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Crystal-field and spin parameters in *Mg*-Mn via transmission electron spin resonance*

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We report transmission-electron-spin-resonance measurements at 9.2 and 35 GHz for a single-crystal 60-ppm *Mg*-Mn alloy. The observed resonance exhibits an angular anisotropy and temperature dependence which is characteristic of unresolved fine structure in an axial field. We find the second-order crystal-field parameter $D = 70 \pm 10$ G when we include a correction for coupling to the conduction electrons. Measurements of the conduction-electron spin resonance in pure Mg at 9.2 GHz are also reported. We suggest that the anisotropic properties of the observed resonances require additional theoretical development in order to satisfactorily interpret the coupled conduction-electron–local-moment spin system.

I. INTRODUCTION

We present transmission-electron-spin-resonance (TESR) measurements at 9.2 and 35 Ghz for a single-crystal 60-ppm *Mg*-Mn alloy. The observed resonance exhibits an angular anisotropy and temperature dependence which we interpret in terms of unresolved fine structure of an $^6S_{5/2}$ ion in an axial field. We have also made TESR measurements on pure Mg single-crystal samples where we find an angular anisotropy and temperature dependence of the linewidth, which suggests that much more work needs to be done to clarify the intrinsic conduction-electron-spin-resonance (CESR) properties.

The first observation of ESR in *Mg*-Mn was included in the pioneering local-moment resonance work of Owen *et al.*[1] Subsequent experiments have been reported,[2-4] but all of these are at sufficiently high concentrations (≈0.5%) that the samples exhibited ordering at cryogenic temperatures.[5] Further, either powdered or polycrystaline samples were used. Our own efforts have been directed towards lightly doped (≈60-ppm) single-crystal samples so as to be able to exploit the sensitivity of the TESR approach in determining the crystal-field environment of the local moment. Our preliminary results which represented the first observation of ESR fine-structure effects for a transition-metal local moment in a metallic host have been reported earlier.[6] In this paper we present an extension of these preliminary data and the results of a quantitative analysis in terms of a spin Hamiltonian. From a study of the variation of resonant field with angle we find the second-order crystal-field parameter $D = 70 \pm 10$ G, where the spread of values is in part indicative of an uncertainty in interpretation which is discussed in Sec. IV. Although we have no theoretical interpretation of the anisotropic behavior of the pure CESR, we have analyzed the temperature dependence of the *Mg*-Mn spectra taken at the angle where the fine-structure lines coalesce in terms of a bottlenecked local-moment–conduction-electron system, thereby obtaining a preliminary determination of the spin properties of Mn in a Mg host.

II. EXPERIMENTAL TECHNIQUES

The pure Mg single crystals were vapor grown following a procedure developed by Stark.[7] Oriented samples were spark cut and then lapped chemically to a thickness of 1.5×10^{-3} cm. The TESR data were taken on slices from a crystal with resistivity ratio (room temperature to 4.2 K) of ≅4500. The Mn-doped crystals were grown via the Bridgeman technique in graphite crucibles. A master alloy was prepared, and then through dilution crystals were grown at 240 and 60 ppm (atomic). Concentrations were determined by atomic absorption and were consistent with values deduced stoichiometrically or from the dc susceptibility.

The susceptibility of an appropriately sized sample cut from the 60-ppm boule was measured for us from 2 K down to 7×10^{-3} K. Deviations from a Curie law were observed only below 60×10^{-3} K.[5]

The TESR spectrometer employs superheterodyne detection, and an optional maser preamplifier.[8] The dc magnetic field may be oriented anywhere in a horizontal plane, which in turn is normal to the plane of the sample. The sample temperatures may be set anywhere from 1.3 to 300 K.

III. DATA

A. *Mg*-Mn crystal-field effects

A single resonance line was observed under all conditions for our *Mg*-Mn samples. In Figs. 1 and

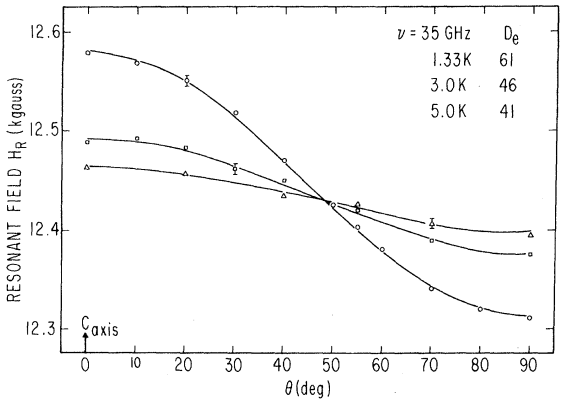

FIG. 1. Resonant field H_R, vs magnet angle for a 60-ppm *Mg*-Mn single-crystal sample at a frequency of 35 GHz. At 0° the field is normal to the sample and parallel to the *C* axis. The solid lines represent first-moment computations which determine the experimental value of the crystal-field-splitting parameter D_e.

