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PHYSICAL REVIEW B VOLUME 5, NUMBER 9 1 MAY 1972

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

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(Received 26 April 1971)

The effective g factor g^* of conduction electrons in degenerate CdTe has been determined by using measurements of the Cd^{113} nuclear spin-lattice relaxation time T_1 and the Knight shift K. It is shown that the magnitude of g^* is given by the Korringa product $T_1TK^2=C(g^*)^2$, where C is a known constant and T is the absolute temperature, and that the sign of g^* is given by the sign of K for a spherically symmetric conduction band. The measured value, $g^*=-1.1\pm0.1$, 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 $|\psi_F(0)|^2\simeq 6.5\times10^{25}\ \mathrm{cm}^{-3}$, about 70% of that found for the free Cd ion in a $5s\,^2S_{1/2}$ 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^*, which is different from two, the free-electron value.[1] This effect has been successfully explained, using the effective-mass formalism,[2] 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.[3] 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[3] that $g^*\simeq-50$.

In the II–VI compound sequence, CdS, CdSe, and CdTe, the band gaps decrease and the spin-orbit energies increase.[4] 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 $g^*_{\mathrm{CdS}}\simeq 1.72-1.79$ and $g^*_{\mathrm{CdSe}}\simeq 0.51-0.7$. For CdTe Cardona[4] has calculated $g^*_{\mathrm{CdTe}}\simeq-0.4$. Evidently, attempts to measure g^*_{CdTe} by EPR have proved unsuccessful.[5]

It is often true that conduction electrons have s-state character and thus interact with magnetic nuclei through the hyperfine-contact coupling.[6] 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.[6] Since the degree of polarization depends upon g^*, 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,[6] and measurements of the relaxation time, in conjunction with the Knight shift, afford a means of eliminating all unknown parameters except g^*. Our result for g^* in CdTe, although somewhat different from Cardona's estimate,[4] 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.[1] 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[2]; 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 Hamiltonian 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 $\vec{k}=0$.[7] Since the conduction-band edge is spherical, it may be shown that the most general form of the effective-mass Hamiltonian is[3,8]

$$\mathcal{H}=\frac{1}{2m^*}\left(\vec{p}+\frac{e\vec{A}}{c}\right)^2+\frac{g^*\mu_B}{2}\vec{\sigma}\cdot\vec{H}\,, \tag{1}$$

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

$$F_k(\vec{r})=e^{i(k_y y+k_z z)}\,\phi_n(x-cky/eH)\,, \tag{2}$$

where ϕ_n is the harmonic-oscillator wave function for the nth excited state.[3] By defining the zero of energy at the bottom of the conduction band the eigenvalues of $\mathcal{H}$ are

$$E_n=\frac{e\hbar H}{m^*c}(n+\tfrac{1}{2})+\frac{\hbar^2k_z^2}{2m^*}\pm\frac{g^*\mu_B}{2}\,, \tag{3}$$

where n is an integer and $\hbar$ is Planck's constant divided by 2π. 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 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 α or spin-down β, but not mixed spin. This is possible because the two s-like wave functions, $\psi_k(\vec{r})\alpha$ and $\psi_k(\vec{r})\beta$, are not mixed, to first order, by spin-orbit coupling.

The effective mass of Eq. (1) is given by[3]

$$\frac{m}{m^*}=1+\frac{2}{m}\sum_{\delta\neq 0}\frac{|(0|p_x|\delta)|^2}{E_0-E_\delta}\,, \tag{4}$$

where $|0)$ denotes the spin-up conduction band of energy $E_0\equiv 0$ and $|\delta)$ denotes other band edges. Here m is the free-electron mass and we have ignored a small correction to $\vec{p}$. The g factor is given by[3]

$$g^*=2+\frac{2}{im}\times\sum_{\delta\neq 0}\frac{(0|p_x|\delta)(\delta|p_y|0)-(0|p_y|\delta)(\delta|p_x|0)}{E_0-E_\delta}\,. \tag{5}$$

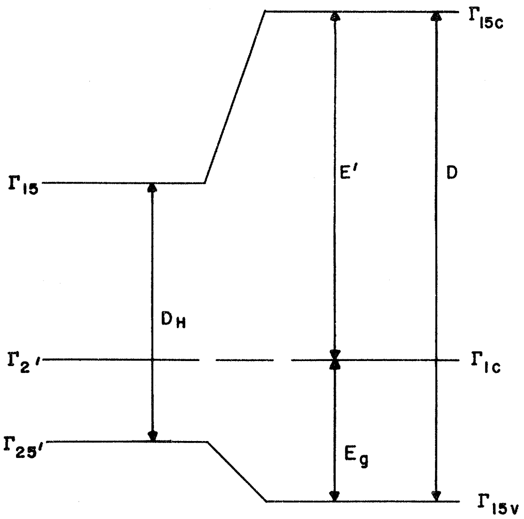

FIG. 1. Schematic diagram of energy levels at the Γ point in the zinc-blende lattice (right-hand side) and the levels in the diamond lattice from which they are derived. For clarity, spin-orbit splittings of the levels are not shown.

