[37] J. Rosenthal, L. Yarmus, and R. H. Bartram, Phys. Rev. 153, 407 (1967); R. A. Serway, Phys. Letters 26A, 642 (1968); C. Y. Huang, J. F. Reichert, and J. Gigante, *ibid.* 26A, 219 (1968); R. Calvo and R. Orbach, Phys. Rev. 164, 284 (1967).

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Impurity-Induced *g* Shift of Conduction Electrons

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(Received 6 January 1971)

A simple theory of the *g* shift of conduction electrons induced by nonmagnetic impurities embedded in a metal is described. A single impurity atom is placed at the center of a large sphere containing a free-electron gas. The major contribution to the *g* shift is obtained by calculating the change in the orbital angular momentum due to the spin-orbit interaction. Quite large *g* shifts obtain when the spin-orbit interaction with the impurities is large, when the scattering phase shifts are not too small, when one or more partial waves go through a narrow resonance, or when the phase shifts change rapidly with energy without becoming large, and when the alloys are concentrated. Application of the theory to very dilute lithium alloys has revealed that the *g* shifts are too small to be observable by means of conduction-electron spin resonance. This was confirmed by performing spin-resonance experiments on dilute Li-Zn, Li-Ag, and Li-Cd alloys. The theory presented here provides the extension of the theory of the *g* factor of atomic electrons to the case of electrons in the continuum states.

I. INTRODUCTION AND CONCLUSION

Recently, Slichter and co-workers[1-3] measured and calculated the spin-flip cross section for scattering of conduction electrons from nonmagnetic impurity atoms embedded in lithium and sodium metal. They showed that satisfactory agreement with experimental data can be obtained if it is assumed that the spin-dependent scattering is due to the spin-orbit interaction of the spin of the conduction electron with its orbital motion in the electric field of the impurity atoms. Furthermore, these authors demonstrated that conduction-electron spin-resonance experiments on the alkali metals containing a small concentration of nonmagnetic impurity atoms with a valence different from 1 provide a convenient way to study the electric screening of an excess charge in these metals.

The main purpose of the present paper is to explore the feasibility of obtaining additional knowledge about the electric screening of an excess charge by also measuring and interpreting the *g* shift of the conduction electrons. Although Slichter *et al.* did not report *g*-shift measurements, Hahn and Enderby[4] measured the *g* shift in three dilute lithium alloys. They obtain *g* shifts of $(-7.8\pm 0.6)\times 10^{-3}$, $(-2.2\pm 0.1)\times 10^{-2}$, and $(-3.5\pm 0.1)\times 10^{-2}$ for the alloys Li-0.05 at.% Zn, Li-12 at.% Mg, and Li-0.032 at.% Ag, respectively. These values should be compared with the very small conduction-electron *g* shift of pure lithium,[5] which is -6.1×10^{-5}. The present work was motivated by the desire to understand the (seemingly) large *g* shifts reported in Ref. 4.

In Sec. II we describe the theoretical aspects of this problem. We assume that the difference in *g* shift of the alloy and the pure host metal is also caused by the spin-orbit interaction of the conduction electrons with the impurity atoms. In order to estimate this impurity-induced *g* shift we consider a single impurity immersed in a free-electron gas. For simplicity, the impurity potential is taken to be spherical. It turns out that the theory is particularly simple when the impurity is placed at the center of a sufficiently large perfectly reflecting sphere containing the free-electron gas, and use is made of the angular momentum representation. We show that in a conduction-electron spin-resonance experiment transitions take place between a predominantly spin-up state and a predominantly spin-down state. The predominantly spin-up state is the sum of a large spin-up component and a small spin-down component. Similarly, the predominantly spin-down state consists of a large spin-down part and a small spin-up part. The large components are eigenfunctions of L_z, so that the two states are characterized by the orbital angular momentum quantum number l, the magnetic quantum number m, and the wave number k. The small components vanish in the absence of the spin-orbit interaction. The *g* factor of a conduction electron is associated with the difference in energy of these two states in the presence of a static magnetic field. The impurity-induced *g* shift δg is defined as the deviation of the g factor from its free-electron value. We find that, to first order in the spin-orbit interaction, the dominant contribution to the average g shift of an electron with wave number k is given by

$$\delta g(k) = \frac{4\nu}{9\pi} \sum_{l=0}^{\infty} l(l+1) k \frac{d}{dk} (\eta_{l+1/2} - \eta_{l-1/2}) \ . \qquad (1)$$