2 we present values of H_R, the field at which TESR resonance occurs as a function of orientation of the dc magnetic field for several temperatures, and at a frequency of 35 and 9.2 GHz, respectively. The same 60±10-ppm (atomic) sample was used at both frequencies. When the magnetic field was normal to the sample it was parallel to the *C* axis. We attribute the angular dependence of H_R to the axial-crystal field and analyze the experimental data as follows.

For a set of H_R-vs-θ data at a particular frequency and temperature, we fit a single constant, the *D* parameter of the axial-field term in the spin Hamiltonian[9] where we incorporate an isotropic *g* factor and take into account the population factors of the $S=\frac{5}{2}$ multiplet in a first-moment calculation. The matrix elements for the transitions between levels are calculated to second order in *D*, which have a $1/H$ dependence. Thus the angle θ_c at which the fine-structure lines all coalesce is not 54°45′ (i.e., where $3\cos^2\theta - 1 = 0$), but slightly shifted to smaller angles depending on the frequency. Therefore, θ_c is not the angle at which the curves for different temperatures shown in either Figs. 1 or 2 intersect. We observe a shift of the resonant field at θ_c with temperature which we attribute to the dynamical behavior of the coupled local-moment conduction-electron spin system. We present the data for this *g* shift and an analysis in (*C*).

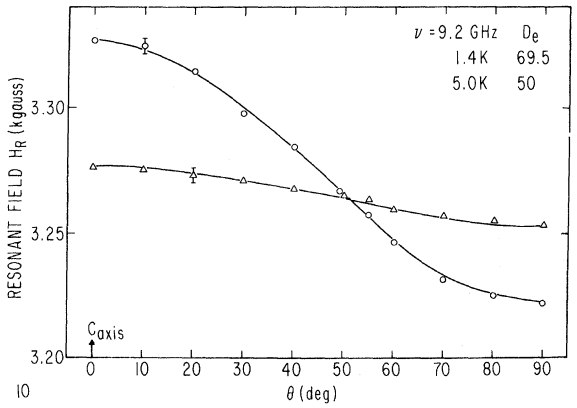

FIG. 2. Resonant field H_R vs magnet angle for a 60-ppm *Mg*-Mn single-crystal sample at a frequency of 9.2 GHz. At 0° the field is normal to the sample and parallel to the *C* axis. The solid lines represent first-moment computations which determine the experimental value of the crystal-field-splitting parameter D_e.

As noted in Fig. 1 and 2, the best fit to the respective data result in different values for *D* (designated D_e). The values of D_e are listed in Table I. We note a monotonic decreasing value with increasing temperature. A possible explanation for this temperature dependence is discussed in Sec. IV.

The linewidth of the TESR signals exhibited appreciable anisotropy as presented in Fig. 3. In contrast to the good fit of the first-moment calculation used to determine D_e from the data of Figs. 1 and 2, we find that the analogous second-moment fit to the linewidth fails completely. Not only is the magnitude off by one order, but the functional dependence is quite different, i.e., the experimental curves do not have a minimum near θ_c. We can understand the discrepancy in magnitude as being due to exchange narrowing within the unresolved fine-structure levels. In cubic hosts such as *Ag*-Gd[10] we found we were able to satisfactorily account for the linewidth anisotropy data following the more detailed calculations of Barnes.[11] However, it is not possible to explain the continued decrease of the experimental linewidth beyond θ_c with this theory. We note that the pure Mg linewidth data exhibit a similar angular dependence as noted in Sec. B, but this may simply be fortuitous.

TABLE I. Values of *D* as determined from the data, D_e, and as corrected by the susceptibility ratio. We have taken $\chi_r(1\text{K}) = 10$, and assume a Curie law for χ_d.

