and there is no assurance of complete ferromagnetic to antiferromagnetic order. Of course, the surface energy K_s must be sufficiently large and $4\pi\Delta M$ must be larger than the line width (so that the surface spins would be nonresonant) for effective pinning to occur. Although this phenomenon could be equally accounted for by inhomogeneous demagnetizing field due to the film's nonellipsoidal shape, our detailed calculations show that the inhomogeneity is only of order $(d/D)4\pi M$, where d/D is the thickness to diameter ratio of the film, entirely too small compared to the line width to account for pinning.

A further word on the experimental determination of the exchange constant A and the surface anisotropy energy density K_s is in order. Using the measured critical angle ϕ_{Hu} at which the spin system becomes unpinned, $2Ak^2/2K_s'$, the ratio of the exchange to surface energy, could be determined from Fig. 3. Then, using this ratio and curves similar to Fig. 4 plotted with A as a constant parameter, K_s and A may be determined simultaneously. Thus, we see that if the surface spins are not completely pinned, the exchange constant cannot be determined independent of the surface energy, as is usually done.

Paramagnetic Resonance of Chromium in CdTe†

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Paramagnetic resonance has been studied for Cr in the $3d^5$ configuration substituting for Cd in CdTe. We find $S=5/2$, $g=1.9997\pm0.0003$, $|a|=(3.1\pm0.6)\times10^{-4}$ cm^{-1}, and $A=(+12.781\pm0.005)\times10^{-4}$ cm^{-1} for Cr^{53}. Using electron-nuclear double resonance the complete tensor describing the anisotropic hyperfine coupling with the nearest Cd neighbors has also been determined. Electrical measurements indicate that the Cr acceptor level lies within 0.6 eV of the conduction band edge.

I. INTRODUCTION

THE technique of electron paramagnetic resonance has been used with moderate success for the study of defect centers, principally transition metal ions of the $3d$ group, in CdTe and related II–VI compounds. Data on manganese ions having a half-filled $3d$ shell are available for all of these compounds, while cobalt in the $3d^7$ configuration has been studied in most of them. Paramagnetic resonance associated with chromium has been reported only in ZnS and CdS.[1,2]

The purpose of the present paper is to report on the paramagnetic properties of chromium in the $3d^5$ configuration in CdTe, a cubic crystal having the zinc-blende structure. If chromium were simply to substitute for cadmium in the lattice with no charge unbalance, its configuration would be expected to be $3d^4$. The fact that one detects Cr$(3d^5)$ implies that chromium can act as an acceptor as it does in ZnS.[1,3] The resonance study of

Cr$(3d^5)$ in CdTe has been unusually successful. It has been possible to determine not only the g factor and the cubic field splitting parameter, but also, using electron-nuclear double resonance (ENDOR) techniques, the hyperfine interaction with Cr^{53}, and the complete tensor describing the hyperfine coupling with the magnetic isotopes Cd^{111} and Cd^{113} occupying second-neighbor positions.

Sample preparation and properties and the resonance spectrum are described in II; III is devoted to a description of the ENDOR experiments; the results are presented and discussed in IV.

II. EXPERIMENTAL TECHNIQUES AND THE RESONANCE SPECTRUM

High-purity CdTe single crystals were prepared by techniques already described.[4] Samples were cut into oriented bars approximately $3\times3\times10$ mm^3 with a [110] axis parallel to the long dimension. The bars were etched in HF·HNO$_3$·2H$_2$O solution and chemically polished in a solution of 70 parts of saturated K$_2$Cr$_2$O$_7$

[1] R. S. Title, Bull. Am. Phys. Soc. **8**, 23 (1963).

[2] For a more complete discussion of paramagnetic resonance of defects in II–VI compounds, including references, see G. W. Ludwig and H. H. Woodbury, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 223.

[3] The configuration of the free chromium atom is $3d^54s$. On an ionic model one writes CdTe as Cd^{2+}Te^{2-}; thus, at a chromium impurity site, assuming no charge unbalance, one would have Cr$^{2+}(3d^4)$. On a covalent model one writes CdTe as Cd^{2-}Te^{2+}, but

the outer Cd electrons are used in the covalent bonding. On such a model one would have Cr$^{2-}(3d^44s4p^3)$ at a chromium site were there no charge unbalance. The $4s4p^3$ electrons participate in covalent bonding leaving the Cr core in the $3d^4$ configuration. Thus with either model Cr$(3d^4)$ is the configuration for no charge unbalance at the Cr site, while Cr$(3d^5)$ implies that the chromium impurity has accepted one electron.