Here, $\eta_{l\pm 1/2}$ are the phase shifts of the $(l \pm 1/2)$ partial waves. We note that $\delta g(k)$ is (correctly) proportional to the impurity concentration ν. A notable property of Eq. (1) is the occurrence of the first derivatives of the phase shifts with respect to k. This means that even if the spin-orbit interaction is small, that is, even if $\eta_{l+1/2} - \eta_{l-1/2}$ is small, the g shift can become quite large in case $\eta_{l+1/2} - \eta_{l-1/2}$ has a large slope for a particular value of k. Another way of obtaining a large δg is to assume that for some l both the $(l+1/2)$ partial wave and the $(l-1/2)$ partial wave are in resonance. Ferrell and Prange[6] postulated the existence of a p-wave resonance in the lithium and sodium alloys investigated by Slichter *et al.* in order to explain the dependence of the spin-flip cross section on the valence of the impurity atoms. We are in a position to check this hypothesis by calculating δg, Eq. (1), under the assumption that the $(l=1)$ p waves are in resonance (Sec. III). We find that the width of the partial-wave resonance needed to obtain agreement with Hahn and Enderby's experimental g shift, in, for instance, the Li-Ag alloy, is at least three orders of magnitude smaller than the width estimated by Ferrell and Prange. Rather than searching for possible theoretical explanations of this discrepancy we have preferred to do g-shift measurements ourselves. We thus performed conduction-electron spin-resonance experiments on small particles of dilute Li-Zn, Li-Ag, and Li-Cd alloys. The concentrations of the impurity atoms were always chosen such that the resulting linewidths were of the order of 100 G. With our equipment we would have been able to detect g shifts of at least 10^{-3}. In all three alloys no g shift was observed, in disagreement with the results of Ref. 4. The details of our experiments are described in Sec. IV.

We must conclude that the impurity-induced g shifts in alloys suitable for conduction-electron spin-resonance experiments are too small to be observable. The reason is, of course, that, since the spin-flip cross sections are so large, one must work with extremely dilute alloys so as to obtain resonance lines of reasonably small width (typically 100 G). There are, however, techniques available which can be used to investigate the spin splitting of conduction electrons in more concentrated alloys. One such technique involves the observation of spin-splitting zeros in a de Haas–van Alphen experiment.[7] It would be interesting to search for impurity-induced shifts of the spin-splitting zeros in suitably chosen alloys. It is here that application of our theory seems most promising. Our theory is also of interest, since it sheds light on the interesting but involved phenomenon of conduction-electron spin resonance. Finally, we may regard our theory as the extension of the theory of the Zeeman effect for electrons in atomic states[8] to the case of electrons in the continuum states.

II. THEORY OF δg

As mentioned in the Introduction, we estimate the impurity-induced g shift by placing a single impurity at the center of a large perfectly reflecting sphere (of radius R) containing a free-electron gas. The potential of an electron in the electric field of the impurity is denoted by $V(r)$. The Hamiltonian of an electron is then

$$\mathcal{H} = \frac{p^2}{2m_0} + V(r) + \left(\frac{\hbar}{4m_0^2c^2}\right)[\vec{\sigma}\times\vec{\nabla}V]\cdot\vec{p} \ , \qquad (2)$$

where the last term is the spin-orbit interaction energy and $\vec{\sigma}$ is the Pauli spin operator. Since $V(r)$ is assumed to be spherically symmetric, the spin-orbit interaction energy can be simplified and Eq. (2) becomes

$$\mathcal{H} = \frac{p^2}{2m_0} + V(r) + \left(\frac{\hbar}{4m_0^2c^2}\right)\left(\frac{1}{r}\right)\left(\frac{dV}{dr}\right)\vec{L}\cdot\vec{\sigma} \ . \qquad (3)$$

