Anisotropic Behavior of Dilute Scandium-Gadolinium Alloys*

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The g value for electron spin resonance of Gd impurities in Sc is found to be anistropic. The anisotropy is shown to result from spin-orbit coupling in the impurity cell.

Gadolinium impurities have long been known[1] to behave like S-state ions in solution. It is somewhat surprising, therefore, that the effective moment of Gd impurities in Sc is strongly anisotropic[2] and considerably larger[3] than the moment in metallic Gd. Fradin *et al.*[3] attributed the large moment to induced spin polarization on nearest-neighbor sites, and the anisotropy, at least in part, to an induced orbital moment in the impurity cell.[4] In order to study this system further, we have made electron-spin-resonance measurements on portions of the crystals used in the susceptibility experiments. Resonance signals were observed in samples with Gd concentrations in the range 500-10 000 ppm. In the more concentrated samples a second, narrower line was observed which did not exhibit the behavior described below. We believe that this line is due to Gd clusters.

Resonance data were obtained by standard methods using an X-band spectrometer. The spectra were fitted to Dyson-type lines, using Lorentzian and Gaussian shapes, by means of a least squares fitting procedure. Somewhat better fits resulted with Gaussian shapes, and these are reported here. The g value is independent of the shape used.

The g value for the 500-ppm sample is shown in Fig. 1(a) as a function of the angle between the dc field and the c axis. The samples were polished to a cylindrical shape in order to avoid demagnetizing effects. Further, the impurity magnetization is negligibly small at this concentration. The g value along the c axis ($\theta = 0$) is considerably larger than in the a-axis direction and passes through $g = 2.00$ at $\theta \cong 60°$. In the simple theory,[1] this requires that the s-f exchange energy vanish, but since the moment per impurity is larger than the ionic value at all angles,[2] some coupling must remain. The deviations from $\cos^2\theta$ behavior are larger than experimental error; a better fit is obtained when g is plotted against $\cos^4\theta$.

Shown in Fig. 1(b) is the anisotropy of the linewidth for the same sample, calculated for Gaussian lines. The errors in the linewidth are much larger than in the g value, but it seems clear that there is a minimum near the angle for which $g = 2$. Since both the linewidth and g shift in metals are dominated by the conduction electrons, we conclude that the observed behavior reflects an anisotropy in the impurity–conduction-electron coupling rather than crystal-field splitting of the impurity f levels. The conjecture is supported by the behavior of Gd ions in a variety of other hosts.[1,5]

Local-moment–conduction-electron coupling has been shown[6] to result from the interplay of two mechanisms: the ferromagnetic exchange interaction and the antiferromagnetic mixing exchange. The mixing interaction can couple the local moment only to conduction states having the same parity as the impurity levels. In the case of Gd, this is further restricted to $l = 3$ partial waves of the conduction-electron wave function.[6] With Sc as the host metal, the situa-

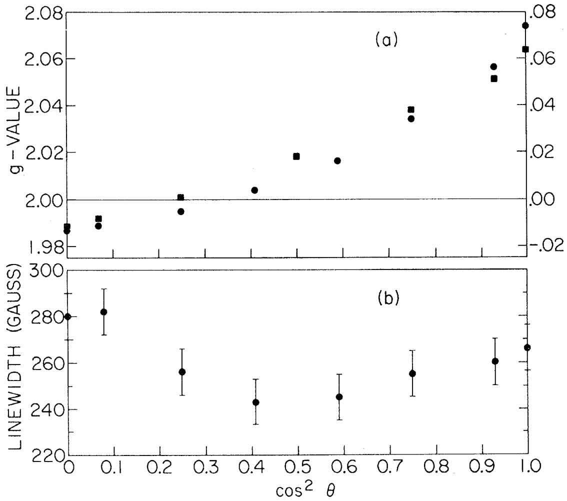

FIG. 1. (a) The g value of the spin resonance of Gd impurities in Sc. The data indicated by circles were taken at 3.0 K, and by squares at 4.2 K. Both sets are for a Gd concentration of 500 ppm. The angle is measured from the hexagonal c axis. (b) Linewidth at 3.0 K for the 500-ppm alloy. The widths are calculated for Gaussian lines.

tion is complicated still further by crystal-field splitting of the d bands and s-d hybridization. There are four bands at the Fermi surface of Sc, which form interlocking hole and electron surfaces.[7] Portions of the hole surface are doubly degenerate. The anisotropy of the nuclear relaxation[8] in Sc has shown that 20% of the density of states at E_F is due to tight-binding d-wave functions of E'' symmetry, and the remainder to s-d states of A_1' symmetry. It is customary, nonetheless, to introduce an effective molecular-field coupling between the impurity moment and the magnetization of the host conduction electrons. This seriously oversimplifies the actual situation and masks the effects of local variations in the conduction-electron susceptibility.

