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Electron-Spin Resonance of Rare Earths in Aluminum*

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The electron-spin resonance of Gd, Dy, and Er has been observed in dilute Al-based alloys. From the temperature-dependent linewidth and the sign of the g shift, a value of the exchange integral $J_{f\text{-}s} = +0.11 \pm 0.02$ eV was extracted for Al : Dy and Al : Er. This value is in agreement with that extracted from the reduction of T_c in Al : Er, on the assumption of little influence of the crystalline field. The more concentrated Al : Gd alloys exhibited a strong magnetic-resonance bottleneck, which was partially opened by (i) reduction of the Gd concentration and (ii) by introducing a third element. The exchange integral was found to equal $J_{f\text{-}s} = +0.17 \pm 0.03$ eV for Al : Gd, and values were obtained for the spin-lattice relaxation rate of the conduction electrons from band effects, the Gd impurities themselves, and the third elements (Ag, Au). A "residual" positive g shift $\Delta g_1 = +0.05$ was noted for Al : Gd (as well as for a number of other dilute Gd alloys), and is tentatively attributed to polarization of the screening electrons of d-like character.

I. INTRODUCTION

Previous ^{27}Al Knight-shift measurements in RAl$_2$,[1,2] RAl$_3$,[3] and RAl[4] (R is a rare earth) intermetallic compounds were interpreted in terms of a negative exchange interaction between the rare-earth ions and conduction-electron spins. A large negative effective exchange coupling has also been extracted from NMR in the liquid phase of dilute rare-earth Al alloys.[5] A mechanism proposed by Anderson and Clogston,[6] Kondo,[7] and others[8,9] suggests "covalent mixing" between the $4f$ states and the conduction electrons as a source for the negative interaction. This mixing depends appreciably upon the proximity of the $4f$ level to the Fermi level.[10] The stability of the localized magnetic moment on the rare-earth (RE) impurity, according to the Anderson criterion,[11] is also related to the amount of covalent mixing. For Yb and Ce, $|E_{4f} - E_F|$ is very small and, as a result, instability of the $4f$ configuration is characteristic of these ions. Both Yb and Ce exhibit localized magnetic moments in some host metals (e.g., La, Au), but are diamagnetic in others (e.g., Mg, Ag). On the one hand, therefore, it is not surprising that many dilute alloys containing Ce and Yb as impurities display strong Kondo[10,12] anomalies. On the other hand, however, the rare-earth ions near the middle of the series, Gd, Er, and Dy, are known to be very stable ($E_{4f} - E_F$ varies from 4 to 9 eV in various host metals) so that one expects the covalent mixing for these RE to be small. Indeed, previous experiments[13,14] with these ions in simple host metals (e.g., Au, Th) exhibit positive exchange interactions between the rare-earth ions and the conduction electrons. We contend that the negative g shifts observed for these RE in transition-metal hosts[15,16] are probably not due to covalent mixing between the $4f$ shell and the conduction electrons as suggested by Coles *et al.*,[17] but more likely caused by direct exchange between the $4f$ electrons and the surrounding d-like host cores.[16] Finally, there is no evidence for a resistivity minimum in any alloy containing Gd, Er, or Dy, suggesting still further that covalent mixing is not significant.

The clear discrepancy between the NMR interpretation of the exchange coupling, and the

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systematics found by EPR in a variety of hosts, make it of extreme importance to determine the magnitude and sign of the exchange integral J_{f-s} in Al using a more direct technique. We report EPR measurements on dilute Al : R(R = Gd, Er, Dy) alloys. For very low rare-earth concentrations, these rare earths are soluble in Al. Our experimental results demonstrate that, for all three RE, the exchange interaction is positive: $J_{f-s} = 0.17 \pm 0.03$ eV for Al : Gd; $J_{f-s} = 0.11 \pm 0.02$ eV for Al : Er and Al : Dy. The magnitude of J_{f-s} for Er is in agreement with T_c measurements on Al : Er alloys, performed by others.[18] The system Al : Gd is bottlenecked at high concentrations[19] because the conduction-electron-spin relaxation rate to the paramagnetic spin exceeds that to the lattice. However, by decreasing the Gd concentration, as well as introducing other nonmagnetic impurities, we are able to reverse the inequality, thereby partially opening the bottleneck. This is manifested by appreciable increases in the slope of the linewidth versus temperature, as well as the g shift. Previous reports on bottlenecked systems, such as Ag : Mn,[19] Cu : Mn,[20,21] Y : Gd,[22] and Ca : Eu[23] exhibit changes in slope of the linewidth, but no appreciable change in the g shift as a function of magnetic-impurity concentration. Our measurements extend over greater magnetic-solute concentration ranges, and thus allow us to move more nearly out of the bottleneck regime. As a result, we can estimate the lattice-spin-flip-scattering cross section for Gd, Ag, and Au, as well as a value for the host Al. A "residual" large g shift ($\Delta g_1 = +0.05$) which does not seem to be dependent on the magnetic-resonance bottleneck, concentration, or lattice relaxation rate of the conduction-electron spin, is exhibited in the Al : Gd alloys, and possible interpretations are given. Finally, a discussion is given of the differences in interpretation between our EPR work and the dilute liquid-alloy NMR work of Flynn *et al.*[5]

II. EXPERIMENTAL RESULTS

Electron-spin resonance of rare earths in Al has been measured as a function of temperature in the liquid-helium range (1.4–4.2 K). Most of the measurements were done at X band, using reflection techniques. The apparatus, technique, and procedures of analysis have been described elsewhere.[24,25a] Samples were prepared by arc melting 99.9999% aluminum from Cominco, with small amounts of rare-earth dopants (usually 99.9% purity or better) in an argon-arc furnace. The dilute alloys were then filed into powders either in an argon atmosphere or in air. Some of the samples were also rapidly quenched in the arc furnace by splat cooling the molten alloys onto a cold copper wall with a jet of argon. However, unlike the cases of Th[14] and Rh,[16] no advantage was found by splat cooling the alloys. Most were made by arc melting eight times, each time from a different side of the button. Metallurgic analyses with an electron microprobe showed that the rare earths were not homogeneously distributed in the aluminum. This was indicated by approximately 2-μm-diam spots of concentrated areas of rare earths in the more highly concentrated samples. Whether or not the rare earths in the spots are each surrounded by aluminum, or well dispersed, is beyond the resolution capability of the microprobe. Such clustering effects are more pronounced in the highly concentrated (1000 ppm) samples than in the very dilute ones. In support of a homogeneous distribution, Maple[25b] has determined that (i) our samples exhibit a lowering of T_c relative to the pure-Al value (so that the Gd is certainty dissolved) and (ii) that the transition to the superconducting state is sharp (implying a reasonably homogeneous distribution). In addition, the presence of EPR of Er and Dy, together with their hyperfine splittings appropriate to a Γ_7 ground state, indicates that at least a significant fraction of the rare earths are in well-defined cubic-symmetry sites of the aluminum host. Without such a local environment, it would have been impossible to observe the Er and Dy resonances. Furthermore, the resonance spectra of Er and Dy in other metallic hosts tends to broaden greatly with increasing solute concentration, while no detectable difference in the line intensity was observed for the same rare earths in the aluminum host. This suggests again that a significant percentage of the rare earths are surrounded by aluminum in the cubic matrix.

