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CONTENTS

Chapter | Page

II. THEORY

III. EQUIPMENT AND EXPERIMENTAL PROCEDURE

TABLES

Table Page

ILLUSTRATIONS

Figure | Page

CHAPTER I

INTRODUCTION

In addition to possessing an electrostatic charge, some nuclei also possess a magnetic moment. A study of nuclear magnetic resonance is in essence a study of the local magnetic environment of a molecular system by means of the magnetic properties of the nuclei. The local magnetic field at a nuclear site is determined by a number of factors such as screening due to orbital motion of electrons, presence and action of electronic and nuclear magnetic moments within and outside the molecule containing the nucleus, and molecular motions. Therefore NMR has been used to investigate such properties as the structure and motions of molecules and the chemical environment of nuclei.

When NMR is used to study the properties of conducting materials, two main differences are found between the behavior of conductors and non-conductors. Both of these arise from the action of conduction electrons.

Because metals are conductors, the penetration of the metal by the radio frequency magnetic field is limited by the skin depth of the metal. Therefore, if large pieces of the metal are used, only those nuclei near the surface will be excited by the radio frequency magnetic field and the resulting NMR signal will be weak. This difficulty may be alleviated by using a suspension of finely-divided particles whose dimensions are small compared with the skin depth. In spite of this difficulty, the first observation of a resonance signal in a metal was made by Pound[1] in 1948. He correctly identified some spurious resonances he observed in his spectrometer as due to Cu^{63} and Cu^{65} in the copper wire of his receiver coil.

The second main difference between metals and non-metals arises from the magnetic interaction between the nuclei and the conduction electrons. This interaction has two important effects. It provides the dominant mechanism for spin-lattice relaxation and also produces a shift in the resonance frequency of the nucleus relative to its resonance frequency in a non-metallic material. Knight[2] discovered that the resonance frequency in metals is higher than for nuclei of the same isotope in an insulating material subjected to the same external

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[1] R. V. Pound, Phys. Rev. 73, 1112 (1948).

[2] W. D. Knight, Phys. Rev. 76, 1259 (1949).

magnetic field. Townes[3] showed that this effect was caused by the local magnetic fields produced by the conduction electrons.

Gutowsky[4] measured the line width of metallic sodium as a function of temperature. He observed that the line width at low temperatures (77°K) could be explained on the basis of dipolar interactions in a rigid lattice. Motional narrowing of the line was observed to begin at a temperature of approximately 1[illegible]0°K. The width of the resonance was observed to continue decreasing with increasing temperature until it attained a constant width of 0.1 gauss, the limit of resolution of the spectrometer, in the range 250° to 300°K. Gutowsky[5] also measured the line width of Li^7 and found a similar temperature dependence. Again the line width at high temperatures was determined by the resolution of the spectrometer.

Holcomb and Norberg[6] measured T_1, the spin-lattice

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[3] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. <u>77</u>, 852 (1950).

[4] H. S. Gutowsky, Phys. Rev. <u>83</u>, 1073 (1951).

[5] H. S. Gutowsky and B. R. McGarvey, J. Chem. Phys. <u>20</u>, 1472 (1952).

[6] D. F. Holcomb and R. E. Norberg, Phys. Rev. <u>98</u>, 1074 (1955).

relaxation time, and T_2, the spin-spin relaxation time, in Na^{23}, Li^6, Li^7, Rb^{85}, and Rb^{87} as a function of temperature by the spin echo technique due to Hahn[7] and Carr and Purcell.[8] They observed a sudden decrease in T_2 for Na^{23}, Li^6, and Li^7 when the metals melted. Because T_2 is inversely proportional to the line width, the decrease in T_2 corresponds to a broadening of the absorption line. The decrease in T_2 upon melting is contrary to what one would expect unless there were observed an accompanying decrease in T_1. A correspondingly sudden decrease in T_1 was not observed.

The subject of the present investigation has been a nuclear magnetic resonance study of the relaxation times T_1 and T_2 and of the absorption spectra of two metals, sodium and rubidium. The relaxation times have been measured by pulse techniques and the absorption spectra have been examined on a high resolution spectrometer. Measurements have been made with improved resolution below and above the melting points of the metals in order to

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[7] E. L. Hahn, Phys. Rev. 80, 580 (1950).

[8] H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954).

investigate further the anomalous behavior of the line width of sodium upon melting. A primary goal of the study has been to try to find a plausible explanation of this behavior.

CHAPTER II

THEORY

A. Bloch phenomenological equations

In this discussion the spin system will refer to the nuclear magnetic moments under consideration. The lattice will consist of the physical system in which the spin system is embedded (atoms, molecules, solids, liquids, and gases). Consider a spin system to be placed in a strong, constant external magnetic field B_0 directed along the positive Z axis. It is observed that the macroscopic magnetization per unit volume $\vec{M}$ grows exponentially in the direction of the Z axis according to the equation

$$M_z = M_0(1 - e^{-\frac{t}{T_1}}) \qquad (1)$$

where M_0 is the magnetization per unit volume of the spin system when the spin system is in equilibrium with its lattice. The longitudinal relaxation time T_1 is the characteristic time of the exponential growth function and will later be identified with spin-lattice relaxation mechanisms.

If $\vec{M}$ is disturbed from its equilibrium position, then there may exist components of $\vec{M}$ in the XY-plane.

Observation shows that the M_x and M_y components tend to decay at an exponential rate T_2 which is always less than or equal to T_1. The transverse relaxation time T_2 will later be identified with spin-spin relaxation mechanisms.

Bloch[9] developed a set of phenomenological equations to describe the observed phenomenon. The results of Bloch's work are reviewed at this point. The magnetization and angular momentum of the spin system are related by the expression $\vec{M} = \gamma \vec{I}$ where γ is the gyromagnetic ratio and $\vec{I}$ is the angular momentum per unit volume of the spin system. The equation of motion of the spin system is

$$\frac{d\vec{M}}{dt} = \gamma(\vec{M} \times \vec{B}). \qquad (2)$$

In most NMR experiments the exciting radio frequency magnetic field is a linear, oscillating field given by $B_x = 2B_1\cos\omega t$ where ω is the angular frequency. This field can be decomposed into two rotating components. Only the rotating component in phase with the precessing $\vec{M}$ is effective, in first order, in producing resonance. Hence the total field effective in NMR has the components

$$B \equiv (B_1\cos\omega t, \mp B_1\sin\omega t, B_0) \qquad (3)$$

Eq. (3) is substituted into Eq. (2), the damping terms T_1 and T_2 are introduced, and a rotating coordinate system is

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[9] F. Bloch, Phys. Rev. 70, 460 (1946).

selected. The U-V frame is selected to rotate about the Z axis at the angular frequency of the rotating magnetic field ω. B_1 is chosen to be directed along the U axis. After the algebraic details are carried out, the following set of equations is obtained:

$$\dot{M}_U \mp (\omega_L - \omega) M_V = -\frac{M_U}{T_2} \tag{4a}$$

$$\pm \dot{M}_V + (\omega_L - \omega) M_U - |\gamma| B_1 M_Z = \mp \frac{M_V}{T_2} \tag{4b}$$

$$\dot{M}_Z \pm |\gamma| B_1 M_V = -\frac{M_Z - M_0}{T_1} \tag{4c}$$

where $\omega_L = |\gamma| B_0$.

The technique of slow passage was used to observe the line widths in this investigation. Under the conditions of slow passage the time of passage through resonance is long compared with the relaxation times T_1 and T_2. In this case $\dot{M}_V$, $\dot{M}_U$, and $\dot{M}_Z$ are almost zero and can be neglected compared to the other terms in Eq. (4). Then the components of magnetization in the rotating frame are obtained as solutions of the resulting equations:

$$M_U = M_0 \frac{|\gamma| B_1 T_2^2 (\omega_L - \omega)}{D + T_2^2 (\omega_L - \omega)^2} \tag{5a}$$

$$M_V = \pm M_0 \frac{|\gamma| B_1 T_2}{D + T_2^2 (\omega_L - \omega)^2} \tag{5b}$$

$$M_Z = M_0 \frac{1 + T_2^2 (\omega_L - \omega)^2}{D + T_2^2 (\omega_L - \omega)^2} \tag{5c}$$

where $D = 1 + (|\gamma| B_1)^2 T_1 T_2$. Under the conditions of slow passage B_1 is very small so that $D \cong 1$. When the above conditions are fulfilled, Eq. (5a) represents the dispersive mode and Eq. (5b) represents the absorptive mode of the NMR signal. With the crossed-coil detection technique it is possible to suppress one mode and observe the signal produced primarily by the other mode. Note that the absorption curve produced by the V-mode has a Lorentzian line shape and a width at half-maximum amplitude given by

$$\Delta \omega = \frac{2}{T_2} \, . \tag{6}$$

B. Spin-lattice relaxation processes

The spin-lattice relaxation time T_1 was introduced into the Bloch equations as a damping term. Spin-lattice relaxation is a process in which an interaction takes place between magnetic moments and molecular motions or lattice vibrations. The result of this interaction is that the nuclear moments make transitions to energetically preferred spin orientations. The connection between T_1 and transition probability can be seen if the case of a system of nuclear spins with spin angular momentum $I = \frac{1}{2}$ is considered.[13] If the system is embedded in a uniform

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[13] R. A. Andrew, Nuclear Magnetic Resonance, Cambridge: The Cambridge University Press, 1956.

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external magnetic field, two energy levels will be established. In thermal equilibrium by the principle of detailed balancing

$$W_2 N_2 = W_1 N_1 \tag{7}$$

where N_2 is the number of spins in the lower level, N_1 is the number of spins in the upper level, W_2 is the probability per unit time for upward transitions, and W_1 is the probability per unit time for downward transitions. In thermal equilibrium N_2 and N_1 are related by the Boltzmann factor

$$\frac{N_2}{N_1} = \exp\left[\frac{2\mu B_0}{kT}\right] \cong 1 + \frac{2\mu B_0}{kT} \tag{8}$$

where the approximation is valid for $kT >> \mu B_0$. In Eq. (8) is the magnitude of the magnetic moment of the nucleus and B_0 is the magnitude of the external magnetic field. By substituting Eq. (7) into Eq. (8) we obtain

$$W_1 = W\left[1 + \frac{\mu B_0}{kT}\right] \tag{9a}$$

$$W_2 = W\left[1 - \frac{\mu B_0}{kT}\right] \tag{9b}$$

where W is the mean of W_2 and W_1.

Consider the case in which the spin system has been disturbed from its equilibrium configuration so that the energy levels are no longer populated according to the Boltzmann distribution. During the time the driving electromagnetic field is applied, there are two competing processes taking place: relaxation processes which tend to establish the populations according to the Boltzmann distribution and the tendency of the driving field to destroy the Boltzmann distribution. After the driving field has been removed, the spin system will return to equilibrium according to the following rate equation

$$\dot{n} = 2W_1N_1 - 2W_2N_2 \qquad (10)$$

where $n = N_2 - N_1$ = excess number of nuclei per cubic centimeter in the lower energy state. Upon substituting from Eq. (9), the result is

$$\dot{n} = 2W(n_o - n) \qquad (11)$$

where $n_o = N \tanh \frac{\mu B_o}{kT}$ is the value of n when the spin system and the lattice are in equilibrium and $N = N_1 + N_2$ is the total number of nuclei per cubic centimeter. Integration of Eq. (11) yields

$$n_o - n = (n_o - n_a)e^{-2Wt} \qquad (12)$$

where n_a is the initial value of n. Eq. (12) shows that equilibrium between the spin system and the lattice is approached with the characteristic time

$$\tau_1 = \frac{1}{2W}\,; \qquad (13)$$

therefore the magnetization, which is proportional to n, approaches its equilibrium value at the same characteristic time as given by Eq. (13). The extension of this analysis to the case involving more than two energy levels is straightforward but tedious.

Spin-lattice relaxation is a process in which energy is exchanged between the spin system and the lattice and thereby tends to bring the two systems to a common temperature. The probability for spontaneous transitions between the nuclear magnetic energy levels is extremely small; therefore essentially all transitions which take place in the relaxation process are induced by a fluctuating magnetic field whose frequency is the resonance frequency.

In non-metallic liquids the principal mechanism in spin-lattice relaxation arises from the thermal motions of the atoms or molecules which constitute the lattice. The atoms or molecules can be regarded as vehicles which carry the nuclear moments about. If attention is fixed on a particular nucleus i, then it is found that a fluctuating magnetic field exists at this nuclear site. The fluctuating field at this site is produced by the motion of other members of the spin system relative to the site under consideration. If frequency components of the Fourier spectrum of this fluctuating field are at the resonance frequency of the nucleus i, then nucleus i may be induced to make a transition. The theoretical problem then involves an analysis of the lattice motion to determine the Fourier spectrum of the fluctuating field.

Bloembergen, Purcell, and Pound[11,12] worked on the problem

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[11] N. Bloembergen, *Nuclear Magnetic Relaxation*, The Hague: Martinus Nijhoff, 1948.

[12] N. Bloembergen, E. Purcell, and R. Pound, Phys. Rev. 73, 679 (1948).