$\vec{L}$ is the orbital angular momentum operator. In the presence of a magnetic field described by a vector potential $\vec{A}(\vec{r})$, the operator $\vec{p}$ in Eq. (2) must be replaced by $\vec{p} + (e/c)\vec{A}$. It becomes now necessary to choose a particular gauge. In this paper we adopt the customary choice $\vec{A}(\vec{r}) = \frac{1}{2}\vec{H}\times\vec{r}$, which describes a homogeneous static magnetic field $\vec{H}$. If we take $\vec{H}$ in the z direction, we obtain for the Hamiltonian $\mathcal{H}_H$ with the magnetic field on

$$\mathcal{H}_H = \mathcal{H} + \mu_e H\sigma_z + \left(\frac{eH}{2m_0c}\right)(x\pi^y - y\pi^x) + \frac{e^2A^2}{2m_0c^2} \ , \qquad (4)$$

where

$$\frac{\vec{\pi}}{m_0} = \frac{\vec{p}}{m_0} + \left(\frac{\hbar}{4m_0^2c^2}\right)\vec{\sigma}\times\vec{\nabla}V \qquad (5)$$

is the velocity operator in the absence of the magnetic field. μ_e is the intrinsic magnetic moment of the free electron. Substituting Eq. (5) into Eq. (4), and neglecting terms which are second order in the magnetic field, the Hamiltonian becomes finally

$$\mathcal{H}_H = \mathcal{H} + \mu_e H\sigma_z + \left(\frac{eH}{2m_0c}\right)L_z + \left(\frac{\mu_B H}{4m_0c^2}\right)[\vec{r}\times(\vec{\sigma}\times\vec{\nabla}V)]_z \ . \qquad (6)$$

The eigenfunctions of $\mathcal{H}$, Eq. (3), corresponding to the one-electron energy $E=\hbar^2k^2/2m_0$ are well known from scattering theory.[9] They are

$$\psi_k^a(\vec{r})=\frac{1}{r}\,u_k^a(r)\left[\left(\frac{l+m+1}{2l+1}\right)^{1/2}Y_l^m\alpha+\left(\frac{l-m}{2l+1}\right)^{1/2}Y_l^{m+1}\beta\right],$$

$$\psi_k^b(\vec{r})=\frac{1}{r}\,u_k^b(r)\left[-\left(\frac{l-m}{2l+1}\right)^{1/2}Y_l^m\alpha+\left(\frac{l+m+1}{2l+1}\right)^{1/2}Y_l^{m+1}\beta\right]. \tag{7}$$

Here, Y_l^m are normalized spherical harmonics, whereas α and β are the familiar pure spin-up and spin-down functions. The superscripts a and b stand, respectively, for $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$, indicating that ψ_k^a and ψ_k^b are eigenfunctions of $(\vec{L}+\frac{1}{2}\hbar\vec{\sigma})^2$ with eigenvalues $\hbar^2j(j+1)$.

The radial functions u_k^a and u_k^b, Eq. (7), satisfy the ordinary differential equations[9]

$$\frac{d^2u_k^a(r)}{dr^2}+\left(k^2-\frac{l(l+1)}{r^2}-\frac{2m_0}{\hbar^2}\,V(r)-\frac{2m_0l}{\hbar}\,\lambda(r)\right)\times u_k^a(r)=0\ ,$$

$$\frac{d^2u_k^b(r)}{dr^2}+\left(k^2-\frac{l(l+1)}{r^2}-\frac{2m_0}{\hbar^2}\,V(r)+\frac{2m_0(l+1)}{\hbar}\,\lambda(r)\right)\times u_k^b(r)=0\ . \tag{8}$$

Here, $\lambda(r)=(\hbar/4m_0^2c^2)(1/r)(dV/dr)$ is the coefficient of the spin-orbit interaction energy appearing in Eq. (3).

