

crease in ΔH at low temperatures.

The usual ESR method¹² of determining the absolute sign of A for $S \geq 1$ consists of (i) the determination of the sign of A relative to that of the fine-structure coupling constant, and (ii) the determination of the absolute sign of the fine-structure coupling constant by investigating the ESR spectrum at a very low temperature. This indirect method is effective only when both the hyperfine and fine structures are experimentally resolved.

When the fine-structure splitting is very small or vanishing, it is usually not possible to determine the correct sign of A by this indirect method. However, by measurements of the hyperfine splitting at low temperatures and an analysis similar to the one presented here for $\text{SrF}_2:\text{Mn}^{2+}$, the absolute sign of A can be determined unambiguously for both S -state and non- S -state ions with electronic spin $S \geq 1$, even if the fine-structure splitting is zero or

very small.

IV. CONCLUSIONS

An anomalous increase in the splitting between hyperfine lines for Mn^{2+} in SrF_2 has been observed at low temperatures and is explained in terms of the high electron spin polarization expected below 4 K. The importance of this effect is stressed in view of the recent interest in the changes in A itself produced at low temperatures by lattice vibration and expansion and by local modes. Finally, the observation of this effect makes possible the direct determination of the sign of A for paramagnetic ions with $S \geq 1$ when the fine-structure splitting is negligible.

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¹E. Šimánek and R. Orbach, *Phys. Rev.* **145**, 191 (1966).

²E. Šimánek and N. L. Huang, *Phys. Rev. Letters* **17**, 699 (1966).

³T. J. Menne, D. P. Ames, and S. Lee, *Phys. Rev.* **169**, 333 (1968).

⁴T. J. Menne, *Phys. Rev.* **180**, 350 (1969).

⁵T. J. Menne, *Phys. Rev. B* **1**, 4496 (1970).

⁶K. Zdansky, *Phys. Status Solidi* **28**, 181 (1968).

⁷V. M. Vinokurov and V. G. Stepanov, *Fiz. Tverd. Tela* **6**, 380 (1964) [*Soviet Phys. Solid State* **6**, 303 (1964)].

⁸B. Bleaney, *Phil. Mag.* **42**, 441 (1951).

⁹E. Abbott and R. A. Serway, *Phys. Status Solidi* **36**, K9 (1969).

¹⁰R. A. Serway, *Phys. Letters* **26A**, 642 (1968).

¹¹C. Y. Huang, J. F. Reichert, and J. Gigante, *Phys. Letters* **26A**, 219 (1968).

¹²See, for example, Ref. 8.

Hyperfine Splitting of a Localized Moment in a Metal

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The hyperfine splitting of the erbium localized moment resonance in silver metal has been observed for nominal concentrations of 28-, 65-, 86-, and 1500-ppm solid solution Ag:Er alloys. A hyperfine coupling constant $A = 75 \pm 1.0$ Oe was found to fit the individual line positions to within experimental accuracy (± 5 Oe). The magnetic-resonance bottleneck is discussed; it is argued that this bottleneck is absent for these measurements, and is the reason for the failure of previous attempts to observe such hyperfine splittings in transition-metal alloys.

I. INTRODUCTION

We wish to report the first observation of hyperfine splitting of the magnetic resonance of a localized moment in a metal. The magnitude of

the splitting, combined with the resonance g value, leaves no doubt as to the orbital occupation number of the observed moment. The fact that previous measurements (on transition-metal alloys) have failed to observe hyperfine splittings, whereas for

the system reported here (Ag:Er) they have been observed,¹ can be understood in terms of the magnetic-resonance bottleneck.

The magnetic resonance of the solid solution Ag:Er was first reported by Griffiths and Coles² for 0.28% Er samples. They quoted a g value of 6.73 ± 0.1 , and observed the resonance signal between 2.5 and 16°K. We have continued their investigation to more dilute concentrations (from 25 to 1500 ppm, see Fig. 1) and have observed the resonance at both X band and 35 kMc/sec. We have observed the hyperfine splitting of the Er resonance clearly in alloys with concentrations of 28, 65, and 86 ppm; and the outermost lines in a 1500-

ppm sample. The natural abundance of the erbium isotope, Er^{167} , with a nuclear moment $I = \frac{7}{2}$, is 22.8%, so that the intensity of one of the hyperfine components is only 4% of the unsplit ($I=0$ isotopes) central line. The derivative spectra are exhibited in Fig. 1. The line positions are not linearly spaced in field because of second-order hyperfine corrections. Using the Breit-Rabi formula, our best fit occurs for $A = 75 \pm 1.0$ Oe. Table I lists the observed and calculated hyperfine line positions. The central component corresponds to a g factor of 6.852 ± 0.05 , only slightly outside the error limits set by Griffiths and Coles.²

