Transmission Electron-Spin-Resonance Measurements of Exchange and Crystal Field Parameters in Dilute *Al*:Er Alloys*

J. F. Siebert,† S. A. Dodds, and R. H. Silsbee
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
(Received 4 March 1974)

We report transmission electron-spin-resonance and EPR measurements on unbottlenecked *Al*:Er dilute alloys. We have derived theoretical expressions for the effects of the exchange and crystal-field interactions on the properties of the resonances. A computer fit of these expressions to the data yields the crystal-field parameters, the sign, magnitude, and a measure of the k dependence of the exchange interaction, and the spin-flip scattering cross section and free-ion g value of the Er impurities.

In this paper we would like to show, using the *unbottlenecked* system of *Al*:Er as our example, that the properties of the conduction-electron spin resonance ($g \cong 2$) combined with the properties of the normal reflection EPR of the Er^{3+} ions ($g \cong 6.8$) yield useful information about the magnitude, sign, and k dependence of the exchange coupling between the two spin systems, the crystal-field splittings of the rare-earth f shell due to its cubic metallic environment, and the spin-flip scattering cross section and free-ion g value of the Er impurities.

The conduction-electron spin resonance was measured by using the transmission electron-spin-resonance (TESR) technique.[1] Aluminum was chosen as the host metal because it has a strong TESR signal up to liquid-nitrogen temperatures, it has a nearly-free-electron conduction band, and there is no charge contrast between it and the trivalent rare-earth impurities. Because of the high reactivity and low solid solubility of rare-earth impurities in aluminum, reliable samples could not be prepared by conventional methods. Instead, a "getter-sputtering" technique[1] was used to prepare Al foils of appropriate thickness (0.05 mm) containing Er impurities in the 5–35-ppm concentration range. Consistent scaling of neutron-activation analysis, TESR results, and resistivity measurements indicate that the samples are metallurgically satisfactory, with absolute concentrations accurate to ± 10%.

The experimental points in Figs. 1 and 2 show the temperature dependence of the impurity-induced g shift and linewidth of the TESR for two *Al*:Er alloys.[2] The main features of the experimental data can be understood qualitatively as follows:

(1) *g value.*—The dramatic increase in g value as the temperature is lowered can be attributed to a *positive* (ferromagnetic) exchange interaction between the conduction-electron spins and the temperature-dependent magnetization of the Er ions, the converse of the Knight shift. Although the temperature dependence of the rare-earth magnetization is dominated by the $1/T$ contribution of the ground-state Γ_7 doublet of the Er impurities, a complete analysis shows that Brillouin saturation effects at low temperatures and contributions from higher crystal-field multiplets produce significant deviations from a simple Curie-like temperature dependence.

(2) *Linewidth.*—We assume that the impurities contribute to the TESR linewidth in two ways. There is a temperature-independent term $\Delta H_{s.o.}$ due to spin-flip scattering via spin-orbit interaction in the outer electron shells of the rare-earth ions[3] (a process assumed to be independent of the presence of a local moment), and a tem-

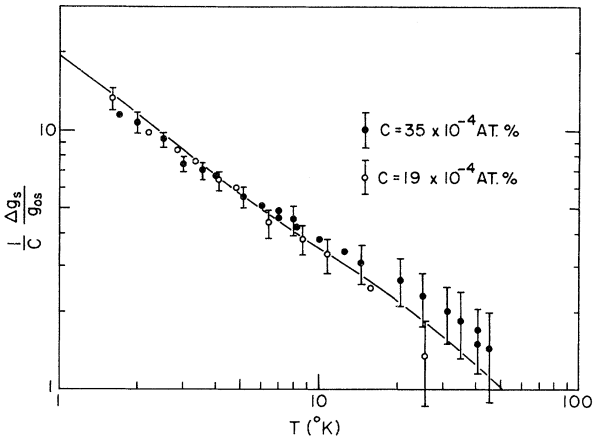

FIG. 1. Temperature dependence of the impurity-induced TESR fractional g shift $\Delta g_s/g_{0s}$ per Er impurity concentration c (expressed in at.%). The solid lines in both figures are theoretical fits to the data, as described in the text. All measurements were made at 9.2 GHz and referenced to the pure-Al g value $g_{0s} = 1.997$ (Ref. 2).