Frequency (GHz)	T (°K)	D_e	$D_e\left(\frac{\chi_r+1}{\chi_r}\right)$
9.2	1.4	69.5±2	79
	2.0	63±3	76
	3.5	57.5±10	78
	5.0	50±4	75
35	1.33	61±3	72
	3.0	46±7	60
	5.0	41±14	62

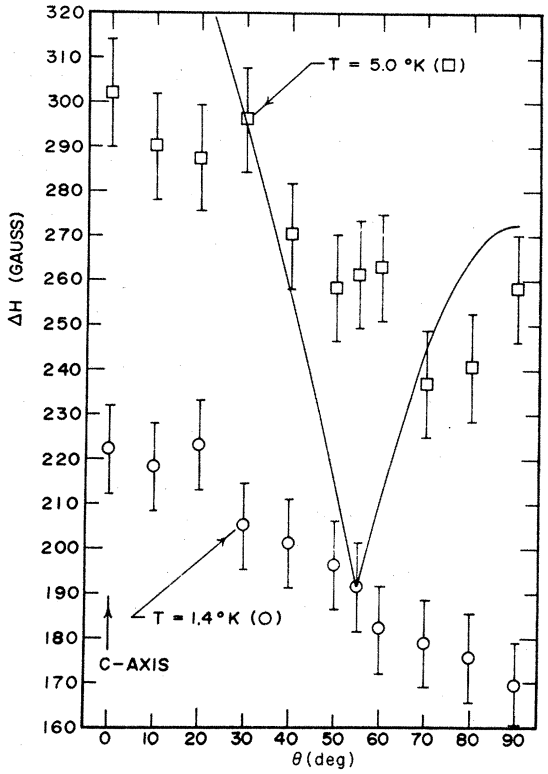

FIG. 3. TESR full linewidth at half-maximum signal amplitude vs magnet angle for Mg doped with 60-ppm (atomic) Mn. The spectrometer frequency was 9.2 GHz, and all data have been corrected for the A/B line-shape factor. The solid line on the figure reproduces a second-moment computation based on $T = 1.4$ °K and $D_e = 69$ G. At 0° the field is normal to the sample and parallel to the C axis.

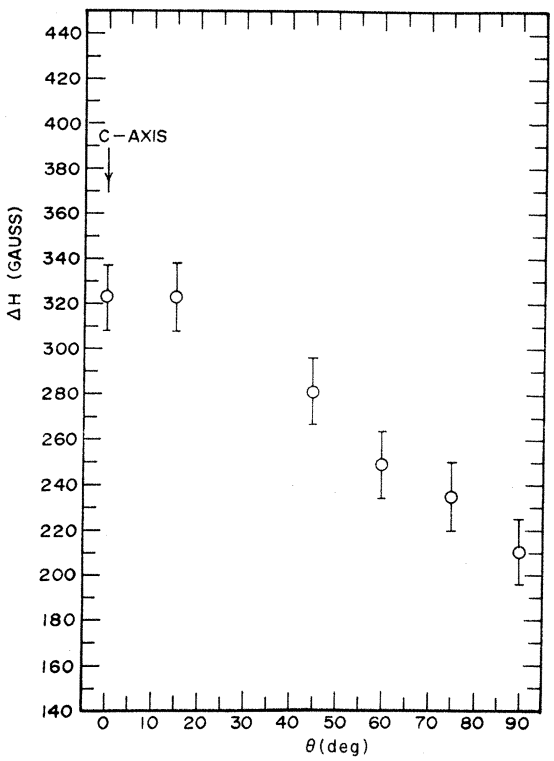

FIG. 4. Full linewidth at half-maximum signal amplitude versus magnet angle for pure Mg CESR. These data were obtained at $T = 40$ °K and spectrometer frequency 9.2 GHz. The sample foil was 1.78×10^{-3} cm thick, oriented with crystalline c axis perpendicular to the sample plane. Data have been corrected for the A/B line-shape factor.

B. Pure magnesium

Conduction electron spin resonance in Mg has been reported in the literature,[6,12] but appears to have an anomalous behavior.[13] We have observed somewhat different characteristics for our samples via TESR, and at the moment do not know if they can be attributed to g anisotropy, surface relaxation, or other complications similar to that for Al.[14] In contrast to reflection measurements, we have been able to observe signals down to 1.4 K. Although the signal to noise is poor (and the linewidths large) for our samples we have found that there is neither a systematic temperature nor orientation dependence of the g value larger than ±0.01. However, we do find an appreciable orientation dependence to the linewidth which extends to surprisingly high temperatures. In Fig. 4 we present the variation in full linewidth (corrected for lineshape factors) as a function of the angle of orientation of the field. At 0° the field is normal to the sample and parallel to the C axis. Comparable ratios were observed in another sample from 1.4 to 20 K.