The spin-resonance spectrum exhibited the following features:

Al : Er and Al : Dy. Spectra of these alloys are very similar to those observed previously for Er and Dy in cubic metals[16] (see Fig. 1). For Er and Dy solutes with natural isotopic abundance, the spectra exhibited strong central lines, corresponding to $I = 0$ isotopes, surrounded by several hyperfine satellites corresponding to Er^{167} ($I = \frac{7}{2}$) and Dy^{163} ($I = \frac{5}{2}$), respectively. The resonance field of the central line ($I = 0$) corresponds to a g factor of $g = 6.82 \pm 0.04$ for the Al : Er alloys and $g = 7.58 \pm 0.05$ for the Al : Dy alloys. These g values are appropriate to a Γ_7 ground doublet. Thermal broadening of the linewidth was fitted by the formula $a + bT$. Both alloys exhibited an a which changes only slightly with concentration. The value of b was concentration independent to within experimental error. As pointed out previously, the total linewidth of Dy alloys is broadened by unresolved hyperfine structure originating from the nuclear isotopes Dy^{161} ($I = \frac{5}{2}$) and Dy^{163} ($I = \frac{5}{2}$).[26,27]

The relatively high natural abundance of these isotopes (18.9% for Dy^{161} and 25% for Dy^{163}), as well as the small hyperfine constant for Dy^{161} ($A = 57$ G), broadens the $I = 0$ line by at least 20%. In order to avoid errors introduced in a and b by these effects, we have also measured Al : Dy^{164} ($I = 0$). Figure 2 is a plot of ΔH as a function of temperature for the Al : Dy^{164} alloy. The results are consistent with the alloys containing natural-abundance Dy isotopes, but considerably more accurate. Figure 3 exhibits linewidth versus temperature for the Al : Er alloys. All experimental data from Al : Dy and Al : Er are summarized in Table I.

The hyperfine constant was measured by using the Breit–Rabi formula[28] for hyperfine splitting. The following values were obtained for Er^{167} and Dy^{163}:

$$A(Er^{167}) = 75.5 \pm 1 \text{ G}, \qquad A(Dy^{163}) = 82 \pm 4 \text{ G} .$$

These values are slightly larger than the values appropriate to a Γ_7 ground state in a nonmetallic host for the same isotopes. A possible interpretation for this behavior has been given recently in terms of conduction-electron s-like polarization in the vicinity of the stable rare earth.[13] It should be mentioned that independent EPR measurements

TABLE I. Values of g, a, b and A/B for the various measured Al : Dy and Al : Er alloys.

Sample	Nominal concentration (ppm)	g value	a (G)	b (G/K)	A/B
Al : Er[a]	250	6.81 ± 0.04	15.5 ± 2	11.0 ± 2	2.1 ± 0.1
Al : Er	250	6.80 ± 0.04	16.5 ± 2	10.1 ± 2	2.0 ± 0.1
Al : Er[a]	530	6.82 ± 0.04	16.5 ± 2	9.9 ± 2	2.0 ± 0.1
Al : Er	530	6.83 ± 0.04	17.0 ± 2	10.2 ± 2	1.86 ± 0.1
Al : Er	1000	6.83 ± 0.04	17.5 ± 2	10.5 ± 2	1.95 ± 0.1
Al : Dy	500	7.57 ± 0.07	37 ± 10	32 ± 10	1.9 ± 0.2
Al : Dy	892	7.61 ± 0.07	46 ± 8	26 ± 7	2.6 ± 0.2
Al : Dy	1000	7.56 ± 0.07	42 ± 7	27 ± 6	2.0 ± 0.2
Al : Dy^{164}	250	7.58 ± 0.05	33 ± 6	26 ± 6	2.0 ± 0.1
Al : Dy^{164}	500	7.58 ± 0.05	33 ± 5	27 ± 5	2.08 ± 0.1
Al : Dy^{164}	1000	7.59 ± 0.05	34 ± 4	27.5 ± 4	2.0 ± 0.1

[a] Splat-cooled samples.

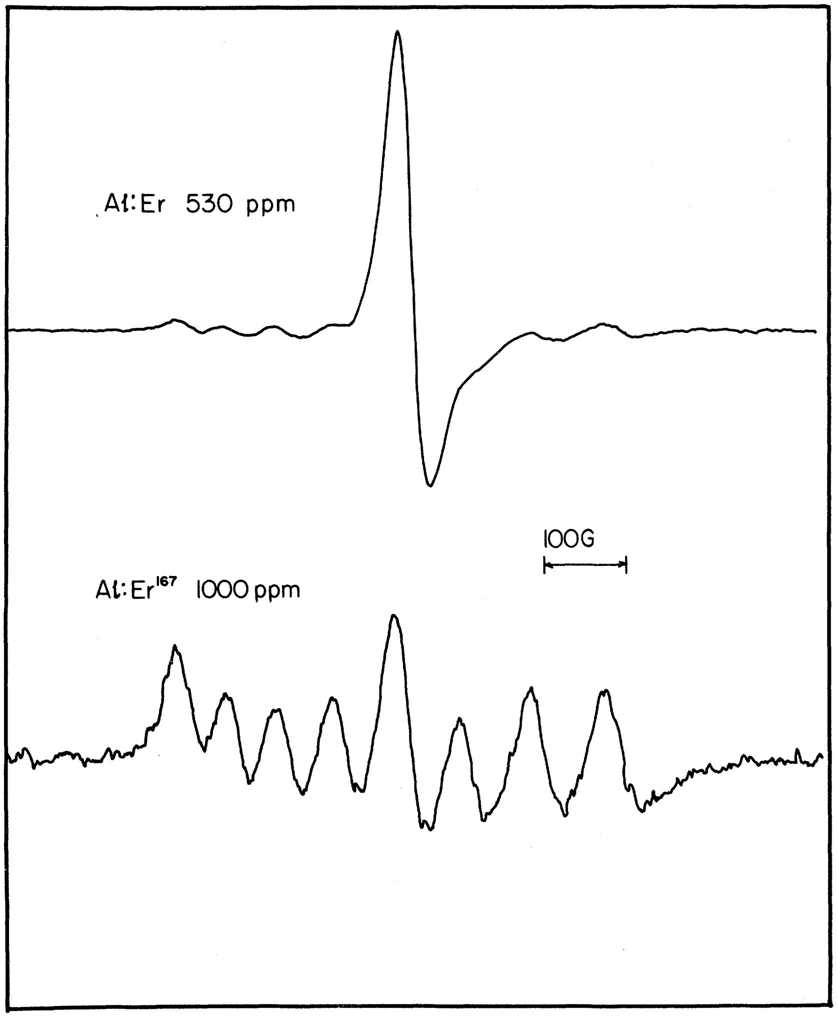

FIG. 1. (a) Electron-spin-resonance spectrum of Er in Al : Er for natural abundance of Er at a nominal concentration of 530 ppm at 1.4 K. (b) Electron-spin-resonance spectrum of Er^{167} in Al : Er^{167} at a nominal concentration of 1000 ppm at 1.4 K.

