamiltonian can be explained in two ways. Abragam and Pryce [17] called attention to the following splitting mechanism. The magnetic dipole interaction of the electron spins inside a paramagnetic atom depends not only on their relative orientation, but also on the electron coordinates. If the electron probability cloud has a cubic or spherical symmetry, then the averaged energy of the spin-spin interaction is independent of the orientations of the spins relative to one another; consequently the ground state of the paramagnetic ion is fully spin-degenerate. A field of tetragonal or trigonal symmetry slightly deforms the electron clouds and makes it ellipsoidal in shape. In this case the spin-spin interaction averaged over the electron cloud will depend on the relative orientations of the spins. The splitting of the energy ground level of a
paramagnetic ion occurs already in the second approximation and it will be proportional to $\frac{3^z_2}{2} - 35/12$. The constant $D$ can be estimated from the formula

$$D \approx \frac{U(f^1)}{E_{DS}}. \quad (3.52)$$

Here $U = <3d|U_2^0|4s>$, and $E_{DS}$ is the interval between the $3d^44s^6D$ and $3d^56S$ terms. According to Watanabe [62] a term of the type $D_S^2 \frac{3^z_2}{2}$ arises in fourth-order perturbation-method calculations, if simultaneous account is taken of the spin-orbit interaction and the effect of cubic and axial symmetry fields. An estimate of the splitting can be made with the aid of the formula

$$D \approx \frac{\lambda KV}{E_{DS}}, \quad (3.53)$$

where $U' = <3d|U_2^0|3d>$. Both formulas (3.52) and (3.53) yield $|D| \approx 0.1 \text{ cm}^{-1}$ if we assume $U = U' = 10^3 \text{ cm}^{-1}$, $E_{DS} = 2.5 \cdot 10^4 \text{ cm}^{-1}$, and $r^{-3} = 5a_0^{-3}$; this is in good agreement with the experimental data.

Analogous splitting mechanisms were considered in other papers [62] devoted to calculations of the principal terms of ions in the S state.

If the paramagnetic resonance spectra of ions in the S state display a hyperfine structure, this structure can be calculated by adding to (3.50) the spin Hamiltonian (3.29). The presence of a hyperfine structure in electron energy levels of ions in the S state is apparently due exclusively to the configuration interaction.

§3.9. Covalent Bonds; 3d, 4d, and 5d Transition Groups

Ionic crystals, the paramagnetism of which is due to elements of the 3d, 4d, and 5d transition groups, frequently contain octahedral complexes $MX_6$: the center of such a complex is occupied by an atom M with unfilled d shell, and the vertices of the octahedron are either
water molecules, CN radicals, or atoms of chlorine, fluorine, etc. The bond inside the $\text{MX}_6$ complex is frequently covalent, something first pointed out by Pauling [63], who attempted to explain the singularities of magnetic properties of potassium ferrocyanide with the aid of the theory of localized pairs. Van Vleck [64] showed, however, that the experimental facts pertaining to static magnetic susceptibility can be equally well explained by assuming covalent forces within the complex $\text{Fe(CN)}_6$ or by advancing the hypothesis that the interaction is purely ionic, but that a strong crystalline field disturbs the normal type of bond between the electrons of the iron atom.

If the molecular orbital method is compared with the localized pair method, it turns out that the results obtained by the former method are more general and closer to the experimental facts. Detailed calculations of the energy splittings in a strong crystalline field were made for an atom with configuration $d^5$ [65]. Van Vleck's theory was later extended to include cyanides of other elements with electron configurations from $d^1$ to $d^4$ [66]. A further impetus in the development of the theory of the covalent bond inside the $\text{MX}_6$ complex was produced by the discovery of the unusual hyperfine structure of the paramagnetic resonance spectrum of iridium [67]. It turned out that the absorption line of the iridium contained in $[\text{IrCl}_6]$ has a structure due to the magnetic moment of the chlorine nucleus, and this fact points clearly to the covalent character of the bond within the complex. A detailed analysis shows that the hyperfine structure of the spectrum of Ir cannot be attributed to the $\sigma$ bond, which was already investigated by Van Vleck, so that it becomes necessary to assume that the $\pi$ bond between the iridium and the chlorine also plays a noticeable role. A general analysis of the theory of paramagnetic resonance in $\text{MX}_6$ complexes with covalent $\sigma$ and $\pi$ bonds was made by Stevens [68].
Data were soon compiled on the absorption of light by hydrated salts of the iron-group elements as well as experimental results on paramagnetic resonance in these substances [69].

Contradictions arose, and these could be eliminated by assuming that the bond in the octahedral complex is partially covalent. Double covalent bonds were established in the vanadium complex of vanadium sulfate [70] by comparing the paramagnetic resonance data with results of observation of optical absorption spectra and x-ray structural analysis. Further generalization of the theory became necessary to explain the spectra of paramagnetic resonance of chelates [71] and fluorites of the iron-group elements [72]; to set up the molecular orbitals for fluorides it was necessary to involve not only the 2s and 2p functions of the fluorine but also states with principal quantum number $n = 3$. We note also that to explain the hyperfine structure of Mn$^{2+}$ ions introduced into the ZnF$_2$ crystal it becomes necessary to take the covalent bonds into account [89].

We shall present a general analysis of the effect of covalent bonds on paramagnetic resonance spectra of the elements of d transition groups by following Stevens [68] and Owen [69] and using the method of molecular orbitals.

a) Energy levels and molecular orbitals of a complex

If the bond were purely ionic in nature, the atom would be a positive ion with unfilled nd shell ($n = 3, 4, 5$), inside of which the electrons are distributed over the following orbitals*: $d_{3z^2-r^2}$, $d_{x^2-y^2}$, $d_{xy}$, $d_{yz}$, $d_{zx}$. The subscripts indicate the angular dependence of the real d wave functions. If we disregard the interaction between the electrons, then the ground level of the atom M splits in a crystal field of cubic symmetry in accordance with (3.11) into a lower triplet and an upper doublet. The first two of the listed orbitals belong to...
the doublet and are called after Bethe [1], the dy-orbitals. The functions \( d_{xy}, d_{yz}, \) and \( d_{zx} \) belonging to the triplet are called dz-orbitals.

In the ion approximation the particle \( X \) is diamagnetic and is a negative ion with a \( p \) shell that is filled as a rule; examples are \( X = Cl^-1 \) or \( O^{2-} \).* The orbital functions of the atoms \( M \) and \( X_6 \) must be used to set up the molecular orbitals of the entire octahedral complex.

We first consider the covalent \( \sigma \) bond, which is formed by the orbitals of the central atom \( nd_y \), \((n + 1)s\), \((n + 1)p\) and the \( p_\sigma \) orbitals of the surrounding atoms, which overlap the former appreciably. We include among the \( p_\sigma \) orbitals also the \( s \) functions of the \( X \) atoms. Altogether, we can construct \( 6[2(dy) + l(s) + 3(p)] \) binding six disintegrating orbitals, four of which contain magnetic \( dy \) orbits \[64\]:

\[
\begin{align*}
\sigma_{1-1} &= \alpha d_{32} + \beta d_{23} - \sqrt{1 - 2\alpha^2} \times \frac{1}{2} \times \left[ 2p_4 - 2p_3 + p_1 + p_4 - p_1 - p_4 \right] \\
\sigma_{1-2} &= \alpha d_{13} + \beta d_{23} - \sqrt{1 - 2\alpha^2} \times \frac{1}{2} \times \left[ 2p_4 - 2p_3 + p_1 + p_4 - p_1 - p_4 \right] \\
\sigma_{1-3} &= \alpha d_{23} - \beta d_{13} - \sqrt{1 - 2\alpha^2} \times \frac{1}{2} \times \left[ 2p_4 - 2p_3 + p_1 + p_4 - p_1 - p_4 \right] \\
\sigma_{1-4} &= \alpha d_{23} + \beta d_{13} - \sqrt{1 - 2\alpha^2} \times \frac{1}{2} \times \left[ 2p_4 - 2p_3 + p_1 + p_4 - p_1 - p_4 \right]
\end{align*}
\]

We denote here the binding orbits by \( \sigma \), the disintegrating orbits by \( \sigma^* \), and use the subscripts 1, 2, 3, 4, 5, and 6 for the \( X \) atoms located on the axes \( X, Y, Z, -X, -Y, -Z \), respectively. The coefficient \( \alpha \) shows to what extent the \( \psi \) functions of the central atom and of the environment are mixed. If \( \alpha = 1 \), the bond is purely ionic; on the other hand, if \( \alpha^2 = 1 - \alpha^2 = 0.5 \), the electrons are shared by \( M \) and \( X_6 \) with equal probability.

The covalent \( \pi \) bond can be formed by mixing the \( dz \) orbitals of the central atom with the \( p_\pi \) orbitals of \( X_6 \). This bond should generally speaking be weaker, since the directions of the combining orbitals are such that they overlap little. The molecular orbitals have the follow-
ing form [68, 69]:

\[ \pi_{xy} = \beta d_{xy} - \sqrt{1 - \beta^2} \frac{1}{2} [p_1 + p_3 - p_4 - p_5], \]  
\[ \pi_{zy} = \sqrt{1 - \beta^2} d_{xy} + \beta \frac{1}{2} [p_1 + p_3 - p_4 - p_5]. \] (3.56) (3.57)

The other four combinations \( \pi_{yz}, \pi^*_{yz}, \pi_{zx}, \pi^*_{zx} \) are obtained from (3.56) and (3.57) by cyclic permutation of the indices. The coefficient \( \beta \) shows how large the \( \pi \) bond is; when \( \beta = 1 \) there is no \( \pi \) bond.

In expressions (3.54)-(3.57) we have neglected the influence of the overlap of the atomic orbitals of \( M \) and \( X \) and the normalizations of the \( \sigma \) and \( \pi \) functions.

Figure 3.3 shows a possible level scheme for the free atoms \( M \) and \( X \) and for the complex \( MX_6 \). We see that the \( \sigma \) bond increases the splitting \( \Delta \) due to the cubic field of the crystal, while the \( \pi \) bond decreases it somewhat. This scheme applies to the cases \( X = Cl^{-1} \) and \( H_2O \); on the other hand if \( X = CN^- \), then the formation of the \( \pi \) bond with \( M \) occurs with the aid of the orbitals of the excited level of the carbon atom, which lies above the \( \delta \) level. Because of this, the sign of \( \beta \) should be reversed in (3.56) and (3.57), so that the binding orbitals become disintegrating orbitals and vice versa. Now the \( \pi \) bond also leads to an increase in \( \Delta \).

To develop the theory further, as already mentioned in §3.1, it is important to compare the action of the cubic field with the interaction between electrons, leading to the formation of the term. In hydrated salts of the iron group elements the value of \( \Delta \) is much smaller than the interval between the different terms of the free paramagnetic ions; in cyanide and in a few other salts of the element of the same group, the inverse relation holds true in the compounds of the elements of the 4d and 5d transition groups. The apparent reason for the latter is that in heavy elements, first, the Russel-Saunders coupling
is weak and, second, the $d$ orbits lie farther away from the nucleus and therefore overlap more strongly the orbits of the $X_6$ atoms.

b) Hydrated salts of the iron group elements

The procedure for calculating the spectrum of the paramagnetic resonance is the same as in §3.3, but only the perturbation matrix elements (3.12) need now be calculated with allowance for the presence of the covalent bonds. For this purpose, it is necessary to expand the wave function of the entire unfilled electron shell in terms of $d$ functions of the individual electrons, and the latter must then be replaced by the orbitals (3.54)-(3.57). Owen [69], who took only $\sigma$ bonds into account, has shown that systematic discrepancies between the optical and magnetic data on the intervals $\Delta$ can be eliminated by choosing suitable values of the coefficient $\alpha$. Thus, for example, for Ni$^{2+}$
we have in accord with the previously developed purely ionic theory
\[ g = 2.0023 - \frac{8\lambda}{\Delta}; \]
on the other hand, if we take the covalent \( \sigma \) bonds into account, we obtain
\[ g = 2.0023 - \alpha \frac{8\lambda}{\Delta}. \]
(3.58)
This result can be interpreted in the following fashion: each of the two unpaired electrons has a probability \( \alpha^2 \) of being in the nickel atom and a probability \( \frac{1}{6}(1 - \alpha^2) \) of being in each water molecule. As a result the spin-orbit coupling is reduced and in place of \( \lambda \) we have \( \lambda' = \alpha^2 \lambda \). For the complex \([\text{Ni(H}_2\text{O)}_6]^{2+}\) the experimental values of \( \Delta \) and \( \lambda \), taken from optical observations, as well as the values of \( g \) obtained by measuring paramagnetic resonance, lead in accord with (3.58) to a value \( \alpha = 0.83 \). The covalent bonds should also decrease the hyperfine splitting, something indeed observed in copper salts [25].

Fig. 3.4. Level splitting scheme of the ground state of the octahedral complex under the influence of the spin-orbit interaction (LS), the tetragonal field (T), and the magnetic field (M). It is assumed that the constant of the tetragonal field is \( \delta > 0 \); if \( \delta < 0 \), then the lower state for the configuration \((de)^2\) will be a doublet. The dashed lines indicate the splitting occurring only in the second perturbation theory approximation.
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exception of $(de)^3$ have triple orbital degeneracy. Therefore, owing to the Jahn-Teller effect, the octahedral symmetry should be lowered.

We shall assume that a weak field of lower symmetry, such as tetragonal, is superimposed on the cubic field. We denote the total splitting due to this field by $\delta$. If we furthermore take the spin-orbit interaction into account, we obtain the following series of values for the energy $E_k^*$:

$$(de)^{1T_1}: \quad E_1 = E_4 = \frac{a}{3} - \frac{1}{2} \lambda,$$

$$E_{24} = E_{14} = \frac{1}{2} \left[ \left( \frac{a}{2} + \frac{1}{3} \right) \pm \sqrt{\frac{9}{4} \lambda^2 - 2\lambda + 5\delta} \right];$$

$$(de)^{1T_2}: \quad E_{13} = E_{43} = \frac{1}{2} \left[ -\frac{5}{3} \pm \sqrt{\frac{9}{4} \lambda^2 + \lambda + 5\delta} \right].$$

The energy levels $(de)^{5T_2}$ are obtained from $(de)^1$ and $(de)^{4T_1}$ are obtained from $(de)^2$ by reversing the signs of $\delta$ and $\lambda$. The splitting of the level $(de)^3$ occurs only if the higher approximations of perturbation theory are included. In the case of an odd number of electrons we have Kramers' doublet, and therefore paramagnetic resonance can always be observed. If the number of electrons is odd, observation of paramagnetic resonance is possible (the ground states are singlets); an exception is the configuration $(de)^2$ if $\delta < 0$. Calculation of doublet splitting in a magnetic field shows that the $g$ factor decreases, owing to the covalent bond. Thus, for $[IrCl_6]^2-$ we have, for example,

$$g = 2 - \frac{2}{3} (1 - \frac{\delta}{\lambda}).$$

We have already indicated that covalent bonds produce a hyperfine structure in paramagnetic resonance lines, due not only to the momentum of the M nucleus, but also the momenta of the $X_6$ nuclei.
tion of the hyperfine structure can be made with the aid of the spin Hamiltonian (3.20), containing an additional series of terms that take into account the spins of the $X_6$ nuclei. Thus, if a strong magnetic field is applied along the Z axis and only the octahedral symmetry of the crystalline field is taken into account, then the spin Hamiltonian has the form

$$\mathcal{H}_{\text{cu}} = \frac{1}{2} g_1 H_{\text{e}} S_z + A (\langle S_z \rangle^2) + A' (\langle S_z \rangle^2 + \langle S_z \rangle^2),$$

(3.62)

where $A' = -(32/15) \beta^2 (1 - \beta^2) g_0 B_0 B_N (r^{-3})$. The subscript 0 pertains here to the central atom and the subscripts 3 and 6 to the $X$ atoms located on the Z axis.

In conclusion we must note that the spin-orbit interaction can be described with the aid of a single constant $\lambda$ only in the case of octahedral symmetry. Deviations of the field symmetry from octahedral cause anisotropy of the spin-orbit interaction.

§3.10. The Actinides

It is firmly established by now that the transition group of elements starting with thorium contains a partially filled 5f shell [44]. The actinides differ from the 4f transition rare-earth group in their tendency to form compounds that contain complexes which are rather stable chemically, similar to the uranyl ion ($\text{UO}_2^{2+}$). A systematic investigation of the magnetic properties of the actinides, and particularly paramagnetic resonance, began only recently, and so far only compounds containing $\text{UO}_2$, $\text{NpO}_2$, and $\text{PuO}_2$ have been well investigated. The experimental data on these complexes have been theoretically interpreted in [74-76].

Let us start with an examination of the complex $\text{UO}_2$, although it does not have normal paramagnetism and therefore does not give rise to paramagnetic resonance.

The structure of this complex is linear: O-U-O. The free uranium
atom has a closed core and six valence electrons, forming a configuration $5f^36d7s^2$. Two of these electrons are lost in $(\text{UO}_2)^{2+}$, and the four remaining ones produce a strong covalent bond with the oxygen atoms. In the simplest model used in [74, 75], only the $\sigma$ bond is assumed. The linear combinations of the $5f_\sigma$, $6d_\sigma$, and $7s_\sigma$ functions form orbitals which are highly elongated in the direction of the oxygen atoms, and strongly overlap the $sp_\sigma$ orbitals of oxygen. Thus, no unpaired electrons remain in the ground state of $(\text{UO}_2)^{2+}$, and consequently compounds containing uranyl will either be diamagnetic or will have a weak temperature-independent paramagnetism.

The ions $(\text{NpO}_2)^{2+}$, $(\text{PuO}_2)^{2+}$ and $(\text{AmO}_2)^{2+}$ have a structure and chemical properties similar to those of $(\text{UO}_2)^{2+}$. It is natural to assume that the character of the bond of all these ions is the same, and that the additional electrons fill the $5f$ shell, similar to the $4f$ electrons of the trivalent ions Ce, Pr, and Nd. However, the transuranyl compounds differ greatly from the solid salts of the lanthanides in that the magnetic properties of the former are more sensitive to the crystalline field, whereas for the $5f$ electrons of the actinides the dominating effect is produced by the axially symmetrical field due to the binding electrons of the complex. In first approximation, the magnetic properties of a compound containing a transuranyl complex will be the same as those of a linear molecule; the crystalline field introduces small corrections.

The complex $(\text{NpO}_2)^{2+}$ contains one unpaired $f$ electron, which moves in a strong field of axial symmetry. Therefore the conserving quantities will in first approximation be the components of its total $J_z$, orbital $L_z$ and spin $S_z$ angular momenta about the symmetry axis, which we choose to be the Z axis. In an axial field, all possible values $|L_z| = 3, 2, 1, 0$ will correspond to different energy
levels. The very lowest level, which is located about 10^4 cm\(^{-1}\) away from the neighboring one, corresponds to a state with \( |\frac{1}{2}z| = 3 \), for in this case the charge of the unpaired electron is located in the equatorial plane, so that the repulsion between it and the electrons forming the \( \sigma \) bond will be minimal. This quadruply degenerate level (\( |\frac{1}{2}z| = +3, s_z = +1/2 \)) is split as a result of the spin-orbit interaction into two doublets: \( J_z = \pm 5/2, \pm 7/2 \). The first doublet lies 3000-4000 cm\(^{-1}\) below the second, and consequently it is the only one responsible for the paramagnetism of neptunyl.

The paramagnetic resonance spectrum can be calculated with the aid of the following simple spin Hamiltonian

\[
\mathcal{H} = g_I \mu_B H_z \hat{S}_z + g_I \beta \left( H_x \hat{S}_x + H_y \hat{S}_y \right) + A \hat{J}_z \hat{S}_z + \frac{1}{3} I(I+1) \frac{\hat{S}^2}{\hbar^2} - g_I \mu_B H \hat{S}
\]  

(3.63)

Here \( g_\parallel = 2<\hat{1}_z + 2\hat{S}_z^2 > \), \( g_\perp = 2<\hat{1}_x + 2\hat{S}_x^2 > \), \( |\rightarrow \rangle \) and \( |\leftarrow \rangle \) denote the wave functions of the lower doublet, while \( S' \) is the effective spin with value 1/2. In the approximation that takes only the \( \sigma \) bond into account we have \( g_\parallel = 4, g_\perp = 0 \). If the possibility of the \( \pi \) bond is also taken into account then, as we have seen in the preceding section, the orbital momentum drops and \( \frac{1}{2}z \) is replaced by \( k \frac{1}{2}z \); \( k < 1 \). Now \( g_\perp \neq 0 \), \( g_\parallel = 6k - 2 \). Comparison with the experimental data shows that \( k = 0.9 \).

Finally, it should be noted that the large electric field gradient produced by the electrons forming the covalent bond will give rise to a large hyperfine structure, due to the quadrupole moment of the Np nucleus.

The complex \((\text{PuO}_2)^{2+}\) contains two unpaired electrons, the motion of which is perturbed primarily by the axial field and by the electrostatic repulsion between them. For the same reason as in the case of neptunyl, it might appear that the unpaired electrons should occupy
the state \( L_z = \pm 3 \). Actually, however, because of the electrostatic repulsion between the electrons, the ground state of the "configuration" \( 5f^2 \) is determined by the modified Hund rule: the electron spin projection should be maximal, \( S_z = 1 \); the projection of the orbital momentum should have a maximum value compatible with \( S_z = 1 \), namely: \( |L_{1z}| = 3 \), \( |L_{2z}| = 2 \) and, consequently, \( L_z = \pm 5 \). The spin-orbit interaction causes further splitting of the energy levels, after which the lower level turns into a doublet with \( J_z = \pm (5 - 1) = \pm 4 \).

Elementary calculation shows that if we again introduce an effective spin \( S' = 1/2 \), then for this doublet \( g_\parallel = 6 \), \( g_\perp = 0 \). The probability of transition between magnetic sublevels is in this case equal to zero independently of the direction of the external magnetic field \( H \). A detailed analysis shows that an account of different corrections does not change the fact that \( g_\perp = 0 \). As a result, the paramagnetic resonance has a maximum when the alternating magnetic field is parallel to the \( Z \) axis. The reason for it is that the previously unaccounted for crystalline field of lower symmetry causes an intermixing of the wave functions with \( J_z = \pm 4 \). It must be kept in mind that the doublet considered here is not a Kramers' doublet, for the number of unbound electrons is even in our case. Thus, the spin Hamiltonian will have the form

\[
\mathcal{H} = g_\parallel \mu_B S_z + \Delta S_z I_z + \mu [\hat{J} - \frac{1}{3}(I + 1)] + \Delta S_z + \Delta \hat{S}_z + \Delta \hat{S}_\hat{S} \tag{3.64}
\]

The last two terms take into account the splitting due to a low-symmetry crystalline field.

\section*{3.11. Influence of Exchange and Dipole Interactions on the Form of the Paramagnetic Resonance Spectrum}

Interesting exchange effects were observed in certain salts of copper. The temperature dependence of the static magnetic susceptibility of copper acetate is unusual [77]. Sharp anomalies in the magnetic
behavior of this substance were also observed by the paramagnetic resonance method [78]. All these singularities can be explained as follows. The crystalline cell of copper acetate has two closely adjacent paramagnetic ions, which behave, as the result of the strong exchange bonds between them, in a manner similar to a single "molecule," capable of being either in a paramagnetic state with spin $S = 1$, or in a diamagnetic state with spin $S = 0$. It is well known [10] that the exchange bond is characterized in the absence of other forces acting on the spins by a cosinusoidal dependence on the spin direction; the exchange energy is equal to $-J S_1 S_2$, where $J$ stands for the exchange integral and $S_1$ and $S_2$ are the spins of the interacting atoms. It has been shown at the same time that if there are other than exchange forces, which also strongly influence the spin directions, then the cosinusoidal law may still be valid, but only for the "effective" spins [21, 22]. In copper acetate the exchange interactions are much stronger than the spin-orbit coupling (which appears only in the second approximation), and therefore the Hamiltonian for the system of two copper ions under consideration will have the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2,$$

where

$$\mathcal{H}_0 = J S_1 S_2 + \beta H,(L_1 + L_2),$$

$$\mathcal{H}_1 = \lambda (L_1 S_1 + L_2 S_2),$$

$$\mathcal{H}_2 = \gamma (L_1 L_2 + S_1 S_2).$$

(3.65)

The subscripts 1 and 2 are the numbers of the copper ions in the crystal cell, while the remaining terms of the Hamiltonian stand for the energy in the crystalline field, the exchange interaction, the spin-orbit coupling, and the energy in the external magnetic field. The exchange interactions split the lower orbital level of the "molecule" into a spin singlet and a triplet. It is possible to explain with the aid of (3.65) in natural fashion all the known facts concerning the static magnetic properties of copper acetate, the paramagnetic resonance spectrum, and its hyperfine structure.
The exchange interactions influence the form of the paramagnetic resonance spectrum also in copper sulfates [79], but here the anomalies have a different character, since the exchange energy is comparable in order of magnitude with the radio frequency quantum; its value is approximately 0.15 cm\(^{-1}\), whereas in copper acetate \(J = 300\) cm\(^{-1}\).

The magnetic dipole interactions usually are causes of broadening of resonance lines. In some cases, however, when the substance is magnetically dilute and contains at the same time magnetic particles that lie closely to each other, these interactions can bring about the appearance of a fine structure of the paramagnetic absorption spectrum. Such a structure was observed in neodymium ethyl sulfate [80]. If the static magnetic field is parallel to the hexagonal axis of the crystal, then the spectrum comprises a symmetrical triplet with intervals of 360 oersteds between the extreme absorption peaks. The central peak has approximately double the intensity of the extreme ones. Simple calculation of the energy of dipole interaction between the ion and the neighboring particles yields values \(\pm 2g_{||} \beta/c^3,0,0\); here \(c = 7A\) is the distance between two closest particles, located along the hexagonal axis. Thus, the satellites may be located \(50g_{||} = 180\) oersteds away from the central peak. A more complicated spectrum structure was established for gadolinium ethyl sulfate, this being due to the larger spin of the \(\text{Gd}^{3+}\) ion.

§3.12. Forbidden Spectral Lines. Multiple Quantum Transitions

So far, when speaking of a paramagnetic resonance spectrum, we had in mind resonance lines pertaining to such spin levels, the transition probabilities between which differ from zero in the first perturbation theory approximation. Let us consider now several causes of the appearance of additional "forbidden" resonance absorption lines.
a) Dipole interaction between magnetic centers

Let us assume that the crystalline field does not split the spin levels and that consequently each level corresponds to a definite value $M$ of the spin momentum projection on the direction of the field $H_0$. Because of this, magnetic dipole transitions are possible in the first approximation only between neighboring levels ($\Delta M = \pm 1$) under the influence of the oscillating magnetic field perpendicular to the field $H_0$. We now take into account the magnetic dipole interactions between the paramagnetic centers of the crystals. Because of the interactions, the wave functions $\eta_M(M = S, S - 1, \ldots, -S)$, pertaining to different spin levels become intermixed and assume the form (see §5.2) $\eta_M + \sum_{i=M-1}^{M+2} \epsilon_i \eta_i$, where $\epsilon_1 \sim \beta^2/a^3(g\beta H_0)^{-1}$; here $a$ is the average distance between two neighboring magnetic centers. Now the nondiagonal matrix elements of the vector $\vec{S}$ will be different from zero not only in the case when $\Delta M = \pm 1$, but also for the transitions $\Delta M = \pm 2$ and $\pm 3$. If we assume the intensity of the principal resonance line ($\Delta M = \pm 1$) to be equal to one, then the intensity of the lines $\Delta M = \pm 2$ and $\pm 3$ will be $4|\epsilon_1|^2$ and $9|\epsilon_1|^2$, respectively, if the oscillating field is perpendicular to the field $H_0$. If the fields are parallel, the transitions $\Delta M = \pm 1$ and $\Delta M = \pm 2$ give rise to two forbidden resonance lines, the intensity of which is $|\epsilon_1|^2$ and $4|\epsilon_1|^2$. The existence of forbidden lines was first established experimentally by Zavoyaskiy in manganese salts [81], and was later on observed by others [82].

b) Hyperfine interactions

With increasing concentration of the paramagnetic centers, the intensity of the additional absorption lines, due to the magnetic dipole interaction between centers, will become weaker. However, other forbidden absorption peaks can arise in this case, if the nuclei of the
paramagnetic atoms have a spin different from zero. Let us assume that the spectrum of the paramagnetic resonance can be described by the following spin Hamiltonian:

\[ \widetilde{H}_e = D \left( \hat{S}_z - \frac{1}{3} \hat{S}(\hat{S} + 1) \right) + \beta \left[ \gamma_0 \hat{H}_0 \hat{S}_z + \gamma_1 \left( \hat{H}_x \hat{S}_x + \hat{H}_y \hat{S}_y \right) \right] + A \hat{S} \hat{I} + B \left( \hat{S}_z \hat{I} + \hat{I} \hat{S}_y \right) + \epsilon \left( \hat{I} - \frac{1}{3} \hat{I}(\hat{I} + 1) \right). \] (3.66)

We assume first that the field \( \hat{H}_0 \) is parallel to the Z symmetry axis of the crystalline field. Figure 3.5a shows the system of energy levels arising under the influence of the magnetic hyperfine interaction for the particular case \( S = 1/2, I = 3/2 \). Because of the quadrupole interaction, the energy levels cease to be equidistant (Fig. 3.5b). To each level there corresponds a wave function \( \psi_{M,m} \) with a definite magnetic quantum number \( M \) of the electron spin and a magnetic quantum number \( m \) of the nuclear spin. The arrows in Fig. 3.5b denote the transitions that are allowed by the selection rule \( \Delta M = \pm 1, \Delta m = 0 \), provided
the oscillating field is perpendicular to the permanent field.

In the second approximation of perturbation theory, owing to the term $B(\hat{s}_x \hat{f}_x + \hat{s}_y \hat{f}_y)$, the wave functions assume the form $\eta_{M,m} + \alpha \eta_{M+1,m+1}$, where $\alpha \sim B/\gamma H_0$. It is easy to verify that now, if the magnetic oscillating field is parallel to $H_0$, there should appear additional absorption peaks, corresponding to the transitions $\Delta M = \pm 1$, $\Delta M = \pm 2$. These transitions are shown in Fig. 3.5c by the dotted arrows. The intensity of the forbidden lines is related to the intensity of the principal lines of paramagnetic resonance approximately as $|\alpha^2|:1$.

Forbidden absorption lines in parallel fields were observed experimentally in salts of cobalt, manganese, and vanadium [83].

If the field $H_0$ is inclined to the Z axis of the crystal, then the possibilities for forbidden transitions become greater. The additional lines appear not only in parallel but also in perpendicular fields. The spectrum becomes particularly enriched with forbidden lines if the quadrupole interactions between the nuclei and the crystalline field are large [84].

c) Multiple quantum transitions

The reason for the appearance of additional absorption lines may be quantum transitions connected with simultaneous absorption of several photons by the paramagnetic atoms. Such transitions, which are forbidden in the first perturbation theory approximation, become possible in the higher approximations via one or several intermediate states of the atom. Multiple quantum transitions produced under the influence of a powerful radio frequency field, were first discovered in experiments with molecular beams [85], and then by the method of nuclear magnetic resonance [86]. Observation of electron paramagnetic
resonance has recently disclosed the existence of multiple quantum transitions in Mn\(^{2+}\) ions introduced into the MgO lattice [87].

Let us assume that among the energy spin levels there are three such levels \(E_k\), \(E_1\), and \(E_m\) (Fig. 3.6) that \(\omega_{\perp k} \neq \omega_{\perp l}\), but \(|\omega_{\perp l} - \omega_{\perp k}| < < 1/2\omega_{mk}\) \(\omega_{ij} = (E_i - E_j)/\hbar\). We assume also that in first approximation the transitions between neighboring levels \(k \leftrightarrow 1\) and \(1 \leftrightarrow m\) are allowed, but the transition \(k \leftrightarrow m\) is forbidden. The state of the paramagnetic center can be described with the aid of the Hamiltonian

\[
\mathcal{H} = \mathcal{H}_{\text{sp}} + \mathcal{H}', \quad \mathcal{H}' = \frac{i}{2} \mathbf{S} \cdot \mathbf{e} \wedge \mathbf{H},
\]

where \(\mathcal{H}_{\text{sp}}\) is the spin Hamiltonian which determines the system of spin energy levels of the paramagnetic center, and \(\mathcal{H}'\) is the time-dependent part of the Hamiltonian representing the interaction with the radio frequency magnetic field, while \(\mathbf{S} \pm = \mathbf{S}_x \pm i\mathbf{S}_y\). In this case we consider, to simplify the calculations, a field rotating with angular velocity \(\omega\) in place of an oscillating field.

We assume that at the initial instant of time the atom is in the state \(k\). Then in first approximation of the theory of time-dependent perturbations, the probability that the atom will be in the state \(l\) at the instant of time \(t\) is

\[
|\psi(t)|^2 = \frac{\mathbf{S}_z \cdot \mathbf{e} \wedge \mathbf{H}}{\hbar} \left| \langle k | \mathbf{S}_z | l \rangle \right|^2 \left| \frac{\hbar \omega_{mk} - \omega}{\hbar \omega_{mk} + \omega} - 1 \right|^2;
\]

and in the second approximation of perturbation theory we have

\[
|\psi(t)|^2 = \frac{\mathbf{S}_z \cdot \mathbf{e} \wedge \mathbf{H}}{\hbar} \left| \langle k | \mathbf{S}_z | l \rangle \right|^2 \left| \frac{\hbar \omega_{mk} - \omega}{\hbar \omega_{mk} + \omega} \right|^2 \times \left| \frac{\hbar \omega_{mk} - \omega}{\hbar \omega_{mk} + \omega} - 1 \right|^2.
\]

We see that the probability of the transition \(k \leftrightarrow m\) is appreciably different from zero if, first, the frequency of the alternating field is equal approximately to \(\omega_{mk}/2\), and, second, if the matrix elements of the perturbation, which relate the levels \(m\) and \(k\) with the inter-
mediate level \( \lambda \), are not equal to zero. Let us now take account of the fact that the absorption line is finite, for which purpose we introduce the form function \( g(\omega) \) (see §1.3). Carrying out, as usual, the integration

\[
\mathcal{W}_{ij} = \int |a_{ij}(t)|^2 g_{ij}(\omega) d\omega, \quad (3.70)
\]

we see that the probabilities of the transition are proportional to the time \( t \). If we take also account of the difference in the populations of the levels \( E_k, E_\lambda, \) and \( E_m \) and recognize that the quantity \( g_{ij}(0) \) is inversely proportional to the absorption line width \( \Delta \nu_{ij} \), then we obtain for the ratio of the intensity \( I_2 \) of the line due to the two-quantum transitions, to the intensity \( I_1 \) of the ordinary \( 1 \leftrightarrow k \) resonant line the following expression:

\[
\frac{I_2}{I_1} = \frac{1}{2} \left( \frac{g \beta H_1}{\hbar} \right) \Delta \nu_{ij} \left| \langle \ell | \hat{S}_z | k \rangle \right|^2 . \quad (3.71)
\]

We see that the intensity of the line, resulting to the two-quantum transitions, becomes larger if the frequency of the Larmor precession, corresponding to the magnetic field \( H_1 \), is comparable with the frequency interval between the ordinary absorption line, connected with the transitions \( k \leftrightarrow \lambda \) and \( \lambda \leftrightarrow m \). We note that when the power of the radio frequency field is so large that \( g \beta H_1 / \hbar \sim (\omega_{\lambda k} - 1/2 \omega_{mk}) \), then the use of perturbation theory is not justified, and formula (3.71) is no longer valid.

Along with the two-quantum transitions which we have considered, other transitions are also possible, due to the absorption of three or more photons. In the third perturbation-theory approximation we obtain for the probability of a three-quantum transition
\[ |a^n_{lm}(t)|^2 = \frac{e^{ipH(t)}}{64\pi^3 (\omega_{ab} - \omega)^2 (\omega_{ab} - 2\omega)^2} \times \left| \frac{e^{i\omega_{ab} - 2\omega t}}{\omega_{ab} - 2\omega} - 1 \right|^2 \]  

(3.72)

Here \( l \) and \( m \) are intermediate states through which the transition under consideration becomes possible.

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Certain exceptions will be discussed later (see §3.11).

In this section we do not concern ourselves with salts having ions in the $S$ state.

Exceptions are encountered. For example, in cerium ethyl sulfate the two lower levels of the ion are noticeably populated even at liquid-helium temperature.

By orbitals we mean, as is customary in quantum chemistry, the "orbital" wave functions of individual electrons.

If the octahedral complex is formed by water molecules, then the oxygen atom faces the M atom.

We use Mulliken's notation for the terms of the octahedral complex [73].

\[\text{kr} = kr = \text{kristallicheskiy} = \text{crystalline}\]
\[\text{tet} = tetr = \text{tetragonal'nyy} = \text{tetragonal}\]
\[\text{trig} = \text{trig} = \text{trigonal'nyy} = \text{trigonal}\]
\[\text{geks} = \text{geks} = \text{geksagonal'nyy} = \text{hexagonal}\]
\[\text{romb} = \text{romb} = \text{rombicheskiy} = \text{rhombic}\]
\[\text{trikl} = \text{trikl} = \text{triklinicheskiy} = \text{triclinic}\]
\[\text{kub} = \text{kub} = \text{kubicheskiy} = \text{cubic}\]
\[\text{sp} = \text{sp} = \text{spin} = \text{spin}\]
\[\text{eff} = \text{eff} = \text{effektivnyy} = \text{effective}\]
Chapter 4

SPECTRA OF IONIC CRYSTALS. EXPERIMENT

§4.1. Introduction. Crystallographic Data

The experimental data on the paramagnetic resonance spectra in solids are listed below in the form of tables in §4.2. The data on spectra in liquid solutions of salts are contained in §4.3. Finally, §4.4 gives information on nuclear spins discovered with the aid of paramagnetic resonance. In the first column of the tables in §4.2 there are contained, in addition to the chemical formulas for the paramagnetic substance, also the degree of its dilution by the diamagnet (usually in atomic percent) and data on the crystal structure. If the latter is included among the ten most important types considered in the present section (see below, pages 126-129), the corresponding number is listed in the first column. For example, cr. st. 1 denotes that the compound is of the alum type. For other crystal structures, reference is made to the corresponding crystallographic literature; the number of such reference is accompanied by the letter "k." A list of these references is given for all the ions at the end of the chapter. The next columns give the temperature of the experiment and the basic spin-Hamiltonian constants in cm$^{-1}$,* determined from the type of the spectrum.

The arrangement of the material follows that used in the preceding chapter. We first consider the ions of the iron group, the lower orbital level of which in octahedral magnetic complexes is a singlet ($V^{2+}$, $Cr^{3+}$, $Ni^{2+}$), and the neighboring ions $Cr^{2+}$, $Mn^{3+}$ and $Cu^{2+}$, which
also have a lower orbital singlet in a crystal field with tetragonal component. Finally, it is necessary to include in the same group such compounds as CsCoCl$_5$, in which the magnetic ion Co$^{2+}$ is surrounded by a distorted tetrahedron of Cl$^-$. In a tetrahedral magnetic complex, the sign of the cubic field is opposite that in an octahedral complex. Consequently, the orbital levels are inverted, and the Co$^{2+}$ ion produces in this compound a spectrum which is similar to the spectra of the compounds of trivalent chromium or divalent vanadium.

The next group of tables contains data on the ions Ti$^{3+}$, V$^{4+}$, V$^{3+}$, Fe$^{2+}$, and Co$^{2+}$ (Table 4.2). These are followed by the rare earths. We first give data for the rare-earth ions with odd number of electrons (Table 4.3), and then for those with even numbers (Table 4.4).

The ions of all the periodic-system groups in the S state (Mn$^{2+}$, Fe$^{3+}$, Ga$^{3+}$, Eu$^{2+}$, and Cm$^{3+}$) are listed separately (Table 4.5).

The next set of tables is devoted to compounds in which strong covalent bonds occur between the paramagnetic ion and its surroundings (individual compounds of the iron group, and also compounds of the palladium and platinum groups, and finally the actinides; see Table 4.6).

Table 4.7 lists some data on the compounds containing atoms of metals in anomalous valence states.

Within each group of tables, the ions appear in order of increasing atomic number of the element in the periodic system.

To facilitate the use of the bibliography, the references are given for each ion separately. The remarks contain certain special information concerning the structure of the given compound and other properties. The symbols used in the tables are explained on page 3.

For each ion, the data obtained with dilute single crystals are followed by a list of substances investigated only in the form of pow-
ders or magnetically concentrated single crystals, together with those constants which were determined by this investigation.

To explain the form of the paramagnetic resonance spectrum of an ionic crystal it is necessary to have certain crystallographic data, usually obtained by x-ray structural analysis. The paramagnetic properties of salts are determined essentially by the magnetic complexes contained in these salts. It is very important to know how many such complexes there are in each crystal cell, and what their arrangement is. We therefore relate with each magnetic complex a rectangular coordinate system $X, Y, Z$. If the crystal cell contains only one magnetic complex or if there are several complexes which are all equivalent and identically oriented, then the axes $X, Y, Z$ coincide with the principal axes $K_1, K_2, K_3$ of the magnetic susceptibility tensor. In the general case, on the other hand, the axes $K_1, K_2, K_3$ are the result of the averaging of the axes $X, Y, Z$ of different magnetic complexes. It must be borne in mind that the axes $K_1, K_2, K_3$ do not coincide in the majority of cases with the crystallographic axes $a, b, c$.

The magnetic complexes of the compounds of the 3d, 4d, and 5d transition groups frequently are octahedra with a paramagnetic ion $M$ at the center and identical particles $X$ on the vertices, at a distance $R$ from the center. Such particles can be water molecules (the interval between $M$ and the oxygen atom is approximately 2 A), halide ions ($R \approx 2.5$ A), CN radicals (distance from $M$ to C $\approx 1.8$ A and to N $\approx 3$ A). Owing to the Jahn-Teller effect and to the particles surrounding the magnetic complex, the octahedron is so deformed that the electric field acting on the ion $M$ acquires either trigonal or tetragonal or even lower symmetry. The first of these factors explains why the crystal field can change appreciably when the particle $M$ is replaced by another one, even if the surrounding remains completely the same. The second
reason explains why perfectly identical complexes $\text{MX}_6$ can have different symmetries in different salts.

We consider first the most widely investigated hydrated salts of the iron-group elements, the octahedral complexes of which contain six water molecules.

1) Alums [1-3]: $\text{M}'\text{M}''\text{M}'''(\text{S}^4\text{O}_4)_2\cdot6\text{H}_2\text{O}$, where $\text{M}' = \text{K, Na, Rb, Cs, NH}_4$, ..., $\text{M}'' = \text{Al, Gd, La, ...}$ or the trivalent ion of the 3d group $\text{S}^* = \text{S, Se}$. The symmetry of the crystal is cubic. Each cell contains four complexes, the positions of which change in different allotropic modifications. The existence of $\alpha$, $\beta$, and $\gamma$ modifications is apparently connected with the difference in the dimensions of the monovalent ions $\text{M}'$. In the $\alpha$ modifications, the octahedral complexes are somewhat deformed along the trigonal axes of the crystal: [111], [111], [111]; the cubic axes of the octahedra, on the other hand, are turned about the [111] crystal axis. All four complexes of the unit cell of the $\beta$ modification are perfectly equivalent; the cubic axes of the octahedra coincide with the cubic axes of the crystal. The paramagnetic resonance in the crystals of the $\gamma$ modification was not investigated. At temperatures $80-160^0\text{K}$ one observes phase transitions which change the symmetry of the magnetic complexes. The $\alpha$ structure of the alums usually occurs in salts with $\text{M}' = \text{K, Rb, Tl, and NH}_4$; $\beta$ alums occur for $\text{M}' = \text{Cs, (NH}_3\text{CH}_3\text{)},$ and $\gamma$ alums occur for $\text{M}' = \text{Na}$.

2) Tutton's salts [1, 4, 5]: $\text{M}'_2\text{M}''(\text{S}^4\text{O}_4)_2\cdot6\text{H}_2\text{O}$, where $\text{M}' = \text{K, Rb, NH}_4$, ..., $\text{M}'' = \text{Mg, Zn, or a divalent ion of the 3d group. The crystal is monoclinic and contains in each cell two M''(H}_2\text{O})_6$ complexes. Four water molecules are located at a distance 1.9 A from M'', forming almost a square, while the two other molecules are 2.15 A away from M''. Thus, the symmetry of the complex is close to tetragonal. One can choose the $Z$ axis as the tetragonal symmetry axis.
A reflection from the ac plane transfers the X, Y, Z axes of one of the complexes into the axes of the other complex. The angle between the Z axis and the ac plane is designated $\alpha$. $\psi$ denotes the angle between c and the projection of Z on the ac plane.

3) Double nitrates [1]: $M''M''_2(\text{NO}_3)_2\cdot12\cdot24\text{H}_2\text{O}$, where $M'' = \text{Mg}, \text{Zn}$, or a divalent ion of the 3d group, $M''' = \text{Bi}$, ..., or a trivalent ion of the 4f group. The crystal is trigonal and contains one trivalent and two divalent ions in each unit cell. The two 3d-magnetic complexes $M''(\text{H}_2\text{O})_6$ have trigonal deformations that are somewhat different in magnitude.

4) Fluorosilicates [1, 6, 7]: $M''\text{SiF}_6\cdot6\text{H}_2\text{O}$, where $M'' = \text{Zn}, \text{Mg}$, or a divalent ion of the 3d group. The crystal is trigonal; it has been assumed that it contains one molecule per cell and that the magnetic complex is slightly deformed in the direction of the trigonal axis. Paramagnetic resonance investigations have shown that there are six magnetic complexes in each unit crystal cell, differing only in the orientation of the deformation axes.

5) Bromates [1, 8]: $M''(\text{BrO}_3)_2\cdot6\text{H}_2\text{O}$, where $M'' = \text{Zn}$ or a divalent ion of the 3d group. The crystal has a cubic symmetry. The four $M''(\text{H}_2\text{O})_6$ complexes contained in the unit cell are octahedra distorted along the trigonal axes, similar to the analogous complexes of the a alums.

6) Sulfates [1, 9]: $M''\text{SO}_4\cdot7\text{H}_2\text{O}$. A study was made of the structure of crystals in which $M'' = \text{Ni}, \text{Zn}, \text{Mg}$; the symmetry is orthorhombic. Each unit cell of the crystal contains four complexes, the axes of which go over into one another upon reflection from the symmetry planes (100), (010), and (001).

In addition to the hydrated salts of the 3d-group elements, the most thorough investigations were made of the cyan compounds, in which
the octahedral complexes contain six CN radicals. Two isomorphic series of cyanides were investigated:

7a) \( K_3^{''''}(CN)_6 \), \( M'''' = \text{Cr, Mn, Fe, Co} \). The crystal has a symmetry which is very close to orthorhombic [1, 10-12].

7b) \( K_4^{''''}(CN)_6 \cdot 3H_2O \), \( M'''' = \text{V, Mn, Fe} \). The symmetry of the crystal is monoclinic and very close to tetragonal [1, 13].

In both series, a unit cell of the crystal contained four magnetic complexes which were pairwise equivalent.

The X, Y, Z axes of one pair can be obtained by reflecting the axes of the second pair of complexes from three mutually perpendicular planes of the crystal. Among the compounds of the 4d and 5d group elements, the crystals investigated in greater detail are those containing octahedral complexes formed by halides, namely:

8a) \( M'^{''''}M'^{IV}X_6 \), \( M'^{''''} = \text{K, NH}_4 \), ..., \( M'^{IV} = \text{Pt, Ir, Mo, ...} \), \( X = \text{Cl, Br} \) [1, 14]. The crystals have a cubic symmetry. In the case when \( X = \text{Cl} \), all the magnetic complexes of the crystal cell turn out to be fully equivalent to one another. On the other hand, if \( X = \text{Br} \), then the octahedra of the three complexes contained in the crystal cell are somewhat distorted along the three different cubic axes.

8b) \( \text{Na}_2M'^{IV}X_6 \cdot 6H_2O \), \( M'^{IV} = \text{Ir, Pt} \), \( X = \text{Cl, Br} \) [1]. The crystal is triclinic; the number of complexes per unit cell is unknown, but they are all perfectly equivalent magnetically. There is a large rhombic predominantly tetragonal distortion of the symmetry of the octahedral complex.

There are apparently no octahedral complexes in salts of the rare earth elements. The following compounds were investigated in detail:

9) Ethyl sulfates [1, 15]: \( M''''(C_2H_5SO_4)_3 \cdot 9H_2O \), where \( M'''' \) is a trivalent ion of the 4f group. The crystals are trigonal, and each unit cell contains two complexes which are perfectly equivalent. Nine
water molecules are located at the vertices of three identical equilateral triangles, which are parallel to one another and whose planes are perpendicular to the trigonal axes of the crystal. In the center of the middle triangle is located the rare-earth ion; the outermost triangles are turned by an angle $\pi/3$ relative to the middle triangle.

The double nitrates $(M_3^"M"_2(NO_3)_{12}\cdot24H_2O)$ were considered above (see item 3). We note that the rare-earth ion is surrounded by $(NO_3)$ groups which produce a field of trigonal symmetry.

10) Nitrates. From among the compounds of the 5f-group elements, the ones investigated in detail are rubidium nitrates, containing groups of the uranyl type [16] $(M^{IV}_2Rb(NO_3)_3$, where $M^{IV} = U, Np, Pu, ...$). The symmetry of the crystal is rhombohedral; each unit cell has two equivalent complexes. Each complex contains the linear group O-IV-O, parallel to the hexagonal axis of the crystal, and surrounded by three nitrate groups situated in a plane perpendicular to the hexagonal axis.

REFERENCES (§4.1)
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[Footnote]

The hyperfine structure constant is sometimes marked by an index indicating the mass number of the isotope to which it pertains.
§4.2. Spin-Hamiltonian Constants for Solid Paramagnets

1. Iron group ions \((L \neq 0)\) with lower orbital singlets (see Table 4.1, pages 138-151).

\[ 3d^3 (V^{2+} \text{ and } Cr^{3+}) \]

The lower orbital singlet arising under the influence of the octahedral field has a fourfold spin degeneracy, which is split by the lower-symmetry fields into two Kramers doublets. The spin Hamiltonian has the form

\[ \mathcal{H} = g_\| (H_0 S_z + H_x S_x + H_y S_y) + D \left( S_z^2 - \frac{3}{4} \right) + E (S_x^2 - S_y^2) + A (S_z I_z + S_x I_x + S_y I_y) \]

with \( S = 3/2, I = 0 \) for the even isotopes \( Cr^{3+} \), \( 3/2 \) for \( 53\text{Cr} \), \( 7/2 \) for \( 51\text{V} \), and \( 6 \) for \( 50\text{V} \). The value of \( I \) for \( 50\text{V} \) has been determined from experiments on paramagnetic resonance.

If the hyperfine structure is disregarded, the levels in a field \( H_0 \parallel Z \) are described by the formula

\[ \frac{1}{2} g_\| H_0 \pm \{(D + g_\| H_0)^\| \cdot 3E^2 \}^{1/2}, \]
\[ -\frac{1}{2} g_\| H_0 \pm \{(D - g_\| H_0)^\| + 3E^2 \}^{1/2}. \]

The hyperfine structure in \( Cr^{3+} \) salts is frequently unresolved owing to the smallness of the constant \( A \) and the considerable width of the absorption lines.

In salts of \( 51\text{V} \), with a field \( H_0 \parallel Z \) and when \( g_\| H_0 \gg E \) and \( A \), account of the hyperfine structure yields for the levels

\[ \pm \frac{3}{2} g_\| H_0 \pm D \pm \frac{3}{2} A m, \pm \frac{1}{2} g_\| H_0 \pm D \pm \frac{1}{2} A m \]

\( \left( m = \frac{7}{2}, \frac{5}{2}, \ldots, -\frac{1}{2} \right) \).

In analogy with the \( V^{2+} \) and \( Cr^{3+} \) in an octahedral environment, the \( Co^{2+} \) in a tetrahedral complex has a lower orbital singlet which is fourfold spin-degenerate. The only investigated compound \( Cs_3CoCl_5 \) yielded a spectrum described by means of a spin Hamiltonian.
\[ \mathcal{H} = g_1 \beta H_0 \mathbf{S}_z + g_1 \beta (H_x \mathbf{S}_x + H_y \mathbf{S}_y) + D \left( \mathbf{S}_z - \frac{S(S+1)}{4} \right) \]

with \( S = 3/2 \), without a resolved hyperfine structure, owing to the large width of the lines.

\[ 3d^4 (\text{Cr}^{2+}, \text{Mn}^{3+}) \]

The cubic field of the octahedron and the trigonal field leave the lower orbital doublet degenerate. The orbital degeneracy is lifted by a tetragonal field; the lower orbital level remains quintuply spin-degenerate, with the degeneracy lifted by a rhombic field.

Only the sulfate of divalent chromium was investigated. The hyperfine structure due to \(^{51}\text{Cr} \) was not resolved. The spin Hamiltonian has the form \( (S = 2) \):

\[ \mathcal{H} = g_1 \beta H_0 \mathbf{S}_z + g_1 \beta (H_x \mathbf{S}_x + H_y \mathbf{S}_y) + D \left( \mathbf{S}_z - 2 \right) + E (\mathbf{S}_z - \mathbf{S}_y). \]

The levels in a field \( H_0 \| \mathbf{Z} \) are situated at

\[ -2D_z; -D \pm (g_1 \beta H_0^2 + 9E)^{1/2}; \] \[ 2D \pm 2g_1 \beta H. \]

The \( \text{Mn}^{3+} \) compounds were not investigated.

\[ 3d^8 (\text{Ni}^{2+}) \]

In an octahedral field the lower orbital level is a singlet that is triply spin degenerate; the trigonal and tetragonal fields split this level into a doublet and a singlet, while rhombic fields split it into three singlets. The experimental results are described by a spin Hamiltonian

\[ \mathcal{H} = g_1 \beta (H_x \mathbf{S}_x + H_y \mathbf{S}_y + H_z \mathbf{S}_z) + D \left( \mathbf{S}_z - \frac{2}{3} \right) + E (\mathbf{S}_z - \mathbf{S}_y) \]

with \( S = 1 \) and isotropic \( g \); no hyperfine structure was observed. For a field \( H_0 \| \mathbf{Z} \) the levels corresponded to

\[ -\frac{2}{3} D; \frac{1}{3} D \pm (E^2 + g_1 \beta H^2)^{1/2}; \] \[ 2D \pm 2g_1 \beta H. \]

\[ 3d^9 (\text{Cu}^{2+}) \]

In an octahedral field, the lower orbital level is a "nornagnetic"
doublet. A field of rhombic or tetragonal symmetry splits this level into two Kramers doublets. A trigonal field does not split the lower orbital doublet; in this case the orbital degeneracy is lifted by the Jahn-Teller effect or by the spin-orbit coupling. The experimental results are described by a spin Hamiltonian

$$\mathcal{H} = g_s^2 H_s \hat{S}_z + g_s^2 H_s \hat{S}_z + \epsilon_s H_s \hat{S}_z + \epsilon_s H_s \hat{S}_z + A_s \hat{S}_z I_z + A_s \hat{S}_z I_z + P(\hat{S} - \frac{3}{4}) + P(\hat{S} - \frac{3}{4}) + \epsilon_s \hat{S} \hat{I}$$

with

$$S = 1/2 \text{ and } I = 3/2.$$  

When $H_0 \parallel Z$ and $g\beta H_0 >> A >> P'$ the levels are at $\pm 1/2g_z \beta H_0 \pm \pm 1/2A_z m + P (m^2 - 5/4)$, where $m = 3/2, 1/2, -1/2, -3/2$. A special case is copper acetate, which was considered above in Chapter 3.

The behavior of the $\text{Ti}^{3+}$ in a tetrahedral surrounding should be analogous to that of the copper ions.

2. Iron-group ions ($L \neq 0$) with lower orbital triplet (see Table 4.2, pages 152-155)

$3d^{11}$ ($\text{Ti}^{3+}, \text{V}^{4+}, \text{Mn}^{6+}$)

In an octahedral field, the lower level is an orbital triplet, which is split into three Kramers doublets by the lower-symmetry field. When the octahedral complex is weakly distorted, the spin-lattice relaxation time is quite short and the effect is observed only at very low temperatures. In the case of strong distortion (the $\text{V}^{2+}$ or $\text{MnO}^{-}$ ion), the relaxation time is long enough to observe the effect at room temperatures. In $\text{Ti}^{3+}$ salts, the results are described by the following Hamiltonian ($S = 1/2$):

$$\mathcal{H} = g_s^2 H_s \hat{S}_z + g_s^2 (H_s \hat{S}_z + H_s \hat{S}_z).$$

The hyperfine structure has not been resolved for $\text{Ti}^{3+}$. It is observed in dilute vanadyl salts ($I = 7/2$ for $^{51}V$).
In an octahedral field, the lower level is an orbital triplet with quintuple spin degeneracy. A rhombic field lifts the degeneracy completely. In the case of (Fe, Zn)F$_2$ one observes a weakly split lower doublet. The spectrum is described by a Hamiltonian ($S = 1/2$, $g_\parallel = 0$)

$$\hat{H} = g_\parallel \beta H S_z + \Delta S_z$$

where $\Delta$ characterizes a weak splitting of the doublet by the low-symmetry components of the crystalline field.

$3d^7 (Co^{2+})$

In an octahedral field the lower orbital triplet is degenerate and is split into Kramers doublets by the lower-symmetry fields and by the spin-orbit coupling. The results of the experiments are described by a Hamiltonian ($S = 1/2, I = 7/2$)

$$\hat{H} = \hat{g} (g_x S_x + g_y S_y + g_z S_z) + A_x S_x I_x + A_y S_y I_y + A_z J_z.$$ 

Sometimes one obtains $g_x = g_y = g_z$; $A_x = A_y = A_z$ (axial symmetry).

3. Rare-earth ions ($L \neq 0$) with odd number of electrons (see Table 4.3, pages 156-158)

$4f^1$ (Ce$^{3+}$), $4f^3$ (Nd$^{3+}$), $4f^5$ (Sm$^{3+}$), $4f^9$ (Dy$^{3+}$), $4f^{11}$ (Er$^{3+}$), $4f^{13}$ (Yb$^{3+}$)

In the investigated cases, the experimental data are described by a Hamiltonian ($S' = 1/2$)

$$\hat{H} = g_\parallel \beta H S_z + g_\perp \beta (H S_x + H S_y)$$

to which one adds in the case of odd isotopes the terms of the hyperfine interaction $A S_z I_z + B (S_x I_x + S_y I_y)$. Sometimes (in ethyl sulfates of Ce$^{3+}$) a second doublet is observed, described by the same Hamiltonian and located several cm$^{-1}$ away from the lower one.
4. Rare-earth ions with even number of electrons (see Table 4.4, pages 159-160)

\[ 4f^2(Pr^{3+}), \ 4f^4(Pm^{3+}), \ 4f^6(Eu^{3+}), \ 4f^8(Tb^{3+}), \ 4f^{10}(Ho^{3+}), \ 4f^{12}(Tm^{3+}) \]

Since the number of electrons in these ions is even, the lower spin doublet can be nondegenerate. However, a trigonal field does not lift the degeneracy, and the components of the lower symmetry in ethyl sulfate and double nitrate crystals are small. Paramagnetic resonance is therefore observable; the available experimental data are described by a Hamiltonian

\[ \mathcal{H} = \frac{g_\|}{2} \mathbf{H}_z \cdot \mathbf{S} + \Delta_x \mathbf{S}_x + \Delta_y \mathbf{S}_y + A \mathbf{S}_x \mathbf{S}_y \]

In this case \( g_\| \) is assumed equal to zero; the terms \( \Delta \) represent small splittings, due to distortion by a field which has a symmetry lower than trigonal.

5. Ions in the \( S \) state (see Table 4.5, pages 160-169)

\[ 3d^5(Mn^{2+}, Fe^{3+}) \]

The lower orbital level is a singlet with sixfold spin degeneracy. The electric field of the water octahedron splits the singlet into three Kramers doublets which are usually spaced less than 1 cm\(^{-1}\) apart. The spin Hamiltonian (for the odd isotopes) has the form

\[ \mathcal{H} = \frac{g}{2} \left( H_x \mathbf{S}_x + H_y \mathbf{S}_y + H_z \mathbf{S}_z \right) + \frac{1}{2} \alpha \left( \mathbf{S}_x^2 + \mathbf{S}_y^2 + \mathbf{S}_z^2 - \frac{\text{27}}{16} \right) + \]

\[ + D \left( \mathbf{S}_x^2 - \frac{35}{12} \right) + \frac{7}{36} \alpha \left( \mathbf{S}_x^2 - \mathbf{S}_y^2 + \mathbf{S}_z^2 \right) + A \left( \mathbf{S}_x \mathbf{S}_y + \mathbf{S}_x \mathbf{S}_z \right) \]

Here \( \alpha \) is the splitting by the cubic field, \( \xi, \eta, \zeta \) are mutually perpendicular axes, with respect to which the Z axis is in the [111] direction.

If the symmetry of the magnetic complex is not higher than orthorhombic (for example, in Tutton's salts of Mn\(^{2+}\)), then a term \( E(\mathbf{S}_x^2 - \mathbf{S}_y^2) \) is added to the Hamiltonian.
4f^7(ad^3+, Eu^{2+})

Because of the large value $S = 7/2$, the spin Hamiltonian is very complicated and will not be written out here. It can be written (without account of the hyperfine structure) in the form

$$\mathcal{H} = \beta (H_x \hat{S}_x + H_y \hat{S}_y + H_z \hat{S}_z) + B_1 \hat{U}_1 + B_2 \hat{U}_2 + B_3 \hat{U}_3 + B_4 \hat{U}_4 + B_5 \hat{U}_5.$$

Here each $\hat{U}_n$ is an operator; the coefficients $B_n$ are determined from experiment. For the sake of convenience, one frequently uses the following notation

$$b_1 = 3B_5, b_2 = 3B_6, b_3 = 60B_7, b_4 = 1260B_8, b_5 = 1260B_9,$$

with $b_2 = D, b_2 = E, 3b_4 = F$.

In the case of Eu^{2+}, which was investigated in a field of cubic symmetry, $g$ and $A$ are isotropic, but the complete spin Hamiltonian was not established.

6. Compounds with strong covalent bond (see Table 4.6, pages 169-173)

Included among such substances are the cyanides of trivalent iron and divalent manganese from the 3d group, and also all the investigated paramagnets from among the compounds of elements of the 4d and 5d groups.

For Fe^{III}, Mn^{II}, Mo^{V}, Ru^{III}, Ag^{II}, and Ir^{IV}, the effective spins have a value $S' = 1/2$ and the spectrum is described by a spin Hamiltonian

$$\mathcal{H} = \beta (g_x \hat{S}_x + g_y \hat{S}_y + g_z \hat{S}_z),$$

to which the corresponding terms that take the hyperfine structure into account are added for the odd isotopes. In some cases one must also take into account the hyperfine structure due to the interaction between the uncompensated electron and the spins of the nuclei of the atoms which are covalently bound with the central atom (for example, in the case of (NH_4)_2[IrCl_6], diluted with the corresponding platinum salt).
For Mo\textsuperscript{III} and Re\textsuperscript{IV}, the spin Hamiltonian has the form

\[ \mathcal{H} = g_1 (\mu_B H \cdot S) + g_2 (\mu_B H \cdot S) + g_3 (\mu_B H \cdot S) + D \left( S^2 - \frac{1}{3} S(S+1) \right) + E \left( S_z - \frac{1}{2} S \right) \]

with effective spin \( S' = 3/2 \). For odd isotopes one should add to the Hamiltonian the terms characterizing the hyperfine structure of the spectrum.

The number of compounds of the elements of the 4d and 5d groups, in which paramagnetic resonance spectra were investigated, is very small; one of the difficulties entailed in the investigation is the choice of isomorphous diamagnetic salts necessary to weaken the magnetic dipole interactions, for the latter are quite appreciable when the indicated compounds are in the undilute state. The last group in the class of substances with strong covalent bonds is made up of the actinide compounds. Paramagnetic resonance in these compounds has also been investigated in a very small number of cases. In double neptunyl nitrate, the spectrum is described by a spin Hamiltonian

\[ \mathcal{H} = g_1 (\mu_B H \cdot S) + g_2 (\mu_B H \cdot S) + g_3 (\mu_B H \cdot S) + D \left( S^2 - \frac{1}{3} S(S+1) \right) + E \left( S_z - \frac{1}{2} S \right) \]

with effective spin \( S' = 1/2 \) and \( I = 5/2 \) (for the odd isotope \( ^{237}\text{Np} \)).

For plutonyl we have \( g_1 = 0 \) and the spin Hamiltonian has the form

\[ \mathcal{H} = g_2 (\mu_B H \cdot S) + A S_z + A_\perp S_z + A_\parallel S_z \]

The effective spin is \( S' = 1/2 \); the value of \( I \) is 1/2 for \( ^{239}\text{Pu} \) and 5/2 for \( ^{241}\text{Pu} \). The last two terms of the Hamiltonian describe small splittings due to the distortions of the crystal and to thermal fluctuations.
### TABLE 4.1

<table>
<thead>
<tr>
<th>Formula</th>
<th>T. °K</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Literature</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4)_2)\text{V(SO}<em>4)\text{\cdot 6H}</em>{2}\text{O})</td>
<td>290</td>
<td>1,051</td>
<td>± 0,002</td>
<td>± 0,005</td>
<td>± 0,049</td>
<td>± 0,0088</td>
<td>± 0,0002</td>
<td>[1]</td>
<td>a = 4°, (\psi = 22°)</td>
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<tr>
<td>\text{V: Zn = 10°}</td>
<td>20</td>
<td>1,93</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>± 0,009</td>
<td>± 0,0018</td>
<td>± 0,0006</td>
<td>[2, 3]</td>
<td>a = 22°, (\psi = 2°)</td>
</tr>
<tr>
<td>\text{K}<em>4\text{V(CN)}\text{\cdot 3H}</em>{2}\text{O})</td>
<td>90, 20</td>
<td>1,9991</td>
<td>± 0,0008</td>
<td>± 0,0016</td>
<td>± 0,0004</td>
<td>± 0,00003</td>
<td>± 0,00002</td>
<td>[4, 5]</td>
<td>± 0,00003</td>
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<tr>
<td>\text{V: Fe = 0,1-5 \cdot 10°}</td>
<td>90, 20</td>
<td>1,9903</td>
<td>± 0,0005</td>
<td>± 0,0001</td>
<td>± 0,0001</td>
<td>± 0,00002</td>
<td>± 0,00002</td>
<td>[6]</td>
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<tr>
<td>\text{Cr: AI + 2: 17}</td>
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<td>1,98</td>
<td>± 0,006</td>
<td>± 0,003</td>
<td>± 0,0003</td>
<td>± 0,0003</td>
<td>± 0,0003</td>
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<tr>
<td>\text{V(C}_6\text{H}_4)\text{4(CN)}\text{8(T = from 270 to 20°K, g = 2,0)}</td>
<td>[8]</td>
<td>± 0,002</td>
<td>± 0,002</td>
<td>± 0,002</td>
<td>± 0,002</td>
<td>± 0,002</td>
<td>± 0,002</td>
<td>± 0,002</td>
<td>± 0,002</td>
</tr>
</tbody>
</table>

Paramagnetic resonance is observed also in \(\text{VSO}_4\) \((T = 290°K)\) [7]; \(\text{V(C}_6\text{H}_4\)\text{4(CN)}\text{8(T = from 270 to 20°K, g = 2,0)}\) [8]; \(\text{V}^2+\) in phthalocyanine \((T = 290, 20°K, g = 2,0)\) [11].

Remarks. a) The direction cosines are:

\[
\begin{align*}
\alpha &= 0.707 \\
\beta &= 0.523 \\
\gamma &= 0.470
\end{align*}
\]

### Cr\(^{3+}\)

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<th>Formula</th>
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<th>β</th>
<th>γ</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Literature</th>
<th>Remarks</th>
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<tr>
<td>\text{CrCr(SO}<em>4)\text{\cdot 12H}</em>{2}\text{O})</td>
<td>290</td>
<td>1,98</td>
<td>± 0,003</td>
<td>± 0,007</td>
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<td>± 0,007</td>
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<td>250</td>
<td>± 0,003</td>
<td>± 0,007</td>
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<td>± 0,007</td>
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<td>± 0,003</td>
<td>± 0,007</td>
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<td>± 0,007</td>
<td>± 0,007</td>
<td>[4]</td>
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<td>± 0,003</td>
<td>± 0,007</td>
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<td>± 0,007</td>
<td>± 0,007</td>
<td>[7]</td>
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- 138 -
TABLE 4.1 (Continuation)

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<th>$D$</th>
<th>$S$</th>
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<td>г) d</td>
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<td></td>
<td>193 1.98</td>
<td>0.063</td>
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<tr>
<td></td>
<td>±0.02 1.98</td>
<td>0.054</td>
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</tr>
<tr>
<td>4</td>
<td>KCr(SeO$_4$)$_3$·12H$_2$O</td>
<td>90 1.98</td>
<td>0.091</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 1.98</td>
<td>0.092</td>
<td></td>
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<tr>
<td></td>
<td>±0.02 1.98</td>
<td>0.099</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Cr: Al = 1:10</td>
<td>90 20</td>
<td>0.098</td>
<td></td>
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<tr>
<td></td>
<td>20 0.099</td>
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- 139 -
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<th>Т.К</th>
<th>q</th>
<th>D</th>
<th>E</th>
<th>A</th>
<th>2</th>
<th>Замечания</th>
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<tbody>
<tr>
<td>2</td>
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<td>1,976</td>
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<td>0,0003</td>
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<tr>
<td>4</td>
<td>KCr (SO₄)₂·12H₂O</td>
<td>90,20</td>
<td>1,976</td>
<td>0,0002</td>
<td>0,0003</td>
<td>0,0003</td>
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<tr>
<td>4</td>
<td>Cr:[Cr:Cl₄]·6H₂O</td>
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<td>1,968</td>
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<tr>
<td>5</td>
<td>Cr : Mn = 0,1-10^-4</td>
<td>90,20</td>
<td>1,983</td>
<td>1,991</td>
<td>1,981</td>
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<td>0,0018</td>
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<tr>
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<td>0,0002</td>
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<td>Cr : Mn = 0,1-10^-4</td>
<td>90,20</td>
<td>1,983</td>
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<td>Cr : Mn = 0,1-10^-4</td>
<td>290</td>
<td>1,98</td>
<td>0,592</td>
<td>0,592</td>
<td>0,592</td>
<td>0,592</td>
<td>0,592</td>
</tr>
<tr>
<td>5</td>
<td>Cr : Mn = 0,1-10^-4</td>
<td>290</td>
<td>1,98</td>
<td>0,59</td>
<td>0,59</td>
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<td>Cr : Mn = 0,1-10^-4</td>
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<td>0,70</td>
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<td>0,70</td>
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<tr>
<td>5</td>
<td>Cr : Mn = 0,1-10^-4</td>
<td>290</td>
<td>1,97</td>
<td>0,55</td>
<td>0,27</td>
<td>0,0007</td>
<td>0,0017</td>
<td>0,0017</td>
</tr>
</tbody>
</table>

Paramagnetic resonance absorption was observed also at room temperature in

A) Orthorhombic; B) hexagonal; C) (enriched with odd isotope).

- 140 -
Remarks:

a) Below 160°K there are two different magnetic complexes.

b) The temperature of the crystalline transition is 157 ± 2°K. Below this point, the spectrum corresponds to rhombic symmetry; the direction cosines of the rhombic axes relative to the tetragonal axes a, b, c are:

\[
\begin{array}{ccc}
X & -0.35 ± 0.05 & -0.35 ± 0.05 \\
Y & +0.71 ± 0.04 & -0.71 ± 0.04 \\
Z & +0.61 ± 0.04 & +0.61 ± 0.04 \\
\end{array}
\]

The directions for the other three ions are obtained by rotating the XYZ system about the c axis through angles π/2. D and E remain unchanged between 90 and 13°K.

c) The temperature of the crystalline transition 170 ± 2°K. Below this point the spectrum corresponds to rhombic symmetry.

d) Crystalline transition near 80°K. Below this temperature there are two different magnetic complexes.

e) $\delta$ decreases at an approximate rate 0.0005 cm$^{-1}$ deg$^{-1}$ in the temperature interval from 295 to 77°K, i.e., the trigonal component of the crystalline field decreases with decreasing temperature.

f) The crystal has three aluminum atoms per unit cell, located on the C$_3$ axis, but only two of them are equivalent. This explains the observed intensities of spectra I and II: spectrum I is twice as intense.

g) Only one line.

h) The direction cosines of the angles at $T = 20°K$ are:

\[
\begin{array}{ccc}
X & 0.104 ± 0.004 & 0 \\
Y & 0 & 1 \\
Z & 0.994 ± 0.004 & 0 \\
\end{array}
\]

j) The direction cosines of the angles at $T = 90°K$ are:

\[
\begin{array}{ccc}
X & 0 & ±0.996 \\
Y & 0 & ±0.996 \\
Z & 1 & 0 \\
\end{array}
\]

- 141 -
k) The nearest surrounding of Cr$^{3+}$ in acetyl acetonate and its fluorine derivatives is a distorted octahedron made up of six oxygen atoms; the local field is essentially axial. Between 290 and 900K one observes in acetyl acetonate a gradual transition wherein the complex splits at 900K into three types with slightly different orientations of the Z axes, or having a somewhat different splitting; $\psi = +22.5^o$, $\alpha = 59^o$.

l) The spectrum, which consists of one isotropic line, shows that Cr$^{3+}$ is in a strictly cubic crystalline field.

m) The spectrum belongs to the Cr$^{3+}$ ions in an axial crystalline field. The axes of the nonequivalent ions are directed along the cubic axes. The spectrum arises at large concentrations of Cr$^{3+}$.

n) The spectrum belongs to the Cr$^{3+}$ ions in a rhombic crystalline field. The directions of the X, Y, and Z axes are: X = (110), Y = (110), Z = (001). The number of Cr$^{3+}$ ions in the rhombic field constitutes 1/2 to 1/4 of the number of Cr$^{3+}$ in the cubic field. The spectrum arises at large concentrations of Cr$^{3+}$.

o) The presence of two spectra is attributed to different relative arrangements of the Cr$^{3+}$ ions and the compensating F$^-$ ions; the hyperfine interaction with the F nuclei causes only a broadening of the lines. The constant of this interaction is approximately 3-5 oersteds. The constant of the hyperfine interaction with the $^{19}F$ nuclei is approximately 20 oersteds. Absorption in zero field occurs at a frequency $\nu = (2847 \pm 2) \cdot 10^{-4}$ sec$^{-1}$. 

