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Nuclear-Magnetic-Resonance Measurement of the Conduction-Electron g Factor in CdTe

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The effective g factor $g_e$ of conduction electrons in degenerate CdTe has been determined by using measurements of the Cd$^{115}$ nuclear spin-lattice relaxation time $T_1$ and the Knight shift $K$. It is shown that the magnitude of $g_e$ is given by the Korringa product $T_1 T K^2 = C g_e^2$, where $C$ is a known constant and $T$ is the absolute temperature, and that the sign of $g_e$ is given by the sign of $K$ for a spherically symmetric conduction band. The measured value, $g_e = 0.98$, is within the range allowed by effective-mass theory. Also, the electronic probability density at the nucleus, normalized to unity in an atomic volume, is calculated to be $|\psi_p(0)|^2 = 6.5 \times 10^{-23}$ cm$^{-3}$, about 70% of that found for the free Cd ion in a $5s^25p^3$ state.

I. INTRODUCTION

For many semiconductors it is found that the magnetic spin splitting of conduction electrons is given by an effective g factor $g_e$, which is different from two, the free-electron value. This effect has been successfully explained, using the effective-mass formalism, as being due to a nearby band which is connected to the conduction band by momentum matrix elements and which is split by spin-orbit interaction. In cases where the band gap is small and the spin-orbit energy large, the g factor can be greatly affected; for example, in InSb it is found that $g_e \approx -50$.

In the II–VI compound sequence, CdS, CdSe, and CdTe, the band gaps decrease and the spin-orbit energies increase. The g factors are expected to decrease in this sequence, and indeed they do for the first two, which have been measured by electron-paramagnetic-resonance (EPR) and magneto-optical methods to be $g_{CdS} \approx 1.72$–1.79 and $g_{CdSe} \approx 0.51$–0.7. For CdTe Cardona has calculated $g_{CdTe} \approx -0.4$. Evidently, attempts to measure $g_{CdTe}$ by EPR have proved unsuccessful.

It is often true that conduction electrons have s-state character and thus interact with magnetic nuclei through the hyperfine-contact coupling. Because the electron spins are polarized in a magnetic field, the diagonal part of the hyperfine Hamiltonian produces a shift in the nuclear-magnetic-resonance (NMR) frequency, the so-called Knight shift. Since the degree of polarization depends upon $g_e$, we would expect to gain information through measurement of this shift. Furthermore, the fluctuating off-diagonal elements of the Hamiltonian produce a nuclear-spin-lattice relaxation mechanism, and measurements of the relaxation time, in conjunction with the Knight shift, afford a means of eliminating all unknown parameters except $g_e$. Our result for $g_e$ in CdTe, although somewhat different from Cardona’s estimate, is not outside the range allowed by his calculation, considering the spread in measured and estimated energy-band parameters.

II. THEORY

A. Effective-Mass Theory

It is well known that the effect of a magnetic field on Bloch functions is quite appreciable and cannot adequately be treated by perturbation theory. However, because the electrons of interest in a semiconductor often occupy only a small region of $k$ space, it is possible to obtain an approximation to the Hamiltonian by carrying out a perturbation expansion in powers of the wave vector; to lowest order, this is the so-called effective-mass Hamiltonian. Furthermore, since the energy levels still remain clustered in bands, and interband matrix elements are usually quite small, the Ham-
iltonian can often be represented by only intraband elements and thus handled more easily.

In CdTe, of zinc-blende structure, the lowest-energy conduction-band minimum and highest-energy valence-band maximum occur at $K = 0$.\(^7\) Since the conduction-band edge is spherical, it may be shown that the most general form of the effective-mass Hamiltonian is\(^\alpha\,\beta\)

\[
\mathcal{H} = \frac{1}{2m^*} \left( \frac{e^2}{c} \right) \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 + \frac{\hbar^2}{2m^*} \mathbf{K} \cdot \mathbf{H},
\]

where $m^*$ is the conduction-band effective mass (to be defined later), $\mathbf{p} = \mathbf{\hat{r}} / i$ is the momentum operator, $e$ is the magnitude of the electronic charge, $c$ is the speed of light, $\mathbf{A}$ is the vector potential for the magnetic field $\mathbf{H}$, $g^*$ is the effective $g$ factor for the conduction band, $\mu_B$ is the Bohr magneton, and $\mathbf{K}$ is the Pauli spin vector. By choosing the $z$ axis along the magnetic field and the appropriate Landau gauge for the vector potential $\mathbf{A} = -H(0, x, 0)$, the spatial part of the eigenfunctions of $\mathcal{H}$ are of the form $\phi_n(\mathbf{r}) = u_0(\mathbf{r}) \exp(i \mathbf{K} \cdot \mathbf{r})$, where $u_0(\mathbf{r})$ is the conduction-band Bloch function at $K = 0$ and