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and obtained for the case of dipolar-interactions of like nuclei the following expression for the dipolar contribution to T_1 in a liquid due to translation of the nuclei

$$\left[\frac{1}{T_1}\right]_d = \frac{8\pi N\gamma^4\hbar^2 I(I+1)}{5}\int_a^\infty \frac{1}{r^4}\left[\frac{\tau_c}{1+\omega_o^2\tau_c^2} \quad \frac{2\tau_c}{1+4\omega_o^2\tau_c^2}\right]dr \qquad (14)$$

where N is the number of nuclei per cubic centimeter, γ is the gyromagnetic ratio, I is the spin quantum number of the identical nuclei, r is the radial distance from the nucleus i, a is the distance to the nearest neighbor of nucleus i, ω_o is the angular resonance frequency, and τ_c is the correlation time. In general τ_c is the length of time over which some correlation exists. For the case in which relative translational motions of the molecules are primarily responsible for the Fourier spectrum, Bloembergen obtained the following expression for τ_c

$$(\tau_c)_{\text{trans}} = \frac{\overline{x^2}}{2D} = \frac{r^2}{12D} \qquad (15)$$

where $\overline{x^2}$ is the mean square displacement of a particle, r is the relative displacement of two particles in any direction, and D is the diffusion coefficient. If different species of nuclei and paramagnetic ions are present, then appropriate modification must be made to Eq. (14).

The motion of the atoms in a solid may be restricted to vibrations of the atoms about fixed lattice points. This case, in which diffusion of the atoms through the solid does not take place, is often referred to in the literature as a rigid lattice. Therefore one would expect that the restricted motion in the solid would result in smaller fluctuating magnetic fields than those found in liquids and hence that T_1 should be longer in the solid than in the liquid. In experiments it was found that T_1 was indeed longer but not as long as theory predicted. Bloembergen[13] investigated the problem and proposed that even in pure materials some paramagnetic ions were present. The large magnetic moments of the paramagnetic ions would therefore make the fluctuating fields stronger than otherwise would be anticipated. By appropriate experiments Bloembergen demonstrated that spin-lattice relaxation via the paramagnetic impurity ions was the dominant mechanism in rigid-lattice, non-metallic solids. In this process excess energy in the spin system is carried by a mutual spin exchange process toward the impurity ion where a magnetic interaction takes place with the ion. Then the

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[13] N. Bloembergen, Physica, 15, 386 (1949).

energy ultimately shows up as an increase in the thermal energy of the lattice.

If a nucleus has an $I > \frac{1}{2}$, it may have an electric quadrupole moment. Such a nucleus will interest with the electric field gradients of the electric field in which it resides. The interaction energy is a function of the orientation of the nucleus with respect to its electrostatic environment and is therefore a function of the magnetic quantum number m which describes its space orientation. Hence an electric quadrupole moment may interact with a fluctuating electric field gradient and thereby provide an additional spin-lattice relaxation mechanism. The electric quadrupole interaction energy is of the order of the product of the electric quadrupole moment and the electric field gradient. An order of magnitude calculation shows that when quadrupole interactions are present in a system, they may predominate over the nuclear dipolar interactions.

C. Spin-lattice relaxation and Knight shift in metals

In 1936, Heitler and Teller[14] pointed out that a spin-spin interaction of the nuclear moments with the conduction electrons of a metal should provide a very

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[14] W. Heitler and E. Teller, Proc. Roy. Soc. (London) A155, 629 (1936).

powerful spin-lattice relaxation mechanism in metals. Closely related to the relaxation phenomenon is the Knight shift. Knight[2] discovered in 1949 that the resonance frequency of a nuclear species in a metal is higher than the resonance frequency of the same isotope of the element in a salt.

The Hamiltonian describing the magnetic interaction of the nucleus with the conduction electrons is discussed by Bloembergen and Rowland.[15] The Hamiltonian is repeated here:

$$H = \frac{8\pi}{3}\beta\gamma_N\hbar\vec{I}\cdot\vec{S}(\vec{r})\,\delta(\vec{r}) - \beta\gamma_N\hbar\vec{I}\cdot\left[\frac{\vec{S}}{r^3} - \frac{3\vec{r}(\vec{S}\cdot\vec{r})}{r^5}\right] - \gamma_N\hbar\frac{e}{mc}\left[\frac{\vec{I}\cdot(\vec{r}\times\vec{p})}{r^3}\right] + H_q \qquad (16)$$

where $\vec{r}$ is the radius vector of the electron with the nucleus at the origin, γ_N is the nuclear gyromagnetic ratio, and H_q is the electric quadrupolar interaction term.

The first term in the Hamiltonian occurs because the electron wave function has a finite value at the nucleus, the second term represents the interaction of the nuclear spin with the electron spin, the third represents an interaction of the nuclear spin with the electron

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[15] N. Bloembergen and T. J. Rowland, Acta Metallurgica **1**, 731 (1953).

orbit, and the last term represents the interaction of the electric quadrupole moment with electric field gradients.

Korringa[16] has examined the contribution which the conduction electrons make to the spin-lattice relaxation process, $(T_1)_e$, and the relation of $(T_1)_e$ to the Knight shift $\frac{\Delta B_0}{B_0}$. His results are

$$\left[\frac{1}{T_1}\right]_e = \frac{4\pi kT}{\hbar} v_0^2 \rho^+(\varepsilon_0)\rho^-(\varepsilon_0) \left[\frac{P_f}{P_a} \frac{\Delta E}{2I+1}\right]^2 \qquad (17)$$

where $\rho^{\pm}(\varepsilon_0)$ are the densities of the electron states per unit volume per unit energy for spins up and spins down respectively, evaluated at the Fermi surface, v_0 is the atomic volume, ΔE is the hyperfine splitting of the ground state of the free atom, P_f is the probability density of an electron in the Fermi surface at the nucleus, and P_a is the probability density of the valence electron in the free atom at the nucleus. Korringa's result for the Knight shift also calculated using Bloch wave functions for the electrons is

$$\frac{\Delta B_0}{B_0} = \frac{\gamma_e}{\gamma_N} \frac{\Delta E\, v_0}{(2I+1)} \rho(\varepsilon_0) \frac{P_f}{P_a}. \qquad (18)$$

Coupling between nuclear electric quadrupole moments and electric field gradients at the nucleus due to the

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[16] Jan Korringa, Physica 16, 601 (1950).

conduction electrons is not included in the Korringa results; however Bloembergen and Rowland[15] do discuss such a term.

D. Line width and spin-spin relaxation processes

The resonance line possesses an observed line width for two reasons: (i) the presence of a static component of local field which has a different magnitude at different nuclear sites; and (ii) the finite lifetime of a nuclear magnetic spin state.

From a classical viewpoint each nuclear moment finds itself in a total magnetic field which is the sum of the externally applied magnetic field and the local magnetic field produced by the nuclear dipole moments of neighboring nuclei. The magnetic field produced by a magnetic moment at distance r from the moment is proportional to $\frac{\mu}{r^3}$. Therefore, in general the local field, B_L, will vary from place to place in the nuclear spin system. Since the resonance condition is determined by

$$\omega_D = \gamma (B_0 + B_L) \qquad (19)$$

one would expect to find a distribution of resonance frequencies, $\Delta\omega_0 \sim \gamma B_L$; hence the observed resonance line will exhibit a width. Consequently, any mechanism which makes a contribution to the static B_L will contribute to observed line broadening. Such broadening is known as inhomogeneous broadening.

Consider the other cause of line broadening: limiting of the lifetime of a nuclear spin state. The lifetime Δt of a state is related to the probability of transition per unit time W from that state to another by the expression

$$\Delta t \cong \frac{1}{W} \tag{20}$$

where W is related to T_1 by Eq. (13). By a consequence of the uncertainty relation, $\Delta E \, \Delta t \sim \hbar$, the energy level of the nuclear spin state will be broadened by the amount

$$\Delta E \cong \frac{\hbar}{2T_1} \tag{21}$$

and finally there will be a spread in the observed resonance frequency given by

$$\Delta \omega_0 \cong \frac{1}{2T_1} \, . \tag{22}$$

Bloembergen[11] has shown that the observed T_2 is related to T_1 and T_2' by the following expression

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2T_1} \tag{23}$$

where T_2' arises from effects due to local static fields and mutual spin-flipping. The above expression is valid only for the case of extreme motional narrowing of the resonance line. Outside this case no simple relation between T_1, T_2, and T_2' can be established.

E. Summary

The observed spin-lattice relaxation time T_1 is the resultant of all the processes which contribute to spin-lattice relaxation. The observed T_1 can then be represented as the sum

$$\frac{1}{T_1} = \sum_i \frac{1}{T_{1i}} . \qquad (24)$$

Similarly, if all the interactions which contribute to the line width correspond to the same line shape, then the observed spin-spin relaxation time T_2 can be represented by the sum of all the contributions as

$$\frac{1}{T_2} = \sum_i \frac{1}{T_{2i}} . \qquad (25)$$

In metals, the main mechanisms of spin-lattice relaxation are: nuclear magnetic interaction of the spin system with lattice motions of the spin system, diffusion of metal atoms through the lattice, diffusion of spin energy to paramagnetic impurity ions, interaction of electric quadrupole moment with electric field gradients, and the predominant source--magnetic interaction of the spin system with the conduction electrons. Factors which contribute to the line width in metals are: (1) the variation in the static component of B_L throughout the spin system (inhomogeneous broadening) and (ii) limiting of the lifetime of the spin state by the spin-lattice relaxation processes and mutual spin-flipping.

CHAPTER III

EQUIPMENT AND EXPERIMENTAL PROCEDURE

A. Equipment

A Varian Type V-4012-A magnet was used in these experiments. This magnet has cylindrical pole faces which are twelve inches in diameter and has a two-inch air gap. It can produce magnetic fields in the range from one to twelve kilogauss. The well regulated power supply for the magnet was designed and built in this laboratory and is described by Farringer.[17] Additional regulation of the magnetic field is attained by using a Varian Super Stabilizer Model V-K3506. The Super Stabilizer also enables one to produce variations of B_o at a low but nearly constant rate.

The experiments in the present investigation were carried out at two frequencies: 3.3 Mc/s and 11.0 Mc/s. The radio-frequency sources consisted of two separate oscillators each of which is crystal-controlled. The output of the oscillators can be continuously controlled

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[17] L. D. Farringer, doctoral dissertation, The Ohio State University (1958).

over a range from several microwatts to about five watts. They are designed so that the output can be modulated by an audio oscillator. This provides a convenient method of calibrating the sweep field. For spin-echo experiments it is desirable to have a pulsed radio-frequency source. Both oscillators were modified so that the screens and plates of the two stages before the final can be pulsed from their quiescent state of twenty-five volts below the cathode potentials to their maximum possible positive potential. This provides a ratio of on to off voltage at the output of ten thousand to one. In this way a coherent source of pulsed radio-frequency power is obtained. In the pulsed mode, the oscillator rises from minimum to maximum output in five microseconds and falls from maximum output to minimum output in three microseconds.

A Tektronix Type 162 Waveform Generator and two Tektronix Type 163 Pulse Generators were used to pulse the oscillators used in the spin-echo experiments.

The probes used in the experiments are the crossed-coil type Varian Model V4331A. One probe was operated at 3.3 Mc/s and another at 11.0 Mc/s. In each probe, there is a set of Helmholtz coils with the axis of the set oriented parallel to the direction of the external magnetic field. The Helmholtz coils can be driven by the sawtooth sweep of an oscilloscope in order to produce at the site of the sample a magnetic field which varies at a constant rate. The magnitude of this field sweep can be varied from a few milligauss to five gauss.

A Varian Variable Temperature NMR Probe Accessory Model V-4340 was used to obtain a variable sample temperature. The temperature accessory was modified so that sample tubes with an outside diameter of 8 mm. could be used. In order to reduce the sensitivity of the probe balance to temperature fluctuations, the transfer Dewar was removed; a piece of high-grade rubber hose was then used to connect the heater tube assembly to the insert Dewar cap.

For detecting the NMR signal, the first stage of a Wallman cascode preamplifier is connected directly to the probe and the second stage is located in a National HRO-60 radio receiver. This system has a capability of detecting a 0.1 microvolt signal at 11.0 Mc/s with a signal-to-noise ratio of about 3:1. For slow-passage work, the output at the detector of the receiver is connected to a low-pass RC filter circuit which has a time constant that can be varied in steps from 0.01 to 3.0 seconds. The signal then passes through a cathode follower and DC balancing system for convenient display on the Tektronix Type 533 oscilloscope. For the pulse experiments the output of the receiver detector is connected directly to the oscilloscope; in this configuration the overall band pass of the detection system is approximately 3 Kc/s.