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| FORMULA | T, K | E || E⊥ | E | LITERATURE | REMARKS |
|---------|------|-----|-----|-----|-------------|---------|
| Co²⁺  |      |     |     |     |             |         |
| Co₂⁺[x 2] | 90, 20 | 2.32 ± 0.04 | 2.37 ± 0.04 | -4.5 | 0 | [1] | M = 4. Each ion is surrounded by a distorted tetrahedron made up of 4 chlorine atoms. M_m = 1, the spectrum corresponds to axial symmetry with an axis parallel to c. |
| Cr²⁺  |      |     |     |     |             |         |
| CrSO₄·5H₂O | 290 | 1.98 | 1.99 | 2.24 | 0.10 | [1] | Mₘ = 2, the angle between the Z axis is 86°. |
| Ni²⁺  |      |     |     |     |             |         |
| NiCl₂(NO₃)₂·24H₂O | 20 | 2.24 | 0.177 | 0 | ± 0.002 | [3] |         |

A) M = 4. Each ion is surrounded by a distorted tetrahedron made up of 4 chlorine atoms. M_m = 1, the spectrum corresponds to axial symmetry with an axis parallel to c.
B) M_m = 2, the angle between the Z axis is 86°.
TABLE 4.1 (Continuation)

<table>
<thead>
<tr>
<th>1 формула</th>
<th>T. K.</th>
<th>ε</th>
<th>D</th>
<th>ε′</th>
<th>D′</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiBr₂·6H₂O (кр. ст. 4)</td>
<td>290</td>
<td>2,3</td>
<td>-0,50</td>
<td>0</td>
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</tr>
<tr>
<td></td>
<td>180</td>
<td>2,29</td>
<td>-0,32</td>
<td>0</td>
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</tr>
<tr>
<td></td>
<td>90</td>
<td>2,28</td>
<td>-0,17</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>2,29</td>
<td>-0,14</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2,29</td>
<td>-0,12</td>
<td>0</td>
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<tr>
<td></td>
<td>14</td>
<td>2,29</td>
<td>-0,12</td>
<td>0</td>
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<tr>
<td></td>
<td>2,34</td>
<td>-0,6</td>
<td></td>
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</tr>
</tbody>
</table>

A) (Powder).

Paramagnetic resonance absorption was observed also at room temperature in: NiBr₂ (g = 2.27) [11]; NiBr₂(NH₃)₆ (g = 2.14 and 2.16) [12, 13]; NiCl₂ (g = 2.21) [11]; NiCl₂·6H₂O [14]; NiI₂(NH₃)₆ (g = 2.14) [13, 7]; Ni(C₆H₄)₄(CN)₈ (g = 2.20; T = 270 - 20⁰K) [15]; Ni(NH₃)₆ClO₄ (g = 2.17) [13].

Remarks:

a) When Zn:Ni = 50, the parameters and the axes remain practically unchanged.

b) When Zn:Ni = 4.16, D is approximately 20% larger than in the undiluted salts at all temperatures.

c) The dependence of D and ε on the hydrostatic pressure p was investigated; ε is independent of p, 3D/3p = 0.834·10⁻⁴ cm⁻¹/kg·cm⁻²; D = 0 when p = 6200 kg/cm².

d) For one complex, the direction cosines of the axes are: Z (0.95; 0.31; 0), Y (-0.31; 0.95; 0.09). The axes of the other complex are ob-
tained by mirror reflection.

e) One line, the width of which hardly changes with temperature.
f) The cubic field is subject to trigonal distortion.
g) The low-temperature measurements may not be accurate (see Orton, J.W., Rep. progr. Phys. 22, 204, 1959). The axes $Z_1$ and $Z_2$ of two ions lie in the $K_1OK_3$ plane, with the angles $Z_1OK_1$ and $Z_2OK_1$ equal to $\pm \theta$, where the angle $K_1C_0 = \psi$. $X_1$ is approximately parallel to $Y_2$, and both axes lie in the $K_2OK_3$ plane with the angle $X_1OK_2$ equal to $\alpha$ and the angle $Y_2OK_2$ equal to $90^0 - \alpha$.

TABLE 4.1 (Continuation)

<table>
<thead>
<tr>
<th>Formula</th>
<th>T. °K</th>
<th>$\epsilon_1$</th>
<th>$\epsilon_2$</th>
<th>$\epsilon_3$</th>
<th>$\epsilon_{\min}(K,\epsilon)$</th>
<th>$\epsilon_{\max}(K,\epsilon)$</th>
<th>$\Theta$</th>
<th>$\Theta^*$</th>
<th>Literature</th>
<th>Comments</th>
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<td>$\text{Cu}^2+$</td>
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<tr>
<td>Tutton's Salts (cr. st. 2)</td>
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</tr>
<tr>
<td>$\text{Cu}_{2} \text{Cu} \text{(SO}_4 \text{)}_2 \cdot 6\text{H}_2\text{O}$</td>
<td>90</td>
<td>2.08</td>
<td>2.06</td>
<td>2.43</td>
<td>$\pm 0.02$</td>
<td>$\pm 0.02$</td>
<td>$\pm 0.02$</td>
<td>+114 40</td>
<td>[1]</td>
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<tr>
<td>$\text{K}_{2} \text{Cu} \text{(SO}_4 \text{)}_2 \cdot 6\text{H}_2\text{O}$</td>
<td>290</td>
<td>2.31</td>
<td>2.07</td>
<td>2.25</td>
<td>$\pm 0.03$</td>
<td>$\pm 0.03$</td>
<td>$\pm 0.03$</td>
<td>+105 [2]</td>
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<tr>
<td>$\text{Cu}<em>{2} \text{Zn} = \text{Zn}</em>{2} \text{Cu} \text{(SO}_4 \text{)}_2 \cdot 6\text{H}_2\text{O}$</td>
<td>290</td>
<td>2.06</td>
<td>2.25</td>
<td>2.26</td>
<td>$\pm 0.03$</td>
<td>$\pm 0.03$</td>
<td>$\pm 0.03$</td>
<td>+105 [2]</td>
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<tr>
<td>$\text{Cu}_{2} \text{Zn} = 2 \cdot 10^{-4} - 3 \cdot 10^{-4}$</td>
<td>20</td>
<td>2.44</td>
<td>2.03</td>
<td>0.0011</td>
<td>$\pm 0.02$</td>
<td>$\pm 0.03$</td>
<td>$\pm 0.03$</td>
<td>+105 42</td>
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TABLE 4.1 (Continuation)

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<th>ε_y</th>
<th>ε_z</th>
<th>А_x</th>
<th>А_y</th>
<th>А_z</th>
<th>P</th>
<th>q</th>
<th>a^*</th>
<th>Литература</th>
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<td>77</td>
<td>2.47 ± 0.05</td>
<td>2.08 ± 0.04</td>
<td>-0.0083</td>
<td>0.0045</td>
<td>0.001</td>
<td>[42]</td>
<td>a</td>
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<tr>
<td>K_2Cu(SO_4)_2·6D_2O</td>
<td>20</td>
<td>2.16 ± 0.02</td>
<td>2.04 ± 0.02</td>
<td>2.42 ± 0.0017</td>
<td>+0.0061</td>
<td>-0.0009</td>
<td>+0.00110</td>
<td>+105</td>
<td>43</td>
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<tr>
<td>Zn : Cu = 200 — 1000</td>
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<tr>
<td>K_2Cu(SO_4)_2·6H_2O</td>
<td>90</td>
<td>2.32 ± 0.02</td>
<td>2.07 ± 0.02</td>
<td>2.46 ± 0.0015</td>
<td>+0.005</td>
<td>+0.0106</td>
<td>+0.00001</td>
<td>47</td>
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<tr>
<td>Zn : Cu = 50 — 2000</td>
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<td>2.04 ± 0.02</td>
<td>2.26 ± 0.02</td>
<td>2.46 ± 0.0015</td>
<td>+0.005</td>
<td>+0.0106</td>
<td>+0.00001</td>
<td>47</td>
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<tr>
<td>(NH_4)_2Cu(SO_4)_2·6H_2O</td>
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<td>2.32 ± 0.02</td>
<td>2.07 ± 0.02</td>
<td>2.46 ± 0.0015</td>
<td>+0.005</td>
<td>+0.0106</td>
<td>+0.00001</td>
<td>47</td>
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<tr>
<td>Zn : Cu = 50 — 2000</td>
<td>290</td>
<td>2.04 ± 0.02</td>
<td>2.26 ± 0.02</td>
<td>2.46 ± 0.0015</td>
<td>+0.005</td>
<td>+0.0106</td>
<td>+0.00001</td>
<td>47</td>
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</tr>
<tr>
<td>(NH_4)_2Cu(SO_4)_2·6H_2O</td>
<td>290</td>
<td>2.32 ± 0.02</td>
<td>2.07 ± 0.02</td>
<td>2.46 ± 0.0015</td>
<td>+0.005</td>
<td>+0.0106</td>
<td>+0.00001</td>
<td>47</td>
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<tr>
<td>Rb_2Cu(SO_4)_2·6H_2O</td>
<td>20</td>
<td>2.15 ± 0.02</td>
<td>2.04 ± 0.02</td>
<td>2.43 ± 0.0020</td>
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<td>-0.0110</td>
<td>+0.00112</td>
<td>+105</td>
<td>42</td>
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<td>Zn : Cu = 200 — 1000</td>
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<tr>
<td>Ti_2Cu(SO_4)_2·6H_2O</td>
<td>90</td>
<td>2.40 ± 0.02</td>
<td>2.08 ± 0.02</td>
<td>2.06 ± 0.0015</td>
<td>+0.005</td>
<td>+0.0106</td>
<td>+0.00001</td>
<td>47</td>
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- 146 -
<table>
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<th>( T ), K</th>
<th>( g )</th>
<th>( A )</th>
<th>( B )</th>
<th>Literature</th>
<th>Notes</th>
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<td>0.2219</td>
<td>0.2217</td>
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<td>0.0026</td>
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<td>( g_x = g_y )</td>
<td>( g_z = g_z )</td>
<td>( A_x = A_y )</td>
<td>( A_z = A_z )</td>
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</tr>
<tr>
<td>( Cu_xLa_y) ((NO_3)_x) \cdot 24H_2O</td>
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<td>2.026</td>
<td>2.454</td>
<td>0.0017</td>
<td>0.0110</td>
<td>[5]</td>
</tr>
<tr>
<td>( Cu : Mg = 1 : 100 )</td>
<td></td>
<td>( g_x = g_y )</td>
<td>( g_z = g_z )</td>
<td>( A_x = A_y )</td>
<td>( A_z = A_z )</td>
<td></td>
</tr>
<tr>
<td>( Cu_xLa_y) ((NO_3)_x) \cdot 24D_2O</td>
<td>90</td>
<td>2.219</td>
<td>2.218</td>
<td>0.00290</td>
<td>0.00275</td>
<td>[4, 5]</td>
</tr>
<tr>
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<td>( g_x = g_x )</td>
<td>( g_y = g_y )</td>
<td>( A_x = A_x )</td>
<td>( A_y = A_y )</td>
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</tr>
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<td>( CuSiF_4 \cdot 6H_2O ) ( \text{up.ctx. 4} )</td>
<td>250</td>
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<td>0.0028</td>
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<td>( g_x = g_x )</td>
<td>( g_y = g_y )</td>
<td>( A_x = A_x )</td>
<td>( A_y = A_y )</td>
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<td>2.46</td>
<td>0.00360</td>
<td>0.0110</td>
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</tbody>
</table>

A) Orthorhombic.
<table>
<thead>
<tr>
<th>Формула</th>
<th>( T ), К</th>
<th>( \epsilon )</th>
<th>( A )</th>
<th>( B )</th>
<th>2 Литература</th>
<th>3 Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu} (\text{CN})_2 \cdot \text{Cu} (\text{NO}_3)_2 \cdot \text{nH}_2\text{O} )</td>
<td>290</td>
<td>2,25</td>
<td>2,05</td>
<td>0,02</td>
<td>0,0199</td>
<td>0,0007</td>
</tr>
<tr>
<td>( [\text{Cu} (\text{CN})_2] \cdot \text{nH}_2\text{O} )</td>
<td>290</td>
<td>± 0,02</td>
<td>± 0,02</td>
<td>± 0,08</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} )</td>
<td>290</td>
<td>2,055</td>
<td>2,124</td>
<td>2,161</td>
<td>0,0199</td>
<td>0,0007</td>
</tr>
<tr>
<td>( \text{Cu} (\text{Cl})_2 \cdot \text{Cu} (\text{Cl})_2 \cdot \text{nH}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{Cu} (\text{Cl})_2 \cdot \text{Cu} (\text{Cl})_2 \cdot \text{nH}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} )</td>
<td>290</td>
<td>± 0,004</td>
<td>± 0,015</td>
<td>± 0,005</td>
<td>± 0,007</td>
<td>[23]</td>
</tr>
</tbody>
</table>

A) Orthorhombic; B) rhombic; C) tetragonal; D) monoclinic; E) or; F) S = 1, three different magnetic complexes, see §3.11.
TABLE 4.1 (Conclusion)

<table>
<thead>
<tr>
<th>Formula</th>
<th>T, K</th>
<th>g</th>
<th>A</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺⁺ + MgO</td>
<td>290</td>
<td>2.100</td>
<td>± 0.002</td>
<td>± 0.0001</td>
</tr>
<tr>
<td>Cu⁺⁺ + NaCl</td>
<td>290</td>
<td>2.07</td>
<td>± 0.009</td>
<td>± 0.0009</td>
</tr>
<tr>
<td>Cu⁺⁺ + KCl</td>
<td>290</td>
<td>2.16</td>
<td>± 0.010</td>
<td>± 0.0010</td>
</tr>
<tr>
<td>Cu⁺⁺ + CdCl₂</td>
<td>290</td>
<td>2.065</td>
<td>2.033</td>
<td>2.136</td>
</tr>
</tbody>
</table>

Paramagnetic resonance is observed also in the following compounds at room temperature:

chlorophyllates of copper (T = 270, 90°C; g = 2.05 ± 0.01; Mg:Cu, g = 2.06) [15, 44]; in silicate glass (g_u = 2.32, g_ξ = 2.06) [38]; persulfate of diorthophenantroline of copper (T = 290, 90, 20°C; g_ξ = 2.05) [22]; copper derivative of salicylaldehyde (Cu:Ni = 1:200) [47]; CuS [20]; chlorinated and nonchlorinated tetraphenylporphin Cu²⁺ (g = 2.18, A_Cu = 0.0250, A_CL = 0.0120) [30].

A) Field of cubic symmetry; B) (powder); c) dimethylglyoxime Cu³⁺.

Remarks:

a) Measurements were made at ν = 5·10⁸ cps.

b) A second anomalous spectrum appears when T > 20°C; the g factors of both spectra differ by less than 1%.

c) Transition temperature from 173 to 273°C.

d) Transition temperature from 33 to 45°C.

e) Transition temperature from 12 to 50°C.

f) Transition temperature from <7 to 35°C.

g) Each Cu²⁺ is surrounded by a distorted octahedron of ⁴H₂O and 20; it can be assumed that the Cu²⁺ is in a tetragonal field (the - 149 -
rhombic field is very small); the angle between the tetragonal axes is $86 \pm 2^\circ$; $g_{\text{max}}$ and $g_{\text{min}}$ are determined in the plane of the tetragonal axes of the nonequivalent ions.

h) The ratio of the constant $\lambda'$ of the spin-orbit coupling of the Cu$^{2+}$ ion in the crystal to the constant $\lambda$ for the free ion is $\lambda'/\lambda = 0.55$.

j) The sharply anisotropic exchange leads to lifting of the hyperfine structure in a direction perpendicular to the $Z$ axes; the structure is resolved in the direction of the $Z$ axes.

k) Each Cu$^{2+}$ has a plane surrounding of two H$_2$O and two Cl; an elongated octahedron results from two additional more remote Cl, belonging to the other ions of Cu. Only one line is observed. The substance is antiferromagnetic below 4.3$^\circ$K.

l) Each Cu$^{2+}$ is surrounded by four Cl's, forming a rhombus in the $aa$ plane, and two molecules of H$_2$O on a normal to this plane. The two rhombi of the nonequivalent ions are turned through $90^\circ$ relative to each other around the $c$ axis — the H$_2$O-H$_2$O line (the Y axis); thus, the Cu is in a field of rhombic symmetry. The spectrum was measured at wavelengths of 5.4 and 6.6 millimeters, with an exchange frequency $1.1 \cdot 10^{10}$ cps.

m) Each Cu$^{2+}$ is surrounded by a square made up of four N.

n) The Cu$^{2+}$ is surrounded with four N; perpendicular to the N plane, opposite the Cu, an O on one side (at a distance 2.68 A) and Cl on the other (at a distance 2.89 A).

o) Each Cu$^{2+}$ surrounded by four O and two H$_2$O, forming a distorted octahedron.

p) Bimolecular cell; each Cu$^{2+}$ surrounded by a distorted octahedron made up of four O, an H$_2$O, and a neighboring Cu$^{2+}$; distance between two neighboring Cu$^{2+}$ is 2.6 A. $D = 0.345 \pm 0.005$, $E = 0.007 \pm 0.003$, 

- 150 -
A_z = 0.008, A_x, A_y < 0.0010. See §3.11.

r) It is seen from the paramagnetic resonance spectrum that the cell contains six magnetic complexes, each with two Cu^{2+}; three complexes are derived from the remaining three by reflection in the ac plane. Each complex is approximately tetragonal.

s) Each Cu^{2+} is surrounded by four O in a single plane. The hyperfine structure is described by the relation

\[ A'g' = A'g'_{||} \cos^2 \theta + B'g'_{\perp} \sin^2 \theta + 2Cg'_{||} \sin \theta \cos \theta, \]

\[ C = \pm 0.0062 \text{ cm}^{-1} \text{ at } T = 77^0\text{K and } C = \pm 0.0043 \text{ cm}^{-1} \text{ at } T = 290^0\text{K}. \]

t) Type A; axial distortion of the crystalline field due to interaction between Cu^{2+} and vacancy of the positive lattice site in the (110) direction; type B: the same, but the vacancy is in the (100) direction; type C: axial distortion of the cubic-symmetry field is due to the Jahn-Teller effect and is directed along (100). The effect is observed only in halogenated crystals.

u) Spectra a) and b) obtained in crystals grown from a melt, while spectrum c) is obtained from the aqueous solution.

v) There are trigonal distortions of the cubic field.

1) Formula; 2) literature; 3) remarks; 4) cr. st.; 5) in; 6) to.
### Table 4.2

| Formula | \( T \) \(^\circ\)K | \( \varepsilon_{||} \) | \( \varepsilon_{\perp} \) | \( \Delta \) | Literature | Notes |
|---------|-----------------|-----------------|-----------------|--------------------|-----------------|-----------------|
| \( \text{A} \) | \( \text{CsTi(SO}_4\text{)}_3 \cdot 12\text{H}_2\text{O} \) | 4.2–2.5 | 1.23 | 1.14 | [1] | |
| | \( \text{KTi(C}_2\text{O}_4\text{)}_3 \cdot 2\text{H}_2\text{O} \) | 90–20 | 1.68 | 1.65 | [2] | |
| | \( \text{Ti}[[\text{CH}_3\text{COO}]_3 \cdot \text{CH}_3 \) | 290 | 2.00 | 1.93 | [3] | |
| | \( \text{Ti:Al} = 10^{-5} \) | (powder) | 7.88 | 1.53 | [4] | |
| | \( \text{CsTi(SO}_4\text{)}_3 \cdot 12\text{H}_2\text{O} \) (powder) | 6.53 | 1.55 | | |
| | \( \text{M}_m = 2 \) | \( \text{M}_m = 2 \) | \( \text{BN} \) | (octahedron) | (cube) | \( \text{BN} \) | | (cube) |

### Notes

A) (Powder); \( \text{M}_m = 2 \). Nearest surrounding of \( \text{Ti}^{3+} \) is an octahedron of 60; local field of axial symmetry. The g factor depends on the temperature, the line width is very large and is determined by the spin-lattice relaxation time. C) A hyperfine structure, due to \( ^{51}\text{V} \) (\( I = 7/2 \)) is observed in powder diluted with a \( \text{Ti}^{3+} \) salt; D) The transition \( \Delta \text{M} = 2 \) is observed.
<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Co:Zn</th>
<th>$g_A$</th>
<th>$g_B$</th>
<th>$A$</th>
<th>$A_{min}$</th>
<th>$A_{max}$</th>
<th>A.M.</th>
<th>A.M.</th>
<th>3 Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$K_2Co(SO_4)_3 \cdot 6H_2O$ (sp. cr. 9)</td>
<td>$1:500 - 10^{-6}$</td>
<td>20</td>
<td>$0.58 \pm 0.13$</td>
<td>$2.50 \pm 0.06$</td>
<td>$3.35 \pm 0.01$</td>
<td>$0.0286 \pm 0.001$</td>
<td>$0.0080 \pm 0.0004$</td>
<td>$\psi = +183^\circ$, $\alpha = 35^\circ$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$(NH_4)_2Co(SO_4)_3 \cdot 6H_2O$ (sp. cr. 3)</td>
<td>$1:500 - 10^{-6}$</td>
<td>20</td>
<td>$0.45 \pm 0.13$</td>
<td>$2.06 \pm 0.06$</td>
<td>$2.06 \pm 0.06$</td>
<td>$0.0245 \pm 0.0020$</td>
<td>$0.0030 \pm 0.0001$</td>
<td>$\psi = +130^\circ$, $\alpha = 34^\circ$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$(NH_4)_2Co(SO_4)_3 \cdot 6D_2O$ (sp. cr. 3)</td>
<td>$1:500 - 10^{-6}$</td>
<td>20</td>
<td>$0.41$</td>
<td>$2.7 \pm 0.06$</td>
<td>$5.3 \pm 0.06$</td>
<td>$0.0251 \pm 0.0006$</td>
<td>$0.0144 \pm 0.0003$</td>
<td>$\mu (Co^{3+}) = 0.8191 \pm 0.0018$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$Co_2ZnCl_2(NH_4)\cdot 2D_2O$ (sp. cr. 9)</td>
<td>Co : Zn</td>
<td>$1:50 - 10^{6}$</td>
<td>20</td>
<td>$6.65 \pm 0.06$</td>
<td>$2.7 \pm 0.3$</td>
<td>$0.093 \pm 0.0049$</td>
<td>$0.0003 \pm 0.0004$</td>
<td>$\psi = +15^\circ$, $\alpha = 37^\circ$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$(Ce + Bi)Co_4(NO_3)_4 \cdot 2D_2O$ (sp. cr. 8)</td>
<td>Co : Mg &amp; Zn</td>
<td>$1:1200$</td>
<td>4</td>
<td>$4.45 \pm 0.02$</td>
<td>$4.45 \pm 0.02$</td>
<td>$0.0004 \pm 0.0103$</td>
<td>$0.0003 \pm 0.0003$</td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>$Co_2ZnCl_2(NH_4)\cdot 2D_2O$ (sp. cr. 9)</td>
<td>Co : Zn</td>
<td>$1:500 - 10^{-6}$</td>
<td>20</td>
<td>$4.12 \pm 0.01$</td>
<td>$4.45 \pm 0.01$</td>
<td>$0.0007 \pm 0.0114$</td>
<td>$0.0009 \pm 0.0007$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A) Two different magnetic complexes.
Table 4.2 (Continuation)

<table>
<thead>
<tr>
<th>Formula</th>
<th>t °K</th>
<th>I</th>
<th>A</th>
<th>( A_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄·7H₂O (cr. st. 6)</td>
<td>20</td>
<td>3.58 ± 0.03</td>
<td>4.09 ± 0.03</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>Co: Zn = 10⁻²</td>
<td>20</td>
<td>3.50 ± 0.08</td>
<td>4.09 ± 0.07</td>
<td>0.0028 ± 0.0001</td>
</tr>
<tr>
<td>Co⁺⁺ as ZnF₄</td>
<td>20</td>
<td>3.50 ± 0.08</td>
<td>4.09 ± 0.07</td>
<td>0.0028 ± 0.0001</td>
</tr>
<tr>
<td>Co⁺⁺ as NaF, 10⁻³</td>
<td>20</td>
<td>3.50 ± 0.08</td>
<td>4.09 ± 0.07</td>
<td>0.0028 ± 0.0001</td>
</tr>
<tr>
<td>Co⁺⁺ as MgO</td>
<td>20</td>
<td>3.50 ± 0.08</td>
<td>4.09 ± 0.07</td>
<td>0.0028 ± 0.0001</td>
</tr>
<tr>
<td>Co⁺⁺ as Al₂O₄</td>
<td>4</td>
<td>3.50 ± 0.08</td>
<td>4.09 ± 0.07</td>
<td>0.0028 ± 0.0001</td>
</tr>
<tr>
<td>Co⁺⁺ as CaF₂, 10⁻³</td>
<td>20</td>
<td>3.50 ± 0.08</td>
<td>4.09 ± 0.07</td>
<td>0.0028 ± 0.0001</td>
</tr>
<tr>
<td>Co⁺⁺ as CdCl₂</td>
<td>20</td>
<td>3.50 ± 0.08</td>
<td>4.09 ± 0.07</td>
<td>0.0028 ± 0.0001</td>
</tr>
</tbody>
</table>

Paramagnetic resonance observed also in: Co(C₆H₄)₄(CN)₂ (T = 270-200 K, two complexes I: \( g = 2.9 \), II: \( g = 2.4-1.98 \)) [9]; (T = 290 K, \( g = 1.98 \); T = 200 K, \( g = 2.90 \)) [10]; \( K_2\text{Co(SO}_4\text{)}_2\cdot 6\text{D}_2\text{O} (T = 200 K, Co:Zn, sample contained } 4 \text{ mC Co}^{56}, \mu^{56}/\mu^{59} = 0.829 \pm 0.002; \text{sample contained } 4 \text{ mC Co}^{58}, \mu^{58}/\mu^{59} = 0.8734 \pm 0.0024 [11, 12, 16].

A) Centers in 0.05 cm⁻³ of the crystal; after irradiation.

Remarks:

a) Principal line, \( g \parallel \) corresponds to the \( c \) axis of the crystal.

b) Much weaker lines (lattice imperfections).

c) For one complex, the \( Z \) axis lies in the plane (110) with \( \angle ZOC = 13° \), the \( X \) axis in (110) with \( \angle XOC = 103° \), the \( Y \) axis is parallel to (110) plane. The axes of the second complex are obtained by mirror reflection. For an undilute salt, \( g \) is anisotropic in the \( ab \) plane and ranges from 1.4 to 5.8.

d) Hyperfine structure due to the F nuclei is observed: \( A_N^Y = (32 \pm 1) \cdot 10^{-4} \text{ cm}^{-1}, A_N^Z = (21 \pm 5) \cdot 10^{-4} \text{ cm}^{-1}. \)

e) There are six types of magnetic ions with similar spectra. A well resolved structure due to the interaction not only with Co nuclei but also with F nuclei, is observed. After irradiation, this spectrum - 154 -
vanishes and two isotropic lines appear, one of which is without a resolved structure and possibly belongs to Co\(^{2+}\) in a weakly distorted cubic surrounding, while the other belongs to Co\(^{+}\) (see page 193). All the irradiated centers vanish after heating to 150\(^\circ\)C.

f) Hyperfine structure is observed, due to the interaction with the F\(^-\) nuclei, \(A_F \approx 0.0030\) cm\(^{-1}\).

g) There are trigonal distortions of the cubic field.

**TABLE 4.2 (Conclusion)**

<table>
<thead>
<tr>
<th>(M=2, M_m=1), (M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</th>
<th>(M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</td>
<td>(M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</th>
<th>(M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</td>
<td>(M=2, M_m=1), каждый Fe окружен искаженным октаздрам из шести F.</td>
</tr>
</tbody>
</table>

Paramagnetic resonance observed also for \(T = 20^\circ K\) in \(K_2Fe(SO_4)_2 \cdot 6H_2O\), \((NH_4)_2Fe(SO_4)_2 \cdot 6H_2O\), \(FeSiF_6 \cdot 6H_2O\) \(4\); \((C_3H_4N_2)_4Fe\) \(T = 290, 20^\circ K\), \(g = 3.8; 2.0\) \(5\).

A) \(M=2, M_m=1\), each Fe surrounded by a distorted octahedron of F.

A hyperfine structure is observed, due to the F nuclei (the constants were determined at \(T = 12^\circ K\):

B) Asymmetrical line.

1) Formula; 2) literature; 3) remarks; 4) cr. st.; 5) in; 6) cm\(^{-1}\)
TABLE 4.3

### Ce³⁺

<table>
<thead>
<tr>
<th></th>
<th>Формула</th>
<th>T, К</th>
<th>$e_1$</th>
<th>$e_2$</th>
<th>$e_3$</th>
<th>$e_4$</th>
<th>Литература</th>
<th>Значения</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Mg₂Ce₄(NO₃)₈ · 24H₂O (кр. ст. 3) Ce:La = 1:20</td>
<td>4,2</td>
<td>0,25</td>
<td>1,84</td>
<td>±0,05</td>
<td>1,84</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{144}$Ce : La = 10⁻⁴</td>
<td>4,2</td>
<td>±0,05</td>
<td>±0,02</td>
<td>±0,02</td>
<td>±0,02</td>
<td>[2]</td>
<td>$A^{144}_{0,002}$</td>
</tr>
<tr>
<td></td>
<td>Ce(C₆H₅NO₃)₂ · 9H₂O Ce:La = 1:200</td>
<td>2,5</td>
<td>1,0</td>
<td>2,25</td>
<td>3,80</td>
<td>±0,4</td>
<td>[3]</td>
<td>$B^{144}_{0,0126}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4,2</td>
<td>0,955</td>
<td>2,185</td>
<td>3,72</td>
<td>±0,05</td>
<td>[3, 4]</td>
<td>$V_{Дублета b на (3 ± 1) cm⁻¹}$</td>
</tr>
<tr>
<td>5</td>
<td>Ce⁺⁺ в CaF₂ Ce:Ca ≈ 10⁻⁴</td>
<td>20</td>
<td>3,030</td>
<td>1,398</td>
<td>±0,003</td>
<td>±0,002</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ce⁺⁺ в LaCl₆ Ce:La = 2:100</td>
<td>4</td>
<td>4,036</td>
<td>0,17</td>
<td>±0,001</td>
<td>±0,01</td>
<td>[6]</td>
<td></td>
</tr>
</tbody>
</table>

### Nd³⁺

<table>
<thead>
<tr>
<th></th>
<th>Формула</th>
<th>T, К</th>
<th>$e_1$</th>
<th>$e_2$</th>
<th>$e_3$</th>
<th>$e_4$</th>
<th>Литература</th>
<th>Значения</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Mg₂Nd₄(NO₃)₈ · 24H₂O (кр. ст. 4) Nd:La = 10⁻⁴</td>
<td>4,2</td>
<td>0,45</td>
<td>2,72</td>
<td>±0,05</td>
<td>±0,02</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nd : La = 10⁻⁴</td>
<td>4,2</td>
<td>2,72</td>
<td>147</td>
<td>±0,004</td>
<td>±0,0005</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Nd(C₆H₅NO₃)₂ · 9H₂O Nd:La = 1:200</td>
<td>20</td>
<td>3,535</td>
<td>2,072</td>
<td>±0,001</td>
<td>±0,001</td>
<td>[2]</td>
<td>$\frac{144A}{145A} = 1,9083$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>2,072</td>
<td>2,072</td>
<td>±0,001</td>
<td>±0,001</td>
<td>[2]</td>
<td>$± 0,0012$</td>
</tr>
<tr>
<td></td>
<td>Nd(NO₃)₂ · 6H₂O Nd:La = 1:250</td>
<td>20−18</td>
<td>±0,1</td>
<td>0,14</td>
<td>±0,01</td>
<td>±0,01</td>
<td>[6]</td>
<td>Даб обоих изотопов</td>
</tr>
<tr>
<td></td>
<td></td>
<td>148</td>
<td>±0,002</td>
<td>±0,002</td>
<td>±0,002</td>
<td>±0,0005</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>145</td>
<td>±0,002</td>
<td>±0,002</td>
<td>±0,002</td>
<td>±0,0005</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Nd⁺⁺ в CaF₂ Nd:Ca = 10⁻⁴</td>
<td>20</td>
<td>4,412</td>
<td>1,301</td>
<td>±0,008</td>
<td>±0,002</td>
<td>[5]</td>
<td>a)</td>
</tr>
<tr>
<td>5</td>
<td>Nd⁺⁺ в SrF₂ Nd:Sr = 10⁻³</td>
<td>20</td>
<td>4,526</td>
<td>1,505</td>
<td>±0,008</td>
<td>±0,002</td>
<td>[5]</td>
<td>a)</td>
</tr>
</tbody>
</table>

A) Doublet b is the lower one; B) doublet b is (3+1) cm⁻¹ higher than doublet a; C) $M_m = 3$, crystalline axis of nonequivalent ions directed along the edges of a cube; D) for both isotopes.

- 156 -
### TABLE 4.3 (Continuation)

<table>
<thead>
<tr>
<th>1 Формулa</th>
<th>( T \text{, K} )</th>
<th>( \epsilon_{I} )</th>
<th>( \epsilon_{\perp} )</th>
<th>Магнитный момент</th>
<th>( A )</th>
<th>( B )</th>
<th>Литература</th>
<th>Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Nd}^{3+} \cdot \text{LaCl}_{6} )</td>
<td>4</td>
<td>0.996 ± 0.001</td>
<td>1.763 ± 0.001</td>
<td>143</td>
<td>0.0425 ± 0.0002</td>
<td>0.0187</td>
<td>0.0001</td>
<td>( 10^{-4} )</td>
</tr>
<tr>
<td>( \text{Nd} : \text{La} = \text{2 : 10}^{a} )</td>
<td>4</td>
<td>0.844 ± 0.001</td>
<td>1.642 ± 0.001</td>
<td>145</td>
<td>0.0084 ± 0.0002</td>
<td>0.0104</td>
<td>0.0001</td>
<td>( 10^{-4} )</td>
</tr>
</tbody>
</table>

Paramagnetic resonance observed also in \( \text{Nd}_{2}(\text{SO}_{4})_{3} \) \( (T = 90^0\text{K}) \) \[3\]; \( \text{Nd}_{2}(\text{SO}_{4})_{3} \cdot 8\text{H}_{2}\text{O} \) \( (T = 90^0\text{K}) \) \[3\]; \( \text{Nd}_{2}\text{O}_{3} \) \( (T = 290^0\text{K}, g = 3.2) \) \[4\].

Remarks. a) \( M_{m} = 3 \). There is an axial electric field near each ion; the crystalline axes of the nonequivalent ions are the axes of a cube.

### Sm\(^{3+}\)

<table>
<thead>
<tr>
<th>1 Формулa</th>
<th>( T \text{, K} )</th>
<th>( \epsilon_{I} )</th>
<th>( \epsilon_{\perp} )</th>
<th>Магнитный момент</th>
<th>( A )</th>
<th>( B )</th>
<th>Литература</th>
<th>Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}<em>{2}\text{Sm}</em>{4}(\text{NO}<em>{3})</em>{14} \cdot 24\text{H}_{2}\text{O} ) ( \text{ср. ст. 3} )</td>
<td>4.2</td>
<td>0.78 ± 0.001</td>
<td>0.604 ± 0.002</td>
<td>147</td>
<td>0.0546 ± 0.0005</td>
<td>0.0010</td>
<td>0.0001</td>
<td>( 10^{-4} )</td>
</tr>
<tr>
<td>( \text{Sm}(\text{C}<em>{6}\text{H}</em>{5}\text{SO}<em>{4})</em>{3} \cdot 9\text{H}_{2}\text{O} ) ( \text{ср. ст. 3} )</td>
<td>4.2</td>
<td>0.598 ± 0.002</td>
<td>0.6127 ± 0.0006</td>
<td>147</td>
<td>0.00002 ± 0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>( 10^{-4} )</td>
</tr>
<tr>
<td>( \text{Sm}^{3+} \cdot \text{LaCl}_{6} ) ( \text{Sm} : \text{La} = \text{1 : 150} )</td>
<td>4</td>
<td>0.584 ± 0.0003</td>
<td>0.6127 ± 0.0006</td>
<td>147</td>
<td>0.00006 ± 0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>( 10^{-4} )</td>
</tr>
</tbody>
</table>

Paramagnetic resonance observed also in \( \text{Sm} \) \( \text{SrS} \) \( (T = 77-20^0\text{K}) \) and in \( \text{Sm} \) \( \text{SrS} \cdot \text{SrSe} \) \[3\].

### Dy\(^{3+}\)

<table>
<thead>
<tr>
<th>1 Формулa</th>
<th>( T \text{, K} )</th>
<th>( \epsilon_{I} )</th>
<th>( \epsilon_{\perp} )</th>
<th>Магнитный момент</th>
<th>( A )</th>
<th>( B )</th>
<th>Литература</th>
<th>Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Dy(CH}<em>{2}\text{COO})</em>{3} \cdot 4\text{H}_{2}\text{O} ) ( \text{Dy} : \text{Y} = \text{1 : 150} )</td>
<td>4.2</td>
<td>13.50 ± 0.06</td>
<td>9.323 ± 0.005</td>
<td>161</td>
<td>0.0003 ± 0.0003</td>
<td>0.0001</td>
<td>0.0001</td>
<td>( 10^{-4} )</td>
</tr>
<tr>
<td>( \text{Dy}<em>{3}\text{Mg}</em>{4}(\text{NO}<em>{3})</em>{14} \cdot 24\text{H}_{2}\text{O} ) ( \text{Dy} : \text{La} = \text{2 : 10}^{a} )</td>
<td>4.2</td>
<td>4.281 ± 0.006</td>
<td>4.023 ± 0.005</td>
<td>161</td>
<td>0.0101 ± 0.0001</td>
<td>0.02463</td>
<td>0.0001</td>
<td>( 10^{-4} )</td>
</tr>
</tbody>
</table>

Remark. a) \( M_{m} = 1 \). Triclinic crystal. All principal values of the \( g \) factor are different; the direction of the magnetic field corresponds to the maximum value of the \( g \) factor.
### Er$^{3+}$

<table>
<thead>
<tr>
<th>1 Формула</th>
<th>Т. К.</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
<th>$\lambda$</th>
<th>$\beta$</th>
<th>Литература</th>
<th>3 Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er(C$_2$H$_3$SO$_4$)$_3$ · 8H$_2$O</td>
<td>4</td>
<td>1,47</td>
<td>8,85</td>
<td>0,0052</td>
<td>0,014</td>
<td>[1]</td>
<td>$P = 0,0009 \pm 0,0003$</td>
</tr>
<tr>
<td>Er$^{3+}$ в CaF$_2$</td>
<td>20, 14</td>
<td>$\delta_3$</td>
<td>$\delta_8$</td>
<td>0,0003</td>
<td>0,0003</td>
<td>[2]</td>
<td>a)</td>
</tr>
<tr>
<td>$\delta_3$</td>
<td>$\delta_8$</td>
<td>0,02</td>
<td>0,0003</td>
<td>0,0003</td>
<td>0,0003</td>
<td>5</td>
<td>0,0003</td>
</tr>
<tr>
<td>$\delta_8$</td>
<td>0,0003</td>
<td>0,0003</td>
<td>5</td>
<td>0,0003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_3$</td>
<td>0,02</td>
<td>0,0003</td>
<td>5</td>
<td>0,0003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_8$</td>
<td>0,0003</td>
<td>0,0003</td>
<td>5</td>
<td>0,0003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er$_3$Mg$_4$(NO$_3$)$_6$ · 24H$_2$O</td>
<td>4,2</td>
<td>0,02</td>
<td>0,0003</td>
<td>0,0003</td>
<td>0,0003</td>
<td>[3]</td>
<td>$P = 0,0013$</td>
</tr>
<tr>
<td>Er$^{3+}$ в LaCl$_4$</td>
<td>1,989</td>
<td>1,001</td>
<td>0,0003</td>
<td>0,0003</td>
<td>0,0003</td>
<td>[4]</td>
<td>$P = 0,00086$</td>
</tr>
</tbody>
</table>

Remarks:
- a) Isotropic line.
- b) Line from ground-state doublet.
- c) Line from excited doublet.

### Yb$^{3+}$

<table>
<thead>
<tr>
<th>1 Формула</th>
<th>Т. К.</th>
<th>$\delta_1$</th>
<th>$\lambda$</th>
<th>$\alpha$</th>
<th>Литература</th>
<th>3 Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb(CH$_3$COO)$_3$ · 4H$_2$O</td>
<td>4,2</td>
<td>4,57</td>
<td>171</td>
<td>0,122</td>
<td>[1]</td>
<td>a)</td>
</tr>
<tr>
<td>Yb: Y = 10$^{-4}$</td>
<td></td>
<td>$\pm 0,02$</td>
<td>173</td>
<td>$\pm 0,001$</td>
<td>$\pm 0,001$</td>
<td>$\pm 0,0003$</td>
</tr>
</tbody>
</table>

Remark. a) $M_m = 1$, triclinic crystal; all principal bodies of the $g$ factor different; direction of magnetic field corresponds to maximum value of $g$ factor.

1) Formula; 2) Isotope; 3) Literature; 4) Remarks; 5) Cr. st.; 6) In.
### Pr\(^{3+}\)

| Formula           | T, K | \(E_{||}\) | \(E_{\perp}\) | \(\Delta E\) | Literature | Notes               |
|-------------------|------|------------|---------------|--------------|------------|---------------------|
| Mg\(_2\)Pr\(_6\)(NO\(_3\))\(_6\) \(\cdot\) 24H\(_2\)O | 4.2  | 1.55 \(\pm 0.02\) | \(< 0.03\) \(\sim 0.19\) | 0.083 \(\pm 0.001\) | [1]        |                     |
| Pr: La = 10\(^{-4}\) |      |            |               |              |            |                     |
| Pr(C\(_2\)H\(_4\)SO\(_4\))\(_4\) \(\cdot\) 9H\(_2\)O | 20   | 1.69 \(\pm 0.01\) | \(0.11 \pm 0.04\) | \(0.0755 \pm 0.0020\) | [5, 7, 8] | \(V_2 = 50\) cm\(^{-1}\), \(V_7 = --100\) cm\(^{-1}\), \(b\) \(V_\text{r} = --46\) cm\(^{-1}\), \(V_\text{r} = 660\) cm\(^{-1}\) |
| Pr: La = 1 : 200 |      |            |               |              |            |                     |
| Pr: Y         |      |            |               |              |            |                     |
| PrCl\(_3\) \(\cdot\) 7H\(_2\)O | 4    | 3.02       | 2.33          | \(\Delta E\)  | [3]        | \(V_6 = 10^2\) cm\(^{-1}\), \(V_7 = 10^2\) cm\(^{-1}\) |
| PrCl\(_6\) | 4.2  | 1.791      | 3.975         | \(\pm 0.005\) | \(\pm 0.01\) | [6]        |                     |
| PrCl\(_6\) | 4    | 1.035      | \(\pm 0.005\) | \(\pm 0.15\) | \(\pm 0.002\) | [8]        |                     |
| Pr: La = 0.11 |      |            |               |              |            |                     |
| PrCl\(_6\) | 4    | 2.87       | \(\pm 0.02\)  | \(\pm 0.003\) | \(\pm 0.003\) | [6]        |                     |

A) \(M_m = 2\), triclinic crystal; B) one line observed; C) crystal of perovskite type.

### Tb\(^{3+}\)

| Formula           | T, K | \(E_{||}\) | \(E_{\perp}\) | \(\Delta E\) | Literature | Notes               |
|-------------------|------|------------|---------------|--------------|------------|---------------------|
| Tb\((C\(_2\)H\(_4\)SO\(_4\))\(_4\) \(\cdot\) 9H\(_2\)O | 20   | 17.72      | \(< 0.3\)     | 0.387 \(\pm 0.001\) | [1, 4] | \(V_7 = (220 \pm 30)\) cm\(^{-1}\), \(V_2 = 37\) cm\(^{-1}\) |
| Tb: Y = 10\(^{-4}\) | 13   | 18.0       | \(< 1\)       | 0.210 \(\pm 0.01\) | [2]        |                     |
| Tb(NO\(_3\))\(_6\) \(\cdot\) 6H\(_2\)O | 20   | 17.8       | \(\pm 0.4\)   | \(0.007 \pm 0.001\) | [5]        | \(V_\text{r} = 10^{-4}\) cm\(^{-1}\), \(V_\text{r} = 10^{-4}\) cm\(^{-1}\) |
| Tb: La = 10\(^{-4}\) |      |            |               |              |            |                     |
| Tb: Ca = \(10^{-4}\) |      |            |               |              |            |                     |
| Tb\(_4\) \(\cdot\) Ca\(_2\) | 4    | 12.78      | \(< 0.1\)     | 0.2010 \(\pm 0.001\) | [6]        |                     |
| Tb: La = 5 \(\cdot\) 10\(^{-4}\) \(\longrightarrow\) 2 \(\cdot\) 10\(^{-4}\) | 4    | 12.78      | \(< 0.1\)     | 0.2010 \(\pm 0.001\) | [6]        |                     |

Paramagnetic resonance observed also in Tb\(^{3+}\) in SrS \((T = 290^\circ\text{K})\) [3].

A) Hyperfine structure due to F\(^+\) observed, number of components even, distances between components on the order of 5 oersted.
TABLE 4.4 (Continued)

<table>
<thead>
<tr>
<th>Сказуемое</th>
<th>Θ</th>
<th>E</th>
<th>A</th>
<th>A</th>
<th>R</th>
<th>Литература</th>
<th>Значения</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho(C₂H₃SO₄)₉·9H₂O</td>
<td>15,410 ±0,010</td>
<td>0,085 ±0,015</td>
<td>0,0200 ±0,0040</td>
<td>0,00003</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ho: Y = 10⁻⁶</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ho⁺⁺ в LaCl₃</td>
<td>3,88</td>
<td>7,705 ±0,005</td>
<td></td>
<td></td>
<td>0,083</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Ho: La = 5·10⁻⁶</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remark. a) A detailed investigation has shown that the best explanation of the experimental data can be obtained by ascribing S = 1 to the ground level.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) Formula; 2) literature; 3) remarks; 4) cr. st.; 5) in; 6) cm⁻¹.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4.5

<table>
<thead>
<tr>
<th>Формула</th>
<th>Θ</th>
<th>E</th>
<th>D</th>
<th>E</th>
<th>a</th>
<th>A</th>
<th>Литература</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂Mn(SO₄)₆·6H₂O (ср. ст. 3)</td>
<td>200</td>
<td>0,0231 ±0,0002</td>
<td>0,0006</td>
<td></td>
<td>0,00000</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Mn: Mg = 1:250</td>
<td>200</td>
<td>0,0221 ±0,0002</td>
<td>0,0004</td>
<td></td>
<td>0,00005</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Mn: Zn</td>
<td>200</td>
<td>0,0238 ±0,0005</td>
<td>0,0005</td>
<td></td>
<td>0,0001</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Mn: Zn = 10⁻⁶</td>
<td>200</td>
<td>0,0238 ±0,0005</td>
<td>0,0005</td>
<td></td>
<td>0,0001</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Mn: Mg = 1:200</td>
<td>200</td>
<td>0,0238 ±0,0005</td>
<td>0,0005</td>
<td></td>
<td>0,0001</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Mn: Mg = 1:200</td>
<td>200</td>
<td>0,0238 ±0,0005</td>
<td>0,0005</td>
<td></td>
<td>0,0001</td>
<td></td>
<td>6</td>
</tr>
</tbody>
</table>

Remark. a) A detailed investigation has shown that the best explanation of the experimental data can be obtained by ascribing S = 1 to the ground level.

1) Formula; 2) literature; 3) remarks; 4) cr. st.; 5) in; 6) cm⁻¹.
<table>
<thead>
<tr>
<th>1</th>
<th>Формула</th>
<th>T, °K</th>
<th>e</th>
<th>D</th>
<th>ε</th>
<th>A</th>
<th>Литера-</th>
<th>3</th>
<th>Значение</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>MnSO₄·H₂O (кр. ст. 4)</td>
<td>195</td>
<td>2000</td>
<td>±0.005</td>
<td>0</td>
<td>0</td>
<td>±0.0002</td>
<td>3</td>
<td>[a]</td>
</tr>
<tr>
<td>5</td>
<td>Mn: Mg</td>
<td>90</td>
<td>2000</td>
<td>±0.0003</td>
<td>0</td>
<td>0</td>
<td>±0.0002</td>
<td>3</td>
<td>[a]</td>
</tr>
<tr>
<td>6</td>
<td>Mn: Ca = 1:2000</td>
<td>90</td>
<td>2002</td>
<td>±0.005</td>
<td>0</td>
<td>0</td>
<td>±0.0002</td>
<td>3</td>
<td>[a]</td>
</tr>
<tr>
<td>7</td>
<td>Mn: Zn</td>
<td>200</td>
<td>2001</td>
<td>±0.0075</td>
<td>0</td>
<td>0</td>
<td>±0.0002</td>
<td>3</td>
<td>[a]</td>
</tr>
<tr>
<td>8</td>
<td>Mn: ZnS</td>
<td>280</td>
<td>2002</td>
<td>±0.0003</td>
<td>0</td>
<td>0</td>
<td>±0.0002</td>
<td>3</td>
<td>[a]</td>
</tr>
</tbody>
</table>

**TABLE 4.5 (Continuation)**

| 11 | (из водного раствора) | 290 | 2000 | ±0.005 | 0 | 0 | ±0.0002 | 3 | [a] |
| 12 | Mn⁺⁺ + 0.01—0.02% по весу | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 13 | Mn⁺⁺ в КС | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 14 | Mn⁺⁺ в К2С и КI | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 15 | Mn⁺⁺ в NaF и CaF₂ | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 16 | Mn⁺⁺ в MgO и ZnO | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |

**TABLE 4.5 (Continuation)**

| 11 | (из водного раствора) | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 12 | Mn⁺⁺ + 0.01—0.02% по весу | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 13 | Mn⁺⁺ в КС | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 14 | Mn⁺⁺ в К2С и КI | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 15 | Mn⁺⁺ в NaF и CaF₂ | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
| 16 | Mn⁺⁺ в MgO и ZnO | 290 | 2001 | ±0.003 | 0 | 0 | ±0.0002 | 3 | [a] |
TABLE 4~.5 (Continuation)

F.F7

1 *OU&
Mn' 4 a Az~1

13

290

10-a

Mn: Ag = 10-4-

290

H3 acniaaa)
MR: AgmiF~0

On+Csx~e

MnCI (nopoulok
Mn:Sr =l:100l,7
Mnl+ a 0o41oPaI
0.1...0

17

1:2,0061:,0!

±0,0004

+0,00
±r0010

0,0077
±0,0004

1181

-0,00425

f19]

AmA..,97

(2

01,0000m
0,00922

[371

77

2,0061

2

zo0
2

+0008

9

p sk
2,004

Mg?,

MggOI.,S-t.4
CO1AP

g .A-O

,00450098
2,006

17

2,002

coo

±t0,0025

16~Z0
MnZn 1-

-

160

050,0
,001
2
0~
2,0024 t,0025006
290
(0,00ux)±0408

13

0,00607

Mn 4= C1-C- 0Mn' 4B LICI

(H3pacnaasa)

18 flapH
+ M nAu a SI

290

29090
29
20

[37210
S 7

~ ia.

0044

2cnlama)

10-±O
Mn:Sr
Mn'SSS
(nopomoac)

[371

,06

292001

13 S
16

W7

0,00856

2,004

ZgI0,MOA.O.kMO-0
Z1S
US
MnS

k

18

±0,003
11:2,000

2,002

2,0

A0,00102,0011
9m
1S.531
8
A
A,,086:4,0004KCNOT

X

[6

0,0065

0.01

1 191
10,0076(0
±A0,007
15

2.073

:L0,001
2A=0,00910

451

TunaCQNepa

proawo

c

2
9 =,00,p

Sr?,KNC
906 (50;mo
gu20 ~,M? ku2O1 A0,00906) [ElCl' g,0,A=0,00
T50;mgsug-20meJae087)
g-,002
d
(50
0,0091
2004
29%9,
(501;
'"l+au0003
noSxxf2=007
007[71
0,00,A
Z003
UTI
n' 5aS~u2O
2
de(
0,0009551;
:t-A0067J[
:t501
0,0729
,K
am
pa
P)
x
O
(Am0
[511
0060
0
A
20
(51 Sdi (g2,01,A0008)5 Zne(
n:I5)