\[
F_n(\mathbf{r}) = \exp(i \mathbf{p} \cdot \mathbf{r}) \phi_n(\mathbf{x} - e \mathbf{y} / c H),
\]

where $\phi_n$ is the harmonic-oscillator wave function for the $n$th excited state.\(^5\) By defining the zero of energy at the bottom of the conduction band the eigenvalues of $\mathcal{H}$ are

\[
E_n = \frac{e^2 H}{m^* c} - \left( n + \frac{1}{2} \right) \frac{\hbar^2}{2m^*} + \frac{g^* \mu_B}{2}
\]

where $n$ is an integer and $\hbar$ is Planck's constant divided by $2\pi$. The first term is appropriate for cyclotron resonance and the last term, of interest to us here, gives the spin splitting, where the positive sign denotes spin parallel to field and the negative sign denotes spin antiparallel. An important point, as will be seen later, is that we are able to represent the spin parts of each of the two eigenfunctions by either spin-up $\alpha$ or spin-down $\beta$, but not mixed spin. This is possible because the two $s$-like wave functions, $\phi_\alpha(\mathbf{r})$ and $\phi_\beta(\mathbf{r})$, are not mixed, to first order, by spin-orbit coupling.

The effective mass of Eq. (1) is given by\(^3\)

\[
\frac{m}{m^*} = 1 + \frac{2}{m} \sum_{n \neq 0} \frac{|\langle 0 | \mathbf{p} \cdot \mathbf{r} | n \rangle|^2}{E_n - E_0},
\]

where $|0\rangle$ denotes the spin-up conduction band of energy $E_0 = 0$ and $|n\rangle$ denotes other band edges. Here $m$ is the free-electron mass and we have ignored a small correction to $p$. The $g$ factor is given by\(^3\)

\[
g^* = 2 + \frac{2}{im} \sum_{n \neq 0} \frac{\langle 0 | \mathbf{p} \cdot \mathbf{r} | n \rangle \langle n | \mathbf{p} \cdot \mathbf{r} | 0 \rangle - \langle 0 | \mathbf{p} \cdot \mathbf{r} | n \rangle \langle n | \mathbf{p} \cdot \mathbf{r} | 0 \rangle}{E_n - E_0}.
\]

We first consider the relevant bands of the diamond lattice at $K = 0$, as shown on the left-hand side of Fig. 1. The $\Gamma_3'$ level is the lowest $s$-like conduction band, while the $\Gamma_{25}$ and $\Gamma_{15}$ levels are $p$-like valence and conduction bands, respectively. Because of inversion symmetry the $\Gamma_3'$ and $\Gamma_{15}$ levels are not connected by momentum matrix elements and, furthermore, only the $\Gamma_{25}$ states will make an appreciable contribution to $g^*(\Gamma_{25})$ since contributions from other bands are small due to the energy denominator in Eq. (5).

The $\Gamma_3$ states may be represented by $|\alpha\rangle$ and $|\beta\rangle$, where $|\alpha\rangle$ represents an $s$-like state and the $\Gamma_{25}$ states, sixfold degenerate without spin–orbit interaction $[\{X, Y, Z|\alpha, \beta\}]$, are split into a fourfold-degenerate band $-\{(1/\sqrt{2})|X + i Y\rangle \alpha, (1/\sqrt{2})|X - i Y\rangle \beta\}$ and twofold-degenerate band $-\{(1/\sqrt{3})|Z\alpha - (X + i Y)\beta\}$, $(1/\sqrt{3})|Z\beta + (X - i Y)\alpha\}$. Here $X, Y$, and $Z$ represent $p$-like states transforming under group operations like $x, y, z$, respectively, and $\Delta_0$ is the spin–orbit splitting in the $\Gamma_{25}$ valence band. By using these states to determine the matrix elements in Eq. (5) we get\(^3\)

\[
g^* - 2 \left( 1 - \frac{\Delta_0}{3E_0(E_0 + \Delta_0)} \right) P^2
\]

where $P^2 = (2/m) \langle \alpha| \mathbf{p} \cdot \mathbf{r} | \alpha \rangle \langle \alpha| \mathbf{p} \cdot \mathbf{r} | \alpha \rangle$. Equation (6), given by Roth, has been applied successfully in, for example, Ge, Si, and InSb. It shows that a $g$ factor different from two is achieved for an $s$-like con-
duction band only if the nearby $p$-like valence band is split by spin-orbit coupling.