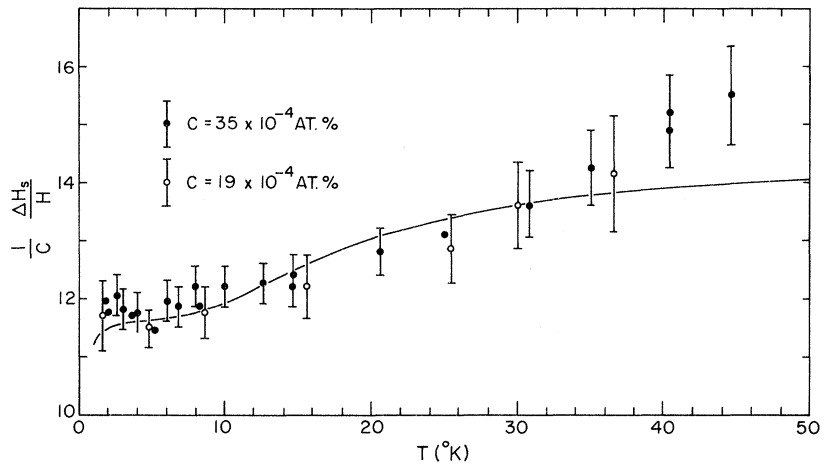

FIG. 2. Temperature dependence of the impurity contribution to the TESR fractional linewidth $\Delta H_s/H$ (where $\Delta H_s \equiv 1/\gamma T_2$) per Er impurity concentration c (expressed in at.%), where H is the measured resonance field. The background linewidth of pure Al over this temperature range (Ref. 2) was assumed to be additive and was subtracted out.

perature-dependent term ΔH_{ex} due to exchange scattering with the local moment of the rare-earth $4f$ shell. This latter process is temperature dependent because the magnetic moment, and therefore the exchange scattering, depends sensitively upon the thermal populations of the various crystal-field levels of the rare-earth f shell. Although both contributions scale with concentration, this temperature dependence allows us to study the exchange-scattering mechanism separately.

This qualitative description can be formalized by assuming an exchange interaction of the form $-(g_J-1)J(\vec{r})\vec{J}\cdot\vec{s}$, where $J(\vec{r})$ characterizes the strength and the range of the interaction between a conduction-electron spin $\vec{s}$ and a local moment of angular momentum $\vec{J}$. Neglecting electron-electron enhancement of the host, we then compute expressions for the local-moment contribution to the fractional change in g value and linewidth of the TESR as[1]

$$\frac{\Delta g_s}{g_{0s}} = \frac{c(g_J-1)\langle J(\vec{k},\vec{k})\rangle_{E_F}\langle J_z\rangle}{g_s\mu_B H}, \tag{1}$$

$$\frac{\Delta H_{ex}}{H} = \frac{\pi\rho c(g_J-1)^2\langle|J(\vec{k},\vec{k}')|^2\rangle_{E_F}\langle G\rangle}{g_s\mu_B H}, \tag{2}$$

where g_J is the Lande g factor, c is the fractional impurity concentration, and ρ is the density of states, per atom, of conduction electrons of one spin direction at the Fermi energy. We have defined $J(\vec{k},\vec{k}') = N_0(\vec{k}|J(\vec{r})|\vec{k}')$, where N_0 is the host atomic density and the states $|\vec{k})$ are the exact one-electron states of electrons moving in the electric field of the lattice *and* the impurity, but neglecting the exchange interaction. In the expressions above the value of the k-dependent exchange energy is averaged over the Fermi surface. The dependence of the g shift and linewidth on temperature and crystal-field splittings is contained in the thermal averages[1]

$$\langle J_z\rangle = Z^{-1}\textstyle\sum_a (a|J_z|a)\exp(-E_a/kT), \tag{3}$$

$$\langle G\rangle = \frac{1}{Z}\sum_{a,b}|(b|J_+|a)|^2 \times \frac{(E_b-E_a)/kT}{\exp(E_b/kT)-\exp(E_a/kT)}, \tag{4}$$

where $|a)$ and E_a are the $2J+1$ exact eigenstates and eigenenergies of the rare-earth f shell in the presence of both the host crystal field and the external magnetic field applied in the z direction, and Z is the appropriate partition function. $\langle J_z\rangle$ is just the mean z component of the total ionic angular momentum, and $\langle G\rangle$ is a similarly defined function that characterizes the exchange scattering. In the high-temperature limit, $\langle G\rangle$ saturates at $\frac{2}{3}J(J+1)$, and Eq. (2) reduces to the usual form for exchange scattering from a degenerate multiplet.[4]

A computer program is used to determine these averages for arbitrary temperatures, magnetic fields, and crystal-field parameters. The solid lines in the figures give the best *simultaneous* theoretical fits to the g-value and linewidth data. These curves were obtained by using the cubic-crystal-field parameters $W=0.6$ and x

$= -0.3$, and establish a (45 ± 20)°K separation between the Γ_7 ground state and the $\Gamma_8^{(1)}$ first excited state, the most sensitive parameter in determining the fit.[5] At high temperatures the data deviate significantly from the theoretical curves. This is not surprising since with increasing temperature the relaxation rates are becoming fast enough that dynamical or bottlenecking effects, neglected in our derivation of Eqs. (1) and (2), may well be influencing the measured shifts and linewidths.[1] Therefore, we have emphasized the lower part of the temperature-dependent data in making the fits.