In order to improve the situation somewhat, we make the assumption that the electrons in the hybridized s-d orbitals are coupled to the impurity by a net antiferromagnetic exchange interaction $-J_1$, while those in the degenerate d levels couple with a net ferromagnetic exchange J_2. This is a reasonable separation since the mixing exchange is inoperative between d electrons and f levels.

We may write, then,

$$\Delta g = (-J_1\chi_1 + J_2\chi_2)/2\mu_B^2, \tag{1}$$

where χ_1 and χ_2 are the contributions to the electronic susceptibility per atom from the s-d and the d orbitals, respectively. We anticipate that local spin-orbit splitting of the d levels is the source of the anisotropy in Δg, modifying the locally enhanced susceptibility χ_2.

We now consider a simplified model in which a twofold degenerate band contains one electron per atom. We restrict ourselves to the case of Sc, for which this band is constructed from tight-binding wave functions of E'' symmetry, which transform as linear combinations of $Y_2^{\pm 1}(\theta, \varphi)$ under the covering operations of the group D_{3h}. The z axis coincides with the hexagonal c axis. Since Gd and Sc are isoelectronic, we assume that the major contribution to the impurity potential is due to spin-orbit coupling, which is $\lambda \cong 1000\ \mathrm{cm}^{-1}$ for Gd as compared with $\lambda < 100\ \mathrm{cm}^{-1}$ for Sc. With the magnetic field along the c axis the impurity potential, ignoring the hybridized band, is[10]

$$\mathcal{H}_i = E\sum_{m\sigma} n_{m\sigma} + \tfrac{1}{2}\lambda \sum_{\sigma}(n_{2\sigma} - n_{1\sigma}) + 2\mu_B H(n_{2-} - n_{2+}) + \tfrac{1}{2}(U-J)\sum_{m\neq m';\sigma} n_{m\sigma}n_{m'\sigma} + U\sum_{mm'} n_{m+}n_{m'-}, \tag{2}$$

where $n_{m\pm} = c_{m\pm}^\dagger c_{m\pm}$, and $c_{m\pm}^\dagger$ creates a d electron in the mth orbital on the impurity. These orbitals are eigenstates of $\mathcal{H}_{\mathrm{s.o.}} = \lambda \vec{l}\cdot\vec{s}$, with $m = 1$ the ground state, and $m = 2$ the excited state. These correspond to $j_z = \pm\frac{1}{2}$ and $\pm\frac{3}{2}$, respectively. For $m = 1$ states, the orbital moment cancels the spin moment $(l_z + 2s_z = 0)$ and there is no splitting in a field. For $m = 2$ states, the orbital moment adds to the spin moment giving twice the usual splitting.

When H is along the a axis, the Zeeman term in (2) is

$$\mathcal{H}_z = i\mu_B H[c_{2-}^\dagger c_{1+} - c_{1+}^\dagger c_{2-} + c_{1-}^\dagger c_{2+} - c_{2+}^\dagger c_{1-}]. \tag{3}$$

The spin-orbit and Zeeman terms are diagonalized by the substitution

$$b_{m+}^\dagger = [(\tfrac{1}{2}\lambda + \Lambda)c_{m\pm}^\dagger \pm i\mu_B H c_{m'\mp}^\dagger]/(2\Lambda^2 + \lambda\Lambda)^{1/2}, \quad m \neq m, \tag{4}$$

where $\Lambda = (\frac{1}{4}\lambda^2 + \mu_B^2 H^2)^{1/2}$. The interaction Hamiltonian then becomes

$$\mathcal{H}_i' = E\sum_{m\sigma} n_{m\sigma}' + \Lambda\sum_{\sigma}(n_{2\sigma}' - n_{1\sigma}') + \tfrac{1}{2}(U-J)\sum_{m\neq m';\sigma} n_{m\sigma}'n_{m'\sigma}' + U\sum n_{m+}'n_{m-}', \tag{5}$$

where $n_{m\sigma}' = b_{m\sigma}^\dagger b_{m\sigma}$. Because the new states are no longer true one-electron orbitals, the Coulomb and exchange terms are only approximate. So long as the admixture is small, this should not be a serious error, but our results are not valid in the limit of small spin-orbit coupling.