In order to normalize the functions u_k^a and u_k^b we assume that the Fermi energy E_F remains unchanged when the impurity is immersed in the electron gas. The same normalization condition was used in the derivation of the Friedel sum rule.[10] This condition implies that at large distances the electron density associated with all occupied states is not affected by the impurity. Let us denote the radial function in the absence of the spin-orbit interaction by u_k. We require that u_k be normalizable in the large sphere of radius R. The asymptotic form of u_k for large r is then expressed by[11]

$$u_k(r)=\left(\frac{2}{R+d\eta/dk}\right)^{1/2}\sin(kr-\tfrac{1}{2}l\pi+\eta)\ , \tag{9}$$

where η is the phase shift of the lth partial wave. Since the density of a states per unit k (for a given l) is equal to $(2/\pi)(R+d\eta_a/dk)$, our normalization condition leads to the following asymptotic form of u_k^a for large r:

$$u_k^a(r)=\left(\frac{2}{R+d\eta_a/dk}\right)^{1/2}\sin(kr-\tfrac{1}{2}l\pi+\eta_a)\ . \tag{10}$$

Here, η_a is the phase shift of the $j=l+\frac{1}{2}$ partial wave. The asymptotic form of the radial function u_k^b is very similar, except that one must replace η_a in Eq. (10) by η_b, the phase shift of the $j=l-\frac{1}{2}$ partial wave.

In our subsequent considerations we need asymptotic expressions for $\int_0^r(u_k^a)^2\,dr$ and $\int_0^r(u_k^b)^2\,dr$. With the help of Eq. (10) and a method described by Friedel[10] we find

$$\int_0^r(u_k^a)^2\,dr=\frac{r+d\eta_a/dk}{R+d\eta_a/dk}\ ,$$

$$\int_0^r(u_k^b)^2\,dr=\frac{r+d\eta_b/dk}{R+d\eta_b/dk}\ . \tag{11}$$

Actually, Eqs. (11) should be augmented with oscillatory terms, but, as in the derivation of the Friedel sum rule,[10] these have been omitted.

We must now direct our attention to the phenomenon of conduction-electron spin resonance itself. In the absence of the spin-orbit interaction we would describe the spin resonance by noting that a small x-directed oscillating magnetic field causes transitions between the pure spin states $(u_k/r)Y_l^m\alpha$ and $(u_k/r)Y_l^m\beta$, separated in energy by the static magnetic field H. An almost identical description is possible in the presence of the spin-orbit interaction. This becomes clear if it is realized that an originally pure spin-up state acquires a small spin-down component when a small spin-orbit interaction is turned on. Similarly an originally pure spin-down state acquires a small spin-up component. The predominantly spin-up state (denoted by $\phi_{k,\uparrow}$) and the predominantly spin-down state (denoted by $\phi_{k,\downarrow}$) are obtained by forming appropriate linear combinations of ψ_k^a and ψ_k^b, Eq. (7). We find

$$\phi_{k,\uparrow}=\frac{1}{2l+1}\left[(l+m+1)u_k^a+(l-m)u_k^b\right]\frac{1}{r}\,Y_l^m\alpha+\frac{1}{2l+1}\left[(l-m)(l+m+1)\right]^{1/2}(u_k^a-u_k^b)\,\frac{1}{r}\,Y_l^{m+1}\beta \tag{12}$$

and

$$\phi_{k,\downarrow}=\frac{1}{2l+1}\left[(l-m+1)u_k^a+(l+m)u_k^b\right]\frac{1}{r}\,Y_l^m\beta+\frac{1}{2l+1}\left[(l+m)(l-m+1)\right]^{1/2}(u_k^a-u_k^b)\,\frac{1}{r}\,Y_l^{m-1}\alpha\ . \tag{13}$$

In a spin-resonance experiment, the small x-directed field causes transitions between $\phi_{k,\uparrow}$ and $\phi_{k,\downarrow}$. The obvious requirement, that the off-diagonal matrix element of the field-dependent part of the Hamiltonian [i.e., the last three terms of Eq. (6)] for $\phi_{k,\uparrow}$ and $\phi_{k,\downarrow}$ be zero, is, of course, satisfied.