We first consider the relevant bands of the diamond lattice at $\vec{k}=0$, as shown on the left-hand side of Fig. 1. The $\Gamma_{2'}$ level is the lowest s-like conduction band, while the $\Gamma_{25'}$ and Γ_{15} levels are p-like valence and conduction bands, respectively. Because of inversion symmetry the $\Gamma_{2'}$ and Γ_{15} levels are not connected by momentum matrix elements and, furthermore, only the $\Gamma_{25'}$ states will make an appreciable contribution to $g^*(\Gamma_{2'})$ since contributions from other bands are small due to the energy denominator in Eq. (5).

The $\Gamma_{2'}$ states may be represented by $|S\alpha)$ and $|S\beta)$, where $|S)$ represents an s-like state and the $\Gamma_{25'}$ states, sixfold degenerate without spin-orbit interaction $\{[X,Y,Z]\times[\alpha,\beta]\}$, are split into a fourfold-degenerate band—$\{(1/\sqrt{2})(X+iY)\alpha$, $(1/\sqrt{2})\times(X-iY)\beta$, $(1\sqrt{6})[2Z\alpha+(X+iY)\beta]$, and $(1/\sqrt{6})\times[2Z\beta-(X-iY)\alpha]\}$—at energy $-E_g$, and a twofold-degenerate band—$\{(1/\sqrt{3})[Z\alpha-(X+iY)\beta]$, $(1/\sqrt{3})\times[Z\beta+(X-iY)\alpha]\}$—at energy $-(E_g+\Delta_0)$. Here X, Y, and Z represent p-like states transforming under group operations like x, y, and z, respectively, and Δ_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]

$$g^*=2\left(1-\frac{\Delta_0}{3E_g(E_g+\Delta_0)}P^2\right)\,, \tag{6}$$

where $P^2\equiv(2/m)\,|(S|p_x|X)|^2$. 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 conduction 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.[4] Thus the zinc blende Γ_{15v} and Γ_{15c} states, shown on the right-hand side of Fig. 1, may be derived primarily from the diamond Γ_{15} and $\Gamma_{25'}$ states. (The $\Gamma_{2'}$ state, although unchanged in first order, is relabeled Γ_{1c}.) Since both the Γ_{15v} and Γ_{15c} states will contain an admixture of the $\Gamma_{25'}$ state, the summation in Eq. (5) must include both bands; i.e., $\delta = \Gamma_{15v}$ and Γ_{15c}. It is straightforward to show that

$$\frac{m}{m^*} = 1 + \frac{P^2}{2D}\left[\left(\frac{D+D_H}{3}\right)\left(\frac{2}{E_g} + \frac{1}{E_g+\Delta_v}\right) - \frac{D-D_H}{E'}\right] \tag{7}$$

and

$$g^* = 2 - \frac{P^2}{3D}\left(\frac{(D+D_H)\Delta_v}{E_g(E_g+\Delta_v)} + \frac{(D-D_H)\Delta_c}{E'(E'+\Delta_c)}\right) , \tag{8}$$

where the notation,[5] as shown in Fig. 1, is as follows: D, E', and E_g are, respectively, the $\Gamma_{15c} - \Gamma_{15v}$, $\Gamma_{15c} - \Gamma_{1c}$, and $\Gamma_{1c} - \Gamma_{15v}$ 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 Δ_v and Δ_c are, respectively, the spin-orbit splittings in the Γ_{15v} and Γ_{15c} levels. Since Cd and Te are in the same row of the Periodic Table, the appropriate D_H would be that of α-Sn. Following Cardona[4] we use low-temperature reflectivity data, which include $D = 5.2$ eV, $E_g = 1.59$ eV, $\Delta_v = 0.81$ eV, $E' \equiv D - E_g = 3.6$ eV, $D_H(\alpha\text{-Sn}) = 2.9$ eV, and we estimate $\Delta_c = \Delta_v$ and $P^2 = 21$ eV to obtain $g^* = -0.47$ and $m^* = 0.11m$. 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 $\Delta_c = \Delta_v$ 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[6]