The zinc-blende band structure may be derived from the diamond structure by assuming the existence of an antisymmetric perturbing potential which mixes bands of opposite parity. The zinc blende $\Gamma_{15c}$ and $\Gamma_{16c}$ states, shown on the right-hand side of Fig. 1, may be derived primarily from the diamond $\Gamma_{15}$ and $\Gamma_{20}$ states. (The $\Gamma_{15}$ state, although unchanged in first order, is relabeled $\Gamma_{1c}$.) Since both the $\Gamma_{15c}$ and $\Gamma_{16c}$ states will contain an admixture of the $\Gamma_{20}$ state, the summation in Eq. (5) must include both bands; i.e., $\delta = \Gamma_{15c}$ and $\Gamma_{16c}$. It is straightforward to show that

$$
\frac{m}{m^*} = 1 + \frac{b_k^2}{2D} \left( \frac{D + D_H}{3} \right) \frac{2}{E_k + \Delta_k} \left( \frac{D - D_H}{E' + \Delta'} \right)
$$

and

$$
g^* = 2 - \frac{b_k^2}{3D} \left( \frac{(D + D_H)\Delta_k}{E_k(E_k + \Delta_k)} + \frac{(D - D_H)\Delta'}{E'(E' + \Delta')} \right),
$$

where the notation, as shown in Fig. 1, is as follows: $D$, $E'$, and $E_k$ are, respectively, the $\Gamma_{15c} - \Gamma_{15s}$, $\Gamma_{15c} - \Gamma_{15p}$, and $\Gamma_{1c} - \Gamma_{1c}$ energy splittings in the zinc-blende structure; $D_H$ is the $\Gamma_{15} - \Gamma_{25}$ splitting in the appropriate isoelectronic group-IV elemental semiconductor; and $\Delta_k$ and $\Delta'$ are, respectively, the spin-orbit splittings in the $\Gamma_{15s}$ and $\Gamma_{15p}$ levels. Since Cd and Te are in the same row of the Periodic Table, the appropriate $D_H$ would be that of $\alpha$-Sn.

Following Cardona we use low-temperature reflectivity data, which include $D = 5.2$ eV, $E_k = 1.59$ eV, $\Delta_k = 0.81$ eV, $E' = 1.29$ eV, $D_H = 0.90$ eV, and we estimate $\Delta_k = 0.77$ and $b_k^2 = 0.24$ eV to obtain $g^* = 0.47$ and $m^* = 0.11 m_e$. These data will be discussed later, but we note here that the third term in Eq. (8), which arises in the zinc-blende lattice because of the antisymmetric potential, is less than a 10% correction to the second term; thus, the approximation that $\Delta_k = \Delta'$ is not too critical.

**B. NMR Theory**

1. Knight Shift

The contact term of the Hamiltonian for the hyperfine interaction between an electron and nucleus may be written

$$
3c_c = 3 \frac{\gamma_n \gamma_e h^2}{\hbar} \mathbf{\tilde{\gamma}} \cdot \mathbf{\delta}(\mathbf{\tilde{r}}),
$$

where $\gamma_n$ and $\gamma_e$ are, respectively, the electronic and nuclear gyromagnetic ratios; $\mathbf{\tilde{\gamma}}$ and $\mathbf{\delta}$ are, respectively, the electronic and nuclear spin vectors; and $\mathbf{\delta}(\mathbf{\tilde{r}})$ is the Dirac $\delta$ function of the radius vector $\mathbf{\tilde{r}}$ between the electron and nucleus. By considering $3c_c$ as a perturbation of the nuclear Zeeman levels, and realizing that the nuclear spin remains quantized along the external magnetic field, $\mathbf{H} = H\mathbf{\tilde{H}}$, it is seen that only the $I_z S_z$ term will have matrix elements between ground-state magnetic field. In fact, it may be shown that $3c_c$ contributes an additional field at the nucleus, in the direction of the applied field, given by

$$
H_c = -\frac{3}{2} \pi g_\mu B \sum_{I_z} \langle \psi_{I_z} \mid S_z \delta(\mathbf{\tilde{r}}) \mid \psi_{I_z} \rangle \int d^3 \mathbf{\tilde{K}} \mathbf{\tilde{r}}(\mathbf{\tilde{K}}) \cdot \mathbf{\tilde{H}},
$$