162011Z,(0)
-

13
1 ap-0,

Mu~ow(,0[
; 2,0).f2;07n,
[130
A 0,008 12H,0072)
MInB; 12,0,0 Mn 2,,0,(9);208In[
0207) 12n(19
0 A &(
(g 2B
nl+
- BeM -(Cas g sw
oeAuueuun
u
6tmama
4H,0Z~
.311,0 (141; (CNOW,
COO),O
,
2,I0)
f , 11
1;W
(92,01,A=0,00) ;n(
(~501 WeC
-0~;,
34241 MnO .110
MnC, ~=00[I2
%004,M~,(0).o
421
14
F'.O.a
2, 1 , Mm
1; ( ,026, 4I -%P
ow02,0,09)[2
,0.A
Cd2)Mm,-2,00 (A, 1 7 4& 4 MgSg
,)
r2,4)M.
(gn
06110
Mn [241;
*OH,0
rl~J~c
I150r
.(-A2
A* ,00)J

~~~~~~~

0,0

r

Oi)
00
162,zm)10]

0

j

0r2

A-0072

51


In addition, the absorption lines of Mn$^{2+}$ were investigated in paramagnetic Tutton's salts R(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O (R = Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Cu$^{2+}$), and also in CuSO$_4$·5H$_2$O [44]). The intermetallic compound MnAu$_2$ was investigated (polycrystal); when T > 90$^\circ$C we have $g = 2.0$; below 90$^\circ$C, MnAu$_2$ is an antiferromagnet [43]. Finally, the paramagnetic resonance was measured for Mn$^{2+}$ in amorphous phthalocyanine ($g = 2.0$) [41].

Remarks:

a) The direction cosines of the Z axis are (0.282, ±0.952, 0.122).

b) The Zn is surrounded in ZnF$_2$ by a distorted octahedron made up of six F ions, four of which (type I) form a rectangle with sides 2.59 and 3.13 Å, and the two other F ions (type II) lie on a perpendicular to the plane of the rectangle at a distance 2.04 Å. The Z axis is chosen along the long side of the rectangle (c axis), the X axis passes through the type II F ions and is parallel to the short side of the rectangle. The following hyperfine structure due to the F nuclei was observed:

$$A_Y^I = (16.5 \pm 0.7) \times 10^{-4} \text{ cm}^{-1}, \quad A_Y^II = (14.6 \pm 1.2) \times 10^{-4} \text{ cm}^{-1},$$
$$A_Z^I = (18.2 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}, \quad A_Z^II = (12.5 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}.$$

c) CaCO$_3$ - calcite, $M = 2$. The nearest neighbors of the Ca are six O with trigonal symmetry. The magnetic complexes with Mn are equivalent. The structure of the crystal is hexagonal.

d) $M_m = 2$, $\psi = +97^\circ$, $\alpha = 62^\circ$, monoclinic structure.

e) $M_m = 1$, $Z \equiv c$, $X \equiv b$, monoclinic structure.

f) $M_m = 2$, $\psi = +47^\circ$, $\alpha = 29^\circ$.

g) If a sample obtained from the melt is heated and soaked for a certain time at a temperature $T$, and then cooled rapidly to room temperature, then: 1) if $T < 300^\circ$C, the resonant curves do not change; 2) if $T > 500^\circ$C, then curve I goes over into II. A superposition of curves
I and II is observed at intermediate temperatures. There are probably two different states of Mn$^{2+}$ in NaCl, one of which is stable above 500°C, and the other stable below. The former is contained in the rapidly cooled samples and the latter in the slowly cooled ones.

h) Lines without structure.

j) Line with hyperfine structure of Mn$^{55}$.

k) There are two types of centers, each containing three nonequivalent magnetic ions. Because of the complexity of the spectrum, the values of D, $g$, and A are determined only along the axis of the crystalline field. The intensity of the second spectrum is one hundredth of that of the first. Each of the hyperfine structure lines of Mn has a resolved structure, due to the interaction with the F nuclei. The constants of this interaction are: $A_s = 0.00144 \pm 0.00003$, $A_p = 0.00028 \pm 0.00007$. The intensity of the Mn$^{2+}$ spectrum is greatly weakened after irradiation.

1) Spectrum I of six peaks corresponds to isolated Mn$^{2+}$ ions. Spectrum II having one peak is observed only in samples with higher concentration of Mn$^{2+}$, and is probably brought about by the aggregation of the Mn$^{2+}$ ions.

m) $\mu^{53}/\mu^{55} = 1.455 \pm 0.002$.

n) $a = (0.6 \pm 0.4) \times 10^{-4}$ cm$^{-1}$, $A_s = (9.5 \pm 0.3) \times 10^{-4}$ cm$^{-1}$, $A_p = (2.7 \pm 0.5) \times 10^{-4}$ cm$^{-1}$. $A_s$ and $A_p$ are the constants of the hyperfine structure due to the interaction between the spin of the F nucleus with the $s$ and $p$ orbitals, respectively.

o) In addition to the ordinary hyperfine structure, a hyperfine structure was also observed due to the magnetic interaction between the Mn$^{2+}$ electrons with the nearest Cd nuclei.

p) The spectrum is due to the complex made up by Mn$^{2+}$ and the Na$^+$ vacancy; the Z axis is directed along the bond between Mn$^{2+}$ and the.
Na$^+$ vacancy, and the y axis is parallel to the cubic axis. The complexes are unstable.

r) At 20°C each Mn$^{2+}$ line is split by the interaction with the Au nuclei; it is suggested that the quadrupole interaction with Au is stronger than the magnetic interaction.

### TABLE 4.5 (Continuation)

<table>
<thead>
<tr>
<th>Formula</th>
<th>$T$, K</th>
<th>$g$</th>
<th>$D$</th>
<th>$e$</th>
<th>$F$</th>
<th>Literature Type</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>KFe(SeO$_4$)$_4$·12H$_2$O (ep. cr. 1)</td>
<td>90</td>
<td>2,003</td>
<td>-0,0103</td>
<td>-0,0127</td>
<td>-0,0002</td>
<td>[1]</td>
<td>$\gamma = (10,50 \pm 0,5)^\circ$</td>
</tr>
<tr>
<td>Al: Fe = 1:300</td>
<td>20</td>
<td>2,003</td>
<td>-0,0115</td>
<td>-0,0127</td>
<td>-0,0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$NH$_4$Fe(SO$_4$)$_2$·12H$_2$O (ep. cr. 1)</td>
<td>4</td>
<td>0,016</td>
<td>(-)0,0128</td>
<td></td>
<td></td>
<td>[23]</td>
<td></td>
</tr>
<tr>
<td>Fe: Al = 1:300</td>
<td>90</td>
<td>2,003</td>
<td>±0,0001</td>
<td>±0,0004</td>
<td>-0,0003</td>
<td>[1]</td>
<td>$\gamma = (7,5 \pm 0,5)^\circ$</td>
</tr>
<tr>
<td>RbFe(SO$_4$)$_2$·12H$_2$O (ep. cr. 1)</td>
<td>20</td>
<td>2,003</td>
<td>±0,0003</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe: Al = 1:300</td>
<td>290</td>
<td>2,00</td>
<td>0,01658</td>
<td>0,01445</td>
<td>0,00045</td>
<td>[15]</td>
<td>$t_1 = 0,058 \text{ cm}^{-1}$, $t_2 = 0,050 \text{ cm}^{-1}$.</td>
</tr>
<tr>
<td>Fe$^{2+}$ in Al$_2$Be$_5$(SiO$_4$)$_6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$ in MgO (ep. cr. 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$ in SrTiO$_3$</td>
<td>77</td>
<td>0,0007</td>
<td>±0,0003</td>
<td>±0,0011</td>
<td></td>
<td>[10, 17]</td>
<td>b</td>
</tr>
<tr>
<td>Fe$^{2+}$ in Ti$^{4+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$ in Si (всегда присутствует)</td>
<td>10</td>
<td>2,099</td>
<td>0,07</td>
<td>0,0037</td>
<td></td>
<td>[19, 21]</td>
<td>$A^{4s} = 7,0 \cdot 10^{-4} \text{ cm}^{-1}$, r) a</td>
</tr>
<tr>
<td>Fe$^{2+}$ in (CH$_3$CO)$_2$CH$_2$</td>
<td>200</td>
<td>0,001</td>
<td></td>
<td></td>
<td></td>
<td>[16]</td>
<td>b</td>
</tr>
<tr>
<td>Fe$^{2+}$ in MgWO$_4$ [6]</td>
<td>75</td>
<td>2,0</td>
<td>-0,687</td>
<td></td>
<td></td>
<td>[23]</td>
<td>$E = +0,174 \text{ cm}^{-1}$, a) Θ</td>
</tr>
<tr>
<td>Fe$^{2+}$ in Al$_2$O$_3$</td>
<td>290</td>
<td>2,003</td>
<td>0,01679</td>
<td>0,0241</td>
<td>0,0028</td>
<td>[12, 22]</td>
<td>a</td>
</tr>
</tbody>
</table>
### Table 4.5 (Continuation)

<table>
<thead>
<tr>
<th>1</th>
<th>Формула</th>
<th>T, K</th>
<th>ε</th>
<th>D</th>
<th>α</th>
<th>Ф</th>
<th>Данные</th>
<th>Значения</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Fe⁺⁺ in BaTiO₃</td>
<td>77</td>
<td>2.003</td>
<td>+0.1716</td>
<td>±0.0001</td>
<td>±0.00004</td>
<td>±0.00002</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>Fe⁺⁺ in BaTiO₃</td>
<td>4.2</td>
<td>2.003</td>
<td>+0.1719</td>
<td>±0.0001</td>
<td>±0.00004</td>
<td>±0.00002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe⁺⁺ in BaTiO₃</td>
<td>290.0</td>
<td>±0.003</td>
<td>±0.00015</td>
<td>±0.00004</td>
<td>±0.00002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Remarks:**

a) $M_m = 2$, nonequivalence due to the difference in the directions of the cubic-field axes.

b) Below the phase-transition point (near 100°K) the single crystal consists of tetragonal domains.

c) $M_m = 2$, the crystal is orthorhombic. Upon dilution of the aluminum, a similar but not identical spectrum was obtained. Thus, the crystalline field acting on the Fe³⁺ may vary from diluent to diluent.

d) Isotropic line.

e) The $Y$ axis is parallel to the $b$ axis, the $Z$ axis lies in the $ac$ plane and forms a 41.5° angle with the $a$ axis. The signs of $D$ and $F$ are determined from a comparison of the intensities at 2 and 4°K.

| 4 | Mg₂Gd₄(NO₃)₁₄·24H₂O | 290,77 | 1.991 | +0.0009 | ±0.00006 | ±0.00012 | [15] |
|   | Gd : Bi = 1 : 5000 |   |   |   |   |   |   |
|   | Gd : Bi = 10⁻⁴ | 90,20 | 1.992 | ±0.0003 | ±0.0001 | ±0.00001 | ±0.0001 | [1] |
|   | Gd (C₆H₅SO₄)₂·9H₂O | 90 | 1.900 | ±0.002 | ±0.0002 | ±0.00003 | ±0.00005 | [2] |
|   | Gd : La = 1 : 200 | 20 | 1.900 | ±0.002 | ±0.00001 | ±0.00005 | ±0.00005 | [15] |
|   | Gd₂(SO₄)₂·8H₂O | 20 | ±0.002 | ±0.00001 | ±0.00005 | ±0.00005 |       |   |
|   | Gd : Sm = 1 : 200 | 300 | ±0.003 | ±0.0005 | ±0.0005 | ±0.0005 |       |   |
|   | Gd CI₄ | 290 | 1.901 | ±0.000038 | ±0.000018 | ±0.000004 | ±0.00005 | [7] |
|   | Gd : (La, Ce) = 10⁻⁴ | 90 | ±0.000038 | ±0.000018 | ±0.000004 | ±0.00005 | [7] |
|   | Gd : La = 5 · 10⁻⁴ | 4 | ±0.000038 | ±0.000018 | ±0.000004 | ±0.00005 | [7] |
|   | GdCl₄·7H₂O | 290 | ±0.0003 | ±0.000038 | ±0.000018 | ±0.000004 | ±0.00005 | [7] |
|   | Gd : La | 200 | ±0.0003 | ±0.000038 | ±0.000018 | ±0.000004 | ±0.00005 | [7] |

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TABLE 4.5 (Continuation)

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\gamma,^\circ$</th>
<th>$\alpha$</th>
<th>$\Delta E, ,\text{cm}^{-1}$</th>
<th>Literature</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdCI₄ · 7D₂O</td>
<td>90–77</td>
<td>1.99</td>
<td>0.00009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd:La = 2 · 10⁻⁴</td>
<td>77</td>
<td>1.00</td>
<td>+0.236</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd⁺⁺ in LaF₄</td>
<td>90</td>
<td>1.00</td>
<td>+0.00001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd⁺⁺ in LaF₄</td>
<td>1.000</td>
<td>±0.00001</td>
<td>±0.00001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remarks:


b) Monoclinic. $M = 8$, $M_n = 2$. The axes are specified by the angles $\psi_z = 28^\circ$, $\alpha_z = +35^\circ$, $\psi_y = 0^\circ$, $\alpha_y = +52^\circ$, where $\psi_1$ is the angle between $c$ and the plane containing the $Z$ axes; $\alpha_i$ is the angle between the $i$-th axis and the $ac$ plane ($i = z, y$).

c) Hexagon. The crystalline field on Gd has a $C_{3h}$ symmetry.

d) The sign of the coefficients $b_n^m$ is determined from measurements of the relative intensities in parallel fields at 20°C.

e) $\Delta E = 8c - 2d$ is the total splitting in the cubic field.

f) $M_m = 3$, the ion is acted upon by a rhombic crystalline field; $b_4^2 = 60b_4^2 = +0.0027 \pm 0.0003$; $b_4^4 = 60b_4^4 = -0.0043 \pm 0.0003$; $b_6^2 + b_6^4 = 1260(b_6^6 + b_6^8) = +0.00085 \pm 0.00030$; $b_6^6 = 1260b_6^8 = -0.0001 \pm 0.0005$. 

$\mu_{\text{iso}}^{144} = 0.75 \pm 0.07$

$\mu_{\text{iso}}^{154} = (5.3 \pm 0.2) \times 10^{-4} \, \text{cm}^{-1}$
<table>
<thead>
<tr>
<th>1</th>
<th>Формула</th>
<th>T, К</th>
<th>g</th>
<th>( \Delta \mathcal{E} )</th>
<th>Инергия</th>
<th>( \lambda )</th>
<th>Литература</th>
<th>3 Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(^{2+}) в CaF(_2)</td>
<td>290</td>
<td>1,971</td>
<td>±0,001</td>
<td>151</td>
<td>0,00346</td>
<td>±0,00001</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>1,9927</td>
<td>±0,0001</td>
<td>151</td>
<td>0,00303</td>
<td>±0,00001</td>
<td>[2, 3, 5, 6, 9]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>Естествен.</td>
<td>(в расплаве)</td>
<td>Eu: Ca = 10^{-4}</td>
<td>290</td>
<td>1,963</td>
<td>±0,002</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>Eu(^{2+}) в SrS</td>
<td>200</td>
<td>1,992</td>
<td>±0,001</td>
<td>151</td>
<td>0,00300</td>
<td>[1, 4, 13]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>00-20</td>
<td>2,0</td>
<td>0,18</td>
<td>153</td>
<td>0,00144</td>
<td>±0,00001</td>
<td>[8, 9]</td>
</tr>
<tr>
<td></td>
<td>Eu(^{2+}) в SrS — SrSe</td>
<td>90-20</td>
<td>2,0</td>
<td>0,18</td>
<td>152</td>
<td>0,00148</td>
<td>±0,00001</td>
<td></td>
</tr>
<tr>
<td>Eu(^{2+}) в CaCl(_2)</td>
<td>290, 77</td>
<td>1,9914</td>
<td>±0,0008</td>
<td>0,00076</td>
<td>[1, 2]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg, Eu(_2)(NO(_3))(_4)·24H(_2)O</td>
<td>290</td>
<td>2,003</td>
<td>0,000020</td>
<td>±0,000002</td>
<td>[1]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

1) Formula; 2) reference; 3) remarks; 4) cr. st.; 5) two different magnetic complexes; 6) in; 7) (slow cooling from melt); 8) (fast cooling from melt); 9) hexagonal; 10) cubic; 11) (from aqueous solution); 12) by weight; 13) (from melt); 14) (from solution); 15) in 0.05 cm\(^3\) of the crystal; 16) (powder); 17) in phosphors; 18) Mn-Au pairs in Si; 19) two spectrum types, apparently depending on the S or Se surrounding; 20) trigonal distortion of cubic field; 21) paramagnetic resonance observed also at room temperature in: a) phosphorus containing small concentrations of ......; 22) b) undiluted compounds: ......; 23) (enriched and
not enriched); 24) paramagnetic resonance observed also at room temperature in .....; 25) the principal axes of the tetragonal field are parallel to the edges of the cube, a = +0.0175; 26) paramagnetic resonance is observed also in Gd$^{3+}$ in LaAlO$_3$ ($T = 4.2, 295, 195, 83^\circ K$, lines without structure with $g = 1.992 \pm 0.002$, six fine-structure maxima with $g = 1.55$); 27) isotope; 28) the magnetic moments of $^{151}$Eu and $^{153}$Eu have the same sign; 29) (natural); 30) paramagnetic resonance was also observed in Eu$^{2+}$ in KCl.....; 31) paramagnetic resonance observed also in Cm$^{3+}$ in ThO$_2$ and CaCl$_2$ [1].

**TABLE 4.6**

**FeIII**

<table>
<thead>
<tr>
<th>1</th>
<th>Formula</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$g_3$</th>
<th>Literature</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>K$_4$[Fe(CN)$_6$] (cr. st. 7)</td>
<td>20</td>
<td>2.40</td>
<td>2.18</td>
<td>0.94</td>
<td>[1]</td>
<td>5</td>
<td>Направляющие косинусы осей</td>
</tr>
<tr>
<td></td>
<td>Fe:Co $= 10^{-6}$</td>
<td>20</td>
<td>±0.02</td>
<td>±0.02</td>
<td>±0.01</td>
<td>[2]</td>
<td></td>
<td>$a$ 0</td>
</tr>
<tr>
<td>6</td>
<td>Fe$^{1111}$ in monocrystals</td>
<td>20</td>
<td>0.7</td>
<td>2.20</td>
<td>6.60</td>
<td>[3]</td>
<td></td>
<td>$X \pm 0.868$</td>
</tr>
<tr>
<td>7</td>
<td>Fe$^{1111}$ in monocrystals</td>
<td>20</td>
<td>±0.01</td>
<td>±0.01</td>
<td>±0.05</td>
<td>[4]</td>
<td></td>
<td>$P \pm 0.500$</td>
</tr>
<tr>
<td>8</td>
<td>Fe$^{1111}$ in in Fe$^{1111}$ in Fe$^{1111}$</td>
<td>200, 20</td>
<td>1.12</td>
<td>2.72</td>
<td>2.50</td>
<td>[4-6]</td>
<td>[5]</td>
<td>$\Delta &gt; 2$ cm$^{-1}$</td>
</tr>
<tr>
<td>9</td>
<td>in Fe$^{1111}$ in Fe$^{1111}$ in Fe$^{1111}$</td>
<td>77</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>[6]</td>
<td></td>
<td>$\Delta &gt; 2$ cm$^{-1}$</td>
</tr>
<tr>
<td>10</td>
<td>in Fe$^{1111}$ in Fe$^{1111}$ in Fe$^{1111}$</td>
<td>17</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
<td>[7]</td>
<td></td>
<td>$\Delta &gt; 2$ cm$^{-1}$</td>
</tr>
<tr>
<td>11</td>
<td>in Fe$^{1111}$ in Fe$^{1111}$ in Fe$^{1111}$</td>
<td>300, 200</td>
<td>1.12</td>
<td>2.72</td>
<td>2.50</td>
<td>[4-6]</td>
<td>[8]</td>
<td>$\Delta &gt; 2$ cm$^{-1}$</td>
</tr>
<tr>
<td>12</td>
<td>in Fe$^{1111}$ in Fe$^{1111}$ in Fe$^{1111}$</td>
<td>400, 200</td>
<td>1.12</td>
<td>2.72</td>
<td>2.50</td>
<td>[4-6]</td>
<td>[9]</td>
<td>$\Delta &gt; 2$ cm$^{-1}$</td>
</tr>
<tr>
<td>13</td>
<td>in Fe$^{1111}$ in Fe$^{1111}$ in Fe$^{1111}$</td>
<td>400, 200</td>
<td>1.12</td>
<td>2.72</td>
<td>2.50</td>
<td>[4-6]</td>
<td>[10]</td>
<td>$\Delta &gt; 2$ cm$^{-1}$</td>
</tr>
<tr>
<td>14</td>
<td>in Fe$^{1111}$ in Fe$^{1111}$ in Fe$^{1111}$</td>
<td>400, 200</td>
<td>1.12</td>
<td>2.72</td>
<td>2.50</td>
<td>[4-6]</td>
<td>[11]</td>
<td>$\Delta &gt; 2$ cm$^{-1}$</td>
</tr>
</tbody>
</table>

**TABLE 4.6**

**FeIII**

<table>
<thead>
<tr>
<th>1</th>
<th>Formula</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$g_3$</th>
<th>Literature</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>K$_4$[Fe(CN)$_6$] $\cdot 3$H$_2$O (cr. st. 7)</td>
<td>12</td>
<td>2.424</td>
<td>2.182</td>
<td>0.972</td>
<td>[1]</td>
<td>5</td>
<td>Направляющие косинусы осей</td>
</tr>
<tr>
<td></td>
<td>Mn:Fe $= 10^{-3}$</td>
<td>12</td>
<td>±0.006</td>
<td>±0.003</td>
<td>±0.05</td>
<td>[1]</td>
<td></td>
<td>$a$ 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>±0.006</td>
<td>±0.003</td>
<td>±0.05</td>
<td>[1]</td>
<td></td>
<td>$b$ 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>±0.006</td>
<td>±0.003</td>
<td>±0.05</td>
<td>[1]</td>
<td></td>
<td>$c$ 0</td>
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</table>
TABLE 4.6 (Continuation)

<table>
<thead>
<tr>
<th>1 Формула</th>
<th>T, K</th>
<th>ε∥</th>
<th>ε⊥</th>
<th>εΔ</th>
<th>Aε</th>
<th>A∥</th>
<th>A⊥</th>
<th>Литература</th>
<th>3 Заметки</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoV в виде загрязнения в K₉[InCl₆]·2H₂O</td>
<td>260, 20</td>
<td>1,06</td>
<td>1,06</td>
<td>0,0008</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td>[1]</td>
<td>В единичной ячейке два магнитно эквивалентных комплекса; наблюдала спиновая структура, обнаружена агрегам Cl 20</td>
</tr>
<tr>
<td>K₉[Mo(CN)₆] (порошок)</td>
<td>290, 20</td>
<td>g: 2,006</td>
<td>±0,005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>K₉[MoCl₆]·2H₂O</td>
<td>90, 20</td>
<td>g: 1,93</td>
<td>±0,06</td>
<td>D &gt;1</td>
<td>E/D = 0,08</td>
<td>±0,0005</td>
<td>±0,0005</td>
<td>[1]</td>
<td>В единичной ячейке несколько магнитно эквивалентных комплексов; измерены только два</td>
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<tr>
<td>MoIV: In = 1: 200</td>
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<tr>
<td>K₉MoCl₆ (порошок)</td>
<td>290</td>
<td>1,76</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₃MoCl₆·H₂O (порошок)</td>
<td>290-20</td>
<td>1,96</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>KMnCl₃ (порошок)</td>
<td>14</td>
<td>1,95</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Tc IV в K₃PtCl₆</td>
<td>4,2</td>
<td>1,9886</td>
<td>±0,0005</td>
<td>Amax</td>
<td>0,01378</td>
<td>±0,00044</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc: Pt =10⁻³</td>
<td></td>
<td></td>
<td>Amin</td>
<td>0,01354</td>
<td>±0,00044</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Ru III

<table>
<thead>
<tr>
<th>1 Формула</th>
<th>T, K</th>
<th>ε∥</th>
<th>ε⊥</th>
<th>εΔ</th>
<th>Aε</th>
<th>A∥</th>
<th>A⊥</th>
<th>Литература</th>
<th>3 Заметки</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NH₃)₅Cl]Cl₆</td>
<td>20</td>
<td>2,06</td>
<td>2,02</td>
<td>1,72</td>
<td>0,0048</td>
<td>0,0048</td>
<td>0,0049</td>
<td>[1][3]</td>
<td>a)</td>
</tr>
<tr>
<td>Ru: Co = 1: 200</td>
<td></td>
<td>±0,01</td>
<td>±0,01</td>
<td>±0,01</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II: 1,80</td>
<td>1,90</td>
<td>2,06</td>
<td>0,0048</td>
<td>0,0048</td>
<td>0,0050</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±0,01</td>
<td>±0,01</td>
<td>±0,01</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III: 1,15</td>
<td>1,84</td>
<td>2,06</td>
<td>0,0048</td>
<td>0,0048</td>
<td>0,0054</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>±0,01</td>
<td>±0,01</td>
<td>±0,01</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₉[RuCl₃]·2H₂O</td>
<td>20</td>
<td>1,0</td>
<td>1,22</td>
<td>3,24</td>
<td></td>
<td></td>
<td></td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>Ru: In = 10⁻³</td>
<td></td>
<td>±0,01</td>
<td>±0,02</td>
<td>±0,01</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td>±0,0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(NH₃)₅Cl]Cl₆</td>
<td>20</td>
<td>2,21</td>
<td>2,05</td>
<td>1,5</td>
<td></td>
<td></td>
<td></td>
<td>[1]</td>
<td></td>
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<tr>
<td>3HgCl</td>
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<td></td>
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</tr>
</tbody>
</table>

22 Параметривный резонанс наблюдал также в неравномерных кристаллах [Ru(NH₃)₅Cl]Cl₆ [Ru(NH₃)₅Cl]Cl₆ при T= 200K [1].

Remark. a) The unit cell contains three pairs of magnetically non-equivalent complexes, types I, II, III. The plane AC is the mirror-symmetry plane for the ions of each pair.
### TABLE 4.6 (Continuation)

<table>
<thead>
<tr>
<th>Формула</th>
<th>T. K.</th>
<th>$I_a$</th>
<th>$I_d$</th>
<th>Литература</th>
<th>Значение</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (C,H,N) S,O</td>
<td>297, 20</td>
<td>2,18</td>
<td>2,04</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>Ag : Cd = 1 : 20</td>
<td>4,2</td>
<td>g = 2,06</td>
<td>g = 2,04</td>
<td>[1]</td>
<td>[2]</td>
</tr>
<tr>
<td>Ди-фенантролин персульфат серебра</td>
<td>250, 90, 20</td>
<td>2,18</td>
<td>2,04</td>
<td>[1]</td>
<td></td>
</tr>
</tbody>
</table>

| K$^+$ [ReCl$_4$] | 90, 20 | g = 1,8 | g = 2,06 | g = 2,04 | [1] | |

| Наблюдено 6 линий (возможно, сверточная структура от $^{185}$Re, $^{187}$Re) |

#### $I_a^IV$

<table>
<thead>
<tr>
<th>1 Формула</th>
<th>T. K.</th>
<th>$I_a$</th>
<th>$I_d$</th>
<th>СТС в Br</th>
<th>СТС в Cl и Br</th>
<th>Литература</th>
<th>Значение</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$ [[IrBr$_4$] _</td>
<td>20</td>
<td>1,80</td>
<td>±0,10</td>
<td>1,87</td>
<td>±0,04</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>Ir : Pt = 1 : 200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$^+$ [IrCl$_4$] _</td>
<td>20</td>
<td>1,78</td>
<td>±0,02</td>
<td></td>
<td></td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>Ir : Pt = 1 : 200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| (NH)$_3$ [IrCl$_4$] \_ | 20 | 1,75 | ±0,001 | ±0,00010 | ±0,00004 | [1] | |
| Ir : Pt = 1 : 200 | | | | | | | |
| Na$_2$ [IrCl$_4$] \_ · 6H$_2$O \_ | 20 | 2,25 | ±0,02 | ±0,000010 | ±0,00002 | [1] | |
| Ir : Pt = 1 : 200 | | | | | | | |
| Na$_2$ [IrCl$_4$] \_ · 6H$_2$O \_ | 20 | 2,20 | ±0,02 | ±0,000010 | ±0,00004 | [1] | |
| Ir : Pt = 1 : 200 | | | | | | | |

| 32 | Парахромный феномен наблюдался также в (NH)$_3$ [IrCl$_4$] при T = 20 — 208 К и разбавленных Ir : Pt = 1 : 10, 1 : 100 [10]. | | | | | |

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### TABLE 4.6 (Continuation)

<table>
<thead>
<tr>
<th>1</th>
<th>Формула</th>
<th>T, °K</th>
<th>$g_{1}$</th>
<th>$g_{J}$</th>
<th>A</th>
<th>B</th>
<th>P</th>
<th>Литература</th>
<th>3 Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>U₃⁺ in CaF₂</td>
<td>20</td>
<td>3,501</td>
<td>1,866</td>
<td>±0,008</td>
<td>±0,002</td>
<td>[1]</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>U:Ca = 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>U₃⁺ in SrF₂</td>
<td>20</td>
<td>3,433</td>
<td>1,971</td>
<td>±0,006</td>
<td>±0,002</td>
<td>[6]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>U:Sr = 10⁻⁴</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>U₃⁺ in BaF₂</td>
<td>20—10</td>
<td>3,337</td>
<td>2,115</td>
<td>±0,002</td>
<td>±0,001</td>
<td>[2, 3]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>U♭ / (обозначен U♭)</td>
<td>20, 4</td>
<td>4,153</td>
<td>1,520</td>
<td>0,0176</td>
<td>0,00375</td>
<td>±0,00055</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>U♭ / (обозначен U♭)</td>
<td>20, 4</td>
<td>3,991</td>
<td>1,789</td>
<td>±0,005</td>
<td>±0,002</td>
<td>±0,00005</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>U♭ / (обозначен U♭)</td>
<td>20, 4</td>
<td>4,149</td>
<td>1,520</td>
<td>0,03786</td>
<td>0,01236</td>
<td>±0,00005</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>U♭ / (обозначен U♭)</td>
<td>200, 90</td>
<td>2,8—2,9</td>
<td>2,1—2,2</td>
<td>±0,00012</td>
<td>±0,00010</td>
<td>[5]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>U♭ / (обозначен U♭)</td>
<td>200</td>
<td>g = 2,1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remark. a) A complex hyperfine structure due to the F⁻ nuclei was observed in CaF₂ and SrF₂. It is well resolved into an even number of components in some directions.

### NpO₂ II, PuO₂ II

<table>
<thead>
<tr>
<th>1</th>
<th>Формула</th>
<th>T, °K</th>
<th>$g_{1}$</th>
<th>$g_{J}$</th>
<th>A</th>
<th>B</th>
<th>P</th>
<th>Литература</th>
<th>3 Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>(NpO₄)₂Ru(NO₃)₃ (пр. ст. 10)</td>
<td>20—12, 4,3</td>
<td>3,40</td>
<td>0,32</td>
<td>±0,01</td>
<td>±0,02</td>
<td>A₄⁰⁷</td>
<td>B₄⁰⁷</td>
<td>[1—3]</td>
</tr>
<tr>
<td>43</td>
<td>NpO₄: UO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>(PuO₄)₂Ru(NO₃)₃ (пр. ст. 10)</td>
<td>20—12</td>
<td>5,22</td>
<td>&lt; 0,4</td>
<td>±0,02</td>
<td>±0,002</td>
<td>A₄⁰⁷</td>
<td>B₄⁰⁷</td>
<td>[1]</td>
</tr>
<tr>
<td>45</td>
<td>PuO₄: UO₃ = 1: 17—1: 200</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>Na₂(PuC₆) (CH₃COO)₆</td>
<td>7—1,5</td>
<td>3,18</td>
<td>~ 0</td>
<td>±0,01</td>
<td>±0,001</td>
<td>~ 0</td>
<td>[3]</td>
<td>a)</td>
</tr>
<tr>
<td>47</td>
<td>(Pu, U)₂Ca₂(NO₃)₆</td>
<td>4</td>
<td>5,92</td>
<td>~ 0</td>
<td>±0,004</td>
<td>±0,001</td>
<td>~ 0</td>
<td>[2]</td>
<td>b</td>
</tr>
</tbody>
</table>

Remarks:

a) Cubic; M = 4. Linear groups O-U-O lie along the body diagonals of the cube; each U is also surrounded with six O from the acetate.

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groups. Eight 0 form a distorted cube.

b) The spectrum is apparently due to unusual oxides of Pu, the composition of which has not yet been established.

1) Formula; 2) reference; 3) remarks; 4) cr. st.; 5) direction cosines of the axes are; 6) Fe\textsuperscript{III} in single crystals of myoglobin obtained from whale muscle; 7) Fe\textsuperscript{III} in single crystals of hemoglobin

\[ \text{ClFe(C}_6\text{H}_4\text{)}_4(\text{CN})_8; \]

8) Fe\textsuperscript{III} in ferrimyoglobin and ferrihemoglobin azide; 9) in borax beads; 10) in polycrystalline hemin; 11) in acid metaferrihemoglobin; 12) in acid metaferrimyoglobin; 13) in fluoride of ferrihemoglobin; 14) in fluoride of ferrimyoglobin; 15) Z axis perpendicular to hemplane; 16) the distance between maxima of the hyperfine structure, due to the \( ^{57}\text{Fe} \) nucleus is approximately 10 oersted; 17) asymmetrical line; 18) Mo\textsuperscript{V} in the form of contamination in \( K_2[\text{InCl}_6] \times 2\text{H}_2\text{O} \); 19) (powder); 20) the unit cell contains two magnetically nonequivalent complexes; a hyperfine structure due to the Cl nuclei is observed; 21) the unit cell has several magnetically nonequivalent complexes; only two were measured; 22) paramagnetic resonance was observed also in undilute crystals of \( [\text{Ru(NH}_3)_6]\text{Cl}_3, [\text{Ru(NH}_3)_5\text{Cl}]\text{Cl}_2 \) at \( T = 200 \text{K} \) \[1\]; 23) di-o-phenanthroline persulfate of silver; 24) six lines observed (possibly the hyperfine structure of \( ^{185}\text{Re}, ^{187}\text{Re} \)); 25) HFS Ir; 26) HFS Cl or Br; 27) \( m_m = 3 \), axes of nonequivalent complexes parallel to the edges of a cubic unit cell; 28) all complexes equivalent; 29) all complexes equivalent; the X, Y, and Z axes are parallel to the edges of the cubic unit cell and to the axes of the Cl\textsubscript{6} octahedron. The value of \( A' \) is for \( ^{35}\text{Cl}; \)

30) all complexes equivalent; the X, Y, and Z axes parallel to the axes of the Br\textsubscript{6} octahedron. The value of \( A' \) is for \( ^{79}\text{Br} \) and \( ^{81}\text{Br} \); 31) all complexes equivalent; the X, Y, and Z axes parallel to the axes of the Cl\textsubscript{6} octahedron. The value of \( A' \) is for \( ^{36}\text{Cl} \); 32) paramagnetic resonance was also observed in \( (\text{NH}_4)_2\text{IrCl}_6 \) at \( T = 20-20^\circ \text{K} \) with a dilution ratio \( \text{Ir:Pt} = 1:10 \) and \( 1:100 \) \[3]\; 33) \( a \); \( m_m = 3 \); the ion is acted upon by an axial field, the crystalline axes of the nonequivalent ions are directed along the edges of the cube; 34) in; 35) (enriched with \( ^{235}\text{U} \)); 36) (specimen enriched); 37) relative signs of A and P determined directly; 38) \( \Delta \) small.
### Compounds with anomalous valence

#### TABLE 4.7

<table>
<thead>
<tr>
<th>№</th>
<th>Вещество</th>
<th>( T, {^\circ}\mathrm{K} )</th>
<th>( \varepsilon )</th>
<th>( A )</th>
<th>Ссылка</th>
<th>Замечания</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cr⁺⁺⁺ NaF</td>
<td>90</td>
<td>2.000</td>
<td>0.00140</td>
<td>±0.0002</td>
<td>±0.00005</td>
</tr>
<tr>
<td>2</td>
<td>Cr⁺⁺⁺ NaF</td>
<td>90</td>
<td>2.31</td>
<td>±0.02</td>
<td><strong>Fe⁺⁺⁺ Na⁺⁺⁺</strong>, ( Fe : Mg = 10^{-4} ), ( Fe : Na = 10^{-4} )</td>
<td>2</td>
</tr>
</tbody>
</table>
| 3 | Ni⁺⁺⁺ NaF | 20 | 2.768 | ±0.002 | ±0.002 | ±0.0002 | 1 | Добавления спектра не наблюдалось до 20° K. После облучения появляется спектр, приписывае- мый Ni⁺⁺⁺. \( A = 0.0016 \pm 0.00003 \), \( A = 0.0011 \pm 0.00003 \), \( A = 0.00005 \) | 3 | Константы сверх-Ф |}

#### Замечание

\( A \) определяется контактным взаимодействием с электронами, \( A \) включает дипольные взаимодействия и связи через \( \pi \)-орбитали. Считается, что \( A \) и \( A \) одинаковы для всех шести \( F \).
Key to Table 4.7

1) Substance; 2) reference; 3) remarks.

A) In 0.05 cm$^3$ of the crystal
B) Prior to irradiation, Cr$^{3+}$ in NaF yields no spectrum down to 20$^0$K, but after irradiation a spectrum appears which is presumed to be due to the Cr$^{3+}$. The value of the cubic splitting parameter is
\[ a = 0.00036 \pm 0.00004. \]

The constants of the interaction with the fluorine nuclei are:
\[ A_8 = 0.00128 \pm 0.00002, \quad A_9 = 0.00009 \pm 0.00007. \]

On heating to 150$^0$C, the irradiation effects disappear.

C) The line appears at 90$^0$K after irradiation and has a flat top, with a width of about 200 oersted; it is presumed that it is due to Co$^{3+}$. After heating to 150$^0$C, the irradiation effects disappear.

D) Prior to irradiation no spectrum is observed down to 20$^0$K. After irradiation spectrum appears, ascribed to Ni$^{3+}$. $M_m = 3$; the spectra of the nonequivalent ions are similar and correspond to axial symmetry; the symmetry axes of the nonequivalent ions are located along the edges of a cube. The interaction constants with the F nuclei are:
\[ A_{8I}^I = 0.0041 \pm 0.0002, \quad A_{9I}^I = 0.0016 \pm 0.0003, \]
\[ A_{8II}^II = \text{very small}. \]

The index I pertains to the four F located in a plane perpendicular to the symmetry axis, and the index II to the two F on the symmetry axis. After heating to 150$^0$C, the irradiation effects drop out.

E) The hyperfine structure constants due to the interaction with F$^{-}$ are:
\[ A_{8I} = 0.00141 \pm 0.00002, \quad A_{9I} = 0.0016 \pm 0.0003. \]

F) Solutions: H) dipyridyl of chromium; I) dipyridyl of vanadium; J) dipyridyl of titanium.

G) Solutions: H) dipyridyl of chromium; I) dipyridyl of vanadium; J) dipyridyl of titanium.

K) Remark. $A_8$ is determined by the contact interaction of the s electrons, $A_9$ includes the dipole interactions and the coupling via

- 175 -
the \( p_\sigma \) orbitals. It is assumed that \( A_s \) and \( A_\sigma \) are the same for all six \( F \).

REFERENCES (§4.2)

To Table 4.1

\( \text{\( V^2+ \)} \)


\( \text{\( \text{Cr}^{3+} \)} \)


\[ \text{Co}^{2+} \]


\[ \text{Cr}^{2+} \]


\[ \text{Ni}^{2+} \]


- 178 -

Cu²⁺
30. Bennett, J.E., Ingram, D.J.E., Phil. Mag. 1, 970, 1956.
43. Lütze, E., Naturwiss. (Natural Sciences) 41, 279, 1954.
48. Vittorelli, M.B.P., Palma, M.U., Palumbo, D., Santangelo, M.,


To Table 4.2

\[ \text{Ti}^{3+} \]


\[ \text{V}^{4+} \]


\[ \text{Mn}^{6+} \]


- 182 -
V8+


Co2+


- 183 -
Fe$^{2+}$


To Table 4.3

Ce$^{3+}$


Nd$^{3+}$


- 184 -

\[ \text{Sm}^{3+} \]


\[ \text{Dy}^{3+} \]


\[ \text{Er}^{3+} \]


\[ \text{Yb}^{3+} \]


To Table 4.4

\[ \text{Pr}^{3+} \]


\[ \text{Tb}^{3+} \]


Ho$^{3+}$


To Table 4.5

Mn$^{2+}$


10. Ingram, D.J.E., Phys. Rev. 90, 711, 1953.


- 186 -
45. Kumagai, H., Ono, K., Hayashi, I., Abe, H., Shimada, J., Shono, H.,
46. Kumagai, H., Hayashi, I., Ono, K., Abe, H., Shimada, J., Shono, H.,

- 188 -

Fe$^{3+}$


\[ \text{Gd}^{3+} \]


- 190 -
17. Manenkov, A.A., Prokhorov, A.M., Trapeznikova, Z.A., Fok, M.V.,
    Izv. AN SSSR, ser. fiz., 21, 779, 1957.
18. Granisher, H., Müller, K.A., Nuovo Cimento 6, suppl. No. 3, 1217,
    1957.
    1958.
    1959.

Eu$^{2+}$

    55, 1956.
10. Manenkov, A.A., Prokhorov, A.M., Trapeznikova, Z.A., Fok, M.V.,
    Izv. AN SSSR, ser. fiz., 21, 779, 1957; Optika i spektroskopiya
    2, 470, 1957.
    1958.
    1958.

\[ \text{Cm}^{3+} \]


To Table 4.6

\[ \text{Fe}^{III} \]


\[ \text{Mn}^{II} \]


\[ \text{Mo}^{V} \]


- 192 -
McIII

TcIV

RuIII

AgII

ReIV

IrIV

**Np**


**Pu**


To Table 4.7

§4.3. Paramagnetic Resonance Spectra in Electrolyte Solutions

Paramagnetic absorption in liquid solutions of salts was first observed by Zavoyskiy [1] in 1944.

From among the inorganic compounds in solution, the salts studied predominantly to date have been those of the iron group ions. The solvent used for the most part was water; in addition, various monatomic and diatomic alcohols, glycerine, acetone, dioxane, and other organic liquids were used.

A measurable resonant effect was found in solutions containing the ions $\text{VO}^{2+}$, $\text{Cr}^{3+}$, $\text{Mn}^{2+}$, $\text{Fe}^{3+}$, and $\text{Cu}^{2+}$. The observation of paramagnetic resonance in solutions of $\text{Gd}^{3+}$ and $[\text{W(CN)}_8]^{3-}$ salts is also reported.

The investigated absorption lines are either single or display a hyperfine structure. The maxima of the fine structure are not resolved, although it is known that in certain polycrystals (for example, in chrome alum powder) they can be observed. In solutions, on the other hand, the fine structure is manifest only in the width of the line.

The values of the effective $g$ factors are close to 2, but for some ions, particularly for $\text{Cu}^{2+}$, their exact value depends appreciably on the nearest surrounding of the ion. In particular, a change in solvent or complex formation lead to a change in $g$.

A hyperfine structure of paramagnetic resonance lines was observed in aqueous solutions of the simple salts $^{55}\text{Mn}^{2+}$ [2-4], $^{51}\text{VO}^{2+}$ [4, 5], and also in solutions of the complex salts $^{63,65}\text{Cu}^{2+}$ [6] and $^{183,185}\text{W}^{5+}$ [7].

The spectrum is described by a spin Hamiltonian

$$\mathcal{H} = g \mu_B H_0 \mathbf{S} + A \mathbf{I} \mathbf{S}.$$  

The resonant value of the field $H_0 = H^{*}_0$ for the transitions $(M,m) \rightarrow (M-1,m)$ are given by the expression

$$H_0^* = H - Am - \frac{A^*}{2H} [(l + 1) - m^2].$$  

- 196 -
where $H = \frac{\nu}{g\beta}$, which is in good agreement with experiment in the case of solutions of $\text{Mn}^{2+}$ and $\text{VO}^{2+}$ in water.

When the frequency of the oscillating field is low ($\nu \approx 100 \text{ Mcs}$), i.e., under conditions corresponding to the Zeeman effect, a single peak with $g = 1.00$ is observed in the hyperfine structure in weak fields in aqueous solutions of $\text{Mn}^{2+}$. The position of this peak is described by the formula

$$\nu = g\beta H,$$

where $F$ is the quantum number of the resultant momentum of the electron shell and of the nucleus and $g_F = \frac{F(F + 1) + J(J + 1) - I(I + 1)}{2F(F + 1)}$.

Indeed, when $J = I = 5/2$ we obtain $g_F = 1$ for $\text{Mn}^{2+}$. This effect, discovered by Al'tshuler, Kozyrev, and Salikhov [2], was the first evidence of the influence of nuclear spin on the electron paramagnetic resonance line. The fact that formula (a) is applicable to the description of the effect in aqueous solutions of $\text{Mn}^{2+}$ salts shows that in this case the fine splittings are quite small as compared with the hyperfine splittings. Measurements in solutions of other ions (for example, $\text{VO}^{2+}$) under weak field conditions have shown no agreement with this formula.

In solutions containing the ions $^{57}\text{Fe}^{3+}$, $^{53}\text{Cr}^{3+}$, and the hydrated ions $^{63,65}\text{Cu}^{2+}$, no hyperfine structure is observed because its constant is small compared with the line width. For $^{57}\text{Fe}^{3+}$ and $^{53}\text{Cr}^{3+}$, the hyperfine structure constants are quite small also in all the solid compounds of these ions. On the other hand, for the ions of $^{63,65}\text{Cu}^{2+}$aq the situation is to some extent close to that observed in solid copper salts, which have trigonal symmetry; in the latter, the hyperfine structure constant is small at sufficiently high temperatures and is close to isotropic; the $g$ factor is likewise close to isotropic (see the foregoing tables for the solid salts of $\text{Cu}^{2+}$).
In aqueous solutions the copper ion is surrounded by a deformed octahedron of water molecules; one of its axes is elongated because of the Jahn-Teller effect. It is obvious that we have three possible deformations of this type, corresponding to the same energy. Transitions can occur between these deformations and impart to the Jahn-Teller effect a dynamic character in this case. Calculation [8] has shown that one can explain on this basis the single line observed in aqueous solutions of copper salts. On the other hand, the presence of a resolved hyperfine line structure in solutions of several complex copper salts is due to the fact that owing to the large mass of the ligands and to their stronger bond with the Cu$^{2+}$ ion, the Jahn-Teller effect loses its dynamic character to some degree. Accordingly, the hyperfine structure constants increase and, like the $g$ factor, they become less isotropic. The values of the $g$ factors and of the hyperfine structure constants of the ions investigated in solution are listed in Table 4.8.

We note in conclusion that paramagnetic resonance was investigated also in certain supercooled solutions (glasses) [12-14]. In this case a hyperfine structure of absorption lines, which was anisotropic for VO$^{2+}$ and Cu$^{2+}$, was observed for the ions $^{51}$Vo$^{2+}$, $^{53}$Cr$^{3+}$, $^{55}$Mn$^{2+}$, and $^{63,65}$Cu$^{2+}$. In the case of Mn$^{2+}$ the structure is isotropic, and at low frequencies a single peak with $g = 1$ is observed, as in aqueous solutions of this ion, but broader. One of the results of work done in this field was the establishment of the value of the spin I = 1/2 for the $^{57}$Fe nucleus [15]. The experiments were set up in cooled melts of borax containing $^{57}$Fe.
### TABLE 4.8

**g Factors and Hyperfine Structure Constants in Liquid Solutions of Paramagnetic Salts at Room Temperature**

<table>
<thead>
<tr>
<th>№</th>
<th>Соединение</th>
<th>Концентрация, моля/л</th>
<th>Растворитель</th>
<th>( g )</th>
<th>( \mu_0 ), м.а.</th>
<th>Литература</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1) VO&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,5±0,1</td>
<td>10 водя</td>
<td>1,962±0.002</td>
<td>110</td>
<td>[4]</td>
</tr>
<tr>
<td>2</td>
<td>VOCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0,3</td>
<td>10 водя</td>
<td>1,962</td>
<td>110</td>
<td>[4]</td>
</tr>
<tr>
<td>3</td>
<td>Cr&lt;sup&gt;++&lt;/sup&gt;</td>
<td>3±0,25</td>
<td>10 водя: ацетон = 1:19</td>
<td>1,972</td>
<td>97</td>
<td>[9]</td>
</tr>
<tr>
<td>4</td>
<td>Cr(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0,2±0,01</td>
<td>10 водя</td>
<td>2,000</td>
<td>95,6</td>
<td>[4]</td>
</tr>
<tr>
<td>5</td>
<td>MnCl&lt;sub&gt;2&lt;/sub&gt;, MnSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0,3</td>
<td>10 водя</td>
<td>2,000</td>
<td>95,6</td>
<td>[4]</td>
</tr>
<tr>
<td>6</td>
<td>Mn(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4±0,01</td>
<td>10 водя</td>
<td>2,184</td>
<td>9</td>
<td>[9]</td>
</tr>
<tr>
<td>7</td>
<td>Cu(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;·3Н&lt;sub&gt;2&lt;/sub&gt;О</td>
<td>2,5</td>
<td>этиловый спирт</td>
<td>2,184</td>
<td>±0,004</td>
<td>[9]</td>
</tr>
<tr>
<td>8</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>2</td>
<td>13</td>
<td>Ацетон</td>
<td>2,158</td>
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<tr>
<td>9</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>2±1</td>
<td>15</td>
<td>Глицерин</td>
<td>2,138</td>
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<tr>
<td>10</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,08</td>
<td>16</td>
<td>Дихлорформ + толуол</td>
<td>2,139</td>
<td>±0,004</td>
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<tr>
<td>11</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
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<td>16</td>
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<tr>
<td>12</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,19</td>
<td>17</td>
<td>Дихлорформ + четыреххлористый углеводород</td>
<td>2,139</td>
<td>±0,004</td>
</tr>
<tr>
<td>13</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,27</td>
<td>18</td>
<td>Дихлорформ + четыреххлористый углеводород</td>
<td>2,139</td>
<td>±0,004</td>
</tr>
<tr>
<td>14</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,15</td>
<td>10</td>
<td>Вода</td>
<td>2,139</td>
<td>±0,004</td>
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<tr>
<td>15</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,15</td>
<td>10</td>
<td>Вода</td>
<td>2,139</td>
<td>±0,004</td>
</tr>
<tr>
<td>16</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,15</td>
<td>10</td>
<td>Вода</td>
<td>2,139</td>
<td>±0,004</td>
</tr>
<tr>
<td>17</td>
<td>Cu&lt;sup&gt;++&lt;/sup&gt;</td>
<td>0,15</td>
<td>10</td>
<td>Вода</td>
<td>2,139</td>
<td>±0,004</td>
</tr>
</tbody>
</table>

**Remark on Table 4.8.** The values of the \( g \) factors and hyperfine structure constants noted with an asterisk have been obtained without account of the second approximation.

1) Compound; 2) ion concentration, mole/liter; 3) solvent; 4) \( \mu_0 \), oersted; 5) literature; 6) Cu – acetyl acetonate; 7) Cu 3-ethylacetonate; 8) Cu ethanolamine; 9) Cu diethanolamine; 10) water; 11) water:acetone = 1:19; 12) ethyl alcohol; 13) acetone; 14) glycerine; 15) dioxane + toluol; 16) chloroform + toluol; 17) chloroform + carbon tetrachloride; 18) dioxane-toluol; 19) dioxane.
REFERENCES (§4.3)

§4.4. Use of Electron Paramagnetic Resonance for the Determination of the Spins of Atomic Nuclei

One of the important results of investigations on the spectra of paramagnetic resonance was the determination of the spins of several atomic nuclei. Table 4.9 lists the corresponding data. It must be noted that this table does not indicate the many cases when the value of the nuclear spin, previously determined by other means (and sometimes unreliable), was confirmed by the electron paramagnetic resonance method. Nor do we present in the form of a separate table the values of the magnetic moments of the nuclei, obtained by this method, since they cannot compete in accuracy with the data obtained by the nuclear paramagnetic resonance method. Some information pertaining to magnetic moments is given in the remarks for Tables 4.1-4.6.

### TABLE 4.9

<table>
<thead>
<tr>
<th>1) Isotope</th>
<th>2) Nuclear Spin</th>
<th>3) Literature</th>
<th>1) Isotope</th>
<th>2) Nuclear Spin</th>
<th>3) Literature</th>
<th>1) Isotope</th>
<th>2) Nuclear Spin</th>
<th>3) Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Mo</em>63</td>
<td>5</td>
<td>[8]</td>
<td>Sm*147</td>
<td>7</td>
<td>[13]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Isotope; 2) nuclear spin; 3) literature.
REFERENCES ($§4.4$)


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Manuscript
Page
No.

[Footnote]

197 Reference [2] was delivered to the USSR Academy of Sciences on 7 March 1948.

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Chapter 5

FORM OF PARAMAGNETIC RESONANCE ABSORPTION LINES IN
IONIC CRYSTALS AND ACOUSTIC PARAMAGNETIC RESONANCE

§5.1. Introduction

The construction of a theory for the form of paramagnetic resonance lines is a much more complicated task than a theoretical interpretation of the paramagnetic spectra. Furthermore, the problem has been very little investigated experimentally. Therefore, in spite of the existence of several basic researches, many unsolved problems still remain.

The deep analogy between the electron and nuclear resonances frequently makes it possible to extend the results obtained in one field to the other field. In investigations of the form of nuclear resonance lines, an important role is played by Bloch's phenomenological equation [1]

\[
\frac{dM}{dt} = \gamma [M, H] - \frac{M_k}{T_1} - \frac{M_j}{T_2} - \frac{M_i}{T_1},
\]

\[H = kH_z + iH_x \cos 2\pi vt,\]

(5.1)

where \(M\) is the magnetization at the instant of time \(t\), \(M_0\) the equilibrium value of the magnetization corresponding to the static magnetic field \(H_0\), \(\gamma\) the gyromagnetic ratio, \(T_1\) and \(T_2\) the times of longitudinal and transverse relaxation, respectively, and \(i, j, \) and \(k\) are the unit vectors of the coordinate system. If the interactions between the magnetic moment of the particle and the surrounding is much stronger, under conditions where the lattice is stationary (spin-spin interactions), than the interactions with the lattice vibrations (spin-lattice inter-
actions), then the longitudinal relaxation time \( T_1 \) can be identified with the spin-lattice relaxation time \( \tau \), and the transverse relaxation time \( T_2 \) can be called the spin-spin relaxation time. If the spin-lattice interactions are stronger than the spin-spin interactions, then both the longitudinal and the transverse relaxation times are determined by the spin-lattice interactions, and therefore \( T_1 = T_2 = \tau \).

Solution of (5.1) under stationary conditions leads to the following expressions for the real and imaginary parts of the paramagnetic susceptibility:

\[
\chi' = \frac{1}{2} \frac{\chi_0 v_0 T_1}{1 + 4\pi^2 T_1^2 (v_0 - v)^2 + \frac{1}{4} \frac{\gamma^2 H_T^2}{T_1 T_2}},
\]

\[
\chi'' = \frac{1}{2} \frac{\chi_0 v_0 T_1}{1 + 4\pi^2 T_1^2 (v_0 - v)^2 + \frac{1}{4} \frac{\gamma^2 H_T^2}{T_1 T_2}}.
\]

In most cases the observation of the electron paramagnetic resonance is carried out under such conditions that the saturation factor is small \((1/4\pi^2 H_T^2 T_1 T_2 << 1)\) and can be neglected. It must be borne in mind that in formulas (5.2) we take into account only the component of the alternating magnetic field which is circularly polarized in the direction of the Larmor precession. The values of \( \chi' \) and \( \chi'' \) depend therefore on the sign of the static magnetic field and consequently on the sign of \( v_0 \). It follows from (5.2) also that \( \chi'' = 0 \) if \( v_0 = 0 \). This is of course incorrect, since absorption exists also in the absence of a static magnetic field. This shortcoming was eliminated by Garsten [2], who obtained the following formulas for a linearly polarized wave:

\[
\chi' = \frac{1}{2} \frac{\chi_0 v_0 T_1}{1 + 4\pi^2 (v_0 - v)^2 T_1^2 + \frac{1}{4} \frac{\gamma^2 (v + v_0)^2 T_1^2}{T_1^2 + 4\pi^2 (v + v_0)^2 T_1^2}},
\]

\[
\chi'' = \frac{1}{2} \frac{\chi_0 v_0 T_1}{1 + 4\pi^2 (v_0 - v)^2 T_1^2 + \frac{1}{4} \frac{\gamma^2 (v + v_0)^2 T_1^2}{T_1^2 + 4\pi^2 (v + v_0)^2 T_1^2}}.
\]

We note that these expressions coincide with the known dispersion formulas of Van Vleck and Weisskopf [3].

Shaposhnikov [4] developed a thermodynamic method of investigating
relaxation phenomena. In considering paramagnetic resonance [5], he arrived at the formulas of Van Vleck and Weisskopf by solving the difference equations for the magnetization of a paramagnet, derived thermodynamically by assuming the existence of a spin system that interacts weakly with the vibrations of the lattice. Skrotskiy and Kurbatov [6], following the Shaposhnikov method, presented a general thermodynamic theory of relaxation and resonance phenomena in two spin systems. Systems of this type are frequently encountered among paramagnets, for many substances contain two sorts of magnetic particles.

Wangsness and Bloch [7] developed a statistical quantum theory for dynamic phenomena in paramagnets, starting out from the equation of motion of a corresponding statistical operator. It turned out that Bloch's phenomenological equation (5.1) is valid if there are no spin-spin interactions and if the paramagnetism is of pure spin nature (there are no splittings of the energy spin levels by electric fields). Thus, Bloch's phenomenological equation (as well as its various modifications) is applicable in a rather limited region. Nevertheless, it is used quite extensively because it gives a qualitative explanation of various aspects of the phenomenon of paramagnetic resonance: 1) it follows from the equation that the form of the resonance line is determined by the time $T_2 = \tau$ and is independent of $T_1 = \tau$ if the spin-spin interactions are stronger than the spin-lattice interactions, and conversely the line shape is determined by the time $T_2 = T_1 = \tau$ and is independent of the spin-spin interactions if they are weaker than the spin-lattice interactions; 2) the equation makes it possible to account for the dependence of the line shape on the intensity of the alternating magnetic field which is capable of producing "saturation"; 3) the equation makes it possible to analyze quantitatively various transients in radio devices containing paramagnets.
The difficulties in constructing a microscopic quantum theory of the processes that determine the paramagnetic resonance line shape make it necessary to consider two extreme cases: either the spin-spin interactions are much stronger than the spin-lattice ones, or are much weaker. Because of this it is possible to assume that in the former case we deal with interactions in a system of magnetic particles that are in adiabatic conditions, and that there is no energy exchange with the lattice vibrations (or with the Brownian movement of the particles in a liquid). In the second case it is usually assumed that the magnetic particles are isolated from one another and each interacts individually with the lattice vibrations. In the sections that follow we shall discuss the theoretical and experimental investigations of spin-spin and spin-lattice interactions in ionic crystals and in their liquid solutions. In addition, we shall consider the theory of acoustic paramagnetic resonance, a phenomenon whose study can yield valuable information on spin-lattice interactions.

§5.2. Spin-Spin Interactions

1. If two neighboring magnetic atoms are at a distance \( r \) from each other, then each Zeeman energy level will be broadened by dipole interaction by an amount \( \sim h/\beta^2 r \). This can be visualized in the following fashion. Each atom is acted upon not only by the external magnetic field \( H_0 \) but also by a local field \( H_{10k} \), produced by the neighboring particles. The resonance condition therefore assumes the form \( \hbar v = g\beta(H_0 + H_{10k}) \). Since the average scatter of the possible values of \( H_{10k} \) is of the order of \( \beta/r^3 \), it is clear that we obtain for the width of the resonant line \( \Delta v \) the value given above.

If all the magnetic particles are identical, then in addition to the "magnetostatic" broadening mechanism which we have already considered, there is also a second broadening mechanism, a "dynamic" one.
Let us consider two precessing dipoles with oppositely directed moments. Each of these produces at the location of the other an alternating field of resonant frequency, under the influence of which the moments can exchange orientations, for the total energy is conserved in this case. The limitation on the lifetime of each particle at a definite Zeeman energy level leads to a broadening, which again, in accordance with the uncertainty relation, has a value $\sim h/\beta^2 r^{-3}$.

The computation methods developed to date make it possible to calculate the moments of the resonance absorption curve. By $k$-th moment of an absorption line is meant the quantity

$$M_k = \int (\nu - \nu_0)^k g(\nu) d\nu. \quad (5.4)$$

If the paramagnetic resonance line has a Gaussian shape (1.20), then at $M_2 = \sigma^2$, $M_4 = 3\sigma^4$. If the line shape is Lorentzian (1.21), then in order for the integrals $M_k$ to converge for positive $k$, the $g(\nu)$ curve must be cut off. If we assume that the function $g(\nu) = 0$ when $M_2 = a\Delta\nu/\pi$, $M_4 = a^3\Delta\nu/3\pi$, then $|\nu - \nu_0| \geq a$.

This method was first used by Waller [8], and then by Broer [9] to estimate the magnitude of the spin-spin interaction. An analysis of the paramagnetic resonance absorption line shape by the method of moments was carried out by Van Vleck [10]. Van Vleck’s theory is based on the following assumptions: a) the particle magnetism is of the pure spin type; b) there is no paramagnetism; c) the frequency of the oscillating field is so high that the Zeeman energy is much larger than the average energy of the spin-spin interaction of the neighboring particles; d) the exchange forces are isotropic; e) the temperature is so high that all the Zeeman levels are equally populated.

The Hamiltonian of the spin system contains the Zeeman energy as well as the dipole-dipole and exchange interactions:
\[ \dot{\mathbf{r}} = \mathbf{R}_{\text{ext}} \cdot \mathbf{r} + \mathbf{R}_{\text{int}} + \mathbf{R}_{\text{def}} \]  

(5.5)

where

\[ \mathbf{R}_{\text{ext}} = g \mathbf{H}_0 \sum_j \mathbf{S}_j \]  

(5.6)

\[ \mathbf{R}_{\text{int}} = g^2 \sum_{j<k} \left( |r_{jk}|^3 (\mathbf{S}_j \cdot \mathbf{S}_k) - 3 |r_{jk}|^5 (r_{jk} \mathbf{S}_j)(r_{jk} \mathbf{S}_k) \right) \]  

(5.7)

\[ \mathbf{R}_{\text{def}} = \sum_{j<k} \mathbf{a}_{jk} \mathbf{S}_j \mathbf{S}_k. \]  

(5.8)

Here \( \mathbf{S}_z \) denotes the z-th component of the vector matrix of the spin momentum of the \( j \)-th atom, \( r_{jk} \) is the distance between the \( j \)-th and the \( k \)-th atoms, \( \mathbf{a}_{jk} = 2Z^2 I_{jk} \), where \( Z \) is the number of electrons in the unfilled atomic shell, and \( I_{jk} \) is the ordinary exchange integral. It is convenient to represent the dipole interaction matrix in the form

\[ \mathbf{R}_{\text{int}} = \dot{\mathbf{a}} + \dot{\mathbf{b}} + \dot{\mathbf{c}} + \dot{\mathbf{d}} + \dot{\mathbf{f}} = g^2 \sum_{j<k} r_{jk} \times \]

\[ \times (\dot{a}_{jk} + \dot{b}_{jk} + \dot{c}_{jk} + \dot{d}_{jk} + \dot{f}_{jk}), \]

\[ \dot{a}_{jk} = (1 - 3 \cos^2 \theta_{jk}) \mathbf{S}_j \mathbf{S}_k, \]

\[ \dot{b}_{jk} = \frac{1}{4} (1 - 3 \cos^2 \theta_{jk}) (\mathbf{S}_j \mathbf{S}_j + \mathbf{S}_k \mathbf{S}_k), \]

\[ \dot{c}_{jk} = \dot{d}_{jk} = -\frac{3}{2} \sin \theta_{jk} \cos \theta_{jk} e^{-i \phi} (\mathbf{S}_j \mathbf{S}_j + \mathbf{S}_k \mathbf{S}_k), \]

\[ \dot{e}_{jk} = \dot{f}_{jk} = -\frac{3}{2} \sin \theta_{jk} \cos \theta_{jk} e^{-i \phi} (\mathbf{S}_j \mathbf{S}_j + \mathbf{S}_k \mathbf{S}_k). \]  

(5.9)

where \( \mathbf{S}_\pm = \mathbf{S}_x \pm i \mathbf{S}_y \) and \( \theta_{jk} \) is the angle between \( \mathbf{H}_0 \) and \( \mathbf{r}_{jk} \).

We choose a representation in which the matrices \( \mathbf{S}_z \) are diagonal; their eigenvalues are denoted by \( m_j \). The magnetic quantum number of the entire spin system will be \( M = \sum m_j \). If we neglect the interactions between the spins, then we obtain a system of equidistant energy levels \( E_M = g \mathbf{S}_0 M \), which will be strongly degenerate, since there exists a tremendous number of combinations of values of \( m_j \) which lead to one and the same value of \( M \). The eigenfunctions \( \mathbf{H}_{\text{zeem}} \) will be denoted \( \psi_M; m_1, m_2, \ldots \). If \( \mathbf{H}_{\text{dip}} + \mathbf{H}_{\text{obm}} \) are considered as a perturbation and the ordinary perturbation method is used for the degenerate case, then to solve the problem in the first approximation we must calculate the

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perturbation matrix elements with the aid of \( \psi \) functions that pertain to only one considered energy level \( E_M \). We can readily see that the application of individual parts of the perturbation operator to \( \psi_M; m_1, m_2, \ldots \) will give new \( \psi \) functions for which the values of \( M, m_i, \) and \( m_k \) will change in the following manner:

\[
\begin{align*}
\hat{a}_{jk}: & \quad \Delta M = 0, \Delta m_j = 0, \Delta m_k = 0; \\
\hat{d}_{jk}: & \quad \Delta M = \ldots 1, \Delta m_j = \begin{cases} 0 & \text{if } j = 1, \\
-1 & \text{if } j = 0 \end{cases}, \Delta m_k = \begin{cases} -1 & \text{if } j = 1, \\
0 & \text{if } j = 0 \end{cases}; \\
\hat{b}_{jk}: & \quad \Delta M = 0, \Delta m_j = \pm 1, \Delta m_k = \mp 1; \\
\hat{e}_{jk}: & \quad \Delta M = 2, \Delta m_j = 1, \Delta m_k = 1; \\
\hat{c}_{jk}: & \quad \Delta M = 1, \Delta m_j = \begin{cases} 0 & \text{if } j = 1, \\
1 & \text{if } j = 0 \end{cases}, \Delta m_k = \begin{cases} 1 & \text{if } j = 1, \\
0 & \text{if } j = 0 \end{cases}; \\
\hat{f}_{jk}: & \quad \Delta M = -2, \Delta m_j = -1, \Delta m_k = -1.
\end{align*}
\]

(5.10)

The operator \( \hat{A}_{obm} \) acts like \( \hat{S}_{jk} \). From (5.10) and (5.8) it is seen that the nonvanishing matrix elements pertaining to the level \( E_M \) contain only the matrices \( \hat{A}, \hat{B}, \) and \( \hat{A}_{obm} \).

The probability of transition between two Zeeman levels \( E_M \) and \( E_M' \) under the influence of a radio frequency field directed along the \( x \) axis will obviously be proportional to \( |<M| \hat{S}_x |M'>|^2 \). Since the matrix element of the operator \( \hat{S}_x = \sum \hat{S}_{xj} \) is in first approximation different from zero, provided only \( M' = M \pm 1 \), then only one bright absorption line can appear, with the Larmor frequency \( v_0 \). In the next approximation we must also take into consideration the operators \( \hat{C}, \hat{D}, \hat{E}, \hat{F} \) in order to calculate the perturbation energy, and consequently the wave functions corresponding to the energy level \( E_M \) assume the form \( \psi_M + \epsilon_1 \psi_{M-1} + \epsilon_2 \psi_{M+1} + \epsilon_3 \psi_{M+2} + \epsilon_4 \psi_{M-2} \), where the \( \epsilon_i \) are of the order of \( \beta^2 r^{-3}/g B H_0 \). It is clear that in the second approximation transitions are also possible from the level \( M \) to the levels \( M' = M, M + 2, \) and \( M + 3 \). Thus, satellites at frequencies 0, 2\( v_0 \), and 3\( v_0 \) appear at the fundamental line of frequency \( v_0 \). The intensity of the satellites will be related to the intensity of the fundamental line.
approximately as \( \varepsilon^2 = 1 \). If still higher approximations are taken into account, then weak satellites at even higher frequencies can appear.

2. When considering the principal resonance line, we must cut off the Hamiltonian (5.5) by discarding from it the terms \( \hat{C}, \hat{D}, \hat{E}, \) and \( \hat{F} \), which do not commute with the principal part of the Hamiltonian \( H_{zem} \). The eigenvalues of the cut-off Hamiltonian \( H^+ \) will be denoted by \( H_{nn} \), and the transition frequencies by \( \nu_{nn'} \). Then, by definition, we have for the mean square of the absorption-line frequency

\[
\langle \nu^2 \rangle = \frac{\sum_{n, n'} |\langle n' | \hat{S}_x | n \rangle|^2}{\sum_{n, n'} |\langle n' | \hat{S}_x | n \rangle|^2}.
\]

This expression can be represented in the form

\[
\langle \nu^2 \rangle = -\frac{S_P}{h^2 S_P} \left( \frac{\hat{S}_x - \hat{S}_y \hat{S}_z}{h^2 S_P} \right)^2.
\] (5.12)

It would be quite hopeless to attempt to calculate the eigenvalues of \( H_{nn} \), for their number is comparable with the number of atoms in the crystal. The great advantage of formula (5.12) lies in the fact that it contains only the diagonal sums, the invariance of which makes it possible to carry out the calculations in an arbitrary representation. The simplest obviously will be a representation in which the spatial quantization is carried out for each spin separately. After calculating the traces of the matrices contained in (5.12), we find that the second moment of the absorption line is

\[
M_s = \langle \nu^2 \rangle = \frac{3}{4} S^2 + 2S(S+1) \sum_k r_k^4 \cdot (3\cos^2 \theta_k - 1)^4.
\] (5.13)

where \( k \) numbers all the magnetic particles of the lattice, and the index \( l \) pertains to a certain atom which is chosen as the reference point for the calculations. For a crystalline powder we have

\[
M_s = \frac{3}{4} S^2 + 2S(S+1) \sum_k r_k^4.
\] (5.14)
For a simple cubic lattice, with a constant equal to \( d \), we obtain

\[
\sum_{i} r_{ij} = 8.5d^4.
\]  

(5.15)

If the quantum mechanical calculations are replaced by the magnetostatic calculations and the influence of the broadening mechanism which we have called dynamic is thereby discarded, then we obtain for \( M_2 \) the same expression (5.13), reduced by a factor \( 9/4 \). This reduced value should be used only when we deal with the broadening due to the interaction between dipoles of different sorts, for example of paramagnetic atoms with nuclear spins of surrounding diamagnetic particles. Thus, if we have magnetic particles of two sorts with spins \( S \) and \( S' \) and spectroscopic-splitting factors \( g \) and \( g' \), then the second moment of the resonance line produced by the particles of the first sort will consist of (5.13) and the following expression:

\[
M_2' = \frac{1}{3} g^4 v^4 (S' + 1) \sum r_{ij}' (3 \cos^2 \theta_{ij} - 1)^2.
\]  

(5.16)

where the index \( j \) pertains to some particle of the first sort, which is chosen to be the reference for the calculations, and \( j \) numbers the particles of the second sort. If \( g' = g \), then these formulas are not suitable, for now the resonance lines produced by the particles of the different sorts coalesce into one. This case was considered in [11].

Van Vleck also calculated the second moment \( \tilde{M}_2 \) of the absorption curve which includes not only the fundamental line, but also the supplementary lines at frequencies \( 0, 2g \beta H_0 \), and \( 3g \beta H_0 \). It turned out that \( \tilde{M}_2 = 10/3M_2 \), and that this relation, as was already pointed out by Broer [9], is independent of \( H_0 \), since the heights of the supplementary absorption curves are inversely proportional to \( H_0 \), whereas the frequencies are approximately linear in \( H_0 \).

Let us turn to an examination of the fundamental paramagnetic res-
onance line. It is seen from (5.13) that the isotropic exchange forces do not affect the value of the second moment of the absorption line at all. Therefore, in order to evaluate the influence of the exchange forces on the line shape it is necessary to make use of higher moments. The fourth moment was calculated in the same paper of Van Vleck, while the sixth moment was calculated later by Glebashev [12]. We note that the odd moments vanish and consequently the absorption line is symmetrical. Calculations have shown that in case of pure dipole interactions the ratios of the moments are close to the values obtained for the Gaussian function, namely: $\frac{M_6^{1/6}}{M_4^{1/4}} : \frac{M_2^{1/2}}{1} = 1.57:1.32:1$. If the exchange interactions predominate over the dipole ones, then $\frac{M_4^{1/4}}{M_2^{1/2}} >> 1$ and consequently the line assumes a Lorentzian form. Insofar as the area of the absorption curve and its second moment do not contain exchange integrals, we can conclude that the absorption line becomes narrower in the center and becomes accordingly less steep on the edges.

This narrowing down of the lines under the influence of the exchange forces, which was noted already in [13, 14] is the consequence of the assumptions on which the Van Vleck theory is based, and which cannot be accepted in many cases for real crystals.

The theory of dipole broadening as developed by Van Vleck was extended by Kittel and Abrahams [15] to the case of solid paramagnetic solutions. It was found that if the concentration of the paramagnetic atoms is $f > 0.1$, then the line retains a Gaussian form and its width is proportional to $\sqrt{f}$; on the other hand, if $f < 0.01$, then the line shape becomes Lorentzian, and the width is proportional to $f$. Glebashev [16] generalized these calculations, taking also account of the influence of exchange isotropic forces.

3. The assumption that the paramagnetism has a purely spin nature
greatly limits the applicability of Van Vleck's theory. In fact, if
the effective spin is $S' > 1/2$ then there are always small splittings
of the spin levels by the electric field of the crystal. On the other
hand, if $S' = 1/2$, then the influence of the crystalline field is
still felt and the $g$ factor becomes anisotropic.

Pryce and Stevens [17] generalized Van Vleck's theory and pointed
out methods of calculating the moments of curves for a great variety
of cases. The general calculation method consists in the following.
The Hamiltonian of the spin system is represented in the form

$$ H = H_0 + W, \quad (5.17) $$

where the principal part of the Hamiltonian $H_0$ determines the energy
levels the transitions between which produce individual lines of the
paramagnetic resonance spectrum, while the perturbation $W$ serves as
the cause of broadening of these lines. Expressions of the type (5.12)
are then set up for the calculation of the moments of the line. In or-
der to separate only the absorption line of interest to us, the opera-
tors $\hat{W}$ and $\hat{S}_x$ are so cut off as to make the cut-off operator $\hat{W}$ com-
mute with $\hat{H}_0$, and the cut-off operator $\hat{S}_x$ contains only nondiagonal
matrix elements, which ensure the necessary quantum transitions. The
matrices $\hat{W}$ and $\hat{S}_x$ are cut off either with the aid of the corresponding
projection matrices, as was proposed by Pryce and Stevens [17], or by
directly crossing out the unneeded matrix elements.

The following cases are considered in [17]: 1) there is one sort
of particles, all the energy intervals of which are different in the
unperturbed state; 2) the particles in the unperturbed state have co-
inciding or nearly degenerate levels; 3) there are two sorts of par-
ticles; 4) there exists a hyperfine structure of the energy levels of
the particles. In addition, Pryce and Stevens considered the question
of the dependance of the absorption line width on the temperature and
on the form of the crystal. The perturbation usually has a two-particle character and can be represented in the form \( \hat{W} = \sum_{i,j} \hat{W}_{ij} \). The resulting second moment, expanded in powers of \( 1/kT \), is

\[
M_i = a_0 \sum_{i,j} |\langle W_{ij} \rangle|^2 + \frac{a_1}{kT} \sum_{i,j} |\langle W_{ij} \rangle| + \ldots ,
\]  

(5.18)

where \( a_0 \) and \( a_1 \) are certain quantities independent of \( W \) and \( T \). By virtue of the fact that \( W_{jk}^2 \) decreases at least as fast as \( 1/r_{jk}^6 \), we can carry out for the temperature-independent part of the moment \( M_2 \) the following transformation:

\[
\sum_{i,j} |\langle W_{ij} \rangle|^2 = N \sum_j |\langle W_{ij} \rangle|^2 .
\]  

(5.19)

It is immaterial whether the particle \( _1 \), chosen as the reference for the calculations, is located at the center of the crystal or near its boundary. The transformation (5.19) cannot be applied to that part of the moment which is proportional to \( 1/kT \), since \( W_{ij} \) decreases slowly with increasing \( r_{ij} \). As a result the paramagnetic resonance line should shift near the Curie point, and the line width will depend on the temperature and on the form of the crystal. From the microscopic point of view it can be stated that the factor of demagnetization of the investigated specimen becomes essential near the Curie point. Glebashev [18] made detailed calculations of the dependence of the moments of the resonance line on the temperature. At sufficiently low temperatures the paramagnetic resonance lines will become asymmetrical and their width will change.

4. Ishiguro, Kambe, and Usui [19] calculated \( M_2 \) for nickel fluorosilicate, which has only one magnetic ion per crystal cell. The principal Hamiltonian has the form

\[
\mathcal{H} = \sum_i (\frac{1}{2} \delta_i \delta_i + D \delta_i^2) ,
\]  

(5.20)
The spin level scheme for the individual particle was shown in Fig. 3.2. If the field $H_0$ is parallel to the hexagonal axis of the crystal (the Z axis) we have for both lines $-1 \rightarrow 0$ and $0 \rightarrow 1$

$$\hbar \mathcal{M}_s = \sum \left[ \mathcal{M}_s + \frac{5}{4} \mathcal{M}_s (3 \cos^2 \theta_s - 1) \right]. \quad (5.21)$$

For the case $H_0 \perp Z$, this same formula will hold true if we assume $g \beta H_0 >> D$. Calculation of the lattice sums yields

$$\hbar \mathcal{M}_s = 6 \lambda + \frac{3.13 \beta H_0}{d^{1/2}} \mathcal{M}_s \parallel Z; \ h \mathcal{M}_s = 6 \lambda + \frac{6.50 \beta H_0}{d^{1/2}} \mathcal{M}_s \perp Z. \quad (5.22)$$

From a comparison with experiment [20] we can estimate the value of the exchange coefficient $|A| = 0.027 \text{ cm}^{-1}$.

Griffiths and Owen [21] observed a discrepancy between their measurements of the line shape of Tutton's salts of nickel and the theory of Ishiguro, Kambe, and Usui. Stevens [22] made detailed calculations and showed that the discrepancies are due, first, to the presence of two nonequivalent paramagnetic ions per crystal cell in Tutton's salts, and second to the more complicated form of the spin Hamiltonian, which contains the additional term $E(S_x^2 - S_y^2)$. From a comparison with the experimental data, Stevens estimated the exchange coefficient at $A = -0.026 \text{ cm}^{-1}$.

Kambe and Ollom [23] calculated the second moment of the central paramagnetic resonance line (transition $-1/2 \rightarrow 1/2$) for half-integer particle spin $S$. Because of the action of the crystalline field, other transitions give lines at different frequencies and are not considered in this work.

a) If all the particles are equivalent, then

$$\hbar \mathcal{M}_s = \left[ \frac{S(S+1)}{3} + \frac{2S(S+1)}{2(S+1)} \right] \sum \lambda_s + \left[ -\frac{2}{3} S(S+1) + \frac{2S(S+1)}{2(S+1)} \right] \sum \lambda_s \beta \frac{H_0}{d} \times$$

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1) If there are particles of a different sort with $g$-factor $g'$ and spin $S'$, they make an additional contribution:

$$\hbar^2 M_b = \frac{1}{3} S' (S' + 1) \sum_{\nu} [\lambda_{j\nu} + \frac{3}{4} g_{j\nu} (1 - 3 \cos^2 \theta_{j\nu}) ]^2.$$  

(5.24)

b) If there are particles of a different sort with $g$-factor $g'$ and spin $S'$, they make an additional contribution:

$$\hbar^2 M_b = \frac{1}{3} S' (S' + 1) \sum_{\nu} [\lambda_{j\nu} + \frac{3}{4} g_{j\nu} (1 - 3 \cos^2 \theta_{j\nu}) ]^2.$$  

(5.24)

c) If there are several nonequivalent particles of one and the same sort in the crystal cell, then the interaction between the considered type of particles with the other nonequivalent particles gives an additional contribution to the second moment:

$$\hbar^2 M_b = \left[ \frac{1}{3} S (S + 1) - \frac{1}{4} (2S + 1) + \frac{(2S + 1)^2}{32} \right] \sum_{\nu} \lambda_{j\nu} +$$

$$+ \left[ - \frac{2}{3} S (S + 1) + \frac{1}{8} (2S + 1) + \frac{(2S + 1)^2}{32} \right] \sum_{\nu} \lambda_{j\nu} \frac{g_{j\nu}}{r_{j\nu}'},$$

$$\times (3 \cos^2 \theta_{j\nu} - 1) + \left[ \frac{1}{3} S (S + 1) + \frac{1}{8} (2S + 1) + \frac{(2S + 1)^2}{128} \right] \times$$

$$\times \sum_{\nu} \frac{g_{j\nu}^2}{r_{j\nu}'} (3 \cos^2 \theta_{j\nu} - 1).$$  

(5.25)

If we denote the second moment, calculated by formula (5.13), which is valid in the absence of crystalline splittings, by $M^*_2$, then we obtain for purely dipole interactions:

<table>
<thead>
<tr>
<th>Spin</th>
<th>$M^*_4$</th>
<th>$M^*_5$</th>
<th>$M^*_4$</th>
<th>$M^*_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>4</td>
<td>9</td>
<td>4</td>
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<td>105</td>
<td>313</td>
</tr>
<tr>
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<td>881</td>
<td>161</td>
</tr>
<tr>
<td>7</td>
<td>756</td>
<td>189</td>
<td>756</td>
<td>189</td>
</tr>
</tbody>
</table>

Abragam and Kambe [24] calculated the dipole broadening of the resonance line due to transitions between energy sublevels arising in
the electric field of the crystal, if the external magnetic field is equal to zero. The following assumptions were made there: a) the spin is \( S = 1 \) or \( 3/2 \); b) the crystalline field has axial symmetry; c) the symmetry axis is the same for all particles. The following expressions were obtained for the second moment of the resonance lines:

\[
S = 1: \quad M_s = \frac{\alpha_{jk}^2}{\hbar^2 a^2} \sum_\alpha r_{jk}^\alpha \times \\
\times \left[ 8(1 - 3\gamma_j^k) - (1 - \gamma_j^k)^2 - 2(1 - 3\gamma_j^k)(\alpha_j^k - \beta_j^k) \right],
\]

\[
S = \frac{3}{2}: \quad M_s = \frac{\alpha_{jk}^2}{90 \hbar^2 a^2} \sum_\alpha r_{jk}^\alpha \times \\
\times \left[ 207(1 - 3\gamma_j^k)^2 + 1512 \gamma_j^k(1 - 3\gamma_j^k) + 459(1 - \gamma_j^k)^2 - 103(1 - 3\gamma_j^k)(\alpha_j^k - \beta_j^k) \right].
\]

where \( \alpha_{jk}^2 \), \( \beta_{jk}^2 \), and \( \gamma_{jk} \) are the direction cosines of the radius vector \( \mathbf{r}_{jk} \); if the \( Z \) axis is taken to be the symmetry axis of the crystalline field. For a cubic lattice with an electric field parallel to one of the axes

\[
S = 1: \quad M_s = 28,1 \frac{\alpha_{jk}^2}{\hbar^2 a^2}; \quad S = \frac{3}{2}: \quad M_s = 60,0 \frac{\alpha_{jk}^2}{\hbar^2 a^2}.
\]

Calculations were also made for the broadening due to the presence of "nonresonant" particles (particles of the second sort, not participating in the production of the resonance line).

5. In all the investigations which we have just considered, where the existence of energy splittings due to the electric field of the crystals was taken into account, it was assumed that the action of the crystalline field is much stronger than the dipole and exchange interactions. If this is not so, then the appearance of the resonance lines becomes possible if the external magnetic field causes splittings that are much larger than the crystalline ones. In this case the Hamiltonian term that takes into account the influence of the crystalline field should be transferred from the main part \( \hat{H}_0 \) into the "perturbed" part \( \hat{W} \). The crystalline field will participate in the broadening of the resonance line along with the dipole and the exchange interactions. This
case was considered by Berson [25], who proposed that the action of the crystalline field can be represented by an axially-symmetrical Hamiltonian $E_S^2 + F_S^2$. Calculations have shown that the second moment is equal to

$$h^2M_2 = \frac{3}{4} g^2S(S+1) \sum \hat{r}_{ia}^2 (3 \cos^2 \theta_{ia} - 1) +$$

$$+ \frac{1}{3} (4S(S+1) - 3) \hat{E}^2 + \frac{1}{18} (48 S^2(S+1)^2 - 76S(S+1) + 30) \hat{E} \cdot \hat{F} +$$

$$+ \frac{1}{105} (120 S^3(S+1)^3 + 208 S^2(S+1)^2 + 336 S(S+1) - 135) \hat{F}^2. \tag{5.28}$$

Here, as in the case considered by Van Vleck, the second moment is independent of the isotropic exchange interactions.

6. In many crystals the paramagnetic ions of which contain an odd number of electrons, the ground level of these ions is a Kramers doublet. Among substances of this type are the investigated salts of rare-earth elements, many salts of the iron-group elements, etc. In spite of the fact that in all these cases the ground level can be characterized by an effective spin $S' = 1/2$, nonetheless the Van Vleck theory is unsuitable here, too. The electric field of the crystal cannot split a level with $S' = 1/2$, but it can give rise to a strong anisotropy of the $g$ factor.

Kopvillem [26] calculated the second moment of the resonance line for this case under the following assumptions: a) the crystal temperature is so low that only the lowest Kramers doublet is populated; b) all the paramagnetic ions are equivalent and consequently have the same $g$-tensor. Since the spin-lattice interactions are for the most part very strong in paramagnets of this type and the observations of paramagnetic resonance must be made at low temperatures, the dependence of the line shape on the temperature can therefore be of importance and was consequently taken into account in the calculations of the moment $M_2$.

The calculations have shown the following: a) the line width de-
pends on the direction of the static magnetic field; b) the isotropic exchange forces influence the value of $M_2$, and consequently the exchange interactions generally speaking increase the width of the resonance line; this broadening is different for different magnetic field directions; c) the line width due to the dipole interactions decreases with decreasing temperature. The magnitude of the second moment due to the dipole interactions was found to be

$$M_2 = \frac{31}{8} \left( \frac{3}{2} + 2e^m + \frac{1}{2} e^{2m} \right) - B_{ij} (B_{ij} + B_{ij}) (1 + 3e^m),$$

where $x, y, z$ are the principal axes of the $g$ tensor, $v_{ij}^{(\alpha)}$ is the angle between $r_{ij}$ and the $\alpha$ axis. Calculation of the lattice sums gives, for example for ethyl sulfates of rare earths and for a field $H_0$ parallel to the crystal symmetry axis,

$$M_2 = 66.7 \frac{g_1}{g_1} \left( x^3 + 3x^2 + 2 \right) - 0.5 e^{2m} + 1.5 - x^4,$$

where $x = \frac{g_1}{g_1}$.

7. If the exchange interactions are sufficiently strong, they influence not only the paramagnetic resonance line widths, but can also change the line positions. One such case was experimentally investigated by Bagley and Griffiths [27] in the salt CuSO$_4 \cdot 5$H$_2$O. The crystal cell of this substance contains two ions with different magnetic axes. Two resonance lines of approximate width 115 oersted were therefore observed with the aid of a radio frequency field at a wavelength $\lambda = 0.85$ cm. Were we to have $\lambda = 3$ cm, then these lines would be approximately 500 oersted apart, but experience has
shown that they coalesce into a single line. A theoretical explanation of this fact was presented by Pryce [28]. The Hamiltonian of the spin system has the form

$$\hat{H} = \beta \hat{S}' g' H_0 + \beta \hat{S}'' g'' H_0 + \hat{H}_{\text{obs}}$$  \hspace{1cm} (5.31)$$

where $S'$ and $S''$ are the total spins of all particles of the first and second kind, and $g'$ and $g''$ are the corresponding $g$ tensors. For simplicity no account was taken here of the dipole interaction. Formula (5.31) can be represented in the form

$$\hat{H} = \hat{H}_0 + \hat{W}$$

$$\hat{H}_0 = \frac{3}{2} (\hat{S}' + \hat{S}'') (g' + g'') H_0 + \hat{H}_{\text{obs}}$$ \hspace{1cm} (5.31a)$$

Were there no "perturbation" $\hat{W}$, then, in view of the fact that both terms of $\hat{H}_0$ commute with each other, a transverse radio frequency field should give rise to transitions between states, for which the components of the total spin $S' + S''$ in the direction $(g' + g'') H_0$ differ by unity, and the exchange energy is conserved. The result should be one sharp absorption line. The perturbation $W$ changes the intervals between the unity levels, the transitions between which are allowed by the selection rules. The line broadens. In addition, the perturbation causes overlapping of the wave functions pertaining to different exchange-energy levels, and consequently the selection rules change together with the line shape. At higher frequencies, at large fields $H_0$, the value of $\hat{W}$ can no longer be regarded as a perturbation, for it becomes comparable with the exchange energy. It is easy to imagine that two absorption peaks can appear under such conditions.

A second example of the influence of exchange interactions on the form of the spectrum is the reduction in the hyperfine splittings of the resonance lines, occurring under the influence of the exchange forces. Assume that the interaction of the magnetic moments of the nu-
ucleus and of the electron shell is characterized by an isotropic hyperfine structure constant $A$. If we disregard the nuclear spin, we can assume for simplicity that all the paramagnetic atoms precess about the external magnetic field with one and the same Larmor frequency. Because of the interaction between the electron and nuclear moments, different atoms will have one of the $2I + 1$ precession frequencies, which differ by small amounts on the order of $A/h$, with equal probability. Let the period of the exchange be $\tau = h/J$ ($J$ is the exchange integral). If $\tau \gg h/A$, then the precession will change during the course of the exchange by an amount $\sim A/h$; if on the other hand $\tau \ll h/A$, then all these changes will average out and the individual peaks of the hyperfine structure will coalesce into a single line. Consequently, the reduction in the hyperfine splitting can be expected only when $J \geq A$. These arguments can be qualitatively confirmed by the method of moments. The Hamiltonian of the spin system can be written in the form

$$\mathcal{H} = g \mu_B H \sum_i \hat{S}_i + \sum_{j,k} \gamma_{jk} \hat{S}_j \hat{S}_k + A \sum_i \hat{S}_i \hat{I}_i.$$

The first term denotes here the Zeeman energy, the second the exchange interactions, and the third the magnetic interactions of the nuclei and the electrons. Calculations made by Van Veringen [29] have led to the following expressions for the second and fourth moments of the resonance line:

$$M_2 = \frac{1}{3} h^2 A^2 I(I+1),$$

$$M_4 = h^4 I(I+1) \left\{ \frac{1}{3} \left[ I(I+1) - \frac{1}{3} \right] A^4 + \frac{2}{5} S(S+1) A^2 \sum \lambda^4 \right\}. \quad (5.32)$$

The exchange forces do not enter into $M_2$, but they do increase $M_4$. We can conclude from this that the exchange interactions shift the absorption from the center of the spectrum to its edges. This redistribution
of the intensities of the different parts of the spectrum can occur in two ways: 1) the intervals between the hyperfine components are decreased and the absorption is increased on the curves of the entire spectrum; 2) the intervals between the hyperfine components remain unchanged, but each line becomes narrower at the center and broader at the skirts. It was shown by the method of random functions that the first possibility is realized.