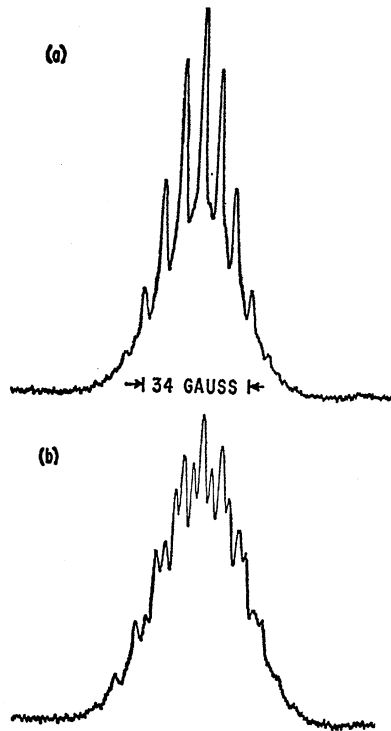[4] M. R. Lorenz and R. E. Halsted, J. Electrochem. Soc., **101**, 343 (1963).

FIG. 1. Spectrum of 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.

→| 34 GAUSS |←

and 30 parts of concentrated H_2SO_4.[5] The latter solution apparently gives rise to an adsorbed layer of chromium ions which is not completely removed even by a thorough rinse in distilled water. The treated bars were sealed in evacuated quartz ampoules to which Cd metal had been added. These were held for 24 h or longer at 950°C, were quenched, and the surface regions were removed. The Hall coefficient and resistivity were measured from 12 to 350°K using conventional techniques.

A number of samples were n type and exhibited electron freezeout into a level 0.056 eV below the conduction band[6] and also into the hydrogenic donor level.[7] When such samples were examined in a paramagnetic resonance spectrometer which has been described previously,[8,9] resonant absorption was detected in the vicinity of $g=2$. The spectrum was not observed if the Fermi level locked onto a level 0.6 eV below the conduction band edge. Thus, the resonant center must have an electrical level located within 0.6 eV of this band edge.

With the magnetic field H restrained to be in the

(110) plane, the resonance spectrum, shown in Fig. 1, is simplest for H in a zero cubic field splitting direction. [This is the direction in which p vanishes, where

$$p=1-5(l^2m^2+m^2n^2+n^2l^2), \qquad (1)$$

l, m, and n being the direction cosines of the magnetic field with respect to the cubic crystalline axes.] For $p=0$ the spectrum consists of seven strong resolved lines having an envelope of intensities. A similar pattern has been described previously for resonant centers in[10] CdS and[11] CdTe, and has been attributed to an essentially isotropic hyperfine coupling of the unpaired electrons with the magnetic isotopes Cd^{111} and Cd^{113} occupying twelve equivalent sites, viz., the twelve nearest Cd sites to an impurity ion occupying a substitutional Cd site.

As the magnetic field is rotated in the (110) plane towards $p=1$ (the [001] direction), each of the Cd hyperfine lines splits into three resolved fine structure components. However, if there were only three fine structure components ($S=\frac{3}{2}$) one would expect no cubic field splitting. One is, thus, led to suspect that $S=\frac{5}{2}$: there are five fine structure components but the splitting between the outer fine structure components is not resolved. Taking for the spin Hamiltonian

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

and assuming $S=\frac{5}{2}$ and $|a|\ll g\beta\mathbf{S}\cdot\mathbf{H}$, the $\Delta M=\pm1$ transitions are given by

$$M=+\tfrac{1}{2} \text{ to } -\tfrac{1}{2}: \quad h\nu=g\beta H,$$
$$M=\pm\tfrac{3}{2} \text{ to } \pm\tfrac{1}{2}: \quad h\nu=g\beta H\mp\tfrac{5}{2}pa, \qquad (3)$$
$$M=\pm\tfrac{5}{2} \text{ to } \pm\tfrac{3}{2}: \quad h\nu=g\beta H\pm2pa,$$

where p is defined by (1).

From the spectrum for $p=0$ one finds $g=1.9997\pm0.0003$. Similarly, from analysis of the angular dependence of the fine structure components we obtain $|a|=(3.1\pm0.6)\times10^{-4}$ cm^{-1}. In arriving at this value it was assumed that the experimentally measured peak positions of the outer fine structure components represent the $\pm\frac{3}{2}$ to $\pm\frac{1}{2}$ transitions, which are stronger than the $\pm\frac{5}{2}$ to $\pm\frac{3}{2}$ transitions and which generally also are narrower. The large uncertainty takes into account the possible inaccuracy of this assumption.

