

UNCLASSIFIED

AD 297 057

*Reproduced
by the*

**ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA**



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

297 057

CATALOGED BY ASTIA
AS AD NO. 297057

RESEARCH ON CdTe

M. R. Lorenz, B. Segall and R. E. Halsted
General Electric Research Laboratory
Schenectady, New York

Seventh Quarterly Progress Report

November 1, 1962 - January 31, 1963

Contract No. AF 33(616)-8264

Aeronautical Research Laboratory
Office of Aerospace Research
United States Air Force
Wright-Patterson Air Force Base, Ohio

FEB 27 1963
JISIA B

RESEARCH ON CdTe

M. R. Lorenz, B. Segall and R. E. Halsted
General Electric Research Laboratory
Schenectady, New York

I. GENERAL INTRODUCTION

In the last quarterly progress report we indicated the initiation of an investigation on the identity and properties of native defects in CdTe. During the present reporting period we have continued this study.

Electrical transport measurements were conducted with the cooperation of Dr. H. H. Woodbury. In the course of studying the electrical properties of high-purity single crystals of CdTe, a new center, thought to be a native double acceptor, has been observed. It is believed to be the first of its kind in compound semiconductors identified by electrical transport measurements. This center is formed during heat treatment in a Cd atmosphere. The doubly ionized acceptor level lies 0.056 eV below the conduction band and when this level is filled the center contains two electrons and is an effective hole trap at low temperatures. In fact, the singly negatively-charged center has such a low cross section for electron capture that it is impossible to observe a normal freeze out of electrons into the second level when the samples are cooled below a critical temperature region. Details of this work are presented in the form of a publication draft to Physical Review Letters in Section II.

Another approach toward the identification of point defects is the technique of electron paramagnetic resonance. In cooperation with Dr. G. W. Ludwig we have studied n-type CdTe by this

method. Two resonance lines have been observed so far. A line with a g value of 1.68 is believed to be due to shallow donor impurities. The exact defects responsible for it are not yet known. Further work is planned to learn their identity. The other resonance line was observed with a g value of 2 and the line has been associated with the Cr^+ ion in a cadmium site. Details of this study are given in Section III.

We have also continued to examine fluorescent emission spectra in the zone-refined CdTe and in CdTe subjected to various heat treatments. Some data has been taken with samples immersed in He. Of current interest is the possibility of correlating the 1.54 eV emission in CdTe (believed analogous with the "green edge emission" of CdS) with transitions between the -2 charged double acceptor level described in this report and the valence band. The energy differences and several other aspects of the correlation appear favorable. Unresolved problems exist in accounting for details such as the origin and temperature dependence of the doublet structure, and correlation with analogous spectra of other II-VI compounds. Further experiments are currently in progress.

II. A DOUBLE ACCEPTOR DEFECT IN CdTe*

M. R. Lorenz and H. H. Woodbury
General Electric Research Laboratory
Schenectady, New York

In the course of studying the electrical properties of high-purity single crystals of CdTe, a new center, thought to be a native double acceptor, has been observed. It is believed to be the first of its kind in compound semiconductors identified by electrical transport measurements. This center is formed during heat treatment in a Cd atmosphere. The doubly ionized acceptor level lies 0.056 eV below the conduction band and when this level is filled the center contains two electrons and is an effective hole trap at low temperatures. In fact, the singly negatively-charged center has such a low cross section for electron capture that it is impossible to observe a normal freeze out of electrons into the second level when the samples are cooled below a critical temperature region. A similar level about 0.09 eV below the conduction band has also been found in CdS.

CdTe samples were prepared by techniques already described.¹ High-purity crystals having a residual impurity donor concentration of about 10^{15} cm^{-3} were used.² Hall bars of approximately $3 \times 3 \times 10 \text{ mm}^3$ were sealed in small evacuated quartz ampoules to which Cd metal was added. These were heated to various temperatures for varying lengths of time and then quenched. The surface regions of the samples were removed by grinding, etching, and a

*The research reported in this paper was supported in part by the Aeronautical Research Laboratory, Office of Aerospace Research, United States Air Force, and in part by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under contract AF19(628)-329.

final chemical polish. The crystals were then studied using conventional d.c. techniques to measure the Hall coefficient, resistivity, and Hall mobility from 350°K to 12°K. There were provisions for exciting the samples with a small incandescent lamp mounted inside the cryostat.