In addition to the crystal-field parameters, these theoretical fits give values for the two measures of the strength of the exchange interaction appearing in Eqs. (1) and (2), namely, $\langle J(\vec{k}, \vec{k})\rangle_{E_F} = 0.19 \pm 0.02$ eV and $\langle |J(\vec{k}, \vec{k}')|^2\rangle_{E_F}^{1/2} = 0.135 \pm 0.025$ eV. (ρ has been computed from specific-heat measurements to be 0.21 states/eV atom spin.[6]) Furthermore, the f-shell exchange and outer-shell spin-orbit contributions to the linewidth can now be separated to determine the *outer*-shell spin-flip scattering cross section $\sigma_{s.f.} = (2\pi f/cN_0V_F)(\Delta H_{s.o.}/H) = (4.6 \pm 0.7) \times 10^{-18}$ cm^2, where V_F is the Fermi velocity for aluminum and f is the microwave frequency.

The small but significant difference between the two exchange averages is to be expected, as a partial-wave expansion for $J(\vec{k}, \vec{k}')$ shows,[7] and we find that our experimental results are in good agreement with the predictions of this simple k-dependent exchange model. Recently however, Schultz *et al.*[8] suggested that their data on spin resonances in *Ag*:Er were just barely consistent with the $J(\vec{k}, \vec{k}')$ model, because of the large difference they found between the two exchange averages. In particular, they found $\langle J(\vec{k}, \vec{k})\rangle_{E_F} \cong 0.75$ eV, a value over 3 times larger than the $\langle |J(k, k')|^2\rangle_{E_F}^{1/2} \cong 0.23$ eV they determined from the temperature dependence of the linewidth of the rare-earth resonance. However, a computer fit to their data using our theoretical model, which includes contributions from higher crystal-field multiplets (neglected by them), gives $\langle J(\vec{k}, \vec{k})\rangle_{E_F} \cong 0.5$ eV, where we have assumed a ground-state isolation of 35°K.[9] Using this value we find that the difference between the exchange averages is still markedly larger in Ag than in Al, but is now much more consistent with the $J(\vec{k}, \vec{k}')$ model.

If we now combine the results of normal EPR measurements of the rare-earth resonance near $g = 6.8$ with our TESR results, we obtain additional information about the alloys. In particular, the rare-earth resonance is characterized by a g shift (Knight shift) relative to the free-ion value g_{0f}, and a temperature-dependent linewidth (Korringa broadening) of the form $a + bT$. Again by assuming the $J(\vec{k}, \vec{k}')$ exchange model, the theoretical expressions for the conduction-electron contribution to the g value and linewidth of the rare-earth resonance[6] can be combined to yield the ratio

$$\frac{(g_f - g_{0f})}{b} = \frac{\mu_B}{\pi k_B \rho} \frac{g_J}{(g_J - 1)} \frac{\langle J(\vec{k}, \vec{k})\rangle_{E_F}}{\langle |J(\vec{k}, \vec{k}')|^2\rangle_{E_F}}. \quad (5)$$

Our experimental values for the rare-earth resonance in the temperature range 1–4°K are $g_f = 6.805 \pm 0.01$ and $b = 10.5 \pm 1.5$ G/°K. (Within experimental error, these results agree with independent EPR measurements on *Al*:Er.[6]) Putting these results, along with the TESR values for the exchange averages, into Eq. (3), we obtain $g_{0f} = 6.74 \pm 0.03$. This result is to be compared with the theoretical g value for the Er Γ_7 ground state of 6.77, which has been corrected for the breakdown of Russell-Saunders coupling in the free atom, but does not include the effects of covalent bonding or crystal-field admixture of excited states on the Er^{3+} ground-state orbital angular momentum.[10]