The originally degenerate states $\phi_{k,\uparrow}$ and $\phi_{k,\downarrow}$ will be separated in energy by the static magnetic field. This energy separation ΔE is directly related to the g shift of a conduction electron. We wish to calculate the average contribution $\Delta E(r)$ of the electrons with wave number k in a sphere of radius r (smaller than R) to this energy separation. This quantity is formally defined by

$$\Delta E(r) \equiv \frac{1}{N(r)} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \left(\int_0^r \phi_{k,\uparrow}^{\dagger} (\mathcal{H}_H - \mathcal{H}) \phi_{k,\uparrow}\, d^3r - \int_0^r \phi_{k,\downarrow}^{\dagger} (\mathcal{H}_H - \mathcal{H}) \phi_{k,\downarrow}\, d^3r \right) , \tag{14}$$

where $N(r)$ is the number of electrons with wave number k in the sphere of radius r. Employing Eqs. (6), (12), and (13), we obtain to first order in the spin-orbit interaction

$$\Delta E(r) = \frac{1}{N(r)} \left(2\mu_e H \sum_{l=0}^{\infty} (2l+1) \int_0^r u_k^2\, dr + \tfrac{2}{3}\mu_B H \sum_{l=0}^{\infty} l(l+1) \int_0^r [(u_k^a)^2 - (u_k^b)^2]\, dr + \frac{\mu_B H}{3m_0c^2} \sum_{l=0}^{\infty} (2l+1) \int_0^r u_k^2 r \frac{dV}{dr}\, dr \right) . \tag{15}$$

Here, $N(r)$ is the number of electrons (of one spin) with wave number k in the sphere of radius r, but now in the absence of the spin-orbit interaction, i.e.,

$$N(r) = \sum_{l=0}^{\infty} (2l+1) \int_0^r u_k^2\, dr . \tag{16}$$

The first term of Eq. (15) is the contribution of the σ_z term of $\mathcal{H}_H$, Eq. (6); the second term is the contribution of the L_z term of $\mathcal{H}_H$; and the last term is the contribution of the last term of $\mathcal{H}_H$. The σ_z term of $\mathcal{H}_H$ does not give rise to first-order (spin-orbit) contributions to $\Delta E(r)$. In deriving Eq. (15) we have used the fact that $2[(l+1)u^a + lu^b][u^a - u^b] = (2l+1)[(u^a)^2 - (u^b)^2]$ to first order in the spin-orbit interaction. We will now rewrite Eq. (15). We write

$$u_k^2 = (2/R)(kr)^2 j_l^2(kr) + [u_k^2 - (2/R)(kr)^2 j_l^2(kr)] ,$$

where $j_l(kr)$ is the spherical Bessel function. Further, we make use of the fact that $\sum_{l=0}^{\infty}(2l+1) j_l^2(kr) = 1$. Next, let there be N electrons in the volume $\frac{4}{3}\pi r^3$ whose wave number is less than k, and let there be n impurities in the same volume. Then, by employing Eqs. (11) we find to lowest order in R^{-1} and for sufficiently large r that

$$\frac{\Delta E(r)}{\mu_B H} - \frac{2\mu_e}{\mu_B} = \frac{4\nu}{9\pi} \sum_{l=0}^{\infty} l(l+1) k \frac{d}{dk} (\eta_a - \eta_b) + \frac{2\nu}{9\pi m_0 c^2} \sum_{l=0}^{\infty} (2l+1) kR \int_0^r u_k^2 r \frac{dV}{dr}\, dr , \tag{17}$$