The temperature dependence of the Hall constant for electrons in several samples is shown in Fig. 1. Curve A represents an unfired sample; curve B, a sample fired at 900°C for 30 min.; and curve C, a sample fired at 900°C for 285 hrs. The solid curves correspond to measurements without light and the dotted curves show the effects following photoexcitation at the lowest temperature. Freeze out of electrons into the level of interest starts near 300°K and is most pronounced in curve B. The thermal activation energy is 0.056 ev. At about 110°K the electronic equilibrium starts to lag the thermal equilibrium. The lag increases as the temperature is lowered and at 85°K it is necessary to wait several hours to establish electronic equilibrium. At lower temperatures it becomes impossible to reach equilibrium with regard to the 0.056 ev level. This sluggishness was observed for the heating as well as the cooling of samples in this temperature region.

The peculiarity of the above behavior suggests that a barrier is associated with the 0.056 ev level. The decay of conduction electrons following photoexcitation was measured at four temperatures in the critical temperature region, i.e., 95 to 115°K. The simple relation $\Delta n = c \exp(-t/\tau)$ was observed over three decades at each temperature and over the limited temperature region the lifetime can be expressed as $\tau = \tau_0 \exp(0.27 \text{ ev}/kT)$, where $\tau_0 = 3.2 \times 10^{-12}$ sec.

In Fig. 2 the Hall mobilities are shown corresponding to the Hall constants of Fig. 1. Curve A again is the unfired sample which also exhibits the intrinsic mobility over the range shown.² Photoexcitation did not change the mobility for this sample. There is, however, a pronounced effect on the mobility of the fired samples, as seen from the dashed curves. After photoexcitation at the lowest temperature, the mobility shows a marked increase. The original mobility curve is rejoined at about 100°K , the temperature at which the excess electrons, thrown out of equilibrium at the lowest temperature, are able to freeze into the 0.056 eV level.

We conclude that the 0.056 eV level, although close to the conduction band, is the doubly ionized state of a two-level acceptor defect. The singly ionized state has a charge of (-1) and is responsible for the barrier observed. Photoexcitation at the lowest temperature produces hole-electron pairs. The holes are captured (trapped) by the filled double acceptor centers resulting in a change of the charge state of the centers from (-2) to (-1). The excess electrons are unable to reach electronic equilibrium with the centers because of insufficient kinetic energy to surmount the barrier about the singly occupied defect. When the temperature is raised to the critical region, the Hall constant increases and the mobility decreases to their original values as electronic equilibrium is re-established.

The explanation of the behavior observed in these crystals is based on a double acceptor model analogous to that established for many impurities in Ge.³ Qualitatively, the observed effects on mobility and Hall coefficient with and without light show a one-to-one correspondence between the effects reported here and those reported, for example, for Mn-doped Ge.⁴ A quantitative

difference appears to be that in the present case, the ratio of the barrier to the second (thermal) ionization energy is much greater than the ratio seen for double acceptors in Ge. This prevents thermal equilibrium from being established as the CdTe samples are cooled but causes no difficulty for the double acceptor centers seen in Ge.

It is to be emphasized that the double acceptor centers described here are not necessarily the dominant defects in the CdTe system. Under the present preparative conditions their formation is accompanied with a concurrent formation of donor centers. The results indicate that for short firing times the samples are slightly more n-type than they were originally but are also more compensated. Hence, the 0.056 ev level appears to be dominant. After long periods of firing the concentration of both acceptor and donor defects increase, but the latter more than the former. There is an additional peculiarity in this system. Short firing times of about one-half hour produce, after surface region removal, a homogeneously-changed sample. Long firing times of several hundred hours also yield homogeneous samples. However, treatment times of intermediate periods result in inhomogeneous crystals. This suggests that at least two processes occur during heat treatment. The fast one is essentially complete after a short time and then is succeeded by a much slower process.

