

of the individual metals. Thus any calculation of the residual values of L_i will probably require a consideration of features pertinent to the metal of interest. To the best of this author's knowledge, this has been carried out only in the case of Pd, where a recent refinement⁹ of the s -electron-paramagnon scattering theory provides an estimate of the low-temperature value of L_i in terms of the Stoner enhancement factor $(1/K_0^2)$.¹⁰ The experimental L_i of 0.7 then yields a $1/K_0^2$ of approximately 5. The value of $1/K_0^2$ for Pd is not known, but the above result is in fair agreement with a recent estimate of 8.¹¹

The author is indebted to B. C. La Roy and R. Williams for the preparation of the Pd specimen and to A. C. Ehrlich for help in data acquisition. He is particularly grateful to A. I. Schindler and M. J. Rice for many stimulating

discussions and for communication of the results of their work prior to publication.

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PARAMAGNETIC RESONANCE OF ERBIUM IN A SINGLE CRYSTAL OF MAGNESIUM*

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(Received 28 July 1967; revised manuscript received 31 August 1967)

The anisotropic electron-paramagnetic-resonance spectrum of an erbium-doped single crystal of magnesium metal is characteristic of a uniaxially distorted Γ_7 doublet of the free-ion $^4I_{15/2}$ multiplet. The observed linewidth anisotropy is consistent with an isotropic conduction-electron-localized-electron exchange interaction.

We wish to report what we believe to be the first observation of an anisotropic electron-paramagnetic-resonance signal in a metal. We have observed the resonance spectrum of erbium-doped single-crystal magnesium metal in the liquid-helium range at both 9 and 35 Gc/sec. The g tensor is uniaxial, with $g_{\parallel} = 8.90 \pm 0.1$ and $g_{\perp} = 5.77 \pm 0.1$. If it is assumed that the uniaxial component of the crystalline field is small compared with the cubic field splitting, and the "parent" state is the Γ_7 level of the free-ion $^4I_{15/2}$ multiplet, these values obey the relation¹ $g_{\parallel} + 2g_{\perp} = 3g_c$, where $g_c = 6.8$. The line shape is found to be that predicted by Bloembergen² with a width which increases linearly with temperature. The broadening is anisotropic, the temperature-dependent part varying from 120 ± 20 G in the parallel direction to 140 ± 20 G in the perpendicular direction at 4.2°K . This anisotropy can be accounted for on the assumption that the conduction-electron-localized-electron exchange interaction is isotrop-

ic, and yields a value for the exchange integral of ± 0.13 eV. This value yields a calculated residual X-band ($T=0$) linewidth³ (cut-off Lorentzian) of 25 G for $h_{rf} \perp c$ axis, to be compared with an observed extrapolated $T=0$ width of $\sim 110 \pm 30$ G. The residual linewidth was found to be $\sim 80 \pm 30$ G for $h_{rf} \parallel c$ axis.

Previous measurements⁴ of the resonance properties of localized moments in metals were performed in cubic hosts. The first observation of the resonance of a non-S-state ion was reported recently by Griffiths and Coles.⁵ They observed the resonance of Er dissolved in Ag in small-particle samples. Geschwind⁶ observed the resonance of Mn in single crystals of Cu and found results similar to those reported earlier by Owen et al.⁴ In order to examine the effects of a crystalline field on a moment dissolved in a metal, single crystals of magnesium doped with a variety of rare-earth metals were grown. The local symmetry of a rare-earth atom, assumed to substitute for a mag-

nesium atom, is expected to be nearly cubic, but with a small hexagonal distortion. Erbium was chosen as a dopant because of the greater solubility of the second half of the rare-earth series in magnesium metal.⁷ Single crystals of magnesium were grown by the Bridgman technique containing concentrations of erbium in the 0.1% range. No additional phases were observed by inspection of the crystal, and back-reflection x-ray photographs showed only the hexagonal structure typical of magnesium metal. Microprobe measurements demonstrated rough uniformity of concentration, varying from a minimum of 0.08 at.% to a maximum of 0.15 at.% over distances of the order of a few microns. At no time were concentrations observed which would have corresponded to the known compounds of the form ErMg_x . Magnetic susceptibility measurements⁸ were made from room temperature down to 2.5°K, and displayed a Curie-like behavior, indicating the absence of magnetic ordering. The samples were oriented using x-ray photographs and cut to approximately cylindrical shape with an acid string saw.