B. Experimental method

In the slow-passage experiments, the external field sweep was obtained by having the oscilloscope sweep drive, by means of an additional amplifier, the Helmholtz coils in the probe. The resonance signal was then displayed directly on the oscilloscope and photographed. The line widths were then determined directly from the photograph. In all the experiments the line width δB is taken as the total separation (in gauss) between the half-maximum amplitude points on the absorption curve as displayed on the oscilloscope. The field sweep was calibrated by modulating the output of the radio-frequency oscillator with a calibrated audio frequency oscillator and then measuring the separation between the central line and the lines due to sidebands which appeared on the oscilloscope. Care was taken to insure that the sweep rate was well below that rate which would produce eddy currents in the probe of sufficient magnitude to cause "artificial" broadening of the line being observed. The time constant of the RC filter network was always adjusted to prevent any artificial broadening. The output of the radio-frequency oscillator was operated in a region where a linear increase in output voltage would result in a linear increase of the amplitude of the NMR signal as displayed on the oscilloscope. This procedure was followed in order to prevent broadening of the line due to partial saturation of the sample.

Before each experiment was begun, the magnet was cycled in order to obtain the best field homogeneity. The Super Stabilizer was then put into operation and finally the field was trimmed using a Varian Field Homogeneity Control Unit Model V-4365. The sample used during this procedure was a 4.5 molar aqueous solution of NaBr in an 8 mm. sample tube. The width of this line was found to be between 13 and 14 milligauss, a result consistent with some unpublished data by Elleman. Therefore the field inhomogeneity over the sample in its active region probably did not exceed several milligauss.

Spin-lattice relaxation times T_1 were measured by the null method due to Carr and Purcell.[8] In this method a 180° pulse is applied and is later followed by a 90° pulse. The time between the two pulses is increased each time the sequence is carried out, and the tail at the end of the second pulse is observed to be a minimum for a certain pulse separation t. Then T_1 can be found from the relation

$$t = T_1 \ln 2 . \tag{26}$$

The spin-spin relaxation time T_2 was measured by the Carr-Purcell[8] technique in which a single 90° pulse is applied and then is followed by a sequence of equally spaced 180°

pulses. This procedure results in a sequence of echoes with a single echo appearing between each pair of 180° pulses. The envelope of this echo sequence decays at a characteristic rate which is very nearly equal to the true T_2 of the material. Artificial shortening of T_2 due to diffusion of nuclei through an inhomogeneous B_o is greatly reduced. The effects on T_2 of inhomogeneities in B_o are less if the spacing between the 180° pulses is reduced. However, experimental difficulties prevent this spacing from being made arbitrarily short. In these experiments, the spacing between 180° pulses was 5 msec.

C. Samples

The metallic sodium used in this work was very kindly donated by U.S. Industrial Chemicals Co., 1275 Section Road, Cincinnati, Ohio. It consisted of metallic sodium dispersed in an oil called Alkylate #775-13 with 0.5% aluminum stearate additive. Alkylate consists of petroleum isoparaffins combined with olefin hydrocarbons. The particle size was alleged to be in the range of 1 to 14 microns and to have an average size of 7 microns. A slide of the sodium dispersion was examined under a microscope and the particle size was compared with the red blood cells of the chicken. The average size of these chicken cells is known to be 7 microns.[18] The sodium particles were observed to be on the average about seven microns in diameter.

The rubidium sample was very kindly donated by Dr. William Gager of Battelle Memorial Institute. The rubidium had been dispersed in paraffin. The particle size of this dispersion is not known.

Both the sodium and the rubidium samples were placed in pyrex tubes which have an outside diameter of 8 mm. and an inside diameter of 6 mm.

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[18] W. E. Bray, Clinical Laboratory Methods, St. Louis: C. V. Moseby Co., 1957, p. 175.

CHAPTER IV

RESULTS OF EXPERIMENTS

The line width δB of the absorption spectrum of metallic sodium was measured over the temperature range 30° to 120° C. at two resonance frequencies: 3.3 Mc/s and 11.0 Mc/s. Melting occurs at 99° C.; therefore observations were made in both the solid and liquid states. The results are presented in Fig. 1 and 2.

The probable error in the data at 3.3 Mc/s is ± 0.0015 gauss in both the liquid and solid states. At 11.0 Mc/s the probable error is ± 0.0005 gauss in the solid state and ± 0.0010 gauss in the liquid state. The probable error was estimated as half of the difference between the maximum line width and the minimum line width observed at each temperature. At least nine measurements were made at each temperature.

At both frequencies, a large increase in line width occurs as the temperature of the sample passes through the melting point. At 3.3 Mc/s, the line width is 0.036 gauss just before melting and the line width is 0.061 gauss just after melting. This is a 70% increase

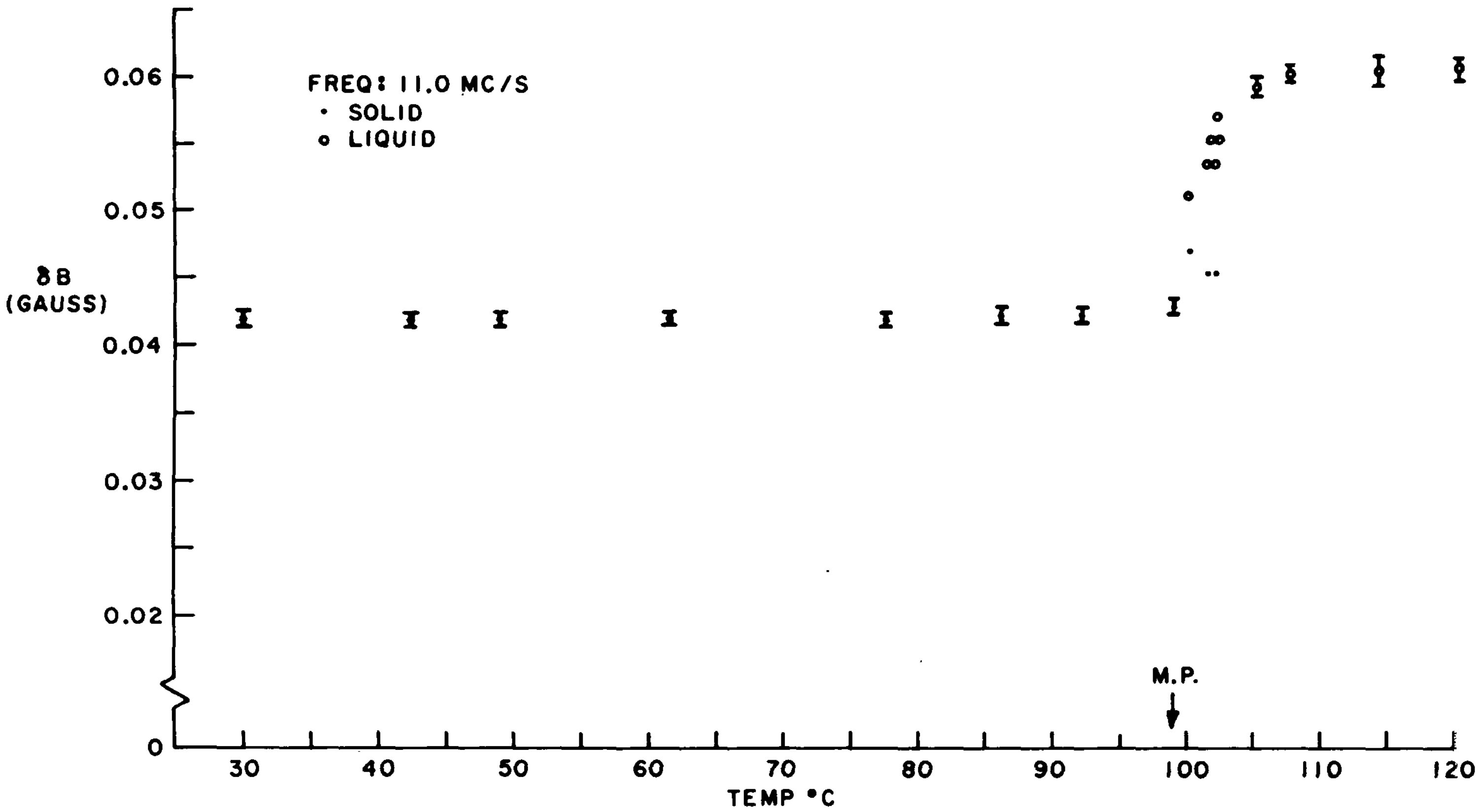


Figure 1. Line Width Of Na^{23} Versus Temperature.

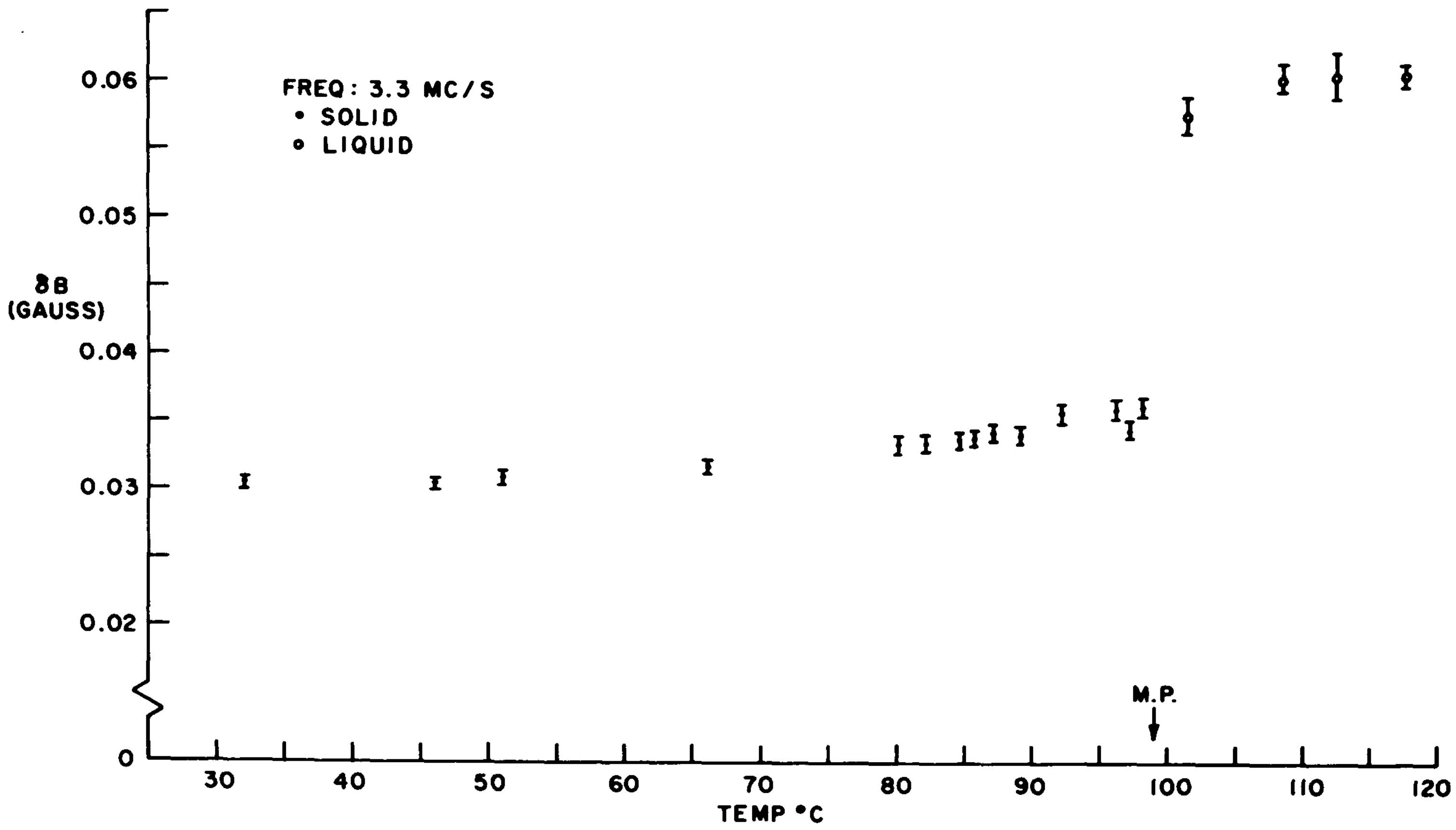


Figure 2. Line Width Of Na^{23} Versus Temperature.

in line width upon melting. At 11.0 Mc/s, the line width is 0.043 gauss just before melting and 0.060 gauss after the sample has melted. This is a 40% increase in line width upon melting.

In Fig. 1, it is seen that at a resonance frequency of 11.0 Mc/s the line width δB of the solid has an essentially constant value of 0.042 gauss from 30° C. to the melting point. The data in Fig. 2 show a different behavior of the line width in the solid at 3.3 Mc/s. In Fig. 2 it is seen that δB is 0.031 gauss at 30° C. At 66° C., δB has risen to 0.032 gauss and then continues to gradually rise until $\delta B = 0.036$ gauss just before melting begins. Therefore in the temperature range from 30° C. to the melting point, the line width of the resonance line of solid sodium exhibits a dependence on the resonance frequence; in addition at a resonance frequency of 3.3 Mc/s, the line width exhibits a slight temperature dependence. This temperature dependence is not observed at 11.0 Mc/s.