where $g_\mu = g_\mu/\hbar$ ($g = 2$ is the free-electron $g$ factor). $\psi_{I_z}$ is a deformed conduction-band Bloch state including spin ($s = \alpha, \beta$), and $f(\mathbf{\tilde{K}}, s, \mathbf{\tilde{H}})$ is the Fermi function, including the magnetic energy. As stated before, since the conduction-band wave functions, degenerate in the absence of magnetic field, are not coupled in first order by the spin-orbit interaction, we may represent them by $\psi_\alpha(\mathbf{\tilde{r}})$ and $\psi_\beta(\mathbf{\tilde{r}})$. By letting the energy be represented by $E(k) \pm \Delta E$, where $E(k)$ is the energy in the absence of the magnetic field and where $\Delta E = g^* \mu_B H/2$, we can approximate

$$
f(\mathbf{\tilde{K}}, s, \mathbf{\tilde{H}}) = f(E(k)) = \frac{E(k)}{\hbar} \frac{\partial f}{\partial E} \left|_{E=k} \right. \Delta E,
$$

if $\Delta E \ll kT$, where $k$ is Boltzmann’s constant and $T$ is the absolute temperature. Then Eq. (10) becomes

$$
H_c = -\frac{3}{2} \pi g_\mu B \int d^3 \mathbf{\tilde{K}} \mathbf{\tilde{r}}(\mathbf{\tilde{K}}) \cdot \mathbf{\tilde{H}} \left| \psi_\alpha(0) \right|^2 \int dE \rho(E) \frac{\partial f(E)}{\partial E} dE,
$$

where $\rho(E)$ is the density of states per unit volume for a single spin and the origin of $E$ is the band edge. Here we must assume that the Landau levels do not strongly perturb $\rho(E)$ from its value in the absence of the magnetic field; this should certainly be true at 77 and 300’ K. For $kT/\Delta E \ll 1$, we can approximate $\partial f/\partial E = -\delta(E - E_F)$ and Eq. (13) becomes

$$
H_c = \frac{3}{2} \pi g_\mu B \int d^3 \mathbf{\tilde{K}} \mathbf{\tilde{r}}(\mathbf{\tilde{K}}) \cdot \mathbf{\tilde{H}} \left| \psi_\alpha(0) \right|^2 \rho(E_F).
$$

The quantity $K = H_c/H$ is called the Knight shift.

The most important point here, that $K \propto g g^*$, has been recognized before. It shows that the sign of $g^*$ is given by the sign of the Knight shift for our simple approximation of a spherical energy.
band with states unmixed by spin-orbit coupling. A more complicated case, involving nonspherical energy bands with states strongly mixed by spin-orbit coupling, has been discussed by Senturia et al.

In such cases (e.g., the lead salts) the hyperfine coupling constant \(\langle |\psi_f(0)|^2 \rangle\) may also be negative, and the relationship between the signs of \(g^*\) and \(K\) must be examined in greater detail.

2. Relaxation Time

A nuclear-spin-lattice relaxation mechanism arises from the fluctuating \(I_x, I_y, I_z\) terms of the hyperfine contact Hamiltonian, Eq. (9). The zero-order wave functions, assuming a nuclear spin of \(\frac{1}{2}\), will now be \(\Psi_{I_x I_y I_z s_n}\), where \(S_n\) and \(S_{\alpha_n}\) denote, respectively, the spin states of the electron and nucleus, represented by either \(\alpha\) or \(\beta\) in the limit of weak spin coupling. The probability per unit time of transition between, say, \(\Psi_{I_x I_y I_z s_n}\) and \(\Psi_{I_x I_y I_z s_n'}\), is given by the "Golden Rule" formula:

\[
W_{I_x I_y I_z s_n \rightarrow I_x' I_y' I_z' s_n'} = \frac{2\pi}{\hbar} \left| \langle \vec{K} \alpha_n | \hat{\beta}_{\alpha_n} | \vec{K}' \beta_{\alpha_n} \rangle \right|^2 \\
\times \delta(E_{I_x I_y I_z s_n} - E_{I_x' I_y' I_z' s_n'}). \quad (15)
\]