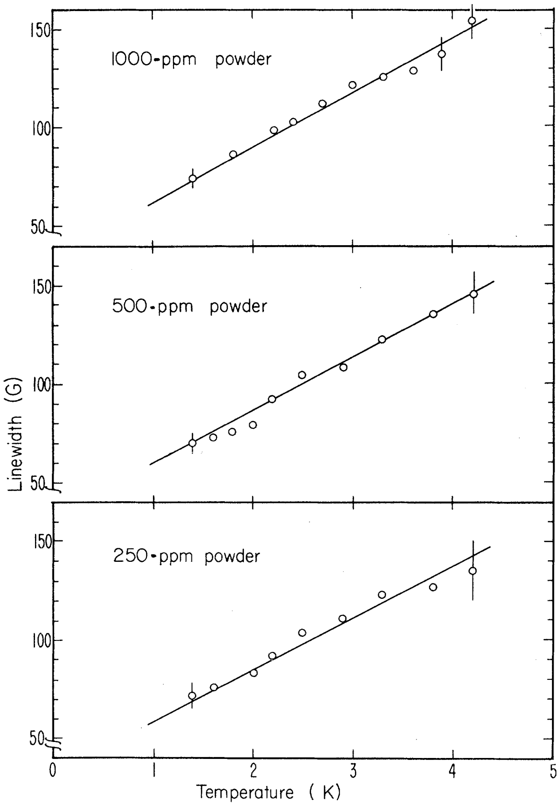

FIG. 2. EPR linewidth of Dy^{164} ($I=0$ isotope) in Al : Dy^{164} dilute alloys as a function of temperature.

on Al : Er dilute alloys at 35-ppm Er concentration have been performed by Siebert *et al.*[29] at Cornell University. Their results for the g value and b agree, to within experimental error, with ours.

Al : Gd. The polycrystalline EPR spectra for these alloys exhibit a single line. The width of the resonance increases almost linearly with temperature, according to the formula $a+bT$. However, in contrast to the Al : Er and the Al : Dy samples, the value of b is concentration dependent. A concentration dependence was also found for the g value, which is temperature independent between 1.4 and 4.2 K. Such behavior usually indicates the presence of a magnetic resonance bottleneck.[30] In order to verify this condition, we prepared three series of samples and measured the linewidth as a function of temperature. The respective results are plotted in Fig. 4. The samples appropriate to Fig. 4(a) were melted many times, beginning with a master sample of 1200-ppm Gd, and using step-by-step dilution to a limiting nominal concentration of 3 ppm. Those yielding the results exhibited in Fig. 4(b) were melted two times during long periods, beginning with the same master, but not diluted step-by-step. Those appropriate to Fig. 4(c) were melted many times starting with the same master, but not diluted step-by-step. The values of b, as well as the g values for all the samples measured, are summarized in Fig. 5. For all three series, we definitely observe (as is clearly seen in Fig. 5) an appreciable increase in b at very low concentrations, as well as a positive increase in the g shift [Fig. 5(b)]. However, the experimental values for b in the higher-concentration region show some variation which is slightly larger than experimental error [see Fig. 5(a)]. We can attribute this behavior to the following: As explained earlier, the inhomogeneity in the samples causes local concentrations to differ from the bulk and the nominal concentrations. The degree of inhomogeneity also depends on the thermal history of the sample. Although each alloy was made by arc melting many times, each time arcing from a different side of the button, the zone refining effect causes the dopant to shift over to one side because of the sharp temperature gradient inherent in the arc-melting technique. In the bottleneck regime, the measured value of b and g are functions of the relaxation rate of the conduction electrons to the lattice δ_{eL} which in turn depends on the magnetic-impurity concentration. Therefore, concentration fluctuations result in macro-

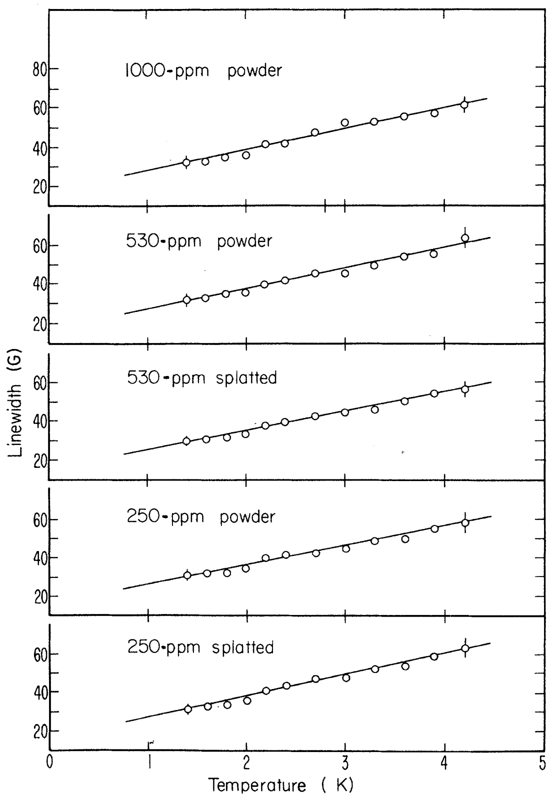

FIG. 3. EPR linewidth of Er (natural isotope) in Al : Er dilute alloys as a function of temperature.