It is clear that a substantial amount of work needs to be done to clarify the pure CESR situation. For the purposes of the present work we can only say that our host Mg has a g value of 2.00 ± 0.01, and an anisotropic linewidth varying between 100 and 500 G. We shall comment further on these values following the analysis of Sec. III C.

C. Local-moment-conduction-electron dynamics

As was mentioned in B, there is a discrepancy between the angles at which the curves for different temperatures cross in Figs. 1 and 2 and θ_c, as calculated for the axial symmetry. We attribute this to an intrinsic temperature dependence in the field for resonance at θ_c. In Fig. 5 we present the temperature dependence of the g values associated with the resonant field at the angle corresponding to θ_c for 9.2 and 35 GHz. Although there are substantial uncertainties, we can readily notice a g shift towards lower g values at increasing temp-

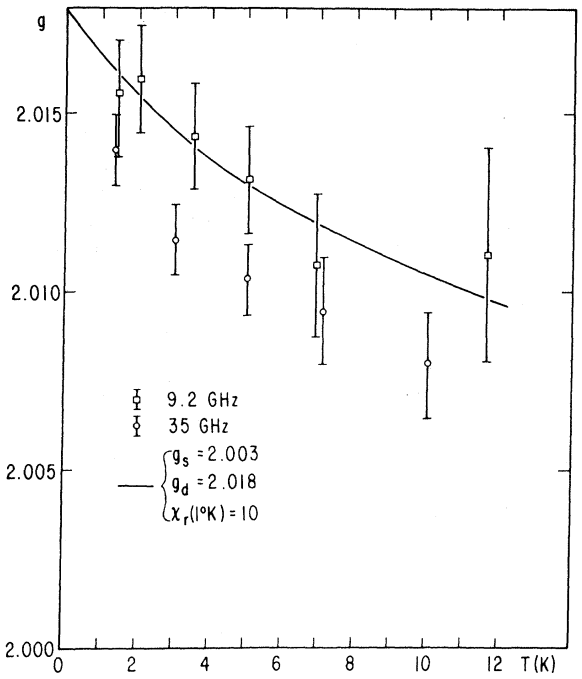

FIG. 5. TESR g value at θ_c vs sample T for a 60-ppm Mg-Mn sample at a frequency of 9.2 and 35 GHz. θ_c is that angle where the fine-structure lines coalesce. The solid line represents the relation appropriate to the bottlenecked limit where the values indicated were chosen to fit the 9.2-GHz data.

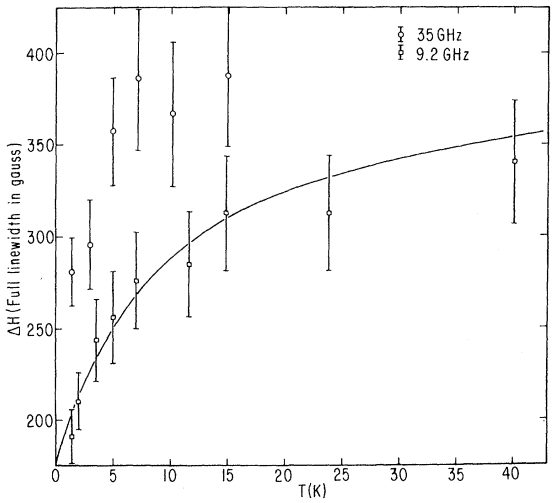

FIG. 6. Full TESR linewidth at half-maximum signal amplitude vs temperature for a 60-ppm *Mg*-Mn single crystal at a frequency of 9.2 and 35 GHz. The dc field orientation was set at θ_c. The data have been corrected for the A/B line-shape factor. The solid line represents the relation appropriate to the bottlenecked limit, where the parameters $\Delta H_{dl} = 175$ and $\Delta H_{sl} = 400$ G were chosen to fit the 9.2-GHz data.

erature.

In Fig. 6 we present the full linewidths (ΔH) (corrected for line-shape factors) of the resonance signal at θ_c as a function of temperature for 9.2 and 35 GHz. Again, despite the large uncertainties, one can discern that the linewidth increases with temperature at both frequencies and expect to obtain a reasonably quantitative result with a fit to the data at 9.2 GHz.