where ν is n/N, i.e., the impurity concentration when k is equal to the Fermi wave number k_F. Since the excess charge introduced by the impurity is screened at a sufficiently large distance, we may interpret Eq. (17) as the impurity-induced g shift, δg, of a conduction electron in a bulk sample. Actually there is another contribution to the g shift arising from the relativistic change in mass.[12,13] This contribution is not likely to be changed significantly by the introduction of the impurities, and will therefore not be included in δg. The last term of Eq. (17) can be estimated by replacing u_k by $(2/R)^{1/2}(kr) j_l(kr)$ and performing a partial integration. For a square-well potential of depth $-V_0$ and width a_0 ($< r$) we find for this term $(4\nu k^3 a_0^3 V_0 / 9\pi m_0 c^2)$ which is only of the order of $2\times10^{-6}\nu$ for $V_0 = 1$ eV, $k = 10^8$ cm^{-1}, and $a_0 = 2$ Å. This contribution to δg will also not be retained. The remaining term of Eq. (17) is the contribution to δg discussed in the Introduction, i.e., Eq. (1). Since this term contains the derivative of the phase shifts with respect to k, it could become rather large. In Sec. III we will estimate this contribution to δg.

We wish to remark that since the phase shifts must obey the Friedel sum rule, the expression, Eq. (1), for δg already contains many-electron effects. We further note that there is no obvious relation between this expression for δg and the spin-flip cross section, e.g., Eq. (13) of Ref. 2.

III. NUMERICAL ESTIMATE OF δg

With Ferrell and Prange[6] we assume that both the $j=\frac{3}{2}$ and $j=\frac{1}{2}$ p waves are in resonance, i.e., we assume that

$$\begin{aligned} \cot\eta_{3/2} &= 2(E - E_{3/2})/\Gamma , \\ \cot\eta_{1/2} &= 2(E - E_{1/2})/\Gamma , \end{aligned} \tag{18}$$

where Γ is the width of the resonance, and $E_{3/2} - E_{1/2} = \Delta$ is the spin-orbit splitting of the $l=1$ p state. Employing Eqs. (18) we obtain for Eq. (1) (keeping only the $l=1$ term)

$$\frac{\delta g}{\nu} = -\left(\frac{64}{9\pi}\right)\left(\frac{E_F\Delta}{\Gamma^2}\right) \sin^2\eta_1 \sin 2\eta_1 . \tag{19}$$

One sees that a large g shift results when the p-wave resonance is narrow and when the corresponding phase shift is large. In fact the factor $\sin^2\eta_1 \sin 2\eta_1$ has a maximum value of $\frac{3}{8}\sqrt{3}$ which occurs for $\eta = \pi/3$. Thus for $E_F = 4.7$ eV (i.e., the Fermi energy of lithium), $\Delta = 1$ eV, and $\Gamma = 1$ eV, $\delta g/\nu$ could become as large as approximately -7.

Let us now apply Eq. (19) to a dilute Li-Ag alloy. For Δ we take 0.114 eV, which is the spin-orbit splitting of the atomic $5p$ state,[12] whereas for Γ we substitute 3 eV, which was approximately the value needed by Ferrell and Prange to obtain agreement with the spin-flip cross-section data. Finally, for η_1 we use the value calculated by Ball *et al.*,[2] namely, 0.046. We find $\delta g/\nu = -2.6\times10^{-5}$. This[4] is seven orders of magnitude smaller than the measured value -1.1×10^{2}! We predict that the g shift in a 0.01-at.% Li-Ag alloy (i.e., an alloy which produces a spin-resonance linewidth of approximately 100 G)[1] is -2.6×10^{-9}. This is completely negligible. The situation is somewhat more favorable in a dilute Li-Sn alloy. We choose again a 0.01-at.% alloy so as to produce a spin-resonance linewidth of approximately 60 G.[1] For Γ we take again 3 eV, whereas Δ is now 0.45 eV,[12] and $\eta_1 = 1.117$ (see Ref. 2). We find $\delta g/\nu = -0.34$ and $\delta g = -3.4\times10^{-5}$. This is still negligibly small. We must therefore conclude that our theory is not capable of reproducing the large values of $\delta g/\nu$ and δg in dilute lithium alloys as reported in Ref. 4. This conclusion receives support from the negative results of our own spin-resonance experiments on some dilute lithium alloys. These experiments will be described in Sec. IV.