8. In most cases it is possible to calculate only the second moment of the absorption line, while calculations of the higher moments are exceedingly difficult. The information obtained on the paramagnetic resonance line shape by the moment method is therefore inadequate. Anderson and Weiss [30] proposed to use the method of random functions so as to obtain more detailed information on the absorption line shapes, particularly the exchange narrowing of these lines. This idea was developed in the papers by Anderson [31], Kubo and Tomita [32], and others. Since we are unable to describe in detail the results of all these investigations, we shall stop to discuss only the principal idea and the most important applications.

The narrowing down of the resonance line under the influence of the exchange forces can be visualized as being the consequence of frequency modulation of the precessional motion of the individual magnetic dipoles. How frequency modulation acts on the width of a resonance line is best understood from the following example, which was analyzed in [33, 31]. Let us consider an oscillator which is subjected to random collisions. Let the average time interval between two collisions be \( \tau \). We assume that the oscillator has two different natural frequencies, \( v_1 \) and \( v_2 \). Assume that after each collision the oscillator changes its frequency, going over from \( v_1 \) to \( v_2 \) and back. If the oscillator "suffers from complete lack of memory" and its state prior
to collision does not influence at all the subsequent motion, then the form function is

\[ g(v) = \frac{1}{2} \left( \frac{1}{2\pi} \right)^2 \left( \frac{1}{(v - v_0)^2 + \frac{1}{(2\pi)^2}} \right) \]

(5.33a)

A more complicated form function is obtained in the case of "good memory." If only the oscillator frequency changes after the collision, while its position and velocity are conserved, then

\[ g(v) = \frac{2}{\pi} \frac{v_m^2}{(v - v_c)^2 + v_m^2 + (v - v_0)^2 \left( \frac{1}{e^{v^2} - 2v_m^2} \right)} \]

where

\[ v_c = \frac{1}{2} (v_1 + v_2), \quad v_m = \frac{1}{2} (v_1 - v_2). \]

(5.33b)

In the case of (5.33a), the intensity under resonant conditions is proportional to \( \tau \), and consequently both resonant lines spread out with decreasing \( \tau \), and finally, when \( \tau \ll 1/2\pi v_m \) they merge into one broad line with resonant frequency \( v_c \). In the case (5.33b), if \( v = v_c \), the intensity is proportional to \( 1/\tau \), and therefore both resonant peaks merge at sufficiently small values of \( \tau \) into one line, which becomes narrower with decreasing \( \tau \). An illustration of the foregoing is seen in Fig. 5.1.

In a paramagnetic crystal the precession frequency of the magnetic moment is \( v_0 + v' \), where \( v_0 \) is determined by the externally applied static magnetic field, and \( v' \) is determined by the internal local fields. It can be assumed that the frequencies \( v' \) have a Gaussian distribution. We denote the mean value of \( (v')^2 \) by \( v_p^2 \). Owing to exchange interactions, the neighboring particles will exchange frequencies, in the mean, after time intervals \( 1/v_1 \approx h/J_{1k} \). If we concentrate our attention on one particle only, we see that its precession frequency will be constantly subject to random variations. If \( v_1 \gg v_p \),
Fig. 5.1. Reduction in the width of the oscillator form function with decreasing collision time $\tau$. It is assumed that the oscillator has alternately the frequencies $v_1$ and $v_2$, and retains its previous velocity and position after each collision. The curves have been drawn for different values of $\tau$. 1) $\tau = 10^{-10}$ sec; 2) $\tau = 0.5 \cdot 10^{-10}$ sec; 3) $\tau = 10^{-11}$ sec; 4) $\tau = 0.5 \cdot 10^{-11}$ sec. A) (in relative units).

This frequency modulation can appreciably narrow down the resonant absorption line. Calculation shows that the form function of the line can be written as

$$g(v) = \frac{1}{2\pi} Re \int_{-\infty}^{\infty} \exp[-2\pi i (v - v_0)t - \nu^2 u] \, dt,$$  

(5.34)

where

$$u = \int_0^t (t - t') \exp(-\pi^2 \nu^2 u') \, dt'.$$  

(5.34a)

The frequencies $v_0$ and $\nu_1$ can be determined from the following equations:
\[ v^2 = M \cdot 3v^2 + \frac{1}{2} \pi v^2 \eta = M \cdot \frac{8.45}{3} \frac{(J_h)^3}{S(S+1)}. \]  

For a simple cubic lattice we have

\[ v^2 = \frac{8.45}{3} \left( \frac{J_h}{k} \right)^3 S(S+1). \]  

Inasmuch as \( v_1 \gg v_p \), it follows from (5.34a) that

\[ u = \frac{1}{2} t^2, \text{ if } v - v_0 \gg v_1, \]

\[ u = \frac{t}{v_1}, \text{ if } v - v_0 \ll v_1. \]

Substituting in (5.34), we obtain in the former case

\[ g(v) = \frac{1}{\sqrt{2\pi} v} e^{-\frac{(v-v_0)^2}{2v_p^2}}, \]  

and in the latter case

\[ g(v) = \frac{1}{\pi} \frac{v_1}{\sqrt{v_1}} e^{-\frac{v}{v_1} + \frac{v}{v_1}}. \]

Thus, in the case of strong exchange interactions, the absorption line, being Lorentzian at the center, assumes on its skirts a Gaussian form, thus ensuring that its second and higher moments are finite. In place of the formula \( \Delta v = 2.35v_p \) (see (1.21)), which is valid in the case of pure dipole interactions, we now have

\[ \Delta v = 2.35v_1. \]

It must be noted that if the exchange energy is very large, so that \( v_1 \gg v_0 \), then the value of \( \Delta v \) given by this formula should be multiplied by \( 10/3 \). The reason for it is that the cutoff of the Hamiltonian carried out in the calculation of (5.13) is no longer justified here, for the energy difference between two neighboring Zeeman levels \( h\nu_0 \) can be strongly modified by the exchange energy. Consequently, the alternating magnetic field of frequency \( v = v_0 \) can give rise not only to transitions \( \Delta M = \pm 1 \), but also transitions such as \( \Delta M = 0, \pm 2, \pm 3 \). Thus, in equating \( v_p^2 \) to the second moment of the ab-
sorption curve, one must recognize that the principal resonance line coalesces with its satellites. Consequently,

\[ \nu_0 = \bar{M}_t = \frac{10}{3} M_t. \]

If the resonant frequency \( \nu_0 \) is increased enough to make \( \nu_0 >> \nu_1 \), observation of the satellites becomes possible and the factor 10/3 in the formula for the width of the principal line must be discarded.

§5.3. Spin-Lattice Interactions

Before we start to consider the results of the spin-lattice interaction theory in different types of ionic paramagnetic crystals, let us dwell on some general problems.

1. Let us consider some pair of spin-system energy levels \( E_k \) and \( E_\perp \) \((E_k > E_\perp)\), the population of which is assumed to be \( N_k \) and \( N_\perp \). We denote by \( A_{kl} \) the per-second probability of transition of the spin system from the level \( E_k \) to the level \( E_\perp \) under the influence of the lattice vibrations. The condition for statistical equilibrium is the equation

\[ N_k A_{kl} = N_\perp A_{lk}. \]

If a Boltzmann distribution can be assumed, it follows that

\[ A_{lk} = A_{kl} e^{-(E_k - E_\perp)/kT}. \] (5.38)

We see that \( A_{kl} > A_{lk} \). This circumstance plays an important role in paramagnetic resonance. Let the oscillating magnetic field of resonant frequency give rise to transitions between the levels \( E_k \) and \( E_\perp \); the probability of such transitions per second will be denoted by \( p_{kl} \) (see formulas (1.3) and (1.4)). Under stationary conditions we have

\[ N_k (\sum_{j} A_{kj} + p_{kl}) = \sum_{j} N_j A_{jk} + N_\perp p_{lk}. \] (5.39)

We can assume with great degree of accuracy that \( p_{kl} = p_{lk} \). If in addition \( A_{kl} = A_{lk} \), then \( N_k = N_\perp \) and no paramagnetic resonance is possible.
sible. The difference $A_{kl} - A_{1k}$ decreases with increasing temperature of the paramagnet, and consequently the resonant paramagnetic absorption decreases.

We have seen in §5.1 that under certain conditions the paramagnetic resonance line width is determined by the spin-lattice paramagnetic relaxation time $\tau$. If the energy levels $E_k$ and the transition probabilities $A_{kl}$ are known, then this time can be calculated by means of the following formula [34]:

$$\tau = \frac{\sum_{E_k} (E_k - E_1)^n}{\eta \sum_{E_k} A_{kl} (E_k - E_1)^n} \quad (5.40)$$

where $\eta$ is the number of all possible states of the spin system. Formula (5.40) has been derived under the assumption that $|E_1 - E_k| \ll kT$ is valid for all $1$ and $k$. It follows from (5.40) that if we choose as the "spin system" a single particle with spin $S = 1/2$, then $\tau = A_{kl}/2$.

Paramagnetic resonance makes it possible to determine the transition probabilities $A_{1k}$ by the saturation method. Experiments of this type are made to determine the saturation factors $q_{1k} = n_{1k}/n_{1k}^0$ (compare with §1.3), where $n_{1k}^0$ is the difference in the populations of the energy levels $E_1$ and $E_k$, if the paramagnet is in thermodynamic equilibrium state, and $n_{1k}$ is the same quantity under saturation conditions. The saturation factors $q_{1k}$ can be readily expressed in terms of the transition probabilities $A_{1k}$ and $p_{1k}$, by setting up equations of the type (5.39) for each spin level of the paramagnetic particle. If all the intervals between these levels are different, and the resonance is observed as a result of transitions between the levels $E_1$ and $E_2$ under the influence of a radio frequency field, then it is easy to show [35] that

$$q_n = (1 + q_x^0)^{-1}. \quad (5.41)$$
where the quantity $W_R$, which Lloyd and Pake call the relaxation probability, is equal to

$$W_R = A_{11} + \frac{1}{C_{2k}} \sum_{k \neq 1} A_{1k} C_{2k}$$

(5.41a)

Here $C_{2k}$ is the cofactor of the elements of the second row and the second column of the following matrix:

$$
\begin{pmatrix}
A_{11} - \sum_{k=3}^{n} A_{1k} & A_{12}, A_{13}, \ldots, A_{1n} \\
A_{12} - \sum_{k=3}^{n} A_{2k} & - \sum_{k=3}^{n} A_{12}, A_{13}, \ldots, A_{1n} \\
\vdots & \vdots & \ddots & \ddots \\
A_{1m} + A_{1m} & A_{1m}, A_{1m}, \ldots, A_{1m} \\
A_{1n} + A_{1n} & A_{1n}, A_{1n}, \ldots, A_{1n} \\
\end{pmatrix}
$$

(5.41b)

The experimental conditions are frequency adjusted in such a way as to make $q_{12} = 1/2$. It is directly evident from (5.41) that in this case $W_R = p_{12}$.

2. For reasons stated in §5.1, the theory of spin-lattice relaxation usually deals not with the entire spin system but with an individual particle interacting with the lattice vibrations. The calculation of the transition probabilities $A_{1k}$ between the energy levels of an individual magnetic particle as a result of energy exchange with the lattice is made by the perturbation method. In the unperturbed state, the system considered by us consists of two noninteracting parts: a paramagnetic ion and an aggregate of oscillators, which represent the elastic vibrations of the crystal. From among all the interactions between the paramagnetic ion and the surrounding particles, we are interested in those that depend on the magnitude of its magnetic moment. Under the influence of the lattice vibrations, the magnitude of these interactions will vary. This variable part of the energy of
the bond between the paramagnetic ion and its surrounding does indeed yield the spin-lattice interaction operator $H'$. We can then use the perturbation theory developed in the theory of radiation [36].

Energy exchange between the paramagnetic ion and the lattice vibrations under the influence of the perturbation $H'$ can occur in different ways, of which the most important are the direct (single-phonon) processes and processes of combination scattering of phonons (two-phonon). We denote the difference in the energies of any two states of the paramagnetic ion by $E_{lk}$. A direct process consists in an increase (or decrease) of the ion energy by an amount $E_{lk}$ due to the vanishing (or occurrence) of one quantum of elastic lattice vibrations (one phonon). Of all the lattice oscillators, the only ones that can participate in such processes are those whose frequency $v$ satisfies the condition

$$E_{lk} = hv.$$  \hspace{1cm} (5.42)

The probability that the paramagnetic ion will go over as a result of the direct processes from level $E_\perp$ to level $E_k$ is

$$
\mathcal{A}_{\perp k} = \frac{\rho_v}{h \rho_v} |\mathcal{X}_{\perp k}|^2.
$$  \hspace{1cm} (5.43)

Here $\rho_v$ is the spectral density of the oscillators with frequency $v$, and $H'_{lk}$ is the matrix element of the spin lattice interaction, averaged over the different states of the oscillators that satisfy condition (5.42). Frequently the matrix element $H'_{lk}$ relating the energy levels $E_\perp$ and $E_k$ turns out to be zero in first approximation. Higher approximations are then used and $H'_{lk}$ is calculated through the intermediate state of the paramagnetic particles.

Combination scattering of phonons is a process consisting of an increase (or a decrease) in the ion energy by an amount $E_{lk}$, owing to the vanishing of an elastic-oscillation quantum of frequency $v$ and the
occurrence of a quantum of frequency $v'$; in this case, obviously, the following condition should be satisfied:

$$E_{1k} = h\nu - h\nu'.$$

(5.44)

For the probability of transition under the influence of combination phonon scattering processes we have

$$A_{ll'} = \frac{4\pi^2}{\hbar^2} \int |\tilde{\kappa}_{ll'}|^2 \rho_{l'} dv'.

(5.45)$$

It is seen from (5.44) and (5.45) that elastic lattice vibrations of all frequencies participate in combination phonon scattering processes. Therefore, in spite of the fact that the combination scattering of phonons is a second-order process, it does play a principal role in the relaxation mechanism if the temperature of the paramagnet is relatively high. At low temperatures, the principal role is assumed by the direct processes.

We denote the quantity $A^{(1)}_{lk}$, averaged over different values of $l$ and $k$, by $A_1$, while the averaged value of $A^{(2)}_{lk}$ is denoted $A_2$. From (5.43) and (5.45) we obtain, if we assume that $E_{1k} \ll kT$,

$$A_1 = K_1 \rho \frac{kT}{\hbar v}, \quad A_2 = K_2 \rho \frac{J_n}{\hbar v}.

(5.46)$$

Here $\rho$ is the crystal density, $T$ is the temperature, $v$ the average velocity of sound, while $K_1$ and $K_2$ are quantities that depend on the nature of the relaxation mechanism and on the energy level structure of the magnetic particles, and consequently also on the applied magnetic field $H_0$. By $J_n$ we denote

$$J_n = \int_{\theta}^{\hbar v} \frac{x \exp \frac{\hbar v}{kT}}{[\exp \frac{\hbar v}{kT} - 1]^2} \, dx,$

(5.47)

where $\theta$ is the Debye temperature. This integral can be calculated from the following approximate formulas [37]:

$$J_n = n! \left( \frac{nkT}{\hbar v} \right)^{n+1} (T < \theta),

(5.48)$$

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\[ J_n = \left( \frac{\hbar}{\Lambda} \right)^{n+1} \left[ \frac{1}{(n+1)(\varepsilon^2 \gamma - 1)^\frac{1}{2}} + \frac{1}{(n+1)(n+2)} \frac{1}{\varepsilon^2 \gamma - 1} + \ldots \right] (T \sim \theta), \]  
(5.49)

\[ J_n = \frac{1}{n-1} \left( \frac{\hbar}{\Lambda} \right)^{n+1} \theta^{n-1} \gamma^n (T > \theta), \]  
(5.50)

The value of \( n \) is usually 6 or 8. Therefore the relatively weak temperature dependence of the relaxation time when \( T \gg \theta \) becomes very strong when \( T \ll \theta \).

3. In the first theory of paramagnetic spin-lattice relaxation, presented by Waller [8], it was assumed that the reorientation of the atomic spin relative to the external magnetic field \( H_0 \) under the influence of the lattice vibrations is the result of a change in the magnetic interaction of the spins, brought about by these oscillations. Waller's calculations lead, however, to values of the relaxation time which are several orders of magnitude larger than the experimental data. A particularly sharp discrepancy between theory and experiment was observed in titanium-cesium alums. Kronig [38] and Van Vleck [37] therefore proposed a different relaxation mechanism. In many cases, however, as was shown by Al'tshuler [39], Waller's mechanism can play a principal role.

Waller's calculations were made for a paramagnet whose magnetic particles have a spin \( S = 1/2 \). Yet the probability of the particle spin reorientation under the influence of oscillations of the magnetic forces acting on it is proportional to the fourth power of the magnetic moment of the particle. In addition, this probability is inversely proportional to \( R^6 \), if \( R \) stands for the equilibrium distance between two neighboring crystal atoms having magnetic moments. Frequently several such atoms are contained in a single crystalline cell.
It is easy to see that in this case a more exact result will be obtained if \( R \) is defined not as the average distance between neighboring particles with magnetic moments, but the shortest one. It is clear therefore that the magnetic forces can determine the spin-lattice interaction in substances with large atomic magnetic moments and with large magnetic particle density. Calculations have shown that

\[
K_i = \frac{4\pi^2 Z}{3k} \left( \frac{g_\mu_B}{R} \right)^3 S(2S+1)(S+1)^6. \tag{5.51}
\]

\[
K_i = \frac{8\pi^2 Z}{3} \left( \frac{g_\mu_B}{R} \right)^3 S(2S+1)(S+1)^6, \quad n = 6. \tag{5.52}
\]

Here \( Z \) is the number of nearest neighbors of the particle. It should be noted that Waller considered the relaxation due to the spin reorientation of one particle under the influence of the lattice vibrations under the condition that the other spins conserve their directions. Yet, as can be seen from (5.10), the matrix elements of the spin-lattice perturbation differ from zero even in the case of simultaneous reorientation of the spins of two neighboring particles. For this case it follows from the calculations that

\[
K_i = -\frac{16\pi^2 Z}{3k} \left( \frac{g_\mu_B}{R} \right)^3 (2S+1)^6(S+1)^4, \quad n = 6. \tag{5.53}
\]

\[
K_i = 3,16\pi^2 Z \left( \frac{g_\mu_B}{R} \right)^3 (2S+1)^6(S+1)^4, \quad n = 6. \tag{5.54}
\]

We see that simultaneous reorientations of the spins of two interacting particles is much more probable than the change in spin orientation of one particle alone.

In substances with large magnetic ion density, exchange forces assume appreciable values. The energy of the exchange interactions has for the most part the isotropic form \( A_{12}(r)\vec{S}_1\cdot\vec{S}_2 \); it is an integral of the motion, and consequently the exchange forces cannot cause, in first approximation, a transfer of energy from the spins to the lattice vibrations. On the other hand, if the exchange forces are anisotropic, the magnitude of the spin-lattice interactions which they pro-
duce has the same order as in the case of magnetic dipole forces.

4. In order to explain why the spin-lattice interaction is very large in titanium-cesium alums, Kronig [38] proposed the following relaxation mechanism. The elastic vibrations of the lattice modulate the electric field of the crystal, and this causes a change in the orbital motion of the magnetic-ion electrons. The action influences the electron spin through the orbital magnetic moment. This mechanism of spin-lattice interaction is the principal one for the majority of salts in the iron-group elements, in spite of the fact that the orbital motion is "frozen" in these salts. Calculations have shown that

\[
K_1 = \left( \frac{\lambda}{A} \right)^n \left( \frac{r_0}{\alpha} \right)^4 \left( \frac{eH_0}{\alpha} \right)^4, \quad K_2 = h^4 \left( \frac{\lambda}{A} \right)^n \left( \frac{r_0}{\alpha} \right)^4 \left( \frac{e'}{\alpha} \right)^4, \quad n = \infty
\]

(5.55)

Here \( \Delta \) is the interval between two lower orbital sublevels, arising in the electric field of the crystal, \( r_0 \) is the average distance from the 3d electron to the nucleus, \( \alpha \) is the equilibrium distance from the center of the magnetic particle to the nearest diamagnetic ion, and \( e' \) is the effective charge of this ion. The factor \( (\lambda/\Delta)^2 \) appears in (5.55) because changes in the crystalline electric field cannot produce directly a reorientation of the electron spin, and acts through the orbital momentum. Since the orbital motion is "frozen," the matrix element of the spin-lattice interaction differs from zero in the higher approximations of perturbation theory.

It is therefore clear that in ionic crystals containing the iron group elements the probabilities of relaxation transitions will always be inversely proportional to a high power of the interval \( \Delta \). It is known from experiment that the spin-lattice relaxation times at the same temperature can differ by several orders of magnitude for different elements. This is explained principally by the fact that the in-
interval $\Delta$ can change on going from one ion to another from about $10^2$ to about $10^4$ cm$^{-1}$. In particular, for the titanium ion (see §4.2) we have $\Delta \approx 500$ cm$^{-1}$.

An analogous but more complete theory of spin-lattice relaxation was developed by Van Vleck [37] independently of Kronig. He considered in addition to titanium salts also salts containing Cr$^{3+}$. Unlike the titanium ion, the simple orbital levels of which are Kramers doublets, in the chromium ion we have $S = 3/2$, and consequently the simple orbital level breaks up into two closely located Kramers doublets, the interval between which will be denoted by $\delta$. The expressions for $\tau$ obtained by Van Vleck are very cumbersome. The principal difference between them and (5.55) lies in the following. In the case of the direct processes $(g\beta H_0)^4$ is replaced by $\lambda^2 \sqrt{4g^4 \beta^4 H_0^4 + c_1 c_2 \beta^2 H_0^2 + c_2 \beta^2}$, where $c_1$ and $c_2$ are certain numbers on the order of unity. In the expression for $K_2$ we have $\lambda^2 J_6$ in place of $h^2 J_8$.

Bashkirov [40] calculated the spin-lattice relaxation time for copper salts, the electric fields of which have tetragonal symmetry. The copper ion Cu$^{2+}$, like the ion Ti$^{3+}$, has $S = 1/2$. However, unlike the titanium salts, the matrix element of the spin-orbit interaction, which relates the lowest orbital states, is in this case equal to zero. Therefore in place of one interval $\Delta$, the formula for the relaxation time contains two intervals, $\Delta_0$ and $\Delta$, where $\Delta_0$ is the splitting in the field produced by the octahedron of the water molecules surrounding the Cu$^{2+}$ ion, and $\Delta$ is the interval between the lowest orbital sublevels, arising in the field of tetragonal symmetry. In formulas (5.55) it is necessary to replace $\Delta^{-6}$ by $\Delta_0^{-2} \Delta^{-4}$.

The following singularities were observed experimentally in many copper salts: 1) the spin-lattice relaxation time at room temperature depends strongly on the angle $\phi$ between the field $H_0$ and the tetragonal symmetry.
axis of the crystal [41]; 2) the paramagnetic resonance spectrum in 
CuSO₄·5H₂O can be explained by assuming the constant λ to have appreci- 
ciable anisotropy [42]. If the constant λ is replaced by a tensor with 
principal values λ∥, λ⊥, then in formula (5.55) λ² must be re-
placed by 1/2[λ∥² sin² 0 + λ⊥² (1 + cos² 0)]. If we take for λ∥ and λ⊥ 
the values assumed in [42], we obtain good agreement with the measure-
ments of [41].

It follows from Kramers' theorem that the spectra of ions with an 
even number of electrons should have many singularities. Avvakumov
[43] undertook detailed theoretical calculations of the spin-lattice 
interaction for crystals with such ions (V³⁺, Cr²⁺, Mn³⁺, Fe²⁺, Ni²⁺).

In the case of Ni²⁺, as in the case of the Cr³⁺ investigated by Van 
Vleck, the lower orbital level is simple under the action of a field 
of cubic symmetry. Therefore the interval is Δ ≈ 10⁴ cm⁻¹ and the re-
laxation time is relatively large. In the other ions considered by Av-
vakumov, the lower orbital level is degenerate under the action of a 
cubic field, and therefore Δ denotes the interval between sublevels 
produced in a weak field of low symmetry. Because of this, the relaxa-
tion time of salts containing these ions turned out to be relatively 
short and observation of paramagnetic resonance is impossible at room 
temperatures.

If the relaxation is due to the combination phonon scattering 
processes, then the temperature dependence of τ is determined by the 
integral Jₙ, in which n = 6 for the Cr²⁺, Mn³⁺, and Ni²⁺ ions and n = 8 
for the Fe²⁺ and V³⁺ ions. Calculations have disclosed a strong de-
pendence of the relaxation time on the value of the spin S; at low tem-
peratures τ ~ S⁻¹² and at high temperatures τ ~ S⁻⁸. A noticeable de-
pendence of the relaxation time on the angle between the field H₀ and 
the axes of the crystal was established also for all ions, except Ni²⁺.
As to the dependence of \( \tau \) on the magnitude of the field \( H_0 \), this dependence becomes noticeable if \( g_\beta H_0 > \delta \).

5. A special analysis is necessary for ions in the S state. Al'tshuler [39], using the salts of trivalent iron as an example, considered relaxation due to the direct processes. Bashkirov [44] made detailed calculations of the relaxation which is due also to second-order processes for the ions \( Mn^{2+}, Fe^{3+}, Eu^{2+} \), and \( Gd^{3+} \). If we denote by \( \delta \) the magnitude of the total splitting of the spin levels by the crystalline field, then the results of the calculations will essentially reduce to the following:

\[
K_1 = \frac{\nu}{\delta} (g\beta H_0)^n, \quad K_0 = \nu, \quad n = 6.
\] (5.56)

Comparison of these formulas with (5.52) and (5.53) shows that Waller's mechanism can play the principal role when

\[
\delta < \frac{\epsilon_{12}}{R} (2S + 1)(S + 1).
\] (5.57)

This is apparently the case with manganese salts, for which the splitting \( \delta \) is relatively small.

6. The theory of spin-lattice relaxation for salts of the rare earth elements was given by Al'tshuler [45] with the cerium ion as an example; it was assumed there that the crystalline field consists of two parts, a strong field of cubic symmetry and a weak field of lower symmetry. Shekun [46] made a theoretical analysis of relaxation in ethyl sulfates of different rare earth elements. We recall that the crystalline field in ethyl sulfates has trigonal symmetry.

In rare earth compounds, the lattice vibrations, by changing the crystalline field, can directly change the direction of the moment of the paramagnetic ion, for in this case the coupling between the spin and orbital momenta is stronger than the action of the electric field of the crystal. One therefore obtains for \( K_1 \) and \( K_2 \) expressions of the
type (5.55), but without the factor \((\lambda/\Delta)^2\). Since the interval \(\Delta\) is relatively small for rare earth ions, on the order of 10-100 cm\(^{-1}\), the spin-lattice interaction turns out to be very strong, in spite of the fact that \(r_0\) for 4f electrons is somewhat smaller than for the valence electrons of the iron group. In ions with an odd number of f electrons, the spin-lattice interaction due to the direct processes turns out to be particularly large if a non-Kramers degeneracy of the ground level exists. In this case we have

\[
K_i = \frac{1}{\hbar^2} \left( \frac{\hbar}{\epsilon} \right)^{1/2} \left( 2 \frac{\hbar}{\epsilon} \right)^{1/2} (g\beta H_0)^i.
\]

(5.58)

Here the matrix element of the spin-lattice interaction differs from zero even in the first approximation of perturbation theory.

7. Great interest is attached to an explanation of how the spin-lattice interaction is changed if the concentration of the paramagnetic particles is decreased by isomorphically replacing them with diamagnetic ions. This question was considered theoretically by Kochelayev [112].

It would seem at first glance that relaxation due to the Kronig-Van Vleck mechanism should not depend on the concentration of the paramagnetic particles, since the forces bringing about the spin-lattice coupling are determined by the relative displacement of the paramagnetic ion and the diamagnetic atoms surrounding it. Actually, however, an appreciable role can be played by the following circumstance: practically any specimen contains crystal-lattice imperfections, on which the plane Debye waves are scattered.

Under the influence of the standing plane Debye wave, two neighboring atoms oscillate with amplitudes whose difference is proportional to the frequency \(v\) of the elastic oscillations. Since the probability of the relaxation transition is proportional to the square of the rela-
tive displacement of the paramagnetic ion and of the neighboring diamagnetic particle, we find in the case of direct processes, in accord with (5.45), that $A_1 \sim E_{kl}^2$. After the Debye wave is scattered by the randomly located paramagnetic center, a spherical wave is produced around this center, with an intensity that increases rapidly, of course, as it propagates. Consequently, two neighboring atoms located at distances $r_1$ and $r_2$ from the scattering center will oscillate with amplitudes whose difference is proportional to $(1/r_1 - 1/r_2)$. In spite of the fact that the intensity of the scattered waves is much smaller than the intensity of the plane Debye waves, simple calculation shows that over a wide range of paramagnetic particle concentrations and at reasonable values of the defect concentrations, the relaxation due to the scattered spherical waves plays the principal role if the amplitude of the scattered wave is independent of the frequency. Besides, whereas in accordance with the ordinary spin-lattice relaxation theory we have $A_1 \sim E_{kl}^n$, now, by virtue of the fact that the relative displacement of the neighboring particles is independent of the frequency $v$, the relaxation probability will be $A_1 \sim E_{kl}^{1-n}$. As we have seen above, in many cases $n = 2$, and consequently the dependence of the probability of relaxation transitions between spin levels $E_k$ and $E_1$ on the magnitude of the interval $E_{kl}$ should disappear. When the number of defects in the crystal is small and when the crystal is strongly diluted by diamagnetic ions, the Kronig-Van Vleck relaxation mechanism will again predominate.

According to the views developed here, the spin-lattice interaction should also be appreciably influenced by such crystal lattice imperfections, whose dimensions are comparable with the length of the incident wave.

The theory developed here is applicable in the case of low tem-
Fig. 5.2. Scheme showing the transfer of energy to the lattice vibrations in the case of strong exchange interactions. 1) Zee- mans; 2) exchange; 3) lattice.

peratures, when the relaxation is due to single-phonon processes. At high temperatures, when the relaxation is determined by two-phonon processes, the principal role is assumed by the phonons with high frequencies \( v \), and consequently the spin-lattice interaction due to the waves scattered by the imperfections ceases to predominate.

8. Akhiezer and Pomeranchuk [47] have considered the question of paramagnetic relaxation at super low frequencies by the method of elementary excitations. They have proposed that the paramagnet is a nonconducting crystal containing ions with an odd number of electrons. The spin system of the paramagnetic crystal has a spectrum whose form is determined by the crystalline electric field and by the magnetic and exchange interactions between the individual lattice ions. Deviations from the ground state of the spin system, a state which occurs when \( T = 0 \), are regarded as an assembly of elementary excitations, which, as in the case of the Bloch model of the ferromagnet, propagate over the entire crystal. Each elementary excitation represents a quasiparticle which can be assigned a definite energy and a certain quasimomentum. The calculations were made under the assumption that the quasiparticles obey the Fermi-Dirac statistics. Because of the interaction between the elementary excitations and the lattice vibrations, energy is exchanged between the spin system and the lattice. By calculating the probabilities of the collisions of the quasiparticles among themselves and with the phonons, one determines the amount of heat \( Q \) which is transferred per unit time from the lattice to the spin system. It was found that \( Q = \text{const} \frac{T^6}{T_1^6} q(T_6/T_1) \), where the function \( q(T_6/T_1) \) is inversely pro-
portional to \((T_s/T_J)^6\) when \(T_s \ll T_J\) and proportional to \(1 - T_s/T_J\) when \(T_s \approx T_J\). If initially \(T_s >T_J\) and \(T_s \sim 10^{-10}\)K, then, as shown by calculation, the time after which \(T_J\) and \(T_s\) differ by 1% does not exceed 1 second.

9. If the exchange interactions are very large (anhydrous paramagnetic salts, free radicals, ferrites), then it is necessary, as shown by Blombergen and Wein [48], to divide the spin system into two parts, a Zeeman part and an exchange part.

The scheme whereby energy is transferred from the Z system to the lattice is shown in Fig. 5.2. Each of the three subsystems can be assigned a certain temperature. Let us denote the temperature of the Z system by \(T_Z\), the temperature of the Ex system by \(T_e\), and the lattice temperature as before by \(T_1\). The possibility of introducing separate concepts of Zeeman and exchange temperatures is connected with the fact that the operators of Zeeman energy \((5.6)\) and exchange energy \((5.8)\) commute. Therefore changes in the Zeeman energy can occur without affecting the exchange energy. The transfer of energy from the Z system to the Ex system is possible because of the existence of relatively weak magnetic dipole interactions which do not commute with \(H_\text{zeem}\) and \(H_\text{obm}\).

It can be assumed that direct transfer of energy from the Z system to the lattice has low probability and consequently the relaxation time \(\tau_{zl}\) is large compared with the times \(\tau_{ze}\) and \(\tau_{el}\). Let us denote by \(\alpha_{ze}\) and \(\alpha_{el}\) the corresponding heat conduction coefficients, and by \(C_Z\) and \(C_e\) the specific heats of the Z and Ex systems. To explain the experimental data it becomes necessary to assume that \(\alpha_{ze} < \alpha_{el}\) and \(C_Z \ll C_e\).

Inasmuch as the relaxation time is determined by the ratio of the specific heat to the corresponding heat conduction coefficient, it
turns out that $\tau_{ze} < \tau_{el}$. Therefore $\tau_{ze}$ plays the role of the spin-lattice relaxation time for ordinary paramagnetics. It is remarkable that the independence of $\tau_{ze}$ of the lattice temperature is confirmed in experiments on saturation. Under stationary conditions the amount of heat transferred from the Z system to the Ex system is equal to the heat flowing from the Ex system to the lattice, i.e., $a_{ze}(T_z - T_e) = a_{el}(T_e - T_l)$. It follows therefore that $T_e$ is much closer to $T_l$ than to $T_z$.

§5.4. Longitudinal Relaxation at Low Temperatures

1. It follows from the theory of spin-lattice relaxation due to single-phonon processes (§5.3) that the relaxation time $\tau$, which is inversely proportional to the temperature $T$, decreases with increasing applied field $H_0$ and is generally speaking independent of the concentration of the paramagnetic centers and of the crystal dimensions. Yet many experiments [49-53] have established facts that are in direct contradiction with all these theoretical conclusions. Moreover, it was observed that in place of one time it becomes necessary sometimes to introduce a whole set of relaxation times. In spite of all these contradictions, there are no grounds for doubting the correctness of the theoretical choice of the mechanism of spin-lattice interaction. At least in some cases, these singularities of the relaxation occurring at helium temperatures can be explained as follows.

In the analysis of relaxation processes it is always assumed that the lattice vibrations can be regarded as a thermostat in which the spin system is embedded. The specific heat of the spin system was always considered to be small compared with the specific heat of the lattice. Yet if the temperature of the spin system is higher than that of the lattice, then establishment of equilibrium with the aid of single-phonon processes will occur by exciting oscillations in a narrow fre-
quency band, satisfying approximately the condition (5.44). The specific heat of these low-frequency lattice oscillators, which are in direct contact with the spin system, is low. The speed with which the energy acquired by these "effective" oscillators is transferred either to the oscillators of other frequencies or to the helium thermostat surrounding the crystal is therefore important. Let us denote the temperature of the spin system by $T_s$, the temperature of the "effective" oscillators by $T_Z$, and the thermostat temperature by $T_0$. If the energy transferred to the "effective" oscillators is drawn away sufficiently rapidly so that the relation $T_s - T_Z \gg T_Z - T_0$ holds true for the temperature differences, then the bottleneck in the chain linking the spin system with the thermostat will be the contact between the spin system and the lattice, and consequently the longitudinal relaxation time $T_1$ will be equal to the time $\tau$. If on the other hand the stationary processes of striking the balance between the spin system and the thermostat is such that $T_s - T_Z \ll T_Z - T_0$, then along with the spin-lattice relaxation time $\tau$ it is necessary to introduce a time characterizing the exchange of energy between the "effective" oscillators and the helium thermostat (or with the oscillators of other frequencies). We shall denote this time $T_1$, since it will now determine the longitudinal relaxation, inasmuch as $T_1 \gg \tau$.

2. For what is to follow, it is necessary to calculate the number $N_f$ of "effective" oscillators per unit volume. Were the energy spectrum of the spins and lattice oscillators a discrete one, then the number of oscillators participating in the energy exchange between the spins and the lattice would be infinitesimally small. Actually, however, owing to the spin-spin interactions on the one hand, and the finite lifetime of the oscillators in the excited state on the other, the energy levels become broadened. We shall see that the most appre-
ciable broadening occurs in the vibrational levels. We denote by $2\Delta v_L$ the frequency interval of the oscillators that interact strongly with distance. In accordance with the usual law governing the distribution of the frequencies of elastic lattice vibrations, we can assume that

$$N_f = \frac{12\pi^3}{a^3} (2\Delta v_L). \quad (5.59)$$

The value of $\Delta v_L$ can be estimated in the following fashion. We assume for simplicity that the effective spin of the paramagnetic particles is 1/2. Then, according to (5.40), the probability per unit time $A_1$ of transition between the spin energy levels under the influence of the lattice vibrations is connected with the time $\tau$ by the relation $A_1 = \frac{1}{2} \tau^{-1}$. Each of the $N_0$ spins contained per unit volume can exchange one phonon with each of the $N_f$ oscillators within a time $2\tau$. Therefore the oscillator vibrations will be interrupted in the mean after time intervals

$$\Delta t = \frac{2N_f}{N_0} \tau.$$

Since $\Delta v_L = \frac{1}{2\pi} \Delta t$, it follows from (5.59) that

$$\Delta v_L = \left( \frac{N_0 \omega}{2\pi N_f} \right)^{\frac{1}{4}}. \quad (5.60)$$

By way of an example let us assume that $N_0 = 10^{14}$ cm$^{-3}$, $v = 2 \cdot 10^5$ cm/sec, and $\nu = 10^{10}$ cps, and $2\tau = 10^{-5}$ sec; then $\Delta v_L = 4 \cdot 10^8$ cps, which is much larger than the frequency interval $4N_0\beta^2/\hbar$, connected with the spin-spin interactions. The number of "effective" oscillators in our example is, in accord with (5.59), $N_f = 5 \cdot 10^{14}$ cm$^{-3}$. We see that there are approximately $10^4$ spins for each effective oscillator.

It is clear that the specific heat of the "effective" oscillators is negligible compared with that of the spin system. Therefore, if $T_1 \gg \tau$, then the establishment of the thermal equilibrium between the spin system and the aggregate of the effective oscillators will consist of hav-
ing the "effective" oscillators assume the spin temperature, $T_z \rightarrow T_s$.

It can be shown that in this case the "effective" oscillators are directly coupled to the spin system.

We note that the formulas obtained are valid if $kT_s << h\nu$. On the other hand, if $kT_s >> h\nu$, then it is necessary to introduce in place of $N_0$ the difference in the populations of two neighboring spin levels, i.e.,

$$\frac{N_0 kT_s}{2h\nu}.$$

3. What is the mechanism determining the longitudinal relaxation if $T_1 > \tau$? Equilibrium between the spin system and a helium thermostat can be established in various ways. Frelikh and Heitler [54] have shown that the heat conductivity of the spin system is very small. Therefore direct transfer of energy from the spin system to the thermostat is of low effectiveness. This can be readily understood by recognizing that the rate of propagation of the spin-system excitations (magnons) in substances that do not have too high a concentration of paramagnetic centers is much smaller than the velocity of sound: $v >> \frac{\beta^2}{h\nu^2}$ (see §5.1).

Two possible mechanisms remain: a) the transfer of the energy of the "effective" oscillators to all other lattice vibrations; b) direct transfer of energy from the "effective" oscillations to the helium thermostat. Van Vleck [55] considered mechanism a), and took the anharmonicity of the lattice vibrations into account. Let $dQ/dt$ be the quantity of heat transferred per second from the "effective" oscillators to the remaining lattice vibrations. Then

$$\frac{dQ}{dt} = b(T_x - T_0) \quad (5.61)$$

where $b$ is the heat conduction coefficient, equal to

$$b = \frac{(3\nu')^2}{\nu'^2}(\frac{18}{A} - \frac{15\nu'}{A'}) + 2\left(\frac{5}{A} - \frac{3\nu'}{A'}\right). \quad (5.62)$$

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If we denote by $\Delta V$ the change in the volume $V$ of the crystal under the influence of the pressure $p$, then the mean of the coefficients $A$ and $B$ becomes clear from the following formula:

$$\frac{\Delta V}{V} = Ap - Bp^2.$$  \hspace{1cm} (5.62a)

For potassium chrome alums [56] $A = 6.3 \cdot 10^{-12}$ cm$^2$/dyn and $B = 1.08 \times 10^{-22}$ cm$^4$/dyn$^2$. If we return to the numerical example considered in this section and assume furthermore that the specimen is in the form of a sphere of radius $R$, we obtain with the aid of (5.62) $b \approx 2 \cdot 10^{-4} \times R^3$ w/deg.

In order to estimate the effectiveness of mechanism b), let us assume first that the elastic waves are not perturbed at all, with the exception of interaction with the spin system and the walls of the crystal [57]. The case which we are considering is most favorable for the penetration of heat from the thermostat inside the specimen. Let us imagine a spherical cavity in which the elastic waves striking the wall have a temperature $T_Z$ and the waves radiated by the wall have a temperature $T_0$. If $u(T)$ denotes the energy density of the "effective" oscillations at temperature $T$, then each unit surface of the wall will absorb per second an energy $vu(T_Z)/4$ and radiate an energy $vu(T_0)/4$. If the difference $T_Z - T_0$ is small, then

$$u(T_z) - u(T_0) = N_f k (T_z - T_0),$$

and consequently the heat transferred per second by the "effective" oscillations to the helium thermostat is $a(T_z - T_0)$, where the heat conduction coefficient is

$$a = \pi R^4 N_f k v.$$  \hspace{1cm} (5.63)

Substituting the previous values of $N_f$ and $v$ we obtain $a \approx 4 \cdot 10^{-3} R^2$ w/deg.

The longitudinal relaxation time $T_1$ can be defined as the ratio
of the specific heat of the spin system $C_S$ to the heat conduction coefficient of the channel coupling the spin system with the thermostat.

If we take both mechanisms a) and b) into account, we obtain

$$T_i = C_s \left( \frac{1}{a} + \frac{1}{b} \right).$$

(5.64)

If $S' = 1/2$, then [34]

$$C_s = \frac{N_v^2 K_{av}^2}{kT_s^2}. \quad (5.65)$$

In the example which we have considered a/b $>> 1$ and consequently mechanism a) is much more effective than b). In this case we obtain with the aid of (5.63)-(5.65)

$$T_i = \left( \frac{1}{2} N_v \nu \right)^{\frac{1}{4}} \left( \frac{A}{kT_s} \right)^{\frac{1}{4}} \nu R. \quad (5.66)$$

If $kT_s << \hbar \nu$, then obviously

$$T_i = \left( \frac{1}{2} N_v \nu \right)^{\frac{1}{4}} \left( \frac{A}{kT_s} \right)^{\frac{1}{4}} \nu \frac{1}{2} R. \quad (5.66a)$$

Substituting again the previous values of the quantities used in our example, we obtain $T_1 \approx 10^{-2}$ sec.

If the mean free path of the "effective" phonons is small compared with the linear dimensions of the crystal, then the mechanism which we have described for the transfer of energy from the effective oscillations to the thermostat will be disturbed by diffusion processes. The mean free path of the phonon, the path of which is interrupted by collision with a magnon, is of the order of $\nu \tau$. Therefore, if $R >> \nu \tau$, the phonon diffusion processes begin to play a predominant role in the transfer of energy from the spin system to the thermostat. An estimate of the longitudinal relaxation time made for this case [58] has shown that for $\hbar \nu << kT_s$ its approximate value is

$$T_i = \frac{R^n N_v K_{av}}{18 \pi^4 (kT_s)^3}. \quad (5.67)$$

We note that in this case one cannot, strictly speaking, define a sin-
gle relaxation time. The temperature of the spin system and of the aggregate of "effective" oscillators will vary from the center of the crystal toward its boundary. As a result, a certain distribution of the relaxation times is produced.

The formulas which we have obtained for the longitudinal relaxation time apparently permit an explanation of the experimental facts concerning the character of the dependence of $T_1$ on the concentration $N_0$ of the paramagnetic centers, on the temperature $T_S$, on the dimensions $R$ of the crystal, and on the intensity of the applied field $H_0$ (of frequency $v$).

Longitudinal relaxation at low temperatures has not been sufficiently well investigated experimentally. The discussion that arose in an examination of this question [59, 60] in connection with the development of paramagnetic amplifiers (see Chapter 8) has thus far not led to any definite results (see §5.9).

§5.5. Experimental Data on Ionic Crystals

1. Line width in solid paramagnets

Various types of interactions in paramagnets are experimentally investigated either by determining the width and the shapes of the paramagnetic resonance lines, or with the aid of a method that makes use of the saturation of these lines. In addition, information on the spin-spin and spin-lattice relaxation times is obtained by measuring parametric absorption and the dispersion of susceptibility on superposition of a static field and a high frequency magnetic field parallel to it.

By line width $\Delta H$ we mean the distance in oersteds between the points on the $\chi''(H_0)$ curve at which $\chi''$ has a value equal to half the maximum. In some papers the width is defined differently, as the distance in oersteds between the points of inflection of the $\chi''(H_0)$ curve.

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Such a definition is convenient when the result of the measurements is the differential curve $d\chi''/dH(H_0)$. We shall designate this width $\delta H$. For curves of Lorentzian shape $\Delta H = 1.73 \delta H$ and for Gaussian curves $\Delta H = 1.26 \delta H$. We note that at measurements at low frequencies it becomes necessary to use the definition of a "right half-width," i.e., the distance in oersteds between the point corresponding to the position of the absorption maximum and the point where $\chi'' = \chi''_{\text{max}}/2$, which lies in the region of $H_0$ above the maximum. The "right half-width" will be designated $\Delta H_{\text{pr}}$.

In addition to measuring $\chi''(H_0)$, the width of resonance lines is also estimated by measuring the dependences of $\chi'$ and $d\chi'/dH$ on the field intensity $H_0$. In the latter case the difference between the Lorentzian and Gaussian line shapes can be readily established by determining the ratio of the values of $d\chi'/dH$ at the maximum and at the minima of the $d\chi'/dH(H_0)$ curve. The values of this ratio are 8:1 and 3.5:1 for Lorentzian and Gaussian shapes, respectively [61].

Measurement of the values of $\Delta H$ (or $\delta H$) gives much less accurate results than a determination of the positions of the lines in the spectrum. The inaccuracy of the resultant line shape and width, which is inherent to some degree or another in all the methods used to determine paramagnetic resonance, is due principally to the impossibility of separating completely the various effects due to the real and imaginary parts of the high-frequency susceptibility.

We shall discuss first data pertaining to pure paramagnetic salts, not diluted by the corresponding diamagnetic ions. The line widths in these salts range from several tens to thousands of oersteds. The lines become sometimes utterly unobservable. If we exclude the case of ions with even number of electrons (in which paramagnetic resonance cannot occur because of the smallness of the quantum of the radio fre-
frequency field as compared with the initial splitting of the spin sub-
levels), then the absence of the effect can be due only to excessively
strong spin-lattice interactions. A sufficient reduction in tempera-
ture decreases these interactions and makes the effect observable. In
general the narrowing down of the lines upon cooling is the most con-
vincing proof that the spin-lattice interactions determine the line
width.

Another way of elucidating the nature of the observed width is to
study the dependence of \( \Delta H \) on the frequency of the absorbed radiation.
In the case when the width increases appreciably with increasing fre-
quency, it is natural to attribute this increase to the influence of
the anisotropy of the \( g \) factor; in this case the measurements aimed at
determining the true relaxation line width should be carried out at
the lowest frequencies. Of course, the influence of the anisotropy
manifests itself most strongly in investigations of polycrystalline
specimens; it is not excluded, however, from single crystals, since in
most cases a unit cell contains several nonequivalent magnetic ions.

One of the most important methods of investigating the internal
interactions in paramagnets is to analyze the absorption line shape.
So far, however, this study has been carried out principally by cal-
culating the second and fourth moments of the experimental \( \chi''(H) \) curves
and comparing the results obtained with the Van Vleck line-width theory
[10]. That this theory has limited applicability to the greater part
of real crystals was already noted earlier.

Some typical results of measurements of absorption line width and
shape in undiluted paramagnetic salts of \( \text{Mn}^{2+} \) are listed in Table 5.1
[62].

From an examination of the data in this table we can conclude the
following:
1) In magnetically concentrated salts, the line widths are considerably smaller than would be expected if only magnetic dipole interactions were taken into account; the line shape is Lorentzian or close to it. It follows therefore that in such salts considerable exchange interactions take place.

2) In salts with smaller magnetic ion concentration (for example, in Tutton's salts of Mn$^{2+}$ and Cu$^{2+}$ or in chrome alums), the line shape is close to Gaussian, and the width deviates little from dipole width; thus, the role of exchange is no longer large.

TABLE 5.1

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\langle \frac{1}{2} \frac{1}{2} \rangle_{\text{theor}}$</th>
<th>$\langle \frac{3}{2} \frac{3}{2} \rangle_{\text{theor}}$</th>
<th>$\frac{\langle \Delta H \rangle^2}{\langle \Delta H \rangle}$</th>
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<td>1.23</td>
</tr>
<tr>
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</tr>
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<tr>
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<td>1246</td>
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<td>1.31</td>
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<td>7020</td>
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</tr>
<tr>
<td>MnS</td>
<td>780</td>
<td>7520</td>
<td>1.40</td>
</tr>
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</table>

1) substance; 2) eksp; 3) teor; 4) oersted; 5) crystalline.

It must be noted, however, that a study of the dependence of the exchange interaction on the average distances between magnetic particles in highly concentrated paramagnets is possible only by comparison of substances that have crystal lattices of the same type; otherwise it is easy to arrive at erroneous conclusions, for at high magnetic concentrations it is meaningless to operate with average ionic distances without taking into account the specific nature of concrete lattices. In particular, it was shown by Kashayev [63], for example, that the absorption line in CuF$_2$·2H$_2$O is considerably narrower.
than in CuF$_2$, in spite of the fact that the average distances between the Cu$^{2+}$ are smaller than in the former salts, and consequently the exchange narrowing of the lines in the latter salts should have been more manifest in the CuF$_2$. The point is that according to crystallographic data the distance between the nearest Cu$^{2+}$ ions in CuF$_2$ is larger than in CuF$_2$·2H$_2$O.

From among the substances with strong exchange interactions, let us stop to discuss CrCl$_3$, polycrystalline specimens of which were investigated many times under various conditions. The form of the absorption line is shown in Fig. 1.2. The value of $\Delta H$ was determined in the frequency interval between $10^{10}$ and $10^7$ cps and was found to be constant and equal to $140 \pm 5$ oersteds [64] within the limits of measurement accuracy (if it is determined at low frequencies by multiplying the "right-hand half-width" by two). Temperature changes in the interval from 290 to 77 K do not affect $\Delta H$. The value of $\Delta H$, calculated following Van Vleck from only the magnetic dipole interactions, is much larger than the observed value and amounts to 1000 oersted. The ratio $\Delta H/\delta H$ corresponds to a Lorentzian form.

A good example of a Gaussian form is the line observed by Bleaney [65], corresponding to the transition $^1S_2 \rightarrow ^3S_2$ in the spectrum of cesium chrome alum CrCs(SO$_4$)$_2$·12H$_2$O with the crystal optical axis oriented along the field. The width of this line is $\Delta H = 280$ oersted, and is shown in Fig. 5.3. The experimental data are marked on the figure by the points, and the curve is drawn to obey a Gaussian law, with a mean square width $\sigma_H = 118$ oersted. This last quantity was calculated by Bleaney after Van Vleck with account of the presence of nonequivalent Cr$^{3+}$ ions in the crystal cell. The good agreement with experiment leads to the conclusion that the role of exchange interactions is small in cesium chrome alum.
Sometimes the line corresponds to neither Lorentzian nor Gaussian shape. In particular, an intermediate form was obtained by Japanese investigators [66] for MnSO$_4$·4H$_2$O and MnSO$_4$·5H$_2$O. Deviations from the form expected by the Van Vleck theory have been observed by MacLean and Kor [67] in organic salts of Mn$^{2+}$.

We shall now stop to discuss the measurements of $\Delta H$ in dilute salts, in which some of the magnetic ions are replaced by diamagnetic ones. From the point of view of spectroscopy, such salts are of great interest. It is necessary to note here first of all that the narrowing down of the lines resulting from the reduction in the magnetic dipole interactions between the ions is observed down to sufficiently small relative concentrations of the magnetic ions ($f \leq 0.01$). If the residual line, which is independent of the further dilution, is not connected with the spin-lattice relaxation, it is usually due to magnetic dipole interactions with the moment of the near-lying atomic nuclei, particularly with the moment of the protons of the water in hydrated salts. Therefore in spectroscopic investigations the H$_2$O is frequently replaced by heavy water D$_2$O, which leads to a certain narrowing down of the line as the result of the smaller magnetic moment of D. During the initial stages of dilution (for $f > 0.1$) the absorption lines are weakly narrowed down, and sometimes they may even broaden a little, as was noted in [63]. The reason for this is that the exchange interactions decrease with increasing distance more rapidly than the magnetic dipole interactions. Examples of experimentally determined width in dilute paramagnetic salts are
1) Substance; 2) dilution; 3) half width; 4) conditions of experiment; 5) state of substance; 6) literature; 7) monocrystalline; 8) \( H_0 \) parallel to the optical axis of the crystal; 9) \( H_0 \) perpendicular to the optical axis of the crystal.

Information on the spin-spin interactions in paramagnets in the absence of constant fields \( H_0 \) can be obtained from absolute measurements of the absorption coefficient at \( H_0 = 0 \). Measurements of this type were made for several salts by Gorter [34] and later by Rivkind [70]. The values of \( \tau'(0) \) obtained by the latter at 10 megacycles are listed in Table 5.3.

**Table 5.2**

<table>
<thead>
<tr>
<th>1 Вещество</th>
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<td>Равве-</td>
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<td>Условия опыта</td>
<td>Литера-</td>
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<td>дение</td>
<td>ширина</td>
<td>( T, ^\circ C )</td>
<td>тур</td>
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<td>(Mn(^{2+}), Zn(^{2+})) S</td>
<td>( 10^{-4} )</td>
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<tr>
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<td>5.5±0.5</td>
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2. Spin-lattice relaxation in solid paramagnets

Investigations of spin-lattice relaxation were started by Gorter [34] even before the discovery of paramagnetic resonance, in the 1930's. His method consisted of measuring the dependence of the coefficients \( \chi' \) and \( \chi'' \) on the intensity of a static magnetic field \( H_\parallel \), situated parallel to an oscillating magnetic field of constant frequency \( v \). The frequency that Gorter used in his experiments was on the order of \( 10^6 \) - \( 10^7 \) cps. A phenomenological theory of spin-lattice relaxation in parallel fields was proposed by Casimir and du Pre [71] for the case \( \tau >> \tau' \).
The phenomenological theory of relaxation phenomena in parallel fields was further developed by Shaposhnikov [4], who took into account the role of the spin-spin interactions in the general relaxation effect. A summary of the experimental values of $\tau$ obtained up to 1947 by Gor- ter and his co-workers is contained in his book [34]. Later measurements of $\tau$ by the method of parallel fields can be found in [72-74, 41] and elsewhere. We shall note here only the principal results, without stopping to describe the experiments.

Measurements at temperatures from 300 to $64^\circ K$ were made in hydrated salts of the iron-group ions and in salts of Gd$^{3+}$. The longest spin-lattice relaxation times were found in salts of Mn$^{2+}$, Gd$^{3+}$ and Cr$^{3+}$; they have an order of $10^{-7}$-$10^{-8}$ sec at room temperatures. Very short values of $\tau$, which are observed for example in salts of Co$^{2+}$ or particularly in salts of Ti$^{3+}$ could not be measured by the parallel-field method in the indicated temperature interval, since the condition $\tau > \tau'$ is not satisfied there.

A small number of salts of Mn$^{2+}$, Fe$^{3+}$, Ud$^{3+}$, Cr$^{3+}$, and Co$^{2+}$ and of a few other ions were investigated in the region of helium temperatures. Their relaxation times are on the order of $10^{-2}$-$10^{-4}$ sec.

We shall consider first the region of high temperatures, where combination processes predominate.

In this region, the dependence of $\tau$ on $H_0$ is well described by a formula proposed by Brons [75], which was theoretically confirmed in a paper by Van Vleck [37]:

$$\tau = \frac{C + m}{T^2 + p}$$

(5.68)

Here $b = C \cdot m^2$ is the constant of magnetic specific heat, $C$ is the Curie constant, $\tau_0$ is the spin-lattice relaxation time at $H_0 \to 0$; $p =$
= \tau_0/\tau_\infty$, where $\tau_\infty$ is the same time when $H_0 \rightarrow \infty$. According to Van Vleck $p < 1$, and therefore the value of $\tau$ should increase with increasing field intensity $H_\parallel$ and tend in the limit to $\tau_\infty$. The temperature dependence is contained essentially in the factor $\tau_0 \sim T^{-2}$ with $T > \theta$. Experiment shows, however, that the value of $p$ sometimes varies with the temperature. The experimental data obtained for the temperature range from 300 to $640^\circ$K agree qualitatively in most cases with the theoretical predictions; the value of $\tau$ calculated by Van Vleck for chrome alums agrees with the experimental values also in order of magnitude. Nonetheless one cannot speak of strict agreement between theory and the experimental data. The main reason for the discrepancies is apparently the fact that the measurements of the spin-lattice relaxation time in parallel fields is possible only if $\tau \gg \tau'$ whereas in Van Vleck's theory the spin-spin interactions are taken into account only very approximately.

Another reason that leads in individual cases to major qualitative disagreements with the theory may be the phase transitions in the paramagnet occurring as the temperature of the experiment is varied. In particular, this may explain the reduction in $\tau$ on cooling, observed by Garif'yanov [76] in iron-ammonia alum, in which the phase transition point lies according to his measurements near $200^\circ$K.

A similar behavior is exhibited by potassium chrome alum (phase transition point near $900^\circ$K) and also by gadolinium sulfate [34].

Tables 5.4 and 5.4a contain certain data pertaining to the values of $\tau$ in the high temperature region ($77-300^\circ$K), obtained by the parallel-field method.

In the region of helium temperatures, where the direct processes should predominate, Van Vleck's theory agrees much worse with experiment. In particular, for the direct processes the theory requires that
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<th>90 K</th>
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<td>0.98</td>
<td>1</td>
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<td></td>
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<tr>
<td>3200</td>
<td>2</td>
<td>2.25</td>
<td>2.25</td>
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</tr>
<tr>
<td>&gt;4000</td>
<td>3.6</td>
<td>3.8</td>
<td>3.8</td>
<td></td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

* - Стабильность при комнатной температуре.
<table>
<thead>
<tr>
<th>Substance</th>
<th>800</th>
<th>1600</th>
<th>2400</th>
<th>3200</th>
<th>4000</th>
<th>5000</th>
<th>6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdCl₄·4H₂O</td>
<td>5,1</td>
<td>0,33</td>
<td>0,59</td>
<td>0,64</td>
<td>0,69</td>
<td>0,64</td>
<td>0,72</td>
</tr>
<tr>
<td>MnCl₂·4H₂O</td>
<td>4,9</td>
<td>1,41</td>
<td>1,51</td>
<td>1,56</td>
<td>1,58</td>
<td>1,6</td>
<td>1,73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>2400</th>
<th>2800</th>
<th>3200</th>
<th>3600</th>
<th>4000</th>
<th>4400</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl₂·4H₂O</td>
<td>1,2</td>
<td>1,94</td>
<td>2,12</td>
<td>2,2</td>
<td>2,4</td>
<td></td>
</tr>
<tr>
<td>Mn(NO₃)₂·6H₂O</td>
<td>0,1</td>
<td>0,3</td>
<td>0,35</td>
<td>0,37</td>
<td>0,38</td>
<td>0,39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>4000</th>
<th>4400</th>
<th>4800</th>
<th>5200</th>
<th>5600</th>
<th>6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSO₄·4H₂O</td>
<td>5,2</td>
<td>3,2</td>
<td>6,2</td>
<td>7,3</td>
<td>8,4</td>
<td>9,5</td>
</tr>
<tr>
<td>Mn(NH₄)₂(SO₄)₆·6H₂O</td>
<td>0,64</td>
<td>5,5</td>
<td>0,40</td>
<td>0,93</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

1) Substance; 2) oersted; 3) sec; 4) other temperatures, °K (in parentheses); 5) literature; 6) at low temperatures.
TABLE 5.4a (Conclusion)

<table>
<thead>
<tr>
<th>Вещество</th>
<th>$H_{10}$</th>
<th>$B_{10}$</th>
<th>$T^*$</th>
<th>$T$</th>
<th>$20^0$</th>
<th>Литера-рура</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>мат.</td>
<td>арт.</td>
<td>K</td>
<td>K</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuK$_2$(SO$_4$)$_3$·6H$_2$O</td>
<td>0,12</td>
<td>0,06</td>
<td>0,8</td>
<td>0,26</td>
<td>0,03</td>
<td>0,03</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O</td>
<td>0,15</td>
<td>0,54</td>
<td>0,01</td>
<td>0,01</td>
<td>0,01</td>
<td>0,01</td>
</tr>
</tbody>
</table>

Remark. $K_1$, $K_2$, and $K_3$ are the principal magnetic axes of the crystal, see §4.1.

1) Substance; 2) oersted; 3) sec; 4) literature; 5) powder; 6) at low temperatures; 7) at $T = 290^0$K.

$\tau$ be proportional to $H_0^{-2}$ and $T^{-1}$; in addition, naturally, there should be no observed dependence of $\tau$ on the magnetic concentration $N_0$. Yet, according to [77], experience shows in concentrated salts a stronger dependence on the temperature than $T^{-1}$, and the dependence on $H_0$ can be expressed up to rather strong fields by means of $\tau \sim (b + CH_0^2)$. Finally, an increase in $\tau$ is observed in most cases upon dilution $\tau(\tau \sim N_0^{-1})$. Moreover, for concentrated salts the Casimir and du Pre formula itself is not in good agreement with the experimental results. They can be described satisfactorily only with the aid of an entire set of values of $\tau$. However, when the magnetic dilution of the specimens increases, the deviations from the Casimir and du Pre formula de-
crease. The dependence of $\tau$ on the concentration also becomes weaker, and at sufficient degrees of dilution the relaxation time becomes constant.

The dependence $\tau(H_0)$ has a complicated form in dilute specimens. At small values of $H_0$ the relaxation time increases with the field but reaches rapidly a maximum (corresponding to several hundred oersted), after which $\tau$ becomes approximately proportional to $H_0^{-1}$. Thus, in dilute paramagnets the deviation from the theory turns out to be somewhat smaller, but is nevertheless not completely eliminated.

### Table 5.5
Spin-Lattice Relaxation at Low Temperatures [72]

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\tau$, °C</th>
<th>$H_{11}$, $\text{sec}^{-1}$</th>
<th>$2\tau$, 104, $\text{sec}$</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCr(SO$_4$)$_2$·12H$_2$O</td>
<td>20,4</td>
<td>4000</td>
<td>0,21</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>14,3</td>
<td>4000</td>
<td>0,31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20,4</td>
<td>800</td>
<td>0,0054</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1600</td>
<td>0,0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2400</td>
<td>0,0074</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3200</td>
<td>0,009</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4000</td>
<td>0,012</td>
<td></td>
</tr>
<tr>
<td>Gd$_3$(SO$_4$)$_2$·8H$_2$O</td>
<td>20,4</td>
<td>670</td>
<td>1,37</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1120</td>
<td>1,52</td>
<td></td>
</tr>
<tr>
<td>MnSO$_4$·4H$_2$O</td>
<td>20,5</td>
<td>670</td>
<td>2,56</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>18,4</td>
<td>670</td>
<td>2,56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1120</td>
<td>2,82</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1685</td>
<td>3,30</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>2250</td>
<td>3,90</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>3370</td>
<td>4,90</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>4030</td>
<td>5,12</td>
<td></td>
</tr>
<tr>
<td>Mn(NH$_4$)$_2$(SO$_4$)$_2$·X$\times$H$_2$O</td>
<td>20,3</td>
<td>670</td>
<td>9,3</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>14,3</td>
<td>670</td>
<td>10,5</td>
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<td></td>
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<td>1120</td>
<td>12,5</td>
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<td></td>
<td></td>
<td>1685</td>
<td>14,5</td>
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<td>2250</td>
<td>16,2</td>
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<td>3370</td>
<td>18,2</td>
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<td>4030</td>
<td>19,0</td>
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<tr>
<td></td>
<td>20,3</td>
<td>0</td>
<td>1,06</td>
<td>6</td>
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<td></td>
<td>14,3</td>
<td>$-\infty$</td>
<td>2,47</td>
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<td>4,21</td>
<td>$-\infty$</td>
<td>5,66</td>
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<tr>
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<td>13,6</td>
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<td>$-\infty$</td>
<td>19,3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-\infty$</td>
<td>117</td>
<td></td>
</tr>
</tbody>
</table>

1) Substance; 2) oersted; 3) sec; 4) method; 5) absorption in parallel fields. Dispersion of susceptibility in parallel fields; 6) absorption and dispersion in parallel fields; 7) the same.
<table>
<thead>
<tr>
<th>Table 5.5a</th>
<th>Average Spin-Lattice Relaxation Times at Low Temperatures [72]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Substance</td>
</tr>
<tr>
<td>2</td>
<td>a</td>
</tr>
<tr>
<td>4 Образец А</td>
<td>KCr(SO$_4$)•12H$_2$O</td>
</tr>
<tr>
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<td></td>
<td>4 Образец В</td>
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<tr>
<td></td>
<td>K$_2$Cu(SO$_4$)•6H$_2$O</td>
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<tr>
<td></td>
<td>Cu(NH$_3$)$_2$(SO$_4$)•6H$_2$O</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe(NH$_3$)$_2$(SO$_4$)•12H$_2$O</td>
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</tbody>
</table>

Remark. In order to calculate these data, which were obtained by measuring $X'(H_0)$ and $X''(H_0)$ in parallel fields $H$, the factors $(1 + \tau_0^2\omega^2)^{-1}$ and $(1 + \tau_2\omega^2)^{-1}$ in the Casimir and du Pre formulas have been replaced by $\int \frac{g(\tau)}{1 + \tau^2\omega^2} d\tau$ and $\int \frac{g(\tau)}{1 + \tau_2\omega^2} d\tau$, with $g(\tau) d\tau = 1$. $\bar{\tau}$ denotes the mean value of $\tau$ in the continuous distribution $g(\tau)$; $\tau_1/2$ denotes the value of $\tau$ given by the relation $g(\tau_1/2) = g(\tau)/2$; the ratio $\tau_1/2/\bar{\tau}$ characterizes the width of the distribution of the relaxation times.

1) Substance; 2) oersted; 3) sec; 4) sample.
Tables 5.5 and 5.5a list some data obtained by Gorter and his co-workers [72] in measurements of paramagnetic relaxation in the region of helium temperatures.

Along with the method of parallel fields, the relaxation time has been measured in recent years by the method of saturation of the paramagnetic resonance line. In this case it is possible to use in principle much greater magnetic dilutions. In addition, the saturation method makes it possible to determine the relaxation constants for individual resonance transitions, whereas the method of parallel fields gives only summary quantities. On the other hand, the saturation method is not free of shortcomings; it is very difficult to use it for the determination of the dependence $\tau(H_0)$ since this calls for measurements over a wide range of frequencies; to study short relaxation times it is necessary to use an oscillating field of very large power; finally, the experiments themselves are much more difficult to set up than in the method of parallel fields.

The first relaxation measurements by the saturation method were made in 1949 by Schlichter and Purcell [78] in undilute salts of Mn$^{2+}$ and Cu$^{2+}$ at room temperature and at the temperature of dry ice. The sample was placed in a resonant cavity used to terminate one of the arms of a T-bridge. To generate the strong microwave magnetic field (with an approximate amplitude of 30 oersteds) needed to saturate the broad absorption lines, a pulse magnetron was used. In view of the transient effects connected with short pulses, the ordinary bridge technique was somewhat modified. The relaxation times $T_1$ for Mn(NH$_4$)$_2$(SO$_4$)$_2$$\cdot$6H$_2$O, the sulfate of Mn$^{2+}$, and the sulfate of Cu$^{2+}$ were found to be on the order of $10^{-8}$ sec.

Schneider and England [79] measured $T_2$ in a specimen of ZnS with a small content of Mn$^{2+}$ at 90°K. Since the absorption lines were nar-
row, experiments on the saturation were carried out with an ordinary klystron as a source of microwave field. The measurements were made at the temperature of liquid air and have led to values of the spin-lattice relaxation time close to those observed by Gorter in undiluted salts of Mn$^{2+}$.

Eschenfelder and Weidner [80] carried out saturation experiments in single crystals of dilute potassium chrome alum and iron ammonia alum at 2.4$^0$K. The measurements were made by the reflection method using a T bridge. The source of the microwave field was a klystron with 1 watt output power. A toroidal sample of the substance was placed in a cylindrical cavity coupled to a waveguide. To ensure thermal insulation, part of the waveguide was made of glass coated with a thin layer of silver.

The spin-lattice relaxation time was determined with the aid of the formula

$$\frac{Q_M}{Q_L} = B \frac{r}{g(v)} + A\Gamma T_1P_i(1-\Gamma)^2.$$

Here $Q_M$ and $Q_L$ are the Q factors of the cavity with and without magnetic losses, $B$ is a certain constant,

$$A = \frac{4(2S+1)\lambda}{N(2S+1)\Gamma_0},$$

$\Gamma$ is the reflection coefficient at the resonant value of the field $H = H_{rez}$, $\Gamma_0$ the same quantity at $H >> H_{rez}$, $P_i$ is the incident power, and

$$\frac{Q_M}{Q_L} = \frac{(1-\Gamma)}{(1-\Gamma_0)}.$$

From the experimental dependence $\Gamma(p_i)$ it is possible to determine the spin-lattice relaxation time $T_1 = 1/2W$, where $W$ is the probability of the relaxation transitions. It is most convenient to do this by plotting the quantity $Q_M/Q_L$ as a function of $p_i(1-\Gamma)^2$; the slope
of the resultant line makes it possible to determine \(T_1\) independently of \(g(\nu)\).

The basic results obtained for \(\text{KCr(SO}_4)_2 \cdot 12\text{H}_2\text{O}\) and \(\text{Fe(NH}_4\text{(SO}_4)_2 \cdot 12\text{H}_2\text{O}\) are shown in Fig. 5.4. On the right side of this figure are indicated, for both salts, the corresponding resonant transitions, the magnetic dilutions, and the crystal orientations. It is seen from the figure that, in accordance with the theory, the time \(T_1\) is inversely proportional to the absolute temperature. The magnetic dilution investigated in iron-ammonia alums lengthens the time \(T_1\) by only a very small amount.

Bloembergen and Wang [48] continued the experiments of Slichter and Purcell on the study of the spin-lattice relaxation time in substances with broad absorption lines, using pulse techniques. Their setup made it possible to obtain in the resonant cavity a microwave magnetic field with a pulsed amplitude up to 50 oersted. The following relation, which is derivable from Bloch's formula (5.1), holds true under paramagnetic resonance conditions:

\[
\frac{M_x}{M_0} = \frac{\chi''}{\chi_0} = \frac{1}{1 + \frac{1}{4} \frac{t^2}{\gamma H_1 T_1}}.
\]

Here \(\chi''\) and \(\chi_0\) are the absorption coefficients for the given amplitude \(H_1\) and when \(H_1 \to 0\), i.e., in the absence of saturation. If the value of \(\gamma\) and the width of the resonance line are known, then the time \(T_1\) can be determined either by measuring \(\chi''/\chi_0\) or by measuring \(M_x/M_0\) at different amplitudes \(H_1\). Measurements carried out by both methods in \(\text{MnSO}_4 \cdot 4\text{H}_2\text{O}\) have shown good agreement with Gorter's data, as can be seen from Table 5.6.
There is no doubt that extensive use of the saturation method will add in the very near future to the far from sufficient experimental data on the spin-lattice relaxation times in crystalline paramagnets.

An appreciable step forward toward the study of relaxation at low temperatures was made in a recent work by Giordmaine, Alsop, Nash, and Townes [58]. These authors measured the relaxation times in $\text{Gd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$; $\text{K}_3\text{Cr(CN)}_6$ and $\text{Cu(NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ at temperatures 1-4°K. Two methods were used: 1) the ordinary method of paramagnetic resonance line saturation, and 2) saturation of the lines by strong microwave pulses with subsequent measurement of the rate of reestablishment of equilibrium by observing the absorption of a weak microwave signal as a function of the time elapsed after the cessation of the strong pulse causing the saturation. This observation was made with the aid of a synchronized frequency sweep of the vicinity of paramagnetic resonance by means of two different klystrons. The pulses were usually repeated at a rate considerably smaller than the relaxation rate. The time between the saturation and the instant of measurement of the absorption can be readily varied by changing the difference in the frequencies radiated by the strong and weak generator or by changing the sweep rate. The relaxation times determined with the aid of both methods turned out to be close to one another, with the excep-
tion of the copper salt. The obtained values of $T_1$ together with the data on the line width are presented in Table 5.7.

For the Gd$^{3+}$ salts, the observed width is connected with hyperfine interactions, and the times $T_1$ vary as functions of the studied transition by approximately two times. They depend also somewhat on the specimen chosen, on the concentration of the Gd$^{3+}$ ion, and on the temperature.

### Table 5.7

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Вещество (концентрация &lt;1:100 ат. %) и переход</td>
<td>Диамагнитный разбавитель</td>
<td>$\Delta H$, ое (ширина на половину максимальной интенсивности)</td>
<td>$T_1$ из времени экспоненциального спада, сс</td>
<td>$T_1$ из насыщения, сс</td>
</tr>
<tr>
<td>Gd,Mg(NO$_3$)$_3$·24H$_2$O</td>
<td>La</td>
<td>20</td>
<td>7·10$^{-4}$</td>
<td>15·10$^{-4}$</td>
</tr>
<tr>
<td>$M\left(-\frac{1}{2}\right)$—$M\left(\frac{1}{2}\right)$</td>
<td>K$_2$Cr(CN)$_6$</td>
<td>Co</td>
<td>12</td>
<td>3·10$^{-4}$</td>
</tr>
<tr>
<td>Cu(NH$_3$)$_4$SO$_4$·6H$_2$O</td>
<td>Zn</td>
<td>20</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>$M\left(-\frac{1}{2}\right)$—$M\left(\frac{1}{2}\right)$</td>
<td>$m\left(\frac{3}{2}\right)$—$m\left(\frac{3}{2}\right)$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Substance (concentration <1:100 atomic %); and transition; 2) diamagnetic diluent; 3) $\Delta H$, oersted (width at half the maximum intensity); 4) $T_1$ determined from the time of exponential decrease, sec; 5) $T_1$ determined from saturation, sec.

§5.6. Solutions of Paramagnetic Salts. Theory

1. Until now, calculations of the line shape of paramagnetic resonance in liquids have been made with the aid of the correlation theory. The use of the correlation method is quite natural, since it permits the simplest evaluation of the effect of Brownian motion of the particles on the width of the absorption lines. We shall describe briefly this method and its application to calculations of the broadening of resonance lines.
Let \( F(t) \) be a certain random function of the time, the mean value of which is denoted \( \langle F(t) \rangle \). Let us assume that \( \langle F(t) \rangle = 0 \). The correlation function, as is well known [81], is defined as
\[
K(\tau) = \langle F(t) F(t + \tau) \rangle. \tag{5.69}
\]
Let us introduce the Fourier transform \( I(\nu) \) of the correlation function defined in the following fashion:
\[
K(\tau) = \int_{-\infty}^{\infty} I(\nu) e^{-2\pi \nu \tau} d\nu, \quad I(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} K(\tau) e^{-2\pi \nu \tau} d\tau. \tag{5.70}
\]

The correlation function obviously decreases with increasing \( \tau \). For most cases considered below, it can be proved that the decrease in the correlation function with time obeys the Markov law:
\[
K(\tau) = \langle |F(t)|^2 \rangle e^{-\frac{\tau}{\tau_c}}, \tag{5.71}
\]
where \( \tau_c \) is a certain parameter called the correlation time. Substituting (5.71) in (5.70) we obtain
\[
I(\nu) = \frac{1}{2\pi} \left( \frac{2\nu}{1 + 4\pi^2 \nu^2 \tau_c^2} \right). \tag{5.72}
\]

Assume that we have a quantum system with energy levels \( E_\perp \), subject to the action of time-varying random perturbations \( \hat{A}'(t) \). The matrix element of the perturbation \( \hat{A}_{lk}'(t) \) will be a random function of the time. Using the ordinary theory of time-dependent perturbations we can readily show that the probability of the transition of a quantum system from the state \( E_\perp \) to the state \( E_k \) under the influence of the perturbation \( \hat{A}'(t) \) per second is
\[
A_{\perp k} = \frac{4\hbar^3}{\pi} I(\nu_0). \tag{5.73}
\]

With the aid of (5.72) we obtain alternately
\[
A_{\perp k} = \frac{2\hbar}{\nu_0} \langle \hat{A}_{\perp k}'(t) \rangle \frac{2\nu_c}{1 + 4\pi^2 \nu_c^2 \hbar^2}. \tag{5.74}
\]
For further calculations it is necessary to clarify the nature of the relaxation mechanism, or in other words, the origin of the perturbation \( \hat{H}'(t) \).