Above the melting point, the line width of the liquid exhibits a different behavior. In the temperature range 105° to 120° C., the width has the average constant value of 0.061 gauss for both resonance frequencies. Hence the line width of the liquid in this range does not exhibit a dependence on either temperature or the resonance frequency.

Some photographs of the absorption spectrum of sodium at a resonance frequency of 11.0 Mc/s are presented in Fig. 3. The calibration of the field sweep in Fig. 3a is 0.028 gauss per division (each division, which has been reduced in the photographic process, represents 1 cm. on the oscilloscope screen for a total of 10 cm.). In Fig. 3b through Fig. 3h the calibration is 0.048 gauss per division. Fig. 3a is the observed absorption spectrum at 30° C. Fig. 3b is a photograph of the spectrum as the sodium begins to melt. Fig. 3c through 3g are photographs of the spectrum taken in sequence as the melting process progresses. Fig. 3h shows three successive photographs of the spectrum taken at 105° C., just after the resonance line of solid sodium has disappeared. The line widths in Fig. 1, which are plotted at 100° and 101.5° C., were obtained from the absorption spectra shown in Fig. 3d, Fig. 3e, and Fig. 3f, in which the resonance lines of solid and liquid sodium are seen to coexist. Fig. 3b through 3g indicate that the resonance frequency is different in solid and liquid sodium. It is for this reason that it is possible to observe the resonance lines of the solid and liquid while the two phases coexist.

The coexistence of the solid and liquid resonance lines at the melting point was observed at both 3.3 Mc/s and 11.0 Mc/s. At 3.3 Mc/s the separation between the centers of the liquid and solid lines is 0.083 gauss in

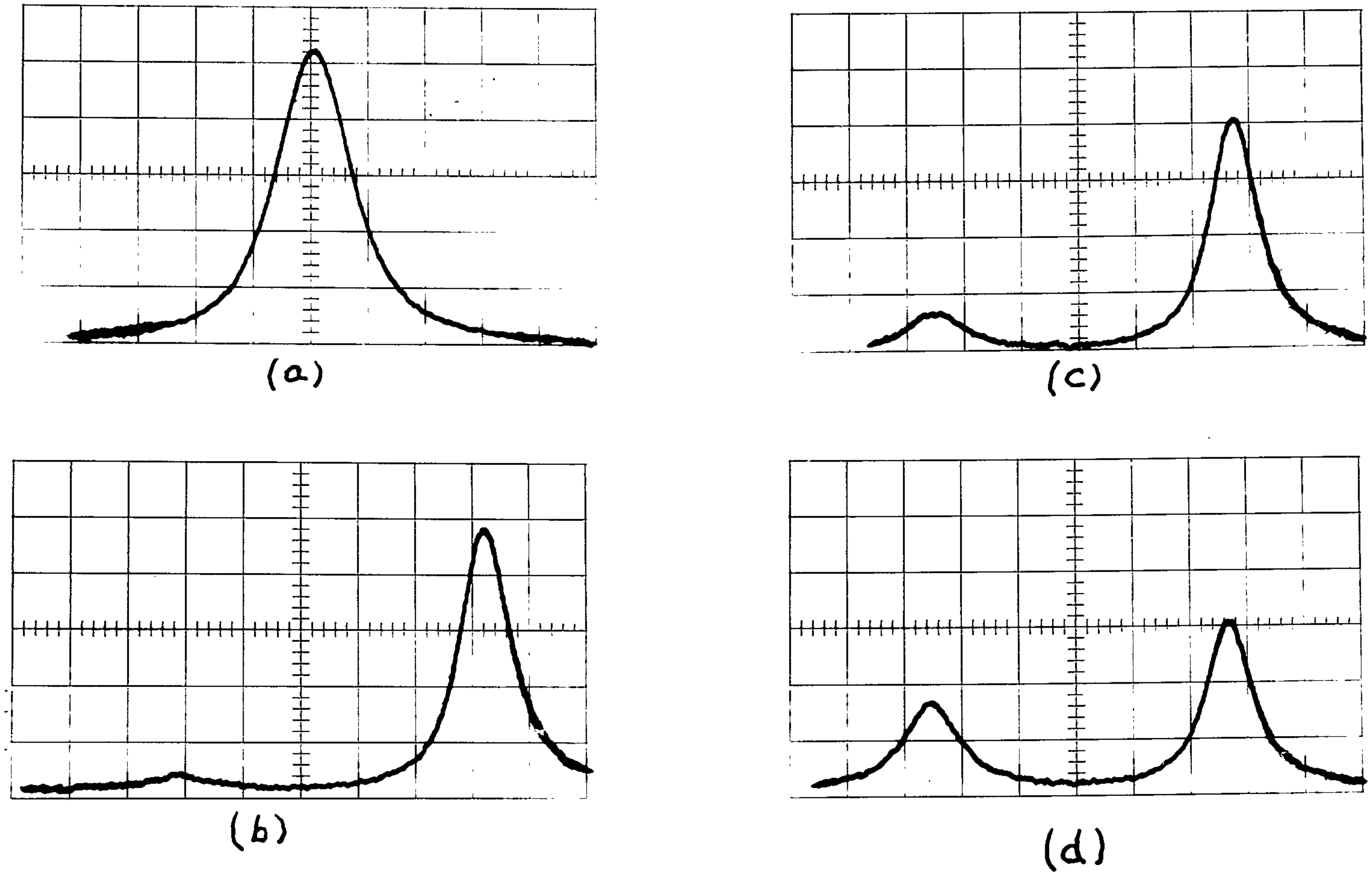
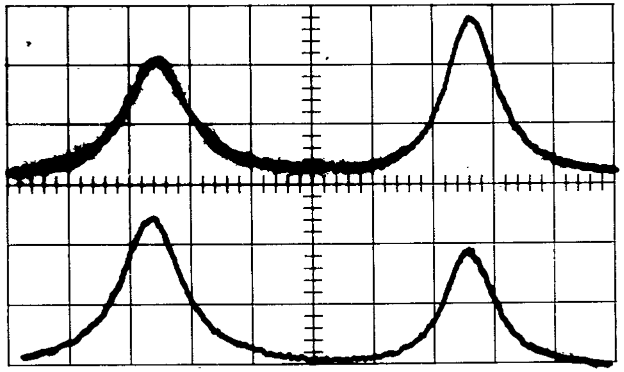
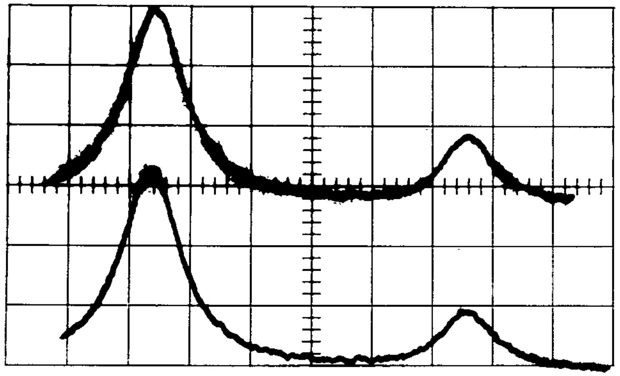


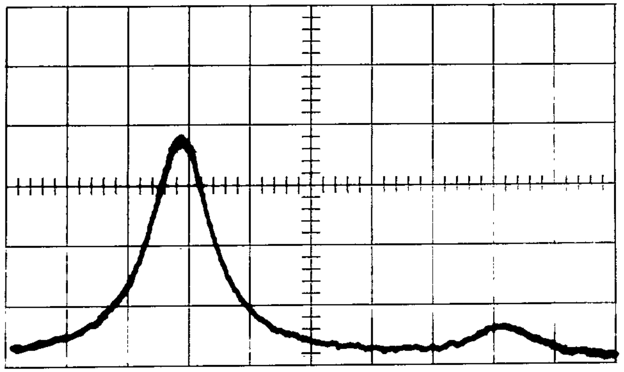
Fig 3. Absorption Spectrum of Na^{23} at 11.0 Mc/s.



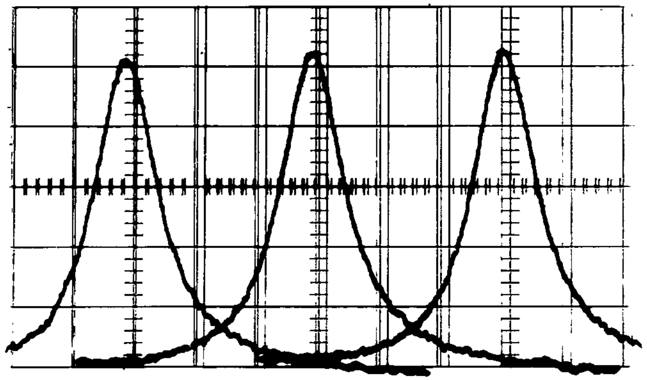
(e)



(f)



(g)



(h)

an external field of 2925 gauss. The separation of the lines does not change as the melting of the sample progresses. At 11.0 Mc/s, the separation of the two lines is observed to be 0.250 gauss in an external field of 9752 gauss. The separation at 11.0 Mc/s does not change as the melting procedure progresses.

The relaxation times T_1 and T_2 of sodium were measured as a function of temperature for two resonance frequencies: 3.3 Mc/s and 11.0 Mc/s. As previously mentioned, the spin-echo technique was used for these measurements. The null method was used to determine T_1 and the Carr-Purcell method (a single 90° pulse followed by a sequence of equally spaced 180° pulses) was used to measure T_2. The results of the T_1-T_2 measurements at 3.3 Mc/s are given in Fig. 4. The spin-lattice relaxation time T_1 decreases at an approximately linear rate with increasing temperature from 14 msec. at 30° C. to about 7.5 msec. at 101° C. The spin-spin relaxation time T_2 is observed to decrease approximately linearly with increasing temperature from 8.5 msec. at 30° C. to 5.5 msec. at 98° C. On account of the poor signal-to-noise ratio, it was not possible to measure T_2 above the melting point at 3.3 Mc/s.

The results of the spin-echo measurements on sodium at a resonance frequency of 11.0 Mc/s are presented in Fig. 5. As a consequence of an improved signal-to-noise ratio (as compared to the signal-to-noise ratio at 3.3 Mc/s),

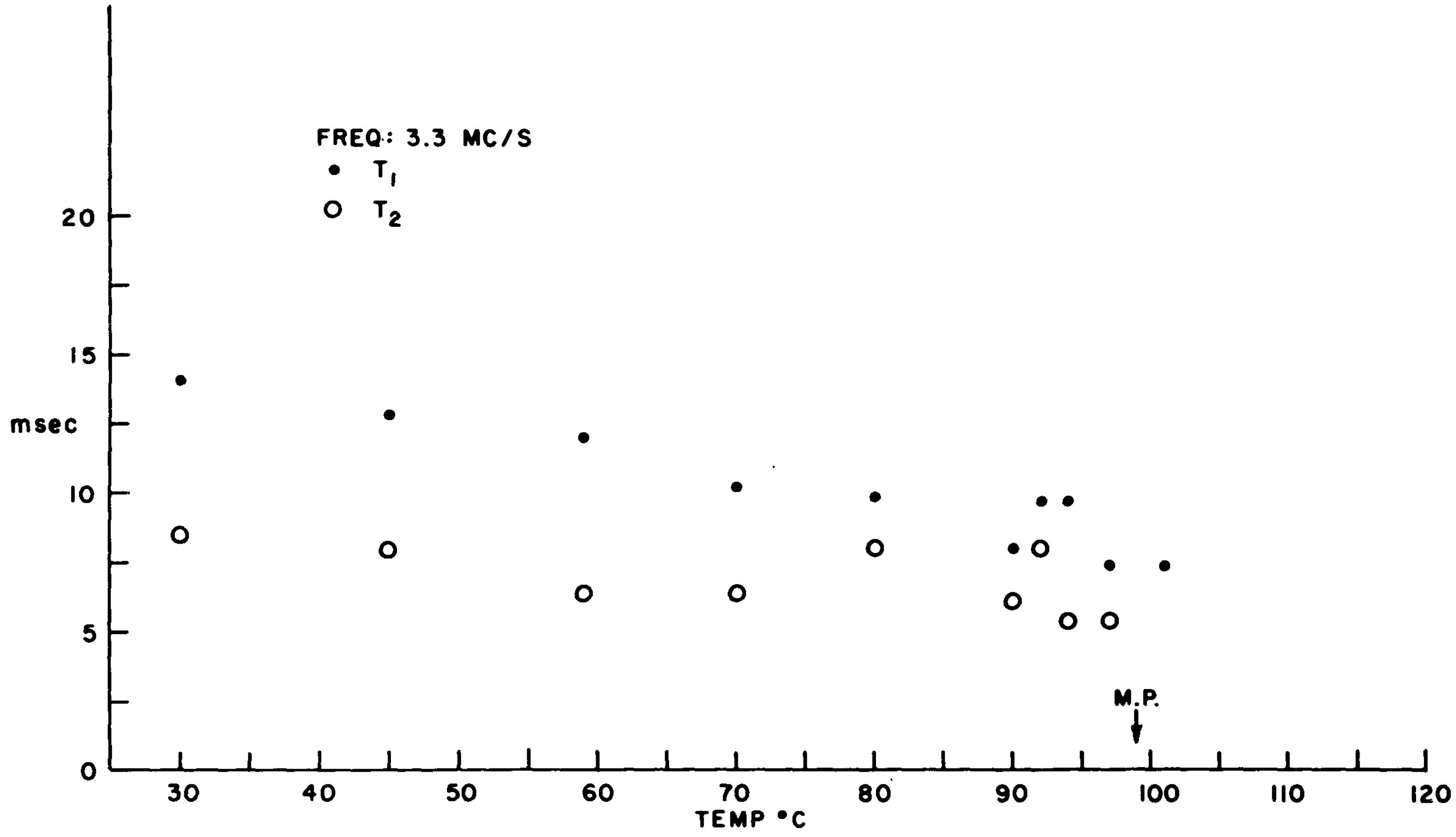


Figure 4. Relaxation Times Of Na^{23} Versus Temperature.