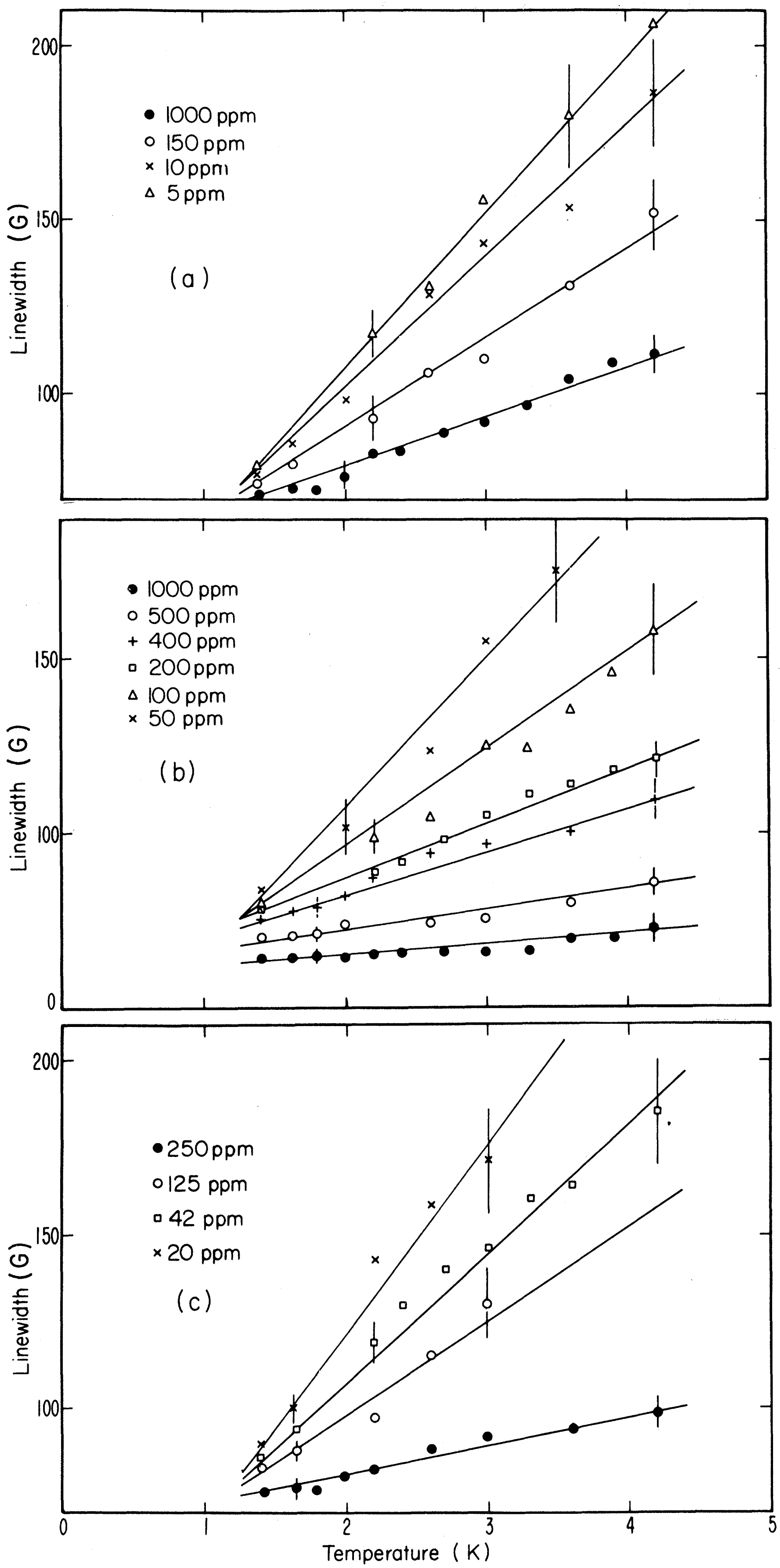

FIG. 4. EPR linewidth of Gd in Al : Gd dilute alloys as a function of temperature. (a) Samples melted many times, starting from master sample and diluted step by step. (b) Samples melted two times during long periods beginning with master but not diluted step by step. (c) Samples melted many times starting with master but not diluted step by step.

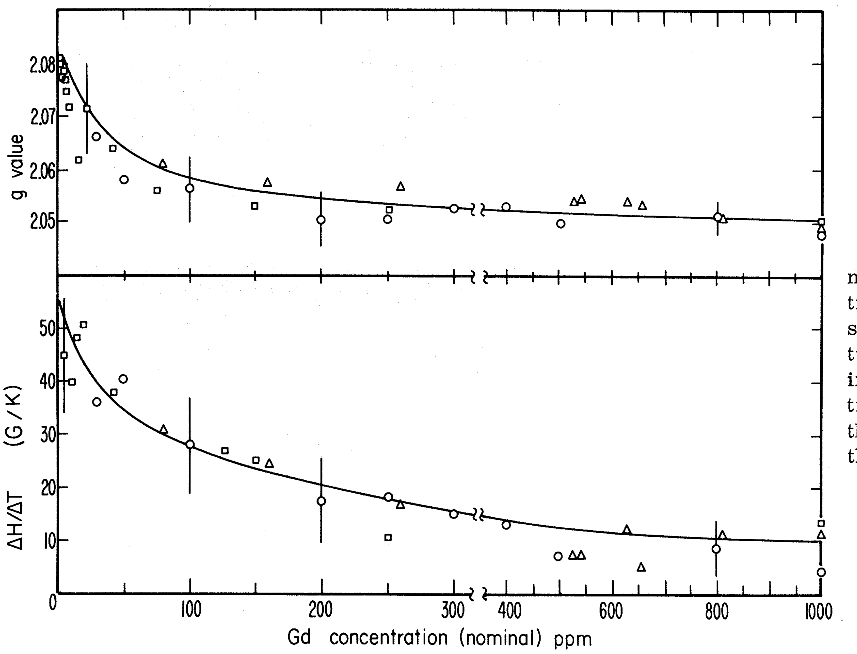

FIG. 5. The g value and the thermal broadening versus concentration for all the Al : Gd samples measured. The squares, circles, and triangles represent results exhibited in Figs. 4(a), 4(b), and 4 (c), respectively. The solid lines represent the theoretical fit to (6) assuming the values of δ_{eL} in Fig. 7.

scopic variations of δ_{eL} and hence of the linewidth and g shift. Indeed, we found that filing from different parts of the same button could result in slightly different b and g values.

Other evidence for the existence of a bottleneck was found by introducing a second impurity which is nonmagnetic, such as Ag, Au, or Pt, into the Al : Gd samples. As expected, we found the slope of the linewidth to increase appreciably with increasing concentration of the nonmagnetic impurities (Fig. 6). It should be stressed that irregularities have been observed in the use of Pt as a dopant in Al : Gd samples. We found that the three series of samples prepared as described above exhibited slightly different results. We attribute the differences in behavior to inhomogeneities as described above, as well as to the difficulty of dissolving Pt in Al.