2. The first theory of paramagnetic resonance line shape in liquids was proposed by Bloembergen, Pound, and Purcell [82]. To be sure, this paper dealt specifically with nuclear resonance, but its results can be directly applied to liquid electronic paramagnets. In the theory of Bloembergen et al, as was done by Waller in the case of crystals, it is assumed that the relaxation is due to magnetic interactions of the particles. Consequently, the perturbation \( \hat{H}'(t) \) can be expressed with the aid of (5.9), assuming that \( r, \varphi, \) and \( \varphi \) are time-varying as a result of Brownian motion. Let us assume that all the Zeeman levels of the magnetic particles are equidistant, so that there is only one Larmor precession frequency \( \nu_0 \). If we calculate the nondiagonal matrix elements \( \hat{H}'(t) \), carry out the necessary averaging, and then substitute the resultant expressions for \( A_{lk} \) in (5.40), we obtain for the time of longitudinal relaxation

\[
\frac{1}{\tau_L} = \frac{8\pi^4}{345\pi^4} \sum_{\mathbf{S}} S(S+1) \left[ \frac{\nu_c^2}{1 + 4\nu_c^2} + \frac{4\nu_c^2}{1 + 16\nu_c^2} \right] \langle \frac{1}{\tau_1^2} \rangle.
\] (5.75)

If \( r \) is the distance between two interacting particles, then we must assume the correlation time to be the average time necessary for this distance to double as a result of Brownian motion. Thus, the quantity \( \tau_c \) will naturally be a function of \( r \), namely \( \tau_c = r^2/12D \), where \( D \) is the diffusion coefficient, the value of which is, by Stokes' formula:

\[
D = \frac{\kappa r^2}{6\pi \eta a_0^2}.
\] (5.76)

Here \( a_0 \) is the radius of the particle and \( \eta \) the viscosity coefficient. Recognizing that the inequality \( 2\pi \nu\tau_c \ll 1 \) holds true for all particles that are sufficiently close to one another to make their interaction significant in the relaxation process we obtain from formula
Bloembergen, Purcell, and Pound took account also of the influence of the Brownian motion on the magnitude of the transverse relaxation time. This question was subsequently investigated in detail in [30-32]. An estimate of the transverse relaxation time due to magnetic interaction of the particles can be carried out in accordance with the following formula:

\[ \frac{1}{T_1} = \sqrt{\frac{3}{\pi}} K_i \text{arctg} \frac{2r_c}{r_i}, \quad K_i = \frac{2}{5} \frac{g_i^2 N_i}{\hbar^2} S(S+1) \sum_i \left\langle \frac{1}{t_i} \right\rangle. \quad (5.78) \]

If \( \tau_c < T_2 \), we obtain from (5.78), after carrying out the transformations involved in going over from (5.75) to (5.77),

\[ \frac{1}{T_1} = \frac{48a_i^2}{5} \frac{g_i^2 N_i}{\hbar^2} S(S+1). \quad (5.79) \]

By way of an example let us point out that for an aqueous solution of a salt of divalent manganese we obtain for \( N_0 = 6 \cdot 10^{20} \text{ cm}^{-3} \) from (5.77) a value \( 1/T_1 \approx 4 \cdot 10^9 \text{ sec}^{-1} \).

It must be borne in mind that at large paramagnetic-ion concentrations the line shape can be appreciably influenced also by exchange interactions. However, experiments on paramagnetic resonance in ionic solutions are set up for the most part at such low magnetic-particle concentrations that the relaxation mechanism is determined no longer by magnetic or exchange interactions.

3. From an analysis of the experimental data on paramagnetic absorption in solutions, Kozyrev [83] arrived at the conclusion that the solvate complex formed of the paramagnetic ion and the dipole molecules of the solvent surrounding it has so high a stability, that it can be regarded in experiments on paramagnetic resonance as a unique type of "microcrystal." Therefore the "spin-lattice" interactions in
solutions turned out to be in many respects analogous to those occurring in solids. The "spin-spin" share of the absorption line width is connected with the fact that the "microcrystals" are randomly oriented in the solution; this should lead to a broadening of the line due to the possible anisotropy of the $g$ factor, and also because the splittings of the spin levels by the "crystalline" electric field depend on the orientation of the "microcrystal" in the external field $H_0$.

McConnell [84] considered the following relaxation mechanism, connected with the presence of stable solvate shells. When the "microcrystal" rotates under the influence of the Brownian forces, the intervals between the spin levels of the paramagnetic ion change. Therefore energy will be exchanged between the paramagnetic ions and the Brownian motion when the "microcrystal" rotates.

McConnell carried out calculations for the Cu$^{2+}$ ion, for which he assumed the following spin Hamiltonian:

$$\mathcal{H}_{en} = \beta [g_\parallel H S_\parallel + g_\perp (H_x S_x + H_y S_y)] + A I_x S_z + B (I_x S_y + I_y S_x).$$  

Here $r$, $g$, and $p$ are unit vectors of the rectangular coordinate system rigidly connected to the octahedron of water molecules. XYZ denotes a stationary system of coordinates; the direction of the external magnetic field $H_0$ is assumed to coincide with the Z axis. The spin Hamiltonian can be represented in the form

$$\mathcal{H}_{en} = \mathcal{H}_0 + \mathcal{H}_1, \mathcal{H}_1 = \frac{1}{3} (g_\parallel + 2g_\perp) \beta HS_z + \frac{1}{3} (A + 2B) SI_z.$$  

The principal part of the Hamiltonian $\mathcal{H}_0$ remains constant in time. Calculating the matrix elements of the time-varying perturbation $\mathcal{H}_1(t)$ and substituting in (5.74) and (5.40), we obtain

$$\frac{1}{T_1} = \frac{8 \hbar^2 \beta^2 \Delta g (\Delta g^2 + b^2)^2}{15 \left(1 + 4 \hbar^2 \beta^2 \Delta g^2 \right)^2},$$

$$\Delta g = g_\parallel - g_\perp, \quad b = A - B.$$  

For the correlation time we can assume an expression that follows from
the well-known Debye theory [82]:

$$\tau_e = \frac{4\pi a^2}{3kT}. \quad (5.83)$$

McConnell considered also the contribution made to the transverse relaxation time $T_2$ by the Brownian rotation of the microcrystals, at which the resonant conditions vary. The broadening of the paramagnetic resonance lines of a particle whose state is described by the spin Hamiltonian (5.80) can be described with the aid of the following formula for the time $T_2$:

$$\frac{1}{T_2} = \frac{32\pi}{45} (1 + \frac{1}{3} S(S+1)) \, \arctg \frac{2\tau_e}{T_1}. \quad (5.84)$$

From formulas (5.82) and (5.84) follow two interesting facts: 1) the absorption line width should depend strongly on the field intensity $H_0$; 2) different hyperfine components of the paramagnetic resonance line should have different widths.

McGarvey [85] extended McConnell's theory to include ions with $S > 1/2$. For Cr$^{3+}$ he assumed a spin Hamiltonian

$$\mathcal{H}_{Ca} = \beta g H S + D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] \quad (5.85)$$

and obtained

$$\frac{1}{T_1} = \frac{32\pi^2 D^2}{5 kT} \left[ 1 + \frac{\tau_e}{4\pi h^2 D^2} + \frac{\tau_e}{1 + 16\pi^2 h^2 D^2} \right], \quad (5.86)$$

$$\frac{1}{T_2} = \frac{64\pi D^2}{15 kT} \arctg \frac{2\tau_e}{T_1}. \quad (5.87)$$

For the ions Mn$^{2+}$ and Fe$^{3+}$, the following term was added to the spin Hamiltonian (5.75):

$$\frac{1}{6} a \left[ (S_x^2 + S_y^2 + S_z^2) - \frac{1}{6} S(S+1)(3S^2 + 3S - 1) \right]. \quad (5.88)$$

Calculations have shown that

$$\frac{1}{T_1} = \frac{16\pi^2 D^2}{25 kT} \left[ 1 + \frac{67\pi^2}{4\pi h^2 D^2} + \frac{52\pi}{1 + 16\pi^2 h^2 D^2} \right], \quad (5.89)$$

$$\frac{1}{T_2} = \frac{64\pi D^2}{5 kT} \arctg \frac{2\tau_e}{T_1} + \frac{656\pi a^2}{105 kT} \arctg \frac{0.6\tau_e}{T_2}. \quad (5.90)$$

In the calculation of $T_1$ it was assumed that $a = 0$. All the cal-
lations were made under the assumption that the fine components of the Cr\(^{3+}\) and of the Mn\(^{2+}\) and Fe\(^{3+}\) lines merge into one line.

4. We shall show below that in many cases the experimental data on the dependence of the resonant line widths on the temperature and on the intensity of the static magnetic field cannot be explained by means of McConnell's theory. Al'tshuler and Valiyev [86] proposed that the principal mechanism that guarantees longitudinal (spin-lattice) relaxation consists of the following.

In solid paramagnetic ionic crystals, the paramagnetic particle M together with the nearest diamagnetic particles X usually forms a paramagnetic complex, for example MX\(_6\) (M is the metal ion and X a water molecule or some other diamagnetic particle), the interactions within which must be taken into account first of all in explaining the magnetic properties of the substances. In liquids, the presence of the solvate shell enables us to make a similar assumption. It can be assumed that, at least for a time longer than the correlation time of the "spin-lattice interaction," the paramagnetic ion together with the nearest solvent molecules forms a stable complex, the oscillations of which can be characterized by a set of normal coordinates \(Q_i\): the Brownian motion of the liquid molecules perturbs the oscillations of the paramagnetic complex and thereby changes the electric field in which the paramagnetic particle is situated. These changes influence the spin-orbit interaction of the electrons of the paramagnetic ion and consequently can lead to a reorientation of its magnetic moment.

If we expand the matrix element of the "spin-lattice perturbation" in normal coordinates

\[
\mathcal{X}_{\lambda}(t) = \sum_{i} \gamma_{\lambda} Q_i(t) \tag{5.91}
\]

and denote the mean oscillation frequency of the paramagnetic complex

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by \( \nu_0 \), we obtain with the aid of (5.74)
\[
A_{ik} = \frac{4\pi^2}{\hbar^2} \sum_i |V_i|^4 \left[ 1 + \frac{2\nu}{1 + 4\pi^2 \omega_i^2} \right].
\] (5.92)

Here \( \overline{Q^2} \) is the average value of the square of the oscillator amplitude, which can be calculated from the formula [81]:
\[
\overline{Q^2} = \frac{h}{8\pi m v_0} \cosh\left( \frac{h\nu_0}{2kT} \right),
\] (5.93)

where \( m \) stands for the mass of the complex. The oscillations of the paramagnetic complex will be perturbed by the action of the surrounding particles, which execute Brownian motion. Therefore the correlation time is naturally defined as the reciprocal of the damping coefficient \( \gamma \), which can be estimated from the line width of the satellites in the combination spectra of the paramagnetic ions: \( \gamma \approx 10 \text{ cm}^{-1} \) and \( \tau_c \approx 1/\gamma \approx 10^{-12} \text{ sec} \). From the experimental data [87] on the temperature dependence of the line width of the vibrational structure of the optical spectra of ions in crystals it follows that the width increases with the temperature approximately as \( \sqrt{T} \).* In this case the temperature dependence of the probability of the relaxation transition will be determined by the formula
\[
A_{ik} \sim \frac{1}{\sqrt{T}} \cosh\left( \frac{h\nu_0}{2kT} \right)
\] (5.94)

when \( 4\pi^2 \nu_i^2 \tau_c^2 \ll 1 \) and
\[
A_{ik} \sim \sqrt{T} \cosh\left( \frac{h\nu_0}{2kT} \right)
\] (5.95)

when \( 4\pi^2 \nu_i^2 \tau_c^2 \gg 1 \).

Let us consider some typical paramagnetic ions.

\( \text{Cu}^{2+} \). The system of energy levels arising in a strong cubic field, a weak field of lower symmetry, and an external magnetic field \( H_0 \) is shown in Fig. 5.5. This case is characterized by the presence of two relatively close orbital levels, the interval between which is on the order of 1000 cm\(^{-1}\) in solid salts. The width of the resonance lines in
liquids turns out to be determined by the relaxation transitions between these energy levels without a change in spin direction. For the width of the resonance line we obtain the following expression

\[ \Delta v = 2 \Delta v_{\alpha \beta} = \frac{1}{12} \left( \frac{1}{\gamma} \frac{1}{R^3} \frac{1}{R^3} \right) \left( \frac{1}{R^2} \frac{1}{R^2} \right) \exp \left( -\frac{A}{kT} \right). \]  

(5.96)

Here \( R \) is the equilibrium distance from the Cu\(^{2+}\) ion to the water molecule, the dipole moment of which is equal to \( \mu \). In contradistinction to the McConnell theory, it follows from this formula that the width should be independent of the field \( H_0 \). If we assume \( v_0 \approx 500 \text{ cm}^{-1} \) [88], then the temperature dependence will be given by the formula

\[ \Delta v = \sqrt{T} \exp \left( -\frac{A}{kT} \right). \]  

(5.97)

The connection between the relaxation time and the half-width is in this case somewhat unusual and has the form

\[ \frac{1}{T_1} \approx \frac{\exp \left( \frac{A}{kT} \right)}{2 \left[ 1 - \exp \left( -\frac{A}{kT} \right) \right]} \]  

(5.98)

It is interesting to note that unlike \( \Delta v \), quantity \( 1/T_1 \) decreases with increasing temperature. This seemingly strange dependence of the relaxation time on the temperature is explained by the fact that in our case the specific heat of the spin system increases more rapidly upon heating than the probabilities of the relaxation transitions. It must be borne in mind that the nonequilibrium distribution of the particles among the levels \( a, -1/2 \) and \( a, 1/2 \) (or the levels \( b, -1/2 \) and \( b, 1/2 \)) cannot be annihilated with the aid of the relaxation transitions \( a, -1/2 \rightarrow b, -1/2 \) and \( a, 1/2 \rightarrow b, 1/2 \). Therefore, in addition to...
time $T_1$, there will exist still another relaxation time $T'_1$, the value of which can be estimated from the formula

$$\frac{1}{T_1} = \frac{96}{5} \left( \frac{2g \mu_B}{\hbar} \right)^2 \left( \frac{16 \alpha_1}{\gamma^3 R^3} \right)^{2/3}. \tag{5.99}$$

$\text{Cr}^{3+}$. Calculations have been made for two extreme cases, a strong magnetic field and a weak one. If the field $H_0$ is strong and the spin levels are equidistant, then

$$\frac{1}{T_1} = \frac{86}{20} \sqrt{\frac{\gamma}{R^4}} (13 \alpha_1 + 4 \alpha_2) \tau_1^2,$$

where

$$\alpha_1 = 54 \sqrt{\frac{3}{4}} \frac{\gamma}{R^4} \tau_1^2,$$

$$\alpha_2 = \frac{12}{175} \frac{324 \tau_1}{44 R^4 (R^3 - 55 \tau_1^2/38 R^4)}. \tag{5.100}$$

On the other hand if $H_0 = 0$, then

$$\frac{1}{T_1} = 36 \sqrt{\frac{\gamma}{R^4}} (\alpha_1 + \alpha_2) \tau_1^2. \tag{5.101}$$

Taking into account the fact that for the chrome complexes $\nu_0 \approx 800 \text{ cm}^{-1} \ [88]$, we obtain $T_1 \approx T_2$.

$\text{Mn}^{2+}$. If we denote by $D$ the spin Hamiltonian constant that determines the splitting of the spin levels in the zero magnetic field, we find that

$$\frac{1}{T_1} = C \sqrt{\frac{\gamma}{R^4}} \tau_1^2, \tag{5.102}$$

where in the case of a strong magnetic field $C = (274.64.12)/35$; on the other hand, if $H_0 = 0$, then $C = (36 \cdot 16 \cdot 157)/7$. At temperatures $300-400^0 \text{K}$ we have $\nu_0 \approx kT$ for $\text{Mn}^{2+}$ [56], and therefore the quantity $1/T_1$ first decreases on heating, and then begins to increase.

§5.7. Solutions of Paramagnetic Salts. Experimental Results

As was indicated in Chapter 4, paramagnetic absorption in liquid solutions of $\text{Mn}^{2+}$ salts was first observed by Zavoyskyi. He investigated this absorption at frequencies 1-10 Mcs in the presence of static
magnetic fields, situated both perpendicular and parallel [89] to the oscillating magnetic field. Later on a series of measurements of the paramagnetic resonance line widths was undertaken not only in solutions of Mn$^{2+}$ [90-94], but also for other ions of the iron group and the ion Gd$^{3+}$ [64, 94, 84, 85]. Some complex ions were investigated along with the simple ones [95, 85]. The measurements have shown that $\Delta H$ in solutions depends strongly on the character of the ion, on the solvent, and on the temperature. The limiting width reached at sufficiently low concentrations, which is independent of further dilution, has different values for different ions. In particular, in solutions of the salts of hydrated ions Ti$^{3+}$, Fe$^{3+}$, and Co$^{3+}$ the lines turned out to be so broad, regardless of the dilution, that no resonance effect was observed. The reason for failure to observe the effect is apparently the rather short spin-lattice relaxation time.*

**TABLE 5.8**

Absorption Line Width in Aqueous Solutions of Iron-Group Salts at Room Temperature

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration, mol/l</th>
<th>$\Delta H$, oersted</th>
<th>$\nu$, Mcs</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$</td>
<td>4.0</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>255</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>200</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>131</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>48</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>41</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>38</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>Cr(NO$_3$)$_3$</td>
<td>3.0</td>
<td>440±20</td>
<td>9452</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>310±20</td>
<td>9452</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>270±20</td>
<td>9452</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>240±20</td>
<td>9452</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>220±20</td>
<td>9452</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>200±20</td>
<td>9452</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>190±20</td>
<td>9452</td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$</td>
<td>4.0</td>
<td>140</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>140</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>140</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>140</td>
<td>207</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>4.0</td>
<td>225</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>185</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>160</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>140</td>
<td>207</td>
</tr>
</tbody>
</table>

1) Substance; 2) concentration, mole/liter; 3) oersted; 4) Mcs.

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In investigations made in the frequency range $10^{-10}$ Mcs [64], the effect is absent in salts of ions having an even number of electrons ($\text{Cr}^{2+}$, $\text{Ni}^{2+}$, $\text{V}^{3+}$); this can be attributed, as in the case of solid salts, to the smallness of the quantum of radio frequency fields as compared with the initial splitting of the spin sublevels.

Certain data on the values of $\Delta H$ in iron-group ions at room temperatures are listed in Table 5.8.

For certain ions ($\text{Mn}^{2+}$, $\text{Cr}^{3+}$, $\text{Cu}^{2+}$), an investigation was made of the temperature dependence of $\Delta H$ [94]. This dependence is shown in Figs. 5.6-5.8.

The following conclusions can be drawn concerning the line width in solutions.

1) In highly concentrated solutions one observes sometimes relatively narrow lines without a hyperfine structure. The lines broaden upon dilution and a hyperfine structure arises. An example of this are solutions of $\text{VOCl}_2$, investigated by Garif'yanov and Kozyrev [96]. It must be assumed that considerable exchange interactions take place in very concentrated solutions of this ion. An analogous fact was noted also in liquid melts of hydrated salts of $\text{Mn}^{2+}$ [93].

2) In solutions of $\text{Cr}^{3+}$ salts one observes at not too high concentrations a narrowing down of the lines on dilution [64, 85]. This narrowing down should be attributed to the reduction in the magnetic dipole interactions, and perhaps partially also to the increase in the symmetry of the local electric fields acting on the ions, and conse-
sequently to the reduction in the "scatter" of the unresolved fine-structure peaks. As to the limiting line-width, which is no longer dependent on further dilution, it may be due either to spin-lattice interaction or to the scatter of the fine-structure peaks.

3) In aqueous solutions of Cu$^{2+}$ salts [64], the line width is independent of the concentration and of the viscosity (inasmuch as the latter decreases to approximately one fifth as the concentration is varied from 4 to 0.5 moles/liter). Therefore the width cannot be related in this case to the spin-spin interactions, and should be ascribed to spin-lattice interactions.

A comparison of the experimental results with the proposed theories is best made for each ion individually.

Cr$^{3+}$. The independence of $\Delta H$ of the field intensity $H_0$ is equally well explained either by the calculations of Al'tshuler and Vallyev or by those of McGarvey. The same pertains also to the qualitative explanation of the $\Delta H(T)$ dependence. There are, however, experimental indications that at approximately 250°C the lines begin to broaden with increasing temperature; this broadening can be understood only with the aid of the theory of Al'tshuler and Vallyev.

Mn$^{2+}$, Fe$^{3+}$. The McGarvey calculations cannot explain the sharp
difference in the line width measured in the solutions of Mn$^{2+}$ and Fe$^{3+}$ ions, and also the broadening of the Mn$^{2+}$ line resulting from heating above 70°C. The theory of Al'tshuler and Valiyev makes it possible to understand the observed $\Delta H(T)$ dependence, while the difference in the width of the Mn$^{2+}$ and Fe$^{3+}$ lines is at any rate not in contradiction with this theory.

Cu$^{2+}$aq For the Cu$^{2+}$aq ion, the Al'tshuler and Valiyev theory explains both the independence of $\Delta H$ of $H_0$ and of the concentration, and the line broadening upon heating. However, in solutions of complex copper salts, which give resolved hyperfine structure peaks [97], one observes that $I_z$ influences the width of the individual peaks. This dependence of $\Delta H$ on $I_z$ in the case of complex copper ions is explained qualitatively by McConnell's theory. The same pertains, apparently, to solutions of vanadium salts, where the width of the hyperfine structure peaks also depend on $I_z$.

Recently, Tishkov [98] measured paramagnetic relaxation in parallel fields in solutions of Mn$^{2+}$ salts in water, glycerine, and water-glycerine mixtures. The principal results obtained by him reduce to the following.

1) The experimental $\chi''(H_\parallel)$ are well described by the theory of Casimir and du Pre with account of the spin-spin relaxation as made by Shaposhnikov.

2) The value of $\tau$ increases with increasing field $H_\parallel$. The dependence of $\tau(H_\parallel)$ is in good agreement with the Brons-Van Vleck formula.

3) When the concentration of Mn$^{2+}$ is decreased from 3 to 1 mole/liter in an aqueous solution of Mn(NO$_3$)$_2$, the value of $\tau$ increases somewhat; further dilution does not affect $\tau$.

4) A change in the microscopic viscosity of the solution does not affect $\tau$. 

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5) A change in the nearest surrounding of the Mn$^{2+}$ ion brings about a change in $\tau$.

6) The value of $\tau$ as a function of the temperature goes through a maximum corresponding to approximately 20°C for 1 mole of solution of Mn(NO$_3$)$_2$ in water.

None of these results contradict the Al'tshuler and Valiyev theory, while the temperature dependence of $\tau$ confirms this theory directly.

Summarizing, we can state that in the case of ions with a small anisotropy of the $g$ factor, the spin-lattice relaxation mechanism is the perturbation of the solvate complex by the Brownian motion. Such ions are, for example, Mn$^{2+}$, Cr$^{3+}$, and the hydrated Cu$^{2+}$ ions. On the other hand, in the case of ions having a strong $g$-factor anisotropy (complex ions of Cu$^{2+}$ and possibly of VO$^{2+}$), the stronger relaxation mechanism is the one connected with the rotation of the solvate complex.

§5.8. Line Shape under Saturation Conditions

One speaks of saturation of paramagnetic resonance when a noticeable dependence of the magnitude of the effect and of the resonance line shape on the power of the alternating field is observed. The character of the saturation can be twofold, corresponding to two possible types of absorption line broadening [99]. We shall call a broadening uniform, if the absorbed energy of the radio frequency field is distributed among all the spins in such a way that thermodynamic equilibrium is not disturbed during the paramagnetic resonance processes. One can name the following sources of uniform broadening:

1) dipole-dipole interaction between identical magnetic particles;
2) spin-lattice interaction;
3) interaction between the spins and the radiation field;
4) exchange interactions;
5) motion of paramagnetic centers in a radio frequency field;
6) diffusion of the excited spin system within the paramagnet.

We are already acquainted with some of these broadening mechanisms, while others are encountered in the study of the effect in metals, semiconductors, and other paramagnets.

If the broadening is due to inhomogeneity of the local magnetic field, then the radio frequency energy is transferred only to those spins for which the intensities of the magnetic field satisfy the resonance condition. If at the same time the processes within the spin system occur at a slower rate than the energy exchange between the spins and the lattice vibrations, then the spin system does not have time to reach thermodynamic equilibrium. A broadening of this type will be called nonuniform. In this case it is convenient to visualize the paramagnet as an aggregate of spin packets, which do not interact with one another at all. To each packet belongs a certain absorption line, the width of which is determined by the dipole-dipole interactions. The reaction of the entire paramagnet to the external interactions consists of the independent reactions of the individual packets. It is therefore clear that such a system will behave entirely differently from a paramagnet with uniform broadening mechanism.

By way of an example we can list the following sources of nonuniform broadening:

1) hyperfine interaction of the spins of the paramagnetic centers with the nuclear moments of the surrounding diamagnetic particles;
2) anisotropy of the spin-level splittings;
3) dipole interaction between spins with different Larmor precession frequencies;
4) inhomogeneity of the applied static magnetic field.
If the broadening is uniform, then it is easy to show that paramagnetic absorption is determined by the following formula:

$$\chi''(\nu) = \frac{\pi}{2} \chi_s v_s \frac{g(\nu - \nu_0)}{1 + \frac{1}{8} \tau'' H T g(\nu - \nu_0)}.$$  \hfill (5.103)

In the present case we write for the form function \(g(\nu)\) (see §1.3) \(g(\nu - \nu_0)\), for we are also interested in its dependence on the resonant frequency \(\nu_0\).

In order to obtain the Bloch formula under resonance conditions, we put

$$g(0) = 2T_1;$$ \hfill (5.104)

then

$$\chi''(\nu_0) = \frac{\pi \chi_s v_s T_1}{1 + \frac{1}{8} \tau'' H T_1}.$$ \hfill (5.105)

which coincides with formula (5.2) when \(\nu = \nu_0\). The dispersion is characterized by the following expression:

$$\chi'(\nu) = \frac{\pi}{2} \chi_s v_s \frac{1}{1 + \frac{1}{8} \tau'' H T g(\nu - \nu_0)} \int_0^\infty \frac{2 g'(\nu') \nu'}{\nu^2 - \nu'^2} d\nu'. \hfill (5.106)$$

Let us assume now that the broadening is not uniform. Let the distribution of the local fields be specified by the function \(h(\nu - \nu_0)\), so normalized that

$$\int_0^\infty h(\nu - \nu_0) d\nu = 1.$$ \hfill (5.107)

In analogy with (5.104) it is convenient to introduce the time

$$T_1 = \frac{1}{2} h(0).$$ \hfill (5.107)

For absorption in the nonuniform case we have

$$\chi''(\nu) = \frac{\pi}{2} \chi_s \int_0^\infty \frac{g'(\nu - \nu) h(\nu - \nu)}{1 + \frac{1}{8} \tau'' H T g(\nu - \nu)} d\nu'. \hfill (5.108)$$
Since the total width is large compared with the width of the line of an individual spin packet, this expression can be simplified to the form

\[
\chi''(v) = \frac{\pi}{2} x^* h_0 (v - v_0) \int \frac{g(v' - v_0)}{1 + \frac{1}{8} \gamma H_0 g(v' - v_0)} dv'.
\]  

(5.109)

The corresponding formula for the dispersion has the form

\[
\chi'(v) = \chi_0 \int \frac{v^* h_0}{v^* - v} dv'.
\]  

(5.110)

We see that in the case of nonuniform broadening the absorption line shape does not change upon saturation, since the integral in (5.109) is independent of \( v \). The character of the dependence of the maximum absorption on the power of the alternating magnetic field is determined by the form function \( g(v - v_0) \). Consequently an experimental study of the saturation of lines with uniform broadening makes it possible to determine the form function \( g(v - v_0) \), though it is masked in the present case by the total broadening.

In conclusion it must be noted that under saturation conditions the Kramers-Kronig relations (1.18) no longer are valid. Relations (1.18) are a direct consequence of the fact that the complex susceptibility becomes an analytic function of the frequency in the lower half of the complex plane. Van Vleck has shown that this condition follows from the linearity of the system. Since the linearity of the system is disturbed under saturation conditions, it is understandable why the Kramers-Kronig relations must be reviewed.

Recently Tomita [100] proposed a general theory of paramagnetic resonance under saturation conditions; he explained at the same time many interesting phenomena that are encountered in the observation of both electron and nuclear paramagnetic resonance.
In many cases of nonuniform broadening, the saturation is nevertheless uniform owing to cross correlation.

§5.9. Cross Correlation

The two characteristic time parameters $T_1$ and $T_2$ (or $\tau$ and $\tau'$) are not always sufficient for a description of the paramagnetic relaxation processes. Thus, at very low temperatures it becomes necessary to take into account the time required to establish thermal equilibrium between the lattice and the helium thermostat. In the case of strong exchange interactions it is necessary to separate the "exchange system" and introduce new time parameters characterizing the rate of establishment of equilibrium between this system and the lattice, the Zeeman system, etc. Developing further the researches of Kronig and Bouwkamp [101], of Gorter [102], and of Abragam and Proctor [103], Bloembergen [104] showed that a large group of phenomena can be explained from a unified point of view by introducing the concept of cross correlation.

We shall henceforth assume always that $T_2 \ll T_1$. The spin-spin relaxation time $T_2$ has a twofold significance: first, the quantity $1/T_2$ is of the order of the resonant paramagnetic absorption line width; second, the quantity $T_2$ is the time necessary to establish thermal equilibrium within the spin system.

If the Zeeman and the intracrystalline Stark splittings of the spin levels are much larger than the average interaction energy between the spins of two neighboring magnetic particles, the second interpretation of the time $T_2$ becomes meaningless. In this case, the conversion of the Zeeman and Stark energies into the energy of dipole-dipole interaction is difficult, and consequently one cannot speak of a single spin system. The rate of establishment of thermal equilibrium between the system of individual spin levels of the paramagnetic par-
articles, on the one hand, and the system of dipole-dipole interactions on the other, will be characterized with the aid of the "cross relaxation time" $T_{21}$. Greatest interest is attached to the case $T_{21} < T_1$, which we shall now consider.

We assume first that the paramagnet contains magnetic particles of one sort with effective spin $S' = 1/2$. Let the Zeeman splitting of the individual ion $\hbar v_{12} = g\beta H_0$ be so large that the energy of interaction between spins of different particles can be regarded as a perturbation. It is necessary to calculate the probability that an energy quantum $\hbar v_{12}$ will be converted as a result of the realignment of the magnetic-dipole system into the energy of dipole-dipole interaction. Direct application of perturbation theory is impossible, owing to the tremendous number of degrees of freedom of the spin system. It is simplest to attain our purpose by means of a mixed method, which combines perturbation theory and the method of moments.

Successive application of perturbation theory calls for the knowledge of the eigenvalues of that part of the dipole-dipole interaction operator which commutes with the Zeeman-energy operator. In order not to consider the tremendous number of energy levels which are eigenvalues of the matrices $A$ and $B$ (5.9), which commute with the Zeeman-energy matrix, we introduce a form function $g(v)$, which has a symmetrical maximum at the point $v_{12}$. The transitions between energy levels of these dipole systems are brought about by that part of the dipole-dipole interactions which is represented by matrices $C$ and $D$, which do not commute with the Zeeman energy matrix. We shall see below that in our case we can disregard the terms $E$ and $F$. In the first approximation of the theory of time-dependent perturbations, the probability of transition of the Zeeman energy $\hbar v_{12}$ into dipole energy is

$$w = (2\pi)^{-1} \int |\psi_0|^2 \int \delta(v - v_{12}) g(v) dv. $$

(5.111)
We denote here by \( c_{12} \) the nondiagonal element of the matrix \( C \), which relates the states 1 and 2. The form function \( g(v) \) can be determined with the aid of its moments. The second moment of this function relative to the frequency \( v_{21} \) can be calculated from the following formula

\[
M_2 = \frac{S_p \left[ \sum_{j=1}^{2} \sum_{i=1}^{2} \delta_{ij} \delta_{ji} - \sum_{j=1}^{2} \delta_{ij} (\Lambda + \delta) \right]^{-1} \left[ \sum_{j=1}^{2} \delta_{ij} \delta_{ji} \right]} {S_p \left[ \sum_{i=1}^{2} \delta_{ij} \delta_{ji} \right]}.
\]  

(5.112)

The difference from formula (5.12) consists in the fact that in place of the operator \( \Sigma \hat{S}_x \), which is connected with the action of the external oscillating magnetic field applied along the \( x \) axis, we have here the matrix of the operator \( \hat{C} = \Sigma \hat{S}_{21}^+ \hat{S}_{12}^+ \), the elements of which determine the intensity of the transitions that we are now considering. The moment (5.112) has obviously the same order as the moment (5.12), which pertains to the absorption line of the radio frequency field, but the two are not equal.

If we assume that \( g(v) \) has a Gaussian form, then we obtain for the cross relaxation probability

\[
w = \frac{3}{4} g^{\mu S(S + 1)} \int \sum_j \frac{r^j \sin^2 \theta \cos \theta e^{-\frac{e^{\mu r_j^2}}{2\hbar^2 M_2}}}{\sqrt{2\pi \hbar^2 M_2}}.
\]  

(5.113)

At large fields \( H_0 \), the time \( T_2 \) increases very rapidly with increasing interval between the Zeeman levels of the ion. Therefore the processes \( \Delta M = \pm 2 \), caused by the terms \( E \) and \( F \), can be neglected.

If \( H_0 \to 0 \), then \( T_{21} \to T_2 \) and we have in accordance with Kronig and Bouwkamp [101]

\[
w = 2\pi \sqrt{M_2^\prime \frac{e^{\mu r_0^2}}{2\hbar^2}}.
\]  

(5.114)

Here \( M_2^\prime \) is the second moment calculated with additional account of the terms \( E \) and \( F \).

It must be kept in mind that the assumed Gaussian character of
the curve \( g(v) \) can lead to serious errors, particularly in the case of strong exchange coupling and random paramagnetic dilution.

We now proceed to consider substances which contain either two sorts of paramagnetic centers, or magnetic particles of one sort but with spin \( S > 1/2 \). The establishment of equilibrium between the Zeeman and the dipole systems can become appreciably accelerated if there are two pairs of levels with almost equal intervals: \( h\nu_\alpha \approx h\nu_\beta \). Then the following processes will take place under the influence of the dipole interactions: the ion \( \downarrow \) will absorb an energy \( h\nu_\alpha \), the ion \( \uparrow \) will lose an energy \( h\nu_\beta \), and the energy \( h(\nu_\alpha - \nu_\beta) \) is transferred to the dipole system. The probability of a process of this kind is

\[
\omega_{ij} = h^{-1} |\langle E_i, E_j | \mathcal{H}_{ij} | E_i + h\nu_\alpha, E_j - h\nu_\beta \rangle|^2 g_{\alpha\beta}(0) \tag{5.115}
\]

where \( \mathcal{H}_{ij} \) is the operator of interaction between the ions \( \downarrow \) and \( \uparrow \), and \( g_{\alpha\beta}(\nu_\alpha - \nu_\beta) \) is a form function which has a maximum at the point \( \nu_\alpha - \nu_\beta = 0 \). The second moment of this function can be determined from a formula analogous to (5.112).

Let us point out a few important cases, where two pairs of energy levels with practically identical intervals are encountered: 1) the ion \( Ni^{2+} (S = 1) \) in an axial crystalline field and a weak magnetic field (Fig. 5.9a); 2) the ion \( Ni^{2+} \) in an intermediate crystalline field and an intermediate magnetic field (Fig. 5.9b); 3) the ion \( Cr^{3+} (S = 3/2) \) in a weak magnetic field parallel to the crystal axis (Fig. 5.9c); 4) two nonequivalent ions of \( Cu^{2+} (S = 1/2) \) (Fig. 5.9d).

We can calculate \( g_{\alpha\beta} \) approximately if we know the form function \( g_\alpha \) and \( g_\beta \) for the paramagnetic resonance absorption lines \( \nu_\alpha \) and \( \nu_\beta \), using the following formula:

\[
g_{\alpha\beta} = \int g_\alpha(\nu') g_\beta(\nu'') \delta(\nu' - \nu'' - \nu) \nu' \nu'' d\nu' d\nu'' \tag{5.116}
\]

if \( g_\alpha \) and \( g_\beta \) have a Gaussian form, then...
Kopvillem [115] made detailed calculations of the form function $g_{ab}(v)$ by the method of moments. He obtained a somewhat unexpected result, which contradicted Bloembergen's statements. It turned out that the form function $g_{ab}(v)$ remains practically unchanged upon magnetic dilution, if the energy $h(v_a - v_B)$ is smaller than the average energy $E_{dip}$ of the magnetic dipole-dipole interactions, calculated per paramagnetic ion in a magnetically concentrated crystal. If on the other hand $h(v_a - v_B) > E_{dip}$, then the increase in energy $h(v_a - v_B)$ will lead to a rapid decrease in $g_{ab}(0)$.

We have assumed in the preceding sections that a change in the spin-level populations can occur under the influence of an external applied oscillating magnetic field and as a result of spin-lattice interactions. The probabilities of the corresponding transitions were denoted by us by $p_{ij}$ and $A_{ij}$. We see now that the populations of the spin levels can also be changed by cross relaxation. Thus, for example, for the case shown in Fig. 5.9a we have

$$w_{ij} = \frac{\omega_{ij}}{\sqrt{2\pi n^2} \int \left(\Delta v_a^2 + \Delta v_B^2\right)} e^{-\frac{(v_a - v_B)^2}{2\left(\Delta v_a^2 + \Delta v_B^2\right)}}. \quad (5.117)$$

![Fig. 5.9. Typical example of cross relaxation transitions.](image)
isolated from the lattice. If $T$ is the lattice temperature and $T_{ad}$ is the temperature of the spin system under adiabatic conditions, then we have the following system of differential equations for the level population of particles with spin $S = 1$:

$$
\frac{dN_s}{dt} = \rho_{ss}(N_s - N_0) + A_{13}(N_s - N_0 - \frac{1}{3} N_s \frac{h \nu_{31}}{kT}) + \frac{1}{3} \sum \nu \left\{ N_s - N_0 - \frac{1}{3} N_s \frac{h \nu_{31}}{kT} \right\}
$$

We have assumed here that the frequency of the applied radio signal is $\nu_{32}$.

A solution of equations such as (5.119) enables us to estimate the behavior of the paramagnet under specified external conditions and the role of cross relaxation. Since we are unable to examine in detail the phenomena that can be explained by cross relaxation, we shall stop to discuss some of them.

a) Intermediate relaxation in measurements made in parallel fields

Measurement of paramagnetic absorption in parallel fields made in dilute paramagnetic salts have shown [105] that in addition to ordinary relaxation maxima, the positions of which are determined by the values of $\tau$ and $\tau'$, intermediate temperature-independent absorption peaks are observed in many cases. A quantitative comparison shows that the experimentally established region of dispersion and absorption corresponds to a frequency $\nu \approx (1/2\pi)T_{21}$.

b) Thermal contact between two different spin systems

If a paramagnetic salt contains two sorts of paramagnetic particles, then the cross relaxation theory makes it possible to estimate
the energy that goes over from one spin system to the other if the thermal equilibrium between these systems has been disturbed.

c) "Crossing" saturation

In the previously mentioned experiments of Giordmaine et al [58], which were carried out at helium temperatures, it was shown that saturation of one of the hyperfine components of copper ions leads to a rapid saturation of all other components which have not been subjected to the action of the radio frequency field. The authors of this experiment have attempted to attribute this to the broadening of the energy levels of the "effective" oscillators of the lattice resulting from the weak coupling between these oscillators and the oscillators of other frequencies and with the helium thermostat (see §5.4). The real reason for the crossing saturation, however, is apparently cross relaxation. A principal role is played here by processes in which four ions participate simultaneously. Let the frequency of three resonant lines \( v_\alpha, v_\beta, \) and \( v_\gamma \) be such that \( (v_\beta - v_\alpha) \approx (v_\gamma - v_\beta); \) besides, \( h v_\alpha, v_\beta, v_\gamma = E_\alpha - E_\beta \). Let us take four ions, of which two are at an energy level \( E_\alpha, E_\beta \) and one each are on the levels \( E_\gamma \). As a result of dipole-dipole interaction between these ions, their spins can become simultaneously reoriented. In this way the energy of the radio frequency field applied at a frequency \( v_\beta \) can be transferred and saturate paramagnetic resonance at the frequencies \( v_\alpha \) and \( v_\gamma \). The numerical estimate of \( T_{21} \) is in good agreement with the experimental data. Bloembergen et al [101] have set up special experiments which led to the following important conclusion: at temperatures above 10°K processes connected with the heating of the system of "effective oscillators" do not play any role whatever in dilute paramagnetic salts.

d) Nonuniform broadening and uniform saturation

In sufficiently diluted paramagnetic salts, the greater part of
the resonance-line width is due to the initial magnetic field of the nuclear spins of the diamagnetic atoms and to the scatter of the parameters of the crystalline field. A nonuniform broadening of this type will be called microscopic to distinguish it from the macroscopic broadening, produced by the inhomogeneity of the external magnetic field and by the polycrystalline nature of the specimens.

Let the total width of the lines be determined by the quantity $1/T_2^*$, and the uniform part of the broadening by $1/T_2$. As a result of cross relaxation, the energy of the radio frequency field absorbed by the fields whose resonant frequencies are distributed within the region $v_0 \pm 1/T_2$ will be transferred to fields with resonant frequencies outside this region. If at the same time the corresponding cross relaxation time is $T_{21} > T_1$, then the saturation of the entire resonant line will occur as if the broadening were uniform; the expression for the saturation factor will contain $T_2^*$ in lieu of $T_2$. The cross relaxation within the resonant line can be due either to processes of the Kronig-Bouwkamp type, or to multiple processes similar to those considered in item c). In the case of Kronig-Bouwkamp processes we readily obtain

$$T_n = \frac{n_1}{(T_2^*)^n}. \quad (5.120)$$

Thus, the saturation is uniform in the majority of practically realized conditions, even in the case of nonuniform broadening. Among the experiments directly confirming the considerations advanced here are those on saturation of paramagnetic resonance in nickel fluorosilicate by means of radio frequency pulses [106].

§5.10. Acoustic Paramagnetic Resonance

In analogy with ordinary paramagnetic resonance, in which a paramagnet selectively absorbs energy from an alternating magnetic field,
it is possible to have also paramagnetic resonant absorption of ultrasonic energy. The theory of this phenomenon was proposed by Al'tshuler [107], while the experimental observations were first made on nuclear paramagnets [108, 109] and recently also on Mn$^{2+}$ ions introduced into quartz crystals [111].

Acoustic paramagnetic resonance consists of a transfer of ultrasonic energy to a system of magnetic particles; this transfer occurs when a quantum of elastic-vibration energy is equal to the difference between the energies of the magnetic levels. Thus, just as in the case of ordinary paramagnetic resonance, the acoustic effect will take place if condition (1.2) is satisfied, except that now $\nu$ stands for the frequency of the ultrasound.

The mechanism that effects the transfer of the energy from the sound oscillations to the paramagnetic particles has the same nature as paramagnetic lattice relaxation, realized with the aid of single-phonon processes. Resonant absorption of ultrasound can therefore be regarded as a phenomenon inverse to paramagnetic relaxation. Under the influence of the sound oscillations, the forces acting on the magnetic particles will vary periodically and transitions will occur from one magnetic energy sublevel to another. The complete population of the lower sublevels will cause the number of transitions connected with absorption of energy to exceed the number of the inverse transitions. Equilibrium will be established by transferring the excess energy of the paramagnetic particles to the thermal vibrations of the lattice.

The calculation of the absorption of ultrasound by paramagnets is analogous to the calculation of the time of paramagnetic lattice relaxation produced by first-order processes. This makes it possible to obtain the following formula for estimating the effect in solids:

$$\sigma = \frac{\hbar^2}{3\pi^2} \frac{N_0\rho}{kT^3} \frac{2\pi e^4}{\hbar^2 \varepsilon_{\text{ab}}^2}$$

(5.121)
Here $\sigma$ is the coefficient of sound absorption, that is, the ratio of the energy absorbed per cubic centimeter to the energy incident on a square centimeter per second; $T$ is the temperature of the body; $T_0$ is the temperature at which the relaxation time $\tau$ was determined. The experimental data lead to values on the order of $0.1\text{ cm}^{-1}$ for the coefficient. Thus, the effect investigated is sufficient to become observable. Calculations of $\sigma$ were therefore undertaken subsequently for many types of paramagnets assuming various mechanisms for the spin-lattice coupling.

The first to be investigated was resonant absorption of ultrasound by paramagnetic salts in which the spin-lattice coupling is by modulation of the internal electrical field of the crystal by elastic lattice oscillations. The coefficient $\sigma$ was calculated for several typical salts of the iron-group elements (titanium and chrome alums), salts of rare-earth elements (cerium nitrate, praseodymium ethyl sulfate), and finally for salts whose magnetic ions are in the $S$ state (iron alums). The absorption coefficient for titanium alum was found to be

$$\sigma \approx \frac{1}{\hbar} \frac{\rho (\frac{1}{\hbar})^i (\frac{1}{\hbar})^i}{\Delta v},$$

(5.122)

where $P = \pi N_0/\rho kT \Delta v$. At $T = 20^0K$, a numerical estimate yields $\sigma \approx 2 \times 10^{-88} \text{ cm}^{-1}$. For chrome alum we have

$$\sigma \approx (\frac{1}{\hbar})^i (\frac{1}{\hbar})^i \rho v^2.$$  

(5.123)

A numerical estimate yields at room temperature $\sigma \approx 10^{-21} v^2 \text{ cm}^{-1}$.

Formula (5.123) pertains to transitions between spin levels belonging to different Kramers doublets. Consequently, unlike the titanium salts, we have here $\sigma \sim v^2$. In the perturbation-theory approximation that yields formula (5.123), we have $\sigma = 0$ for transitions within the Kramers doublets. In the higher-order approximation we obtain, as ...
for the ion Ti\(^{3+}\), \(\sigma \sim v^4\). Physically this result is understandable and has general significance. The lowering of the symmetry of the crystalline field, brought about by the elastic lattice vibrations, can change the splitting of the spin levels pertaining to different Kramers doublets, but can hardly influence the distribution of the Kramers doublets themselves.

Calculation for the salts of rare-earth elements has shown that the effect of resonant absorption of ultrasound is small in those cases when the crystalline field leaves in the magnetic ions only a Kramers energy-level degeneracy, which cannot be lifted by the changes induced in the electric field by the lattice vibrations.

In ethyl sulfates of rare earths, the crystalline field has hexagonal symmetry. If the rare-earth ion contains an even number of electrons, the energy levels retain the Kramers degeneracy and the effect of sound absorption should therefore be large. Thus, for praseodymium ethyl sulfate we obtain

\[
\sigma \approx \rho \left( \frac{e^2}{\hbar} \right)^2 \left( \frac{2}{R^3} \right)^\nu.
\]

From this we have \(\sigma \approx -10^{-15} \text{ cm}^{-1}\) when \(T = 20^0\text{K}\). The effect is so large that this salt is apparently the most suitable for experimental observation of the effect. The acoustic effect in rare-earth salts is analyzed in detail in [110].

For iron alums in which the Fe\(^{3+}\) ion is in the S state, the absorption coefficient is relatively small, on the order of \(10^{-24} v^2 \text{ cm}^{-1}\) at room temperature.

In gadolinium salts, in which, as is well known, the splitting of the ground energy level of the paramagnetic ion by the electric field of the crystal is much larger than in the iron ion, we can expect the acoustic effect to be approximately \(10^4\) times stronger.
Resonant absorption of ultrasound was considered also under the assumption that the spin-lattice coupling is produced by a change in the magnetic interaction of the particles by the elastic oscillations of the lattice (the Waller mechanism). In this case the absorption coefficient turns out to be

\[ \sigma = \frac{233}{31} \rho_{\text{f}} \left( \frac{e_{\text{m}}^2}{4} \right) S(S+1)(2S+1)v^4. \]  

(5.125)

In substances with large density of magnetic atoms, of the MnF\(_2\) type, this mechanism may make the coefficient \(\sigma\) at room temperature equal to approximately \(10^{-19} \, v^2 \text{ cm}^{-1}\).

Resonant absorption of ultrasounds will obviously take place not only in electronic paramagnets, but also in substances having nuclear paramagnetism. Favorable circumstances for the nuclear effect are the small line width of the paramagnetic absorption and the large density of the magnetic particles. Small values of nuclear magnetic and quadrupole moments are the cause of a relatively weak spin-lattice coupling, which naturally decreases the effect.

In solid dielectrics, in which the spin-lattice coupling is due to magnetic interaction between the nuclei, the coefficient of resonant absorption of ultrasound can be calculated by means of formula (5.125), where \(\beta\) now stands for the nuclear magneton. For example, for a NaBr crystal at \(T = 300^0\text{K}\) we have \(\sigma \approx 10^{-25} \, v^2 \text{ cm}^{-1}\). For substances in which the spin-lattice coupling is due to quadrupole nuclear interactions, the coefficient \(\sigma\) can become appreciably larger, on the order of \(10^{-20} \, v^2 \text{ cm}^{-1}\). An even larger effect can be expected in metals in which the coupling between the nuclear spins and the lattice vibrations becomes intensified by the interaction between the nuclei and the conduction electrons. An appreciable effect can also be obtained in singlet electronic levels of paramagnetic particles, the nuclei of which
have nonzero magnetic moments [110].

It is interesting to compare the resonant absorption of ultrasound with paramagnetic resonance under the influence of variable magnetic fields.

a) A comparison of the magnitudes of both effects can be readily carried out by recognizing that the coefficient of absorption of the electromagnetic-field energy is

$$\alpha = \frac{8\pi}{\epsilon} \chi'' \approx \frac{8\pi}{\epsilon} \chi'$$

(5.126)

In many "electronic" paramagnets $\Delta \nu \approx 10^9$ cps, $\chi_0 \approx 10^{-6}$, and therefore $\sigma \approx 10^{-22} \text{ v}^2 \text{ cm}^{-1}$. In many cases we have also obtained for the coefficient of ultrasound absorption an expression proportional to $v^2$, with the proportionality factor strongly dependent on the matrix element of the spin-lattice interaction operator. If this matrix element differs from zero in first approximation, then the values obtained for $\sigma$ are much larger than $\sigma_e$. On the other hand, if higher approximations are needed, usually $\sigma$ and $\sigma_e$ are of the same order of magnitude.

It must be noted that the absorption coefficient for the longitudinal and transverse waves will generally speaking be different. We have cited in all cases the average values of the coefficient $\sigma$ for solid bodies.

b) Ordinary paramagnetic resonance is strongly dependent on the angle between the static and alternating magnetic fields. The acoustic effect is little sensitive to changes in the direction of sound-wave propagation relative to the field $H_0$.

c) Absorption of ultrasound is frequently made possible by transitions between such sublevels, for which the magnetic dipole transitions are forbidden.

d) The absorption line shapes in the case of acoustic and ordinary
effects can be quite different. The reason for it is that in both phenomena we deal with the same energy-level bands, produced by the magnetic and other interactions, but the laws governing the transition probabilities between these levels under the influence of ultrasound and under the influence of an alternating magnetic field are quite different in nature.

In spite of the fact that in many cases the coefficient of ultrasound absorption greatly exceeds the coefficient of absorption of the energy from the radio frequency field, the low sensitivity of ultrasonic research methods makes it desirable to use indirect methods of detecting acoustic paramagnetic resonance. Such resonance can be observed by "saturation" of the magnetic sublevels of the nuclei, a saturation occurring at high sound intensities [108]. Another method can be based on the changes produced in the magnetization of the body under the influence of the ultrasound.

The generation, and particularly the transmission of sound oscillations at microwave frequencies from the generator to the investigated substance constitutes a very complicated experimental problem. Therefore great interest is attached to a determination of the conditions under which one can expect a noticeable effect in electronic paramagnets at relatively low frequencies, on the order of 100 Mcs. This question was considered in [113]. Since the greatest effect is connected with transitions between different Kramers doublets, it is apparently very convenient to observe transitions between spin levels near the points where the levels cross, as occurs, for example, in the case shown in Fig. 1.3.

We note finally that if magnetically diluted crystals are used, the scattering of the sound waves on the imperfections of the crystal lattice can become most appreciable. For reasons indicated in §5.3,
item 7, resonant absorption of these waves will be very strong. Therefore indirect measurement methods, which make it possible to evaluate directly the difference in the spin-level populations, should be very convenient.

An experimental study of resonant paramagnetic absorption of ultrasound can greatly supplement the data obtained by investigating ordinary resonance and paramagnetic relaxation; it makes possible a deeper explanation of the nature of the spin-lattice interaction, and a determination of the constants characterizing this interaction; it discloses new absorption lines, the appearance of which under the influence of a radio frequency field is impossible because of the absence of magnetic dipole transitions.

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See footnote for page 215.

The only exception is the Tutton's salt of $\text{Cu}^{2+}$.

A detailed analysis of the interaction between the oscillators $Q_i$ and the Brownian motion, carried out by K.A. Valiyev (unpublished work), has shown that the constant $\tau_0$ can be given a different interpretation; the character of the temperature dependences of $A_{ik}$ remains the same in this case.

Confirming this fact is the possibility of observing resonance in $\text{V}^{2+}$ [96], and also the reported [84] observation of the effect in a complex salt of $\text{Ti}^{3+}$. In these cases a strong low-symmetry component of the crystalline field can explain the sufficiently long time $\tau$.

лок = lok = lokal'nyy = local

зеем = zeem = zeemanovskiy = Zeeman (adj.)

дип = dip = dipol'nyy = dipole

обм = obm = obmen = exchange

эксп = eksp = eksperimental'nyy = experimental

теор = teor = teoreticheskiy = theoretical

рез = rez = rezonansnyy = resonance

сп = sp = spin = spin

сth = coth

крossrel = krossrel = krossrelaksatsiya = cross-relaxation

ад = ad = adiabatichekiy = adiabatic
Chapter 6
METALS AND SEMICONDUCTORS. IMPERFECTIONS IN CRYSTALS

§6.1. Effect on Conduction Electrons

The carriers of paramagnetism in metals are the conduction electrons. In transition metals, paramagnetism may also be associated with the ions that form the core of the crystal lattice. One could expect in metals the appearance of paramagnetic resonant absorption lines, the positions of which would be determined by the $g$ factors of both the conduction electrons and of the $d$ and $f$ shells of the atoms. However, the observation of paramagnetic resonance in metals entails several difficulties: 1) the skin effect reduces the absorption of energy from the radio frequency field and makes the form of the resonance line more complicated; 2) small paramagnetic inclusions may cause results that are quite erroneous; 3) in many metals, the spin-lattice interactions smear out the paramagnetic resonance curve.

To reduce the skin effect one usually employs minute metal particles, pulverized by ultrasound and embedded in paraffin. The metal specimens must be subjected to multiple purification to rid them of paramagnetic impurities. A confirmed effect on the conduction electrons was obtained in the following metals: Li, Na, K, Be, Cs [1-11]. Investigations of many other substances, such as Al, Mg, Pd, W, produced no positive results, apparently owing to the excessive width of the resonance line.

The first calculation of the $g$ factor for conduction electrons was made by Jafet [12] with sodium as an example. Only the spin-orbit
interaction was taken into account there, since the correlation and exchange effects were insignificant, and the influence of interaction between the electronic and nuclear spins became noticeable only at temperature \( T < 1^0\text{K} \). The closeness of the experimental values of the \( g \) factors to the pure spin value \( g_{\text{spin}} = 2.0023 \) shows that the spin-orbit interaction can be regarded as a perturbation. The Bardeen method [13], in which it is possible to avoid calculation of the matrix elements, was used in the computations. This yielded \( \Delta g = g - g_{\text{spin}} = -3.7 \cdot 10^{-4} \), whereas experiments [8, 9] implied that \( \Delta g = -(8 \pm 12) \cdot 10^{-4} \). Brooks [14] made calculations based on the atomic value of the spin-orbit coupling constants. The value \( \Delta g = -6.6 \cdot 10^{-4} \) which we obtained agrees within the limits of error with the experimental data. The value \( \Delta g = -6 \cdot 10^{-5} \) obtained theoretically for lithium [15] is very small, in agreement with the measurement results [8, 9]: \( |\Delta g| \leq 10^{-4} \). For beryllium, experiment [8] yields \( \Delta g = +(9 \pm 1) \cdot 10^{-4} \), and there are no theoretical calculations. For potassium, the \( g \) factor could at first not be determined, since the effect was small and became observable only at temperatures below \( 4^0\text{K} \).

An original method of obtaining pure and finely ground specimens of metals was proposed by Levy [9]; he froze solutions of alkali metals in ammonia at liquid nitrogen temperature. He was thus able to measure paramagnetic resonance absorption in potassium at \( 180 \text{K} \) and in cesium at \( 25 \text{K} \). The measured values of the \( g \) factor were 1.99 and 1.93, respectively, in good agreement with the theoretical [14] values 1.99 and 1.94.

In metals in which the paramagnetism is due to the conduction electrons, the form of the resonance line is determined by the spin-lattice interactions. The spin-spin relaxation is insignificant, owing to the high velocity of the electrons and the relatively small value.
of the spin-spin interactions. A theoretical analysis of paramagnetic relaxation in metals was first made by Overhauser [16], who used the single-electron model of degenerate gas for the calculation of the interactions between the conduction electron spins and the other parts of the metal. The interactions themselves were regarded in this case as small perturbations.

One might think that, just as in the case of ionic paramagnetic crystals at high temperatures, the principal role in the energy exchange between the electron spins and the lattice vibration would be assumed by second order processes (combination scattering of phonons). This assumption, however, must be rejected for the same reasons for which two-phonon processes are disregarded in the calculations of the electric resistivity of metals.

Overhauser considered the following relaxation mechanisms.

1) Interaction with transverse phonons. Let us assume that the relaxation is brought about by interaction between the magnetic moments of the electrons and the magnetic field produced by the charged particles (ions) participating in the lattice vibrations. It is obvious here that only transverse vibrations are significant. We denote the Fermi energy in the absence of an external magnetic field by \( \varepsilon_0 = \frac{\hbar^2 k_F^2}{2m_0} \), the metal particle diameter by \( d \), the length of the side of the atomic dimension cube by \( a \), the number of electrons per cubic centimeter by \( N_e \), and finally the density of the metal by \( \rho \). If we neglect the correlation between the translational motion of the conduction electrons and the vibrational motion of the lattice, the calculations yield for the relaxation time the following expression:

\[
\tau = \frac{3m_e \hbar k_F}{16\pi^2 N_e T \ln \frac{d}{a}}.
\] (6.1)

From this we get, for example in the case of lithium, \( \tau \approx 6 \times 10^{-2} \) sec
at room temperature.

2) Interaction with longitudinal phonons. Relaxation can be due to interaction between the electron spins and the electric field produced by the vibration of the positive lattice ions. Interactions of this type in atoms give rise to spin-orbit coupling. Transverse vibrations produce a relatively weak electric field; we can therefore confine ourselves to an analysis of longitudinal oscillations. Calculation shows that the relaxation time is

\[ \tau = \frac{9\pi \hbar m_e^2 c^3 v}{k^2 \lambda^2 \sqrt{1 - \frac{\lambda}{\theta}}} \]  

(6.2)

Here \( v \) is the average velocity of sound and \( \theta \) is the Debye temperature.

It follows from (6.2) that for lithium at room temperature \( \tau \approx 3 \times 10^{-4} \) sec.

3) Magnetic dipole interaction of the electron spins. In this case the relaxation process may be the result of both simultaneous re-orientation of the spins of both interacting electrons and of the spin of one electron only (see §§5.2 and 5.3). If only the former processes which play the principal role, are taken into account, we obtain for the relaxation time

\[ \tau = \frac{15m_e \hbar c^4}{8k^2 \lambda^2 \theta} \]  

(6.3)

At room temperature we have hence \( \tau \approx 6 \times 10^{-3} \) sec.

4) Interaction with nuclear spins. The relaxation may also be caused by interaction between the electrons and the nuclear spins. In this case, as in atoms, the principal role is assumed by the hyperfine interaction with the electrons in the \( S \) state [17]. Calculation shows that

\[ \frac{\tau_N}{\tau} = \frac{9(1 + 1)}{8k^2} \tau_e \]  

(6.4)

where \( \tau_N \) denotes the relaxation time of the nuclear spins; according
to calculations by Korringa [17], this time is equal to

\[ \tau = \frac{9\pi eH_0^2}{2m_e^2k_BT|\psi(0)|} \]  

(6.5)

Here \( \psi(0) \) is the wave function of the electron situated on the Fermi surface; the vanishing of the argument denotes that it is necessary to take the value of the given function at the location of the nucleus. It is interesting that the relaxation time \( \tau \) is independent of the temperature. One can therefore expect this relaxation mechanism to have the decisive significance at sufficiently low temperature.

5) Interaction of the electron spins with the magnetic field of the currents arising during the translational motion of the conduction electrons. This relaxation mechanism leads to the following expression:

\[ \tau = \frac{9\pi e^2A}{20\pi k_BT^2H_0^2} \]  

(6.6)

The weak dependence on the applied magnetic field \( H_0 \), which is implied in this formula, can be used to ascertain whether this mechanism plays an appreciable role in paramagnetic relaxation processes. Numerical calculation shows that when \( H_0 = 5 \) oersted and \( T = 293^\circ K \) we obtain \( \tau \approx 8 \times 10^{-7} \) sec.

Experimental determinations of the relaxation time [8, 9] have shown that even the shortest values of \( \tau \) given by the latter of the mechanisms proposed by Overhauser are approximately two orders of magnitude higher than the measurement results. In addition, in contradiction to Formula (6.6), it was observed that the relaxation time is constant as the field \( H_0 \) is varied from 300 to 3000 oersted.

The inadequacy of the Overhauser theory lies evidently not in the fact that some important relaxation mechanism has been left out. The use of plane waves for the description of the conduction electron motion probably leads to excessively crude results. Elliott [18] obtained
good agreement with experiment by calculating the relaxation time using the ordinary band theory of metals, under the assumption that the energy exchange between the electron spins and the lattice vibrations is due to the spin-orbit interaction. The connection between the lattice vibrations and the motions of the electrons is so much stronger than the direct interaction between the electron spins and the lattice that even a weak orbit coupling is sufficient to create the most effective relaxation mechanism. Elliott obtained the following formula for the relaxation time

$$\tau = \frac{\tau_R}{(\Delta g)^2}. \quad (6.7)$$

Here $\tau_R$ is the impact time of the conduction electrons which, as is well known, can be readily determined if the electric resistivity of the metal is known. For lithium, sodium, and potassium the impact time is $\tau_R = 1 \times 10^{-14}, 3 \times 10^{-14}, 2 \times 10^{-14}$ sec, respectively. The impact time can be assumed, with sufficiently good approximation, to be proportional to the electric conductivity of the metal, and therefore it will be approximately proportional to $1/T$ at temperatures $T > \theta$, whereas at low temperatures $\tau_R \sim 1/T^5$. For temperature $T > \theta$, the numerical factor is $\alpha = 1/2^{5/3} \ln (d/a)$ (see (6.1)); when $T < \theta$, the factor $\alpha$ depends on the temperature and besides, as in the case of high temperatures, $\tau \sim 1/T$.

The attractive feature of Elliott's theory is the simple connection between the relaxation time $\tau$ and the deviation of the $g$ factor from the pure spin value, which, as we have seen, is due to the spin-orbit interaction. Formula (6.7) readily explains why it was impossible to observe paramagnetic resonance in heavy metals. After all, with increasing atomic number of the element, the spin-orbit coupling increases rapidly, and with it also the deviation $\Delta g$. 

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Andreyev and Gerasimenko [19] have analyzed the problem of paramagnetic relaxation in metals by solving the kinetic equation for the conduction electrons. They have shown that at temperatures $T \gg \beta H_0/k$, under paramagnetic resonance conditions, the magnetization vector obeys Bloch's equation (5.1), in which the longitudinal and transverse relaxation times are equal to each other. At the same time they have made more precise and corrected Elliott's formula for the paramagnetic relaxation time, for which they obtained the following expression:

$$\tau = \left(\frac{\theta}{\ln \frac{T}{T_0}}\right)^{-1}, \quad u = \frac{3\beta \theta \rho \nu^*}{16 \pi \hbar^3 (4 \pi)^{3/2}},$$  \hspace{1cm} (6.8)$$

where $\bar{\varepsilon}$ is the average electron energy in the lattice, and $T_k = (\nu/kv_F)2\beta H_0$, if the dimensions of the metal specimen are such that $d > \hbar v_F/2\beta H_0$; if on the other hand the specimen dimensions do not satisfy this inequality, then $T_k = \hbar v_k d$; by $v_F$ we denote here the velocity of the electron on the Fermi boundary. At a temperature $T \gg \theta$, Formula (6.8) assumes the form

$$\tau = \frac{u}{T} \ln \frac{T}{T_0}. \hspace{1cm} (6.9)$$

On the other hand, if $T \ll \theta$, then

$$\tau = \frac{u}{T} \ln \frac{T}{T_0}. \hspace{1cm} (6.10)$$

Experimental investigations of the relaxation time have shown that in the case of sodium, $\tau \sim 1/T$ as the temperature varies from 4 to 293°C, as called for by the theory.

The value $\tau = 9 \cdot 10^{-8}$ sec obtained by measurements at room temperature is in good agreement with the theoretical value $\tau \approx 10^{-6} T^{-1}$ sec.

In lithium and beryllium, experiment has disclosed that the relaxation time is constant as the temperature is varied over a wide range.* At the same time, it was established that if the specimen is purified

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and the amount of lithium in it is raised from 99.0 to 99.9%, the relaxation time increases from $3 \cdot 10^{-9}$ to $2.5 \cdot 10^{-8}$ sec. All these facts can be simply explained. Because the value of $4g$ of light metals is small, the paramagnetic relaxation is determined by the spin-orbit coupling of the conduction electrons with the impurities. Success in the measurement of the "true" relaxation time will probably be attained in the case of specimens subjected to an exceedingly careful purification.

In potassium the width of the resonance line is approximately 50 times larger than in sodium [9]. In cesium at helium temperatures, the line width is approximately $2 \cdot 10^8$ cps.

Garif'yanov and Starikov [11] have established that negligible impurities of heavy metals (mercury or lead) in specimens of sodium and lithium are capable of broadening the resonance curve by a factor of $10^4$. This broadening is apparently the result of the shortening of the relaxation time due to the strong spin-orbit coupling in the heavy-metal atoms.

In conclusion we note that the area under the paramagnetic resonance absorption curve is proportional to the purely paramagnetic part of the static susceptibility. Therefore, measurements of the paramagnetic resonance make it possible to separate the diamagnetic part of the susceptibility from the paramagnetic one [20]. The main difficulty arising in realization of this idea lies in the fact that it is exceedingly difficult to make absolute measurements of paramagnetic absorption. This difficulty was cleverly circumvented by Schumacher, Carver, and Slichter [5] who observed simultaneously both electronic and nuclear resonance in metallic lithium, at one and the same frequency, $1.7 \cdot 10^7$ cps. The absolute value of the intensity of the nuclear line could be readily calculated. By comparing both resonance curves...
it was found that the static susceptibility is \((2.0 \pm 0.3) \cdot 10^{-6}\) CGS; theoretical calculation [21] yields \(1.87 \cdot 10^{-6}\).

§6.2. Effect of Skin Effect and Diffusion of Electrons on the Form of the Resonance Line

It has been demonstrated theoretically and experimentally that the skin effect and the diffusion of electrons within the skin layer change appreciably the form of the paramagnetic resonance line. The distortion of the resonance line form should result even from the fact that, unlike paramagnetic dielectrics, in which the variable part of the magnetization is determined by the magnitude of the applied oscillating field, in a metal there exists also an inverse dependence of the local values of this field on the magnetization, owing to the skin effect. By virtue of this, whereas in dielectrics the absorbed energy is proportional to the coefficient \(\chi''\), in a metal it will also be proportional to the real part of the dynamic susceptibility, \(\chi'\). In addition, the line shape will be distorted also because diffusion causes the same electron, which moves inside the skin layer, to be subjected to the action of the oscillating magnetic field, the amplitude and phase of which are continuously varying. Thus, the interesting information concerning the nature of the metallic state, obtained by the paramagnetic resonance method, can be rid of distortion only if account is taken of the skin effect and of electron diffusion. A theoretical analysis of this question was made by Dyson [22] who used a very simple model of the metal in order to obtain formulas that are convenient in practical use. He suggested that the conduction electrons diffuse like free particles, and that the spin of each electron can be regarded as an independent quantum variable. The spin is very weakly coupled to the orbital motion and is therefore very weakly affected by the collisions experienced by the electrons. Judging from the value of the
spin-lattice relaxation time in the case of sodium, for example, only one out of $10^5$ collisions causes reorientation of the spin. One can therefore assume that the spin responds primarily to changes in the local magnetic field.

We denote the thickness of the skin layer by $\delta$ and the mean free path of the electron by $\lambda$. In order for the electron to traverse the skin layer the time required on the average is

$$t_D = \frac{3}{2} \frac{\delta}{\lambda}.'$$

During the time $t_D$, the amplitude and phase of the oscillating magnetic field change by approximately $e$ times. Consequently, in place of a definite frequency of magnetic field acting on the electrons within the layer, we have a frequency band of width $1/t_D$. Since usually $t_D \ll \tau_R$, it appears at first glance that the width of the resonance line should increase from $1/\tau$ to $1/t_D$. Actually, however, the width remains practically constant, but the form of the line changes.

This unexpected result is explained as follows. The alternating magnetic field can be represented in the form

$$F(t) = f(t) e^{-i\omega t} + f^*(t) e^{i\omega t},$$

where $f(t)$ is a modulation factor which, however, cannot be regarded as a perfectly random function of the time. After a time $\tau$, each electron experienced a large number of individual pulses, separated by unequal intervals. The pulses arise near the surface of the metal, where the amplitude $f(t)$ is large. During the intervals between the pulses, the electron is for the most part away from the surface, where $f(t)$ is close to zero. The decisive facts are as follows: 1) there is a large probability that the electron will encounter the surface of the metal many times during the time $\tau$; 2) every time that the electron approaches the surface, the phase of $f(t)$ assumes the same value, and consequently
the integral of $f(t)$ taken over the time interval between two pulses differs from zero.

Let us examine the spectral composition of $F(t)$. Each pulse produces a spectrum distributed with approximately equal intensity over a band of width $1/t_D$. Owing to factors 1) and 2), the interference between the spectra produced by a large number of pulses causes a central maximum, corresponding to the frequency $v$, to become separated within a band of width $1/r_D$. The interval between two successive pulses is a random quantity, which can assume values from zero to $\tau$. Therefore, if we average the spectrum of each electron over all the electrons, we obtain a curve with a flat maximum of width $1/r_D$, on which is superimposed a sharp peak of approximate width $1/\tau$.

We present the results of Dyson's calculations. In addition to the time parameters $\tau$ and $t_D$ which we have already encountered, we find it useful to introduce a third one, namely the time $t_T$ needed by the electron to traverse the entire metal specimen. If the metallic particles are so fine that $t_T << t_D$, then the skin effect is negligible and the power absorbed by the paramagnetic material in the volume $V$ can be represented, in accordance with (1.9), (1.19), and (5.2), in the following form:

$$P_v = \pi^2 \nu^2 V_\nu \nu^2 \frac{1}{\tau + \frac{4\pi^2 (\nu - \omega)^2}{\nu^2 \tau^2}}.$$  \hfill (6.13)

We assume here and throughout that there is no saturation; thereupon we assume that in the metal $T_2 = \tau$. In addition, we neglect here and in what follows the nonresonant absorption proportional to $g_2$ (see §§1.4 and 5.1).

In the opposite case, when $t_T >> t_D$, it is necessary to distinguish in the solution of the problem concerning the form of the resonance line in metals between regions of normal and anomalous skin ef-
fect. In the former case the depth of penetration of the alternating field into the metal is determined by the classical value \( \delta = c/2\pi\sqrt{\sigma} \), where \( \sigma \) is the electric conductivity of the metal, while in the latter case the depth of penetration is characterized by the mean free path \( \lambda \).

We first consider the case of normal skin effect. The general formula for the absorbed power is

\[
P_s = -\pi^4 \hbar^2 (3A_0) \nu \chi_s \frac{t_D}{2\pi} \left\{ \frac{R^4(x-1)+1-2R^4}{(R^4-1)^2+R^4} \times \right. \\
\left. \times \left[ \frac{2}{R(1+x^2)} + R^4(x+1) - 3 \right] + \frac{2R^4-2xR^4}{(R^4-1)^2+R^4} \times \right. \\
\left. \times \left[ \frac{2}{R(1+x^2)} + R^4(x-1) - 3 \right] \right\},
\]

(6.14)

where

\[
x = 2\pi(\nu - \nu_0) t, \quad t = \frac{x}{|1|}[((1+x^2)^2 - 1)^{1/2},
\]

\[
\eta = ((1 + x^2)^2 + 1)^{1/2}, \quad R = \left( \frac{t_D}{4} \right)^{1/2}
\]

and \( A_0 \) is the area of the metal surface. This formula can be simplified for certain cases of practical importance.

Let us assume that \( t_D/\tau \ll 1 \). If this condition, which applies to metals with high conductivity (low temperatures and narrow lines), is fulfilled then, accurate to quantities proportional to \( R \), we have

\[
P_s = -[\pi^4 \hbar^2 (3A_0) \nu \chi_s t_D] \frac{t_D}{2\pi} \left\{ \frac{1}{|1|} \left[ ((1+x^2)^2 - 1)^{1/2} \right] \frac{1}{(1+x^2)^2} \right\}.
\]

(6.15)

If \( t_D/\tau \gg 1 \), which holds true when the diffusion of the magnetic dipoles is very slow, then (6.14) assumes the form

\[
P_s = \pi^4 \hbar^2 (3A_0) \nu \chi_s t_D \frac{1}{2} \frac{1-2\pi(\nu - \nu_0)}{1 + 4x^2(\nu - \nu_0)^2}.
\]

(6.16)

This formula was derived already by Bloembergen [23], who investigated the influence of skin effect on the form of the resonance line in the case when diffusion does not play any role. The present case is encountered when one deals with paramagnetic resonance in metals, brought
about by paramagnetic impurities, nuclear spins, or the core of the crystal lattice (transition metals).

At low temperatures the skin effect becomes anomalous. If we assume furthermore that \( t_D/\tau \ll 1 \), then the formula for the absorbed power assumes the form

\[
P_v = \frac{\pi^2 \hbar^2 (\hbar A) \gamma_0 (\omega - \frac{1}{2})}{\pi} \frac{1}{2 \lambda} \left( \frac{Z_1 - Z_2}{[(1 + \lambda)^2 + 1]} \right) + 2Z_1Z_2 \left( \frac{1}{1 + \lambda^2} \right),
\]

where \( Z_1 \) and \( Z_2 \) define the complex impedance \( Z = Z_1 + iZ_2 \).

Many authors have rigorously established and developed the theory of paramagnetic resonance under conditions of both normal and anomalous skin effect. By means of a brilliant method using the kinetic equation for the statistical conduction electron density operator, Silin [24] derived for the magnetization vector the differential equation which served as the basis for Dyson's work. Lifshits, Azbel', and Gerasimenko [25], who derived independently of Silin an analogous kinetic equation, carried out a general analysis of the behavior of the conduction electrons in a constant magnetic and in an arbitrary alternating electron magnetic field.

From among the many results which they obtained, we note that they calculated the paramagnetic resonance line form under saturation conditions. It is interesting that resonance saturation in bulky spec-
imens calls for much larger amounts of power than in the case when the skin effect is insignificant. The question of paramagnetic resonance in superconductors is considered in [26] where, in particular, it is shown that this effect is impossible in bulky conductors.

Let us proceed to compare the theoretical results with the experimental data, which are cited principally in [8]. Figure 6.1 shows the characteristic curve of paramagnetic resonance absorption in a thick layer of metal. We see that the curve is the result of a certain superposition of the usual curves for $\chi'$ and $\chi''$. Figure 6.2 shows an analogous curve for the derivative of the absorption with respect to the field, $dP_v/dH$, which is frequently measured in the experiments. For comparison with experiment, it is convenient to trace the values assumed by the ratio $A/B$ or $A'/B'$. Figure 6.3a shows the varia-