The following evidence strongly suggests that the double acceptor center described here is a native defect. It is observed only when samples were quenched and is seen in excess of the number of donors and acceptors normally found in slow cooled or annealed samples. Spectroscopic analysis on CdTe has revealed that likely common metal impurities are below the defect

concentrations observed. After heat treatment in excess Cd, a similar double acceptor defect with the doubly ionized level 0.09 ev below the conduction band has also been seen in CdS. Its electrical properties are identical to the center described here in CdTe. Furthermore, CdTe samples showing the behavior illustrated in curve B of Fig. 1 go to high resistance within several days on standing at room temperature. This decay is suggestive of recombination of Frenkel defects or precipitation of Schottky centers. The present results, however, do not permit an unambiguous identification of the native double acceptor center. Although we believe that the center is a simple native defect, we cannot rule out the possibility that the actual defects involved may be complexes of interstitials and/or vacancies or even chemical impurities that are not normally electrically active. However, such complexes must maintain the properties of a double acceptor.

The authors thank their associates for helpful discussions on the observations reported here. They are particularly grateful to Dr. B. Segall and Miss E. L. Kreiger for analysis of the data. B. B. Binkowski and L. H. Esmann assisted in the experimental work.

REFERENCES

1. M. R. Lorenz and R. E. Halsted, J. Electrochem. Soc., April 1963 (to be published).
2. B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev., March 15, 1963 (to be published).
3. See, for example, W. W. Tyler and H. H. Woodbury, Phys. Rev. 102, 647 (1956).
4. Compare Figs. 11 and 10 of Ref. 3 with Figs. 1 and 2, respectively, of this letter.

FIGURE CAPTIONS

Fig. 1. The temperature dependence of the Hall coefficient, R_H , of n-type CdTe samples. The dashed curves show R_H after photoexcitation at the lowest temperature.

A - original high-purity material.

B - Cd fired for one-half hour at 900°C .

C - Cd fired for 285 hours at 900°C .

Fig. 2. The electron Hall mobility, μ_H , of the samples shown in Fig. 1.