Impurity ions in CdTe which might have electron spin $\frac{5}{2}$ are Cr, Mn, and Fe. To check whether the above spectrum is associated with Cr($3d^5$) a sample was prepared containing chromium enriched in the isotope Cr^{53}, which has a nuclear spin of $\frac{3}{2}$. Indeed, a spectrum was detected in this sample which was similar to that of Fig. 1 except that there were 13 strong lines for $p=0$ instead of 7. Thirteen strong lines are to be expected if the hyperfine interaction with the Cr^{53} nucleus is

[5] T. Ichimiya, T. Niimi, K. Mizuma, O. Mikami, Y. Kamiya, and K. Ono, in Solid State Physics in Electronics and Tele-communications (Proceedings of the International Conference held at Brussels, 1960) (Academic Press Inc., New York, 1960), Vol. 2, p. 845.
[6] M. R. Lorenz and H. H. Woodbury, Phys. Rev. Letters 10, 215 (1963).
[7] B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev. 129, 2217 (1963).
[8] G. W. Ludwig and H. H. Woodbury, Phys. Rev. 113, 1014 (1959).
[9] H. H. Woodbury and G. W. Ludwig, Phys. Rev. 117, 102 (1960).

[10] P. B. Dorain, Phys. Rev. 112, 1058 (1958).
[11] J. Lambe and C. Kikuchi, Phys. Rev. 119, 1256 (1960).

FIG. 2. ENDOR transitions of the Cr^{53} impurity nucleus in CdTe for $M=-\frac{5}{2}$. The three lines correspond to the three possible m to m-1 transitions for $I=\frac{3}{2}$, as described by (5).

ESR SIGNAL

94.0   94.5   95.0

ENDOR FREQUENCY
(Mc/sec)
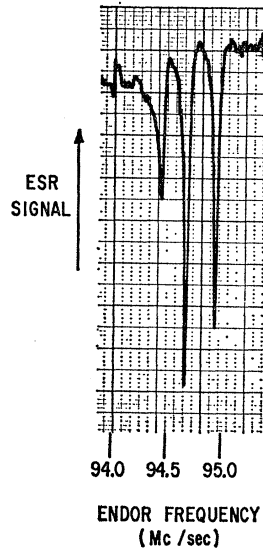
roughly twice as large as that with the neighboring Cd^{111} and Cd^{113} nuclei.

III. ENDOR MEASUREMENTS

In order to gain additional information about the hyperfine interaction with Cr^{53} and with the magnetic Cd isotopes the sample was examined using the electron-nuclear double resonance (ENDOR) technique developed by Feher.[12] In this technique, one detects transitions in which a nuclear spin reorients, the electron spin retaining its orientation ($\Delta M=0$, $\Delta m=\pm1$), via the associated change in intensity of an electron paramagnetic resonance line. Experimentally, one adjusts the magnetic field to resonance on an electron paramagnetic resonance line and simultaneously exposes the sample to an rf magnetic field which induces the nuclear transitions. In analyzing the ENDOR transitions, we assume that the nuclear sublevels are described by the Hamiltonian

$$3C_N = A\mathbf{S}\cdot\mathbf{I} - \gamma\beta_N\mathbf{H}\cdot\mathbf{I} + \sum_k(\mathbf{S}\cdot\mathbf{T}_k\cdot\mathbf{I}_k - \gamma_k\beta_N\mathbf{H}\cdot\mathbf{I}_k). \quad (4)$$

Here the first two terms describe the isotropic hyperfine interaction with Cr^{53} while the kth of the remaining terms gives the anisotropic interaction with Cd^{111} or Cd^{113} occupying the kth of the nearest Cd neighbor positions to the impurity site.

A. Cr^{53}

Supplementing (2) with (4) and assuming the hyperfine interaction terms to be small, one finds that the frequency f of a Cr^{53} ENDOR transition is approximately

$$hf = |AM - [S(S+1) + (2m-1)M - M^2]$$
$$\times (A^2/h\nu) - \gamma\beta_N H|. \quad (5)$$

[12] G. Feher, Phys. Rev. 114, 1219 (1959).