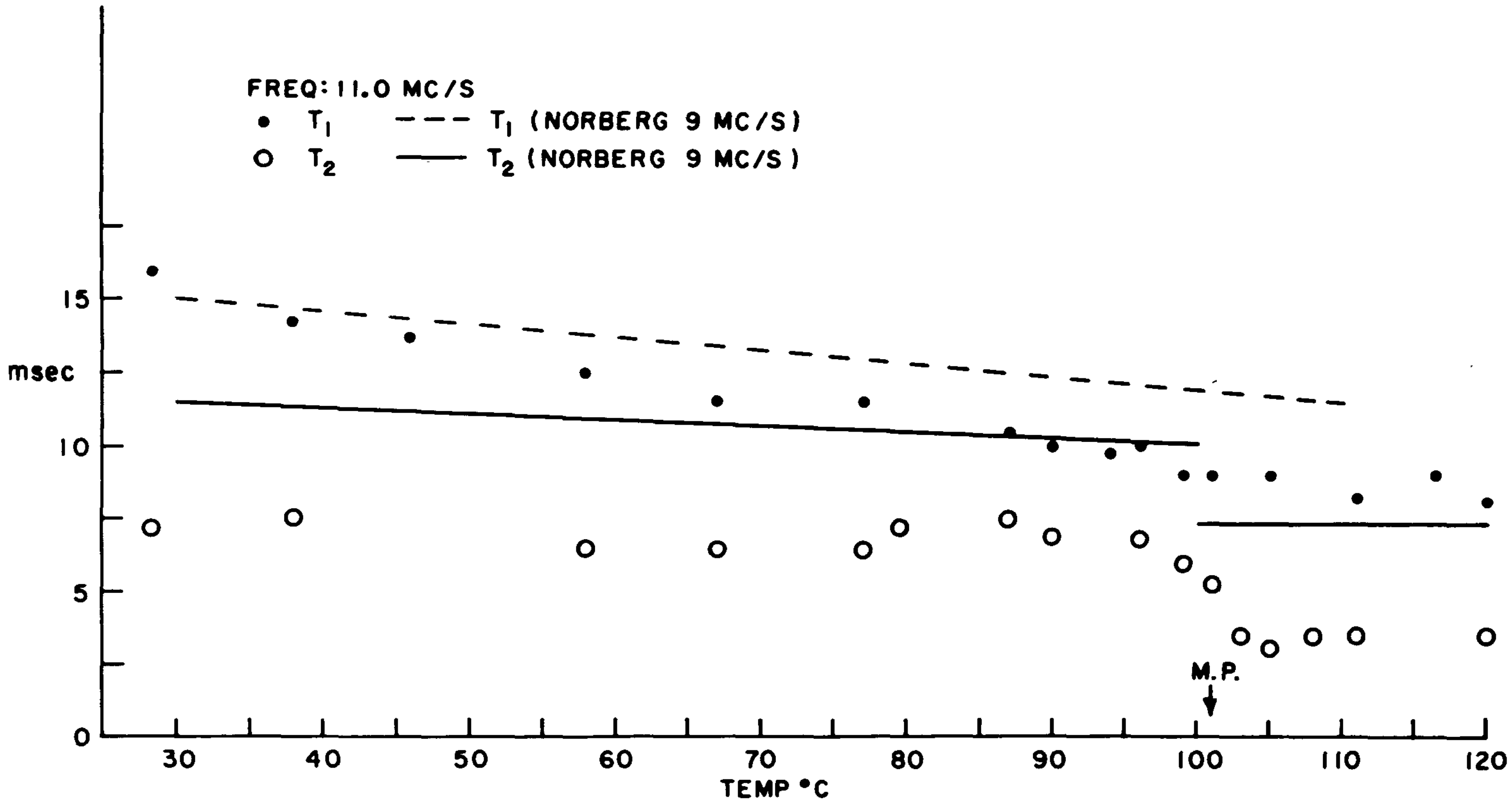


Figure 5. Relaxation Times Of Na^{23} Versus Temperature.

these measurements were extended to 120° C. The relaxation time T_1 is observed to decrease approximately linearly with increasing temperature from a value of 16 msec. at 28° C. to 8 msec. at 111° C. Within the limits of experimental error, this is equivalent to the observed behavior of T_1 at 3.3 Mc/s. In the solid, T_2 remains essentially constant from 30° to 90° C. and has an average value of 7 msec. Melting begins at 99° C.; at this temperature T_2 has an average value of 6 msec. At 103° C. the sample is completely melted, and T_2 has decreased to 3.5 msec. The relaxation time T_2 then remains constant as the temperature increases to 120° C. Since T_2 is inversely proportional to the line width of the absorption spectrum, the decrease in T_2 upon melting is consistent with the observed increase in line width (see Fig. 1). A change from $T_2 = 3.5$ msec. in the liquid to $T_2 = 6.0$ msec in the solid is an increase of 70% in relaxation time.

In order to study further the mechanisms which may contribute to the line broadening exhibited by sodium, the relaxation times of the proton in the oil in which the sodium was dispersed were investigated. A portion of the oil was decanted from the sodium dispersion and placed in a glass sample tube with an inside diameter of 3 mm. The relaxation times T_1 and T_2 were measured by the spin-echo technique at room temperature and in the neighborhood of the melting point of sodium. The results are shown in

Fig. 6. The relaxation times do not show any anomalous behavior in the region of the melting point of sodium. The relaxation times of the proton in the sodium dispersion were measured by the spin-echo technique. The sample used in the sodium experiments was also used for these measurements. The results are shown in Fig. 7.

No anomalous behavior of T_1 and T_2 of the proton in the sodium dispersion is observed at the melting point of sodium. If the T_1 data in Fig. 6 and 7 are compared, it is seen that T_1 of the proton is longer in the dispersion than in the bulk oil. For example, at 30° C., $T_1 = 1.5$ sec. in the dispersion and $T_1 = 0.8$ sec. in the bulk oil. At 100° C., $T_1 = 4.1$ sec. in the dispersion and $T_1 = 2.1$ sec. in the bulk oil. Hence the slope of the T_1 curve is greater for the proton in the dispersion than the proton in the bulk oil. A marked difference in the magnitude of T_2 in the two samples is observed throughout the temperature range in which measurements were made. If 100° C. is selected as a point for comparison, it is seen that in the bulk oil $T_2 = 0.6$ sec. and in the dispersion $T_2 = 0.03$ sec. Hence the relaxation time T_2 of the proton in the dispersion is only 1/20 as large as it is in the bulk oil at this temperature.

In order to gain further insight into the mechanisms causing the line broadening of sodium, the two

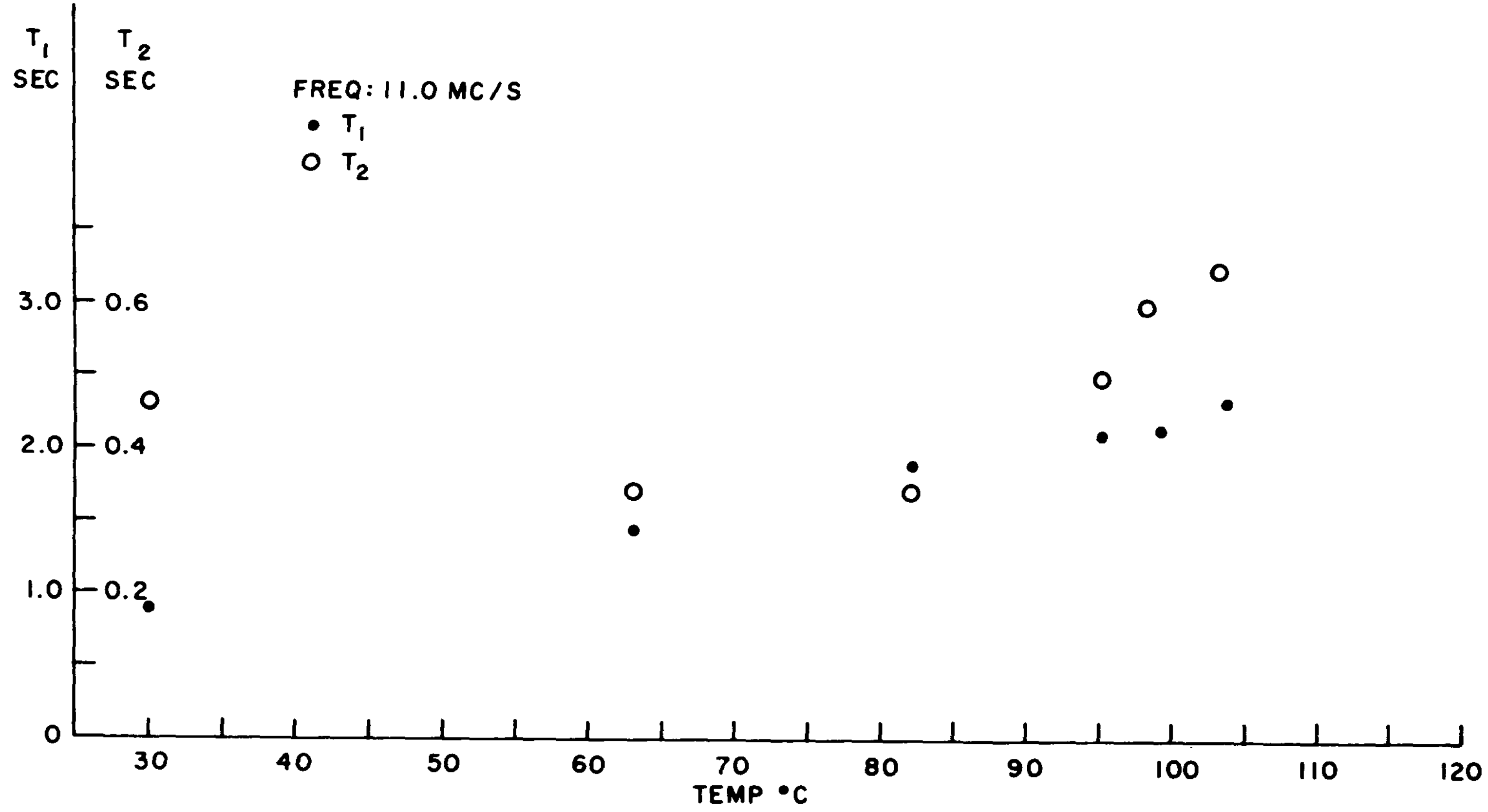


Figure 6. Relaxation Times Of Proton In Alkylate Versus Temperature.