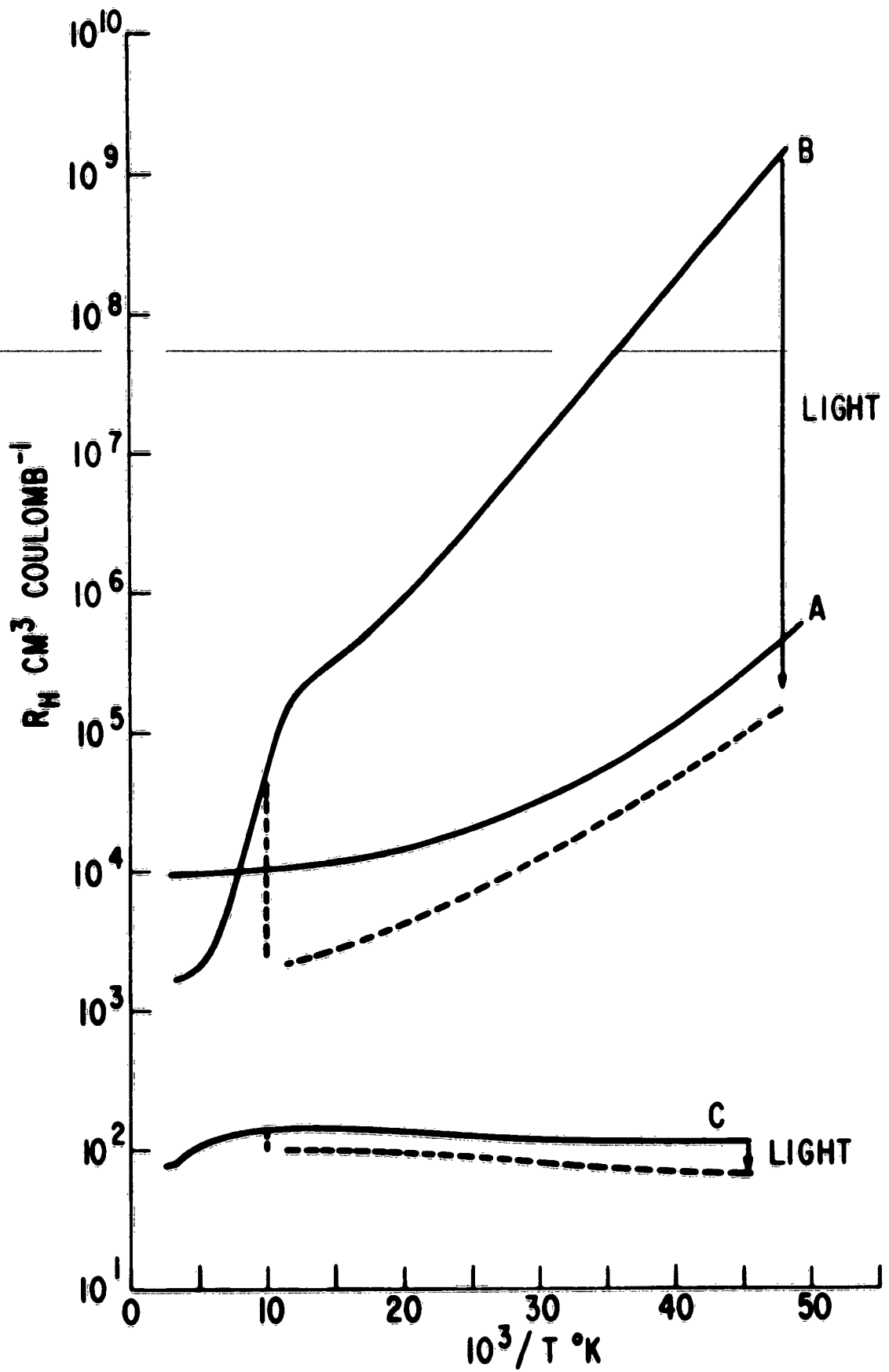


Fig. 1

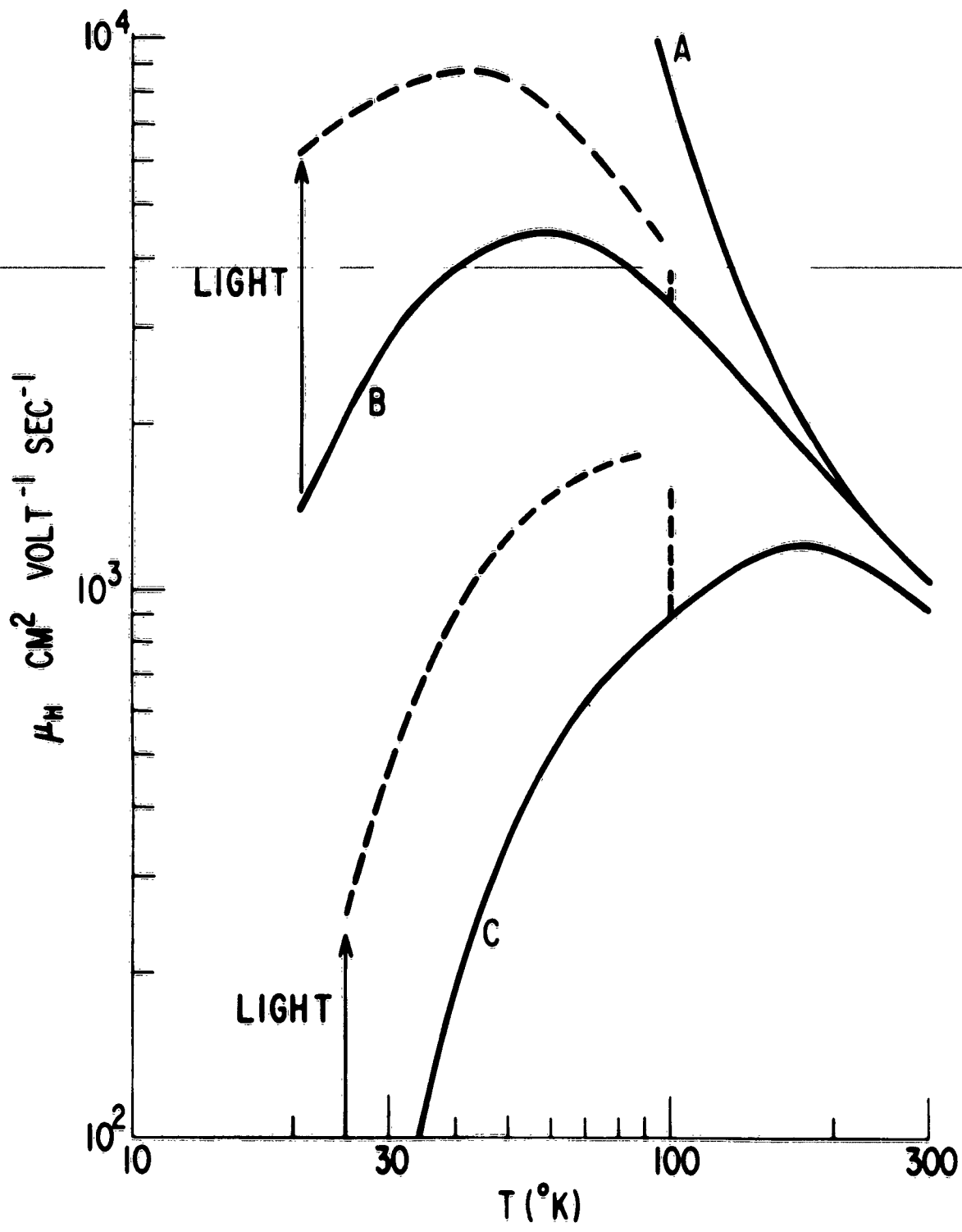


Fig. 2

III. PARAMAGNETIC RESONANCE IN CdTe - G. W. Ludwig and M. R. Lorenz

The technique of electron paramagnetic resonance has been utilized relatively little for the study of defect centers in II-VI compounds. In CdTe the only centers for which such data appears in the literature¹ are the transition metal impurity ions Mn^{2+} and Co^{2+} . We have initiated a program of study of paramagnetic resonance in CdTe, hoping to correlate such measurements with data from other techniques, notably Hall coefficient and resistivity studies. Thus far, we have tentatively associated a resonance line at $g = 1.68$ with shallow donor impurities (not yet further identified). We have also studied the spectrum of the impurity ion Cr^{+} , which will now be discussed in somewhat greater detail.

When CdTe crystals are chemically polished with a dichromate-sulfuric acid solution, they retain an adsorbed layer of presumably dichromate ions. The most thorough rinsing with triple distilled water fails to remove this layer completely. When samples "cleaned" this way are heat treated in a Cd atmosphere, they become Cr doped and give rise to paramagnetic resonance absorption in the vicinity of $g = 2$. If the magnetic field H is restrained to be in the (110) plane, the spectrum is simplest for H in a zero cubic field splitting direction (see Fig. 1a). There it consists of a pattern of lines having an envelope of intensities. The pattern is consistent with assigning the structure to hyperfine interaction with the magnetic isotopes Cd^{111} and Cd^{113} occupying twelve essentially equivalent sites, the mean hyperfine interaction being $\sim 5 \times 10^{-4} \text{ cm}^{-1}$.