Since $S=\frac{5}{2}$, M can take on the values $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, $\pm\frac{5}{2}$, while for $I=\frac{3}{2}$ there are three m to $m-1$ transitions. Thus one has the possibility of detecting eighteen ENDOR transitions of widely differing frequencies from which the two parameters A and γ are to be determined. Of these eighteen transitions, we have studied all but the $M=+\frac{5}{2}$ transitions, which are weak because of the Boltzmann factor. The $M=-\frac{5}{2}$ transitions are shown in Fig. 2. The value for A (including its sign, which can be determined knowing the signs of M and γ) and a value for γ, the nuclear g factor of Cr^{53}, are given in IV. In addition, the experimentally determined magnitude of the second-order terms in (5) confirms the supposition that $S=\frac{5}{2}$.

B. Cd^{111} and Cd^{113}

The analysis of the Cd^{111} and Cd^{113} ENDOR spectrum is more involved than the Cr^{53} analysis because the Cd hyperfine interaction tensor is anisotropic. Since Cd^{111} and Cd^{113} each have nuclear spin $\frac{1}{2}$, one has only the $m=\frac{1}{2}$ to $-\frac{1}{2}$ transition. However, besides the six values of M there are twelve values of k. For the magnetic field in the (110) plane, one can show by symmetry that the twelve k yield seven spectra of relative intensity $1:1:2:2:2:2:2$. Moreover, in high symmetry directions some of these seven coalesce; for example, in the [110] direction one has four spectra of intensity $2:2:4:4$.

The detection of the Cd ENDOR transitions is a relatively difficult experimental problem because of the low natural abundance of the relevant isotopes (Cd^{111} and Cd^{113} are 12.7 and 12.3% abundant, respectively). ENDOR transitions have been detected for all k only for $M=-\frac{3}{2}$ and H in the [$\bar{1}$10] direction. For Cd^{113} these transitions are at 20.42, 20.51, 21.04, and 21.12 Mc/sec. The analysis of this spectrum will now be described.

The second neighbors to a substitutional site in the CdTe lattice lie in the (110) planes, which are planes of reflection symmetry. As a result one of the principal axes of the tensor describing the hyperfine interaction of the $Cr(3d^5)$ center with its nearest Cd neighbors (which occupy the 220 positions) is the corresponding [110] direction. The other two principal axes lie in the corresponding (110) plane (see Fig. 3). Since the magnetic interaction between the Cd nucleus and the unpaired electrons is strong compared to the nuclear Zeeman
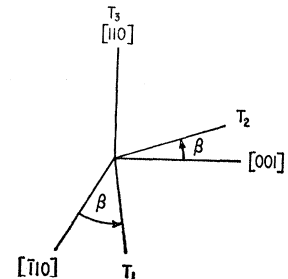
FIG. 3. Principal axes of the tensor describing the hyperfine coupling between the Cr center and its nearest Cd neighbors. Experimentally we find $\beta=37\pm5°$, using the convention $T_1 > T_2$.

T_3
[110]

T_2

β

[001]

β

[$\bar{1}$10] T_1

interaction $(g\beta \mathbf{S}\cdot\mathbf{H}\gg\mathbf{S}\cdot\mathbf{T}_k\cdot\mathbf{I}_k\gg\gamma_k\beta_N\mathbf{H}\cdot\mathbf{I}_k)$, the Cd^{113} ENDOR transitions are given approximately by

$$hf = |MT_k - \gamma_k\beta_N H(T_1\cos^2\theta_1 + T_2\cos^2\theta_2 + T_3\cos^2\theta_3)/T_k|,$$ (6)

where γ_k is the nuclear g factor of Cd^{113} and θ_i is the angle between the magnetic field and the ith principal axis of the tensor T_k. For H in a $[\bar{1}10]$ direction, the four possible T_k, having intensities $2:2:4:4$, are as follows:

$$T_a = T_3,$$ (7)

$$T_b{}^2 = T_1{}^2\cos^2\beta + T_2{}^2\sin^2\beta,$$ (8)

$$4T_c{}^2 = 2T_1{}^2[(\cos\beta/\sqrt{2})\text{-}\sin\beta]^2$$
$$+ 2T_2{}^2[(\sin\beta/\sqrt{2})+\cos\beta]^2 + T_3{}^2,$$ (9)

$$4T_d{}^2 = 2T_1{}^2[(\cos\beta/\sqrt{2})+\sin\beta]^2$$
$$+ 2T_2{}^2[(\sin\beta/\sqrt{2})-\cos\beta]^2 + T_3{}^2.$$ (10)