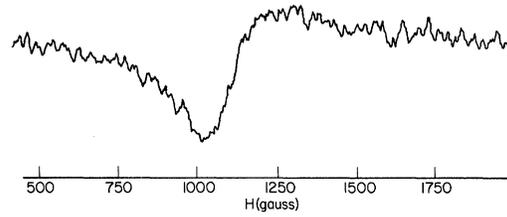


FIG. 1. X-band resonance line (derivative of absorption) for a 0.1% Er:Mg single crystal at 4.2°K.

Observations of the resonance were made between 4.2 and 1.4°K (see Fig. 1) and showed a characteristic² metallic line shape with an A/B ratio (low-field peak height to high-field peak height) of about 2.6. The resonance signal was observed to disappear very rapidly as the sample warmed up above helium temperature. We could not determine whether this was caused by a decrease of signal intensity (as found by Griffiths and Coles⁵) or by a rapid increase in linewidth.

The observed linear increase⁹ of the linewidth with temperature is expected from the usual Heitler-Teller-Overhauser¹⁰ formula. We adopt an s - f exchange interaction of the form¹¹

$$\begin{aligned} \mathcal{H} &= -(2J_{s,f}/n_0) \sum_i \vec{S}_i \cdot \vec{s}(\vec{r}) \delta(\vec{R}_i - \vec{r}) \\ &= -(2J_{s,f}/n_0) [(g_J - 1)/g_J] \sum_i \{g_{\parallel} s_{iz} s_z(\vec{r}) + g_{\perp} [s_{ix} s_x(\vec{r}) + s_{iy} s_y(\vec{r})]\} \delta(\vec{R}_i - \vec{r}), \end{aligned} \quad (1)$$

where \vec{S}_i is the spin of the i th erbium ion; $\vec{s}(\vec{r})$ the spin of the conduction electron at the position $\vec{r} - \vec{R}_i$, relative to the i th erbium ion; n_0 is the number of lattice sites per unit volume; g_J is the Landé g factor ($=6/5$ for Er^{3+}); and (s_x, s_y, s_z) ($s = \frac{1}{2}$) is the effective spin. We have projected¹² \vec{S}_i onto \vec{J}_i , assuming a ${}^4I_{15/2}$ term value appropriate to an f^{11} configuration. Moriya's^{13,14} expression for the linewidth (derived for nuclear relaxation) yields, for $H \parallel c$ axis,

$$\Delta\omega_{\frac{1}{2}}^{\parallel} = (2J_{s,f}/\hbar)^2 [(g_J - 1)/g_J]^2 [g_{\parallel}^2 \int_0^{\infty} \langle \delta s_z(\tau) \delta s_z \rangle d\tau + g_{\perp}^2 \int_0^{\infty} \langle \delta s_x(\tau) \delta s_x \rangle d\tau]; \quad (2)$$

for $H \perp c$ axis,

$$\Delta\omega_{\frac{1}{2}}^{\perp} = (2J_{s,f}/\hbar)^2 [(g_J - 1)/g_J]^2 [g_{\perp}^2 \int_0^{\infty} \langle \delta s_x(\tau) \delta s_x \rangle d\tau + \frac{1}{2} g_{\parallel}^2 \int_0^{\infty} \langle \delta s_z(\tau) \delta s_z \rangle d\tau]. \quad (3)$$

These expressions are valid in the short-correlation-time limit.¹⁵ This is certainly appropriate here, since the conduction-electron correlation time is of the order of \hbar/E_f . In (2) and (3), $\langle \delta s_i(\tau) \delta s_i \rangle$ is the symmetrized time-correlation function of the i th component of the conduction-electron spin fluctuation. We have assumed in (2) and (3) that the spin fluctuations in the x and y directions (the z axis

taken along the c axis of the Mg crystal structure) are the same. If we make the additional assumption that the spin fluctuations are isotropic (as should be the case for Mg, since ultrasonic measurements¹⁶ have shown that the electrons are nearly free), we can then relate the widths (2) and (3). In particular, we find, for the ratio of the temperature-de-

pendent part of the linewidth in the parallel and perpendicular orientations,

$$\frac{\Delta H_{\frac{1}{2}}^{\parallel}}{\Delta H_{\frac{1}{2}}^{\perp}} = \frac{2g_{\perp}^2 g_{\parallel}^2 + g_{\perp}^2}{g_{\parallel}^2 g_{\parallel}^2 + 3g_{\perp}^2} = 0.81, \quad (4)$$

where we have used $g_{\parallel} = 8.9$ and $g_{\perp} = 5.77$, as found in this investigation. Though our rather large error limits in the parallel direction (± 20 G) do not allow a precise experimental determination of this ratio, the most probable value appears to be in excellent agreement with the result of (4).

