Anisotropic Behavior of Dilute Magnesium-Gadolinium Alloys*

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The electron spin-resonance spectrum of Mg:Gd single-crystal alloys in the concentration range 50-1000 ppm exhibits a single anisotropic line. Both the field for resonance and the angular variation of linewidth can be described in terms of unresolved fine structure, but with substantially different values for the axial crystalline field constant. We propose a possible explanation for this difference. We discuss discrepancies between our conclusions and those of Salamon on a similar system.

We report the observation of the magnetic resonance of single-crystal (hexagonal) Mg:Gd alloys with Gd concentrations between 500 and 1000 ppm at frequencies of 8.7 and 35 GHz. The spectra exhibit axial symmetry with a field for resonance which is both angle and temperature dependent (Figs. 1 and 2). Using a conventional axial field term in the spin Hamiltonian, using an isctropic g factor, and taking into account the population factors appropriate to an $S=\frac{7}{2}$ resonance in a combination of magnetic and axial crystalline fields, we compute a first moment (shift) of the resonance line which matches our experimental results. Using the value for D so determined

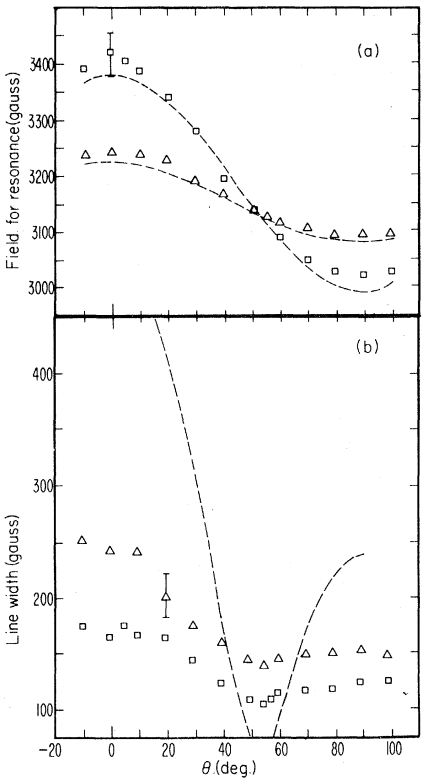

FIG. 1. (a) The field for resonance as a function of the angle θ between the magnetic field and the c axis for Mg:Gd (500 ppm) at a frequency of 8.7 GHz. The squares indicate measurements at 1.4°K; the triangles, 4.2°K. The dashed lines are the first moments, as calculated from (2) using (1) with $D=155$ G and $g=1.98$, at the respective temperatures. (b) The linewidth as a function of angle for the same sample (Mg:Gd, 500 ppm). The dashed line is the square root of the second moment, as calculated from (3) using (1) with the same values of D and g given in (a).

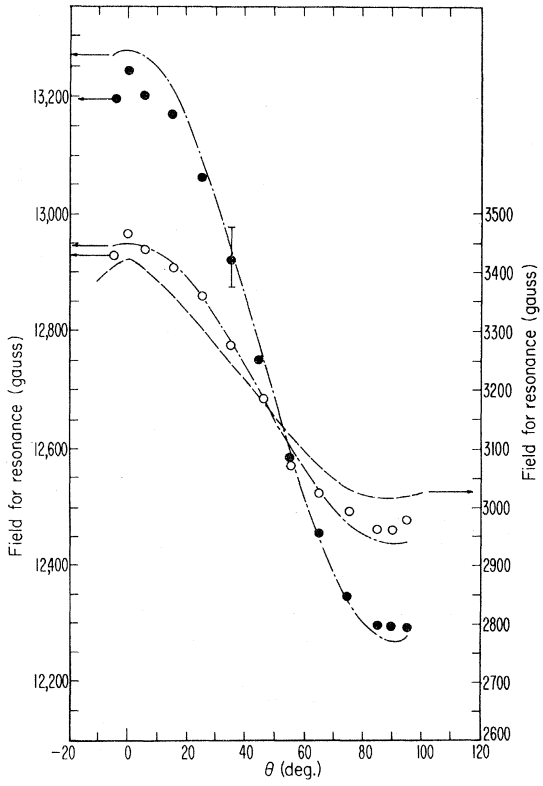

FIG. 2. The field for resonance as a function of the angle θ between the magnetic field and the c axis for Mg:Gd (500 ppm) at a frequency of 35 GHz. The solid circles indicate measurements at 1.6°K; the open circles, 4.2°K. The dash-dot lines are the first moments, as calculated from (2) using (1) with the same values of D and g given in Fig. 1. For comparison we exhibit also, on the same scale, the angular dependence of the field for resonance at 8.7 GHz for 1.4°K (dashed line).