III. ANALYSIS OF THE RESULTS

The linear dependence of the linewidth on temperature suggests that the line broadening is related to thermal fluctuations of the conduction electrons via an exchange coupling. Assuming an interaction of the form $(g_J - 1)J_{f-s}(\vec{J}\cdot\vec{s})$, one can compute the linewidth appropriate to microwave transitions within the $|\pm\rangle$ levels of the Γ_7 doublet as follows[31]:

$$\frac{1}{T_2} = \frac{\pi}{2\hbar}\left([(g_J - 1)J_{f-s}\eta]^2 \frac{K(\alpha)}{(1-\alpha)^2}\right)(A+B+C)\ , \quad (1)$$

where

$$A = (\langle + | J_z | + \rangle - \langle - | J_z | - \rangle)^2 k_B T \quad ,$$

$$B = \tfrac{1}{2}(|\langle + | J_+ | - \rangle|^2 + |\langle - | J_- | + \rangle|^2)\Delta_0/(e^{\Delta_0/k_B T} - 1),$$

$$C = \frac{1}{2}\sum_i (|\langle + | J_+ | i\rangle|^2 + |\langle + | J_- | i\rangle|^2 + |\langle i | J_+ | - \rangle|^2$$

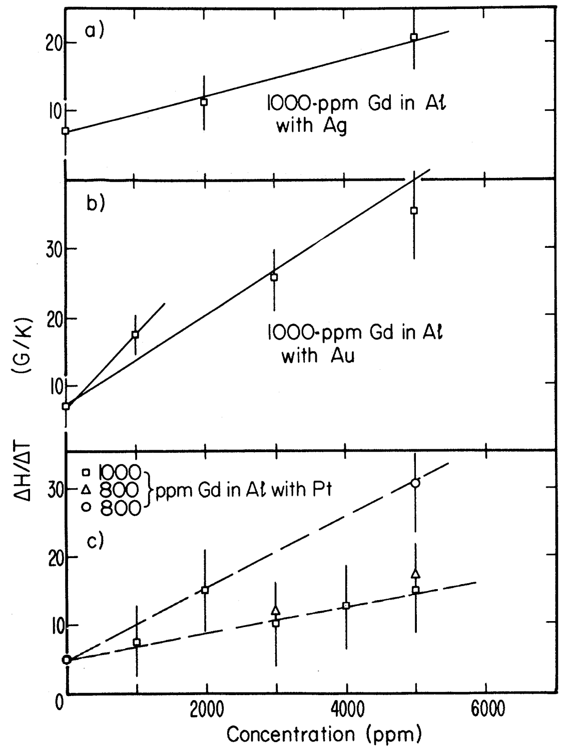

FIG. 6. Slope of the linewidth of Gd vs temperature b as a function of the concentration of the nonmagnetic impurities: (a) Ag, (b) Au, (c) Pt.

$$+\left|\langle i|J_-|-\rangle\right|^2+2\left|\langle +|J_z|i\rangle\right|^2$$
$$+2\left|\langle -|J_z|i\rangle\right|^2)\Delta_i/(e^{\Delta_i/k_BT}-1) \;.$$

Here g_J is the Lande g factor (equal to $\frac{4}{3}$ for Dy and $\frac{6}{5}$ for Er) and η is the conduction-electron density of states per one spin direction at the Fermi level. $J=\frac{15}{2}$ for both Dy and Er. The factor $K(\alpha)/(1-\alpha)^2$ allows for exchange enhancement of the conduction electrons, and is defined in Ref. 32. Δ_0 is the Zeeman-energy splitting between the ground doublet levels $|+\rangle$ and $|-\rangle$ and Δ_i is the difference in energy between the ith-excited cubic-field state and the ground Γ_7 state ($\Delta_i \gg \Delta_0$).

The term A in (1) arises from frequency modulation contributions to the linewidth, B to spin-flip transitions within the Γ_7 doublet. The term C is the contribution to the $|-\rangle \longleftrightarrow |+\rangle$ resonance linewidth arising from transitions to and from higher levels $|i\rangle$, arising from both longitudinal and transverse fluctuations of the conduction-electron spin. In deriving (1), we work to second order in J_{f-s}. For an isolated ground state, and for $k_BT \gg \Delta_0 = g\mu_BH$, (1) yields the usual expression for the slope of the linewidth versus temperature[14]:

$$b=\frac{\hbar}{g\mu_B}\frac{1}{T_2T}=\frac{\pi g k_B}{\mu_B}\left(\frac{(g_J-1)J_{f-s}\eta}{g_J}\right)^2\frac{K(\alpha)}{(1-\alpha)^2}\;. \qquad (2)$$

Al: Er and Al: Dy. The crystalline field splittings of the rare earths in aluminum are not known, but it is easy to see from (1) that only low-lying crystalline field levels ($\Delta_i \lesssim 10$ K) would contribute to the exchange induced linewidth. If these levels are partially populated at the high-temperature end of the helium range, one would expect to observe anomalous temperature dependences of the intensity of the EPR line. Such behavior was not observed to within our experimental error. On this basis, we ignore the term C in (1), and use the limiting expression (2).

In order to extract J_{f-s} from b, we need to determine the various quantities appearing in (2). The value of η can be found from specific-heat measurements $\gamma_e(\mathrm{Al}) = 3.3$ cal/mole K.[33] We use the McMillan relation[34]

$$\gamma_e=\tfrac{2}{3}\pi^2k_B^2\eta(1+\lambda) \;, \qquad (3)$$

where λ is the electron-phonon mass enhancement. McMillan finds, in the strong-coupling model, $\lambda = 0.38$ for Al. This yields, according to (3), $\eta = 0.21$ states/eV atom spin.

The value of $K(\alpha)/(1-\alpha)^2$ was obtained for pure aluminum from Matzkanin *et al.*[35] They applied Moriya's[36] (as modified by Narath and Weaver[37]) exchange-enhancement relation for the Korringa product to available data for aluminum to obtain $K(\alpha)$, and thence α. They found $K(\alpha)^{-1} = 1.2$ and $\alpha = 0.33$. The experimental values for b, according to Table I, are $b = 10 \pm 3$ G/K for Al : Er; and $b = 27 \pm 5$ G/K for Al : Dy. These values, together with the experimental g factors from Table I, yield $J_{f-s} = 0.11 \pm 0.02$ for both alloys.

The cubic Γ_7 ground-state g factors equal 6.77 and 7.55 for Er and Dy, respectively. We observe $g(\mathrm{Er}) = 6.81 \pm 0.04$ and $g(\mathrm{Dy}) = 7.58 \pm 0.06$ in Al, or, respectively, $\Delta g(\mathrm{Er}) = 0.04 \pm 0.03$ and $\Delta g(\mathrm{Dy}) = 0.04 \pm 0.05$.[38] In spite of the relatively large error bars, we claim an unmistakable tendency towards a positive shift. This is consistent with the positive g shift observed for Al:Gd, as shown below. A positive g shift implies a positive value for J_{f-s}, according to the relation[39, 24]

$$\Delta g = g\left(\frac{g_J-1}{g_J}\right)\frac{J_{f-s}\eta}{1-\alpha}\;. \qquad (4)$$

Using $J_{f-s} = 0.11$ and Eq. (4), we calculate the g shift expected for Er and Dy to be $\Delta g(\mathrm{Er}) = 0.04$ and $\Delta g(\mathrm{Dy}) = 0.065$. These results agree to within experimental error with the observed g shifts.