To get the total probability for such a simultaneous spin flip we must multiply by \(Z(\vec{K}) Z(\vec{K}') \langle f(E_{I_x I_y I_z s_n}) \rangle \times \{1 - f(E_{I_x I_y I_z s_n'})\}\), where \(Z(\vec{K})\) is the density of states in \(\vec{K}\) space, and integrate over all \(\vec{K}\) and \(\vec{K}'\) space. If we assume that \(\vec{K}'\) and \(\vec{K}\) do not need to be very different in order to provide energy conservation, which will be true if \(E^* \mu_B H \ll E_f\), then the usual integration in energy space gives

\[
\frac{1}{T_1} = 2W_{I_x I_y I_z s_n \rightarrow I_x' I_y' I_z' s_n'} = \frac{64\pi^3}{9} \gamma_x^2 \gamma_y^2 \gamma_z^2 \frac{3}{\hbar^2} V^2 \\
\times |\psi_f(0)|^4 \{\rho(E_f)|^2 hT, \quad (16)
\]

where \(T_1\) is the nuclear-spin-lattice relaxation time. Here we have assumed that the probability of a \(\beta_{\alpha_n} \rightarrow \alpha_{\beta_n}\) flip is the same as that of an \(\alpha_{\beta_n} \rightarrow \beta_{\alpha_n}\) flip; both, of course, contribute to the relaxation, giving the factor 2.

Note from Eq. (16) that \((T_1)^{-1} \propto \gamma_x^2 \gamma_y^2 \gamma_z^2\), independent of \(g^*\). The reason that \(K\) depends upon \(g^*\), and \(T_1\) does not, may be seen from a consideration of the Fermi function \(f(E_f)\) for the electron spin-up and spin-down cases, respectively, neglecting nuclear-spin energy. The Knight-shift contribution for a given \(\vec{K}\) vector depends upon the difference in probability of occupation, \(f(E_f^+ - f(E_f^-))\), which is proportional to \(g^* \mu_B H \ll kT\), while the relaxation-time contribution depends upon the product of the factors \(f(E_f^+)\) and \(1 - f(E_f^-))\), neither of which is very dependent upon \(g^*\) if \(k^* \mu_B H \ll kT\), \(R^2 h^2/2m^*\).

By combining Eq. (16) with the Knight-shift result, Eq. (14), we get the Korringa product

\[
T_1 TK^2 = (g^*)^2 \mu_B^2 / 4\pi v_F^2 \hbar, \quad (17)
\]

in which the only unknown parameter is \(g^*\). Thus, if \(T_1\) and \(K\) are due to degenerate electrons in the host-lattice conduction band, Eqs. (14), (16), and (17) should apply. Also, since we have used one-electron wave functions in the derivations, electron-electron effects must be negligible; this should be true in a sample with only \(10^{16}\) electrons/cm\(^3\).

It is useful to evaluate Eqs. (14) and (16) in the nearly free-electron approximation which gives \(\rho(E_f) = (3/8\pi)^1/3 m^* N_e^{1/3} V / \hbar^2\), where \(N_e\) is the electron concentration:

\[
K = \left( \frac{8}{9\pi} \right)^{1/3} \frac{E^* \mu_B^2}{\hbar^2} m^* N_e^{1/3} V |\psi_f(0)|^2, \quad (18)
\]

\[
(T_1)^{-1} = \frac{1}{8} (9\pi)^{1/3} \frac{E^* \mu_B^2}{\hbar^2} m^* N_e^{1/3} V^2 \\
\times |\psi_f(0)|^4 hT. \quad (19)
\]

In this approximation, if \(m^*\) is known and \(N_e\) can be measured, then \(|\psi_f(0)|^2\) can be determined.

III. EXPERIMENTAL PROCEDURES AND RESULTS

Several polycrystalline CdTe samples were grown by the vapor-deposition and Stockbarger techniques, in order to obtain a nondegenerate sample for use as a standard and a completely degenerate sample for which Eqs. (14), (16), and (17) would apply.

A typical as-grown sample, doped with about \(10^{15}\) In(donor) atoms/cm\(^3\), has only about \(10^{16}\) electrons/cm\(^3\), due to compensation. By baking for several hours in a Cd atmosphere at about 1 torr, it was possible to obtain an electron concentration \(N_e \approx 9.7 \times 10^{17} \text{cm}^{-3}\). Other attempts at higher Cd pressures for longer times did not increase \(N_e\) beyond \(10^{18} \text{cm}^{-3}\). Another sample, doped with about 50 ppm Cl and not heat treated, was \(p\) type with about \(10^{16}\) holes/cm\(^3\). We designate the relevant samples as follows: sample 1, \(1 \times 10^{16}\) electrons/cm\(^3\); sample 2, \(1 \times 10^{16}\) holes/cm\(^3\); and sample 3, \(9.7 \times 10^{17}\) electrons/cm\(^3\). Other samples were of intermediate concentrations and will not be discussed.