It should be noted that the Er g shift, as determined by Eq. (5), is significantly different from that predicted by the Knight-shift expression $(g_f - g_{0f}) = (g_{0f}/g_J)(g_J - 1)\rho \langle J(\vec{k}, \vec{k})\rangle_{E_F}$. This discrepancy can be attributed to our neglect of electron-electron enhancement in the host metal.[11] For the special case of a spherical moment and Fermi surface, expressions modified to include the effects of enhancement have been calculated for the Knight shift, Korringa broadening, and TESR exchange linewidth,[12] and can be used to resolve the above inconsistency as well as to determine the host susceptibility enhancement factor. However, our calculations show that only the determination of $\langle |J(\vec{k}, \vec{k}')|^2\rangle_{E_F}^{1/2}$ is affected by enhancement (it is reduced by about 10%). In view of the inadequacies of a spherical-model approximation for *Al*:Er, this result is probably not quantitatively significant. It is significant to note that the consistent inclusion of enhancement effects in all three of Eqs. (1)–(3) leads to an expression for the free-ion g value in terms of the experimentally observed widths and shifts which is unaffected by the enhancement, which is the justification for using Eq. (5) rather than the more familiar Knight-shift expression. A more de-

tailed discussion of the effect of enhancement on our results will be given in Ref. 1.

In summary, these experiments demonstrate that the TESR technique can be used effectively in determining some of the details of the exchange coupling and crystal-field splittings for rare-earth impurities in a metallic environment. In addition, direct measurements of the rare-earth resonance can be combined with the TESR results to determine the free-ion g value of the host. Note, however, that direct observation of the rare-earth resonance is not necessary in order to extract the exchange and crystal-field parameters. The TESR technique is applicable as well to ions whose ground states are nonmagnetic as long as there are magnetic low lying crystal-field levels which can be thermally populated. Indeed, we have studied thulium, which has a singlet and hence nonmagnetic ground state, and again we observe an easily measurable temperature-dependent broadening and shift of the TESR line.[1]

We wish to acknowledge valuable discussions with Professor John Wilkins, Professor R. Orbach, and Professor A. Portis. One of us (J.F.S.) would like to thank the National Science Foundation for support during a summer when part of this work was performed.

*This work has been supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-3150, Technical Report No. COO-3150-20. Additional support was received from the National Science Foundation under Grant No. GH-33637 through the Cornell Materials Science Center, Report No. 2161.

†Present address: Bacharach Instrument Co., 2300 Leghorn Street, Mountain View, Calif. 94040.

[1]A preliminary account is given by J. F. Siebert, S. A. Dodds, and R. H. Silsbee, in *EPR of Magnetic Ions in Metals, Proceedings of the Conference of Haute-Nendaz,* edited by G. Cohen and B. Giovannini (University of Geneva, Geneva, Switzerland, 1973). In a forthcoming publication we will present the results of TESR, EPR, and resistivity measurements on several rare-earth–aluminum dilute alloys, along with a detailed description of the TESR apparatus and sample preparation technique.

[2]In determining the impurity contributions to the g value and linewidth of these alloys, we have referenced our data to TESR measurements made on pure Al over this same temperature range. Our results for pure Al are in agreement with those reported by D. Lubzens, M. Shanabarger, and S. Schultz, Phys. Rev. Lett. 29, 1387 (1972).

[3]J. R. Asik, M. A. Ball, and C. P. Slichter, Phys. Rev. 181, 645, 662 (1969).

[4]H. Hasegawa, Progr. Theor. Phys. 21, 483 (1959).

[5]For a given separation, the dependence of the fit on W and x is very weak. The values of W and x given were obtained by correlating the Er data with TESR measurements on other rare-earth impurities in aluminum, and by requiring the parameters to have similar values within a given host. For a discussion of the crystal-field formalism, see K. R. Lea, M. J. Leask, and W. P. Wolff, J. Phys. Chem. Solids 23, 1381 (1962).

[6]C. Rettori, D. Davidov, R. Orbach, E. P. Chock, and B. Ricks, Phys. Rev. B 7, 1 (1973).

[7]R. E. Watson, A. J. Freeman, and S. Koide, Phys. Rev. 186, 625 (1969); D. Davidov, K. Maki, R. Orbach, C. Rettori, and E. P. Chock, Solid State Commun. 12, 621 (1973).

[8]S. Schultz, D. R. Fredkin, B. L. Gehman, and M. R. Shanabarger, Phys. Rev. Lett. 31, 1297 (1973).

[9]G. Williams and L. L. Hirst, Phys. Rev. 185, 407 (1969).

[10]R. W. Reynolds, Y. Chen, L. A. Boatner, and M. M. Abraham, Phys. Rev. Lett. 29, 18 (1972).

[11]P. A. Wolff, Phys. Rev. 120, 814 (1960), and 129, 84 (1963).

[12]A. Narath and H. J. Weaver, Phys. Rev. 175, 373 (1968); J. Zitkova-Wilcox, Phys. Rev. B 7, 3203 (1973).