It is worthwhile to compare the value of J_{f-s} derived by us from EPR with that observed via superconducting T_c measurements on Al : Er alloys. Carven *et al.*[18] found that, by alloying Al with Er, the transition temperature is reduced by $\Delta T_c/\Delta c = 1$ K/at.% Er. The Abrikosov–Gorkov[40] (AG) pair-breaking model would generate a reduction of

$$\left|\Delta T_c/\Delta c\right| = (\pi^2/8k_B)J_{f-s}^2\eta(g_J-1)^2J(J+1)\;. \qquad (5)$$

From (5), we can extract $J_{f-s} = 0.12$ eV, which, at first sight, agrees very closely with the value we extracted from EPR linewidth measurements. However, the AG equation (5) does not take into account crystalline field splittings of the ground Russell–Saunders multiplet. If we assume a completely isolated Γ_7 ground state, and $\Delta_i \gg k_BT$, the (trivially modified) AG theory would yield $J_{f-s} = 0.17$ eV, substantially larger than that needed to explain the EPR linewidth data. Recently, Fulde *et al.*[41] have shown that even excited levels with energies Δ_i substantially larger than T_c can contribute to $\Delta T_c/\Delta c$. Fitting to their results would place J_{f-s} somewhere between the two limits quoted above. To obtain a precise fit, one would need a complete knowledge of the excited crystal field levels. We are attempting to extract this information from magnetic susceptibility measurements and will present our conclusions in a future report. At the present time, we are only able to state that the no-crystal-field expression for $\Delta T_c/\Delta c$ yields the better agreement with EPR results than does the large-crystal-field limit.

Al : Gd. It has been shown that when the relaxation rate of the conduction electrons to the lattice δ_{eL} is much smaller than relaxation rate to the localized-moment spin δ_{es}, the linewidth and shift are limited by a magnetic-resonance bottleneck. In such a limit, the linewidth and shift of the magnetic resonance are no longer related to the exchange interaction, but rather to δ_{eL} for the former, and the susceptibility weighted localized and conduction electron resonance fields for the latter. Experimentally, the presence of a bottleneck leads to a reduction of both the thermal broadening and the g shift. However, by decreasing δ_{es}, or increasing δ_{eL}, it is possible in principle to "break" the bottleneck so that the exchange interaction again can become effective.

The theory of Hasegawa (his case B, and Giovannini[42]) gives the following relations for the linewidth and the g shift in the presence of the magnetic-resonance bottleneck:

$$\Delta H = \frac{\delta_{eL}}{\delta_{es} + \delta_{eL}}\, \delta_{se} \;, \quad \Delta g = \frac{\delta_{eL}^2}{(\delta_{eL} + \delta_{es})^2}\, \Delta g_0 \;. \qquad (6)$$

Here we have neglected the term $\gamma\lambda\chi_s H$, responsible for the dynamic effect.[43] The Korringa relaxation rate is given by (1) and is denoted here by δ_{se}; Δg_0 is the Yosida shift due to the conduction electrons and is given by (4). The value of δ_{es} is related to δ_{se} by the detailed balance condition

$$\delta_{es}\,\chi_e = \delta_{se}\,\chi_s \;, \qquad (7)$$

where χ_e and χ_s are the enhanced static susceptibilities of the conduction electrons and paramagnetic impurities, respectively.[44] Recent EPR measurements of Gd in the cubic metal Au [14] indicate that the value of b found for powdered samples of Au:Gd dilute alloys are identical with those obtained from single crystals at the field angle where the fine-structure lines collapse. We neglect, therefore, any effects due to crystalline fields in our analysis.

The fitting of our experimental results (Figs. 4 and 5) to (6) requires knowledge of the various parameters appearing in (6). Our procedure was as follows.

(a) In the high-concentration regime (Fig. 5), the observed $g = 2.05$ indicates a positive g shift of 0.05 relative to $g = 1.993$ found for Gd in nonmetallic hosts. The thermal broadening appropriate to such a shift, according to the Korringa relation, is approximately 50 G/K. The observed thermal broadening in this concentration range varied only between 3 and 12 G/K, leading us to believe that this shift does not originate with the conduction electrons via the $J_{f-s}\vec{S}\cdot\vec{s}$ exchange mechanism, and must be attributed to another source. It should be noted that a similar positive shift has been observed for Au:Gd, Th:Gd,[14] and very recently for Ag:Gd.[45] We shall present a possible mechanism for this peculiar shift at the end of this section. For the present, we shall measure the g shift caused by the polarization of the conduction electrons relative to 2.05.

(b) At very low concentrations, the observed thermal broadening increases as roughly $b = 50 \pm 10$ G/K. If we assume that this is the full Korringa width (unbottlenecked limit), this would lead to a g shift of 0.045 at these concentrations. The experimental g shift, relative to $g = 2.05$, is between 0.025 and 0.03. Thus, the bottleneck cannot be completely broken, even at 3 ppm, and we must assume a value of $b = 65$ G/K for the full Korringa width in order to fit both $\Delta H/\Delta T$ and the g value to (6).

The value of $\delta_{se} = bT = 65T$ G is consistent also with the following picture: The total exchange interaction J_{f-s} is the sum of a positive atomic exchange J_{at} and a negative covalent mixing exchange J_{cm}. J_{at} is believed to be independent of the $4f$ occupation number for the second half of the rare-earth series. A negative J_{cm} should vary as the square of the $4f$ occupation number and is expected to be larger for Er than for Gd. This is consistent with the value of J_{f-s} we derive from $\Delta H/\Delta T$: $J_{f-s} = 0.17 \pm 0.03$ eV. The calculated Yosida shift appropriate to this value of the exchange is $\Delta g_0 = 0.053$. Thus, the values of δ_{se}, δ_{es}, Δg_0, and the experimental values of ΔH and Δg, are all known. δ_{eL} can then be found from (6). The values obtained are exhibited in Fig. 7. The solid lines in Figs. 5(a) and 5(b) are the theoretical fit using the parameters mentioned above. Using the relation

$$\delta_{eL} = \delta_{eL}^{(0)} + \left(\frac{\partial \delta_{eL}}{\partial c}\right) c \;,$$

we find from the initial slope in Fig. 7

$$\delta_{eL}^{(0)} = (1.4 \pm 0.5) \times 10^{10}\ \text{sec}^{-1} \;,$$

$$\frac{\partial \delta_{eL}}{\partial c} = (1.4 \pm 0.7) \times 10^{8}\ \text{sec}^{-1}/\text{ppm} \;.$$

Addition of nonmagnetic impurities increases the value of b appreciably (Fig. 6) by virtue of an increase in δ_{eL} via impurity spin-orbit-induced spin-flip scattering. Table II summarizes the experimental values for σ, the cross section for spin-flip scattering. σ is related to $\partial\delta_{eL}/\partial c'$, where c' is the nonmagnetic-impurity concentration, by

$$\sigma = \frac{1}{N_0 v_F}\,\frac{\partial \delta_{eL}}{\partial c'} = \frac{1}{N_0 v_F}\left(\frac{\partial}{\partial c'}\,(bT)\right)\frac{\delta_{es}}{\delta_{se}} \;. \qquad (8)$$

For comparison, we also list in Table II the value of σ derived from conduction-electron-spin-resonance measurements on Li- and Na-based alloys.