In the Hartree-Fock approximation we obtain one-electron energies from (2) and (5) which are

$$E_{m\pm}^c = E + (-1)^m\lambda \mp 2(m-1)\mu_B H + (U-J)\sum_{m'\neq m} \bar{n}_{m'\pm} + U\sum_{m'} \bar{n}_{m'\mp},$$

$$E_{m\pm}^a = E + (-1)^m\Lambda + (U-J)\sum_{m'\neq m} \bar{n}_{m\pm}' + U\sum_{m'} \bar{n}_{m'\mp}' \tag{6}$$

for H parallel to the c and a axis, respectively. The bar denotes the average occupancy of a level. The absence of a splitting of the orbitals when the magnetic field is along the a axis reflects the anisotropic g factors of the spin-orbit-split levels.

We now assume the density of states for the d band to be a Lorentzian of the form[10] $\rho_d(\epsilon) = w/\pi(w^2+\epsilon^2)$. In the pure metal each sub-band contains $\frac{1}{4}$ electron which implies that $E_F = -w$ and that $\rho_d(E_F) = (2\pi w)^{-1}$ in each sub-band. The occupancy of the impurity levels is well known[10] to be $\bar{n}_{m\sigma} = \pi^{-1}\cot^{-1}(1+E_{m\sigma}/w)$ for these conditions. Assuming that the impurity potential E adjusts to localize one screening electron, we expand about the average occupancy and solve the resultant set of linear equations to find that

$$\bar{n}_{m\pm} = \tfrac{1}{4} + (-1)^{m+1}\frac{\lambda\rho_d(E_F)/2}{1-(U-J)\rho_d(E_F)} \pm \frac{2(m-1)\mu_B H\rho_d(E_F)}{1-(U+J)\rho_d(E_F)} \tag{7}$$

for H along the c axis, and

$$\bar{n}_{m\pm}' = \tfrac{1}{4} + (-1)^{m+1}\Lambda\rho_d(E_F)/[1-(U-J)\rho_d(E_F)] \tag{8}$$

for H parallel to the a axis. The splittings are sketched in Fig. 2. In the first case, the moment in the impurity cell due to the spin is

$$\begin{aligned} m_c &= \mu_B \textstyle\sum_m(\bar{n}_{m+}-\bar{n}_{m-}) \\ &= 4\mu_B^2\rho_d(E_F)H/[1-(U+J)\rho_d(E_F)]. \end{aligned} \tag{9}$$

In the second case the moment is due to the admixture of up- and down-spin states. An electron in the mth orbital contributes $(-1)^{m+1}\mu_B^2H/\Lambda$ to the magnetic moment in the impurity cell, so that

$$\begin{aligned} m_a &= (\mu_B^2H/\Lambda)\textstyle\sum_{m\sigma}(-1)^{m+1}\bar{n}_{m\sigma}' \\ &= 4\mu_B^2\rho_d(E_F)H/[1-(U-J)\rho_d(E_F)]. \end{aligned} \tag{10}$$

The anisotropy in the moment arises from the effect of the exchange interaction on the impurity orbitals: It opposes the Coulomb interaction in the splitting of like-spin states under the spin-orbit interaction, but assists in the splitting of opposite-spin states. This difference in enhancement is responsible for the quenching of the orbital moment in the Anderson model, for which more detailed calculations have been made.[11]

We have shown that the enhanced conduction-electron susceptibility becomes anisotropic under the influence of spin-orbit coupling. It will, therefore, give rise to an anisotropic Knight shift of the Gd local-moment resonance through Eq. (1). To compare the anisotropy with experiment we make the simplifying assumptions that $U=J$, that the locally enhanced susceptibility given by (9) is the same as for a Sc site, and that the d band contributes a fraction $f \cong 0.2$ to the total susceptibility per atom. From (1) we find that

$$\begin{aligned} \Delta g_c &= [-(1-f)J_1 + fJ_2]\chi_{\mathrm{Sc}}/2\mu_B^2N, \\ \Delta g_a &= [-(1-f)J_1 + fJ_2/\zeta]\chi_{\mathrm{Sc}}/2\mu_B^2N, \end{aligned} \tag{11}$$