The carrier concentrations were determined by Hall-effect measurements using a five-lead configuration. The contacts were indium, soldered with an ultrasonic iron after the samples were treated with a prescribed chemical etch. For the degenerate sample (3) we assumed \(N_e = (R_H eC)^{-1}\), while for the nondegenerate samples (1 and 2), \(N_e = \frac{1}{2} \pi (R_H eC)^{-1}\), where \(R_H\) is the Hall constant.

The NMR measurements were carried out using a Varian V-4200B wide-line spectrometer. Observation of the dispersion mode with high rf field...
strengths enhanced the signal-to-noise ratio. The spin-lattice relaxation times \( T_1 \) were determined by a direct technique in which first the nuclear-spin system is saturated (randomized) by applying the strong rf field at resonance, then the magnetic field is moved off resonance for a time \( t \) allowing the spin system to relax, and finally the field is swept rapidly back through the resonance to observe the fraction of recovered magnetization. This sequence could be performed manually or electronically. The recovery was exponential, obeying \( M(t) = M(\infty)(1 - e^{-t/T_1}) \), and \( T_1 \) was easily extracted from a semilog plot.

The Knight shifts \((K)\), confirmed as such by their dependence upon carrier concentration, were measured with respect to the resonance positions of samples 1 and 2, which were the same. Since sample 1 is \( p \) type and sample 2 is \( n \) type, it is obvious that the carriers did not influence the resonance positions of these two samples. However, it should be noted that all the samples have a chemical shift, about \( 1.6 \times 10^{-4} \) with respect to aqueous CdCl\(_2\), as already shown by Weinberg. The resonance position of each sample was obtained by sweeping the field both ways and taking the average position. Each such point was taken about 15 times and the accumulated data were statistically analyzed.

The results for sample 3 are as follows: at 4.2, 77, and 300 K we measured \( N_e = 9.7 \pm 0.2 \) cm\(^{-3} \) and \( K = (-4.1 \pm 0.1) \times 10^{-4}; \) at 77 and 300 K and at 2-4 K and 6-8 MHz resonance frequencies we measured \( T_1 T = 950 \pm 150 \) sec K, at 4.2 K we measured \( T_1 T \approx 130, 500, \) and 600 sec K at 2.4, and 8 MHz, respectively.

In order to be able to deduce \( g^* \) from Eq. (17) we must show that, at some temperature, \( T_1 \) and \( K \) are entirely due to degenerate, independent conduction electrons in the host-lattice conduction band. We first note that this is obviously not true at 4.2 K since the measured \( T_1 \) is frequency dependent, whereas Eq. (16) predicts it should not be. At this temperature paramagnetic impurities are undoubtedly the dominant influence, but this point will not be discussed further.

The degeneracy of the electrons may be shown by a number of arguments, both theoretical and experimental. When a typical semiconductor is doped with increasing amounts of donor impurities (e.g., In in CdTe) a concentration \( N_e \) is reached at which the electrons may move quite freely in an impurity band, and at a higher concentration \( N_{ea} \) the impurity band "overlaps" the host-lattice conduction band and the electrons become characteristic of this band. These concentrations are easily calculated approximately, and for CdTe are \( N_e \approx 1 \times 10^{17} \) cm\(^{-3} \) and \( N_{ea} \approx 5 \times 10^{17} \) cm\(^{-3} \). Since our sample has \( N_e \approx 1 \times 10^{14} \) cm\(^{-3} \), we can assume that the electrons are in the host-lattice conduction band. Furthermore, in the nearly free-electron approximation the Fermi temperature is \( T_F \approx 440 \) K, well above our measurement temperatures. Experimentally, if the impurity band is separated from the conduction band a hump in \( R_H \) vs \( T \) is normally observed. No such hump was seen in our data. Furthermore, the fact that \( T_1 \approx T_1 \) shows that the electrons are degenerate in the range 77-300 K (cf. Eq. (16)), and the temperature independence of \( K \) shows that the electrons are both degenerate and in the conduction band in the range 4.2-300 K. (The Knight shift would be considerably diminished if the electrons were localized near impurity centers at 4.2 K.) Finally, the independence of the electrons is assumed because correlation effects should not be present in a sample with only \( 10^{18} \) electrons/cm\(^3\). Thus we have shown that Eq. (17) should be valid at 77 or 300 K, and from this equation we calculate \( g^* = -1.1 \pm 0.1 \), the sign being given by the negative sign of the Knight shift.