It has been shown previously that the conduction-electron-spin-flip scattering from nonmagnetic impurities should be proportional to the square of the spin-orbit coupling of the core state of an im-

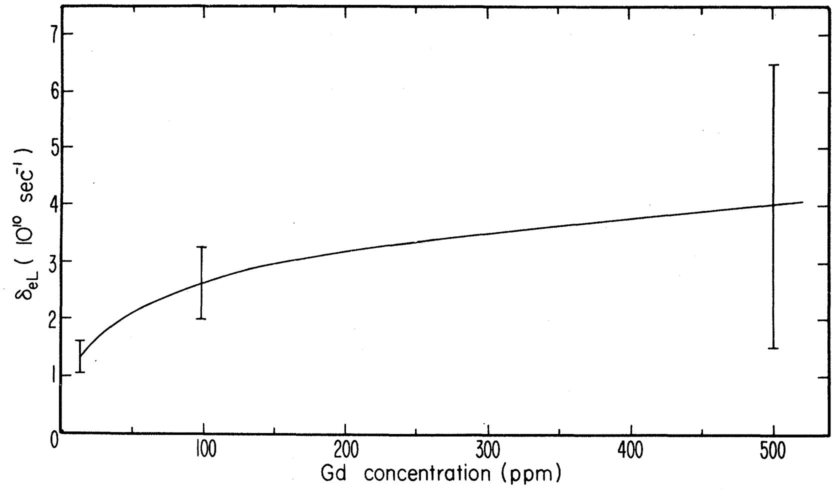

FIG. 7. Value of δ_{eL} as a function of Gd concentration observed by fitting (6) to the experimental data.

purity, as well as the energy overlap of this core state with the conduction electrons. Asik, Ball, and Slichter[46] have shown that the main contribution comes from p or d states immediately below the valence level of the impurity. Thus, the relatively larger cross section for Au, as compared to Ag, is because of the relatively larger spin-orbit coupling of the former as compared to the latter. Huisjen *et al.*[47] have extracted the cross section σ for transition-metal impurities (V, Cr, Mn, Fe) in aluminum. They explain the appreciable changes in σ on the basis of the amount of admixture of the $3d$ virtual state with the conduction electrons at the Fermi level, using the theory developed by Yafet.[48] For the case of Al : Mn, they obtain $\sigma = 8\times 10^{-18}$ cm^2. This value is slightly smaller than the value $\sigma = (12 \pm 6)\times 10^{-18}$ cm^2 observed by us for Al : Gd. The comparative values represent a trade-off between the much larger spin-orbit coupling for Gd, and the much larger overlap (and therefore, admixture) of the Mn d electrons with the conduction states at the Al Fermi surface (the positive exchange observed for Al : Gd indicates that the admixture of the $4f$ electrons with the conduction electrons at E_F is small).

TABLE II. Comparison of the spin-flip scattering cross section of Gd, Ag, and Au impurities in Al with those found for other hosts (Li, Na).

Alloy	$\sigma\times 10^{18}$ (cm^2)	
Al : Gd	12 ± 6	a
Al : Ag	1.5 ± 0.7	a
Al : Au	6 ± 3	a
Li : Au	68	b
Na : Au	30	b
Li : Ag	3.5	b

[a]This work. [b]See Ref. 46.

The value of σ observed for Al : Gd was extracted from low-concentration measurements where inhomogeneities are reduced appreciably. Although the actual Gd concentration is not known, and may deviate from the nominal concentration, we have some confidence in the extracted value of σ. The spin-flip scattering cross section from Ag and Au impurities were obtained from alloys with high Gd concentrations, however, and should be treated with care. In future work, we hope to extract values for σ using more homogeneous samples.[49]

There remains the question of the origin of the positive "residual" g shift of $\Delta g_1 = 0.05 \pm 0.01$ for Al : Gd. We propose the following possible mechanism for this effect. The orthogonality condition of pseudopotential theory,[50] as well as the work of Flynn,[51] leads one to expect that the screening electrons in the immediate vicinity of the rare-earth impurity in aluminum will exhibit $5d$-like character. The energy width of the screening state will be so great as to preclude magnetization, but an enhanced susceptibility (over that of the conduction electrons) can certainly be expected. Using the results of Caroli *et al.*[52] and of Dworin and Narath,[53] a static susceptibility equal to

$$\chi_{(d)}(0) = 2\rho_d \mu_B^2 [\, 1 - \tfrac{1}{5}(\bar{U} + 4\bar{J}\,)\rho_d \,]^{-1} \tag{9}$$

can be expected, where ρ_d is the density of impurity d screening states at the Fermi level for one direction of the spin, $\bar{U}$ the intra-atomic screened-Coulomb interaction and $\bar{J}$ the intra-atomic screened Hund's-rule exchange interaction. Equation (9) applies to the case of little or no crystalline field splitting for the fivefold-degenerate d levels, as compared to their energy width. In a similar manner, the contribution to the linewidth arising from fluctuations of the d electron moment will be proportional to[53]

$$\lim_{\omega\to 0} \mathrm{Im}\chi_{(d)}(\omega)/\omega = \tfrac{2}{5}\pi\hbar\rho_d^2\mu_B^2\,[1-\tfrac{1}{5}(\bar{U}+5\bar{J})\,\rho_d]^{-2}\,. \quad (10)$$

The important character of (9) and (10) is that the enhancement factors are the same. This makes it possible to derive the quite general Korringa relation:

$$(\Delta g_1)^2\, T_{2(d)}\, T = 5(\hbar/\pi k_B)\ , \quad (11)$$

where the factor in parentheses is the electronic analog of the nuclear Korringa factor. The Gd g shift from the screening electron Δg_1 is approximately $J_{4f\text{-}5d}\chi_{(d)}(0)$. Because the exchange is positive, the sign is correct, though the magnitude clearly depends on a number of undetermined factors in (9). It seems to us that a result equal to 0.05 would not be difficult to obtain for reasonable values of $J_{4f\text{-}5d}$ (~0.1 eV) and $\chi_{(d)}(0)$ (~1 eV^{-1}). The linewidth associated with a shift of this magnitude would only be about 10 ± 3 G/K using (11). Such a value can be subsumed within our experimental results in the bottlenecked regime. Hence, it is possible that the shift associated with the screening 5d states could be the origin of the "residual" shift, and that the linewidth associated with that mechanism would be sufficiently small to lie within our error limits. This would then justify the analysis presented earlier in this section. Implicit in this development is that the 5d electrons relax rapidly to the lattice, so that at no Gd concentration used in these experiments would a bottleneck within the 5d state be present. Though the emphasis was different, the work of Salamon[54a] on Sc : Gd is of a very similar nature and forms the basis for the above discussion.