Fig. 6.2. Paramagnetic resonance absorption in a thick layer of metal. Curves showing the dependence of the derivative $dP_v/dH_0$ of the absorbed power with respect to the field on the quantity $\gamma(H_0 - H^*)\tau$ for various values of $R$. 1) $R = \infty$; 2) $R = \sqrt{0.1}$; 3) $R = 0$.

Fig. 6.3a. Dependence of the ratio $A/B$ on $R = (t_D/\tau)^{1/2}$.

Fig. 6.3b. Dependence of the ratio $A'/B'$ on $R = (t_D/\tau)^{1/2}$. 

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tion of these ratios as functions of \( R = (t_D/\tau)^{1/2} \). It is easy to vary 
\( R \) over a wide range by changing over from room temperature to helium 
temperature. For sodium and beryllium, the specimen surfaces of which 
were very smooth, the experimental curves are quite close to the the-
oretical ones. For other metals, discrepancies were observed apparently 
connected with the appreciable variation of the diffusion time \( t_D \) re-
sulting from uneveness in the metal surface.

The experimental values of \( A/B \) can obviously be used to determine 
the diffusion times \( t_D \). The diffusion time measured in this fashion 
for beryllium turned out to be in good agreement with the value ob-
tained with the aid of (6.11).

Knowledge of the ratio \( A/B \) or \( A'/B' \) is very important also because 
it makes possible separation of the effect exerted on the conduction 
electrons from the effect due to the paramagnetic impurities. It is 
seen from Fig. 6.3b that for the conduction electrons the ratio \( A'/B' \) 
always exceeds 2.7. It can be shown that for impurities \( A'/B' < 2.7 \).

For alkali metals the depth of penetration of a field of frequency 
\( 3 \cdot 10^8 \) cps at a temperature \( 40^0K \) becomes equal to the mean free path. 
It is therefore understandable why the experimental absorption curve 
obtained for sodium at \( 4^0K \) corresponds to Formula (6.17), which holds 
true under the conditions of anomalous skin effect.

§6.3. Transition Metals

We can expect the paramagnetic resonance due to the atoms that 
form the core of the crystal lattice to be observable in transition 
metals. The first positive result in the case of the iron-group ele-
ments was obtained in copper-manganese alloys containing from 1 to 
0.07% manganese [27, 28]. The choice of the substance was dictated by 
the following considerations: a) the conduction band of copper has a 
simple structure, since it contains 4s electrons with isotropic effec-
tive mass close to the mass of the free electrons; b) from data on the static susceptibility one can conclude that two 4s electrons of the manganese atoms are included among the particles that fill the conduction band, and therefore the manganese ions are in the $6s^{5/2}$ state; c) by virtue of the fact that the manganese ions are in the $S$ state, we can expect those mechanisms of spin-lattice relaxation, the effect of which depends on the magnitude of the spin-orbit coupling, to be of little effectiveness; d) we can expect the paramagnetic coupling between the manganese atoms to be due to indirect $sd$ exchange forces.

The operator of $sd$ exchange interaction has the simple form

$$\mathcal{H} = J \hat{s} \hat{s},$$

(6.18)

where $\hat{s}$ pertains to the spin of the manganese ion, and $\hat{s}$ pertains to the spin of the conduction electron. On the basis of optical data concerning the magnitude of the exchange interactions in the free manganese atom, we can estimate the $sd$ coupling constant at $I = -7 \cdot 10^{-13}$ erg. The operator (6.18) has the same form as the operator $A\hat{s}$ of the hyperfine interaction between the conduction electrons and the nuclear spins of the metal. This interaction, as is well known, determines the form of the paramagnetic nuclear resonance line in metals [17]. It brings about, first of all, the so-called Knight shift [29] of the position of the resonant peak; owing to the magnetization of the conduction electrons under the influence of the external magnetic field $H_0$, the nuclear spins will be acted upon not only by this field but also by the internal field $H_A = \lambda M_e$, where

$$\lambda = -\frac{\lambda}{4\pi N_e},$$

(6.19)

and $M_e$ is the length of the magnetization vector of the conduction electrons. Second, the $A\hat{s}$ interaction gives rise to the main mechanism of spin-lattice relaxation.
Applying the deduction of nuclear theory to our case, we obtain for an alloy containing say 5% manganese the following formula, which determines the relative change in the $g$ factor:

$$\frac{\Delta g}{g} = \frac{12}{T}.$$  \hspace{1cm} (6.20)

The formula for the spin-lattice relaxation time (6.5) can be rewritten in the form

$$\tau = \frac{8\gamma^2}{5\pi kT^3}.$$  \hspace{1cm} (6.21)

The experimental investigations were carried out at wavelengths 3.3 and 1.2 cm in the temperature interval from 2 to 300°K. The values of the $g$ factor corrected for the line form distortion by the skin effect, using the method indicated in the preceding section, turned out to be very close to 2. On the other hand, the measured width of the resonance line turned out to be approximately 5 times smaller than the value given by Formula (6.21). Thus, if the exchange $sd$ interactions do indeed determine the magnetic properties of the alloys which we are considering, then their magnitude should be approximately one order of magnitude smaller than in the case of free atoms.

The splitting of the spin levels by the electric field of the crystal could not be discerned at all experimentally; the reason for it is that the screening action of the conduction electrons makes these splittings very small. Nor was it possible to observe the hyperfine structure of the absorption lines, a fact which apparently indicates a very weak $s$-configuration interaction.

Along with copper-manganese alloys, silver-manganese and magnesium-manganese alloys were also investigated. All these alloys acquired antiferromagnetic properties at low temperatures.

Let us proceed to consider the rare earth metals. Experimental data on the paramagnetic resonance of this group of transition metals
are exceedingly scanty [30, 31] and do not allow us to make reliable theoretical generalizations. Some theoretical conclusions are given in [32].

With respect to their magnetic properties, the rare earth element metals occupy a special place, for the paramagnetism of these metals is almost completely due to the 4f electrons which lie deep inside the atoms; the conduction electrons exert a negligible influence on the magnetic susceptibility. Because of this we can assume that the general methods for calculating the paramagnetic properties, developed and applied successfully to the salts of the rare earth elements, are applicable in first approximation also to metals. The interpretation of the paramagnetic resonance spectra for rare earth metals becomes simpler by the fact that, unlike the salts, the symmetry of the internal electric field of a metal always coincides with the symmetry of the crystal lattice.

Of particular interest are the paramagnetic absorption lines, the positions of which are independent of the direction of the static magnetic field relative to the crystal axes, since the available experimental data pertain only to polycrystalline specimens. Such lines can appear in crystals that have a cubic lattice, for it is easy to show that if doubly or triply degenerate energy levels are produced under the influence of the cubic-symmetry electric field, then further splitting of these levels by a weak magnetic field will be independent of the direction of this field relative to the cube axes. Among the rare earth metals possessing a cubic lattice are β-cerium, β-praseodymium, europium, and ytterbium. The theoretical conclusions concerning the spectrum of β-cerium turn out to be in good agreement with the experimental results. It was assumed in the calculations that the metal atom lacks three electrons. This assumption follows from data on the static
susceptibility and is confirmed here directly.

From among the metals possessing hexagonal lattices, we shall dwell primarily on \(\alpha\)-cerium, neodymium, and dysprosium, the ions of which have odd numbers of electrons.* The energy levels produced in these ions by the electric field of the crystals are doubly degenerate. If we make certain natural assumptions we find that there should exist only one absorption line, the position of which is determined by the spectroscopic splitting factor

\[
g = g_0 \sqrt{1 + q \sin^2 \theta}, \quad q = J^2 + J - \frac{3}{4},
\]

where \(g_0\) is the Lande factor for the free ion and \(\theta\) is the angle between the direction of the static magnetic field and the crystal hexagonal axis. Calculation shows that for a polycrystalline specimen the absorption line intensity is proportional to

\[
P \sim \left(J + \frac{1}{2}\right)^4 g^0 \sin^2 \frac{2q \sin \theta}{1 + q \sin^2 \theta}.
\]

Elimination of \(\theta\) from Formulas (6.22) and (6.23) enables us to establish with the aid of (1.2) the dependence of the magnitude of the paramagnetic absorption on the intensity of the static field. The theoretical curves obtained in this fashion are in satisfactory agreement with the experimental absorption curves for cerium and neodymium.

The only rare earth metal with a tetragonal lattice, samarium, should have the same spectrum as \(\alpha\)-cerium, provided very simple assumptions are made concerning the coefficients that determine the potential of the crystalline field. Metals whose ions contain an odd number of electrons (\(\alpha\)-Pr, Tb, Ho, and Tm) have a hexagonal lattice. It is easy to show that in this case the probabilities of the magnetic dipole transitions between nearby Zeeman sublevels are equal to zero in first approximation.

If it is assumed that the theory of spin-lattice relaxation de-
veloped above for the rare earth element salts (see §5.3) is also app-
licable to metals, then we obtain for the time $\tau$ values that are sev-
eral times larger because the density and velocity of sound in metals
are appreciably larger; in addition, it is necessary to bear in mind
that the electric field inside metal crystals is much weaker, owing to
the screening effect of the conduction electrons. This probably makes
it possible to observe paramagnetic resonance in rare earth metals at
room temperature.

Gadolinium, the triply charged ion of which is in the $S$ state,
occcupies a special position. Gadolinium is paramagnetic at temperatures
above $16^\circ$C. The measurements of resonant absorption [30], made at a
frequency $2.43 \cdot 10^{10}$ cps and at a temperature $105.5^\circ$C, have shown that
$g = 1.95$, and the line width is independent of the temperature and has
a value of approximately 4000 oersted.

The question of resonant absorption of ultrasound by rare earth
metals was also considered theoretically [33]. In some cases this ef-
fect should be quite appreciable.

§6.4. Impurity Semiconductors

In the first work [34] devoted to paramagnetic resonance in im-
purity semiconductors, the effect was established at a frequency $\nu =
= 9 \cdot 10^9$ cps in powdered specimens of $n$-type silicon, containing be-
tween $1 \cdot 10^{18}$ and $2 \cdot 10^{18}$ phosphorus atoms per cubic centimeter. To elim-
inate the skin effect, minute silicon grains, with radius one order of
magnitude smaller than the depth of the skin layer, were embedded in
paraffin. The measurements were made at temperatures between 4 and
$300^\circ$K. One absorption line was observed with Lorentzian shape. The po-
position of the absorption peak was independent of the temperature and
was determined by a factor $g = 2.001 \pm 0.001$. The width of the reso-
nance line increased rapidly with temperature from about 2 oersted at

- 324 -
40 K to 30 oersted at 3000 K. When working with a klystron generator, no paramagnetic resonance saturation could be observed even at helium temperatures. We can therefore conclude that the longitudinal relaxation time is $T_1 < 10^{-3}$ sec at a temperature 40 K. Willenbroek and Bloembergen [35] have observed at this same alternating field frequency paramagnetic resonance in both n-type and p-type silicon. The measurements were made at 780 K, and the impurity concentration was varied from $5 \times 10^{17}$ to $5 \times 10^{18}$ atoms per cubic centimeter. The position of the absorption peak was the same for electrons and for holes, and corresponded to $g = 2.00$. The intensity of the absorption line was proportional to the impurity concentration.

Fletcher et al. investigated paramagnetic resonance at helium temperatures in single crystals of silicon doped with phosphorus, arsenic [36], and antimony [37]. At concentrations of about $10^{18}$ atoms per cubic centimeter, one absorption peak is observed, the position of which varies somewhat depending on the slope of the static magnetic field relative to the crystal axes. When the field is parallel to the [100] axis, we have for the case of arsenic $g = 2.0004 \pm 0.0005$. The line width was always less than 3 oersted.

From all the foregoing we can conclude that paramagnetic resonance absorption is due to the conduction band electron spins. This conclusion follows first of all from the possibility of observing the effect at temperatures corresponding to an average energy of thermal motion much larger than the ionization energy of the impurity atom (approximately 0.05 ev). Other evidence in favor of this conclusion is the relatively high impurity concentration in the tested specimens and the absence of hyperfine splitting of the resonance line.

The broadening of the paramagnetic absorption line has apparently a spin-lattice character. Indeed, it is easy to calculate that the
width due to magnetic dipole interactions of the electron spins should be of the order of 0.1 oersted. Hyperfine interactions of electron spins with phosphorus nuclei and with nuclei of the odd isotope of silicon cannot make a noticeable contribution to the line width, owing to the rapid motion of the electrons. Nor can surface recombination of the electrons and holes play any appreciable role, since this process is quite slow.

Elliott [18] considered the influence of spin-orbit interaction of conduction electrons on the magnitude of the $g$ factor and the spin-lattice relaxation time of semiconductors. He found that the change in the $g$ factor is

$$
\Delta g \approx \frac{1}{\Delta E},
$$

(6.24)

where $\Delta E$ is the interval between the lowest conduction band and the nearest band having the same transformation properties. If it is recommended that the spin-orbit coupling constant for a silicon atom is $\lambda \approx 100 \text{ cm}^{-1}$ and that experiment yields $\Delta g \approx 3 \cdot 10^{-3}$, we obtain with the aid of (6.24) a sensible value of approximately 4 ev for $\Delta E$.

The spin-lattice relaxation time can be calculated from the following formula (see (6.7))

$$
\tau \sim \frac{\tau}{(\Delta g)^2},
$$

(6.25)

if $\Delta g$ is small. For n-type silicon, the impact time at high temperatures is independent of the impurity concentration and its value is [38]

$$
\tau_R \approx 10^9 T^{-\frac{3}{2}} \text{ sec.}
$$

(6.26)

Hence $\tau \approx 10^{-9} \text{ sec}$ at $T = 300^\circ K$, i.e., the line width is equal to approximately 50 oersted, which is in good agreement with the measured value of approximately 30 oersted. For germanium, the constants $\tau_R$ and $\lambda$ are larger than for silicon by 5 and 20 times, respectively. Conse-
quently, the line width of germanium should be approximately $10^2$ times larger than for silicon, which apparently explains the negative results of the first experiments with germanium.*

At low temperatures and low impurity concentrations, the paramagnetic resonance absorption is due to the spins of the electrons bound to the donors. This fact manifests itself most clearly in the presence of a hyperfine structure of the resonance lines, which indicates that there is a definite coupling between the electron spin and the moment of the impurity atom nucleus. Measurements [36] carried out at a frequency $\nu = 2.4 \cdot 10^{10}$ cps at a temperature of $4.2^\circ K$, on specimens containing from $5 \cdot 10^{16}$ to $10^{18}$ atoms of arsenic per cubic centimeter, have disclosed four equidistant lines in accordance with a nuclear spin of $3/2$ for As$^{75}$. The interval between neighboring hyperfine components is approximately 73 oersted, and the width of each component is about 10 oersted. If silicon is doped with acceptors (boron), the magnitude of the effect is decreased. In addition, it was established that prior elastic deformation of the semiconductors at a temperature of $1000^\circ C$ leads to a considerable increase in the intensity of the absorption lines; the nature of this phenomenon is not quite clear.

In the case of phosphorus-doped specimens, two components spaced 42 oersted apart were observed, in conformance with a value of $1/2$ for the nuclear spin of P$^{31}$.

In specimens containing $4 \cdot 10^{17}$ atoms of antimony per cubic centimeter, owing to the presence of two odd isotopes Sb$^{121}$ and Sb$^{123}$ with nuclear spins $5/2$ and $7/2$, respectively, the paramagnetic spectrum consists of $6 + 8$ hyperfine components [37]. The ratio of the intensities of these two groups of lines corresponds rigorously to the percentage content of the given isotopes, while the total splittings of these line groups (69 and 38 oersted) correspond exactly to the magnetic mo-
ments of the nuclei $\text{Sb}^{121} (\mu = 3.360 \beta_N)$ and $\text{Sb}^{123} (\eta = 2.547 \beta_N)$.

An attempt to observe paramagnetic resonance in semiconductors containing $10^{17}$ atoms of boron and $3 \cdot 10^{17}$ atoms of aluminum per cubic centimeter yielded negative results.

Honig and Kip [39] observed paramagnetic resonance at a frequency $\nu = 8.8 \cdot 10^9$ cps in the temperature range 4-200 K, in a silicon specimen containing $7 \cdot 10^{16}$ atoms of lithium per cubic centimeter. No hyperfine structure was established. The position of the single absorption peak corresponded to $g = 1.999$, the line width was 1.5 oersted, and the line shape was Gaussian.

Kohn and Littinger [40] undertook to ascertain to what degree the experimentally obtained values of the hyperfine splittings of paramagnetic resonance lines are compatible with the assumption that the hyperfine structure is due to the interaction between the donor nuclei and the electrons localized near the donors and situated in well-known donor states with ionization energy 0.04-0.05 ev. The total hyperfine splitting $(\Delta H)_{\text{HFS}}$ of the energy level, expressed in oersted, can be represented in the form

$$ (\Delta H)_{\text{HFS}} = \frac{16\pi}{3} |\psi(0)|^2 \mu_B, $$

(6.27)

where $\mu_D$ is the nuclear magnetic moment, $\psi(r)$ is the wave function of the electron bound to the donor, and $r$ is the radius vector drawn from the nucleus to the electron. Table 6.1 lists the experimental values of $|\psi(0)|^2$.

The function $\psi(r)$ obeys the Schrödinger equation

$$ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) + U(r) - E \right] \psi(r) = 0, $$

(6.28)

where $V(r)$ is the potential energy of the electron in the periodic field of the crystal lattice of silicon, and $U(r)$ is the initial energy that arises when one of the silicon atoms is replaced by an impurity.
atom. At distances large compared with interatomic distances we have
\[ U(r) = -\frac{e^2}{\varepsilon r} \]
where \( \varepsilon \) is the dielectric constant of the medium; for silicon, \( \varepsilon = 13 \). The solution of (6.28) entails great difficulties since, first, the band wave function is unknown for silicon, and, second, the introduction of the concept of the electron effective mass is not allowed near the donor. As a result of detailed calculations undertaken for phosphorus, it was found that \( |\psi(0)|^2 = 0.4 \cdot 10^{24} \text{ cm}^{-3} \), which is in much better agreement with the experimental data than would be expected from the assumptions made. A rough estimate gives a ratio \( |\psi(0)|^2_{\text{P}}/|\psi(0)|^2_{\text{Li}} = 0.004 \). So small a value of \( |\psi(0)|^2_{\text{P}} \) fully explains the negative results of attempts made to observe the hyperfine structure of the absorption line in silicon doped with lithium.

### TABLE 6.1

**Experimental Values of \( |\psi(0)|^2 \)**

<table>
<thead>
<tr>
<th>( I )</th>
<th>( \varepsilon_N )</th>
<th>( \frac{\varepsilon_{N}}{\varepsilon_{\text{Si}}} \times 10^6 )</th>
<th>( A\chi_{e2} \times 10^{-14} )</th>
<th>( \tau_{\text{rad}} \text{ (min.)} )</th>
<th>( \tau_{\text{rad}}/\tau_{\text{S}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li( ^{3+} )</td>
<td>( 3/2 )</td>
<td>2.17</td>
<td>0.055</td>
<td>0.056</td>
<td>3.64 \times 10^4</td>
</tr>
<tr>
<td>P( ^{3+} )</td>
<td>( 3/2 )</td>
<td>2.26</td>
<td>0.44</td>
<td>7.5</td>
<td>560</td>
</tr>
<tr>
<td>As( ^{3+} )</td>
<td>( 3/2 )</td>
<td>0.957</td>
<td>1.80</td>
<td>14.0</td>
<td>58</td>
</tr>
<tr>
<td>Sb( ^{3+} )</td>
<td>( 5/2 )</td>
<td>1.37</td>
<td>1.20</td>
<td>13.0</td>
<td>41</td>
</tr>
<tr>
<td>Sb( ^{5+} )</td>
<td>( 7/2 )</td>
<td>0.724</td>
<td>1.20</td>
<td>7.0</td>
<td>97</td>
</tr>
</tbody>
</table>

1) \( \text{cm}^{-3} \); 2) \( \text{erg} \); 3) \( \text{min} \).

During the observation of the hyperfine structure of paramagnetic resonance spectrum in silicon containing impurities of group V elements, weak satellites, located halfway between each pair of hyperfine components, were observed in addition to the \( 2I + 1 \) lines [36, 37]. Slichter [41] has shown that such satellites should appear if one admits of exchange interactions of the type \( I S_1 S_2 \) between an electron.
pair belonging to two donors that are accidentally in the vicinity of each other. From this interpretation of the nature of the satellite it follows that: a) the intensity of the central satellite is twice that of the outer ones; b) the intensity of the satellites should depend on the concentration of the impurities: at low concentrations the intensities should be proportional to the concentration, and at large concentrations additional satellites should appear, connected with families of three or four electrons; c) if $I \approx kT$, then the intensity of the satellites should depend strongly on the temperature of the semiconductor, approximately as $\exp(-I/kT)$; d) a dependence on the mechanical working is also possible, if this working influences the character of the donor distribution.

In the experiments undertaken to check on Slichter's theory [42], the measurements were carried out at $1.2^0K$ and with an alternating field of frequency $\nu = 9 \cdot 10^9$ cps using two samples of silicon, containing $10^{17}$ and $4 \cdot 10^{17}$ phosphorus atoms per cubic centimeter. Additional absorption maxima, corresponding to the exchange between a pair, a triplet, and a quartet of electrons, were observed in the positions predicted by the theory.

Let us proceed to an analysis of the spin-lattice relaxation of the electrons localized near the donors. As a result of experiments made on silicon samples containing up to $10^{17}$ impurity atoms per cubic centimeter, it was established that the spin-lattice relaxation time at helium temperatures amounts to minutes [43, 44]. Such large relaxation-time values are usually characteristic of nuclear spins. With increasing impurity concentration, the time $\tau$ begins to decrease rapidly, apparently owing to the stronger interaction between the bound electrons and the conduction band electrons. The correctness of this explanation is confirmed directly by the fact that the time $\tau$ decreases
to several milliseconds if the semiconductor is exposed to light [45].

The theory of this phenomenon was presented by Pines, Bardeen, and Slichter [46] and was later developed by Abrahams [47]. The calculations were made in order to estimate the order of magnitude, and consequently several simplifications were made: a) the complex wave function of the bound electron was replaced by the function of an electron with effective mass \( m^* = 0.3m_e \) in a minimal-energy state; b) all the angular dependences were left out; c) the action of only longitudinal phonons was taken into account. The following were considered from among the various relaxation mechanisms.

1. **Modulation of electron-nuclear hyperfine interaction.** Changes brought about by lattice vibration in the potential energy \( V(r) \), which is contained in Eq. (6.28), manifest themselves on the wave function and consequently on the magnitude of the interaction between the electronic and nuclear spins. The relaxation time is

\[
T_x = \frac{\hbar \nu_0}{8\pi^2 \alpha^2 \sqrt{\Delta^4} A^4},
\]

(6.29)

where \( \nu_0 \) is the resonant frequency, \( A \) is the hyperfine structure constant, and \( \alpha \) is a numerical factor of order 10-100.

Table 6.1 lists the values of \( T_x \) for different impurities in silicon, calculated under the assumption that \( \alpha = 50 \), \( \nu_0 = 9 \cdot 10^9 \) cps, and \( T = 1.2^0K \).

2. **Modulation of the hyperfine interaction of the bound electrons with the \( \text{Si}_{29} \) nuclei.** We designate the relaxation time due to the given mechanism by \( T_{Si} \). Calculation shows (see Table 6.1) that \( T_{Si}/T_x \gg 1 \) in all cases, except lithium. Consequently, this mechanism can be significant only for silicon with lithium impurity.

3. **Modulation of spin-orbit interaction of the electrons.** This mechanism, which is the most important for the conduction electrons,
is of little effectiveness in our case, if single-phonon processes are taken into account. Combination scattering of phonons yields for the relaxation time

\[ T_{\text{L}} \sim 10^{14} \tau. \]  

(6.30)

It follows therefore that at temperatures above that of hydrogen, this mechanism should play the principal role.

4. Modulation of exchange interactions between neighboring impurity atoms. At the donor concentrations employed, the mechanism is quite ineffective.

To explain the dependence of the relaxation processes on the impurity concentration, mechanisms were considered, based on the following interactions between the bound electrons and the conduction band electrons:

1) Coulomb interactions; spin reorientation is possible if the spin-orbit coupling of the electron in the donor state is taken into consideration;

2) interaction between the bound electron spins and the magnetic field of the currents produced by the conduction electrons;

3) magnetic dipole-dipole interactions;

4) exchange interactions.

The most effective, in accordance with the calculations, is the last mechanism, since the spins of the bound electrons are subject after the exchange, when they enter the conduction band, to the strong influence of the lattice vibrations. However, even with this mechanism it is impossible to explain the experimental data. It is possible that a stronger spin-lattice interaction mechanism, which is not considered here, exists.

§6.5. Color Centers in Ionic Crystals

It is known that crystals of halides of alkali metals become
strongly colored if their stoichiometric composition is disturbed in some manner and if they contain an excess of metal atoms. It was established that the reason for the coloring is the occurrence of color centers. There exist various methods for obtaining colored crystals: passage of x-rays and γ rays, bombardment with α and β particles, neutrons, or protons; passage of current through a crystal placed between metallic electrodes; heating the crystal in vapors of alkali metals, etc. We note that the color centers are produced not only in alkali halide salts, but in other dielectric and semiconductor crystals. The experimental and theoretical study of various types of color centers has been the object of a large number of investigations (see, for example, the reviews [48]).

In most cases the color centers are also paramagnetic centers, so that their properties can be investigated by magnetic means, particularly with the aid of paramagnetic resonance.

From among the various types of color centers, the best investigated were the F centers, which have a characteristic light absorption band. It can be regarded as proved that the F center in an alkali halide crystal is an electron localized near a vacancy produced after a negative ion has been removed from the crystal lattice site (Fig. 6.4). Thus, a qualitative analogy exists between the hydrogen atom and the F center, since the vacancy of the anion can be identified with the positive charge.

The first to observe paramagnetic resonance on F centers was Hutchison [49], who used for this purpose crystals of LiF bombarded for 24 hours by a neutron flux of $10^{12}$ particles/sec·cm². The measure-
ments were made at a frequency of 9350 megacycles; one absorption peak was observed, the position of which corresponded to $g = 2.00$, while its width was approximately 160 oersteds. The effect was lost when the crystal was bleached by heating it to 500°C. Later, the circle of investigated substances was greatly broadened. A summary of the principal experimental results is given in Table 6.2.

As can be seen from the table, the values of the spectroscopic splitting factors are very close to the $g$ factor of the free electron, thus evidencing the insignificant role of the orbital magnetism. Experiments show that the resonance line has a Gaussian form and that its width in alkali halide crystals is independent of the $F$ center concentration. From this we can conclude that the dipole-dipole interactions of the electron spins of the $F$ centers do not play a major role in the absorption line broadening. This conclusion is reached by simple calculation which shows that at the experimentally investigated $F$ center concentrations the width should not exceed 0.1 oersted. It is seen from Table 6.2 that the experimental values for the line widths of the alkali halide crystals are 2 or 3 orders of magnitude higher.

Kip, Kittel, and others [53] have suggested that the resonance line broadening of the $F$ centers is due to hyperfine interactions between the electron localized near the vacant lattice site and the nuclei of the surrounding atoms. This hypothesis was irrevocably proved. Measurement of paramagnetic resonance in KCl crystals [53], both with natural mixture of potassium isotopes and strongly enriched with the isotope $K^{41}$, have shown that the widths of the resonance lines are quite different in the two cases, and the ratio of these widths corresponds precisely to the values of the magnetic moments of the $K^{39}$ and $K^{41}$ nuclei.

Portis [58] measured by the saturation method the longitudinal
<table>
<thead>
<tr>
<th>Вещество</th>
<th>Количество F-центров в 1 см³</th>
<th>Способ окраски</th>
<th>g-фактор</th>
<th>Ширина линии в ортестдах</th>
<th>Литература</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>$10^{14} - 10^{17}$</td>
<td>Поток нейтронов, протонов; рентгеновские лучи</td>
<td>2,008±0,001</td>
<td>77—160</td>
<td>[49, 54, 55, 60, 79, 108]</td>
</tr>
<tr>
<td>NaCl</td>
<td>$5 \cdot 10^{14} - 10^{15}$</td>
<td></td>
<td>1,987</td>
<td>162</td>
<td>[53]</td>
</tr>
<tr>
<td>NaF</td>
<td></td>
<td></td>
<td>2,002±0,0001</td>
<td></td>
<td>[55]</td>
</tr>
<tr>
<td>KBr</td>
<td>$10^{14} - 10^{15}$</td>
<td>γ-лучи; электролитический</td>
<td>1,980</td>
<td>146</td>
<td>[50, 51, 52, 53]</td>
</tr>
<tr>
<td>KCl</td>
<td>$5 \cdot 10^{14} - 5 \cdot 10^{15}$</td>
<td>Рентгеновские лучи</td>
<td>1,995±1</td>
<td>54</td>
<td>[51, 52, 53, 59]</td>
</tr>
<tr>
<td>K'Cl</td>
<td>$5 \cdot 10^{14}$</td>
<td></td>
<td>1,995±1</td>
<td>36</td>
<td>[53]</td>
</tr>
<tr>
<td>KI</td>
<td></td>
<td></td>
<td>1,971±0,001</td>
<td>200</td>
<td>[109]</td>
</tr>
<tr>
<td>MgO</td>
<td>$10^{14} - 10^{15}$</td>
<td>Поток нейтронов, прогревание в парах</td>
<td>2,0028±0,0001</td>
<td>0,7—0,9</td>
<td>[56]</td>
</tr>
<tr>
<td>NaNO₃</td>
<td></td>
<td></td>
<td>2,000±0,003</td>
<td></td>
<td>[57]</td>
</tr>
</tbody>
</table>

1) Substance; 2) number of F centers per cubic centimeter; 3) method of coloring; 4) g-factor; 5) line width in oersted; 6) literature; 7) neutron or proton flux; x-rays; 8) γ-rays; electrolytic; 9) x-rays; 10) neutron flux, heating in vapor.

Relaxation time for F centers of a KCl crystal at room temperature, and obtained $T_1 = 2.5 \cdot 10^{-5}$ sec. These experiments have shown that the broadening is uneven in character, as should be the case if it is due to hyperfine interactions (see §5.8). We note that questions concerning the nature of spin-lattice relaxation of colored crystals or concerning the dependence of $T_1$ on the temperature, on the static magnetic field intensity, etc., have as yet not been investigated either theoretically or experimentally.

Lord [55] succeeded in resolving the hyperfine structure of the F center resonance lines in LiF and NaF crystals. A large number of components was observed, due to the interaction between the spin of the F electron and the nuclei of the six surrounding alkali metal atoms;
interactions with the following layer of fluorine atomic nuclei yield an unresolved structure and determine the width of the resonance line. The experiments make it possible to determine the hyperfine interac-
tion constants $A$ and the values of $|\psi|^2$ on the nuclei of the alkali metal and fluorine atoms (see Formula (6.27)). The corresponding data are listed in Table 6.3, where the constants $A_1$ and $A_2$ are in oersteds.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$A_1$ (alkali metal)</th>
<th>$A_2$ (alkali metal)</th>
<th>$A_3$ ($\mu$)</th>
<th>$\psi/(\mu)$ cm$^3$/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>14.1 ± 0.1</td>
<td>1.55 · 10$^{-4}$</td>
<td>4.6 ± 0.5</td>
<td>0.21 · 10$^{-4}$</td>
</tr>
<tr>
<td>NaF</td>
<td>37.8 ± 0.3</td>
<td>6.05 · 10$^{-4}$</td>
<td>8.6 ± 0.1</td>
<td>0.39 · 10$^{-4}$</td>
</tr>
</tbody>
</table>

Feher [59] used a double resonance technique (see §8.2) to disclose the hyperfine structure of the paramagnetic resonance line in a colored KCl crystal. The measurements were carried out with samples containing $2 \cdot 10^{17}$ centers per cubic centimeter at a temperature 1.2$^0$K; the electron resonance absorption line was observed at a frequency $\nu \approx 9000$ megacycles and had a width of approximately 150 megacycles, while the frequency of the nuclear resonance was varied from 10 to 100 megacycles and the width of the nuclear resonance was approximately 20,000 cps. Since the nuclear resonance line is approximately 7500 times narrower than the electron line, it is natural for the nuclear resonance to influence noticeably the form of the electron resonance line, in spite of the relatively low intensity of its absorption lines. The results obtained in this fashion can be explained with the aid of the spin Hamiltonian

$$\mathcal{H} = a (i \dot{S}) + b (i \mathbf{\vec{S}} \cdot \mathbf{i} \dot{\mathbf{\mathbf{S}}}) + Q' (\mathbf{i} \mathbf{\mathbf{H}} + \frac{1}{3} i (i + 1)),$$

(6.31)
from which it follows that the resonant frequencies due to the nuclear transitions are

\[ h\nu = \pm q_N h \Omega + \frac{1}{2} [a + b (3 \cos^2 \theta - 1)] + Q \left( 3 \cos^2 \theta - 1 \right) \left( m - \frac{1}{2} \right). \]  

(6.32)

where \( \theta \) is the angle between the field \( H_0 \) and the axial symmetry axis. If this formula is used, then it follows from the experimental data on the nuclear resonance frequencies that \((a/h) = 2.16 \text{ megacycles, (b/h)} = 0.95 \text{ megacycles, and (Q'/h)} = 0.20 \text{ megacycles for K}^{39} \text{ and (a/h)} = 700 \text{ megacycles, (b/c)} = 0.5 \text{ megacycles for Cl}^{35}. \) The value of \( a \) in the case of \( K^{39} \) is in good agreement with the value obtained earlier from the width of the resonance line with unresolved hyperfine structure. Lord [60] applied Feher's double resonance technique to F centers in LiF crystals. He succeeded in making the previous results concerning the hyperfine interaction between the F electron and the nuclei of the second coordinate sphere more precise.

It is clear from all the foregoing that it would be of undoubted interest to measure paramagnetic resonance in crystals containing only atoms whose nuclear spins are equal to zero. Wertz and his coworkers [56] came close to solving this problem by setting up paramagnetic resonance experiments on F centers in MgO crystals. These crystals, to be sure, cannot be classified as ionic, but we shall consider them in the present section, since the properties of interest to us are independent of the character of the chemical bond.

Two methods were used for coloring single crystals of MgO: bombardment with a flux of neutrons of intensity \((1-3) \cdot 10^{19} \) particles per square centimeter (between 5 and 7 neutrons are necessary to form one center) and heating in magnesium vapor to a temperature of 1500°C, followed by rapid cooling and x-raying.

Only the odd isotope Mg\(^{25}\), the abundance of which in natural mag-
nesium is 10 or 11%, has in magnesium oxide a nonzero nuclear spin. Consequently, 53% of the magnesium isotope octahedra surrounding the vacancy contain only the isotopes Mg$^{24}$ and Mg$^{26}$, 36% of the octahedra contain only a single Mg$^{25}$ atom, and 10% contain each two Mg$^{25}$ atoms. One can expect the paramagnetic resonance spectrum to consist of a narrow bright central line, a broad weak line containing six hyperfine components ($I(Mg^{25}) = 5/2$), and a family of 11 even weaker lines. The central line actually turns out to be very narrow, approximately 0.7 oersted wide; its position corresponds to the $g$ factor, which coincides accurate to 0.0001 with the value for the free electron. The hyperfine structure has a rather complicated character, owing to the anisotropy of the electron-nuclear coupling constant.

From the value of the isotropic part of the hyperfine structure we can conclude with the aid of (6.2) that $|\psi(Mg)^2 = 0.276 \cdot 10^{24} \text{ cm}^{-3}$, whereas in the free doubly charged magnesium ion $|\psi(Mg^{2+})^2 = 17.1 x x 10^{24} \text{ cm}^{-3}$. It is interesting to compare these values with the corresponding values for potassium in the KCl crystal: for the F center we have $|\psi(K)^2 = 0.70 \cdot 10^{24}$, and for the free potassium ion $|\psi(K^+)^2 = 7.5 \cdot 10^{24} \text{ cm}^{-3}$. From these data we see that the electron is localized in the MgO crystal inside the vacancy to a considerable greater degree than in KCl, and this apparently is explained by the relatively larger Madelung energy in divalent crystals.

Paramagnetic resonance on F centers can be used for certain practical purposes. By measuring the relative intensity of the paramagnetic absorption lines it becomes possible to determine the number of F centers with an accuracy which is 1 or 2 orders of magnitude higher than the accuracy of all other methods. Gordy [61] points out that paramagnetic resonance absorption on F centers can be used to construct a meter to measure the intensity of neutron and x-ray fluxes.
Let us proceed to consider the theory of paramagnetic resonance on F centers. As is well known, in the general theory of F centers, two models are used, the continual [62] and the orbital [63]. It is shown in [59, 64] that even elementary calculations based on the orbital model yield the correct order of magnitude of the displacement of the $g$ factor and the width of the resonance line. According to the orbital model, the F center electron is a valence electron, bound in succession to each of the six atoms in the nearest surrounding of the vacancy. In other words, the wave function of the F electron is in first approximation a linear combination of the $g$ functions pertaining to the metal atoms situated around the vacancy:

$$\psi = \frac{1}{\sqrt{\delta}} \sum_{i=1}^{6} \psi_i$$

(6.33)

It is assumed here that the $\psi$ functions of the different atoms do not overlap one another. Since a negative vacancy is equivalent to a positive charge, it is necessary to take into consideration the polarization of the metal atoms under the influence of the given charge. Calculation by a perturbation method shows that a $p$ function is added to the $g$ function of the valence electron, so that for one of the atoms we have

$$\psi_i = C \left[ \psi_r - \frac{1}{\sqrt{2}} (\phi^1_r - \phi^{-1}_r) \right]$$

(6.34)

where $\epsilon$ is a numerical factor smaller than unity and $C$ is a normalization factor. The wave functions of the other atoms are constructed in analogous fashion. Calculations with the aid of hydrogen functions yield $\epsilon = 0.9$. In the next approximation it is necessary to take into account the spin-orbit coupling $\lambda LS$, as a result of which the $\psi$ function assumes the form
Here $\Delta$ is the interval between the $s$ and $p$ levels. Calculation with the aid of this function yields the following expression for the displacement of the $g$ factor [64]:

$$
\Delta g = -\frac{4}{3} \frac{\lambda}{\Delta} \varphi(x).
$$

(6.36)

If we use the known value for potassium $\Delta = 13,200$ cm$^{-1}$ and $\lambda = 38$ cm$^{-1}$, we obtain $\Delta g = -1.7 \cdot 10^{-3}$, which coincides in order of magnitude with the experimental value $\Delta g = -0.007 \pm 0.001$.

To calculate the resonance line broadening due to the hyperfine interactions of the F electron with the nuclei of the atoms surrounding the vacancy [53], we employ the Hamiltonian

$$
\mathcal{H}' = \sum_i A_i \delta_h.
$$

(6.37)

where

$$
A_i = -\frac{16\pi}{3} \frac{\mu_i}{I_i} |\psi(0)|^2.
$$

(6.38)

Here $\mu_i$ is the magnetic moment of the nucleus of the $i$-th atom, $I_i$ is the spin of the given nucleus, and $\psi(i)$ is the value of the normalized wave function of the electron at the location of the $i$-th nucleus.

With the aid of the Hamiltonian (6.37) we can readily calculate the second moment of the paramagnetic resonance absorption line; its value is

$$
M_s = \frac{1}{3} \sum_i A_i I_i(I_i + 1).
$$

(6.39)

It can be shown that the absorption line has a nearly Gaussian shape, and consequently, the line width is $\Delta v = 2.36 \sqrt{M_2}$. The hyperfine structure will be anisotropic, owing to the presence of the $\psi_p$ functions in Expression (6.35). If we take into account only the principal isotropic part of the hyperfine structure, then we readily ob-
tain from (6.35), (6.38), and (6.39)

\[ \Delta \nu = \frac{2 \beta}{\sqrt{1 + \frac{1}{4} A} \cdot \frac{V}{18} \frac{V/18}{1 + s} \cdot A. } \]  

(6.40)

Here \( A \) is the constant of the hyperfine interaction between the electron and the metal nucleus closest to the vacancy, and \( I \) is the spin of this nucleus. For potassium \( I = 3/2, A = 0.0077 \text{ cm}^{-1} \), and the line width is therefore 50 oersted, which is in splendid agreement with the experimental value \((54 \pm 2)\) oersted.

The authors of [53] have also estimated the width by using the continual model. According to this model, the F center is made up of an electron moving in a spherically symmetrical potential field, the center of which coincides with the vacancy, and the wave function of the electron covers a large number of atoms. The calculated resonance line width turned out to be several orders of magnitude lower than the experimental value. It was therefore concluded that the continual model is incompatible. The correctness of this conclusion was disputed by several workers [65, 66, 67]. Deygen [67] called attention to the following important circumstance. Kip, Kittel, et al. use in their calculations Formula (6.38), in which the value of the wave function taken for \( \psi(1) \) is the one given by the continual model at the point where the nucleus \( i \) is situated. Yet the formula (6.38), which is due to Fermi [68], holds true only when the symmetry center of the wave function coincides with the nucleus, something that precisely does not occur in the F center, since the nuclei of the ions are shifted relative to the symmetry center of the wave function by an amount equal to the lattice constant. The question of the hyperfine interaction between the electron and a nucleus shifted relative to the symmetry center of the wave function calls for a special analysis. Deygen offers a solution of this problem, using for the wave function of the F center the
following expression [69]:

\[ \psi(r) = \frac{1}{\Omega} \left( 1 + ar \right) e^{-\frac{r^2}{\Omega^2}}. \]  

(6.41)

Assuming that the length \((1/\alpha)\) does not far exceed the lattice constant, and therefore confining himself to a consideration of the hyperfine interaction with the nuclei of the first coordination sphere, he obtained for the resonance line width in KCl a value on the order of 1-2 oersted. With an aim toward improving this result, Deygen replaced the "smoothed" function (6.41) by a so-called detailed wave function in the form

\[ \psi(r) = \Omega^2 \psi_u. \]  

(6.42)

Here \(\Omega\) is the volume of the principal region in the crystal and \(\psi_u\) is the normalized Bloch wave function of the electron at the bottom of the conduction band, which, as is well known, represents in the strong-coupling approximation a linear combination of the atomic wave functions. The line width calculated with the aid of the detailed function turned out to be equal to 15 oersted, which is already quite close to the experimental value.

In order to ascertain whether the line width is affected by an account of relativistic corrections, the usual Pauli equation for the motion of the electron was replaced in the calculation of the hyperfine structure by the Darwin relativistic approximation [70]; the corrections turned out to be negligible. Zevin [71] developed the theory proposed by Deygen and obtained a general expression for the spin Hamiltonian, describing the interaction between the F center electron and the nuclei of the atoms surrounding the vacancy. Shul'man [72], using the given spin Hamiltonian, calculated the broadening brought about by the second coordination sphere, consisting of the halide atoms. For the KCl crystal, the contribution made by the chlorine atoms to the
Gourary and Adrian [73] used a wave function obtained by a simplified Hartree method to calculate the hyperfine structure of paramagnetic resonance on F centers. The lattice ions were regarded here as being point charges. The distortions of the lattice near the vacancy were also taken into account. The theoretically obtained hyperfine splittings are in good agreement with the experimental results for LiF.

The method of Gourary and Adrian was applied to calculations of the isotropic and anisotropic structures of the KCl spectrum [74]; the theoretical results are in good agreement with the experimental data of Feher [59]. Adrian [75] pointed out the possibility of establishing a simple connection between the displacement of the $g$ factor and the anisotropic hyperfine structure, since both these quantities are determined by the average value of $1/r^3$. Thus, for KCl, starting from the experimental value of the hyperfine structure anisotropy, theory yields $\Delta g = -0.0053$ while experiment gives $\Delta g = -0.007$. A good agreement with the experimental results of Feher was also obtained by Blumberg and Das [76], who used in their calculations of the hyperfine structure the $g$ factor displacement and the wave function obtained under the following assumption: the vacancy is replaced by a potential well and the lattice by a system of corresponding point charges.

In developing the theory of paramagnetic resonance on F centers, we used the de Boer model [62], according to which the F center is an electron localized near a vacant lattice site. It is universally accepted that centers of this type are formed in alkali halide crystals. In silver halide crystals one might think that the F centers would be of the Hilsch and Pohl type [62], i.e., they would comprise metal atoms that have penetrated the interstices of the crystal lattice. Glinchuk and Deygen [77] calculated the hyperfine structure of the en-
ergy levels of an F center of this type, using the NaCl crystal as an example. Using the wave functions of both the continual and the orbital models, they obtained spin Hamiltonians with which they calculated the paramagnetic resonance spectrum, the line shapes, and the line widths. It turned out that the results differ qualitatively from those previously obtained for the de Boer model. Thus, a study of paramagnetic resonance uncovers a possibility of choosing between two existing F center models, something particularly valuable inasmuch as so far no other effective methods have been proposed for solving this problem.

Lord et al. [78] have found indirect proof for the existence of paramagnetic resonance absorption on an M center (a combination of an F center and a pair of vacant sites). It was established that the second moment of the resonance line increases appreciably whenever a LiF crystal is exposed to x-rays so as to be able to observe in it, by optical means, an increase in the number of M centers compared with the number of F centers.

Paramagnetic resonance was investigated in greater detail on V centers [79, 84]. In the studied alkali halide crystals, these centers were produced by means of x-rays at liquid nitrogen temperatures. Castner, Knzsig, and Woodruff [82, 83], who have made the most complete study of this problem, interpret their experimental results with the aid of the following V center model: 1) the x-radiation causes an electron to break away from the halide ion, and the resultant electron hole is distributed among two neighboring ions oriented along the [110] axis of the crystal; 2) the molecular ion $X_2^-$ produced in this fashion (where $X$ stands for the halogen) is connected with neither the vacancy formation nor with the distortions of the crystal lattice.

Paramagnetic resonance was investigated in crystals of LiF, KCl,
KBr, and NaCl. The resonance lines had a hyperfine structure due to the interaction between the electron hole and the nuclei of both atoms, forming the $X^-$ molecule. The number and intensity of the hyperfine components in the LiF crystal agrees with a value $I = 1/2$ for the nuclear spin of fluorine, if one takes into account the selection rules for the singlet and triplet nuclear spin states; in precisely the same manner, the spectra of the remaining investigated crystals consisted of seven approximately equidistant components with intensity ratio 1:2:3:4:3:2:1, which corresponds to a nuclear spin $I = 3/2$ for the Cl or Br atoms. To interpret the paramagnetic resonance spectrum, starting with the $X^-$ molecular ion model, one can obtain a spin Hamiltonian of the type (6.31) by taking the [110] crystal axis to be the Z axis. The principal values of the g-tensor components are listed in Table 6.4, which shows also the absorption line widths.

**TABLE 6.4**

<table>
<thead>
<tr>
<th>Substance</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>Maximum error</th>
<th>Width, oersted</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>2.023</td>
<td>2.032</td>
<td>2.003</td>
<td>±0.0010</td>
<td>12.1±0.3</td>
</tr>
<tr>
<td>KCl</td>
<td>2.043</td>
<td>2.047</td>
<td>2.010</td>
<td>±0.0001</td>
<td>1.34±0.03</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.089</td>
<td>2.087</td>
<td>2.009</td>
<td>±0.0001</td>
<td>4.5±0.01</td>
</tr>
<tr>
<td>KBr</td>
<td>2.179</td>
<td>2.173</td>
<td>1.980</td>
<td>±0.0001</td>
<td>2.8±0.1</td>
</tr>
</tbody>
</table>

1) Substance; 2) maximum error; 3) width, oersted.

The main reason for the broadening of the resonance line are the hyperfine interactions between the electron hole and the nuclei surrounding the V center. The line shape is nearly Gaussian.

For Cl$_2^-$, calculations of the $g$ factor were made by the molecular orbital method [85], and yielded values close to the experimental ones.

Kmnzig and Woodruff [86] observed paramagnetic resonance in the KCl crystal on H centers, which have a spectrum similar to that of V centers, but of more complicated nature. The latter is due to the fact...
that in the case of the H centers the electron hole is shared by four chlorine ions arranged on a single line.

Kawamura and Ishiwatari [87] observed paramagnetic resonance on Z\textsubscript{1} centers in KCl crystals. The Z\textsubscript{1} centers are produced in alkali halide crystals in which divalent metals have been introduced. A possible model of the Z\textsubscript{1} center is that of a singly ionized divalent metal atom, which occupies the place of the alkali metal ion. The experiments involved crystals doped with Ca and Sr atoms in amounts of approximately \(10^{17}\) cm\(^{-3}\). Since the spins of the calcium and strontium nuclei are equal to zero, there is a deep analogy between paramagnetic resonance on Z\textsubscript{1} and on F centers. The essential difference lies in the fact that the broadening of the Z\textsubscript{1}-center resonance line occurs primarily as a result of hyperfine interactions with the nuclei of the anions, whereas in F centers the principal role is assumed by the nuclear spins of the cations. Measurements have shown that the absorption line has a Gaussian form, a width \(\Delta H = 79\) oersted, with \(g = 1.999\).

§6.6. Irradiated Crystals with Covalent Bond

Paramagnetic resonance can serve as an effective method for investigating imperfections in crystals. This possibility is connected, first of all, with the fact that the occurrence of many types of imperfections in diamagnetic crystals is accompanied by formation of paramagnetic centers. Second, in paramagnetic crystals, imperfections of the dislocation type change the intercrystalline field and cause shifts in the paramagnetic resonance lines and a change in the spin-lattice interaction. In the last two sections we have considered paramagnetic resonance due to lattice defects of the inclusion, electron, or hole type. In the present section we discuss also a few examples and primarily the effect in neutron-bombarded diamond.

Griffiths, Owen, and Ward [88] carried out measurements at fr€-
quencies $v \approx 9000$ and $25,000$ megacycles in the temperature interval $20-280^\circ K$. The existence of two types of resonance lines was established:

a) Isotropic line with a spectroscopic splitting factor \( g = 2.0028 \pm 0.0006 \). The intensity and width of the line increase with increasing duration of irradiation. Heating to $1000^\circ C$ causes the effect to disappear. An analogous change occurs in the coloring of the crystal. After prolonged neutron bombardment, the line width reaches $100$ oersted at a temperature of $290^\circ K$; the width of the line is reduced to one half when the temperature is decreased to $90^\circ K$.

b) Family of $12$ weak anisotropic lines, symmetrically situated relative to the central peak. The width of each of these lines is independent of the temperature and is approximately equal to $5$ oersted. In this case the effect does not decrease upon heating to $1000^\circ C$. The paramagnetic absorption spectrum can be described with the aid of a spin Hamiltonian $\hat{H} = \vec{g} \cdot \vec{H} S + D S_z^2$ if one admits the existence of paramagnetic centers with spin $S = 1$. It is necessary to assume here that the axis of the crystalline field is parallel to one of the edges of the tetrahedron made up of the carbon atoms. Thus, there exist six different orientations of paramagnetic centers, each of which has two absorption lines corresponding to the transitions $-1 \rightarrow 0$ and $0 \rightarrow 1$. The spin Hamiltonian constants have the following values: $D = 0.010 \text{ cm}^{-1}$, average value of the $g$ factor $\bar{g} = 2.0027 \pm 0.0005$ and $g_u/g_d = 1.00035 \pm 0.00005$.

The central isotropic line has apparently the following nature [89]. Let us consider an isolated vacancy, formed in the crystal lattice after the removal of one of the carbon atoms. Since diamond is not an ionic crystal, there are no grounds for expecting the vacancy to attract an electron or to contribute to its removal; it is more
likely that the vacancy is to be regarded as an electrically neutral stable formation. The vacancy is surrounded by four carbon atoms, in each of which one of the two covalent bonds is saturated and therefore each has an unpaired electron. It can be shown that one can apply to this four-electron system Hund's rule, according to which all electron spins are parallel to one another in the ground state, and consequently the spin of the entire system is $S = 2$. In this state, the orbital wave function is nondegenerate and consequently the paramagnetism will in first approximation be of pure spin nature.

The spin orbit coupling in the free carbon atom is very weak. Furthermore, owing to the high symmetry of the crystalline field, the spin level splitting due to the spin-orbit interaction becomes different from zero only in the fourth perturbation theory approximation. We can therefore conclude that this splitting should be negligibly small. An estimate shows that its order is $10^{-5}$ cm$^{-1}$. For the same reason, the deviation of the $g$ factor from its value for the free electron should also be very small.

It is more difficult to present a theoretical interpretation of all the peculiarities of the anisotropic paramagnetic resonance spectrum. It is evidently connected with the carbon atoms which are situated in the interstices of the crystal lattice.

Let us proceed to an examination of paramagnetic resonance on color centers produced in quartz after exposure to x-rays; these centers disappear upon heating to $350^\circ$C. Griffiths, Owen, and Ward [88] first observed this effect in quartz and established that the paramagnetic absorption is proportional to the optical absorption. Measurements of the paramagnetic resonance spectrum were made at temperatures of 90 and 20$^\circ$K; at higher temperatures, the lines broadened strongly. The existence of six types of paramagnetic centers was established,
with different magnetic-axis orientations. A complicated hyperfine structure of the lines was also observed, and could be resolved at 20⁰K. The spectrum can be described with the aid of a spin Hamiltonian with the following constants: \( S = \frac{1}{2}, I = \frac{5}{2}, g_H = 2.06 \pm 0.005,\)
\( g_i = 2.00 \pm 0.005, A = 4.8 \cdot 10^{-4} \text{ cm}^{-1}, B = 5.6 \cdot 10^{-4} \text{ cm}^{-1}, \) and \( P = -0.4 \times 10^{-4} \text{ cm}^{-1}. \) The symmetry axes of \( g \) tensors of paramagnetic centers of different types are approximately parallel to the lines joining the pairs of silicon atoms within the crystal cell. The principal axes of the \( g \) tensor and of the hyperfine structure tensor do not coincide. The symmetry axes of the hyperfine structure tensor are parallel to the Si-O bonds.

![Fig. 6.5. Electronic structure of paramagnetism carriers in irradiated quartz.](image)

The following interpretation can be offered for all these experimental facts [82]. The various impurities contained in the quartz include also aluminum, the atoms of which replace a small part of the silicon atoms. Before the quartz is irradiated, the aluminum atoms are \( \text{Al}^- \) ions, which have the same number of electrons as the silicon atoms. Consequently, the crystal is not colored and there are no paramagnetic centers. The negative charge of the \( \text{Al}^- \) ions is neutralized by the positive ions \( \text{H}^+, \text{Li}^+, \text{and Na}^+ \), which are located in the interstices of the crystal lattice. Irradiation with x-rays causes the atoms to be ionized and uncompensated electron spins appear. Calculations made by the electronic orbital method show [90] that the electron structure of the paramagnetism carriers has essentially the form shown in Fig. 6.5a. The nonzero spin belongs to the positive oxygen ion. Partially mixed
in with this structure is another one (Fig. 6.5b), containing neutral oxygen and aluminum atoms, and consequently, a hyperfine structure of the paramagnetic resonance lines is produced.

Paramagnetic resonance in single crystals of quartz was observed also by irradiation with fast neutrons \[91, 92, 85a\]. The observations were made at room temperature. The effect is apparently not connected with impurities and has an entirely different nature, as evidenced even by the absence of a hyperfine structure for the absorption lines. It is probable that the resonant absorption, as in the case of diamond, is due to broken bonds which result from the occurrence of the vacancies in the basic SiO$_4$ tetrahedron. An analogous effect was observed at $4.2^\circ$K in silicon bombarded by neutrons \[93\]. In explaining the effect in irradiated quartz crystals it must be borne in mind that a similar paramagnetic resonance spectrum occurs in silicate glasses \[92, 94\].

Paramagnetic resonance was observed at temperatures 4-225$^0$K in $\gamma$-irradiated ice \[95, 96\]. The hyperfine structure of the line is connected with the protons in ordinary ice and the deuterons in D$_2$O. The nature of the paramagnetism carriers cannot be regarded as fully explained as yet.

§6.7. **Metal-Ammonia Solutions. Paramagnetic Resonance on Polarons and Excitons**

Alkali and alkali-earth metals are readily dissolved in ammonia. The solubility of sodium and potassium at the boiling temperature of ammonia (-33.35$^0$C) is approximately 5.4 and 4.9 mole per liter, respectively; the solubility changes little with temperature. A distinguishing property of these solutions is their high electric conductivity, which approaches that of metals in order of magnitude. Measurements of the dependence of the static magnetic susceptibility on the
concentration of the solution have shown that at large concentrations the addition of metal is not accompanied by an increase in the susceptibility.

The first measurements of paramagnetic resonance in metal-ammonia solutions were made in the microwave band [97, 98, 99]. One exceedingly narrow absorption line, with a width not larger than 0.2 oersted, was established. Later experiments were made usually at lower frequencies [100, 101, 9], which called for the application of a static magnetic field with intensity of only a few oersteds; it was necessary besides to take account of the earth's field. The measurements were carried out at temperatures from -80 to 20°C. For potassium solutions, the spectroscopic splitting factor is \( g = 2.0012 \pm 0.0002 \). For other metals it deviates by less than 0.005. We see that the \( g \) factor is close to (but noticeably smaller than) the \( g \) factor of the free electron. Table 6.5 lists data for the resonance line widths, showing that the width decreases with increasing temperature and increases with increasing concentration. In addition to metal-ammonia solutions, solutions of lithium in methylamine [99, 9] and in ethylenediamine [99] were investigated. Galkin et al. [102] observed paramagnetic resonance in solutions of NaCl in ammonia after passing current through the solution. Apparently the current causes decomposition of the NaCl and thus results in an ordinary solution of Na.

Blume [103] measured the times of longitudinal and transverse relaxation (\( T_1 \) and \( T_2 \)) at 17.4 megacycles by means of pulse techniques. The time \( T_2 \) was determined by measuring the time of fall-off of the free induction signal, which was followed at 90° by a pulse (see §8.4). It ranges from 3.2 to 0.7 microseconds when the sodium concentration in \( \text{NH}_3 \) increases from 0.03 to 0.75 mole/liter. The time \( T_1 \) was measured in solutions having concentrations from 0.24 to 0.5 mole/liter.
TABLE 6.5

<table>
<thead>
<tr>
<th>Substance</th>
<th>2 Width, Å</th>
<th>3 Temperature, °C</th>
<th>4 Concentration, cm⁻³</th>
<th>5 Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-NH₃</td>
<td>0.1</td>
<td>-72</td>
<td>0.2</td>
<td>[9]</td>
</tr>
<tr>
<td>Na-NH₃</td>
<td>0.13</td>
<td>-75</td>
<td>0.1</td>
<td>[9]</td>
</tr>
<tr>
<td>K-NH₃</td>
<td>0.1</td>
<td>-70</td>
<td>0.08</td>
<td>[9]</td>
</tr>
<tr>
<td>K-NH₄</td>
<td>0.05</td>
<td>-33,45</td>
<td>0.08</td>
<td>[100]</td>
</tr>
<tr>
<td>K-NH₅</td>
<td>0.027</td>
<td>20</td>
<td>0.08</td>
<td>[100]</td>
</tr>
<tr>
<td>K-NH₆</td>
<td>0.08</td>
<td>20</td>
<td>0.43</td>
<td>[100]</td>
</tr>
<tr>
<td>Rb-NH₃</td>
<td>0.16</td>
<td>-70</td>
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<td>[9]</td>
</tr>
<tr>
<td>Cs-NH₃</td>
<td>0.4</td>
<td>-70</td>
<td>0.5</td>
<td>[9]</td>
</tr>
<tr>
<td>Ca-NH₃</td>
<td>0.14</td>
<td>-70</td>
<td>0.05</td>
<td>[9]</td>
</tr>
<tr>
<td>Li-CH₄NH₃</td>
<td>0.8</td>
<td>-70</td>
<td>0.1</td>
<td>[9]</td>
</tr>
<tr>
<td>Li-NH₂CH₂NH₃</td>
<td>0.6</td>
<td>20</td>
<td>0.1</td>
<td>[9]</td>
</tr>
</tbody>
</table>

1) Substance; 2) width, cm; 3) temperature, °C; 4) concentration, mole/liter; 5) literature.

It was found that $T_1 = T_2$ accurate to within 10%.

Kaplan and Kittel [104] explained the experimental fact by means of the Ogg model [105], which is based on the following assumptions: 1) the alkali metal atoms dissociate when dissolved; 2) the electrons separated from the metal atoms are localized in the cavities formed in the liquid, which have volumes equal to that of from 2 to 4 molecules of NH₃; 3) the wave function of the electron connected with the cavity is a linear combination of hydrogen functions pertaining to the protons of the NH₃ molecules located around the cavity; 4) the conduction band lies one electron volt below the energy level of the bound state of the electron; 5) some cavities contain one electron each (e centers) and some contain two electrons (e₂ centers); the distribution of the electrons among the e and e₂ centers is determined by the equilibrium conditions with respect to the reaction $e + e \rightleftharpoons e₂ + 0.2$ ev.

Between the e centers and F centers considered in §6.5 there is a great similarity. Kaplan and Kittel therefore assume that the absorption line broadening has in both cases the same nature, namely the hy-
perfine interaction between the localized electron and the spins of the surrounding nuclei. An estimate of the width, made as in the case of §6.5 by the method of molecular orbitals, yields $\Delta v_0 = 7g\beta/h$. However, there exists an essential difference, which we did not take into consideration, between the $e$ and $F$ centers. The large mobility of the liquid is capable of appreciably decreasing the width of the resonance line. The correlation time (see §5.6) can be estimated with the aid of the Debye expression for the rotational dipole relaxation:

$$\tau_c \approx \frac{3kV}{M},$$

(6.43)

where $V$ is the volume of the molecule. Hence $\tau_c \approx 10^{-11}$ sec. We see that the correlation time is much smaller than the transverse relaxation time $\sim 1/\Delta v_0$ and therefore the motion of the molecules should narrow down the resonance line appreciably. The width obtained as a result can be estimated by the formula $\Delta v \sim (\Delta v)^2\tau_c$, from which it follows in our case that $\Delta H \approx 0.01$ oersted. So good an agreement with the experimental data is accidental, bearing in mind the crudeness of the theoretical estimate.

At large solution concentrations one can expect the dipole-dipole interactions between different localized electrons to start playing a role. The influence of dipole-dipole interactions on the resonance width can be estimated by means of Formula (5.14). Numerical calculation shows that this broadening mechanism can become significant at concentrations exceeding 0.1 mole/liter.

We know that if $\tau_c \ll 1/\Delta v_0$, we have $T_2 = T_1$, which, as we have seen, has been confirmed by direct measurements. We note that both mechanisms which we have considered for the broadening lead to a proportionality between the line width and the coefficient of viscosity. Experiment confirms this theoretical conclusion, too.
The Ogg e-center model, on which the theory of paramagnetic resonance line broadening considered here is based, was seriously criticized by Deygen [106], who developed a theory of optical, magnetic, and other properties of metal-ammonia solutions by assuming that upon dissociation of the metal atoms in the ammonia the electrons go over into the polaron state. According to Deygen, it is the polarons and not the local electron centers that cause the remarkable features of solutions of metals in ammonia. Deygen and Pekar [107] have shown that, in first approximation, the hyperfine interaction does not change the polaron energy and consequently it cannot cause broadening of the paramagnetic absorption line. The exceeding narrowness of the resonance lines in metal-ammonia solutions was regarded as a direct proof of the existence of polarons in these substances.

Deygen and Pekar considered also the possibility of producing exciton concentrations high enough to permit observation of paramagnetic resonance absorption of energy from a radiofrequency field by excitons. The stationary exciton concentration \( N \) can obviously be determined from the following formula

\[
N = \frac{\eta n}{\pi},
\]  

(6.44)

where \( \tau \) is the exciton lifetime, \( \Pi \) the flux of light energy per square centimeter per second, \( \kappa \) the coefficient of exciton absorption of light in the crystal, and \( \nu \) the frequency of absorbed light. If we assume \( \tau = 10^{-8} \) sec, \( \hbar \nu \approx 1 \) ev, \( \kappa \approx 10^5 \) cm\(^{-1} \), \( \Pi \approx 1 \) w/cm\(^2\), then we obtain \( N \approx 10^{16} \) cm\(^{-3}\). Thus, observation of paramagnetic resonance with the aid of modern technological means is fully feasible. In order to reduce the nonradiative deexcitation of the excitons, it is desirable to choose crystals free of impurities and to use low temperatures. It must be borne in mind that, as in the case of polarons, there will be
no broadening of paramagnetic resonance line due to hyperfine interaction between the exciton and the spins of the surrounding nuclei.

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Levy [9], investigating the temperature dependence of the resonance line width of lithium, established the presence of a jump at approximately 800K, this being apparently connected with the existence of a phase transition.

Gadolinium, the ions of which also have an odd number of electrons, will be considered separately.

A natural sample of silicon contains 4.68% of the isotope Si$^{29}$.

Recently, investigations of paramagnetic resonance in germanium have yielded positive results [110].
Chapter 7
FREE RADICALS

§7.1. Introduction. Hyperfine Structure of Paramagnetic Resonance Lines in Solutions of Free Radicals

The study of free radicals, i.e., molecules in which at least one electron has uncompensated spin, is one of the most important fields of application of paramagnetic resonance and attracts at present a very large number of investigators. It is sufficient to state that the total number of papers devoted to this problem already amount to several hundreds. We are therefore unable to give in our book an exhaustive exposition of all the results obtained. We refer the reader for details primarily to Ingram's book [1], and also to the reviews by Wertz [2] and by Blyumenfeld and Voyevodskiy [3].

The variety of substances that have to be considered in the present chapter is so great that their rigorous classification is very difficult.

Paramagnetic resonance in free radicals was first observed in 1947 by Kozyrev and Salikhov [4] with pentaphenylcyclopentadienyl $C_{35}H_{25}$ as an example. Solid $C_{35}H_{25}$ disclosed a single line with a $g$ factor which, within the limits of the low measurement accuracy, differed little from two. It was therefore concluded that this free radical has essentially a spin magnetism, in accordance with the measurements of the static magnetic susceptibility of this substance.

In 1949, a systematic study of the paramagnetic spectra in free radical was initiated. By now numerous classes of these substances have
been investigated, for example organic derivatives of divalent nitrogen, radical ions of hydrocarbons, heptaquinones, compounds of the peroxide type, biradicals, etc.

An essential feature of paramagnetic resonance spectra in free radicals is the fact that the $g$ factor is very close to its value for the free electron $g_{\text{spin}} = 2.0023$, i.e., pure spin magnetism. Thus, for ordinary organic free radicals containing only C, H, O, and N atoms, the difference $g - g_{\text{spin}} = \Delta g$ does not exceed 0.002-0.003. This practically complete lack of orbital magnetism is due to the fact that the molecules of the free radical have low symmetry, and consequently the orbital degeneracy is completely lifted; there is no doubt that in many of these cases the lowering of the symmetry is brought about by the Jahn-Teller effect. In connection with so strong a suppression of the orbit, the spin-orbit coupling in free radicals is small and the spin-lattice relaxation time is long (usually on the order of $10^{-7}$ sec).

A second feature characterizing practically all free radicals which in the condensed phase are in pure undiluted state is the exceeding naturalness of the paramagnetic resonance lines: their width as a rule is of the order of one or several oersted. This value is approximately 100 times smaller than that calculated from magnetic dipole interactions without account of exchange. Thus, in free radicals we have an example of a system with tremendous exchange forces. Accordingly, the absorption line shape in these radicals is close to Lorentzian, and the line width is determined by the spin lattice interactions [5].

It must be noted that in addition to exchange in free radicals, there exists still another important mechanism whereby the paramagnetic resonance lines become narrower; this mechanism was considered in [6]. It consists in a reduction in the effectiveness of the local magnetic fields, due to the motion of the strongly delocalized unpaired electron.
within the molecule of the free radical. There are certain experimental confirmations of the reality of this mechanism.

The narrowness of the lines makes the height of the resonance peaks in free radicals very large, thus facilitating their detection. Thus, for the substance extensively used as the standard calibrating substance in research on paramagnetic resonance, αα-diphenyl-β-picrylhydrazyl (DPPH) this line can be observed with modern apparatus in the presence of only $10^{-13}$ mole of DPPH in the sample. Paramagnetic resonance is therefore the best of the existing methods for detecting free radicals (at least in condensed phases).

The significance of paramagnetic resonance to chemistry is not limited to this. An investigation of the spectra of paramagnetic resonance in solutions containing free radicals yields very valuable information with respect to the nature and properties of the latter. This information is obtained primarily by studying the hyperfine structure of paramagnetic resonance spectra. A well resolved hyperfine structure is observed only at sufficiently low concentration $N$ of the free radical in the solution (usually with $N \leq 10^{-3}$ mole/liter), when the exchange interactions between the molecules of the free radicals turn out to be practically completely eliminated. In this case the number of hyperfine line components is frequently very large and their relative intensities vary. The occurrence of such a structure is explained by the considerable delocalization of the unpaired electron interacting with the summary spin $I_{\text{summ}}$ of the several atomic nuclei contained in the molecule. Therefore an analysis of the observed hyperfine structure leads to conclusions both concerning the nature of the radical itself and concerning the character of the delocalization of the molecular orbit of the unpaired electron. We shall illustrate this using the simplest example of αα-diphenyl-β-picrylhydrazyl, the structure
The spectrum observed in dilute solutions of this radical consists of five lines with intensity ratio 1:2:3:2:1. It can be explained by assuming that the density of the unpaired electron cloud is equally distributed between the two central nitrogen atoms. Inasmuch as the spin of the \( ^{14}\text{N} \) nucleus is equal to one, we must have \( 2I_{\text{sum}} + 1 = 5 \) hyperfine components. The ratio of the intensities of the individual components follows directly from an examination of Fig. 7.1, which shows first the hyperfine splittings of the ground level, due to the first \( ^{14}\text{N} \) nucleus, and then the splittings of equal magnitude, due to the second nucleus of \( ^{14}\text{N} \), superimposed on the former splittings.

A solution containing the negative p-benzoheptaquinone ion also displays five peaks, but with intensity ratio 1:4:6:4:1. Simple arguments analogous to the preceding ones show that in this case there are identical interactions between the electron spin and all four protons of the molecule, i.e., that the unpaired electron density is distributed over the entire ring (we recall that the spin of the nuclei \( ^{12}\text{C} \) and \( ^{16}\text{O} \) is equal to zero, and consequently these nuclei do not influence the hyperfine structure).
If the electron does not interact to the same degree with all the nuclear spins, the picture of the spectrum becomes more complicated. In particular, if the constant of hyperfine interaction with one group of nuclei, having a summary spin $I_1$, turns out to be much larger than the constant of interaction with another group with summary spin $I_2$, then each hyperfine structure peak resulting from the stronger interactions and consisting of $(2I_1 + 1)$ components breaks up into $(2I_2 + 1)$ close-situated peaks due to the weaker interaction. Finally, in the case when the constants for the interaction between the electron spin and each of the atomic nuclei a, b, c, ... of the molecule, enclosed by the delocalized orbit, turn out to be different and their ratios to one another are not whole numbers, we should have a spectrum consisting of $(2I_a + 1)(2I_b + 1)(2I_c + 1) ...$ components.

We note that, strictly speaking, direct conclusions concerning the distribution of electron density can be drawn from data on paramagnetic resonance only if the atoms enclosed in the delocalized orbits are completely equivalent (as is the case, for example, in heptaque none). For atoms that are not chemically equivalent (as are the nitrogen atoms in DPPH), such a treatment is only very approximate [3].

Let us proceed now to discuss the causes of the very possibility of occurrence of a hyperfine structure in paramagnetic resonance spectra of aromatic free radicals, such as, for example, the negative ions of aromatic hydrocarbons.

In order for hyperfine splitting different from zero to exist it is necessary that the electron density on the nuclei also be finite. Therefore, a direct interaction between an unpaired $\pi$-electron of an aromatic free radical with ring protons is impossible, for the latter are located in the plane of the ring, where the density of the $\pi$-electron cloud is equal to zero. Thus, it appears at first glance that the
hyperfine structure in paramagnetic resonance spectra of aromatic free radicals should be generally nonexistent. Yet experience shows the opposite to be true.

An attempt to explain the observed effect with the aid of an analysis of the proton vibrations normal to the plane of the ring has not led to any success. It was therefore assumed (in analogy with the assumption of the theory of hyperfine structure in ionic crystals, considered in Chapter 3), that the unpaired electron of the aromatic radicals actually has a small admixture of the excited \( \sigma \) state. A quantitative calculation of the configuration interaction for aromatic radicals was made by Weissman [7], McConnell [8], and others [9], [10].

According to [7], the ground state of the free aromatic radical is described as follows: (filled orbits) \( \sigma_B^2 \pi \), where \( \sigma_B \) is the molecular orbital binding C and H. A possible excited state that mixes with the ground state is: (filled orbits) \( \sigma_B^1 \pi (\sigma_A)^1 \), where \( \sigma_A \) is the disintegrating orbit. Since one of the conditions of the configuration interaction is the requirement that both interacting states have the same symmetry with respect to reflection in the plane of the ring, an admixture of the state: (filled orbits) \( \sigma_B^1 \pi^2 \) is impossible.

It follows from theory that the hyperfine splitting \( A' \), expressed in oersted, produced by the proton bound with the given carbon atom, is directly proportional to the density \( \rho_1 \) of the unpaired electron cloud on the nucleus:

\[
A' = Q \rho_1. \tag{7.1}
\]

Here \( Q \) is a constant which is the same for all the aromatic free radicals, calculated to be approximately 28 oersted. This quantity is the distance between the peaks of the hyperfine structure under the condition that \( \rho_1 = 1 \), i.e., that the density of the electron cloud is entirely connected with a single C atom; on the other hand, if the den-
sity per one atom is < unity, then the constant $A'$ should be accordingly smaller. Therefore, if the unpaired electron is delocalized over the entire ring, then the distance between the extreme peaks of the hyperfine structure should again be close to 28 oersted.