Equations (7)–(10) are four equations in the four unknowns T_1, T_2, T_3, and β. There is the additional uncertainty that experimentally one does not know which of the two weaker ENDOR transitions is described by (7) and which by (8). [With the convention $T_1 > T_2$, this single choice serves to allocate the measured transitions among (7)–(10).] If one assigns the transitions at 20.42, 21.04, 20.51, and 21.12 Mc/sec to T_a, T_b, T_c, and T_d, respectively, and substitutes into (6), one obtains the hyperfine parameters quoted in IV.[13] By interchange of T_a and T_b one obtains $T_1 = +5.77$, $T_2 = +5.55$, $T_3 = +5.75$, all in units of 10^{-4} cm^{-1}, and $\beta = 60°$. This result is considered unlikely because of the large angle between the axis of T_1 and the Cr-Cd internuclear axis, which corresponds to $\beta = 0$.

IV. RESULTS AND DISCUSSION

The parameters of the complete spin Hamiltonian (2) plus (4) at 1.4°K determined as described in II and III are

$S = \frac{5}{2}$,

$g = 1.9997 \pm 0.0003$,

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

$\left.\begin{array}{l} A = (+12.781 \pm 0.005) \times 10^{-4}\text{ cm}^{-1}, \\ \gamma = 0.3161 \pm 0.0008, \end{array}\right\}$ for Cr^{53}

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[13] The frequency range in which the ENDOR transitions occur is such that agreement with the hyperfine splitting of Fig. 1 is obtained only if $|M| = \frac{3}{2}$ and, in addition, the first and second terms of (6) tend to cancel. Since the $M = +\frac{3}{2}$ level is depopulated we assume that the transitions correspond to $M = -\frac{3}{2}$. The cancellation of the terms in (6) then implies that γ_k and the components of T_k have opposite signs, from which we conclude that the components of T_k are positive.

$\left.\begin{array}{l} T_1 = (+5.82 \pm 0.05) \times 10^{-4}\text{ cm}^{-1}, \\ T_2 = (+5.63 \pm 0.05) \times 10^{-4}\text{ cm}^{-1}, \\ T_3 = (+5.61 \pm 0.05) \times 10^{-4}\text{ cm}^{-1}, \\ \beta = 37 \pm 5°. \end{array}\right\}$ for Cd^{113}

The magnitude of γ given above agrees within the experimental error with published values of γ for Cr^{53} but not with γ for any other common nuclide. Thus, the center under study undoubtedly is a chromium ion. Since $S = \frac{5}{2}$ and $g \sim 2$ it seems clear that the chromium ion has a half-filled $3d$ shell. Moreover, the magnitudes of g, a, and A are similar to those reported by Title for Cr($3d^5$) in cubic ZnS.[1]

The number and relative intensities of the hyperfine lines shown in Fig. 1 are consistent with the notion that the hyperfine interaction is with Cd^{111} and Cd^{113} occupying twelve equivalent sites. The ENDOR spectrum discussed in III B confirms this notion. If the chromium were substituted for Te in the lattice, it would have four nearest Cd neighbors (the hyperfine interaction with these would be expected to be larger than that with the twelve Cd neighbors at the 311 positions). If the chromium ion were interstitial, it would have either four or six nearest Cd neighbors. Agreement with the spectrum is obtained only if one assumes that the chromium substitutes for Cd, in which case it does have twelve nearest Cd neighbors.

Chromium which substitutes for Cd in the lattice and has the configuration $3d^5$ must have accepted an electron.[3] The electrical measurements referred to in II show that the acceptor level lies within 0.6 eV of the conduction band edge.

Superhyperfine interaction with Cd in the 220 positions has been observed previously for Mn($3d^5$) in CdS[10] and CdTe.[11] The hyperfine splitting which we observe (~ 6 G) for Cr($3d^5$) is roughly four times as large. Thus, the wave function of the Cr($3d^5$) center is more spread out, which might be expected since the Cr center has trapped an electron. The principal axes of the Cd hyperfine interaction are as given in Fig. 3.

Unfortunately, the hyperfine interaction with tellurium neighbors to the Cr center was not detected. Thus, one cannot decide experimentally how the wave function of the Cr center is divided among the Te and Cd sublattices. No explanation is offered for the magnitude of the anisotropy of the Cd hyperfine coupling.

ACKNOWLEDGMENTS