A final point which needs discussion is the discrepancy between our values for $J_{f\text{-}s}$ (relatively small and positive), and those extracted by Flynn *et al.*[5] in their analysis of the Al NMR Knight shift in dilute liquid Al : R alloys (relatively large, and negative). Flynn *et al.*[5] relate the Al Knight shift to the average conduction-electron polarization, brought about by the differential phase shifts for the conduction electrons caused by differing occupation of the "up"- and "down"-localized-spin states, or, alternatively, an effective exchange coupling between the localized spins and the conduction electrons. The latter requires an effective exchange integral equal to −1 eV, which is to be compared to that which we have extracted from EPR measurements: +0.11 and +0.17 eV for Al : Dy, Al : Er, and Al : Gd, respectively. The discrepancy is huge. We suggest a resolution of the difficulty due to Narath.[54b]

In an EPR experiment, the g shift is directly proportional to the $\vec{q}=0$ component of the conduction-electron susceptibility. For the NMR Knight shift in a liquid alloy, one measures a spatial average of the conduction-electron magnetization. At first sight, the two quantities seem directly related. However, the spatial average in the latter case is of restricted volume—the (moving) cell containing the rare earth is not accessible to the Al core. Therefore, the Al nucleus does not sample the entirety of space containing polarized conduction electrons. Indeed, Kittel[55] has demonstrated that, for a single magnetic impurity, the nonoscillatory part of the conduction-electron polarization falls off as $1/r^3$, where r is the distance from the magnetic impurity. This is sufficiently rapid that the majority of net conduction-electron polarization must lie either within or in the immediate vicinity of, the magnetic-impurity site. Thus, though there may be substantial conduction-electron polarization, a large fraction may occur in a region which the Al cannot sample. On top of this, it is well known that the spin density in the outer reaches of the rare-earth ion (the extended 5s and 5p core shells) is negative.[56] Indeed, the magnitude in insulators of this core polarization is ten times that expected from 4f overlap alone at the site of the surrounding ligands, and of opposite sign.[56] Hence, in the liquid alloy, it is not surprising that the Al nuclei might experience a spatially averaged negative spin density. But it is by no means obvious that that negative density is associated with the conduction-electron polarization.

One can be more explicit about the situation. It is certainly true that the total magnetization induced in the conduction electron gas by the magnetic impurity $\int \vec{M}(\vec{r})d^3r$ is proportional to the $\vec{q}=0$ conduction-electron susceptibility. However, there is no reason for asserting that there is any necessary relationship between this quantity and the excluded volume spatial average which the Al nuclei carry out. Our g-shift measurements exhibit a positive effective exchange coupling. Therefore, we expect the conduction electrons to be polarized positively within the rare-earth cell (the contact part of the hyperfine contribution from the conduction electrons is positive[13]). Hence, of the total magnetization induced in the conduction-electron gas, a region of large positive polarization may be forbidden to the Al nuclei. Should the magnetization reverse sign outside of the rare-earth cell (as it is known to do[55]), then it is not difficult to imagine a situation where the Al nuclei would sample a predominantly negative conduction-electron-spin polarization even though the over-all spin polarization of the conduction electrons is positive. Adding to this effect the known large and negative spin density in the outer reaches of the 5s and 5p core states, the experiments of Flynn *et al.*[5] could exhibit a large negative Knight shift for the Al nuclei having nothing to do with that exchange interaction which gives rise to the g shift and linewidth of the local-moment resonance. We suggest that this explanation can remove the discrepancy between our interpretation of the EPR in dilute magnetic alloys and the analysis of Flynn *et al.* on NMR in dilute liquid magnetic alloys.

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[49] As shown in Table II, the values for σ observed by Asik *et al.* for Li : Au and Na : Au dilute alloys are larger by a factor of 5–10 relative to those observed by us for Al : Au. As was pointed out in the text, metallurgical difficulties might be the reasons for this difference (i.e., the effective Au or Gd concentration due to inhomogeneities in the high-concentration samples may be much less than the nominal. This may be especially true here because the samples were not prepared from a master.) However, it should be stressed that the tendency described in Table II is expected because the difference in valence between the Au impurity and the Al (−2) causes a strong repulsive potential for the conduction electrons. This will reduce the overlap integrals and thus the spin-flip cross section of Al : Au relative to that of Na : Au. (For this alloy the difference in valence is zero.) In a future publication we hope to report more accurate values for σ.

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Theoretical Description of the Proton Magnetic Resonance Line Shapes of Ammonium Ions under the Influence of Tunneling*

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A theoretical treatment for the NMR absorption line shape of a tetrahedral group of protons under the influence of tunneling has been developed for the particular case of NH_4^+ ions. For the applied field parallel to a twofold axis of the ion the derived line shapes depend on a single splitting parameter J. This is a measure of the tunneling splitting of the torsional ground state in comparison to the dipolar energy of the ion. As J varies from 0 to ∞ the calculated line shapes are found to vary between the limiting cases of the distinguishable proton (four spin $\frac{1}{2}$) and indistinguishable proton (spin isomeric) situations, respectively. These theoretical line shapes are compared with the observed "rigid-lattice" line shapes reported for the halides NH_4Cl, NH_4Br, and NH_4I. NH_4Cl and NH_4Br are found to be consistent with $J=0$ although the line shape of the latter exhibits an unexplained departure near the center of the resonance. NH_4I is found to exhibit observable splitting effects ($J=3.3$) in which tunneling has displaced one absorption component sufficiently into the wings to be resolved.

I. INTRODUCTION

The problem of the low-temperature NMR absorption line shape for a four-proton group has been considered by a number of authors. Bersohn and Gutowsky[1] calculated the line shape for a system of four-spin-$\frac{1}{2}$ protons (the so-called four-spin-$\frac{1}{2}$ system) in an ammonium ion (NH_4^+) and used their results to explain the line shapes observed in a single crystal of NH_4Cl at − 195 °C. Itoh *et al.*[2] performed an essentially similar calculation, but included the nitrogen-proton interaction to discuss the line shapes of single crystals of NH_4Cl and NH_4Br at 90 °K. They found good agreement between the theoretical and experimental line shapes for NH_4Cl, but not so good for NH_4Br.

In order to explain the narrow absorption line observed in solid methane at 1.29 and 1.42 °K, Tomita[3] calculated the line shape for a four-proton system on the basis that the total spin of the molecule ($I=0, 1, 2$) was a good quantum number. These two theories have been compared by Watton *et al.*[4] in the discussion of the line shapes of a group of ammonium salts. They point out that the four-spin-$\frac{1}{2}$ and nuclear-spin-isomeric pictures are just limiting cases of particle distinguishability. The