For the majority of the investigated aromatic free radicals, experience has yielded quite good agreement with theory (see Table 7.3). In some cases, however, for example in perinaphthene, the total hyperfine splitting turns out to be appreciably larger than 28 oersted. This was attributed to the possibility of "negative spin density" on certain carbon atoms. The "negative spin density" is the result of the perturbing action of the unpaired electron on the orbit of the paired electrons. This perturbation leads to a partial decompensation of the initially paired spins and thus again gives rise to a new unpaired electron density with a spin direction opposite that prevailing on the perturbing electron. The new density has therefore a negative sign. The initial, positive density in turn increases further, so that the algebraic sum of the densities on all the atoms of the ring remains equal to unity as before. For the hyperfine interactions, however, the sign of the spin density is immaterial, and therefore the total hyperfine splitting, which is proportional to the sum of the absolute values of the spin densities, should become larger than 28 oersted as a result of the perturbation [11].

The theory of configuration interaction does not explain, however, the hyperfine splittings that arise as the result of the protons in the groups that replace the ring hydrogen atoms, such as the $\text{CH}_3$, which replace the hydrogens of the ring in tetramethylbenzoheptquinone.
The mechanism that ensures the hyperfine interaction with the protons of the substitutes consists of direct overlap of the $2p_z$ orbit of the carbon atom of the ring with a linear combination of the orbits of the two protons of the methyl group. To the extent that the $p_z$ orbit is a part of a system containing an unpaired electron, it becomes possible for spin density on the methyl group to appear. On the other hand, rotation of the methyl group relative to the ring causes the overlap of the electron clouds to become possible for all three hydrogen atoms of CH$_3$. This mechanism, due to the superconjugation phenomenon, is discussed in greater detail in [48, 49].

In the paramagnetic resonance spectra with which we dealt up to now and which are observed in liquid systems with low viscosity, containing free radicals, only the isotropic part of the hyperfine interactions plays an important role; the anisotropic part of these interactions is effectively averaged by the Brownian movement. In reference [12], which is devoted to paramagnetic resonance in the inorganic free radical ClO$_2$ (chlorine dioxide), it is shown that whereas in dilute liquid solutions of this radical one observes four hyperfine structure peaks (from $^{35,37}$Cl with $I = 3/2$) with distance $A' = 17$ oersted between peaks and with each peak $\Delta H = 8$ oersted wide, after freezing the solutions $A'$ becomes equal to 52 oersted with a corresponding increase in $\Delta H$. The increase in both $\Delta H$ and in $A'$ are due to the fact that freezing removes the averaging action of the motion.

An analogous result was obtained by Berthet [13], who investigated the hyperfine structure of the free radical (CH$_3$OC$_6$H$_4$)$_2$NO in solid and liquid solutions. Whereas in the liquid solution we have for the constant $A' = 11$ oersted and the intensities of all three peaks (from the $^{14}$N nucleus) are equal to one another, in solid solution we have $A' = 18$ oersted and the components have different intensities. Worthy of
notice is also the fact that the observed hyperfine structure appears in the solid solution at a 25% concentration of the free radical, whereas in liquid solutions it is observed only at 0.3% concentration. This difference may be evidence of the fact that in liquid solutions the free radicals are contained in the form of individual molecules only under appreciable dilutions.

§7.2. Free Radicals in the Pure State

Before we present the results obtained for different classes of pure free radicals, it is advantageous to dwell on the most investigated among these substances, αα-diphenyl-β-picrylhydrazyl, DPPH, as being one of the chemically most stable free radicals, widely used for an estimate of the sensitivity of magnetic spectrosopes, for an estimate of the number of paramagnetic centers in the investigated specimens, and finally, in some cases to determine the $g$ factors.

Resonance in solid DPPH was first measured in 1950 [14]; the $g$ factor in polycrystalline specimens was found to be $2.0036 \pm 0.0003$; the line width is $\Delta H = 2.7$ oersted. Later on it was observed in single crystals of DPPH that a slight anisotropy exists both in the values of $g$ and in the values of $\Delta H$ [15, 77]. The saturation method was used to measure the longitudinal relaxation time $T_1$, which was found to be $6.3 \times 10^{-8}$ sec, which is close in magnitude to $T_2$, as should be the case for systems with strong exchange [5] (see §5.3). The theory of DPPH absorption lines in weak fields was developed in [16] and later on confirmed experimentally [17].

A characteristic, long-unexplained feature in paramagnetic resonance of solid DPPH was the great difference in the values of $\Delta H$ (from about 1 to about 7 oersted), obtained by different researchers.

The main reason for these discrepancies was explained in a paper by Arbuzov, Valitova, Garif'yanov, and Kozyrev [18], who investigated
TABLE 7.1
Width of Paramagnetic Resonance Lines in DPPH Specimens Obtained with Different Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>100(^\circ) K</th>
<th>10(^\circ) K</th>
<th>200(^\circ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Бензол</td>
<td>6.8</td>
<td>4.6</td>
<td>4.7</td>
</tr>
<tr>
<td>5 Тoluol</td>
<td>2.9</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>6 Ксиол (смесь)</td>
<td>2.5</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>7 Пиридин</td>
<td>3.3</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>8 Бромоформ</td>
<td>2.2</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>9 Четыреххлори-</td>
<td>1.9</td>
<td>2.7</td>
<td>2.3</td>
</tr>
<tr>
<td>стный углерод</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Хлороформ</td>
<td>1.7</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>11 Серауглерод</td>
<td>1.3</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

The results of their measurements, made in fine crystalline powders in vacuum are listed in Table 7.1.

It is seen from the table that the nature of the solvent greatly influences the line width; this is expected, incidentally, since it has already been known that some solvents enter into the crystalline lattice of DPPH (it is not without interest to note here that the chemical analyses show that in no case is there a guarantee that the solvent enters into the lattice in stoichiometric proportions).

The investigated specimens of DPPH are divided into two groups: in the first (cyclic solvents) the lines narrow down upon cooling and upon increase in the frequency; in the second (noncyclic solvents), both relations are reversed. A slight narrowing down with increasing frequency, observed in the first group, agrees qualitatively with the theory of Kubo and Tomita for pure isotropic exchange (see Chapter 5) and is probably the result of the vanishing of the nonsecular line broadening in strong fields \(H_0\). The narrowing down upon cooling can be explained as being the result of the dependence of the nonsecular broadening on the correlation time.

However, the dependence of the line narrowing in DPPH of the second group on the frequency cannot be explained simply. One could assume this dependence to be the consequence of the large anisotropy of the g factor in the second group, but measurements made by Yablokov...
[20] in single crystals of DPPH have shown that this anisotropy is approximately the same for a benzene specimen \((g_{\|} = 2.0031 \pm 0.0003; g_{\perp} = 2.0039 \pm 0.0003)\) and for a chloroform specimen \((g_{\|} = 2.0030 \pm 0.0002; g_{\perp} = 2.0040 \pm 0.0002)\). Thus, there is still no complete explanation of the line width in modifications of DPPH.

The nature of the solvent is not the only factor that influences \(\Delta H\) in DPPH. As was established in [21, 18], a reversible line broadening, due to the adsorption of \(O_2\) molecules from air, was observed in fine crystalline specimens pertaining to the second group. Pumping out the air narrows the line down to the value of \(\Delta H\) corresponding approximately to the coarse crystalline specimen. This effect is analogous to one previously observed on carbons [22] and is due to shortening of the spin-lattice relaxation time in DPPH under the influence of the magnetic moments of the \(O_2\) molecules. Indeed, it has been shown by the saturation method that along with broadening the lines, adsorption of oxygen causes also a shortening of \(T_1\). The \(O_2\) causes a particularly strong broadening of the narrowest line obtained in specimens that crystallize out of carbon bisulfide [18]. For specimens crystallized out of chloroform, the influence of oxygen is much greater at temperatures 90-273\(^\circ\)K than at temperatures above 273\(^\circ\)K [21].

It follows from all the foregoing that if DPPH is used as a standard, it is necessary to indicate the method by which it has been obtained, to know the chemical composition of the specimens, and to use specimens that have been isolated from the action of oxygen. Apparently the most suitable standard is DPPH crystallized out of benzene, where the adsorption of oxygen has a negligible influence.

It is necessary to take account of the fact that the dependence of \(\Delta H\) on the fine points of its production technique and on the medium from which the specimen is crystallized is not confined to DPPH, but
| №  | Radical; 2) oe; 3) literature; 4) benzoquinhydrone adsorbed on Ba(OH)₂·8H₂O; 5) biphenylenetriphenylethyl; 6) Wurster's blue (perchlorate); 7) Wurster's blue (picrate); 8) (ferricyanide); 9) nitrogen diparaanisyl oxide (monocrystalline); 10) diparaxylenymethyl; 11) diphenyltriphenylmethyl; 12) diphenylquinooxaline chlorostannite; 13) Kenyon-Banfield radical; 14) 2-nitrophenanthrophenazine chlorostannite; 15) pentaphenylcyclopentadienyl; 16) porphyrindine; 17) porphyrindine; 18) tetramethylenbenzidine formate; 19) tetramethylenbenzidine perchlorate; 20) tetramethylstiboniumperoxylamido disulfonate; 21) thymoquinhydrone, adsorbed on Ba(OH)₂·8H₂O; 22) tri-p-xenylmethyl; 23) tri-tetra.-butylphenoxyl; 24) triphenylamine perchlorate; 25) tri-p-anisylamine perchlorate; 26) tri-p-aminophenylamine perchlorate; 27) tri-p-nitrophenylmethyl; 28) phenantraquinhydrone adsorbed on Ba(OH)₂·8H₂O; 29) N-phenyl- N-9-dearyl-N-oxoaminyl; 30) phenyl (N-phenyl ether oxime-2-methylpentene-4 or 2) nitrooxide (monocryst.); 31) chromocene. | $g$ | $d/d$, хром | Литература |
| --- | --- | --- | --- |
| 4 | Бензохинингидрон, адсорб. на Ba(OH)₂·8H₂O | 2,003 | несколько | [28] |
| 5 | Бифенилентрифенилметион | 2,008 | 5 | [36] |
| 6 | Бензолтрифенилметион (перхлорат) | 2,003 | 2,7 | [30] |
| 7 | Вурстера голубой (пинквар) | 2,003 | 6 | [33] |
| 8 | Дипараанисилазот окись (монкр.) | 2,0028 | 2,7 | [33] |
| 9 | Дипараанисилазот окись (мокн.) | $g_1=2,0095$; $g_2=2,0035$ |  |  |
| 10 | Дипарасинцилазитетра | 2,00 | несколько | [32] |
| 11 | Дифенилтрифенилметион | 2,0036 | 5 | [32] |
| 12 | Кеньона — Банфилда радикал | 2,0057 | 8,9 | [32, 33] |
| 13 | Пентагеницилциклопентадиен | 2,0025 | [4, 23] | |
| 14 | Порфириксид | 2,0065 | 17,0 | [35] |
| 15 | Порфириксид | 2,0057 | 10,7 | [35] |
| 16 | Тетраметиленбензидин формат | 2,00 | 8,4 | [32] |
| 17 | Тетраметиленбензидинен перхлорат | 2,00 | 2 | [32] |
| 18 | Тетраметилтрифенилметиламина дисульфат | 2,00 | 100 | [32] |
| 19 | Тимозинцилазид, адсорб. на Ba(OH)₂·8H₂O | 2,0031 | 5,7 | [32] |
| 20 | Три-п-ксенилметион | 2,0032 | 7,7 | [32] |
| 21 | Три-п-ксенилметион перхлорат | 2,003 | 2 | [32] |
| 22 | Три-п-ксенилметион перхлорат | 2,0037 | 0,7 | [32] |
| 23 | Фенил (N-фенилэтил эфир оксигена-2-метилпентан-4-на) 2) нитрооксид (монокрист.) | 2,0036 | 0,7 | [32] |
| 24 | Фенил (N-фенилэтил эфир оксигена-2-метилпентан-4-на) 2) нитрооксид (монокрист.) | 2,0042 | 38 | [58] |
| 25 | Фенил (N-фенилэтил эфир оксигена-2-метилпентан-4-на) 2) нитрооксид (монокрист.) | 2,0064 | 38 | [58] |
| 26 | Фенил (N-фенилэтил эфир оксигена-2-метилпентан-4-на) 2) нитрооксид (монокрист.) | 2,0083 | 38 | [58] |

**TABLE 7.2**
may occur also in many other radicals. Thus, for pentaphenylocyclopenta-
dienyl, a value of $\Delta H$ amounting to several times ten oersteds was ob-
tained in [4], 0.62 oersted was obtained in [23], and from 5 oersted
upward was obtained in [24] (depending on the solvent).

Unfortunately, in most work on DPPH and its derivatives it is not
indicated from which solvent the radical was crystallized.

In addition to DPPH, several polycrystalline free radicals of sim-
ilar structure were investigated [25]; these were of the type

\[
\begin{align*}
\text{X} & \quad \text{N} \quad \text{N} \\
& \quad \text{NO}_2 \\
& \quad \text{NO}_2
\end{align*}
\]

where $X$ is Cl

\[(g = 2.0042; \delta H = 1.2 \text{ oe}); \text{ Br} (g = 2.002; \delta H = 2.2 \text{ oe}); \text{ OCH}_3 (g = 2.000; \delta H = 2.6 \text{ oe}); \text{ F} (g = 2.000; \delta H = 4.1 \text{ oe}). \] Here $\delta H$ is the line width at
the points of inflection. Also investigated was diphenyloxypicrylhy-
drazyl powder, with the same value of $g$ as in DPPH and $\delta H = 3$ oersted
[26] and single crystals of N-picryl-9-aminocarbazyl, with $g = 2.0041-$
2.0024; $\delta H = 0.5$ oersted [27, 28]. The last substance differs very lit-
tle from DPPH, having a structural formula

\[
\begin{align*}
\text{N} \quad \text{N} \\
& \quad \text{NO}_2 \\
& \quad \text{NO}_2
\end{align*}
\]

Nonetheless, its line width is considerably smaller than in any mod-
fication of DPPH.

Certain results of measurements of paramagnetic resonance in solid
organic free radicals of other types are listed in Table 7.2. They do
not claim to be exhaustively complete.

§7.3. Free Radicals in Solutions

In §7.1 we pointed out that from the chemical point of view the
most interesting is an investigation of the paramagnetic resonance line

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hyperfine structure observed at sufficiently low free radical concentrations in solutions. We give here some results obtained in a study of solutions of free radicals.

We have seen that DPPH in solution yields five lines. N-picyrl-9-aminocarbazyl, which is very close to it, yields seven lines, corresponding to a ratio of 2 between the constants \( A'_{\text{1}} \) and \( A'_{\text{2}} \) of interaction with the nuclei of the first and second atoms of the nitrogen. The maximum possible number of lines, namely nine, could be obtained in solutions of diphenyldinitroso sulfophenylhydrazyl salt

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array}
\]

where the constant of interaction with the first nitrogen atom is \( A_{\text{1}} = 12 \) oersted, while \( A_{\text{2}} = 8 \) oersted [38, 39]. We see from this example how sensitive the hyperfine structure is to the least changes in the distribution of the electron densities in the molecule.

In order to verify the hyperfine structure theory, great interest attaches to solutions containing ions of aromatic hydrocarbons. One of the first to be investigated [40] was the negative naphthalene ion

\[
\begin{array}{c}
\text{a} \\
\text{a} \\
\end{array}
\]

which is obtained when alkali metals act on solutions of naphthalene in tetrahydrofurane or dimethyoxyethane. The nature of the metal and solvent does not change the spectrum, which consists of 17 lines with intensities 1:1:1:2:2:1:2:2:1:2:2:1:2:2:1:1:1 and with a distance of 27.2 oersted between the outermost peaks ("total splitting"). This quantity is in very good agreement with the theoretical value of the total splitting (28 oersted). The number and intensity of the lines
were explained on the basis of an approximate calculation of the molecular orbitals, made as long ago as in 1931 by Hückel [41]. If the constants $A_\alpha$ and $A_\beta$ of the hyperfine structure due to the $\alpha$ and $\beta$ protons of the naphthalene ion are equal, we should have nine lines; if $A_\alpha >> A_\beta$ five groups of lines should be obtained, each containing five nearby-lying components. The number 17, on the other hand, corresponds to a ratio $A_\alpha/A_\beta = \rho_\alpha/\rho_\beta = 3:1$, which is obtained indeed from calculations made following Hückel. The most exact value of the ratio $A_\alpha:A_\beta$, obtained from a detailed analysis of the paramagnetic resonance spectrum, is 5.01:1.79.

Partial replacement of $^{12}\text{C}$ by $^{13}\text{C}$ has made it possible to obtain for the naphthalene ion the constant of the hyperfine structure due to the interaction between the electron spin and the spin of the $^{13}\text{C}$ nucleus ($I = 1/2$). It turned out to be equal to 7.1 oersted, from which the density of the electron cloud on the C nucleus was calculated. Several other negative aromatic ions were investigated in similar fashion (see Table 7.3), and the electron densities on the protons were calculated and found likewise to be in good agreement with the calculations based on [41]. In addition, experiments on paramagnetic resonance have made it possible to establish an electronegativity scale for the aromatic ions, and if it is assumed that the lifetime of the electron on the ion determines the line width, one can also determine the speed of electron transition between the aromatic molecule and the ion [42].

By treating aromatic hydrocarbons with concentrated $\text{H}_2\text{SO}_4$, it is possible to obtain positive ions of these hydrocarbons which are also, naturally, free radicals. Several such radicals were investigated by the paramagnetic resonance method [43, 44].

Treatment of several organic substances of other classes with sulfuric acid (for example, anthraquinone, thiophene, and many others),
also leads to the occurrence of paramagnetic resonance spectra \([45, 46]\).

In these cases, however, one obtains not positive ions with the character of radicals, but radical oxidation products of the corresponding organic substances, as was convincingly shown in \([47]\).

A large group of investigations was devoted to solutions containing various heptaquinones and their derivatives. The experimental values of the hyperfine structure constants were compared with those calculated on the basis of the superconjugation theory, developed in \([48, 10]\) and gave good agreement \([49]\).

The picture of the spectrum is frequently very complicated. Thus, for monomethyl-\(n\)-benzoheptaquinone it becomes necessary to assume that the hyperfine structure constant for the two ring protons is \(A'_{1} = A'_{2} = 2.48\) oersted, while that for the third ring proton is \(A'_{3} = 1.73\) oersted, and for the methyl protons the same constant is \(B' = 2.02\) oersted \([50]\). The spectrum becomes simpler if the substituents are chlorine atoms, inasmuch as the hyperfine splitting due to these atoms is small and does not produce resolved lines, since it participates only in the width of the components. Thus, in trichlorobenzoheptaquinone one observes only two components, due to the single ring proton \([51]\). On the contrary, fluorine-substituted heptaquinones disclose a hyperfine structure due both to the protons and to the \(^{19}\text{F}\) nuclei, owing to the large magnetic moment and the small spin \((I = 1/2)\) of the latter \([1]\).

From among the numerous free radicals of other classes, investigated in solution, we shall discuss only a few and refer the reader for more details to Ingram's book \([1]\). Thus, we point out that the spectra in solutions of triphenylmethyl \([52]\) and a few other radicals disclose anomalously large hyperfine splittings. Triphenylmethyl
should yield, assuming that the corresponding H atoms in all three rings are equivalent, a total of \((2I_{\alpha} + 1)(2I_{\beta} + 1)(2I_{\gamma} + 1) = 196\) lines. These are not fully resolved, and the total splitting is 25 oersted. But an investigation of a specimen containing \(^{13}\text{C}\) in the methyl position has shown the occurrence of a doublet due to the \(^{13}\text{C}\) nucleus with a splitting of 22 oersted, which indicates that a considerable fraction of the density of the unpaired electron is concentrated precisely on the methyl carbon, and consequently, \(\Sigma\rho_1\) on the remaining atoms should be considerably less than unity. An explanation of the spectrum of triphenylmethyl, which we shall not discuss, was given in [53, 54].

In the radicals considered so far, both in solid form and in solutions, the \(g\) factor is very close to 2.0023. More significant deviations from this value are observed in solutions of radicals containing sulfur, and also in radicals of the peroxide type [55]. This indicates a much stronger localization of the unpaired electron in the latter cases. Radicals containing sulfur were obtained by dissolving thiophenol, thiocresol, thionaphthol, and diphenyldisulfide in concentrated sulfuric acid [45, 46]. All give a paramagnetic resonance spectrum consisting of two groups of lines with \(g_1 = 2.0151\) and \(g_2 = 2.0081\) (the values of \(g\) are determined for the centers of the groups). These groups are due to two different radicals, since the second group turned out to be more stable in time, and remains when the first vanishes completely. A group of five lines with \(g = 2.0081\) is produced by the thiatrene ring with four protons. The group with \(g = 2.0151\) apparently is
due to the \((C_6H_5S)H^+\) radical with appreciable localization of the unpaired electron on the sulfur atom.

We note that along with organic sulfur derivatives with radical-like character, paramagnetic resonance was observed also in pure molten sulfur [56, 57]. It is observed at temperatures from 189 to 414°C. One line was noted (the spin of the \(^{32}\)S nucleus is zero), with a near-Lorentzian shape and \(g = 2.024\). Neither the line width nor \(g\) depend on the temperature. This resonance is due to a partial breaking of the bonds of the ring molecules \(S_6\). A solution of sulfur in fuming sulfuric acid [1] also discloses two lines (at 20% \(SO_3\)) with \(g\) factors that fluctuate between 2.003 and 2.018 for one line and between 2.025 and 2.032 for the other. The latter is apparently due to the broken \(S_6\) rings, and the former to some other radical containing sulfur.

Great interest is attached to an investigation, made by Voyevodskiy and his coworkers [58, 59], of solutions containing chromo-aromatic compounds of "sandwich" structure. Compounds of this type (metallo-ocenes) have a structure \((C_6H_6)_2\)Me or \((C_5H_5)_2\)Me, etc., where the metallic atom is situated between two parallel ring structures. The nature of the covalent bond of the metal with the addend in these compounds cannot be described within the framework of the theory of ordinary two-electron bonds. Quantum mechanical calculations on compounds of this type are developed in [60].

An investigation [58, 59] of paramagnetic resonance spectra in chromocene cations of the type

\[
\begin{bmatrix}
C_6H_5X^- \\
Cr \\
C_6H_5X
\end{bmatrix}^+
\]

where \(X = H, C_6H_6, \text{cyclo-}C_6H_{11}, \text{COOH}, \text{etc.}\), have shown the presence of a hyperfine structure in which the number of components corresponds to the number of protons on the two rings; on the other hand, a binomial
distribution of the component intensities has led to the conclusion that all these protons are equivalent. The summary spin density on both rings amounts to 1.92. It follows from this that 0.92 of the density of the unpaired electron with opposite spin orientation is localized on the chromium atom.

It was shown in [61] that the width of the paramagnetic resonance spectrum components in chromocenes depends strongly not only on the substitutes, but also on the nature of the solvent and on the temperature.

In addition to the stable radicals, one can sometimes detect in liquid solutions radicals that are formed during the course of the reactions. Thus, for example, in [62] there was investigated the paramagnetic resonance of pyrogallol, which oxidizes in air, in aqueous and alcohol solutions. At room temperatures, the lifetime of the free radical turned out to be on the order of several minutes; \( g = 2.005 \); the spectrum consists of two triplets. In most cases, however, in solutions with low viscosity, the unstable radicals have so short a lifetime that their dynamic concentration lies on the borderline of the sensitivity of modern apparatus. Furthermore, the short lifetime causes broadening of the absorption lines, which makes their detection even more difficult. Unstable radicals are therefore investigated usually by rapidly freezing the solutions.

To conclude this section, we present Table 7.3, taken from [1]. It illustrates the experimental results obtained in the investigation of several types of stable free radicals in solutions.


1. Irradiation of organic substances with ultraviolet, x-rays, and \( \gamma \)-rays frequently damages their molecular structure and leads to the
TABLE 7.3
Stable Free Radicals in Solutions [1]

<table>
<thead>
<tr>
<th>Radical</th>
<th>ΔH or distance between outermost hfs peaks, oe</th>
<th>Number of hfs components</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) Aromatic ions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>anisidine</td>
<td>28</td>
<td>21</td>
<td>[63]</td>
</tr>
<tr>
<td>benzene</td>
<td>22.5</td>
<td>7</td>
<td>[61]</td>
</tr>
<tr>
<td>m-dinitrobenzene</td>
<td>26</td>
<td>8</td>
<td>[65]</td>
</tr>
<tr>
<td>diphenoxy</td>
<td>25</td>
<td>9</td>
<td>[63]</td>
</tr>
<tr>
<td>naphthalene</td>
<td>27</td>
<td>17</td>
<td>[60]</td>
</tr>
<tr>
<td>naphthalene with 13C</td>
<td>34.3</td>
<td>34</td>
<td>[67]</td>
</tr>
<tr>
<td>naphthalene with D</td>
<td>29</td>
<td>15–16</td>
<td>[60]</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>25</td>
<td>10</td>
<td>[60]</td>
</tr>
<tr>
<td>nitrophenyl</td>
<td>49</td>
<td>7X4</td>
<td>[68]</td>
</tr>
<tr>
<td>diphenyl</td>
<td>24</td>
<td>9</td>
<td>[64]</td>
</tr>
<tr>
<td>tetracene</td>
<td>25</td>
<td>31</td>
<td>[67]</td>
</tr>
<tr>
<td>trinitrobenzene</td>
<td>25</td>
<td>8</td>
<td>[66]</td>
</tr>
<tr>
<td>B) Semihydrogenated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) p-benzoquinone</td>
<td>9,48</td>
<td>5</td>
<td>[69]</td>
</tr>
<tr>
<td>monomethyl-p-benzoquinone</td>
<td>14</td>
<td>5</td>
<td>[70]</td>
</tr>
<tr>
<td>tetramethyl</td>
<td>13</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>monochloro</td>
<td>6,0</td>
<td>4</td>
<td>[51]</td>
</tr>
<tr>
<td>trichloro</td>
<td>2,1</td>
<td>7</td>
<td>[51]</td>
</tr>
<tr>
<td>tetrazol</td>
<td>0,4</td>
<td>1</td>
<td>[51]</td>
</tr>
<tr>
<td>2.5-dihydro-2.5-dimethyltetrazol</td>
<td>4,3</td>
<td>19</td>
<td>[71]</td>
</tr>
<tr>
<td>2) 1,4-naphthosilylene</td>
<td>8</td>
<td>3X5</td>
<td>[72]</td>
</tr>
<tr>
<td>2,2-dimetethyl-1,4-naphthosilylene</td>
<td>12</td>
<td>3X5</td>
<td>[72]</td>
</tr>
<tr>
<td>1,4-dimethyl-1,2-dimethylnaphthalene</td>
<td>10</td>
<td>3X3</td>
<td>[73]</td>
</tr>
<tr>
<td>1,4-dibutyl-1,4-dimethylnaphthalene</td>
<td>6</td>
<td>2X11</td>
<td>[73]</td>
</tr>
<tr>
<td>3) 3-fluorenyl</td>
<td>8</td>
<td>7</td>
<td>[73]</td>
</tr>
<tr>
<td>3) 3-fluorenyl, 2X3</td>
<td></td>
<td></td>
<td>[62]</td>
</tr>
<tr>
<td>V) Peroxides and triaryllamines</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tropylium</td>
<td>20</td>
<td>3</td>
<td>[74]</td>
</tr>
<tr>
<td>triphenyl</td>
<td>20</td>
<td>3</td>
<td>[74]</td>
</tr>
<tr>
<td>V) Salts of Vormlet (positive ions)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-metilammonium</td>
<td>28</td>
<td>15</td>
<td>[75]</td>
</tr>
<tr>
<td>N,N-dimethylamine</td>
<td>48</td>
<td>24</td>
<td>[75]</td>
</tr>
<tr>
<td>N,N,N-trimethylamine</td>
<td>73</td>
<td>27</td>
<td>[75]</td>
</tr>
<tr>
<td>N,N,N,N-tetramethyl-1,3-dimethylamine</td>
<td>76</td>
<td>9X3</td>
<td>[75]</td>
</tr>
<tr>
<td>N,N,N,N-dimethyl-1,3-dimethylamine</td>
<td>51</td>
<td>7X3</td>
<td>[75]</td>
</tr>
<tr>
<td>tetrateraclidine</td>
<td>88</td>
<td>13X3</td>
<td>[75]</td>
</tr>
<tr>
<td>D) Miscellaneous radicals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbazone</td>
<td>60</td>
<td>7</td>
<td>[38]</td>
</tr>
<tr>
<td>dihydrocarbazone</td>
<td>9</td>
<td>14</td>
<td>[40]</td>
</tr>
<tr>
<td>diphenyl</td>
<td>48</td>
<td>2X35</td>
<td>[76]</td>
</tr>
<tr>
<td>diphenyl</td>
<td>14</td>
<td></td>
<td>[65]</td>
</tr>
<tr>
<td>diphenylphenylcarbzone</td>
<td>60</td>
<td>9</td>
<td>[38]</td>
</tr>
<tr>
<td>diphenylphenylcarbzone</td>
<td>58</td>
<td>5</td>
<td>[77]</td>
</tr>
<tr>
<td>diphenylphenylcarbzone</td>
<td>58</td>
<td>5</td>
<td>[77]</td>
</tr>
<tr>
<td>diphenylphenylcarbzone</td>
<td>58</td>
<td>5</td>
<td>[77]</td>
</tr>
<tr>
<td>diphenylphenylcarbzone</td>
<td>42</td>
<td>4</td>
<td>[40]</td>
</tr>
<tr>
<td>diphenylphenylcarbzone</td>
<td>25</td>
<td>21X4</td>
<td>[78]</td>
</tr>
</tbody>
</table>

1) Radical; 2) ΔH or distance between outermost hfs peaks, oe; 3) number of hfs components; 4) literature; 5) A) aromatic ions of; 6) anthracene; 7) benzene; 8) m-dinitrobenzene; 9) diphenyl; 10) naphthalene; 11) naphthalene with 13C; 12) naphthalene with D; 13) nitrobenzene; 14) perinaphthenone; 15) perillene; 16) tetracene; 17) trinitrobenzene; 18) B) heptaquinones; 19) 1) p-benzoheptaquinone; 20) monomethyl-p-benzoheptaquinone; 21) tetramethyl; 22) monochloro-.
Key to Table 7.3 (Continued)

23) trichloro-; 24) tetrachloro-; 25) 2,5-di-tert-butyl-; 26) 2) 1,4-naphthoheptaquinone; 27) 2,3-dimethyl-1,4-naphthoheptaquinone; 28) 3) o-benzoheptaquinone; 29) 4-tert-butyl-o-benzoheptaquinone; 30) 3-phenyl; 31) oxidized 1,2,3-benzenetriol; C) perchlorates of triarylamines; 33) trianisyl; 34) tridiphenyl; 35) D) Wurster's salts (positive ions) non-substituted Wurster's salt; 36) N-methyl substituted salt; 37) NN-di-methyl; 38) NN'-dimethyl; 39) NN-di-methyl-NN'-deutero; 40) tetramethyl substituted salt; 41) E) various other radicals; 42) carbazyl; 43) difluoronitrogen; 44) dimesitylmethyl; 45) di-p-anisyl-nitroxide; 46) diphenylidinitrosulfonilhydrazyl; 47) adiphenyl-β-picyryl-hydrazyl; 48) peroxylamine disulfonate; 49) phenazine; 50) sodium-trimesityl-boron; 51) triphenylmethyl.

formation of free radicals. A study of such radicals by the paramagnetic resonance method is of great scientific and practical interest; by now a considerable literature has been devoted to this problem. Usually the substances are investigated in the solid phase or in liquids with high viscosity, for in this case it becomes possible to accumulate the radicals that are obtained as a result of the irradiation.

An investigation of objects irradiated with ultraviolet has advantages over work with x-rays or γ-rays, for in the former case the smaller size of the quantum makes the destruction of the molecules and the formation of free radicals much more selective in character, and therefore the observed spectra are simpler and easier to interpret. In the case of x-rays, and particularly γ-rays, one obtains sometimes a whole set of different free radicals; consequently the paramagnetic resonance spectra becomes highly complicated.

The first work on the study of free radicals in irradiated sub-
stances was carried out in 1951 by Shneider and his coworkers [80], who investigated paramagnetic resonance in the polymer polymethylmethacrylate, which was exposed to x-rays. A large-scale study of irradiated substances began, however, only in 1955.

It was found that many substances (ethyl iodide, benzylamine, benzyl chloride, and others), dissolved in a suitable mixture of hydrocarbons (the most suitable one turns out to be a mixture consisting of 5 parts of ether, 5 parts of isopentane, and 2 parts of ethanol*) and vitrified by deep freezing, produce after exposure to ultraviolet a paramagnetic resonance spectrum [81]. An analogous effect was observed also in high-temperature organic glasses [82]. It turned out further that along with the primary radicals, arising as a result of direct action of the ultraviolet quantum, secondary radicals are produced as a result of interaction between the primary radicals and the solvent [83]. It thus turned out to be possible to obtain paramagnetic resonance spectra from radicals of substances on which ultraviolet does not act directly. A particularly successful converter for radicals was hydrogen peroxide, which produced the radicals OH upon irradiation with ultraviolet.

From the hyperfine structure of the spectrum it is possible to establish the nature of the secondary radicals. Thus, in the vitreous solution of hydrogen peroxide in alcohol \((\text{CH}_3)_2\text{HCOH}\), a spectrum of certain lines from six protons was observed after irradiation; it obviously belongs to the radical \((\text{CH}_3)_2\text{COH}\).

The widths of the lines in solid and vitreous systems containing free radicals is larger than in liquid solutions, in view of the absence of the narrowing due to the Brownian motion. However, the width observed in glasses is nonetheless smaller than that expected for the true solid-state arrangement of the atoms. This can be attributed to
the internal rotation of the protons in the molecules of the free radicals, which remain also at low temperatures [84].

In this connection, it is of interest to investigate the dependence of the secondary spectra on the temperature of the vitreous system. This investigation yields information on internal motion in the glass, and sometimes makes it possible to separate the effects due to individual radicals from the mixed spectrum, because the dependence of the line width on the temperature is not the same in different radicals. In particular, it was shown in [84] that the secondary radicals in a solution of \( \text{H}_2\text{O}_2 \) in methanol are \( \text{CH}_2\text{OH} \) and the biradical \( \text{CH}_2\text{..H} \).

Let us proceed to discuss the results obtained by irradiation with x-rays and y-rays. The spectrum of polymethylmethacrylate obtained in 1951 [80] is so complicated that it took 7 years to interpret [85]. It turned out to be due to a radical of the type \( \text{R} \cdot \text{CH}_2 - \cdot \text{C}(\text{CH}_3)(\text{COOCH}_3) \). It is easier to interpret the spectra of x-irradiated amino acids. Thus, a triplet due to the radical \( \cdot \text{CH}_2 \) [86] was observed in glycine. Anisotropy of the spectrum in an irradiated single crystal of glycine was reported in [87].

An investigation of y-irradiated paraffin hydrocarbons [88, 89] has shown that in the case when the carbon chain does not contain too large a number of atoms, the spectrum has one central component of maximum intensity, and higher molecular radicals of this type have two components. This is evidence that in the former case the number of equivalent protons closest to free valency is even, and in the latter case it is odd. One can assume therefore that in hydrocarbons with a short chain one obtains essentially radicals of the type \( \cdot \text{CH}_2\text{..CH}_2\text{..} \), while in high-molecular ones one obtains the type \( \cdot \text{CH}_2\text{..CH} \). The simplest of the hydrocarbons, methane, produces at 20.4°K upon-y-irradiation a paramagnetic resonance spectrum [90] consisting of four...
components with intensity ratio 1:3:3:1, which agrees with expectation for the radical $\text{CH}_3$.

Thus, paramagnetic resonance makes it possible to establish the nature of the radicals that form upon irradiation of solid organic substances. We mention here still other work on paramagnetic resonance in substances irradiated with x-rays and $\gamma$-rays. The following were investigated in [91]: methyl alcohol, which produces three hyperfine components; ethyl alcohol (five components); acetamide (three components); propionamide (five components); acetaldehyde (three components), and sodium methoxide (three components). Spectra of dimethyl-Hg (five components) and diethyl-Hg (three components) were obtained in [86]. Reference [94] reports an investigation of glycine (three components); alanine (five components); valine (complex spectrum); leucine (two groups of five or more lines); isoleucine (without resolved structure); cysteine (asymmetrical structure with four components); glycolic acid (two components); and glycocyanine (two components). There is no doubt that further systematic study of the influence of irradiation will continue [93]. It is of particular importance to the investigation of polymers, to the analysis of which we now proceed.

2. As is well known from chemical considerations, polymerization of molecules frequently proceeds via free radicals. However, a study of the kinetics itself of this process with the aid of paramagnetic resonance is difficult because of the low concentration of the free radicals. We therefore confine ourselves to a determination of the free radicals, which form on the ends of the growing polymer chains and which are fixed in the substance for steric reasons. This "freezing" takes place when the polymer has already become partially polymerized to form a gel or when the polymer is insoluble in the monomer and precipitates around the growing chains.
The first investigation of this type pertained to polyvinyl gels [94]. The spectrum observed in glycoldimethacrylate consisted of two partially overlapping groups, containing five and four lines; the spectrum turned out to be independent of the initiator of the polymerization and identical with the spectrum of irradiated polymethylmethacrylate. Both groups were recognized to belong to one radical

\[
\text{COOR} \\
\text{-CH}_2\text{-C}^\cdot \\
\text{CH}_3
\]

as a result of superconjugation of the \( p_\pi \) orbit of the C atom with 15 orbits of the protons from the CH\(_2\) and CH\(_3\) groups [85].

In addition to investigating free radicals "frozen" in gels or in polymer precipitates, the determination of radicals arising in ready polymers upon irradiation is used. An interesting example of such research is work on \( \gamma \)-irradiated frozen (77\(^{\circ}\)K) teflon [95]. After freezing with the access of air prevented, a spectrum of 11 lines was obtained; 10 of these form two partially overlapping groups of five lines each and are due to the radical \( \cdots \text{CF}_2\text{-CF-CF}_2\cdots \), in which the central \( ^{19}\text{F} \) nucleus produces the principal doublet splitting, and the four more remote fluorine nuclei split each line of the doublet into a quintuplet. The eleventh line is connected with the peroxyd radical \( \cdot \text{-O}_2\cdot \), inasmuch as action of the oxygen in the air on the irradiated teflon converts the entire spectrum into a single asymmetrical line which coincides in position with the eleventh line of the oxygen-free spectrum [95, 96]. The asymmetry of the line is connected with the great localization of the unpaired electron on the oxygen.

In addition to the foregoing case, irradiation was used to investigate the paramagnetic resonance spectra of the following polymers: polymethacrylic acid, polyethylmethacrylate [97], polymethylchloracryl-
ate, polyacrylic acid, polyvinyl alcohol, hydrolyzed polyvinyl acetate, polystyrol, polythene, nylon, and polyacrylonitrile [98].

The method of "freezing" in gels or in precipitates was used to investigate the free radicals obtained on polymerization of the following monomers: acrylonitrile, methacrylonitrile, vinyl bromide [85]; acrylic acid [1], methylvinylacrylate [94], and a few other polymers.

The change in concentration of free radicals during the course of polymerization was investigated with copolymerization of methylvinylacrylate and glycol dimethacrylate as an example [99]. The action of inhibitors on the polymerization process was investigated in [100].

3. A rather unexpected discovery was the large resonance effect in carbonized organic substances, discovered independently in [101-103].

In low-temperature pyrolysis products, the $g$ factor of the only observed line is very close to 2.0023, and the line width fluctuates from 1 to 100 oersted. The intensity of the effect corresponds to between 0 and $10^{20}$ paramagnetic centers per gram of substance, and increases rapidly with increasing carbon content from 80 to 94% [104]. X-ray diffraction investigations have shown that it is precisely in this region of concentrations that the formation of large groups of carbon rings (from four rings upward) begins. It is noted that the spin-lattice relaxation time also shortens with increasing concentration of the free carbon [105]. The shortest times $T_1$, on the order of $10^{-7}$ sec, are found in coal of the anthracite type [106, 107], which gives rather narrow lines ($\delta H$ from 0.7 to 0.3 oersted) and with strong exchange effect ($T_1 = T_2$).

The disorganized ring structure and the arbitrary arrangement of the carbon rings apparently weaken the exchange and lengthen the spin-lattice relaxation time in carbonlike substances with small contents of free carbon. The properties of the paramagnetic resonance line...
change also with the temperature of the carbonization: the line intensity increases with increasing temperature from approximately 350 to approximately 550°C [108]. This is the temperature interval in which the volatile pyrolysis products are removed and a ring carbon structure begins to arise. Above about 600°C, a sharp decrease in the intensity of the effect begins. A decrease in intensity is observed also if the concentration of the free carbon in the specimen is higher than 94%. The last two circumstances are apparently connected with the graphitization of the specimens, on which multilayer three-dimensional ring structures are produced, and this can lead to a partial pairing of the free electrons and consequently to a weakening of the paramagnetic resonance.

The intensity of the effect increases sharply upon removal of oxygen of the air by pumping. The effect of the oxygen is reversible [109, 110, 106]. One can propose two possible mechanisms for the action of O₂ or other paramagnetic gases (in particular, for example, NO₂ [106]), which influence the effect in complete analogy with oxygen.

The first type of mechanism is purely physical; it consists of the perturbation of the energy of the unpaired electron by the motion of the biradical molecule of the adsorbed O₂ relative to the electron, or, to the contrary, by the motion of the electron relative to the stationary fixed O₂ molecule. As a result of this perturbation, the lifetime of the excited state of the electron should become shorter, that is, the spin-lattice relaxation time T₁ becomes shorter. In this mechanism the number of paramagnetic centers in the irradiated substance, and consequently the area under the resonance absorption curve, should remain constant with increasing width δH.

The other possible explanation has a chemical character. One can assume that some very weak "quasichemical" bonds [1] (weak because they
break when the oxygen is pumped out) are produced between the oxygen and the carbon, such that the spin of the uncompensated electron loses its effectiveness, becoming "paired" with one of the spins of the $O_2$ molecules. The remaining unpaired second electron of $O_2$ should be strongly localized on the oxygen atom and should therefore result in a strongly isotropic and broad line, which is consequently unobservable. In such a mechanism, the area under the resonance curve should decrease. It was shown in [111] that it is possible to select carbon specimens in which the action of the oxygen follows either the first or the second mechanism.

Many investigations devoted to the influence of the chemical processing of carbons has shown that in general paramagnetic resonance in carbon is not connected with any separate chemical group, and is due to the presence of uncompensated and strongly delocalized electrons in condensed carbon rings as a whole [1]. The paramagnetic centers are the result of a break in the bonds on the edges of the condensed rings, leading for the most part only to a growth in the ring structure, but which in individual cases can ensure also the appearance of uncompensated spins; another possibility of spin decompensation lies in imperfections of the ring structures: the presence of individual five- or seven-member rings should lead to the appearance of trivalent carbon atoms. The electron of the "broken bond" should have a $\pi$ orbit (which guarantees the possibility of rather strong delocalization) with admixture of the $\sigma$ state. The presence of very large exchange in the majority of the investigated carbons [106] shows that the electron clouds of the neighboring ring formations overlap in noticeable fashion.

In graphite and other high temperature carbons obtained at $t > 1400^\circ C$, paramagnetic resonance was also observed [112]. It is due not to the conduction electrons, as was initially assumed, but to de-
fects in the graphite lattice [113]. The unpaired electrons have in this case a much more strongly localized σ orbit. No resonance was observed in carbons obtained in the temperature interval 1000-1400°C.

A very important role can be played in future by research on paramagnetic resonance in various blacks. These apparently represent a mixture of high and low temperature carbons, since they are produced by very rapid heating at 1000-1700°C. Their spectrum, however, is near to low temperature carbons; in particular, it turns out to be quite sensitive to oxygen, whereas paramagnetic resonance in graphite is not affected by oxygen. The presence in blacks of unpaired electrons on delocalized π orbits should undoubtedly play a role in the reinforcing action of black introduced into rubber as a filler [1].

We note that paramagnetic resonance was observed in several tar-like substances (asphalt, carbolite, etc.) and in petroleum oil [106].

4. A unique type of organic paramagnet is a biradical, namely a molecule containing not one but two unpaired electrons. Among the biradicals one can distinguish a whole gamut of substances, starting with those in which the conditions brought about by the construction of the molecule cause the spins of both unpaired electrons to be separated from each other and not to add up to unity spin, and ending with such in which the spins interact quite strongly. The most reliable results on paramagnetic resonance were obtained for biradicals with noninteracting spins. These are, for example, 4,4'-polymethylene-bis-triphenylmethyl biradicals and para-substituted polyphenols, obtained in [114]. All g factors of these substances are very close to 2.0023, thus evidencing that the bond between the spins is practically nonexistent. The character of their spectrum, however, is the same as in monoradicals but naturally with twice the intensity per molecule.

Among the substances in which there are no grounds for assuming
the coupling between the molecule spins to be negligibly small, paramagnetic resonance was observed in the so-called Chichibabin hydrocarbon [115]

\[
\begin{array}{c}
\text{structure image}
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\]

which should have the following structure in the excited triplet state:

\[
\begin{array}{c}
\text{structure image}
\end{array}
\]

The observed resonance signal corresponded to 4% of the triplet state. In Ingram's opinion [1], one has no firm assurance that this signal was not due to some paramagnetic impurity. On the basis of several negative results on paramagnetic resonance, obtained on optical excitation of the molecule to the triplet state, he believes that these molecules have a very powerful relaxation mechanism which leads to so strong a line broadening that the lines become unobservable.

However, in addition to Chichibabin's hydrocarbon, there are many other compounds in which one can assume the presence of excited triplet states and which display paramagnetic resonance. These, in particular, are the two highly conjugate systems: 1,9-bis(2 furyl)-5 oxo-1,3,6,8-nonatetraene and 1,9-diphenyl-5 oxo-1,3,6,8-nonatetraene, in which the weak resonance effect was noted in [116].

Further, many solid molecular compounds between various phenylenediamines and halide-substituted quinones, investigated by Biyl, Kainer, and Rose-Innes [149], also displayed paramagnetic resonance. Its occurrence was interpreted as the result of the formation of biradical ionic molecules due to the transfer of an electron from the donors (phenylenediamine) to the acceptors (quinone). Finally, paramagnetic
resonance in such compounds as heated bianthrone \((g = 2.0036; \Delta H = 10\) oersted) [29], violanthrene \((g = 2.00; \Delta H = 26\) oersted) [31], and violanthrone \((g = 2.00; \Delta H = 30\) oersted) [31] could hardly be assigned, without stretching the point, to any other factor except the presence in these compounds of a certain fraction of molecules in the triplet state.

5. To conclude this section, we mention investigations of paramagnetic resonance in biological objects, which undoubtedly have a great future and which already now have yielded interesting results. Thus, in [117] there were investigated three radicals which are the intermediate products in the oxidation-reduction processes that occur with adrenaline, vitamin K, and other biologically important substances. In [118] free radicals were observed in lyophilized tissues and liquids of animals and vegetables, belonging to the albumins. In [119] an investigation was made of the time dependence of the concentration of free radicals upon illumination of an aqueous suspension of chloroplasts and of the decrease in this concentration after turning off the illumination. Of great interest to biology are also investigations of iron in hemin, methemoglobin, and their derivatives, results of which are listed in the tables of Chapter 4 of the present book.

Particularly interesting are the investigations of Blyumenfel'd and his coworkers, devoted to questions of paramagnetic resonance in irradiated and nonirradiated albumins, and also in compounds of albumins with ribonucleic acids [120-123]. Since we cannot stop to detail these investigations, we must note that they uncover entirely new prospects with respect to many problems in theoretical biology, and particularly perhaps with respect to the question of the nature of inheritance.

We point out, finally, that an attempt was made [1] to establish
a correlation between the content of free radicals in tissues and the growth of cancerous cells. This attempt, however, has not led to any success.

§7.5. Inorganic Free Radicals. Paramagnetic Gases

So far we have considered organic substances with radical-like character. The class of inorganic radicals is much less rich, but in it we include, alongside with a small number of stable radicals, also several unstable ones, which are produced in discharges, upon irradiation, during the course of chemical reactions, etc. Among these radicals there are some that are very important from the chemical point of view. One can classify arbitrarily as free radicals various atomic substances. A class of free radicals which is unique in the character of its spectra is made up of paramagnetic gases. We shall consider briefly in this section first free inorganic radicals in condensed phases and then paramagnetic gases.

1. The spectrum of atomic hydrogen obtained upon γ-irradiation of the acids $H_2SO_4$, $HClO_4$, and $H_3PO_4$ frozen at 77°K turned out to be a doublet with splitting $A' = 500$ oersted and with $g = 2.00$ [124, 125]. The maximum intensity of the effect in $H_2SO_4$ was observed at a ratio $H_2SO_4:H_2O = 1:5$; further dilution weakens the effect, which disappears in pure ice. These measurements were made in the centimeter wavelength band. At low frequencies (350 megacycles) an effect due to atomic hydrogen in pure ice was observed with $A' = 30$ oersted [126]. The appearance of this resonance in weak fields $H$ only can be attributed apparently to the large anisotropy of the $g$ factor for "atomic" hydrogen, observed in pure ice. The effects of atomic hydrogen and deuterium in frozen systems were observed in [127, 128].

The radical products produced upon discharge in water vapor and condensed at 77°K were investigated in [129]. The authors observed one
line with \( g = 2.0085 \) and with weakly pronounced inflection corresponding to \( g = 2.027 \). Upon heating to \( 138^0 K \), the resonance disappeared. Analogous results were obtained with \( D_2O \) and \( H_2O_2 \). In [130], in an investigation of the products produced at low temperature from vapors of \( H_2O, H_2O_2, \) and \( D_2O \) dissociated in a glow discharge, one line was likewise obtained with a weak additional maximum on one of its skirts. This maximum was interpreted by the authors of [130] not as an indication of the presence of a second radical, but as a consequence of the anisotropy of the \( g \) factor. The observed effect was ascribed on the basis of chemical considerations to the radical \( HO_2 \), and not \( OH \).

Irradiated nitrates of several salts gave a spectrum ascribed to \( NO_2 \) and consisting of a triplet with \( A' = 50 \) oersted [131, 132].

Among the stable inorganic radicals, mention should be made of the peroxides and ozonates of alkali metals (of the type \( MeO_2 \) and \( MeO_3 \), respectively). In the former the spectrum is due to the radical ion \( \cdot O_2^- \) and consists of one asymmetrical line with \( g_\parallel = 2.157 \) and \( g_\perp = 2.002 \) [133]. In ozonates (\( NaO_3 \) and \( KO_3 \)) the line turned out to be somewhat more symmetrical: \( g_\parallel = 2.003, g_\perp = 2.015 \) [134]. Dithionate of sodium, in which the resonance is apparently due to the \( SO_2^- \) ions, gave a line with \( g = 2.01 \) and \( \Delta H = 12 \) oersted [135].

Investigations of chlorine dioxide \( (ClO_2) \) were already mentioned earlier (see page 368) [12].

Let us mention, finally, the inorganic radical ion \( [(SO_3)_2NO]^{2-} \), the investigation of which in solution has been the subject of several papers. It gives a triplet picture, due to the interaction between the unpaired electron and the spin of the \( ^{14}N \) nucleus. The energy levels of the system, in investigations in weak fields, agree well with the Breit and Rabi formulas for the case \( I = 1, S = 1/2 \), as was shown in [135]. The mechanism of paramagnetic relaxation in solutions contain-
ing the \([(\text{SO}_3)_2\text{NO}]^{2-}\) ion was analyzed in detail by Lloyd and Pake [136].

2. Diatomic and polyatomic molecules of certain gases are, in accordance with the definition given at the beginning of this chapter, free radicals, inasmuch as they contain uncompensated electron spins. These gases include, in particular, \(\text{O}_2\), \(\text{NO}\), \(\text{NO}_2\), \(\text{ClO}_2\), and also vapors of some paramagnetic compounds. In addition to such stable gaseous free radicals, there is also a large number of unstable substances of radical-like nature, existing in a gaseous medium, for example \(\text{CH}_3\), \(\text{OH}\), etc., the investigation of which were discussed above for the case when they enter in the condensed phases.

Paramagnetic gases differ from the paramagnets considered above in the strong coupling between the magnetic moment of the unpaired electron and the moments of the rotational motions of the molecule. Consequently the system of levels observed in the investigation of paramagnetic resonance in gases turns out to be quite complicated.

The resolution of the spectral lines of paramagnetic resonance in gases can be observed only at reduced pressures \(p\). When \(p > 20\) mm Hg, the resolved lines are not observed in even a single case; actually, the pressure employed usually does not exceed \(1\) mm Hg. This brings about (considering the large number of spectral lines) difficulties in the experimental work with gases, which calls for installations of high sensitivity; the greater part of the research in this direction was carried out by Beringer and Castle.

From among the investigated gases, the one with the weakest coupling between electron spin and the rotation of the molecule is nitrogen dioxide \(\text{NO}_2\). At a pressure \(p = 10\) mm Hg, a triplet structure is observed, due to the nitrogen nucleus; at \(p = 1\) mm Hg, it begins to be resolved into a large number of components; this was interpreted by
Beringer and Castle as the Paschen-Back effect of free magnetic moments of the molecule: the electron spin moment, the nuclear spin moment, and the moment due to the rotation of the molecule. The level system can be described by the expression

\[ E_{N_p M_p M_J} = g_P H M_S + A M_S M_I + B M_S M_H \]  

(7.2)

where \( M_J \) is the rotational quantum number of the molecule. It was impossible to attain full resolution of the individual components [137, 138].

The NO molecule contains one unpaired electron and its ground state is \( ^2 \Pi \). It is split by the spin-orbit coupling into two doublet levels with distance 120 cm\(^{-1}\) between them; of these, the lower level \( ^2 \Pi_{1/2} \) is diamagnetic, since its projections of the spin and orbital momenta along the axis are equal and opposite; the upper level, \( ^2 \Pi_{3/2} \), is paramagnetic. It splits further into several components because of the interaction with the rotation. The resultant states are characterized by the total angular momentum \( J \). The momentum \( J = 3/2 \) corresponds to \( g = 4/5 \); this sublevel, split by the external magnetic field \( H \) into a fine structure triplet, was indeed observed in [139]. Each peak of the triplet has in turn a triplet hyperfine splitting due to the \(^{14}\)N nucleus. The theory of the Zeeman effect in NO was presented in [140].

The \( \text{O}_2 \) molecule is a biradical; it contains two unpaired electrons with parallel spins, while its angular moment along the axis is zero. Its ground state is therefore \( ^3 \Sigma \). Its orbital momentum combines with the spin momentum, producing levels corresponding to \( J = K, K \pm 1 \), where \( K \) is the quantum number of the total orbital angular momentum (molecular + electronic). The levels \( K \pm 1 \) are practically degenerate and are 2 cm\(^{-1}\) away from the level \( J = K \). Therefore at a wavelength of approximately 5 mm one can observe absorption in the absence of an external magnetic field \( H \). Superposition of the field \( H \) leads to a split-
ting of the J levels and to the possibility of observation of magnetic dipole transitions between the sublevels. In the region of fields $H \approx 3000 \text{ oersted}$, the coupling between the spin and orbital motion is disrupted, and this leads to the appearance of a large number (approximately 40) of resonance lines, due to the rotational levels. These lines were described in [141]. The theory of the spectrum was presented in [141-143].

In addition to stable paramagnetic gases, Beringer and his co-workers investigated also atomic hydrogen [144], oxygen [145], and nitrogen [146] in the gaseous phase. They used for this purpose a high-voltage gas discharge in a U-shaped discharge tube, in which they placed the corresponding molecular gases. This tube was directly connected to a vertical tube passing along the axis of a cylindrical cavity in the $H_{011}$ mode. Recombination on glass was prevented as far as possible by using suitable anticatalysts.

Dehmelt [147] proposed to add to the investigated gas (which had a partial pressure of about $0.01-0.1 \text{ mm Hg}$) inert gases at pressure $10-100 \text{ mm Hg}$. At such pressures it turns out to be possible to maintain a high arc temperature and thus dissociate by purely thermal means molecules of all types. In addition, the inert gas decreases the possibility of recombination, by slowing down the diffusion to the walls. They used this method to investigate atomic phosphorus ($^4S_{3/2}$). The line turned out to be a hyperfine doublet with $A' = 20 \text{ oersted}$. Another method was used in [148] for the investigation of atomic iodine; for this purpose photodissociation induced by irradiation of $I_2$ vapor directly in a resonant cavity was employed.

REFERENCES TO CHAPTER 7


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98. Abraham R.J., Whiffen D.H. (cited from [1]).
101. Ingram D.J.E., Bennett J.E., Phil. Mag. 45, 545, 1954.
- 401 -

- 402 -
130. Gorbanev A.I., Kaytmafov S.D., Prokhorov A.M., Tsentsiper A.B., 


- 403 -
For two solvents - benzene and carbon bisulfide - this influence was observed still earlier in [19].

Special experiments have shown that the ultraviolet does not act on the molecules of the solvent.

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<th>Manuscript Page No.</th>
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§8.1. Introduction

So far we have considered resonant absorption of an alternating electromagnetic field of one fixed frequency. Yet double resonance, which consists of simultaneous resonant absorption of electromagnetic radiation at two different frequencies, has found a variety of uses. We consider the most important examples of double resonance: 1) the Overhauser effect and other dynamic methods of nuclear polarization; 2) paramagnetic amplifiers and 3) optical investigations of paramagnetic resonance.

In the Overhauser effect one investigates simultaneously electron and nuclear paramagnetic resonance. Therefore, one of the frequencies employed lies in the microwave range and the other at high radio frequencies. An interesting application of this effect is the polarization of atomic nuclei.

Paramagnetic resonance is used for technical purposes to build amplifiers with exceedingly low noise level. In these amplifiers one uses for the most part fields with two different frequencies, lying in the microwave band. Radiation at one frequency is used to supply energy to the working medium; the other frequency pertains to the signal to be amplified.

In many investigations, the medium studied was subjected to the simultaneous resonant action of radiation at optical and microwave
frequencies. The combination of optical and radio research methods turned out to be very fruitful and within a short time it yielded many interesting data both in the field of atomic spectroscopy and on the theory of atomic collisions.

§8.2. Dynamic Methods of Nuclear Polarization

I. Overhauser effect in metals and semiconductors

Let us assume that the substance contains, along with particles that have an electron magnetic moment, also particles that have a non-zero nuclear moment. In a particular case, the electron and nuclear moments can pertain to one and the same atom. In many cases the mechanisms of electronic and nuclear spin lattice relaxation are such that the saturation of the electron paramagnetic resonance leads to considerable polarization of the nuclei. This effect was first considered theoretically by Overhauser [1] for metals.

At first glance the increase in nuclear polarization upon saturation of electron resonance may appear paradoxical, since the equalization of the populations of the different energy sublevels of the spin system means an increase in its temperature. But an increase in temperature should cause a reduction in the differences in population of the different nuclear Zeeman sublevels. This paradox is resolved, as indicated in particular by Van Vleck [2], by the fact that in our case there is no single electron-nuclear spin system. In the processes of interest to us there are involved three weakly interacting systems: the K system, connected with the kinetic energy of the conduction electrons of the metal; the Z system, the energy of which is due to the interaction between the electrons and the external static magnetic field (the Zeeman energy of electrons), and finally the N system, which includes the Zeeman energy of the nuclei. These systems can have different temperatures: $T_K$, $T_Z$ and $T_N$. 

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Overhauser [3] has shown that nuclear spin-lattice relaxation in metals is due essentially to the interaction between the moments of the nuclei and of the conduction electrons:

\[ \mathcal{H}_{SN} = a \mathbf{S} \cdot \mathbf{I} = a (I_z \delta_z + I_y \delta_y + I_z \delta_z), \tag{8.1} \]

where

\[ a = \frac{8}{3} \beta \gamma g_n g_n \delta(r). \tag{8.2} \]

Here \( r \) is the distance from the conduction electron to the nucleus and \( \delta(r) \) is the delta function. The interaction (8.1) has a contact character and is isotropic, from which we see that the sum \( S_z + I_z \) is the integral of the motion. Thus, it follows from the law of conservation of the angular momentum that under the influence of interaction (8.1) the following transitions are possible:

\[ M, m \rightarrow M - 1, m + 1. \tag{8.3} \]

Reorientation of the electron spin is accompanied by a reversal of the direction of the nuclear spin.

It must be kept in mind that the electron Zeeman energy \( E_Z = g \beta H_0 M \) is approximately \( 10^3 \) times larger in absolute magnitude than the nuclear Zeeman energy \( E_N = -g_\gamma H_0 M \). Consequently simultaneous reorientation of the electron and nuclear spins is possible if the \( K \) system, into which the excess of the energy released goes, participates in this process. Assume that the process (8.3) is accompanied by a change in the kinetic energy of the conduction electrons \( E_K \rightarrow E'_K \).

It then follows from the law of energy conservation that

\[ E_K - E'_K = g \beta H_0 - g_\gamma H_0 M = 0. \tag{8.4} \]

We denote by \( N_K, N_M, \) and \( N_m \) the number of particles per unit volume in the states \( K, M \) and \( m \) respectively. For each pair of interacting particles the probabilities of the direct and inverse transitions (8.3) are the same. Therefore the number of direct transitions will
be proportional to $N_K N_M N_m$, and the number of inverse transitions proportional to $N_K N_M - 1 N_m + 1$. Under stationary conditions we have

$$N_K N_M N_m = N_K N_{M-1} N_{m+1}. \quad (8.5)$$

Since

$$\frac{N_K}{N_{K'}} = \exp\left(\frac{E_K - E_{K'}}{kT_K}\right) = \exp\left[\frac{(g^3 + g_N \beta_N) H_0}{kT_K}\right],$$

$$\frac{N_M}{N_{M-1}} = \exp\left(-\frac{g^2 H_k}{kT_2}\right), \quad \frac{N_m}{N_{m+1}} = \exp\left(-\frac{g_N \beta_N H_0}{kT_N}\right), \quad (8.6)$$

it follows from (8.5) that

$$\frac{1}{T_N} = \frac{g^2 + g_N \beta_N}{g_N \beta_N T_K} - \frac{g^2}{g_N \beta_N T_Z}. \quad (8.7)$$

Under electronic resonance saturation conditions we have $T_Z \rightarrow \infty$. If we recognize in addition that $g_N \beta_N \ll g\beta$, we get

$$T_N = T_K \frac{g_N \beta_N}{g\beta}. \quad (8.8)$$

Thus, saturation of electron resonance reduces the temperature of the nuclear Zeeman system by a factor $\frac{g_N \beta}{g\beta}$. Therefore, if we assume that $g\beta H_0 \ll kT_K$, we obtain

$$\frac{N_m}{N_{m+1}} = 1 - \frac{g^2 H_0}{kT_K}. \quad (8.9)$$

The polarization of the nuclei proceeds as if their magnetic moments were to increase by $\frac{g_N \beta}{g\beta}$ times. We note that the nuclear $g$ factor can be both positive and negative. Accordingly, the temperature of the nuclear Zeeman system can assume both positive and negative values. For simplicity, a Boltzmann distribution was used in the derivation of (8.9). It is easy to verify that a Fermi distribution leads to the same result.

Under the influence of the radio frequency field that saturates the electron resonance, transitions are produced predominantly from the lower electronic Zeeman level to the upper one. The relaxation transitions of the electrons occur with large probability in the
opposite direction, and consequently a stationary mode is established. Among the various relaxation mechanisms, the one of importance to the Overhauser effect is that based on the electron-nuclear interaction (8.1). The electrons going from the upper Zeeman level to the lower one will continuously flip the nuclear spins in one direction or another. The nuclear polarization will grow until the number of transitions \( M, m \rightarrow M - 1, m + 1, \) occurring under the influence of the given relaxation mechanism becomes equal to the number of inverse transitions. It is clear therefore that with increasing difference between \( T_N \) and \( T_K \) the number of transitions contributing to the equalization of these temperatures will also increase. The Overhauser effect is an irreversible process of continuous transition of the electron Zeeman energy into lattice vibrations. This effect can therefore be readily interpreted by methods of thermodynamics and statistical physics [4-9]; it can serve as a good illustration of the principal premises of these theories. For the general theory of the Overhauser effect it is important to consider the relaxation processes in two spin systems [10, 11], that is, in systems containing two sorts of particles having different magnetic moments.

In the derivation of (8.9) we have assumed that the mechanism based on the interaction (8.1) is the only relaxation mechanism for the nuclei. The relaxation time due to this mechanism will be denoted by \( T'_1 \). Yet there are also other spin-lattice coupling mechanisms. If we denote the total spin-lattice relaxation time by \( T_1 \) and, in addition, take into account the fact that the saturation factor \( q_{12} \) of electron resonance can differ from 0, we obtain in place of (8.9)

\[
\frac{N_m}{N_{m+1}} = 1 - \frac{g\beta H_0}{kT_K}(1 - q) \frac{T_1}{T_i} - \frac{g\beta \rho N H_0}{kT_K}.
\]

(8.10)

This formula can be used only for specimens whose linear dimensions
are small compared with the skin layer depth $\delta$. Azbel, Gerasimenko and Lifshits [12] have shown that the Overhauser method makes it possible to polarize nuclei in specimens for which $d >> \delta$. The point is that the mean free path of the electron in the metal is much shorter than the distance covered by the electron between two such collisions, which change the spin orientation. There exists therefore a unique "anomalous skin effect" for the magnetic moment. The polarization of nuclei in specimens of arbitrary thickness has been calculated in [12].

The increased nuclear polarization resulting from saturation of the electron Zeeman levels should change the line shape of the electron paramagnetic resonance [13], since the field produced by the polarized nuclei will be superimposed on the external magnetic field.

The Overhauser effect was first investigated experimentally in lithium [14]. To avoid the difficulties connected with simultaneous utilization of a resonant cavity and a coil, the experiments were set up at relatively low frequencies, 13.4 megacycles and 7.96 kilocycles. Figure 8.1 shows a photograph in which it is seen how much the nuclear resonance signal is amplified as a result of the saturation of the electron resonance. The Overhauser effect was later on investigated in detail in sodium and lithium [15].

The use of the Overhauser effect to increase nuclear polarization was extended also to semiconductors, which offers the following advantages: 1) the poor conductivity eliminates the difficulties connected with the skin effect at microwave frequencies; 2) owing to the
small number of conduction electrons, the nuclear relaxation times are very large, so that the nuclear polarization effected with the aid of the high frequency field can be separated both in space and in time from the succeeding experiments on the observation of this polarization with the aid of a relatively low-frequency field.

The experiments were carried out with silicon crystals doped with phosphorus [16]. The polarization of the Si\(^{29}\) nuclei was retained for several minutes.

It must be noted that Honig [17] drew erroneous conclusions from his experiments on electron resonance in silicon containing arsenic impurities. Measurements have shown that the resonance absorption line has four hyperfine components in accordance with the value \(3/2\) of the nuclear spin of As\(^{75}\). Upon repeated passage through one end of the same component, the absorption decreases exponentially as \(1 - e^{-t/\tau}\) with \(\tau = 16\) sec. If one goes in succession through two neighboring components within a time interval which is much shorter than 16 seconds, by varying the field \(H_0\), then the intensity of the second peak will strongly increase. Honig assumed at first that he had discovered a method of 100 per cent polarization of nuclei at not too low temperatures. He thought that the transitions between the electron Zeeman sublevels, excited by the resonant radio frequency field, will rapidly align the nuclear spins as a result of the hyperfine interaction. The appropriate calculations were made by Kaplan [18]. However, later experiments made by Honig and Combrisson [19] have shown that the reason lies in the exceptionally long relaxation time.

2. Overhauser effect in nonmetals

The Overhauser effect can occur in substances which are not metals or semiconductors [20-22]. Indeed, for the effect which we have been considering in metals, the following two circumstances are
significant: 1) one of the mechanisms whereby the electron spins are relaxed is based on their coupling with the nuclear moments, which calls for conservation of the total angular momentum; 2) this coupling plays a decisive role in the relaxation of the nuclear spins; 3) the possibility of conserving the energy during the time of these relaxation transitions is guaranteed by the continuity of the kinetic energy spectrum of the conduction electrons; 4) under saturation conditions, relaxation transitions from the upper Zeeman level to the lower one exceed in number the transitions in the opposite direction.

Perfectly analogous conditions exist in many nonmetals: 1) to increase nuclear polarization it is not essential to conserve the sum of the electron and nuclear spins; it is merely important that the probabilities of the nuclear spin flips $m \rightarrow m'$ and $m \rightarrow -m'$ be unequal; 2) the hyperfine interactions determine the nuclear relaxation not only in metals but in many other substances; 3) the conservation of energy during the time of simultaneous flip of electron and nuclear spins can be guaranteed by transfer of the excess energy to the lattice vibrations in solids or to the Brownian motion of the particles in liquids and gases; 4) if the lattice is in the state of thermodynamic equilibrium, then the a priori probabilities of the relaxation transitions from the upper Zeeman levels to the lower ones will always exceed the probabilities of the inverse transitions.

Abragam [23] considered in detail the question of the Overhauser effect in nonmetals for several important cases. He made the following assumptions: a) the nuclear spin is $I = 1/2$; b) the external magnetic field is strong, so that one can speak with good approximation of the quantum numbers of the projections of the electron and nuclear spins on the $H_0$ direction; c) there is no direct coupling between the nuclear moments and the lattice vibrations; nuclear relaxation is
realized by the magnetic interaction of the nuclear and electron spins, which in general case has the form
\[ \mathcal{H}_1 = i \mathbf{a} \mathbf{S}, \]  
(8.11)
where \( \mathbf{a} \) is a symmetrical tensor. The operator \( \mathbf{\hat{a}} \) can be written in the form
\[ \mathcal{H}_1 = -\varepsilon \mathbf{N} \mathbf{B} \mathbf{N} \mathbf{S}, \]  
(8.12)
where \( \mathbf{\hat{B}} = -(a/g_N) \mathbf{S} \) can be called the magnetic field produced by the electron at the location of the nucleus.

The field \( \mathbf{H}_e \) is a random function of the time because random changes are possible both in the tensor \( \mathbf{a} \) and in the direction of the spin \( \mathbf{S} \). We shall speak of relaxation of the first type if it is due to changes in the tensor \( \mathbf{a} \), brought about by the lattice vibrations in solids or by Brownian motion in liquids. Responsible for the relaxation of the second type are electron spin flips resulting from the ordinary mechanisms of electron spin-lattice interaction, independent of the coupling with the nuclear moments.

We denote the states \((M = 1/2, m = 1/2), (-1/2, 1/2), (1/2, -1/2), (-1/2, -1/2)\) by \(a', a, b', b\) (Fig. 8.2), the summary population of the levels \(a\) and \(a'\) by \(N_+\), and that of levels \(b\) and \(b'\) by \(N_-\). In addition, we introduce the probabilities of the relaxation transitions between the different electron sublevels:
\[ A_{a'\to a} = A_{b'\to b} = A_{a\to a'} = A_{b\to b'} = A (1 - s), \]
(8.13)
\[ A_{a\to b} = A (1 + s), s = \frac{g_N H}{2kT}. \]

For the probabilities of the other relaxation transitions we assume
\[ A_{a'\to a} = A_{b'\to b} = A_{a\to a'} = A_{b\to b'} = \lambda_1 A, \]
\[ A_{a\to b} = \lambda_2 A (1 + s), A_{b\to a} = \lambda_3 A (1 - s), \]
(8.14)
\[ A_{a'\to b'\to a'\to b'} = \lambda_4 A (1 + s), A_{b'\to a'\to b'} = \lambda_5 A (1 - s). \]

If the electron transitions \(a \to a'\) and \(b \to b'\) are saturated by a
radio frequency field, then, as shown by Abragam, the nuclear polarization is determined by the following expression:

\[
\frac{N_+}{N_-} = 1 - \frac{2(\lambda_1 - \lambda_3)}{\lambda_1 + \lambda_2 + \lambda_3}.
\]

(8.15)

Let us consider the following particular cases.

1. In the metals which we considered above, relaxation of the first type takes place, determined by the interaction (8.1); therefore \(\lambda_1 = \lambda_3 = 0\) and consequently

\[
\frac{N_+}{N_-} = 1 - 2s,
\]

(8.16)

which agrees with formula (8.9).

2. In liquids, if we assume that the nuclear relaxation pertains to the first type and is determined by the magnetic dipole interactions between the nuclei and the paramagnetic impurities, the coefficients \(\lambda_1, \lambda_2\) and \(\lambda_3\) are related as 3:2:12, that is, as the mean values of the squares of the matrix elements of the operators \(\hat{\epsilon}_{ijk}, \hat{\delta}_{jk}\) and \(\hat{\epsilon}_{jk}\) (5.9). For the nuclear polarization we obtain

\[
\frac{N_+}{N_-} = 1 - 4s.
\]

(8.17)

3. In diamagnetic crystals containing paramagnetic impurities, the relaxation is of the second type. In this case \(\lambda_3 = \lambda_2\) and there is no Overhauser effect.

This result can be explained in the following fashion. Let us consider the transitions that lead to the nuclear spin flip \(1/2 \rightarrow -1/2\), namely \(a' \rightarrow b \rightarrow b'\) and \(a \rightarrow b' \rightarrow b\). The transitions \(b \rightarrow b'\) and \(b' \rightarrow b\) are realized under the influence of the saturating radio-frequency field and are not accompanied by a change in the nuclear spin orientation. On the other hand, the transitions \(a' \rightarrow b\) and \(a \rightarrow b'\) are due to the coupling with the lattice vibrations. Since the relaxation is of the second type and is due to magnetic interactions of the electron
and nuclear spins, the probabilities of both processes turn out to be the same \((\lambda_2 = \lambda_3)\); as a result the lattice acquires no energy whatever, meaning that additional polarization of the nuclei due to electron resonance saturation is impossible.

4. For substances containing paramagnetic atoms with nonzero nuclear spin, the calculations have been carried out under the assumption that the hyperfine structure of the resonance line is resolved and has an isotropic character. In this case \(\lambda_3 = 0\) and the polarization is

\[
\frac{N_+}{N_-} = 1 + \frac{2i}{2 + i},
\]

where \(\xi = \lambda_2/\lambda_1\). If we saturate not both but one of the electron transitions, then

\[
\frac{N_+}{N_-} = \frac{1 + i}{2 + i}.
\]

The theory of relaxation transitions between hyperfine energy sublevels was developed by Valiyev [24], who calculated the values of \(\lambda_1 A\) for typical ions of the iron and rare earth groups. The appropriate calculations for ions in the S states were made by Bashkirov [25]. The Overhauser effect was considered also theoretically for the case \(S = 1/2, I = 1\) with the ion \(^{64}\text{Cu}\) as an example. It was shown there that simultaneous saturation of one electron and one nuclear resonance results in nuclear polarization of the same magnitude as in the saturation of all the electron transitions [26].

Khutsishvili [27] has considered the question of polarization of nuclei belonging to paramagnetic atoms in nonmetals, by saturating only one of the hyperfine structure components. It turned out that it is most convenient to saturate the \(m = 0\) line if the nuclear spin \(I\) is even and the \(m = \pm 1/2\) if \(I\) is odd.

The Overhauser effect in nonmetals was investigated experimentally.
in many cases: on the protons of the free radical diphenylpicrylhydrazyl [28], on protons [29], on Li\(^7\) and F\(^{19}\) nuclei [30] in solutions containing the free radical (SO\(_3\))\(_2\)NO\(_2\), and on protons contained in benzene absorbed by carbon [31].

3. Method of adiabatic passage

The Overhauser method of nuclear polarization is applicable if the mechanism of nuclear spin-lattice relaxation obeys definite conditions. The method proposed by Feher [32], based on adiabatic rapid passage through the paramagnetic resonance lines (see §8.4) is suitable for substances that have a resolved hyperfine structure independently of the nature of the nuclear and electron spin-lattice relaxation mechanisms. The idea of the method will be illustrated with the aid of Fig. 8.3, which shows the Zeeman energy levels as functions of the applied magnetic field \(H_0\) in the case \(S = 1/2\), \(I = 1/2\). By \(v_e\) and \(v_N\) we denote the frequencies of the microwave and radio frequency fields applied perpendicular to \(H_0\). By decreasing the field \(H_0\) to a value \(H_1\), we excite the electron transitions \(M = -1/2\), \(m = 1/2\) to \(M = 1/2\), \(m = 1/2\).

If this is done under conditions of adiabatic rapid passage, then the vector of electronic magnetization will turn through 180°, and this will cause an inversion of the populations of the corresponding sublevels. The difference in populations of each pair of nuclear sublevels, pertaining to one and the same electron state, will now be determined not by the nuclear but by the electronic Boltzmann factor, something that can be readily observed by the nuclear resonance method. In this case, however, the population of both sublevels with \(m = +1/2\) is equal to the population of the sublevels with \(m = -1/2\),