(155 ± 10 g), a computation of the second moment mirrors somewhat the angular variation of the linewidth but is a factor of from 3 to 4 too large. We hypothesize that the discrepancy is caused by exchange-relaxation narrowing of the unresolved fine structure. These conclusions are in marked contrast with those of Salamon[1] for (hexagonal) dilute Sc:Gd alloys. He attributes the anisotropy of the field for resonance to an anisotropic g factor. We claim that our description, which is successful for Mg:Gd, may also be the more appropriate one for Sc:Gd, and suggest temperature and frequency measurements to settle the issue.

Our measurements were performed on single-crystal Mg:Gd samples in the form of cylinders, cut with the c axis perpendicular to the symmetry axis of the cylinder. The resonance line shapes were characteristic of a localized moment in a metal with A/B^2 of approximately 2. No resolved fine structure was observed. Rather, the single line which was observed possessed an angular shift in position which was temperature and frequency dependent. These results are exhibited in Figs. 1 and 2.

An interpretation of the angular shift of the resonance field can be given in terms of unresolved fine structure. The spin Hamiltonian of the Gd^{+3} ion in an axial crystalline field, assuming an isotropic g value, is given by

$$\mathcal{H} = g\beta H S_z + \tfrac{1}{2}D[S_z^2 - \tfrac{1}{3}(S+1)S](3\cos^2\theta - 1) - D(S_x S_z + S_z S_x)\cos\theta\sin\theta + \tfrac{1}{4}D(S_+^2 + S_-^2)\sin^2\theta. \quad (1)$$

The center of gravity of *all* the fine-structure lines is given by the following expression for the first moment:

$$\langle\omega\rangle = \sum_M C_M (E_M - E_{M-1})/\hbar \sum_M C_M, \quad (2)$$

with

$$C_M = [\exp(-E_{M-1}/kT) - \exp(-E_M/kT)]\,|\langle M|S_x|M-1\rangle|^2;$$

the E_M are the energy levels determined by (1). The appropriate Boltzmann factors must be taken into consideration in the computation of the first moment (in the liquid-He range) because the Zeeman interaction generates an overall splitting of the spin levels of from 3°K at X-band frequencies to 10°K at 35 GHz. Assuming that (2) holds for the center of gravity of the observed resonance line, we can obtain a fit to the experimental results in Figs. 1(a) and 2 (for all temperatures and frequencies) with the choice of $D = 155$ G. Note the frequency dependence of the field for resonance, arising not only from the usual g factor (which we choose to be isotropic) but also from the population factors.

It is interesting at this point to compare our results with those of Salamon[1] on dilute Sc:Gd alloys. He too finds an anisotropic field for resonance, but he attributes this behavior to an anisotropic g factor. He finds a "minimum g shift" when the field makes an angle of roughly 60° from the c axis. We should like to point out that an unresolved axial field splitting also exhibits a minimum (zero to first order) shift of the field for resonance at $\cos^{-1}\theta = \frac{1}{3}\sqrt{3}$, or $\theta \approx 55°$ (see Eq. 1). Also, the shift is greater at $\theta = 90°$ than at $\theta = 0°$, in agreement with Salamon's results. Hence, we argue that (2) is capable of explaining his observation of anisotropy in the field for resonance if we hypothesize that his signal is appropriate to an unresolved fine structure. The crucial test is quite simple: Equation (2) exhibits both a temperature and frequency dependence which is quite specific. It would be of great interest to see how Sc:Gd behaves in these respects.