As the magnetic field is rotated toward the [001] direction, each of the hyperfine lines splits, it being clear that there are

at least three fine structure components ($S \geq 3/2$). Actually, one would guess that five fine structure components are present in all ($S = 5/2$), since the fine structure splitting vanishes in a purely tetrahedral crystalline field for $S \leq 3/2$. Cr^+ is an impurity which would be expected to have a half-filled 3d shell and $S = 5/2$. Therefore, a crystal containing chromium enriched in the isotope Cr^{53} was prepared. Indeed a spectrum (see Fig. 1b) similar to that of Fig. 1a except for the presence of Cr^{53} hyperfine structure, was detected. This sample was then examined by the electron-nuclear double resonance technique of Feher.² The spin-Hamiltonian which we deduce for Cr^+ in CdTe is

$$\mathcal{H} = g\beta S \cdot H + \frac{a}{6} [S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1)]$$

$$+ AS \cdot I - \gamma\beta_n H \cdot I$$

$$+ \sum_k (S \cdot T_k \cdot I_k - \gamma\beta_n H \cdot I_k)$$

with the parameters shown below:

$$S = 5/2$$

$$g = 1.9997 \pm 0.0002$$

$$|a| = (3.1 \pm 0.6) \times 10^{-4} \text{ cm}^{-1}$$

$$A = (12.781 \pm 0.005) \times 10^{-4} \text{ cm}^{-1}$$

$$\gamma = 0.3161 \pm 0.0008$$

$$T_1 = (5.82 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$$

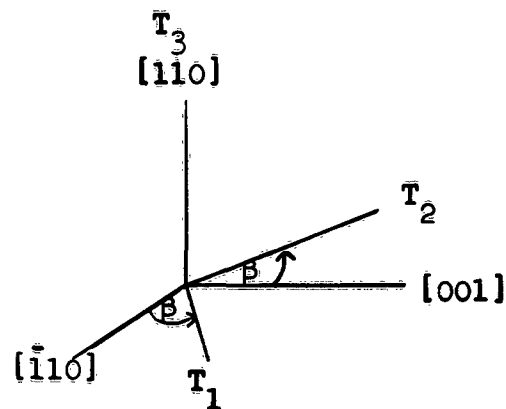
$$T_2 = (5.63 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$$

$$T_3 = (5.61 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$$

$$\beta = 37 \pm 5^\circ$$

} for Cr^{53}

} for Cd^{113}



The paramagnetic resonance transitions for such a spin-Hamiltonian have been discussed previously and lead to the quoted value of $|a|$.