and consequently on the whole there is no nuclear polarization. In order to obtain it, we pass adiabatically through nuclear resonance, to which the field $H_2$ corresponds. Since the energy interval $\hbar \nu_N$ between one pair of nuclear sublevels is not equal to the interval between the other pair of sublevels, as a result we obtain nuclear polarization equal to

$$\frac{N_+}{N} = 1 - 2z.$$  \hspace{1cm} (8.20)

This polarization vanishes after a time interval equal approximately to the nuclear relaxation time; the situation can be restored by repeated variation of the field $H_0$.

If we effect adiabatically the fast transition $\Delta m = 1, \Delta M = 0$, then the electron resonance will change strongly. Thus, we have a sensitive method of investigating nuclear resonance by observing the electron paramagnetic resonance absorption.

An experimental verification of the adiabatic passage method was carried out by Feher and Gere [33]. The experiments were set up with a silicon crystal containing phosphorus amounting to approximately $3 \cdot 10^{16}$ atoms of $^{31}$P per cubic centimeter. Earlier investigations (§6.3) have shown that it is possible to observe in this substance the hyperfine structure of paramagnetic resonance lines as a result of interaction between the donor electron and the magnetic moment of the $^{31}$P; the electron relaxation time was found to be quite long.

In the experiments of Feher and Gere, the external field at which the transitions were investigated was approximately 3130 oersted, and the specimen temperature was 1.25°K. The electron resonance line was observed by a superheterodyne method without the use of field modulation. The microwave cavity was made of pyrex coated on the inside surface with a thin layer of silver. This insured the penetration
into the cavity of the radio frequency field necessary for excitation of the transitions between the nuclear sublevels. The amplitudes of the microwave and radio frequency fields in the specimen were on the order of 0.001 oersted. The constant field $H_0$ changed within approximately four seconds from an initial value 3150 oersted to 3110 oersted, after which it again returned to 3150 oersted.

The results of the experiments confirmed Feher's calculations. In the absence of a radio frequency field, the amplitude of the electron resonance line changed little in the secondary passage through resonance; on the other hand, if a radio frequency field was applied during the interval between the first and second passages to induce the transition $h\nu_N$ (see Fig. 8.3), then the intensity of the electron resonance line decreased sharply during the second passage, thus evidencing the presence of nuclear polarization. An analogous method was used in [34].

4. Method of parallel fields

Jeffries [35] proposed to use for nuclear polarization the forbidden transitions that appear in the case when the alternating and static magnetic fields are oriented parallel to each other, as a result of the fact that the hyperfine interactions cause a slight overlapping of the states with different values of $M$ and $m$. If the hyperfine interaction operator has the form $A\hat{I}_z\hat{S}_z + B(\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y)$ then the wave functions, which in the zero approximation are equal to $\psi(M,m)$, will assume in the next approximation the form $\psi(M,m) + + \alpha(B/H)\psi(M + 1, m + 1)$.

By way of illustration we consider the case $S = 1/2$, $I = 1/2$ (Fig. 8.4). The solid arrows denote the transitions that are possible in the usual mutually-perpendicular arrangement of the alternating and static magnetic fields ($\Delta M = 1$, $\Delta m = 0$). The dashed arrows show the...
"forbidden" transitions, which arise in the case when the fields are parallel. With this, from the form of the perturbed wave functions it follows that \( \Delta (M + m) = 0 \). If we saturate the transition \( M = -\frac{1}{2}, m = + \frac{1}{2} \rightarrow M = \frac{1}{2}, m = -\frac{1}{2} \), with a radio frequency field, polarization is immediately produced:

\[
\frac{N_+}{N_-} = 1 - \varepsilon.
\]

If the polarized nuclei are radioactive, then the polarization can be detected from the resultant anisotropy of the gamma radiation. The effect will in this case be proportional not to the number of atoms participating in the paramagnetic resonant absorption, but to the number of radioactive decays. This method is therefore particularly convenient for the study of short-lived nuclei.

The Jeffries method was used to polarize radioactive \( \text{Co}^{60} \) nuclei contained in the single crystal \( \text{La}_2\text{Mg}_3(\text{NO}_3)_12\cdot 24\text{D}_2\text{O} \) [36]. The ratio of magnesium to its isomorphic cobalt-isotope substitutes was \( \text{Mg:Co}^{59} : \text{Co}^{60} = 10^4 : 50 : 1 \). The measurements were carried out at a frequency of 9.3 \( \times \) 10\(^9\) cps at a temperature 1.6\(^\circ\)K. The Z axis of the crystal was perpendicular to the static and the oscillating magnetic fields. The paramagnetic absorption in \( \text{Co}^{60} \) is very weak and cannot be measured directly. Paramagnetic resonance is detected by the anisotropy of the gamma radiation. The spectrum contained 21 lines in accordance with the well known value of the spin of the \( \text{Co}^{60} \) nucleus. The following ratios were obtained for the line intensities: 83:100:83:52:18 in good agreement with the predictions of the theory [37].

5. The method of Abragam and Proctor [38]

Let us assume that the substance contains electron and nuclear...
paramagnetic centers. For simplicity we assume that the spins of the centers are \( S = 1/2, I = 1/2 \). Assume that some interaction exists between the electron and nuclear spins, say magnetic dipole coupling. This coupling causes an overlap of the electron and nuclear states, so that the wave functions assume the form \( \psi(M,m) + \alpha\psi(M',m') \) where \( \alpha \ll 1 \).

Let us assume that an alternating field of frequency \( \nu = \nu_e + \nu_N \) is applied perpendicular to the static field \( H_0 \). Then, with a certain probability \( P \) proportional to \( \alpha^2 \), simultaneous reorientation of the electron and nuclear spins begins. We denote the time of the electron spin-lattice relaxation by \( T_{1e} \) and the corresponding time for the nucleus by \( T_{1N} \). Let \( 1/T_{1N} < P < 1/T_{1e} \). Then obviously after the onset of dynamic equilibrium the ratio of the populations of the Zeeman levels of the nuclei will be the same as that of the electron levels.

A similar effect can be obtained by applying energy at the difference frequency \( \nu_e - \nu_N \). In this case, obviously, the electron spin flip will be accompanied by a reorientation of the nuclear spin in the opposite direction.

Abragam and Proctor [38] verified experimentally their proposed method using a LiF single crystal. The experiments were carried out at a frequency \( \nu = \nu_e + \nu_N = 9.4 \) megacycles. The attained increase in polarization of the Li\(^6\) nuclei was approximately by \( \gamma(F^{19})/\gamma(Li^{6}) = 6.5 \) times.

The further development of this method is described in [120]. In particular, it became possible to polarize nuclei of aluminum in corundum with chromium impurity [121].

§8.3. Paramagnetic Amplifiers and Generators

Ordinary radio devices which use vacuum tubes, klystrons, magnetrons, etc. convert the kinetic energy of charged particles into energy of a radio frequency electromagnetic field. For many reasons,
the possibility of obtaining radio frequency electromagnetic energy by using the internal energy of atoms and molecules in an excited state is very attractive. This idea was first realized with the aid of molecular beams* [39-41]. Molecular generators have found many important applications because of their exceedingly high frequency stability, but cannot be used extensively for technical purposes owing to their unusually low power and limited range of operating frequencies. Such a device can be used in principle also as an amplifier with exclusively low noise level. However, such an amplifier has not found practical use because of the exceedingly narrow band of the frequencies amplified by it and the impossibility of tuning it.

It has recently become possible to use paramagnetic resonance in solids to produce amplifiers which have equally low noise, but have a much larger band width and can be readily tuned over a wide range. Along with paramagnetic amplifiers, it is possible that paramagnetic generators will also find technical applications, particularly in the range of millimeter and submillimeter wavelengths.

The operating principle of paramagnetic amplifiers and generators consists in the following. We have seen in §1.5 that unlike the optical range the probabilities of spontaneous transitions in the radio frequency band are exceedingly small. We can therefore speak here of the use of induced emission. In addition, whereas in optical light sources each atom radiates independently of the other and the radiation is therefore not coherent, in the radio band the radiation is coherent; there exist definite phase relationships between the induced emission and the radio frequency electromagnetic field that causes it.

We now consider a medium containing a large number of paramagnetic centers, each of which has a definite system of energy levels. Let $E_m$ and $E_n (E_m > E_n)$ be a pair of levels, the interval between which lies
in the radio frequency band.* We denote by \( N_m \) and \( N_n \) the number of paramagnetic centers per unit volume at the levels \( E_m \) and \( E_n \). We assume that the medium has in some manner been placed in such an equilibrium state, by which the number of centers in the upper level is larger than in the lower one. A discussion of different methods of exciting the medium will be presented in the following sections. We assume also that the relaxation mechanisms are of low efficiency and that therefore the transition of the paramagnet into equilibrium state resulting from internal interactions is relatively slow. Let now a weak radio signal of frequency \( \nu_{mn} = (E_m - E_n)/h \) be incident on the medium. Under the influence of this signal, transitions \( E_m \leftrightarrow E_n \) occur, the probabilities of which are the same for both possible directions. But since \( N_m > N_n \), the paramagnetic resonant absorption will be negative. In other words, radiation will take place, the power of which, according to (1.7) and (1.11), can be estimated with the formula

\[
R'_{Am} = \frac{\kappa^2 (N_m - N_n) \langle m | \mu_x | n \rangle |^2 \varepsilon_{mag} H_y^2}{\hbar \Delta \nu}.
\]

We note that the quantities \( (N_m - N_n) \), \( \langle m | \mu_x | n \rangle \) and \( \Delta \nu \) cannot, strictly speaking, be regarded as independent of one another. Indeed, the more appreciable the spin \( S \) of the paramagnetic centers, the larger will be the matrix elements of the magnetic moment. But an increase in \( S \), that is, in the number of spin levels, brings about a decrease in \( N_n \) and \( N_m \). At the same time, the increase in \( S \) can bring about an increase in the resonant width \( \Delta \nu \). In speaking of the width of a resonance line it is necessary, as we already know (see §5.8), to distinguish between the "inhomogeneous broadening," due to the inhomogeneity of the fields acting on the different paramagnetic centers, and the "homogeneous broadening," which is a result of dipole-dipole and exchange interactions between like particles and due to other
factors. The sources of the inhomogeneous broadening — the spins of the nuclei belonging to the diamagnetic atoms, the inhomogeneity of the applied magnetic field, the inhomogeneity of the crystalline fields, etc. — begin to play a lesser role with increasing concentration of the paramagnetic centers. An increase in the concentration, and consequently also in \((N_m - N_n)\) is accompanied, starting with a certain minimum value, by an increase in the width \(\Delta v\).

The simplest amplifier, and at the same time the one having many advantages, can be visualized as consisting of a wave guide filled with an active paramagnetic substance. The traveling wave will increase in power as it propagates, so that the power gain, neglecting losses in the wave guide, turns out to be

\[
g^* = \exp(\alpha l),
\]

where \(l\) is the length of the wave guide and \(\alpha = \frac{A P_{iz} I}{P_{pad}}\), while \(A\) is the area of the transverse cross-section of the wave guide. The power of the incident wave is

\[
P_{xax} = \frac{1}{8\pi} A c H',
\]

It follows from (8.21) and (8.23) that

\[
\alpha = \frac{8\pi}{c \chi} \left| \frac{N_a}{N_n} \right| < \frac{\mu_0}{\mu} |a| \frac{1}{\chi H^2}.\]

Calculation shows that for real values of \((N_m - N_n)/\Delta v\) the length of the wave guide must be very large, on the order of several meters, in order to obtain noticeable amplification.

In order to reduce the amplifier dimensions one employs resonant cavities in lieu of wave guides. If the nonmagnetic losses in the medium and the losses in the cavity walls are smaller than the power radiated by the paramagnet, then the energy stored in the cavity will build up and in this case the induced emission of the paramagnetic centers will occur not only under the influence of the weak radio
signal, but also under the influence of the radiation previously emitted by the paramagnet. Thus, a cavity filled with an active paramagnetic medium can be regarded as a resonant system with positive feedback.

This system can be characterized by means of a negative figure of merit \( Q_m \), connected with the magnetic "losses," the figure of merit \( Q_o \), determined by the nonmagnetic losses inside the cavity, and by the figure of merit \( Q_e \), due to the external losses resulting from the coupling with the wave guide or with the coaxial line. According to (1.10) we have

\[
-\frac{1}{Q_m} = \frac{4P_{\text{nm}}}{(\mathbf{H})_v^2},
\]

where \((\mathbf{H}_r^2)_v\) is the value of \(\mathbf{H}_r^2\) averaged over the volume of the cavity.

Our system will operate like a generator if the self-excitation condition

\[
-\frac{1}{Q_m} > \frac{1}{Q_o} + \frac{1}{Q_e},
\]

is satisfied. The power of the generated oscillations will be limited by the saturation effect, for if the populations of the levels \(E_m\) and \(E_n\) start to become equalized, the increase in the power of the induced emission will stop. The saturation causes the self-oscillating system considered here to be nonlinear and thereby determines the amplitude of the steady-state oscillations in the cavity. The system will operate like an amplifier if

\[
\frac{1}{Q_o} + \frac{1}{Q_e} > -\frac{1}{Q_m} > \frac{1}{Q_o}.
\]

If we denote again the power gain by \(g^2\), we can readily conclude that for a cavity type amplifier the following formula holds true*

\[
g^2 = \frac{Q_o^{-1} - Q_o^{-1} - Q_m^{-1}}{Q_o^{-1} + Q_o^{-1} + Q_m^{-1}}.
\]
The amplifier bandwidth $B$ can be defined as the ratio of the frequency $v$ to the $Q$ of the apparatus:

$$B = v\left(\frac{1}{Q_e} + \frac{1}{Q_m} + \frac{1}{Q_s}\right).$$  (8.29)

Usually $Q_0$ is sufficiently large so that the last two formulas assume the simpler form

$$g_a = \frac{Q_m - Q_e}{Q_m + Q_e},$$  (8.28a)

$$B = v\left(\frac{1}{Q_e} + \frac{1}{Q_m}\right).$$  (8.29a)

Multiplying these expressions we obtain

$$g_a B = v\left(\frac{1}{Q_e} - \frac{1}{Q_m}\right).$$  (8.30)

If the gain is large, then $Q_e$ and $|Q_m|$ should be practically the same. We therefore have

$$g_a B = \frac{2v}{Q_e} = \frac{2v}{|Q_m|}.$$  (8.31)

We see that the product of the square root of the gain and the bandwidth is a quantity that remains approximately constant for an amplifier in which the configuration of the resonant cavity and the volume of the paramagnetic medium remain constant. It is seen from (8.28) and (8.29a) that if the gain is large, then the power gain $g_a^2$ and the bandwidth $B$ are very sensitive to relatively small variations of $Q_e$ and $Q_m$. However, no matter how large the variations of $g_a$ and $B$ may be, the product of these quantities remains almost constant.

Paramagnetic amplifiers and generators have important advantages. First, the amplifiers are rid of many noise sources that are inherent in electronic devices, and their noise temperature amounts to several degrees Kelvin. Second, paramagnetic generators and amplifiers have no upper frequency limits, since the frequencies of the generated and amplified oscillations are determined by the intervals between the spin energy levels. These intervals can be made sufficiently large
by a suitable choice of the medium and by increasing the static magnetic field within permissible limits.

No practical paramagnetic generators have been created to date. We shall therefore consider henceforth only amplifiers and only of the cavity type.

The main advantage of paramagnetic amplifiers, namely their high sensitivity, is connected with the low level of the intrinsic noise. Many special investigations have been devoted to this problem [43-45]. The low noise level in these devices is insured primarily by the fact that they, unlike devices using vacuum tubes and semiconductors, contain no free charges and therefore are not subject to the shot effect, nor are there any flicker noises, excess noises, etc. The lower noise limit of paramagnetic amplifiers is determined by the spontaneous emission. Noise in paramagnetic amplifiers can be characterized by an effective noise temperature $T_n$, the magnitude of which is approximately equal to the absolute value of the effective spin temperature $T_s$.

The use of low (helium) temperatures, which is necessary for effective operation of the amplifier (so as to increase the difference in level populations and to lengthen the relaxation time $T_1$) contributes at the same time to a reduction in the noise levels.

Strandberg [45] calculated the noise figure $K_{sh}$ of a paramagnetic amplifier.* The formula he obtained for a resonator type amplifier has the following form:

$$K_m = \left( \frac{\xi_a + 1}{\xi_a} \right) \frac{1}{\rho_a(T_a)} \left[ (1 - t) \rho_a(T_a) + t \rho_a(T_a) + \right.\
\left. + \frac{Q_a}{Q_a} \left[ \rho_a(T_a) - \rho_a(T_m) \right] - \left( \frac{\xi_a - 1}{\xi_a + 1} \right) \rho_a(T_a) + \right.\
\left. + (\xi_a + 1) \rho_a(T_a) \right].$$

(8.32)

The values of many of the quantities contained in this formula can be understood by referring to the schematic diagram of the amplifier (Fig. 8.5). $T_a$, $T_t$, and $T_c$ denote the temperatures of the antenna...
Fig. 8.5. Temperature parameters determining the noise figure of a paramagnetic amplifier. (signal sources), transmission line, and the paramagnetic medium, respectively. \( T_0 \) is the temperature at the output of the cavity (load temperature), \( t \) is the power loss factor in the transmission line, that is, the ratio of the output power to the power at the input of the transmission line. The parameter \( T_m \) has the dimension of temperature and can be determined from the following formula:

\[
\frac{N_m - N_n}{N_m + N_n} = \text{th} \left( \frac{h\nu m}{2kT_m} \right).
\]  

(8.33)

If \( \eta \) is the number of spin levels of one particle, then

\[
N_m + N_n \approx \frac{2N_h}{\eta}.
\]  

(8.34)

From (8.33), (8.34), (8.21) and (8.25) it follows that

\[
T_m = \frac{h\nu m}{2k} \left[ \text{Arth} \frac{h\nu}{8\pi^2 \eta N_k Q_m (|n| |n|)} \right].
\]  

(8.35)

In accordance with Planck's formula, the mean oscillator energy at temperature \( T \) is

\[
p(T) = \frac{h\nu}{\exp(h\nu/kT) - 1}.
\]  

(8.36)

Usually \( h\nu \ll kT \) and therefore \( p(T) \approx kT \). If we assume furthermore, first, that the losses in the transmission line are small and \( t \approx 1 \), and second that the gain is appreciable \( g_a \gg 1 \), then (8.32) assumes the simpler form

\[
K_a = 1 - \frac{T_m}{T_a} \left( 1 + \frac{Q_{a}}{Q_{r}} \right) + \frac{T_r}{T_a} \frac{Q_{a}}{Q_{r}},
\]  

(8.37)

and the noise temperature will accordingly be

\[
T_a = (K_a - 1) T_a = - T_m \left( 1 + \frac{Q_{a}}{Q_{r}} \right) + T_r \frac{Q_{a}}{Q_{r}}.
\]  

(8.37a)

It is easy to see that by choosing the amplifier parameters we can...
make the noise $K_{nh}$ close to unity and $T_n \approx T_m$. An additional noise source is produced if the excitation of the working medium is carried out by the saturation method (see §8.5). Weber [46] has shown that the corrections to formula (8.32) brought about by this fact have no practical significance.

The most important problem arising in the construction of a paramagnetic amplifier is the choice of the working medium and the determination of the methods for its excitation. It is obvious that there is a great variety in the methods of exciting paramagnetic centers in the case of particles with effective spin $S' > 1/2$, that is, in the case when the number of spin levels exceeds two. We shall therefore consider in the following sections two- and three-level amplifiers separately.

§8.4. Two-level Paramagnetic Amplifier

All the methods proposed for the excitation of paramagnetic centers with effective spin $S' = 1/2$ consist in inverting the populations of the Zeeman energy sublevels. In the equilibrium state, the ratio of the populations of the lower [1] and upper [2] spin levels is

\[ \frac{N_1}{N_2} = \exp\left(\frac{\mu B}{kT}\right) \exp\left(\frac{h \omega}{kT}\right). \]  

(8.38)

The problem consists of inverting this ratio for a more or less prolonged time interval. Let us stop to discuss three possible methods of inverting the populations of the spin levels.

a) Nonadiabatic change in direction of the static magnetic field

The simplest method of accomplishing the indicated purpose is by rapid (nonadiabatic) change in the sign of the applied static magnetic field $H_0$. The ratio $N_1/N_2$ is then reversed, the most populated lower level becomes the upper level, and vice versa. The reversal in the field $H_0$ must be so fast as to satisfy the nonadiabaticity condition
which in our case has the form

\[
\frac{1}{H_0} \frac{dH}{dt} > 2 \pi v_0.
\]  

(8.39)

The lower the precession frequency \( v_0 \), that is, the smaller the field \( H_0 \), the easier it is to satisfy this condition. However, the field \( H_0 \) cannot be made as small as desired, for it must appreciably exceed the width of the resonance line: \( H_{\text{min}} \gg \Delta H \).

It is therefore most advantageous to proceed in the following fashion: Reduce the field \( H_0 \) adiabatically and slowly to a value \( H_{\text{min}} \), and then carry out nonadiabatically and rapidly the reversal \( H_{\text{min}} \rightarrow -H_{\text{min}} \) followed by an adiabatic and slow reduction of the field to \(-H_0\). It is obvious that this entire procedure should be performed within a time much shorter than \( T_1 \). By way of an example let us assume that \( \Delta H \approx 0.1 \) oersted, \( H_{\text{min}} \approx 0.5 \) oersted; then, in order to change the field \( H_0 \) by 1 oersted, it is necessary in accord with (8.39) to have a time interval of about \( 5 \cdot 10^{-8} \) sec. Field changes of this type can be produced presently by modern pulse techniques. The method described by us has been used for the time being only in nuclear paramagnetism [48]. However, it has a great advantage over other methods of excitation of paramagnetic centers in that it does not need the application of an additional radio frequency field. One can therefore expect that nonadiabatic change of magnetic field direction will be used for the construction of microwave generators of very high frequencies.

b) Adiabatically rapid passage

Bloch [49] has shown that the spin level populations can be inverted by rapid but adiabatic passage through resonance, by changing the frequency of the alternating field or the intensity of the static field. Without dwelling on the calculations which lead to this result by a solution of (5.1) (see, for example, [50,51]), let us illustrate
this method with the classical model.

The behavior of a dipole in a magnetic field $H$ is best investigated by changing over to a coordinate system rotating with a certain angular velocity $\omega$. In the rotating coordinate system the motion of the dipole will be determined by the same equations of motion as in the inertial coordinate system, provided we assume that the dipole is acted upon not by the field $H$ but by the effective field

$$H_{\text{eff}} = H - \frac{\omega}{\gamma}, \quad \gamma = \frac{\gamma H}{\hbar}. \quad (8.40)$$

The magnetic moment of the dipole will precess in this case with circular frequency $\omega_{\text{eff}} = \gamma H_{\text{eff}}$. We now put, as usual $\overrightarrow{H} = \overrightarrow{H_0} + \overrightarrow{H_1}$, where $\overrightarrow{H_0}$ is the static field and $\overrightarrow{H_1}$ is a small field rotating uniformly with frequency $\omega$ in a plane perpendicular to $\overrightarrow{H_0}$. Figure 8.6 shows the three possible cases:

- $\gamma H_0 > \omega$,
- $\gamma H_0 = \omega$,
- $\gamma H_0 < \omega$.

We see that if the change in $H_{\text{eff}}$ is adiabatically slow, then the sign of the magnetization vector reverses after passing through resonance,
and consequently the distribution of the particles over the spin levels is reversed: \( N_2 > N_1 \). The adiabatic change in \( H_{\text{eff}} \) denotes that the relative reduction in \( H_{\text{eff}} \) during the time \( 1/\omega_{\text{eff}} \) should be small. The smallest value of \( H_{\text{eff}} \) is \( H_1 \). Therefore the adiabaticity condition has in our case the form

\[
(tH_0)^{-1} \ll \Delta t
\]  
(8.41)

if we denote by \( \Delta t \) the time necessary to change the field \( H_0 \) by an amount equal to the half width \( \Delta H \) of the resonance line. At the same time, passage through resonance should be rapid, for it is necessary to satisfy also the condition

\[
\Delta t \ll T_1
\]  
(8.42)

The method of adiabatically rapid passage has the following advantages:  
1) there is no need for good stabilization of the frequency \( \nu \) of the field \( H_1 \); 2) the time of passage \( \Delta t \) can change over a wide range.

c) 180° pulse

Let us assume that the paramagnet is under resonance conditions. If we change over to a coordinate system rotating with resonant frequency, then \( H_{\text{eff}} = H_1 \). Consequently, the magnetic dipole is acted upon only by the constant magnetic field \( H_1 \) (Fig. 8.6b). The magnetization vector will precess about \( H_1 \) with angular frequency \( \omega_1 = \gamma H_1 \). If we use in place of a continuously acting alternating magnetic field only a pulse of duration

\[
t_p = \frac{\pi}{\omega_1},
\]  
(8.43)

then the direction of the magnetization vector will change by 180° and the spin levels will be inverted. The inversion, however, will not be complete if, first, \( H_1 \) is not appreciably larger than the resonance width \( \Delta H \), and second if the condition (8.43) is not satisfied with great accuracy. It goes without saying that the duration of the pulse
should be much shorter than the relaxation time $T_1$. The "180° pulse" method is more convenient than the "rapid adiabatic passage" in that it consumes less alternating magnetic field power and a shorter time interval for the inversion of the spin levels [50].

The operation of a two-level amplifier can be visualized in the following fashion. At first the working medium is in the equilibrium state. Then the spin levels are inverted for a time $t_1$ by one of the methods considered above. Following this, for a time $t_2 \ll T_1$, the amplification process occurs. Then the thermal equilibrium is restored for a time $t_3$. We see that the two-level amplifier is an intermittently acting device. The time intervals $t_2$ of active operation are divided by "dead" intervals $t_3 + t_1$. If the thermal equilibrium occurs in a medium that is left alone, then the time $t_3$ will be very large, on the order of $T_1$. We propose here two methods for accelerating the transition to the equilibrium state.

The first method consists of illuminating the paramagnet. This method is suitable if the working medium is a doped semiconductor, such as silicon doped with elements of group V (P, As, Sb) or lithium. In these semiconductors, at heating temperatures and at concentrations $N_0 \approx 10^{17} - 10^{18} \text{ cm}^{-3}$, the time $T_1$ runs into many seconds (see §6.2). Under the influence of the illumination, the relaxation time is shortened to several microseconds. If we take account of the fact that the time $t_1$ amounts to in the worst case several milliseconds, we see that the "dead" time can be made negligibly small, and the amplifier operates almost continuously.

The second method of shortening $t_3$ consists in the following. We use as the working medium crystals containing paramagnetic particles of two types. Let the relaxation time $T_1$ of the particles of one type (A) be several orders of magnitude higher than that of particles of
the second type (B). These two sorts of particles, of course, have different spin level systems. The active paramagnetic centers of the amplifier are the particles A. After the end of the period $t_2$, the static field $H_0$ is changed such as to make the interval between the spin levels of particles A equal to the interval between any pair of spin levels of the particles B. Then, owing to the spin interaction, the energy will be transferred from particles A to particles B, and then very rapidly to the lattice. This type of decrease in relaxation time was experimentally investigated in several cases [53].

Let us determine the condition for the amplification, assuming that relaxation losses can be neglected. We denote by $(H_1^2)_S$ the square of the alternating magnetic field intensity averaged over the volume of the paramagnetic specimen. We assume that $| \langle m | \mu_x | n \rangle | = \beta$, $N_m - N_n = N_0 h\nu/2kT$. Then from (8.27), (8.25) and (8.21) it follows that amplification will take place if

$$N_o > \frac{kT\Delta\nu}{2\pi\gamma^2Q_s} \frac{(H_1\nu)}{(H_1)_S}. \quad (8.44)$$

The first attempt at constructing a paramagnetic amplifier was carried out using silicon doped with phosphorus under the following experimental conditions [54]: $\nu = 9000$ megacycles, $Q_0 = 10,000$, $T = 2^0K$, $\Delta\nu = 4 \cdot 10^6$, $(H_1^2)_S \approx (H_1^2)_V$. After substitution of these values, condition (8.44) assumes the form $N_0 > 10^{17} \text{ cm}^{-3}$. In the experiments described this condition was not fulfilled and therefore the sought effect was not observed. Positive results were obtained by Feher et al. [55], who replaced the natural silicon by isotopically pure $(99.88 \pm 0.08%)$Si$^{28}$, as a result of which the paramagnetic resonance line was narrowed down from 2.7 to 0.22 oersted, since the inhomogeneous broadening due to the hyperfine interaction of the electron shell of the phosphorus with the Si$^{29}$ nuclei disappeared.
experiments were set up under the following conditions: \( N_0 = 4 \cdot 10^{16} \) cm\(^{-3}\), \( T_1 \approx 1 \) min at temperature \( 1.2^\circ \)K, \( \nu = 9000 \) megacycles, \( Q_0 \approx 20,000 \). Excitation of paramagnetic centers was by the method of rapid adiabatic passage.

Working media successfully used for two-level amplifiers were quartz and magnesium oxide, the paramagnetic centers in which were produced by strong neutron bombardment [56]. The level inversion was by the method of adiabatic passage. The frequency of the amplified signal was \( \nu = 9000 \) megacycles, the \( Q \) of the loaded cavity was \( Q \approx 6000 \), and the temperature was \( 4.2^\circ \)K. In the experiments with quartz, the number of paramagnetic centers was \( N_0 \approx 10^{18} \). The inverted state lasted about 2 milliseconds. If the signal is amplified 1.2 milliseconds after the level inversion, then \( g \alpha B = 5 \cdot 10^6 \) sec\(^{-1}\) with the gain changing from 8 to 21 db. In experiments with MgO, the number was \( N_0 \approx 10^{17} \). The inverted state lasted approximately 2.5 milliseconds. A gain of 20 db was observed 125 microseconds after the level inversion.

In conclusion, we note that continuously operating two-level amplifier designs were proposed [57], based on the use of mechanically rotating devices.

§8.5. Three-level Paramagnetic Amplifier

1. Operating principle

If the number of spin levels of paramagnetic centers exceeds two, then the excitation of the working medium can be effected by saturating the electron resonance. Let us assume that the particles have three spin levels (Fig. 8.7). We assume also that saturation has been produced with the aid of an oscillating field of frequency \( \nu_{31} \) and of sufficient power, so that the populations of levels \( E_1 \) and \( E_3 \) have become equalized: \( N_1 \approx N_3 \). Then, obviously, either \( N_2 < N_3 \) and an ampli-
fier can be produced for signals of frequency $v_{32}$, or else $N_2 > N_1$ and signals of frequency $v_{21}$ can be amplified. The idea of the possibility of producing a molecular generator using this excitation method was first stated by Basov and Prokhorov [58]. The possibilities of constructing a three-level paramagnetic amplifier excited by the saturation method were considered by Bloembergen [59]. The advantages of an amplifier of this type are the continuous operation and the possibility of using media with relatively short relaxation times. These times should be sufficiently long to permit practical saturation of the paramagnetic resonance.

Let us find the conditions for the excitation of a three-level amplifier. Let $A_{1k}$ be the per second probability for the transition of a particle from the level $E_1$ to the level $E_k$ under the influence of the lattice vibrations (see §5.3), and let $p_{1k}$ be the probability of transition between the same levels under the influence of the radio frequency field, calculated in accordance with (1.3). If $h
u_{1k} << kT_c$, then the populations of the individual levels will obey the equations

$$
\frac{dN_1}{dt} = A_{11} \left( N_1 - N_3 - \frac{N_3 h
u_{11}}{3 kT_c} \right) + \\
+ A_{12} \left( N_2 - N_3 + \frac{N_2 h
u_{12}}{3 kT_c} \right) + p_{11} (N_1 - N_3) + p_{22} (N_3 - N_4),
$$

$$
\frac{dN_2}{dt} = A_{22} \left( N_2 - N_4 + \frac{N_4 h
u_{22}}{3 kT_c} \right) + \\
+ A_{32} \left( N_3 - N_4 - \frac{N_3 h
u_{32}}{3 kT_c} \right) + p_{31} (N_3 - N_4),
$$

$$
\frac{dN_3}{dt} = A_{33} \left( N_3 - N_4 + \frac{N_4 h
u_{33}}{3 kT_c} \right) + \\
+ A_{32} \left( N_3 - N_4 + \frac{N_3 h
u_{32}}{3 kT_c} \right) - p_{31} (N_3 - N_4).
$$

If it is assumed that $p_{31} >> p_{32}$ and $p_{31} >> A_{1k}$, we obtain

$$
N_1 - N_3 = N_2 - N_4 = \frac{h
u_{31} A_{32} - A_{32} A_{33}}{A_{33} + A_{32}}.
$$

This quantity will be positive, and consequently negative absorption
will take place at a frequency $v_{32}$ if

$$A_{n^*n} > A_{n^*n}.$$  \hspace{1cm} (8.47)

If the opposite inequality holds true, then the negative absorption will take place at frequency $v_{21}$. Substituting (8.46) in (8.21) and using (8.25) and (8.27) we obtain the following condition for the presence of amplification:

$$\frac{4\pi^2 q N_0 (2|\psi_0|\psi_0^T)^2}{3kT} \frac{1}{A_{n^*n}} \frac{A_{n^*n} - A_{n^*n}}{A_{n^*n} + A_{n^*n}} > \frac{1}{Q}.$$  \hspace{1cm} (8.48)

If the number of spin levels exceeds three, analogous calculations can be carried out, which, however, become quite cumbersome.

In the derivation of relation (8.47) we disregarded cross-correlation. Equation (8.45) would have to be replaced by equation (5.119), and we would then obtain in lieu of (8.47)

$$A_{n^*n} > (A_n + w + \frac{1}{3} \sum_i w_i) v.$$  \hspace{1cm} (8.47a)

Since the probabilities of the cross-correlation transitions increase rapidly with increasing paramagnetic center concentration, it becomes understandable why appreciable increase in the center concentration causes the amplifier to stop operating.

The linear amplifier theory which we have presented can be regarded as correct if the "illumination" power of frequency $v_{31}$ is sufficient to overcome the spin-lattice relaxation and produce saturation, but is still not large enough to exceed the spin-spin interactions and bring about coherent ordered spin systems. In other words, the average time interval necessary for the spin reorientation under the influence of the saturating rate of frequency field must exceed the spin-spin relaxation time. If this condition is not satisfied, nonlinear effects arise [60] which result in a paramagnetic amplifier of the parametric type. Linearity can be readily maintained if the spin-lattice inter-
actions are much weaker than the spin-spin ones. The latter condition is usually satisfied in most media at low temperatures and not too low paramagnetic center concentrations.

It is interesting to note that the temperature $T_m$, which determines the minimum value of the noise figure, may turn out to be much lower when the amplifier is excited by the saturation method than the temperature $T_c$ of the working medium. Indeed, if we assume $kT_m \gg h\nu_3^2$, then it follows from (8.33), (8.34) and (8.46) that

$$T_m = T_e \left( \frac{A_{11} + A_{22}}{A_{11} - A_{22}} \right).$$

(8.49)

If we can neglect $A_{23}$ in this expression, we obtain $T_m < T_c$ by suitable choice of the energy intervals.

2. Choice of medium

The first and principal problem that must be solved in the production of a paramagnetic amplifier is the choice of a medium with suitable properties. The working medium of a three-level amplifier must satisfy the following main requirements: a) the number of spin levels of the paramagnetic particle should exceed 2, and consequently particles with effective spin $S' = 1/2$ are eliminated; b) the splittings of the spin levels in the crystal field in the absence of an external magnetic field (initial splittings) should be of order $h\nu_3^1$, in order to attain saturation readily at the frequency of the auxiliary radiation; if the initial splittings are small, then the only magnetic dipole transitions that differ noticeably from zero are those between neighboring spin levels; c) the probabilities of the spin-lattice relaxation transitions should be sufficiently small so that saturation sets in at attainable elimination powers; d) the relation between the probabilities of the relaxation transitions should satisfy for different spin level pairs the condition (8.47); e)
the number of magnetically nonequivalent ions per elementary crystal cell should be as small as possible; f) absence of hyperfine structure of the energy levels is the most favorable; g) the width of the individual spin levels due to the spin-spin interactions should be sufficiently small so that, first, the spin levels do not overlap and second, that saturation can be reached sufficiently readily; it is therefore necessary that the chosen medium be magnetically diluted in an isomorphous diamagnetic substance; h) finally, there are requirements that do not concern the magnetic properties of the medium: chemical stability, low dielectric losses, sufficient mechanical strength.

It must be noted that of great importance to the operation of a paramagnetic amplifier is the longitudinal relaxation mechanism. If the latter is defined as the rate of energy transfer from the system of effective lattice oscillators to the helium thermostat, then the resonance saturation due to transitions between levels $E_1$ and $E_3$ may influence the populations of other levels (see §5.4). Unfortunately, the available experimental data are incomplete and scanty and consequently the question of the nature of paramagnetic relaxation in different substances is still debatable. Bloembergen [61] states that the very existence of three-level amplifiers at temperatures below $4.2^\circ K$ indicates that longitudinal relaxation in the employed paramagnetic crystals is not determined by the coupling between the effective lattice oscillators and the helium thermostat. However, he admits the possibility that the bottleneck of the energy transfer from the spin system to the lattice are the phonon-phonon interactions. Strandberg [62, 63], in an analysis of the results of experiments with three-level amplifiers, reached the conclusion that the phonon-phonon processes play an appreciable role. On the basis of subsequent investi-
gations Bloembergen [122] reached the conclusion that all the effects observed by Strandberg could be attributed to cross-correlation.

The only ones among the various paramagnets capable of satisfying the foregoing requirements are apparently crystals containing ions of the intermediate groups. The most investigated among these are the compounds of the iron group of elements. We know that in most crystals the iron group ions have a surrounding of octahedral symmetry; these are the compounds we shall consider primarily.

In this case ions with electron configuration \(d^1, d^2, d^6, d^7\) have very short spin-lattice relaxation times (see §5.3). Therefore, naturally, we eliminate from consideration the compounds of \(\text{Ti}^{3+}, \text{V}^{4+}, \text{V}^{3+}, \text{Cr}^{2+}\) and \(\text{Co}^{2+}\). The ions that remain suitable from this point of view are \(\text{V}^{2+}, \text{Cr}^{3+}, \text{Cr}^{2+}, \text{Mn}^{3+}, \text{Mn}^{2+}, \text{Fe}^{3+}, \text{Ni}^{2+}\) and \(\text{Cu}^{2+}\). Among these ions, copper has a spin \(S = 1/2\), so that its compounds are not suitable for three-level amplifiers; however, the presence of a hyperfine structure in the paramagnetic resonance line of copper apparently makes it possible to use its salts to produce an amplifier at frequencies \(10^8 - 10^9\) cps [64]. Further, the ions of vanadium and manganese are little suitable because they have a large nuclear spin (\(\text{V}^{51}: I = 7/2, \text{Mn}^{55}: I = 5/2\)). We are thus left for our primary choice ions of divalent and trivalent chromium, trivalent iron, and divalent nickel.

We have seen in §3.9 that it is necessary to distinguish between paramagnetic complexes with a small fraction of covalence and those with strong covalent bonds. The only compounds with strong covalent bonds suitable for our purposes are those containing \(\text{Cr}^{3+}\); atoms with configuration \(d_e^1\) and \(d_e^5\) will have an effective spin \(S = 1/2\). Atoms with configuration \(d_e^2\) and \(d_e^4\) have \(S = 1\), but their initial spin level splittings are apparently too large. The atom \(\text{Cr}^{3+}\) has a \(d_e^3\) con-
figuration, and is in an effective $S$ state with spin $S = 3/2$. It is analogous to the $Fe^{3+}$ and $Mn^{2+}$ ions in compounds with weak bond.

Let us dwell in somewhat greater detail on different compounds of the iron group ions selected by us.

$Cr^{2+}$ $S = 2$. Salts of divalent chromium are chemically less stable than all others. In addition, this ion in a cubic field has a double lower orbital level; the orbital degeneracy is lifted by a weak field of lower symmetry, and consequently we can expect the initial splittings of the spin levels in the crystalline field to be too large. This is confirmed by the only substance investigated to date, $CrSO_4 \cdot 5H_2O$, for which the spin Hamiltonian constant is $D = 2.24\; cm^{-1}$, which would require the use of a wave four millimeters long for illumination.

$Cr^{3+}$ $S = 3/2$. Compounds of this ion have been well investigated; they have relatively long spin-lattice relaxation times; the zero level splittings of many lie in a convenient region of standard microwave frequencies. From among the compounds of this ion, the hexacyanide of chromium and corundum doped with $Cr^{3+}$ are already used as working media for amplifiers.

$Fe^{3+}$ $S = 5/2$. The free ion is in the $S$ state. The relaxation times are of the same order as in $Cr^{3+}$. The initial splittings of the spin levels are large in some cases. $Fe^{3+}$ compounds may be of interest for the construction of an amplifier without the use of a constant magnetic field [65, 42] or with the use of weak magnetic fields, for the $Fe^{3+}$ ions have three spin levels even in the absence of a magnetic field.

$Ni^{2+}$ $S = 1$. At first glance $Ni^{2+}$ is the most suitable for use in working medium compounds, in view of the fact that this ion has only three spin levels. However, an attempt at creating an amplifier using
nickel fluorosilicate [68] was not successful because of the excessively short relaxation time $T_1$ and owing to internal stresses in the crystal, which have led to an excessive broadening of the paramagnetic resonance lines. There are many known paramagnetic salts of divalent nickel the only investigated magnetic property of which is the static susceptibility. It is possible that some of them, unlike nickel fluorosilicate, turn out to be suitable. We note that if the symmetry of the crystalline field surrounding the $\text{Ni}^{2+}$ ion is so low that the spin Hamiltonian contains terms of the type $E(S_x^2 - S_y^2)$, then the spin degeneracy will be lifted even in the absence of an external magnetic field. Such compounds of $\text{Ni}^{2+}$ may possibly turn out to be suitable for an amplifier without the use of a constant magnetic field [65].

So far we have considered octahedral paramagnetic complexes. An analysis of the structure of the energy levels of the iron group ions in a tetrahedral surrounding shows that for some reason or another (short spin-lattice relaxation time, large hyperfine structure, etc.) the only promising compounds of this type can be only the salts of divalent iron, which of course must be diluted by suitable diamagnets.

From among the group of rare earth elements, only compounds of $\text{Gd}^{3+}$ and $\text{Eu}^{2+}$ ions in the $S$ state can be used, and in the remaining ions of this group the spin-lattice relaxation times are excessively short. $\text{Eu}^{2+}$ is less suitable because of its appreciable hyperfine structure. The spin of $\text{Gd}^{3+}$ is $S = 7/2$ and in the absence of an external magnetic field there are four spin levels, making compounds of $\text{Gd}^{3+}$ promising for the construction of an amplifier without a magnetic field.

The magnetic complexes of compounds of the palladium and platinum group elements are characterized by a strong covalent bond. Therefore, in accordance with the considerations advanced with respect to com-
pounds of the iron group, the only complexes suitable for our purpose can be those with electron configuration $d_3^3$, that is, complexes containing trivalent molybdenum, trivalent tungsten, and pentavalent ruthenium. Complexes containing $Re^{4+}$ are not suitable since the nuclear spin of $Re^{185}$ or $Re^{187}$ is $5/2$.

Most elements of the actinide group are radioactive. The uranium compounds have been little investigated. It is possible that some of the compounds of trivalent and tetravalent uranium will be found suitable.

Concluding the review of the substances that offer promise as being useful in three-level amplifiers, we note in addition the cubic lattice crystals of the type MgO, CaO, CaF$_2$, in which ions of Cr$^{3+}$, Fe$^{3+}$, Gd$^{3+}$, Mn$^{2+}$, etc., are introduced. The paramagnetic resonance absorption lines observed in these cases are very narrow (in Cr$^{3+}$, for example, the line width is merely 3 oersted). It is possible that these substances will find application in amplifiers at relatively low frequencies.

3. Choice of orientation of constant magnetic field

The orientation of the constant magnetic field relative to the crystal axes determines important characteristics of the working medium of a three-level amplifier, such as the position of the spin energy levels, the probabilities of transitions between them under the influence of the alternating magnetic field, and the probabilities of transitions under the influence of the lattice vibrations. The dependence of the probabilities of the relaxation transitions between the different spin levels on the constant magnetic field has hardly been investigated. The positions of the spin levels and the probabilities of the magnetic dipole transitions between them can, on the other hand, be calculated if we know the parameters of the spin
Hamiltonian (see Chapter III).

In choosing the direction of the magnetic field it is important to have not only suitable energy intervals, which give the required values of the frequencies $v_{32}$ (or $v_{21}$) and $v_{31}$; it is also important to have the probabilities of the magnetic dipole transitions, $p_{32}$ (or $p_{21}$) and $p_{31}$ (1.3), sufficiently large. If $p_{32}$ (or $p_{21}$) is small, then the gain will be small; if $p_{31}$ is small, a large elimination power is necessary to obtain the saturation effect. Therefore, as already mentioned, the spin level splittings due to the application of an external static magnetic field should not exceed greatly the initial crystal splittings. If the external magnetic field is very large, then the spin levels will be practically equidistant, and transitions under the influence of the radio frequency field will be possible in practice only between neighboring levels, and consequently illumination will not be feasible.

In the case when $S \leq \frac{3}{2}$ the spin Hamiltonian has a very simple form, since the part in it $\hat{H}_{kr}$ representing the action of the crystalline field contains only quadratic terms in the components of the spin vector $\vec{S}$. If the field has trigonal or a tetragonal symmetry, then $\hat{H}_{kr} = D[\vec{S}^2 - 1/3S(S + 1)]$; the symmetry axis coincides here with the Z direction. If the static magnetic field $\vec{H}_0 \parallel Z$, then the spin Hamiltonian represents a diagonal matrix and consequently the selection rule $\Delta M = \pm 1$ holds true for the magnetic dipole transitions.

The possibilities for choosing suitable transitions for obtaining the required values of $v_{32}$ (or $v_{21}$) and $v_{31}$ are clear from Fig. 1.3. If the spin Hamiltonian contains also a rhombic term $E(\hat{S}_x^2 - \hat{S}_y^2) \equiv 1/2E(\hat{S}_+^2 + \hat{S}_-^2)$ then the latter, obviously, causes an overlap of the states in which the quantum numbers of the spin projection on the Z axis differ by $\pm 2$, that is, states with $M = -1, M = +1$ in the case
$S = 1$, states with $M = -3/2, M = 1/2, M = -1/2, M = 3/2$ in the case with $S = 3/2$. The number of level pairs between which transitions are allowed now increases.

We note that in the case of an even number of electrons, a rhombic field lifts the spin degeneracy completely, so that for ions with $S = 1$ we have three definite spin levels even in the absence of a magnetic field. As indicated, this opens up the possibility of using compounds of these ions as working media for the amplifier without the use of a magnetic field.

Assume now that the field $\vec{H}_0$ is perpendicular to the trigonal or tetragonal axis of the crystal. If as before we choose $\vec{H}_0 \parallel Z$, then the term $[\Delta_2^2 - 1/3S(S + 1)]$ becomes $1/2[\Delta_2^2 + \Delta_2^2]$ and causes overlapping of states with $\Delta M = \pm 2$ even without a rhombic field.

In the case $S = 5/2$ (and $S = 7/2$) the form of the spin Hamiltonian becomes appreciably more complicated, for it represents a fourth (sixth) degree polynomial in the components of the spin vector $S$. The position of the spin levels and the selection rules will depend essentially on the relationships between the values of the different spin Hamiltonian parameters.

Under certain orientations of the constant magnetic field, a symmetrical energy splitting is possible, making it possible to cause illumination at a single frequency to produce transitions between two pairs of spin levels. The use of such a symmetrical version increases the gain by several times.

We know that in the presence of initial crystalline splittings of the spin levels the resonant absorption is possible not only when the static and alternating magnetic fields are mutually perpendicular. To find the optimal conditions of amplifier operation it is necessary also to take into account the dependence of the absorbed power of
radio frequency field on its orientation relative to the constant magnetic field and to the crystal axes.

In conclusion we note that amplifiers operating without an externally applied magnetic field apparently assume great significance [42]. Such amplifiers would have many advantages: 1) no electromagnet is necessary; the difficulties involved in attaining high homogeneity of the magnetic field, current stabilization, and large working space are eliminated; 2) no single crystals are necessary; 3) all the ions of the crystal cell are used; 4) superconductors can be used in the construction of the microwave circuit; 5) the dimensions of the Dewar are not limited to the gap between poles; 6) there is no broadening due to the scatter of the angles between the crystal axes and the magnetic field.

TABLE 8.1
Initial Splittings of Spin Levels in Substances Containing Fe$^{3+}$, Ni$^{2+}$, and Gd$^{3+}$

<table>
<thead>
<tr>
<th>Ion</th>
<th>Substance</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>RbFe(SO$_4$)$_2$·12H$_2$O</td>
<td>0.043</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NH$_4$Fe(SO$_4$)$_2$·12H$_2$O</td>
<td>0.085</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>KFe(SO$_4$)$_2$·12H$_2$O</td>
<td>0.043</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$_2$(CH$_3$CO)$_2$CH$_3$</td>
<td>0.28</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BaTiO$_3$</td>
<td>0.332</td>
<td>0.166</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SrTiO$_3$</td>
<td>0.023</td>
<td>0.044</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(NH$_4$CH$_3$)$_2$Fe(SO$_4$)$_2$·12H$_2$O</td>
<td>0.134</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al$_4$Be$_4$(SiO$_4$)$_6$</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgWO$_4$</td>
<td>2.05</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>(NH$_4$)$_2$Ni(SO$_4$)$_2$·6H$_2$O</td>
<td>1.5</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(NH$_4$)$_2$Ni(SeO$_4$)$_2$·6H$_2$O</td>
<td>0.91</td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti$_2$Ni(SeO$_4$)$_2$·6H$_2$O</td>
<td>2.5</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K$_2$Ni(SO$_4$)$_2$·6H$_2$O</td>
<td>2.85</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>NiSO$_4$·7H$_2$O</td>
<td>2.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Gd$_2$(NO$_3$)$_17$·24H$_2$O</td>
<td>0.0766</td>
<td>0.0479</td>
<td>0.0246</td>
</tr>
<tr>
<td></td>
<td>GdCl$_3$·7H$_2$O</td>
<td>0.0827</td>
<td>0.0504</td>
<td>0.0243</td>
</tr>
<tr>
<td></td>
<td>GdCl$_3$</td>
<td>0.0087</td>
<td>0.0077</td>
<td>0.00065</td>
</tr>
<tr>
<td></td>
<td>Gd$_2$(CH$_3$CO)$_2$SO$_4$·9H$_2$O</td>
<td>0.13</td>
<td>0.085</td>
<td>0.0466</td>
</tr>
<tr>
<td></td>
<td>Gd$_2$(SO$_4$)$_3$·8H$_2$O</td>
<td>0.291</td>
<td>0.055</td>
<td>0.008</td>
</tr>
</tbody>
</table>

1) Ion; 2) substance; 3) initial splittings, cm$^{-1}$.

Table 8.1 gives the initial splittings of the spin levels of
paramagnetic centers for substances that can be used in amplifiers without field as of now.

4. Amplifier with gadolinium ethyl sulfate

The first three-level paramagnetic amplifier [66, 67] was constructed with diamagnetic lanthanum ethyl sulfate containing 0.5% gadolinium and 0.2% cerium. The role of the active paramagnetic centers was played by the Gd$^{3+}$ ions. A static magnetic field of intensity 1800 oersted was placed perpendicular to the symmetry axis of the crystal. Of the eight spin levels of Gd$^{3+}$, which we shall designate in accordance with the value of the magnetic quantum number in a strong magnetic field, the following three neighboring ones were used: $M = -5/2, -3/2$ and $-1/2$. The illumination frequency was $v(-1/2, -5/2) = 11,500$ megacycles, the signal frequency was $v(-3/2, -5/2) = 6000$ megacycles, the magnetic field of signal and the magnetic field of the illumination were perpendicular and parallel to the static field $H_0$, respectively. The frequencies $v(-1/2, -3/2)$ and $v(-3/2, -5/2)$ were so close to each other that in order to invert the populations of the levels $M = -5/2$ and $M = -3/2$ it is necessary to have, in accordance with (8.43) $A(-1/2, -3/2) > A(-3/2, -5/2)$. This requirement can be readily satisfied by using a small admixture of Ce. The described experimental conditions are such that the interval between the spin levels of Ce$^{3+}$ is precisely equal to the interval $(-1/2, -3/2)$ of the Id$^{3+}$ ion. The spin-lattice relaxation time of Id$^{3+}$ is about $10^{-4}$ sec at helium temperatures, and the relaxation time of Ge$^{3+}$ is several orders of magnitude shorter. Because of the resonant spin interaction of gadolinium and cerium, the spin levels of Ce$^{3+}$ are rapidly excited as a result of the transitions $M = -1/2 \rightarrow M = -3/2$ of the Gd$^{3+}$ ion. The excited Ce$^{3+}$ ions transfer in turn their energy to the lattice vibrations very rapidly.
The illumination was effected by means of a radio-frequency field of 88 mW power. The resonant cavity had a $Q_0 \approx 6000$. The gain reached an order of 20 db at a band width of about $10^5$ cps. The effective noise temperature of the entire installation, including the circulator and the control unit, was approximately $150^\circ K$, but it can be greatly reduced in many ways.

Owing to the chemical instability of gadolinium ethyl sulfate, it is hardly likely that it will assume a practical significance as a working medium for paramagnetic amplifiers.

5. Amplifier with chromium hexacyanide

The exceedingly long longitudinal relaxation time, on the order of 0.2 sec at $1.25^\circ K$, has attracted attention to chromium hexacyanide as a working medium for a paramagnetic amplifier [68]. The substance used in practice was the diamagnetic salt $K_3Co(CN)_6$, which contained 0.5% of chromium. In the complex $Cr(CN)_6$ there is a very strong covalent bond (see §3.8), owing to which the electron configuration $d^3$ gives a zero resultant orbital momentum and a resultant spin $S = 3/2$. The upper three of the four spin levels were used: $M = 3/2, 1/2, -1/2$, the signal frequency was $v(3/2, 1/2) = 2800$ megacycles, the illumination frequency was $v(3/2, -1/2)$ megacycles. In this case there was no need to take any measures to satisfy the condition (8.47), since $v(1/2, -1/2) >> v(3/2, 1/2)$. The central part of the amplifier, a resonant cavity, had to be specially constructed in order to be able to excite simultaneously oscillations at both the signal and illumination frequencies.

Figure 8.8 shows a block diagram of the installation, with the aid of which a gain of 37 db was obtained with a band width of $2.5 \cdot 10^4$ cps. It was possible to obtain saturation with 1 milliwatt of power. No change was noticed in the gain as the signal power was
Fig. 8.8. Block diagram of microwave amplifier installation [68].

1) Generator 2800 megacycles (75 mv); 2) variable attenuator, 50 db maximum; 3) matching load; 4) generator 9400 megacycles (50 mv); 5) crystal modulator; 6) directional coupler; 7) bolometer, 8) power meter; 9) amplified input signal; 10) generator 100 kcs; 11) ferrite circulator; 12) saturated power; 13) directional coupler, 30 db; 14) low pass filter (microwave band; 15) spectrum analyzer; 16) variable attenuator; 17) output of amplifier; 18) to vacuum pump; 19) thermostat with liquid nitrogen; 20) thermostat with liquid helium; 21) detector; 22) cathode ray oscilloscope; 23) magnet pole piece; 24) resonant cavity with working medium.

increased from $10^{-11}$ to $10^{-10}$ watt; a further increase in the power resulted in a decrease in the gain and an increase in the band width.

It was shown experimentally that the relation $g_aB = \text{const}$ (8.31) holds true with great accuracy if the volume of the medium and the configuration of the resonant cavity remain unchanged. It was found in this case that $g_aB = 1.8$ megacycles while theoretical calculations gave a close value of about 2.6 megacycles.

Chromium hexacyanide was used [69] also to produce an amplifier at a frequency of 1373 megacycles (the frequency of the interstellar hydrogen line). The illumination was at a frequency of 8000 megacycles.
With the aid of 9 milliwatts of illumination, the apparatus turned into a generator. Chromium hexacyanide was also used by others to build an amplifier [62, 70].

6. Ruby amplifier

Corundum with chromium added (ruby) is used to produce amplifiers for different frequencies [71, 72]. Ruby has the following favorable distinguishing properties: a) the initial crystalline splitting is of the order of the most widely used frequencies in practice; b) relatively long time of longitudinal relaxation, 0.1 sec at 4.2°K; c) the crystal cell contains only 1 Cr$^{3+}$ ion or the Al$^{3+}$ ion which is isomorphous to it; d) low dielectric losses; e) high mechanical strength and chemical stability; f) good heat conductivity.

Makov et al. [71] constructed an amplifier for a signal frequency $v(-1/2, 1/2) = 9300$ megacycles; the illumination was at $v(-3/2, 1/2) = 24,000$ megacycles; the static magnetic field of intensity 4200 oersted was at an angle $54^\circ 44'$ to the trigonal axis of the crystal. The chromium concentration in the specimen employed was 0.1%. The illumination was with the aid of a klystron with 120 milliwatts of power. The gain reached 20 db.

Prokhorov et al. [72] produced an amplifier at a frequency $v(-1/2, 1/2) = 3000$ megacycles with an illumination frequency $v(3/2, -1/2) = 15,000$ megacycles. When the temperature was reduced to 2°K, the system became self excited and operated as a generator.

A recent communication [1] reports on a paramagnetic amplifier using a ruby with traveling wave (that is, of the wave guide type), having the following parameters: gain approximately 25 db, band width approximately 23 megacycles, noise temperature approximately 10°K, working frequency tunable within several per cent near an operating point of approximately 6000 megacycles. Practical realization of such
an amplifier became possible by using slow-wave systems.

In the case of ruby, the dependence of the spin level splitting on the field $H_0$ and on its inclination to the optical axis of the crystal were plotted [118] and investigations were made of the influence of the admixture of Co$^{2+}$ ions and other ions on the probability of the relaxation transitions [119].

7. Amplifier using corundum with Fe$^{3+}$ impurity

Kornienko and Prokhorov [34] constructed an amplifier for a frequency of about 10,000 megacycles with an illumination frequency of about 25,000 megacycles, using as the working medium corundum with iron ions added. The optical axis of the crystal made a small angle with the direction of the constant magnetic field. We shall denote the spin levels by the magnetic quantum numbers that can be ascribed to them in a strong field $H_0$. The levels with $M = -3/2, -1/2$ were used for the amplification and the levels $M = -5/2, -1/2$ for illumination. We note that since the spin Hamiltonian of the Fe$^{3+}$ ions contains terms with not only axial but also cubic symmetry, transitions between any pair of the selected levels are allowed.

§8.6. Optical Methods of Investigating Paramagnetic Resonance

Many interesting results were obtained in recent years with the aid of experiments consisting of applying simultaneously to gases electromagnetic radiations at two different frequencies in the optical and in the radio bands. Investigations of this type were carried out both with atoms (or molecules) whose ground state is a singlet one and consequently nonmagnetic, and with atoms which are paramagnetic in the ground state. In the former case the radio frequency resonance occurs in the optically excited atoms, and in the latter it occurs on atoms in the ground state.
1. Resonance on optically excited atoms

The idea of paramagnetic resonance experiments on optically excited atoms was advanced in 1949 [73, 74] and consists of the following. Let us consider an assembly of diamagnetic atoms placed in a static magnetic field $H_0$ and subject to the action of polarized light of resonant frequency. The excitation of the atoms will obviously be selective. If the atoms are paramagnetic in the excited state, then only some of the Zeeman sublevels will be occupied. Consequently, the radiation produced upon the excitation of the atoms will be polarized. The radio frequency field, producing transitions between the Zeeman sublevels, changes the character of the polarization of the emitted light. Thus, measurements of the polarization of the emitted light make it possible to establish the occurrence of magnetic resonance.

The investigation method which we have described was first experimentally realized by Brossel and Bitter [75], who applied it to even isotopes of mercury. Using linearly polarized light, they excited the 2537 angstrom ultraviolet resonance line ($6^1S_0 \rightarrow 6^3P_1$). The field $H_0$ was applied parallel to the electric vector of the light wave. In this case, as is well known [76], only the Zeeman sublevel $M = 0$ is excited. The radiation therefore contains only the $\pi$ components. Then an oscillating magnetic field of frequency $\nu = 2.9625 \times 10^{10}$ cps was applied perpendicular to the field $H_0$. By varying the intensity of $H_0$, the resonance condition $\nu = g\beta_0 H^* \beta_0$ was attained, where $g = 1.5$ is the Lande factor for the state $^3P_1$. Owing to the transitions $\Delta M = \pm 1$, produced by the radio frequency field, circularly polarized components appear in the optical
radiation. The dashed lines show the transitions arising as a result of the radio frequency field. In Fig. 8.10 curve I gives the dependence of the intensity of the $\sigma$ components on the field $H_0$. The maximum intensity corresponds to a field intensity $H^*_{0}$ satisfying the resonance condition.

The method described makes it also possible to investigate the Stark effect with great accuracy. Blamont [77] produced parallel to $H_0$ an electric field $E = 40$ kv/cm. In the absence of the field $E$, the energy intervals $0 \rightarrow 1$ and $-1 \rightarrow 0$ are equal, and therefore only the resonance line I appears (Fig. 8.10). The levels $M = 0$ and $M = \pm 1$ shift differently in the electric field $E$; this causes the appearance of two resonance lines (curve II in Fig. 8.10). Within the limits of the measurement accuracy, it was shown that the effect is quadratic. The interval between the resonance peaks is

$$v_r - v_i = 2KE,$$

where the Stark constant is $K = (2.13 \pm 0.05) \cdot 10^5$ cps/kv cm$^{-1}$.

2. Magnetic resonance line shape

If the gas is highly rarefied so that $N_0 < 10^{12}$ then the width of the optical resonance line $\Delta v = g\beta \Delta H$ is determined by the lifetime $t_0$ of the excited state. According to the uncertainty relation

$$t_0 \sim \frac{1}{\Delta v} = \frac{\hbar}{g\beta \Delta H}.$$  

(8.51)

If the width $\Delta H$ is estimated from curve I of Fig. 8.10, we obtain for
the lifetime at the $6^3P_1$ level $t_0 = 1.19 \cdot 10^{-7}$ sec, which is in good agreement with the pure optical data. The double resonance method was used [78] also to determine the much shorter lifetime at the excited level $7^3S_1$.

It is easy to show [75] that the shape of the resonance line is given by the following expression:

$$y = \frac{1}{\pi} \int_0^\infty P(M, M', t) e^{-\frac{t}{\tau}} dt,$$  \hspace{1cm} (8.52)

where $y$ is the relative intensity of the line and $P(M, M', t)$ is the probability that a transition $M \rightarrow M'$ will occur within a time $t$. This probability is calculated by means of the well known Majorana formula [79]. For the line $6^3P_1 \rightarrow 6^1S_0$ we obtain in this manner

$$y = \frac{\gamma \rho^2 (\gamma \rho^2 + \frac{1}{\rho} + 4\omega^2)}{(\gamma \rho^2 + \frac{1}{\rho} + \omega^2)(\gamma \rho^2 + \omega^2 + \frac{4}{\rho})}.$$  \hspace{1cm} (8.53)

Here $\omega = 4\pi(v - v_0)$. Under resonance conditions $\omega = 0$ and consequently

$$y_{res} = \frac{\gamma \rho^2}{\frac{1}{\rho} + \gamma \rho^2}.$$  \hspace{1cm} (8.54)

If the amplitude of the alternating field is small, then the width of the resonance curve can be determined from the following approximate formula:

$$(\Delta \nu)^I = \frac{4}{\rho} \left[ 1 + 1.45 (\gamma \rho^2)^I \right].$$  \hspace{1cm} (8.55)

If the Zeeman levels are shifted by the Stark effect, then formulas (8.53) - (8.55) should, of course, be modified [80].

3. Multiple coherent photon scattering

Blamont [77] in an investigation of the dependence of the line width $y_\theta(H)$ on the vapor density for the even isotopes of mercury, obtained the following unexpected result: an increase in density is accompanied by noticeable narrowing down of the resonance line. Thus,
for example, when the number of atoms per cubic centimeter is increased from $10^{11}$ to $10^{13}$, the width is reduced to one-third. With increasing vapor density, the number of collisions between atoms increases. Under the conditions of this experiment it is evident that this cause of line broadening is insignificant. Detailed investigations undertaken by Brossel et al. [81] have shown that the narrowing down depends on the dimensions of the resonant cavity; it is determined by the concentration of the investigated isotope only and is not at all connected with the amount of other isotopes. All these facts have been explained by the circumstance that under the conditions of these experiments the multiple coherent scattering of the photons plays a major role [82].

The process of multiple photon scattering can be visualized in the following fashion: The photon is absorbed by atom A, which is de-excited after a time interval $t_0$; the photon is then absorbed by another atom B, etc. It is important that the scattering be coherent; then the resonance line width will be determined not by the lifetime $t_0$ but by the "duration of coherence" $t_k > t_0$. Theoretical analysis of multiple coherence scattering was carried out long ago by Weisskopf [83].

It should be noted that when $N_0 > 10^{14}$, collisions between atoms begin to exert a noticeable influence on the line width.

4. Investigation of hyperfine splittings

So far we have assumed that the investigated energy levels do not have hyperfine structure. If the nuclear spin is not equal to zero, then the double resonance method makes it possible to measure with great accuracy the hyperfine splittings. These measurements are particularly valuable when $J = 0$ or $1/2$ in the ground state, and consequently, only a study of the excited states makes it possible to
determine the quadrupole moments of the nuclei. This method was used for an analysis of the hyperfine structure of the \( ^3P_1 \) level of the zinc atom [84] and the \(^2P_{3/2}\) of the following alkaline metal atoms: sodium [85], potassium [86], rubidium [87] and cesium [88]. This method was used to determine the quadruple moments of the nuclei, for which the following values were obtained: \( \text{Na}^{23}, Q = (0.11 \pm 0.01) \cdot 10^{-24} \text{ cm}^2; \) \( \text{K}^{39}, Q = (0.11 \pm 0.035) \cdot 10^{-24} \text{ cm}^2; \) \( \text{Rb}^{85}, Q = (0.29 \pm 0.02) \cdot 10^{-24} \text{ cm}^2; \) \( \text{Rb}^{87}, Q = (0.14 \pm 0.01) \cdot 10^{-24} \text{ cm}^2; \) \( \text{Cs}^{133}, Q = (-0.003 \pm 0.002) \cdot 10^{-24} \text{ cm}^2. \) Related to this series of investigations is the work done on the Stark effect for the levels of the odd mercury isotopes, which, as is well known, have a hyperfine structure [89].

Rabi [90] supplemented his original beam method by optical excitation of the atoms. Measurements carried out in this way have yielded for the quadrupole moments of alkali element nuclei values that agreed with those mentioned above.

5. Orientation of atoms in the ground state

We proceed from a study of magnetic resonance on optically excited atoms to the effect on the ground atomic levels. We first stop to discuss the method of optical pumping, which makes it possible to orient atoms in the ground state. We shall illustrate the idea of the method using the \( D_2(^2P_{3/2} \leftrightarrow ^2S_{1/2}) \) lines of sodium. For simplicity we first neglect the hyperfine structure of the levels. Let the sodium atoms be in a static magnetic field \( H_0 \). The scheme of the Zeeman splittings arising thereby and of the possible electric dipole transitions is shown in Fig. 8.11. Let us assume that a circularly polarized light beam propagates along the field \( H_0 \) and gives rise to the \( \sigma^+ \) transitions indicated in Fig. 8.11 by the solid arrows. Upon de-excitation of the so excited atoms, the greater part of these atoms
will go over into the state $M = +1/2$. After multiple repetition of this process, the level $M = -1/2$ becomes empty, and all the atoms gather at level $M = +1/2$. Thus, as a result of the optical pumping all the atoms will be oriented against the field direction, and magnetization to saturation will set in. Actually the orientation of the atoms will never be complete, principally as a result of collisions with the walls of the vessel. Experiments show that it will nevertheless be appreciable. The extent to which the atoms are oriented can be evaluated from the character of the polarization of the radiation emitted by the optically excited atoms. In our example of the $D_2$ sodium line, the radiation will contain only the $\sigma$ component if 100% atomic orientation is attained.

The idea of orienting atoms by optical pumping was advanced by Kastler [91]. The first experiments were carried out with atomic sodium beams [92, 93]. They were successfully repeated with sodium vapor, which greatly simplified the experimental technique [94]. In addition to the sodium atoms [95], other alkaline metals were later studied: K [96], Rb [97] and Cs [98]. Various modifications of the optical pumping method were proposed and realized [99, 100]. It was shown, in particular, that under the influence of natural light propagating along a magnetic field, the atoms become "aligned."

6. Orientation of nuclei

If the nuclei have a nonzero spin, then the interaction between the electron and nuclear moments causes the orientation of the atoms to be accompanied by orientation of the nuclei. Attempts were made
to determine this orientation from anisotropy of the γ-radiation on the nuclei of alkali-metal atoms [102]. The result turned out to be negative, apparently because of adsorption of atoms on the vessel walls.

If the ground state is diamagnetic, then the method of optical pumping makes it possible to obtain a pure nuclear orientation. The first experiments with odd mercury isotopes were not successful because the light intensity was not sufficient [103]. Positive results were obtained [104] with mercury enriched to 90% with the $^{201}$Hg isotope. The optical excitation was produced by natural light propagating in the direction of the magnetic field. Thus, alignment of the nuclei was obtained in these experiments.

7. Magnetic resonance on atoms in the ground state

Optical pumping causes the paramagnetic resonance absorption to increase appreciably. Usually, however, the detection of magnetic resonance is carried out by optical methods based on the depolarization of the resonant (optical) radiation resulting from transitions between the Zeeman levels under the influence of the radio frequency field. The first experiments, carried out with sodium atoms [105], have shown that in addition to the resonance peaks corresponding to the transitions $\Delta M = \pm 1$, other peaks appear if the intensity of the radio frequency field is sufficient and these are connected with the transitions $\Delta M = \pm 2, \pm 3, ...$. The additional peaks appear as a result of absorption of 2, 3, ... radio frequency quanta. A theoretical analysis has shown [106] that the intensity of the n-th order resonance is proportional to $(H_1/H_0)^{2n}$.

Winter [107] has predicted the possibility of resonance on multiple frequencies even when the atoms contain only two magnetic sublevels each. For this effect to appear it is necessary that the
radio frequency field not be polarized circularly, but that it con- 
tain photons of differing polarizations. The effect was observed ex-
perimentally on sodium atoms [108].

8. Effect of extraneous gases

The double resonance method which we have described is very con-
venient for the study of the influence of extraneous gases on the 
orientation of the investigated atoms. If the atoms are oriented and 
are an excited state, then it is well known that collisions with the 
molecules of the extraneous gas will cause depolarization of the 
resonant radiation [76], since the collisions mix up the states with 
different values of M.

Oriented atoms in the ground states are affected by the extrane-
ous gases in two ways:

a) First, the extraneous gases produce disorientation, as in the 
case of excited atoms;

b) second, they play the role of a buffer preventing the atoms 
from colliding with the vessel walls.

If the density of the extraneous gases is relatively low, the 
buffer action plays the principal role and brings about an increase 
in the resonant absorption intensity by a factor 10-15 [99, 109]. 
If in the absence of impurities the straight line motion of the atoms 
is interrupted predominantly because of collisions with the vessel 
walls, then in the presence of extraneous gases the trajectory of 
the atoms becomes zigzaglike and therefore the orienting action of 
the incident light becomes more prolonged. This effect increases with 
increasing mass of the extraneous gas molecules. Atoms in the $^2S_{1/2}$ 
state are less sensitive to collisions. Dicke [110] has predicted that 
the collisions should give rise not only to an increase in the in-
tensity but also to a narrowing of the resonance line. This was soon
observed in experiment [111].

In conclusion, let us dwell on several prospects in the development of the method of double optical-radio frequency resonance.

a) The measurement accuracy of ordinary optical spectroscopy is limited by the Doppler broadening of the lines. The double resonance method which we described is free of this shortcoming, making it valuable for measurement purposes.

b) Investigations made on vapors in the presence of extraneous gases yield valuable experimental material for the theory of collisions of oriented atoms. The weak influence of the collisions on the orientation of the atoms can be used to orient radioactive nuclei and to obtain polarized electrons [112].

c) In the experiments which we described, optical methods play a double role: 1) they are used for selective excitation of the atoms; 2) they are used to detect radio frequency resonance. Interesting results can be obtained by combining optical methods with other methods for either selective excitation of atoms or detection of magnetic resonance.

Let us point out some possible combinations which have yielded positive results:

1) Selective excitation of atoms can be carried out by the Frank and Hertz method of inelastic electron collisions, while detection of magnetic resonance can be carried out by the optical method; Dehmelt [113] investigated in this fashion magnetic resonance on the metastable mercury state $^6\!^3P_2$, and Pebay-Peyroula [114] made measurements for the $^6\!^3P_1$ level;

2) we have already mentioned that Rabi [90] combined optical excitation and resonance detection by the Stern and Gerlach beam method;
3) selective excitation can be carried out by optical means, and detection by ordinary methods of paramagnetic resonance [115].

d) Great interest attaches to the use of optical pumping in solids. The suitability of the substance for this purpose is determined by the following two conditions: 1) the spin-lattice relaxation time should be longer than the duration of one cycle of optical pumping; 2) optical transitions should exist in a practically convenient frequency region. A preliminary study [116] has shown that these conditions can be satisfied above all by salts of ions in the S state. Apparently the most suitable ones are salts of divalent europium.

We note that the changeover to solids is particularly important for experiments with oriented nuclei, since the use of gases is inconvenient, owing to the disorienting action of adsorption on the vessel walls.

3) It is possible to obtain by the optical pumping method a higher population for the upper Zeeman levels as compared with the lower ones. It follows therefore that this effect can be used to construct a low noise amplifier or generator [112]. The need for using rarefied gases so as to avoid multiple incoherent scattering of the photons greatly limits the practical applications of such devices. They may, however, turn out to be quite valuable as frequency standards.

REFERENCES TO CHAPTER 8

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[Footnotes]

407 It should be remembered that $g_N$ may be either positive or negative.

421 Such devices are customarily called masers abroad, which stands for "microwave amplification by stimulated emission of radiation."

422 We know that such splittings can be readily attained in magnetic fields of readily accessible intensities.

423 This formula pertains to an amplifier that is turned on with the aid of a ferrite circulator.

425 The misprints that have crept into the formulas [45] have been corrected in [46].

455 Alignment of atoms, unlike their polarization, denotes that levels with magnetic numbers $M$ and $-M$ have equal populations; levels with different $M$ are unequally populated.
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