IV. ANALYSIS

The dominant characteristics of the data in Figs. 5 and 6 are suggestive of the behavior of a coupled local-moment–conduction-electron system in the bottlenecked limit. While the uncertainties in the data, and in our knowledge, of the intrinsic CESR properties of pure Mg prohibit making a detailed quantitative analysis, we have attempted to obtain some idea of the spin properties of the system. The theoretical curves in Figs. 5 and 6 represent an attempt to fit the g value and linewidth data at 9.2 GHz self-consistently to the relations of the extreme bottlenecked limit,[15] $g = (g_s + g_d\chi_r)/(1+\chi_r)$ and $\Delta H = (\Delta H_{sl} + \Delta H_{dl}\chi_r)/(1+\chi_r)$, where $\chi_r = \chi_d/\chi_s$, where χ is the dc susceptibility, and where subscripts s and d refer to the conduction electrons and local moments, respectively, and l implies relaxation to the lattice. We have restricted our initial analysis to the 9.2-GHz data because χ_d can still be taken as a simple Curie law dependence, whereas for 35 GHz, saturation becomes significant at the lowest temperature. While there is no problem in making the corrections, there are some features of the data that can not be simply explained, and given our overall uncertainty in the intrinsic properties of the *Mg*-Mn system, we suggest that it does not warrant such a detailed analysis at this stage.

A preliminary analysis of the data suggested that it could be fit with a $\chi_r(1\text{ K}) \cong 10$. This value is consistent with our measured value of χ_d for a 240-ppm sample scaled for concentration, and assuming χ_s is close to the free-electron value. For the g-value analysis, if we take $g_s = 2.003$, $g_d = 2.018$, and χ_r as discussed, we get the theoretical relation shown in Fig. 5. For the model we are discussing, the g values should be basically independent of frequency (barring saturation), although the data at 35 GHz is suggestive that this may not be the case. Whether there is a real frequency dependence, and if it is related more to the properties of the Mg host than the local moment, requires clarification.

For the linewidth analysis at 9.2 GHz, we use the same χ_r and take $\Delta H_{dl} = 175$ G and $\Delta H_{sl} = 400$ G (independent of temperature). We obtain the theoretical curve as shown in Fig. 6. While the sub-

stantial change in ΔH_{dl} needed to attempt to fit the 35-GHz data is not ruled out (or for that matter even a change in ΔH_{sl}), it is clear that these data are not sufficient to provide more than the suggestion of such increases. If we take the $\langle \Delta H_{sl} \rangle$ of the host Mg to be ≈250 G, we can attribute the ΔH_{sl} of 400 G to include 150 G of broadening by the 60 ppm of Mn, or ≈3 G/ppm.

We now return to the apparent temperature dependence of D_e discussed earlier. If we regard the spin system as consisting of five independent subsystems each with the appropriate "g_d" value as determined by the crystal field, then there exists 5 separate relations of the bottlenecked form. Assuming that the first-moment calculation still correctly represents the center of the resultant line shape, the excursion of the resonant field as actually observed is reduced from that of the true D by the factor $\chi_r/(\chi_r+1)$. Thus we expect the D determined from the experimental data to be related to the true D by $D_e = D\chi_r/(\chi_r+1)$. If we take χ_r as was used in the g-value and linewidth analysis, we get the values listed in Table I. The average D so obtained at 9.2 GHz is 77 G with a very small statistical spread. The average value at 35 GHz is 68 G, but as can be seen the spread in values is considerably larger than at 9.2 GHz. Given the evidence for strong exchange narrowing, as exemplified by the linewidth data of Fig. 3, one can question the validity of the simple model used. Indeed, one may also question whether the system is correctly represented as being in the completely bottlenecked limit. In view of the foregoing considerations, we feel that a reasonable range of D is represented by 70 ± 10 G. This may be compared with a reported value of 54 G obtained from an analysis of the susceptibility anisotropy.[16]

To our knowledge, the analysis of comparable systems to determine D have not included the possible χ_r correction.[17] However, it should be pointed out that in most other cases the concentrations used are such that the changes in $(\chi_r+1)/\chi_r$ are small over the range of temperatures of interest.[18]

In conclusion, we strongly suggest that more theoretical attention be paid to questions raised by this interesting system. On the experimental side, a large effort is required to first clarify the frequency, temperature, and anisotropy behavior of pure Mg, followed by extended measurements of the type reported here.

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