IV. EXPERIMENTAL ASPECTS

Experimental determinations of the g shift of conduction electrons are complicated by resonance line shapes. For particle sizes less than the skin depth conduction-electron spin-resonance line shapes are Lorentzian. Most measurements, however, are made in the microwave frequency region (10 GHz) to achieve high sensitivity and the ability to measure very broad lines. Under these circumstances it is difficult to prepare lithium particles smaller than the skin depth which is of the order of 1 μ for 300 °K at X band. The resonance line shapes which result for samples larger than the skin depth are affected by eddy currents and diffusion of electrons into and out of the skin depth. Dyson[14] was the first to perform a calculation of the line shape taking diffusion into account. More recent calculations include those of Lampe and Platzman,[15] and of Lewis and Carver.[16]

Our initial attempt to measure impurity-induced g shifts in dilute lithium alloys entailed using mineral oil dispersions with particle sizes large with respect to the skin depth. However, erratic deviations from Dyson's results, believed to be caused by surface oxidation, produced errors too large to maintain desired sensitivity. Consequently, our efforts were directed toward producing particles small with respect to the skin depth. In the small-particle limit, the center of the resonance line is well defined and the determination of g values is straightforward. Furthermore, the increased surface area of small-particle samples enhances the signal-to-noise ratio.

The dilute lithium alloys were prepared from 99.9% lithium. The doping materials (Ag, Zn, and Cd) had purities of 99.95% or better. The alloying technique has been described elsewhere.[1] The dispersions were prepared by placing 2 cm^3 of alloy, $\frac{1}{10}$ cm^3 oleic acid, and 10 cm^3 of degassed mineral oil in a stainless-steel cup, heating this under an inert atmosphere to 200 °C, and then agitating with a 750-W/in.^{2} ultrasonic cell disrupter for 5 min. This high-power cell disrupter provided sufficient agitation to produce particles smaller than the skin depth.

The conduction-electron spin-resonance signals were measured using a Varian X-band spectrometer with 100-kHz field modulation and phase-sensitive detection. The signal from the phase-sensitive detector was repeatedly fed into a Hewlett-Packard signal averager to enhance the signal-to-noise ratio. The impurity-induced g shifts were measured by comparing the center of the broad alloy signal (typically 100 G) with that of the narrow signal of pure lithium (2 G). Magnetic fields were measured by monitoring a proton resonance fluxmeter.

Several concentrations of three different alloy systems were investigated. No measurable g shifts were observed. By estimation of the experimental error we were able to put an upper bound on $\delta g/\nu$. These values are $|0.015|$ for Li-Zn, $|0.1|$ for Li-Ag, and $|0.15|$ for Li-Cd. These upper bounds are at least an order of magnitude smaller than the values of $\delta g/\nu$ reported in the literature.[4] It should be noted that the primary factor involved in determining the experimental error is finding the center of the signal. Consequently, using higher concentrations to give larger g shifts does not yield better limits on $\delta g/\nu$, since the broader lines result in a poorer signal-to-noise ratio.

We may conclude that conduction-electron spin resonance is not ideally suited to observe impurity-induced g shifts. As was shown in the previous sections, large g shifts occur when the spin-orbit interaction is large, when the phase shifts are not too small, when one or more partial waves are in resonance, or when the phase shifts go through rapid changes without necessarily becoming large, and, of course, when the concentration is high. These are precisely the conditions which result in broad conduction-electron spin-resonance lines, or under which spin resonance is not observable at all. There exist, however, other methods which can be used to study the spin splitting of the conduction electrons more easily. One of these involves the observation of spin-splitting zeros in a de Haas–van Alphen measurement.[7] It would be interesting to perform de Haas–van Alphen measurements on suitable not too dilute nonmagnetic alloys[17] and search for impurity-induced shifts of the spin-splitting zeros.

*Supported in part by the U. S. A. E. C., Contract No. AT(11-1)-1054.

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[1] J. R. Asik, M. A. Ball, and C. P. Slichter, Phys. Rev. 181, 645 (1969).

[2] M. A. Ball, J. R. Asik, and C. P. Slichter, Phys. Rev. 181, 662 (1969).

[3] E. K. Cornell and C. P. Slichter, Phys. Rev. 180, 358 (1969).