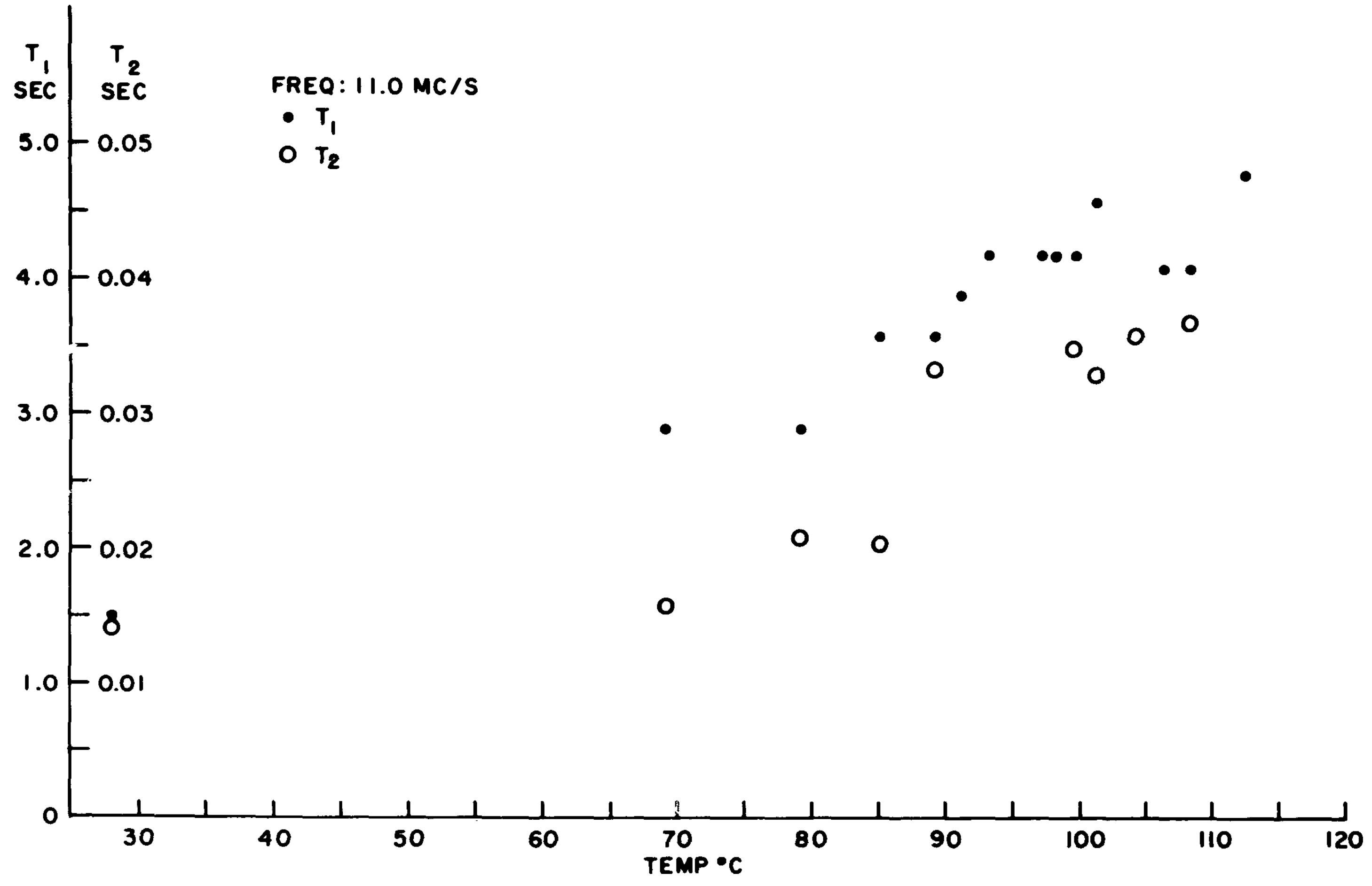


Figure 7. Relaxation Times Of Proton In Sodium Dispersion Versus Temperature.

isotopes of rubidium, Rb^{85} and Rb^{87}, were investigated. The results of the measurement of line width as a function of temperature for Rb^{87} are presented in Fig. 8. Due to a poor signal-to-noise ratio, the statistical variation in these data is rather large. The probable error is estimated to be ± 0.1 gauss. The probable error for the rubidium data was estimated in the same way as it was for the line width measurements of sodium. Within the limits of experimental error, the line width of Rb^{87} is observed to be the same in the liquid and the solid. Two clearly resolved resonance lines were not observed at the melting point as was the case with sodium. Instead, during the melting process, the signal amplitude is observed to decrease to a level such that it is nearly obscured by the noise. After the rubidium has melted, the signal amplitude is the same as before melting occurred. At the melting point, the Knight shift in the liquid is different from the Knight shift in the solid. However the difference is small compared with the line width. Hence, as a result of the change in Knight shift and a poor signal-to-noise ratio, the line width at the melting point is observed to behave as described above.

The line width of Rb^{85} as a function of temperature is presented in Fig. 9. The probable error is estimated to be ± 0.05 gauss. The line width has an average value of 0.68 gauss at 30° C. and decreases with increasing

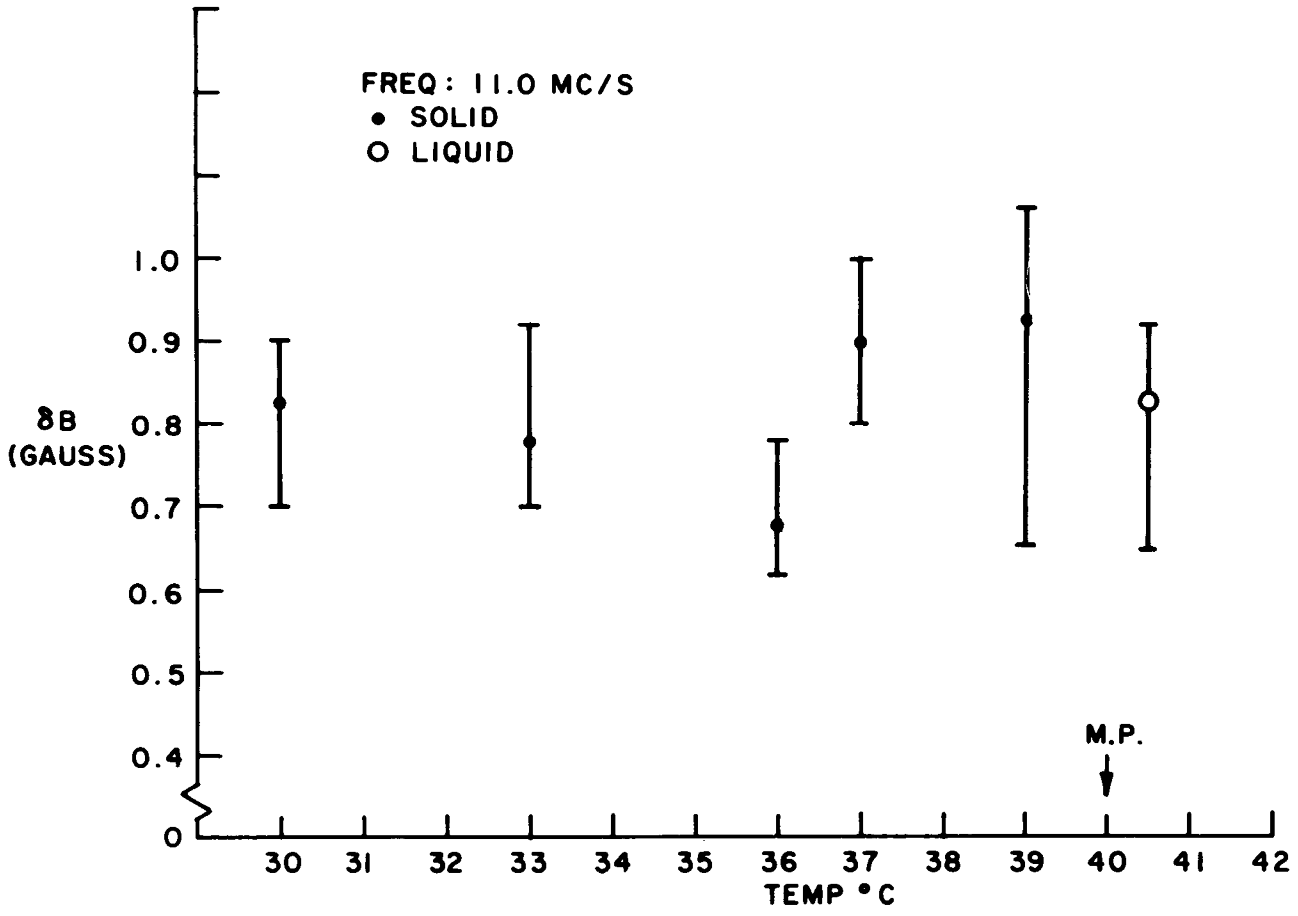


Figure 8. Line Width Of Rb^{87} Versus Temperature.

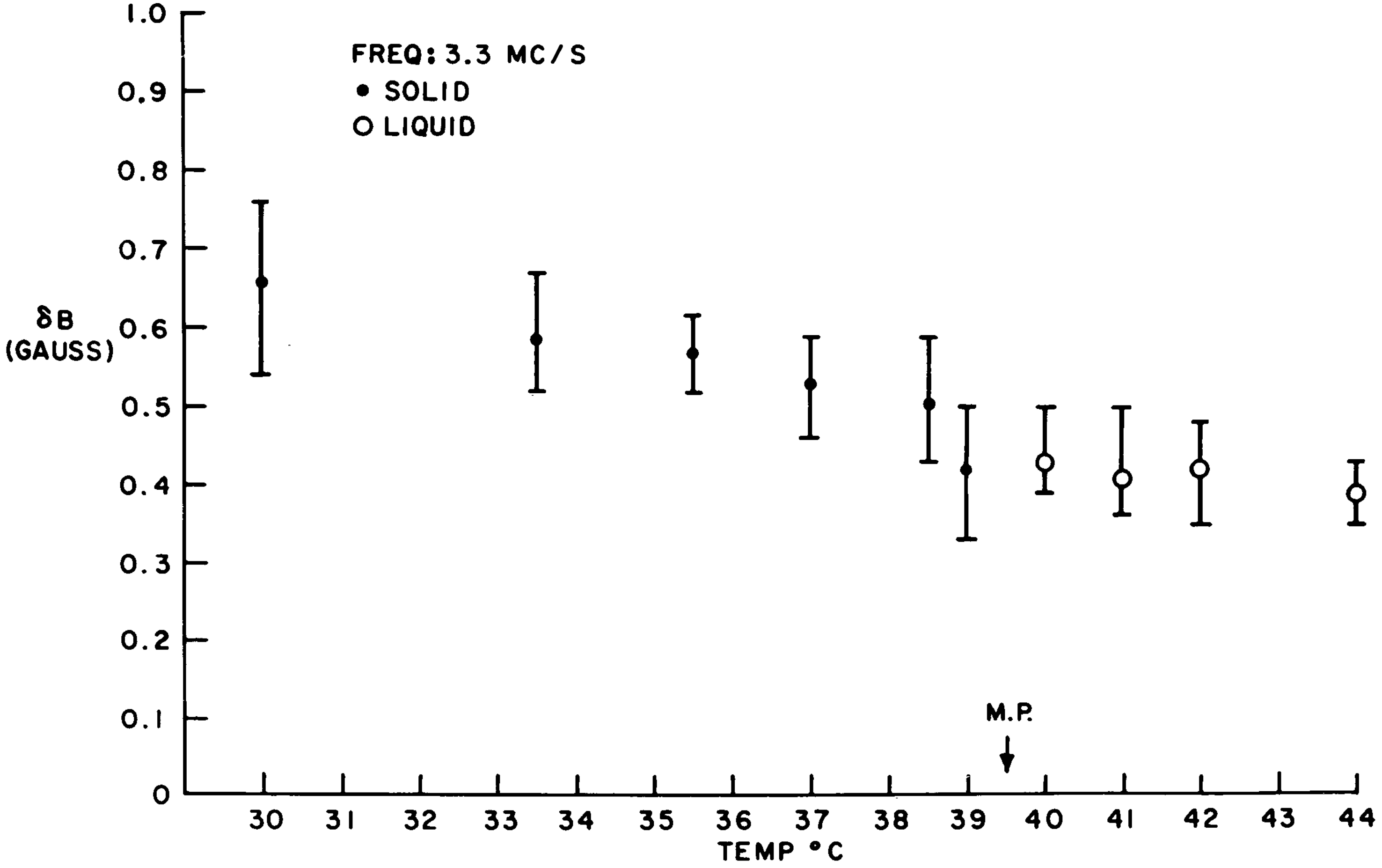


Figure 9. Line Width Of Rb^{85} Versus Temperature.

temperature to an average value of 0.50 gauss at 38.5° C. Just below the melting point at 39° C., the line width suddenly decreases to an average value of 0.41 gauss. The line width is observed to be 0.41 gauss above the melting point also. Instead of exhibiting a line broadening as sodium did at the melting point, Rb^{85} shows a line narrowing. Furthermore, in the case of Rb^{85} the transition takes place just below the melting point.

The liquid and solid resonance lines of Rb^{85} were observed while they coexisted at the melting point. The centers of the lines were observed to be separated by 0.9 gauss in an external field of 7975 gauss. The liquid lines appeared at the lower field for the constant frequency 3.3 Mc/s.

CHAPTER V

DISCUSSION OF RESULTS

Eq. (6) which is valid only for a Lorentzian line shape, can be used to compare the spin-spin relaxation time T_2 as determined by the slow passage technique. In the following tabulation, $T_2(\delta B)$ represents the spin-spin relaxation time which has been determined from a measurement of the line width δB, and T_2 (pulse) is the spin-spin relaxation time as determined by the pulse technique for sodium.

TABLE 1

COMPARISON OF LINE WIDTHS AND T_2 OF Na^{23}

Freq Mc/s	Temp °C	δB (gauss)	$T_2(\delta B)$ (msec)	T_2(pulse) (msec)
3.3	30	0.031 ± 0.0015	9.14 ± 0.4	8.5 ± 1.0
3.3	98	0.037 ± 0.0015	7.65 ± 0.4	5.5 ± 1.0
3.3	102	0.061 ± 0.0015	4.64 ± 0.4	- -
11.0	30	0.042 ± 0.0005	6.74 ± 0.07	7.5 ± 0.5
11.0	99	0.043 ± 0.0005	6.59 ± 0.07	6.0 ± 0.5
11.0	109	0.061 ± 0.0010	4.64 ± 0.07	3.5 ± 0.5

A measurement of T_2 above the melting point by the pulse technique at 3.3 Mc/s was not possible because of the poor signal-to-noise ratio. The data in the above tabulation indicate that in these experiments the greater precision in measuring T_2 was achieved by using the slow passage technique with the high resolution spectrometer.