The ENDOR transitions of Cr^{53} are given by

$$hf = |AM - [S(S + 1) + (2m - 1)M - M^2] (A^2/2h\nu) - \gamma\beta_n H|$$

Such transitions were detected for $M = \pm 1/2, \pm 3/2$ and $-5/2$; from their analysis one obtains the quoted value of A , a value for γ in good agreement with published values for Cr^{53} , and confirmation of the spin $S = 5/2$. ENDOR transitions of Cd^{111} and Cd^{113} were detected with good signal-to-noise only for H in a $[110]$ direction. From their analysis one obtains the parameters given above describing the hyperfine interaction with Cd^{113} .

We conclude that we have identified paramagnetic resonance of Cr^+ in CdTe . The hyperfine interaction with twelve equivalent Cd neighbors leads us to believe that the Cr^+ substitutes for Cd , leading to twelve nearest Cd neighbors; substitution for Te would lead to four nearest Cd neighbors. The resonance parameters are similar to those reported recently by R. S. Title³ for Cr^+ in ZnS .

REFERENCES

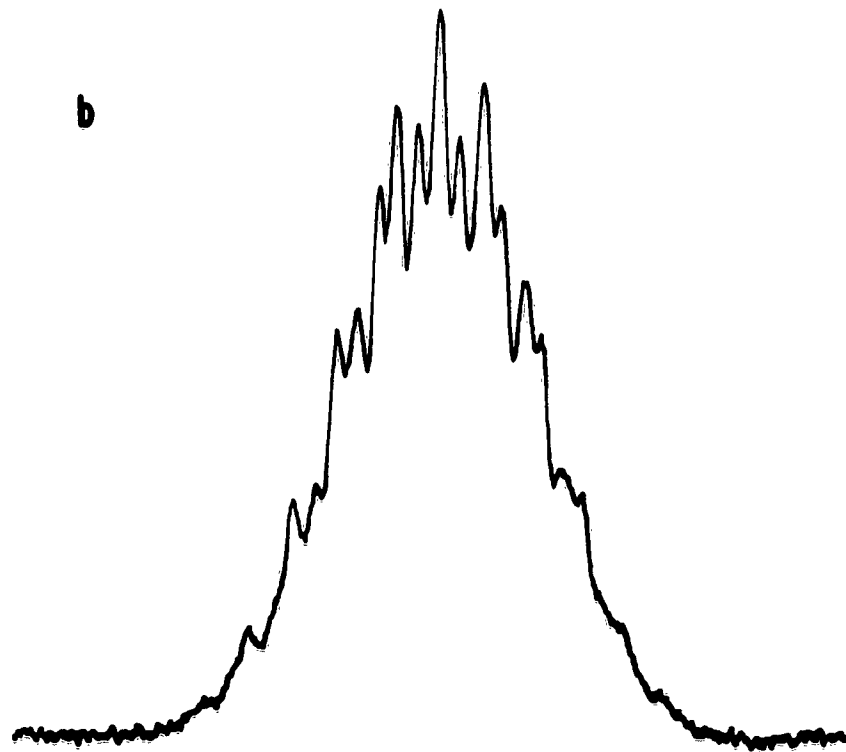
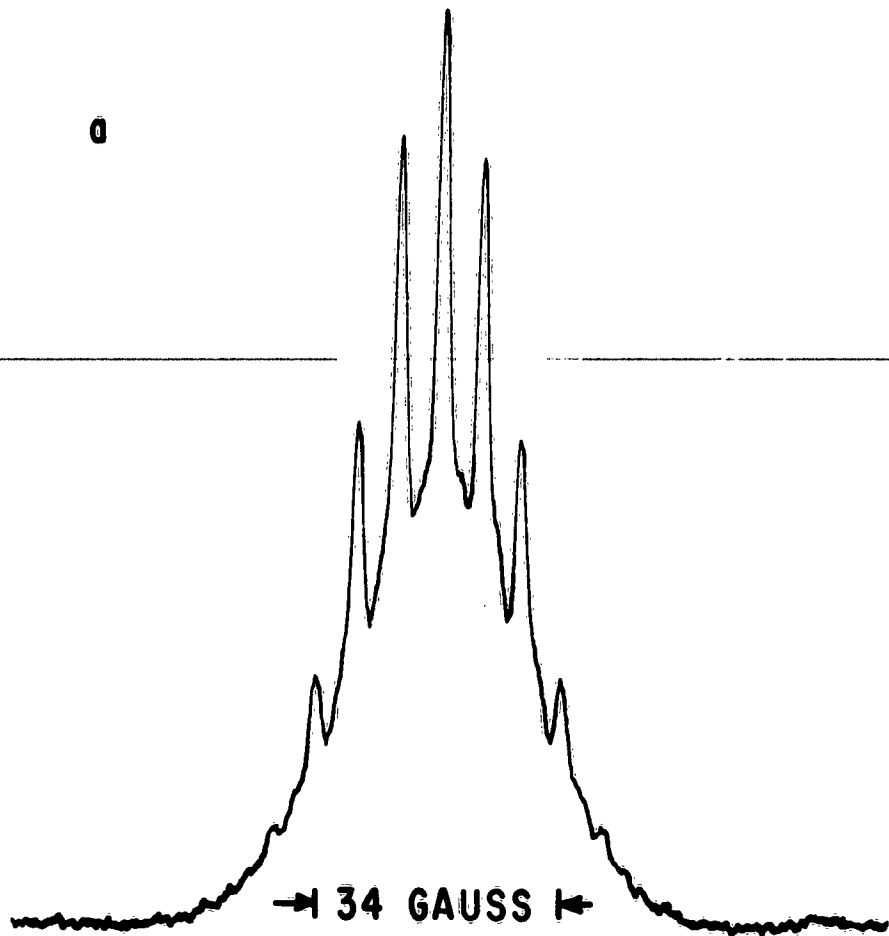
1. G. W. Ludwig and H. H. Woodbury, *Solid State Physics* 13, 223 (1962).
 2. G. Feher, *Phys. Rev.* 114, 1219 (1959).
 3. R. S. Title, *Bull. Am. Phys. Soc. Ser. II* 8, 23 (1963).
-