If one hypothesizes an unresolved fine structure for Gd in these hexagonal metals, it is also interesting to investigate the angular field and temperature dependence of the linewidth ΔH. In the presence of an axial field splitting (assumed unresolved in our measurements), one can compute a second moment arising from the fine structure according to the formula

$$\langle\Delta\omega^2\rangle = \sum_M C_M (E_M - E_{M-1})^2/\hbar^2 \sum_M C_M - \langle\omega\rangle^2. \quad (3)$$

For the same value of D (155 G) which generates the observed angular variation of the resonance field, (3) results in the anisotropic linewidth exhibited in Fig. 1(a) (dashed line). It is clearly seen from Fig. 1(a) that the measured values for the resonance line width are much smaller, though they exhibit roughly the same angular dependence as that predicted by (3) (i.e., the experimental linewidth appears appropriate to a much smaller value of D). We suggest that this "discrepancy" is caused by an exchange narrowing of

the unresolved fine structure, in much the same way as has been argued for the hyperfine structure of localized moments in metals.[3] The relaxation arising from the exchange coupling to the conduction electrons (sometimes called Korringa relaxation or $1/T_{fs}$), is responsible for a hopping between axial-field–split resonance lines. This hopping can narrow the otherwise observable fine-structure splitting into a single line centered at the center of gravity of the fine-structure–split level pattern.

A lower limit for $1/T_{fs}$ may be obtained from the temperature dependence of the linewidth at 55°. At this angle, the fine-structure lines collapse to first order[4] and a temperature-dependent linewidth of 15 G/deg is observed. This value could be too small, however, because of the possibility of a magnetic resonance bottleneck. Another method for the estimation of $1/T_{fs}$ arises from a comparison with the Mg:Er system.[5] We argue that the total exchange coupling between the localized moment and the conduction electron should be approximately the same in both Mg:Er and Mg:Gd for the following reasons: The total exchange coupling is the sum of the positive atomic exchange J_{at} and the negative covalent mixing J_{cm}. The former is expected to be the same in both systems because the Fermi energy remains the same.[6] We argue that the latter is small (compared to the former) for the case of a Mg metal host from our experience[7] with rare-earth ions in Ag and Au, and from the inherent stability of the Gd($4f^7$) and Er($4f^{11}$) configurations.[8] We therefore assume a rough equality of values for the total exchange coupling for Mg:Gd and Mg:Er, leading to a value of $[g_{\parallel}/(g_{\parallel}^2+g_{\perp}^2)] \times [(g_J-1)/g_J]^2 = 2.8$ for the ratio between $(1/T_{fs})_{Gd}$ and $(1/T_{fs}^{\parallel})_{Er}$. ($g_{\parallel}$, $g_{\perp}$, and g_J are the values appropriate to Mg:Er, and are given in Ref. 5.)

The measured temperature dependence of the linewidth[5] in the parallel direction for Mg:Er yields a value of $(1/T_{fs})_{Gd} \cong 70T$ G. This "hopping rate" is approximately equal to (at 1.4°K) or even larger (at 4.2°K) than the fine-structure splitting D for Mg:Gd. Therefore, it could explain the apparent narrowing of our observed spectrum. We are not prepared at this stage to push the argument further, because of the obvious fact that we are not in the extreme narrowing limit. A complete microscopic theory of line narrowing in the intermediate region, appropriate to an $S=\frac{7}{2}$ system, is involved. We are currently in the process of accomplishing this task. The numerical estimates made above indicate a likelihood of success for such an approach.

Comparing our approach with that of Salamon,[1] we note that for his case (Sc:Gd) the linewidth is a minimum near 55° and increases rather more rapidly towards 0° than towards 90°. This is in agreement with (3) as can be seen from Fig. 1(b). We suggest, therefore, that the observed angular dependence of the linewidth in Sc:Gd can also be explained on the basis of unresolved fine structure. Otherwise there seems little likelihood for an explanation of the lack of correlation between the size of the measured "g shift" and resonance linewidth in this alloy.

In conclusion, we feel that our analysis demonstrates that the anisotropic resonance behavior of Gd in hexagonal host metals, reported by us for Mg:Gd and by Salamon[1] for Sc:Gd, can be attributed to unresolved fine structure and not to anisotropic g factors. We further suggest that angular- and temperature-dependent measurements can distinguish between the two models, and that the data available at this time appear to favor the former.

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