By assuming the density of states given in the nearly free-electron approximation, discussed in Sec. II B 2, and an effective mass \( m^* = 0.0985 \) m, we calculate from either Eq. (18) or Eq. (19) \( V |\psi_0(0)|^2 = 4.15 \). Normalizing \( \psi_0(T) \) to an atomic volume \( [V_{at} = \text{molecular weight/}[\text{density} \times \text{Avagadro's number}]) \), we get \( |\psi_0(0)|^2 \approx 6.5 \times 10^{18} \) cm\(^{-3} \). The free-ion value, calculated for the Cd 5s \( S_{1/2} \) state from Goudsmit's formula, is \( 92 \) \( \times 10^{18} \) cm\(^{-3} \). The factor \( \xi = |\psi_0(0)|^2/|\psi_0(0)|^2 \approx 0.70 \) is quite typical of that found in metals and semiconductors and gives additional evidence that our analysis is basically correct.

**IV. DISCUSSION**

The data for CdTe and also several other compounds, for which \( T_1 TK^2 \) has been measured, are presented in Table I. (The resonant nuclei are Si and Cd as well as the Si and Cd compounds, respectively. For dopings and other details the reader should consult the references. The magneto-optical measurements of \( g^* \) are from Zeeman splittings of exciton levels.) The \( T_1 TK^2 \) values for Si, CdO, and CdS are each averaged over three samples which obey the \( T \) and \( N_e \) dependences given by Eqs. (18) and (19). The \( T_1 TK^2 \) value for CdSe was determined in this laboratory from measurements at 77 and 300 K on a single sample of concentration \( N_e \approx 1.5 \times 10^{14} \) cm\(^{-3} \). (The Fermi temperature for this sample is \( T_F = 430 \) K, and the theoretical donor concentration necessary to make CdSe "metallic" is \( N_m \approx 1 \times 10^{14} \) cm\(^{-3} \).) Since the NMR samples are powders, the tabulated \( g^* \)'s of any single-crystal samples of CdS and CdSe are averaged over field direction \( [i.e., g^* = \frac{3(g_f^* + 2g_i^*)}{5}] \) in order to facilitate comparison. As seen in Table I the...
NMR MEASUREMENT OF THE CONDUCTION-ELECTRON...

TABLE I: Some comparisons of theoretical and experimental $g^*$ values in semiconductors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$T_1T_2^2(10^{-6})$</th>
<th>$g^*$[NMR: Eq. (17)]</th>
<th>$g^*$[Other methods]</th>
<th>$g^*$[Theor: Eq. (6) or Eq. (8)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>diamond</td>
<td>$6.3 \pm 7^b$</td>
<td>$1.95 \pm 0.10$</td>
<td>$1.9885[\text{ENDOR}]^8$</td>
<td>$1.95$</td>
</tr>
<tr>
<td>CdO</td>
<td>rocksalt</td>
<td>$5.0 \pm 0.4^d$</td>
<td>$1.93 \pm 0.08$</td>
<td>$1.81[\text{EPR}]^4$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>CdS</td>
<td>wurtzite</td>
<td>$3.3 \pm 0.5^f$</td>
<td>$1.56 \pm 0.12$</td>
<td>$1.78[\text{EPR}]^6$</td>
<td>$1.88$</td>
</tr>
<tr>
<td>CdSe</td>
<td>wurtzite</td>
<td>$0.38 \pm 0.05^i$</td>
<td>$0.53 \pm 0.04$</td>
<td>$0.54[\text{Mag, Opt.}]^j$</td>
<td>$0.83$</td>
</tr>
<tr>
<td>CdTe</td>
<td>zinc blende</td>
<td>$1.6 \pm 0.3^e$</td>
<td>$-1.09 \pm 0.10$</td>
<td>$0.7[\text{Mag, Opt.}]^k$</td>
<td>$0.52[\text{Mag, Opt.}]^j$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$0.68[\text{EPR}]^m$</td>
<td>$-0.47$</td>
</tr>
</tbody>
</table>

$^a$Reference 4.
$^i$This paper (Sec. IV).
$^m$Reference 5.
$^n$This paper.

NMR values of $g^*$ agree reasonably well with values deduced by other methods for Si, CdO, CdS, and CdSe; this fact lends credibility to the NMR value calculated for CdTe. A detailed analysis of the relative merits of each method would be interesting, but is outside the scope of this paper. However, we do note that the NMR samples have higher carrier concentrations ($10^{17}$–$10^{18}$ cm$^{-3}$) than most of those used in other studies.