FIGURE CAPTION

Fig. 1. Spectrum of $\text{Cr}(3d^5)$ in CdTe at 4.2°K with the spectrometer tuned to dispersion under rapid passage conditions.

- a) H in the zero cubic field splitting direction ($p = 0$).
- b) H in a $[001]$ direction.

SPECTRUM OF Cr^{+} IN CdTe



This report is being circulated to the listed addresses in accord with the provisions of Air Force Contract 33(616)-8264.

ARA (Mrs. Koch)
c/o D. C. Reynolds
Research Physicist
Solid State Physics Research Branch
Aeronautical Research Laboratory
Wright-Patterson Air Force Base, Ohio

Air University Library
Maxwell Air Force Base, Ala.

ASTIA (TIP)
Arlington Hall Station
Arlington 12, Virginia

ARA (Library)
c/o D. C. Reynolds
Research Physicist
Solid State Physics Research Branch
Aeronautical Research Laboratory
Wright-Patterson Air Force Base, Ohio

Technical Research Center
ATTN: L. C. Stork
P. O. Box 509
Beacon, N. Y.

EWAPL (Library, Area B)
c/o D. C. Reynolds
Research Physicist
Solid State Physics Research Branch
Aeronautical Research Laboratory
Wright-Patterson Air Force Base, Ohio

Raytheon Company
Research Division Library
28 Seyon Street
Waltham 54, Mass.

Federal Aviation Agency
Bureau of R and D
ATTN: Records Officer
Washington 25, D. C.

Air Force Cambridge Research Labs.
ATTN: Research Library, CRXL-R
L. G. Hanscom Field
Bedford, Mass.

Air Force Office of Scientific Research (SRT)
ATTN: Dr. Knox Millsaps
Washington 25, D. C.

Air Force Office of Scientific Research (SRGL)
Washington 25, D. C.

AFSC LO
ATC
Randolph Air Force Base, Texas