The agreement with the predictions of the simple relation (4) for the linewidth anisotropy, and the observed linear temperature dependence of the linewidth (Fig. 2), give us some confidence that this simple broadening mechanism is dominant. This enables us to estimate the magnitude of the localized-conduction-electron exchange integral $J_{S,f}$. We have measured the (static) susceptibility of pure Mg metal, and find $\chi = 13.7 \times 10^{-6}$ emu/mole, in rather close agreement with previously published values.¹⁷ This magnitude of χ is a factor of 2 larger than that which would be estimated for a free electron gas with a density appropriate to Mg metal, after the inclusion of diamagnetic corrections. We attribute this difference to exchange enhancement.^{13,18} Using Moriya's¹³ wave-vector-dependent susceptibility average in the static limit, we obtain a value for $|J_{S,f}| = 0.13$ eV. The magnitude of $J_{S,f}$ is larger than that found by Kasuya¹⁹ for pure Er metal (0.056 eV) and may be due to a differing magnitude of the covalent²⁰ (antiferromagnetic) exchange for the rare-earth ion in Mg metal, as compared with the concentrated rare-earth metal.

The Ruderman-Kittel-Yosida²¹ indirect exchange interaction, in conjunction with the observed anisotropy of the field for resonance, results in a nonvanishing second moment if the microwave field has a component perpendicular to the c axis of the Mg host crystal. Using the value $|J_{S,f}| = 0.13$ eV, determined from the temperature-dependent part of the linewidth, and making use of the Kittel-Abrahams³ result for the (cut-off Lorentzian) linewidth of a dilute paramagnet, we calculate a ($T=0$) residual width $\delta = 25$ G for $h_{\text{rf}}, H_0 \perp c$ axis. This contribution must vanish for $h_{\text{rf}} \parallel c$ axis. Experimentally, we find $\delta = 110 \pm 30$ G for $h_{\text{rf}}, H_0 \perp c$ axis, and $\delta = 80 \pm 30$ G for $h_{\text{rf}} \parallel$,

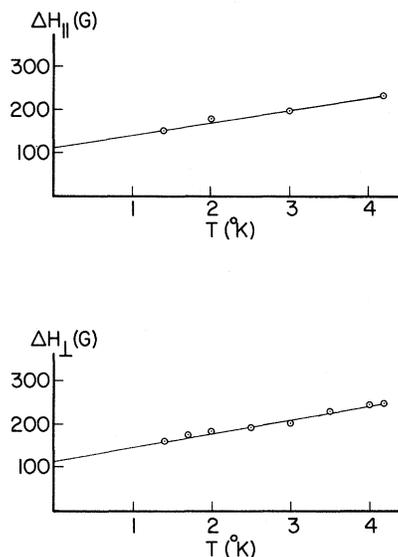


FIG. 2. Temperature dependence of the peak-to-peak resonance linewidth for a 0.1% Er:Mg single crystal.

$H_0 \perp c$ axis. The error limits are unavoidably large, but we do believe we have observed a difference in residual width for the two orientations of the microwave field in agreement with our theoretical estimate. We attribute the remainder of the residual width for $h_{\text{rf}} \parallel c$ axis to a distribution of g values, arising from random strains in the crystal. Unfortunately, however, the low signal-to-noise ratio of our high-frequency (35 Gc/sec) measurements makes it impossible at this time to determine if this assumption is valid.

We have also observed the magnetic resonance of Gd- and Eu-doped Mg metal, but as yet only in polycrystalline samples. The observed g shifts (positive) are consistent with a ferromagnetic $J_{S,f}$ exchange coupling, but a precise value cannot be reported at this time because the line shape deviates from the expected shape. We expect that single-crystal measurements will remove this difficulty and enable us to estimate the magnitude of $J_{S,f}$. We also expect to observe the axial field splitting associated with an S-state ion in a hexagonal crystalline field.

We wish to thank Dr. S. Schultz, Dr. E. Šimánek, Dr. Z. Šroubek, and Dr. R. S. Rubins for many helpful discussions. Special thanks are given to Dr. M. Tachiki for his considerable help in the analysis of our results, and to Dr. L. Hirst for pointing out an error in an

earlier version of this Letter.

*Work supported in part by the National Science Foundation and the U. S. Office of Naval Research, Contract No. NONR 233(88).

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