The observed anomalous broadening of the sodium line will be discussed in terms of several known broadening mechanisms. A decrease in the lifetime of the nuclear spin states when sodium melts would cause broadening of the line. Two principal mechanisms affect the lifetime of the spin states in NMR: (i) spin-lattice relaxation processes, and (ii) mutual exchange of energy within the spin system. The latter process is often termed spin-flipping. The spin-lattice relaxation process is not believed to be the cause for the following reasons: The relaxation time T_1 does not undergo any sudden change at the melting point. Instead, T_1 continues to decrease at the same rate with increasing temperature in the liquid as it did in the solid. Also, if the spin-lattice relaxation process were an important mechanism in determining T_2 in the liquid, then the line width of the liquid would also show a variation with temperature. This is not the case; the line width of the liquid is observed to remain constant up to 120° C. A decrease in lifetime of the spin states due to an increase in the spin-flipping process upon melting would not affect T_1. However this does not appear to be a probable cause since the probability of spin-flipping should decrease due to the expected decrease in τ_c as the rate of self-diffusion of the sodium atoms increases. A line narrowing due to self-diffusion in sodium is observed[4] to begin at 190° K., and there is no reason to expect the diffusion process to be slowed down at higher temperatures. On the contrary the coefficient of self-diffusion in some metals has been observed to increase by several orders of magnitude upon melting.[19]

Inhomogeneous broadening provides another mechanism which must be considered. Each nucleus precesses at a rate determined by the magnitude of the total static field in the z-direction, $B_z = B_o + B_L$, at each nuclear site. Therefore nuclei at nuclear sites, which have different values of B_z, will precess at different rates. In these experiments the variation of B_o, the external field, over the active region of the sample is negligible compared with the natural line width. Therefore in this case any appreciable variation in B_z is due to B_L (the local field produced by factors such as nuclear neighbors, paramagnetic ions, and motions and spins of electrons).

In 1959, Yost[20] measured T_1 and T_2 of the proton

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[19] G. Careri, A. Paoletti, and F. L. Salvetti, Nuovo Cimento **11**, 399 (1954).

[20] I. G. Yost, thesis, The Ohio State University (1959).

in mixtures of water and silicon dioxide as a function of particle size (range of particle diameters--50 to 700 microns). He found that T_2 decreases as the particle size decreases, but that T_1 remains constant over a large range of particle sizes. Fost suggested that because water and silicon dioxide have different magnetic susceptibilities, inhomogeneities in the static component of magnetic field H_z would exist near the interface of the particle and water. Therefore the protons near the surface of the particle would have a spin-spin relaxation time T_{2S} which is shorter than the spin-spin relaxation time T_{2B} of the protons in bulk water. Hence $1/T_2$ may be considered to be due to the weighted sum of two relaxation ratios: $1/T_{2B}$ due to protons in the bulk and $1/T_{2S}$ due to the protons near the surface of the particle. Thus the relaxation time T_2 will depend on diffusion processes near the surface. For example, if the time required for a proton to diffuse from bulk liquid to the surface is small compared with T_{2S}, then there is a greater probability that it will relax according to T_{2S} if it stays near the surface for a long time compared to T_{2S}. This would be an explanation of why T_2 for the mixture decreases as the distance from any point in the bulk liquid to a surface is reduced and the surface to volume ratio is increased; this is the case when the particle size is reduced.

In order to study the influence which surface effects may have on the anomalous broadening of the sodium line; T_1 and T_2 of the proton was measured in the sodium dispersion and in a sample of the bulk oil which had been decanted from the sodium dispersion. The results are given in Fig. 7 and 8, respectively. At room temperature, T_2 of the proton in bulk oil is 30 times longer than T_2 of the proton in the dispersion. This result is similar to the result reported by Lost for the mixture of water and silicon dioxide particles. Also it is noted that T_1 is almost twice as long in the dispersion as it is in the bulk oil sample. The relative susceptibilities of sodium and petroleum (information on alkylate, the oil in which the sodium is dispersed, is not available) are respectively +0.51 and - 0.83. Hence inhomogeneities in the magnetic field near the sodium-oil interface will exist. On the basis of Lost's model, there would be two relaxation terms T_{2S} and T_{2B} for the proton. Similarly, the possibility exists that the spin-spin relaxation time of sodium will consist of two terms: T_{2S} for nuclei near the surface and T_{2B} for nuclei in the interior of the sodium particle. How can the existence of two different relaxation times T_{2B} and T_{2S} account for the line broadening upon melting? Although sodium is a solid in the temperature range from 300° K. to its melting point at 372° K., there is evidence that narrowing of the resonance line[4] due to self-diffusion of the sodium atoms begins at 193° K. Even though self-diffusion is well established below the melting point, the time necessary for the average sodium atom to pass from bulk sodium to the sodium-oil interface is evidently long compared with T_{2B} and T_{2S}. If sodium behaves as some other metals,[19] the self-diffusion coefficient of sodium may increase by several orders of magnitude when it melts. In this way the probability that a given nucleus would approach the surface of the sodium particle and relax according to T_{2S} would be greatly enhanced upon melting. This process could then account for the anomalous line broadening of sodium. Information on the coefficient of self-diffusion in the solid is available;[6,21] however no data on self-diffusion in liquid sodium are available. This information would be desirable in order to check the above information.

Yost[20] has suggested that T_{2S} and T_{2B} are different because the difference in susceptibilities of oil and sodium create inhomogeneities in the magnetic field near the surface of the sodium particles. If this were the case, then one would expect the magnitude of the inhomogeneities to increase as H_0, the external magnetic

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[21] N. H. Nachtrieb, E. Catalano, and J. A. Weil, J. Chem. Phys. 21, 1185 (1952).

field, is increased. This should be reflected in a decrease in T_{2S} and ultimately T_2 as B_0 is increased. This decrease in T_2 is not observed. An inspection of Fig. 1 and 2 reveals that the line width in liquid sodium is the same for the two resonance frequencies, 3.3 Mc/s and 11.0 Mc/s. Evidently no noticeable difference in T_{2S} and T_{2B} arises from the difference in magnetic susceptibilities of oil and sodium.

Another inspection of Fig. 6 and 7 shows that T_1 of the proton is longer in the sodium dispersion than it is in the bulk sample of the oil and T_2 is much shorter in the dispersion than it is in the oil. This behavior of T_1 and T_2 suggests that the protons, being in most cases near the surface of the sodium particles, may be immobilized as if they were in a solid; hence the long value of T_1 and the short T_2. The relaxation time T_1 would not be expected to be extremely long as in a true solid since no attempt was made to remove paramagnetic impurities such as oxygen from the sodium dispersion. In a like manner the sodium nuclei near the inside surface of the sodium particle may behave as a solid after melting and therefore have a T_{2S} shorter than T_{2B}. Then sodium nuclei diffusing to the surface would be exposed to a semi-rigid lattice; hence they would experience an inhomogeneous magnetic field and dephasing of the nuclei would occur just as previously suggested. If the diffusion process suddenly increases upon melting, the probability of a given nucleus reaching the surface is speeded up and the dephasing process is enhanced thus causing a broadening of the resonance line upon melting. If the inhomogeneities near the surface are primarily caused by nuclei near the surface being bound together as a solid, one would not expect the effect to be dependent upon the external magnetic field. This is in agreement with experiment since the line width in the liquid state is not field dependent, at least for the two resonance frequencies investigated.

In order to gain further insight into the line broadening which occurs when sodium melts, the isotopes of rubidium, Rb^{85} and Rb^{87}, in metallic rubidium were investigated. Gutowsky[5,22] has reported data on the line width of Rb^{87} below and above its melting point. He reported that the line width of Rb^{87} showed a sudden decrease upon melting. Just below the melting point he found the line width to be of the order of 0.6 gauss and just above the melting point to be about 0.5 gauss. The results of the present measurements with Rb^{87} are shown in Fig. 5. As can be seen, the statistical variation in the data is large (order of ± 0.1 gauss) so a small change in line width upon melting can not be detected. Gutowsky no doubt was able to use a larger sample with his equipment and thus achieve a better signal-to-noise ratio than that obtained in this experiment. However it must be noted that the line width as reported here is on the average 40 to 50% greater than that reported by Gutowsky. There is a slight difference in the method of dispersing the rubidium. Gutowsky used mineral oil while paraffin was used as the dispersing agent in this experiment. However it seems unlikely that the dispersing agents could account for the large discrepancy in line widths.

The line width of Rb^{85} at 3.3 Mc/s as a function of temperature is displayed in Fig. 9. These data look almost identical in character to those reported by Gutowsky[5,22] for Rb^{87}. There is also some statistical variation in the data in Fig. 9; however there are enough points to indicate that the line width undergoes a sudden decrease of about 0.1 gauss just below the melting point and then remains constant in the liquid up to 44° C. This decrease in line width upon melting is contrary the behavior exhibited by sodium. Therefore this case must be examined to see if it invalidates the proposed explanation of the observed line broadening in molten sodium. Also this decrease in line width of Rb^{85} when it melts contradicts the conclusion of Holcomb and Norberg,[6] based on their spin-echo measurements, that the line width broadens as in the case of sodium.

The relative susceptibilities of several substances are given (data on mineral is unavailable, hence petroleum is given):

TABLE 2

COMPARISON OF RELATIVE SUSCEPTIBILITIES

Paraffin	- 0.60
Petroleum	- 0.83
Rubidium	+ 0.09
Sodium	+ 0.51

Therefore if the difference in susceptibilities of the metal and the agent in which it is dispersed is contributing to a difference between T_{2S} and T_{2E}, then one would expect the difference to be less in the rubidium-paraffin system than in the sodium-mineral oil system. The reason is that the difference in susceptibilities between rubidium and paraffin is less than the differences in relative susceptibilities between sodium and mineral oil.

The rubidium line widths are observed to be 20 to 30 times greater than the line widths of sodium. This suggests a different and stronger relaxation process than that observed in sodium. The hyperfine splitting in the free atom for Na^{23} is 189 Mc/s. The hyperfine splittings in the free atom for Rb^{85} and Rb^{87} are 362 Mc/s and

818 Mc/s respectively. Therefore one would expect a stronger electron-nuclear interaction in the case of rubidium since it has a larger hyperfine splitting than sodium. An inspection of the T_1 and T_2 data on rubidium, which Norberg and Holcomb[6] obtained by spin-echo technique, reveals that $T_1 \cong T_2$ for Rb^{87} above the melting point. No appreciable change in T_1 was observed upon passing through the melting point. They were unable to obtain any reliable T_2 data in the solid. On the basis of the information which is available, it appears that the spin-lattice relaxation mechanism is extremely strong in Rb^{87} and is the dominant mechanism in determining the line width of Rb^{87}.

Norberg and Holcomb[6] also measured T_1 and T_2 in Rb^{85}, and again they were hampered by a poor signal-to-noise ratio and other instrumental problems associated with measuring short relaxation times. They observe T_1 to increase with increasing temperature in the solid and to suddenly increase from 1.5 msec. to 2.6 msec. at the melting point. No measurements of T_2 in the solid were made; but they did measure T_2 in the liquid and found it to be slightly less than T_1 near the melting point. The line width data in Fig. 9 can be converted to the relaxation time T_2 (δB) and compared with Holcomb's T_1 and T_2 data. A Lorentzian line shape has been assumed for this conversion. The melting point is 39.5° C.

TABLE 3

COMPARISON OF LINE WIDTHS, T_1, AND T_2 OF Rb^{85}

Temp °C	T_1 (Holcomb) msec	T_2 (Holcomb) msec	T_2(B) msec
30	1.0	--	1.1
38.5	1.4	--	1.6
40	2.6	2.0	1.9

In light of the two different methods used to measure T_2 and the poor signal-to-noise ratio, the agreement between the two independent measurements of T_2 at 40° C. is remarkable. A comparison between T_1 and T_2 (δB) at 30° and 38.5° C. suggests that the line width in the solid is being determined by spin-lattice relaxation processes. One can see that T_2 is definitely less than T_1 in the liquid at 40° C., a fact which indicates a rather strong spin-spin relaxation mechanism in the liquid. However the domination of T_2 in the solid by spin-lattice relaxation processes and the discontinuity in T_1 at the melting point make it difficult to compare the behavior of rubidium with the anomalous behavior of sodium.