where $\chi_{\mathrm{Sc}} = 3.7\times10^{-4}$ emu/mole and the enhancement factor $\zeta = 3.5$.[8] Solving for J_1 and J_2 from the observed g values we find $J_1 \cong 0.01$ eV and $J_2 \cong 0.1$ eV. This value for J_2 agrees with the direct exchange energy calculated for Gd impurities using orthogonalized plane wave functions.[6] The small value for J_1 is probably due to a near cancelation of mixing- and direct-exchange interactions in the s-d band. If $U-J \neq 0$, the anisotropy is reduced and ζ tends toward unity.

The linewidth data is not sufficiently accurate to obtain the temperature-dependent part. The width of the resonance indicates that the bottle-

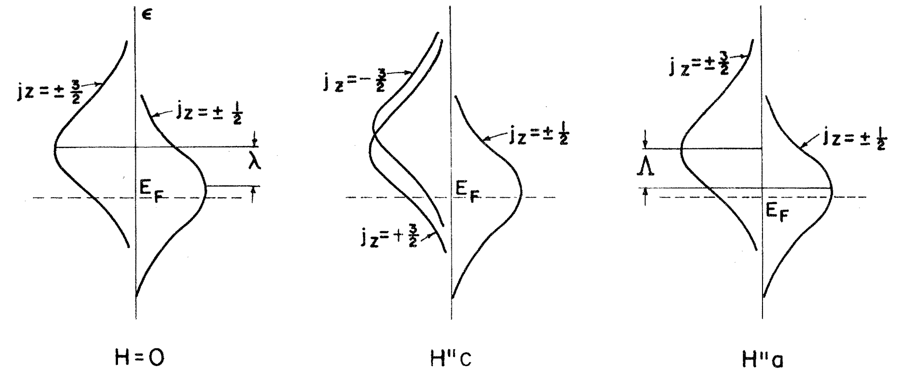

FIG. 2. Occupations of the four E'' sub-bands in the impurity cell as a function of magnetic field. The splittings are exaggerated. The right-hand curve corresponds to $m=1$. The enhanced splitting of the $j_z = \pm\frac{3}{2}$ states gives rise to the large spin moment when $H\|c$.

neck[12] is not effective. The minimum may then be attributed to a Korringa relation between the g shift and the linewidth, and will occur where $\Delta g = 0$.

In summary, we have shown that suppression of the Zeeman splitting by the spin-orbit interaction produces an anisotropically enhanced local susceptibility. This anisotropy is reflected in the g value of the impurity resonance. In our model it is the cancelation of the molecular fields from the various bands in Sc rather than the disappearance of the local-moment–conduction-electron coupling which allows the g shift to pass through zero. Since the anisotropic orbital moment will remain, and since the cancelation need not extend beyond the impurity cell, the presence of an excess moment at all angles does not seem to be in contradiction with our results.

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Electronic Heat Capacity and Susceptibility of Small Metal Particles*

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Detailed calculations of the temperature dependence of the heat capacity and magnetic spin susceptibility of small metal particles are presented. The results depend sensitively upon the symmetries or near symmetries of the dynamics, and exhibit the usual thermodynamic behavior only as the particle size becomes sufficiently large.

The electronic properties of an assembly of small metal particles are determined by and reflect the distribution of the electronic energy levels. This distribution may contain strong correlations arising, for example, from the presence of localized impurities or surface states. Alternatively, if such correlations are absent, one has a more universal problem in which it becomes reasonable to treat the level distribution statistically. The statistical characteristics of the energy level distribution are then determined by (1) the particle size distribution, (2) a mean single-electron-level spacing δ for particles of a particular size, and (3) the symmetry of the dynamics. The problem of a statistical level distribution was first considered by Kubo[1] who assumed a random distribution and calculated the electronic heat capacity and spin susceptibility for the limiting cases $\delta \ll kT$ and $\delta \gg kT$. Subsequently Gor'kov and Eliashberg[2] showed that the correlations between levels could lead to qualitatively different results for these quantities at low temperatures.

In this Letter we present detailed calculations of the heat capacity and magnetic spin susceptibility of metal particles for the whole temperature range and for different statistical assumptions. Our special aim is to encourage experi-