$$\mathcal{H}_c = \tfrac{8}{3}\pi\gamma_e\gamma_n\hbar^2\,\vec{\mathrm{I}}\cdot\vec{\mathrm{S}}\,\delta(\vec{\mathrm{r}}) , \tag{9}$$

where γ_e and γ_n are, respectively, the electronic and nuclear gyromagnetic ratios; $\vec{\mathrm{I}}$ and $\vec{\mathrm{S}}$ are, respectively, the nuclear and electronic spin vectors; and $\delta(\vec{\mathrm{r}})$ is the Dirac δ function of the radius vector $\vec{\mathrm{r}}$ between the electron and nucleus. By considering $\mathcal{H}_c$ as a perturbation of the nuclear Zeeman levels, and realizing that the nuclear spin remains quantized along the external magnetic field, $\vec{\mathrm{H}} = H\hat{z}$, it is seen that only the $I_z S_z$ term will have matrix elements between ground-state wave functions. In fact, it may be shown that $\mathcal{H}_c$ contributes an additional field at the nucleus, in the direction of the applied field, given by[9]

$$H_c = -\tfrac{8}{3}\pi g\mu_B \sum_{\vec{\mathrm{k}},s} \langle \psi_{\vec{\mathrm{k}},s} \,|\, S_z\delta(\vec{\mathrm{r}}) \,|\, \psi_{\vec{\mathrm{k}},s}\rangle f(\vec{\mathrm{k}}, s, \vec{\mathrm{H}}) , \tag{10}$$

where $\gamma_e \equiv g\mu_B/\hbar$ ($g = 2$ is the free-electron g factor), $\psi_{\vec{\mathrm{k}},s}$ is the single-particle conduction-band Bloch state including spin ($s \equiv \alpha, \beta$), and $f(\vec{\mathrm{k}}, s, \vec{\mathrm{H}})$ is the Fermi function, including the magnetic energy. As stated before, since the two 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 $\psi_{\vec{\mathrm{k}}}(\vec{\mathrm{r}})\alpha$ and $\psi_{\vec{\mathrm{k}}}(\vec{\mathrm{r}})\beta$. 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

$$f(\vec{\mathrm{k}}, s, \vec{\mathrm{H}}) \equiv f(\vec{\mathrm{k}}, \pm) = f(E(k)) \pm \left.\frac{\partial f}{\partial E}\right|_{H=0} \Delta E , \tag{11}$$

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

$$H_c = -\tfrac{4}{3}\pi g g^* \mu_B^2 H \sum_{\vec{\mathrm{k}}} V\,|\psi_{\vec{\mathrm{k}}}(0)|^2 \left.\frac{\partial f}{\partial E}\right|_{H=0} , \tag{12}$$

where the $\psi_{\vec{\mathrm{k}}}(\vec{\mathrm{r}})$ are normalized to unity in sample volume V. For degenerate electrons $\partial f/\partial E$ is small except at $E = E_F$, the Fermi energy, so that we may take $|\psi_{\vec{\mathrm{k}}}(0)| \equiv |\psi_F(0)|$, a constant, as long as ψ is not a strong function of $\vec{\mathrm{k}}$ at this energy. Then a conversion of the summation over $\vec{\mathrm{k}}$ to an integration over E yields

$$H_c = \tfrac{4}{3}\pi g g^* \mu_B^2 H V\,|\psi_F(0)|^2 \int_0^\infty \rho(E)\,\frac{\partial f(E)}{\partial E}\,dE, \tag{13}$$

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 $kT/E_F \ll 1$, we can approximate $\partial f/\partial E \simeq -\delta(E - E_F)$ and Eq. (13) becomes

$$H_c = \tfrac{4}{3}\pi g g^* \mu_B^2 H V\,|\psi_F(0)|^2 \rho(E_F) . \tag{14}$$

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

The most important point here, that $K \propto g g^*$, has been recognized before.[9,10] 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.*[9] In such cases (e.g., the lead salts) the hyperfine coupling constant ($\sim |\psi_F(0)|^2$) 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_+S_- and I_-S_+ terms of the hyperfine contact Hamiltonian,[6] Eq. (9). The zero-order wave functions, assuming a nuclear spin of $\frac{1}{2}$, will now be $\psi_{\vec{k},S_e,S_n}$, where S_e and S_n denote, respectively, the spin states of the electron and nucleus, represented by either α or β in the limit of weak spin coupling. The probability per unit time of transition between, say, $\psi_{\vec{k}}(\vec{r})\alpha_e\beta_n$ and $\psi_{k'}(\vec{r})\beta_e\alpha_n$, is given by the "Golden Rule" formula:

$$W_{\vec{k}\alpha_e\beta_n\to\vec{k}'\beta_e\alpha_n}=\frac{2\pi}{\hbar}|(\vec{k}\alpha_e\beta_n|\mathcal{H}_c|\vec{k}'\beta_e\alpha_n)|^2 \times\delta(E_{\vec{k}\alpha_e\beta_n}-E_{\vec{k}'\beta_e\alpha_n})\,. \quad (15)$$