One more factor concerning the line width data of sodium is worthy of discussion. In Figs. 1 and 2 it can be seen that the line width exhibits a field dependence in the solid. At 11.0 Mc/s, the line width has a constant value of 0.042 gauss from 30° C. to the melting point. At

3.3 Mc/s, the line width is 0.031 gauss at 30° C. and gradually increases to 0.036 gauss at the melting point. Spin-lattice relaxation processes cannot be an important factor in determining the line width at 11.0 Mc/s in the solid because in this same temperature range T_1 was observed to decrease from 15 msec. at 30° C. to 9.0 msec. at the melting point. If spin-lattice relaxation processes were influencing the line width, this temperature dependence would be reflected in the line width data. Spin-lattice processes do account for the temperature dependence of the line width in the solid at 3.3 Mc/s. At 3.3 Mc/s, T_1 is observed to decrease from 14 msec. at 30° C. to 7.5 msec. at the melting point. A line width of 0.036 gauss at the melting point corresponds to a $T_2 = 7.7$ msec. Therefore the gradual increase of line width with temperature at 3.3 Mc/s is due to the increasing role which spin-lattice relaxation processes play in determining T_2 as the temperature increases. However at the lower temperatures where spin-lattice relaxation processes are not important in determining T_2 at either resonance frequency, the field dependence of the line width is clear and its cause needs an explanation.

In a previous part of this discussion it was stated that any electric quadrupole interaction which is present in sodium could not account for the anomalous broadening of the sodium upon melting. If the quadrupole interaction were strong enough to account for the anomalous broadening, its effect would be reflected in the behavior of T_1 upon melting. No anomalous behavior in T_1 at the melting point was observed. However the possibility that there is a weak quadrupole interaction in the solid that may account for the field dependence of the line width should be investigated. The first order energy correction to the nuclear Zeeman levels due to an electric quadrupole interaction in a single crystal is

$$E_m = \frac{eQV_{zz}}{4I(2I - 1)} \left[3m^2 - I(I + 1)\right] \left[\frac{3}{2}\cos^2\alpha - \frac{1}{2}\right] \qquad (27)$$

where an axially symmetric electric field has been assumed, Q is the electric quadrupole moment of the nucleus, V_{zz} is the Z-component of the gradient of the electric field at the site of the nucleus, α is the angle between B_o and V_{zz}, and m is the magnetic quantum number. For sodium $I = \frac{3}{2}$, therefore if there is an effective non-zero V_{zz}, the absorption spectrum of a single crystal of sodium will be split into three spectral lines with the following resonance frequencies when $\alpha = 0$

$$\nu_a = \gamma B_o + \frac{eQV_{zz}}{2h} \qquad (28)$$

$$\nu_b = \gamma B_o \qquad (29)$$

$$\nu_c = \gamma B_o - \frac{eQV_{zz}}{2h} \qquad (30)$$

In these experiments, a polycrystalline specimen of sodium was used. In this case the continuous distribution of directions causes the frequencies ν_a and ν_c to have a continuous distribution over a range from $\nu_b - \frac{eQV_{zz}}{4h}$ to $\nu_b + \frac{eQV_{zz}}{4h}$. Therefore in a polycrystalline sample the electric quadrupole interaction may cause a broadening of the resonance line instead of splitting the line as is possible with single crystals.

Sodium has a body-centered cubic crystalline structure; therefore each nucleus in a perfect sodium crystal is at a site of cubic symmetry and V_{zz} would be zero. However in reality vacancies and impurities may exist in the lattice of sodium. The vacancies and impurities may create electric field gradients at lattice sites adjacent to them. In this way a non-zero value of V_{zz} could be produced at certain sites in the sodium lattice; thus an electric quadrupole interaction could take place at these sites. The electric field gradients in solids vary with temperature. Also the number of vacancies is a function of temperature. Therefore the quadrupole interaction should be temperature dependent. The external magnetic field does not appear in the quadrupole energy term; therefore the quadrupole interaction will be independent of the magnitude of B_o. The conclusion is that the electric quadrupole interaction does not contribute to the line width of solid sodium since the line width is observed to be independent of the temperature and dependent on the external magnetic field.

The effects of skin depth will be considered. Chapman[22] *et al.* have made a theoretical analysis of the problem and verified their theory with experiment. They found that if the particle size is larger than the skin depth, the line shape may be distorted and the line position shifted due to a mixing of the absorptive and dispersive modes. This effect is a function of particle size, skin depth, and geometrical shape. The sphere is less sensitive to the effects of skin depth than the flat plate or cylinder, which were the other shapes considered. The conclusion of their study is that as long as the relevent particle dimension (in the present case, the radius of the sodium spheres) is small compared to the skin depth, no effect on line shape or position is observable. Sodium has a skin depth of 65 microns at 3.3 Mc/s and 35 microns at 11.0 Mc/s. The particles in the sodium dispersion are spherical in shape and have an average radius of 3.5 microns. Therefore it is concluded that skin depth is not important in the above considerations.

Another factor involving skin depth must be considered. Earlier, it has been proposed that in the

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[22] A. C. Chapman, P. Rhodes, and E. F. Seymour, Proc. Phys. Soc. B70, 345 (1957).

molten state there exists the possibility that sodium nuclei near the surface of the particle relax according to a term T_{2S} and those away from the surface, according to T_{2B}. If the existence of these two terms in the solid is admitted, it is possible that attenuation of the rf magnetic field due to skin depth effects makes T_{2S} more important at 11.0 Mc/s than at 3.3 Mc/s. If a spherical particle of radius r_o is considered, it is found that 80% of the nuclei reside in the outer shell between $r = r_o/2$ and $r = r_o$. If a plane wave is assumed, then to a first approximation B_1 is reduced by 3% at a penetration depth of $r_o/2$ at 11.0 Mc/s and by 1% at a penetration depth of $r_o/2$ at 3.3 Mc/s. Therefore it is very unlikely that skin effects could account for the difference in line width observed in the solid at 3.3 Mc/s and 11.0 Mc/s in the above way.

If sodium possesses an anisotropic Knight shift, then this could account for the dependence of line width on B_o. If this broadening mechanism is present, then the absorption line should be asymmetric.[15] Absorption lines at both 3.3 Mc/s and 11.0 Mc/s at 30° and at 105° C. were examined for asymmetric characteristics. The peak amplitude of the absorption curve was taken as the center of the line; then the areas under the curve on both sides of this center were compared. At 11.0 Mc/s a slight asymmetry of the order of 4% was noted in the absorption lines at both 30° and 105° C. At 3.3 Mc/s, where the signal-to-noise ratio is poorer, a larger asymmetry of the order of 10% was noted. If an anisotropic Knight shift is causing the asymmetry, the asymmetry should be greater the higher the external B_o. This is contrary to what was observed. Also at both frequencies, the area under that half of the curve toward the higher B_o was greater than the area under the curve toward the lower B_o. Just the reverse would be the case if an anisotropic Knight shift were causing the broadening. This essentially eliminates an anisotropic Knight shift as the mechanism causing the field-dependent broadening.

The nuclear spins may be interacting via the conduction electrons. The electron spin polarization is field dependent; the polarization increases with increasing applied field. However it is independent of temperature since the conduction electrons behave as a degenerate Fermi gas even at room temperature. The broadening which is observed is both field dependent and temperature independent, but the details of such a mechanism are not understood.

Bloembergen and Rowland[15,23] have studied a system in which they allege that the line width is determined

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[23] N. Bloembergen and T. J. Rowland, Phys. Rev. 97, 1679 (1955).

primarily by an exchange interaction and pseudo-dipolar interaction between the nuclear spins. They have measured the line widths of the absorption spectra of Tl^{203} and Tl^{205} in metallic thallium. Because sodium and thallium differ in atomic mass, number of naturally occurring isotopes possessing magnetic moments, and crystalline structure; one would not expect a direct correlation between their absorption spectra. However there are certain similarities; so Bloembergen's results are briefly reviewed here.

They found the line width of both isotopes to be independent of temperature from 77° to 400° K. This rules out spin-lattice relaxation as a broadening mechanism. The line width of Tl^{205} is 33 kc/s; whereas the line width due to pure dipole broadening would be 5 kc/s. The line width of Tl^{205} is independent of the resonance frequency from 5 Mc/s to 16 Mc/s. However the line width of Tl^{203} was observed to increase from 17 kc/s at 5 Mc/s to 33 kc/s 16 Mc/s. The preceding data are for a sample containing a natural abundance of isotopes. An investigation of enriched samples showed the line width to be a function of isotopic abundance.

Bloembergen interpreted the results in terms of an exchange interaction between a pair of nuclear spins which exceeds the normal dipole interaction in the cases where more than one isotope was present in an appreciable amount.

for the case where the abundance of one isotope was over 98%, the line width was still several times broader than would be expected if the direct dipole-dipole interaction were the sole broadening agent. In this case they appealed to an anisotropic Knight shift and the pseudo-dipolar interaction as the broadening mechanisms. The field dependence of the line width in Tl^{203} was not adequately explained. The exchange and pseudo-dipole interactions are not field dependent and there is no evidence of an anisotropic Knight shift in sodium. Therefore their results do not help to explain the field dependence of the line width in solid sodium.

Bloembergen and Rowland were surprised that they were unable to detect a resonance in metallic thallium above 150° C. The melting point of thallium is 302° C. They concluded that the line was quite broad in the liquid.

CHAPTER VI

SUMMARY

The absorption spectrum of Na^{23} in metallic sodium was observed as a function of temperature in the range 30° to 120° C. by means of a high resolution NMR spectrometer. The observed melting point was 99° C. The spectrum was investigated at two resonance frequencies: 3.3 Mc/s and 11.0 Mc/s. The relaxation times T_1 and T_2 of Na^{23} were measured by the spin-echo technique under the same conditions.

At both resonance frequencies the absorption spectrum of Na^{23} consisted of a single resonance line with no observable fine structure. The width of the line was observed to increase upon melting. The line width of liquid sodium was observed to be independent of the resonance frequency for the two frequencies investigated; the line width of solid sodium was found to be broader at the higher resonance frequency. A decrease in T_2 upon melting was observed; however no discontinuity in T_1 at the melting point was observed. The frequency dependence of T_2 in solid sodium was hardly observable. In this case computing T_2 from line width data obtained from a high resolution spectrometer proved to be more precise than measuring T_2 directly by pulse techniques.

Several explanations of the anomalous broadening of the sodium resonance line upon melting were explored; however no completely satisfactory explanation was found. The known mechanisms which may account for the frequency dependence of the line width in solid sodium were considered. No explanation was found. The frequency dependence may be due to an indirect interaction of the nuclei via the conduction electrons; however the details of how this may take place are not understood.

The coexistence of the solid and liquid resonance lines of sodium at the melting point was observed at both 3.3 Mc/s and 11.0 Mc/s. At 3.3 Mc/s the separation between the centers of the liquid and solid lines is 0.083 gauss in an external field of 2925 gauss. The separation of the two lines at 11.0 Mc/s is observed to be 0.250 gauss in an external field of 9752 gauss. At both frequencies the liquid line appeared at the lower external magnetic field.

The absorption spectra of two isotopes of rubidium, Rb^{85} and Rb^{87}, in metallic rubidium were investigated over the temperature range 30° to 44° C. Rubidium was observed to melt at 39.5° C. No change in line width upon melting was observed in the case of Rb^{87}; however the signal-to-noise ratio was poor, so a small change could have been obscured. The Rb^{85} line was observed to become narrower upon melting. However the line width is determined mainly by spin-lattice relaxation processes for both isotopes. Therefore any anomalous behavior in the resonance line is largely obscured by the overwhelming influence of T_1 processes. Thus no conclusions relevant to the anomalous behavior of sodium can be made from the rubidium line width data.

The liquid and solid resonance lines of Rb^{85} were observed while they coexisted at the melting point. The centers of the lines were observed to be separated by 0.9 gauss in an external field of 7975 gauss. The liquid line appeared at the lower field for the constant frequency 3.3 Mc/s.

Several experiments are suggested which may provide additional information about the behavior of the line width in solid and liquid sodium. Post's work should be extended to at least another resonance frequency in an attempt to determine if T_{2S} and T_{2B} are caused by a difference in the magnetic susceptibilities of water and silicon dioxide. A determination of the coefficient of self-diffusion of sodium in the liquid state would be desirable to aid in explaining the anomalous broadening of the width of sodium when it melts. Experiments with sodium should be conducted at several other resonance frequencies to study further the frequency dependence of the line width in solid sodium.

Absorption spectra, T_1 and T_2 in other metals should be investigated systematically in order to try to find an explanation for the behavior of the line width in sodium. A measurement of the line width of Li^7 in metallic lithium would be a good material to begin with. Holcomb and Norberg[6] have already measured T_1 and T_2 in Li^7.

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AUTOBIOGRAPHY

I, Frank Judson Leech, was born in Lexington, Virginia, 24 December 1932. I received my secondary-school education in the public schools of Lexington, Virginia and my undergraduate training at Virginia Military Institute, which granted me the Bachelor of Science degree in physics in 1955. From June 1955 until July 1956, I worked in the research laboratories of the International Business Machines Company in Poughkeepsie, New York. In July 1956, I went on active duty with the Regular Air Force and spent the next three years in the Aeromedical Laboratory at Wright-Patterson Air Force Base, Ohio. I received the Master of Science degree from Ohio State University in 1961. While in residence at Ohio State University, I have worked for Professor L. Carlton Brown.

For my next duty assignment, I shall serve as an Instructor in the Department of Physics at the United States Air Force Academy in Colorado.