[4] C. E. W. Hahn and J. E. Enderby, Proc. Phys. Soc. (London) 92, 418 (1967).

[5] N. S. VanderVen, Phys. Rev. 168, 787 (1968).

[6] R. A. Ferrell and R. E. Prange, Phys. Rev. Letters 17, 163 (1966).

[7] S. Hornfeldt, J. B. Ketterson, and L. R. Windmiller, Phys. Rev. Letters 23, 1292 (1969).

[8] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, New York, 1957), p. 205.

[9] L. S. Rodberg and R. M. Thaler, *The Quantum Theory of Scattering* (Academic , New York, 1967), p. 281.

[10] J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958).

[11] J. Kondo, Solid State Phys. 23, 183 (1969).

[12] Y. Yafet, Solid State Phys. 14, 1 (1963).

[13] A. W. Overhauser and A. M. de Graaf, Phys. Rev. Letters 22, 127 (1969).

[14] F. J. Dyson, Phys. Rev. 98, 349 (1955).

[15] M. Lampe and P. M. Platzman, Phys. Rev. 150, 340 (1966).

[16] R. B. Lewis and T. R. Carver, Phys. Rev. 155, 309 (1967).

[17] Our theory is not applicable to magnetic alloys. It might prove interesting to extend the theory to magnetic alloys where impurity-induced shifts of the spin-splitting zeros apparently have been observed; see P. T. Coleridge and I. M. Templeton, Phys. Rev. Letters 24, 108 (1970).

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EPR and Optical Studies of Cu^{2+} in Dodecahedral Configuration

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(Received 31 July 1970)

The EPR and polarized optical spectra of copper calcium acetate hexahydrate and Cu^{2+} doped in isomorphous cadmium calcium acetate hexahydrate have been investigated in the range of temperature 300–77 °K. g values in both concentrated and doped crystals are found to be the same, indicating the identical ligand fields. The spin-Hamiltonian parameters remain unchanged throughout the temperature range. The parameters are $g_{\parallel} = 2.360 \pm 0.005$, $g_{\perp} = 2.060 \pm 0.005$, $|A_{\parallel}| = 0.0119 \pm 0.0002\ \text{cm}^{-1}$, $|A_{\perp}| = 0.0013 \pm 0.0002\ \text{cm}^{-1}$. Detailed study of the linewidth has established the important contributions of the exchange, hyperfine, and crystal fields. The observed optical bands at 12 800 and 14 000 cm^{-1} exhibit polarization and have intensities characteristic of ligand field bands. With the knowledge of relative magnitudes of g ($g_{\parallel} > g_{\perp}$), assignments of the bands have been made, consistent with the D_{2d} symmetry of the ligand field. The analysis has revealed that the $3d^9$-$3d^84p$ configuration interaction is rather small (at most 2%) in these noncentrosymmetric complexes, and the covalent metal-ligand interaction is more pronounced in the ground state than in the excited states.

I. INTRODUCTION

X-ray structure investigations[1] of isomorphous copper calcium acetate hexahydrate and cadium calcium acetate hexahydrate reveal that in these crystals, M^{2+} ions (Cu^{2+} and Cd^{2+}) are coordinated with oxygen ligands in an irregular dodecahedral configuration (Fig. 1), the distortion being more pronounced in the former case. Preliminary EPR[2,3] and magnetic studies[2,4] only in the case of copper calcium acetate have appeared in the literature. Detailed EPR and optical studies of Cu^{2+} in copper calcium acetate hexahydrate and Cu^{2+} in cadmium calcium acetate have been undertaken with the following objectives: (i) to see whether the observed distortions are solely due to solid-state forces or whether the configurational stability of the molecular complex $[MO_8]$ has a positive role, (ii) to obtain an understanding of the relative magnitudes of various dynamical interactions and to assess the contribution from an anisotropic hyperfine coupling tensor, if any, to the anisotropic EPR linewidth, and (iii) to probe into the nature of the Stark pattern of a Cu^{2+} ion in the metal acetate hexahydrate crystal environments.

The paramagnetic complex has approximate D_{2d}