To get the total probability for such a simultaneous spin flip we must multiply by $Z(\vec{k})\,Z(\vec{k}')f(E_{\vec{k}\alpha_e\beta_n})\times[1-f(E_{\vec{k}',\beta_e\alpha_n})]$, 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 greatly different in order to provide energy conservation, which will be true if $|g^*\mu_BH|\ll E_F$, then the usual integration in energy space gives

$$\frac{1}{T_1}=2W_{\vec{k}\alpha_e\beta_n\to\vec{k}'\beta_e\alpha_n}=\frac{64\pi^3}{9}\gamma_e^2\gamma_n^2\hbar^3V^2 \times|\psi_F(0)|^4[\rho(E_F)]^2kT\,, \quad (16)$$

where T_1 is the nuclear-spin-lattice relaxation time. Here we have assumed that the probability of a $\beta_e\alpha_n\to\alpha_e\beta_n$ flip is the same as that of an $\alpha_e\beta_n\to\beta_e\alpha_n$ flip; both, of course, contribute to the relaxation, giving the factor 2.

Note from Eq. (16) that $(T_1)^{-1}\propto\gamma_e^2\propto g^2$, 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 $f(E_{\vec{k}'},\pm)$ 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, $f(E_{\vec{k}},+)-f(E_{\vec{k}},-)$, which is proportional to g^* if $|g^*\mu_BH|\ll kT$, while the relaxation-time contribution depends upon the *product* of the factors $f(E_{\vec{k}},+)$ and $[1-f(E_{\vec{k}'},-)]$, neither of which is very dependent upon g^* if $|g^*\mu_BH|\ll kT$, $\hbar^2k^2/2m^*$.

By combining Eq. (16) with the Knight-shift result, Eq. (14), we get the Korringa product[6]

$$T_1TK^2=(g^*)^2\mu_B^2/4\pi\gamma_n^2\hbar k\,, \quad (17)$$

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^{18} electrons/cm^3.

It is useful to evaluate Eqs. (14) and (16) in the nearly free-electron approximation which gives $\rho(E_F)=(3/8\pi^4)^{1/3}m^*N_e^{1/3}V/\hbar^2$, where N_e is the electron concentration[11]:

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

$$(T_1)^{-1}=\tfrac{16}{9}(9\pi)^{1/3}\frac{g^2\mu_B^2\gamma_n^2}{\hbar^3}(m^*)^2N_e^{2/3}V^2 \times|\psi_F(0)|^4kT\,. \quad (19)$$

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.[12] A typical as-grown sample, doped with about 10^{18} 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 $N_e\simeq 9.7\times10^{17}$ cm^{-3}. Other attempts at higher Cd pressures for longer times did not increase N_e beyond 10^{18} 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, 1×10^{16} electrons/cm^3; sample 2, 1×10^{16} holes/cm^3; and sample 3, 9.7×10^{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.[13] The contacts were indium, soldered with an ultrasonic iron after the samples were treated with a prescribed chemical etch.[14] For the degenerate sample (3) we assumed[15] $N_e=(R_Hec)^{-1}$, while for the nondegenerate samples (1 and 2), $N_e=\frac{3}{8}\pi(R_Hec)^{-1}$, 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[16] 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 1.6×10^{-4} with respect to aqueous $CdCl_2$, as already shown by Weinberg.[17] 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 $N_e = 9.7\pm0.2$ cm^{-3} and $K=(-4.1\pm0.1)\times10^{-5}$; at 77 and 300 °K and at 2-, 4-, and 8-MHz resonance frequencies we measured $T_1T=950\pm150$ sec °K, while at 4.2 °K we measured $T_1T\simeq130$, 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,[6,16,18] 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_c is reached at which the electrons may move quite freely in an impurity band,[19] and at a higher concentration N_{cb} the impurity band "overlaps" the host-lattice conduction band and the electrons become characteristic of this band.[20] These concentrations are easily calculated approximately, and for CdTe are $N_c\simeq1\times10^{17}$ cm^{-3} and $N_{cb}\simeq5\times10^{17}$ cm^{-3}. Since our sample has $N_e\simeq1\times10^{18}$ 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[11] is $T_F\simeq440$ °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.[19] No such hump was seen in our data. Furthermore, the fact that $T_1 \propto T^{-1}$ 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[16] 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 $g^*=-1.1\pm0.1$, 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 $m^*\simeq0.0985$ m,[21] we calculate from either Eq. (18) or Eq. (19) $V|\psi_F(0)|^2\simeq4150$. Normalizing $\psi_F(\vec{r})$ to an atomic volume [$V_{at}\equiv$ molecular weight/(density × Avogadro's number)], we get $|\psi_F(0)|^2\simeq6.5\times10^{25}$ cm^{-3}. The free-ion value, calculated for the Cd $5s\ {}^2S_{1/2}$ state from Goudsmit's formula,[22] is $|\psi_A(0)|^2\simeq9.2\times10^{25}$ cm^{-3}. The fraction $\xi=|\psi_F(0)|^2/|\psi_A(0)|^2\simeq0.70$ is quite typical of that found in metals and semiconductors[6] and gives additional evidence that our analysis is basically correct.