All of the measured values of the $g$ shift, $\Delta g = 2 - g^*$, are significantly larger than the respective theoretical values in CdS, CdSe, and CdTe. Part of this problem seems to be in Cardona's choice of $P^2 = 21$ eV as the best value for the II–VI compounds in spite of the fact that $P^2 = 23$ eV works best for the III–V and group-IV compounds. If we choose $P^2 = 24$ eV, then Eqs. (7) and (8) yield the following values of $g^*$ and $m^*$: CdS, $g^* = 1.86$ and $m^*/m = 0.158$; CdSe, $g^* = 0.66$ and $m^*/m = 0.111$; and CdTe, $g^* = 0.82$ and $m^*/m = 0.100$. These $g^*$'s are closer to the measured values and the $m^*$'s are closer to those given by cyclotron-resonance data. Another approximation, that $\Delta \sigma = \Delta \epsilon$, could probably be better handled by assuming that $\Delta \epsilon \approx 0.3$ eV the Cd atomic spin-orbit splitting, since electrons in the conduction bands of these compounds are mostly concentrated about the Cd. This assumption increases $\Delta g$ in CdS by about $5\%$ and decreases $\Delta g$ in CdTe by about the same amount; the $\Delta g$ in CdSe is affected very little. Finally, recent room-temperature electroreflectivity data yield somewhat different energy-band splittings and give, for $P^2 = 24$ eV, $m^*/m = 0.109$ and $g^* = -1.15$, close to our measured value. Thus we conclude that our value of $g^*$ is within the range allowed by Cardona's formula.

In summary, it has been demonstrated that the magnitude and sign of the effective $g$ factor can be determined from the magnitude and sign, respectively, of the Kramers product and Knight shift, under the conditions that the electrons are independent and degenerate in a spherical conduction band. These conditions are shown to be valid for the lowest-energy conduction band in a CdTe sample with about $10^{18}$ electrons/cm$^3$. The NMR determination of $g^*$ compares favorably with determinations by other methods in Si, CdO, CdS, and CdSe. However, theoretical estimates of $\Delta g = 2 - g^*$ are too small in CdS, CdSe, and CdTe, at least under the assumption that $P^2 = 21$ eV; a seemingly more accurate value for these compounds would be $P^2 \approx 24$ eV.

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$^2$A good review of $g$ factors for conduction electrons
Physics Interactions in the Samarium Monochalcogenides

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In the insulating state of the samarium monochalcogenides SmS, SmSe, and SmTe, the Sm$^3^+$ (4f$^3$) ion has a nonmagnetic $F_2$ ground state exhibiting Van Vleck paramagnetism at low temperatures. From an analysis of the susceptibility, information about the Sm--Sm exchange interactions is obtained. The deduced variation of this exchange with lattice parameter is shown to be consistent with the pressure dependence of the susceptibilities. Electron paramagnetic resonance of Eu$^{2+}$, Gd$^{2+}$, and Mn$^{2+}$ present as dilute impurities has also been observed. The resonance fields are subject to large shifts (nearly 50% for Mn$^{2+}$ in SmS) due to the impurity-host lattice interaction; this enables one to deduce the Sm--impurity exchange interactions. It is found that the Eu--Sm and Sm--Sm interactions are nearly identical in each lattice and furthermore that they follow the same systematic trend as the Eu--Eu exchange in the corresponding europium chalcogenides. The magnitude however is much larger in the Sm lattice, directly reflecting the closer proximity of the conduction band. The Gd--Sm exchange interaction is roughly twice as large as that found for Eu--Sm in each host lattice. This increase in exchange in going from the larger Eu$^{2+}$ ion to the smaller isoelectronic Gd$^{2+}$ ion implies that the extra electron accompanying the Gd$^{2+}$ ion plays an active role in the exchange process. The Mn--Sm interactions are found to be of opposite sign (antiferromagnetic) and approximately four times larger than those for Eu--Sm.

I. INTRODUCTION

Since the discovery$^1$ of high-temperature ferromagnetism in EuO, there has been considerable interest in the magnetic, transport, and optical properties of the europium chalcogenides.$^2$ Particular effort has been directed towards obtaining an understanding of the microscopic origins of the anomalously large Eu$^{2+}$--Eu$^{3+}$ exchange in these compounds.$^3$ It is now generally recognized that the 5d, 6s conduction states play an important intermediary role in the exchange interaction. However, because of the large number of possible high-order processes, it has proven extremely difficult to isolate the dominant mechanisms. It is therefore of interest to obtain additional empirical information on the magnetic interactions in similar systems.

In this paper we report a study of exchange interactions in the samarium monochalcogenides