IV. DISCUSSION

The data for CdTe and also several other compounds, for which T_1TK^2 has been measured, are presented in Table I. (The resonant nuclei are Si^{29} and Cd^{113} for 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 lines.) The T_1TK^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_1TK^2 value for CdSe was determined in this laboratory from measurements at 77 and 300 °K on a single sample of concentration $N_e\simeq1.5\times10^{18}$ cm^{-3}. (The Fermi temperature for this sample is $T_F\simeq430$ °K, and the theoretical donor concentration necessary to make CdSe "metallic"[16,20] is $N_{cb}\simeq1\times10^{18}$ 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., $g^*=\frac{1}{3}(g^*_\parallel+2g^*_\perp)$] in order to facilitate comparison. As seen in Table I the

TABLE I. Some comparisons of theoretical and experimental g values in semiconductors.

Compound	Structure	$T_1TK^2(10^{-6})$	g^*[NMR: Eq. (17)]	g^*(Other methods)	g^*[Theor: Eq. (6) or Eq. (8)][a]
Si	diamond	6.3 ± 7[b]	1.95 ± 0.10	1.9985(ENDOR)[c]	1.95
CdO	rocksalt	5.0 ± 0.4[d]	1.93 ± 0.08	1.81(EPR)[e]	...
CdS	wurtzite	3.3 ± 0.5[f]	1.56 ± 0.12	1.78(EPR)[g] 1.74(Mag. Opt.)[h]	1.88
CdSe	wurtzite	0.38 ± 0.05[i]	0.53 ± 0.04	0.54(Mag. Opt)[j] 0.7 (Mag. Opt.)[k] 0.52(Mag. Opt.)[l] 0.68(EPR)[m]	0.83
CdTe	zinc blende	1.6 ± 0.3[n]	-1.09 ± 0.10	...	-0.47

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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^{18}–10^{20} cm^{-3}) than most of those used in other studies.

All of the measured values of the *g shift*, $\Delta g \equiv 2 - g^*$, 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.[4] 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 $\Delta_c = \Delta_v$, could probably be better handled by assuming that $\Delta_c \simeq 0.3$ 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 Δg in CdS by about 5% and decreases Δg in CdTe by about the same amount; the Δg in CdSe is affected very little. Finally, recent room-temperature electroreflectivity data[23] 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.[4]

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 Korringa 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 $\Delta g \equiv 2 - g^*$ are too small in CdS, CdSe, and CdTe, at least under the assumption that $P^2 \simeq 21$ eV; a seemingly more accurate value for these compounds would be $P^2 \simeq 24$ eV.

ACKNOWLEDGMENTS

We would like to thank D. E. Naas and C. H. Chung for growing the CdTe crystals, and D. R. Locker for experimental assistance and helpful discussions.

[†] Research sponsored by the Aerospace Research Laboratories, Air Force Systems Command, U. S. Air Force, Contract No. F33615-67-C-1027.

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Exchange Interactions in the Samarium Monochalcogenides

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(Received 29 November 1971)

In the insulating state of the samarium monochalcogenides SmS, SmSe, and SmTe, the $Sm^{2+}(4f^6)$ ion has a nonmagnetic $^7F_0$ 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^{3+}, 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^{3+} ion implies that the extra electron accompanying the Gd^{3+} 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^{2+} exchange in these compounds.[3] It is now generally recognized that the 5*d*, 6*s* 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