The magnetic resonance of Er^{3+} in ThO_2 has

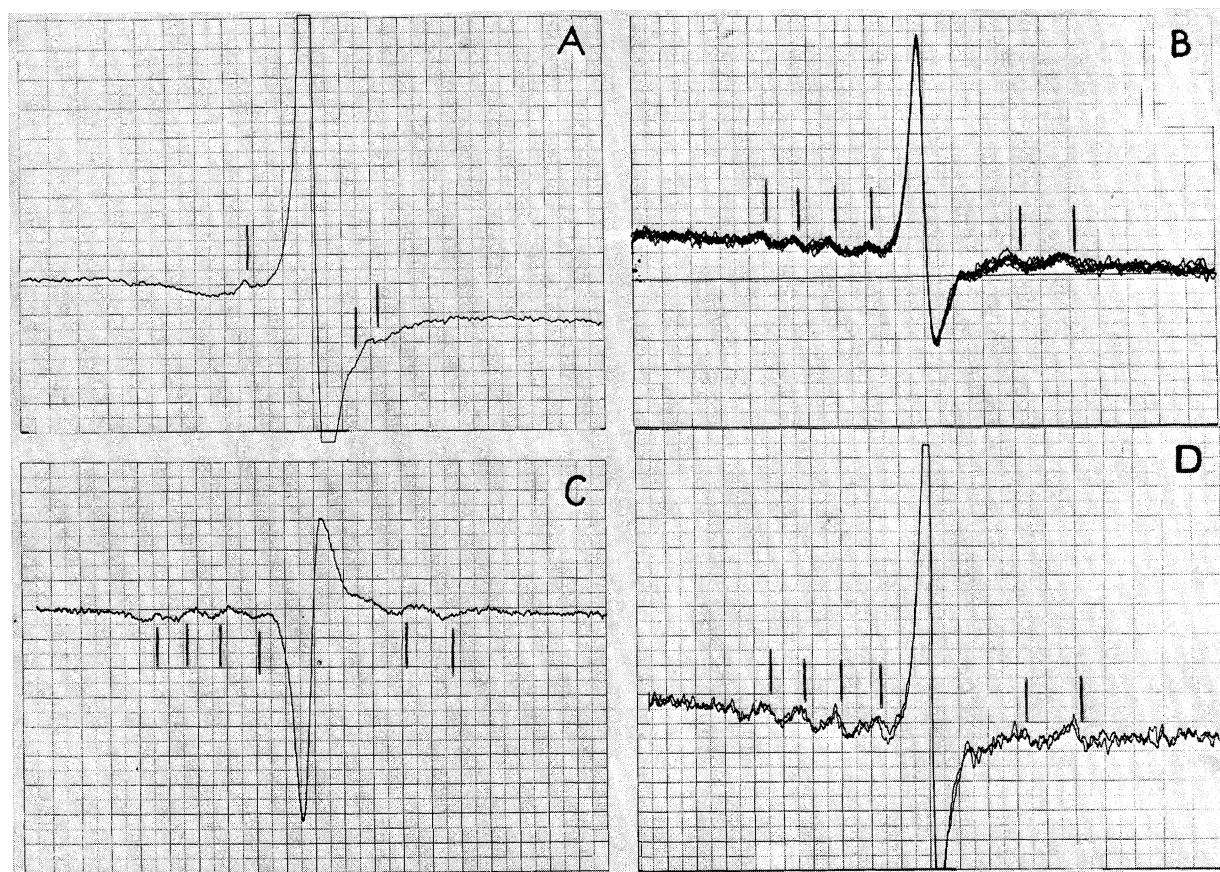


FIG. 1. Absorption derivatives of four different concentration Ag:Er alloys. Measurements are made in reflection at X-band frequency. The central ($I=0$) line occurs at 916.3 Oe in all four cases. Full chart field sweep is 2.5 kOe for the chart labeled A, and 1 kOe for charts B-D. Chart A refers to a 1500-ppm, B to a 86-ppm, C to a 65-ppm, and D to a 28-ppm sample. Multiple traces (Chart B and D) mean multiple sweeps superimposed upon one another. Effect of residual widths (see text) upon the resolution of the hyperfine splittings of Ag:Er¹⁶⁷ ($I = \frac{7}{2}$) is quite apparent. Vertical lines drawn on the figures represent the second-order hyperfine positions as predicted by $H_{\text{res}} = 916.3 - 75M_I - 3.07 \times (15.75 - M_I^2)$, in oersteds. Coefficient $3.07 = A^2/2H_0$, where $H_0 = 916.3$ Oe, the position of the unshifted central line. Higher-order corrections are negligible.

been observed by Abraham *et al.*³ They reported a g factor of 6.752 ± 0.005 , and a hyperfine coupling constant of $A = 73.8 \pm 0.1$ Oe. Because almost all of the hyperfine field for a rare-earth ion with significant orbital moment (non-S-states) is orbital in origin, we can scale their value for A by the ratio of the g factors. The result A (scaled) = 74.9 Oe is in excellent agreement with our measurements. There is no question but that these results confirm the $4f$ character of the Ag:Er resonance. The relative intensities of the hyperfine and central lines are in agreement with the predicted ratio (4%). The central ($I=0$) line has the characteristic Bloembergen⁴ shape for magnetic resonance of fixed centers in thick metallic slabs with a ratio of derivative peak heights (A/B in the notation of Feher and Kip⁵) approximately equal to $2.5 (\pm 0.3)$.

The most obvious question which remains to be answered is why previous measurements (indeed, even in the Ag:Er alloy system²) have not exhibited hyperfine splittings. We believe we can account for the lack of observation in the non-S-state rare-earth dilute alloys by residual ($T=0$) broadening, and in transition-metal (and S-state rare-earth) alloys by the magnetic-resonance bottleneck⁶ (but see below). We consider each in turn.

II. RARE-EARTH DILUTE ALLOYS

The presence of the unsplit $I=0$ Ag:Er resonance enables us to achieve sufficient signal (even at 28 ppm) to perform a significant least-squares

TABLE I. Resonance line positions (in oersteds) for Ag:Er¹⁶⁷ ($I=\frac{7}{2}$). The calculated values are appropriate to a hyperfine coupling constant $A=75$ Oe. The line appropriate to $M_I = -\frac{5}{2}$ may just be seen in Fig. 1; that appropriate to $M_I = -\frac{1}{2}$ is obscured completely by the $I=0$ line. The asymmetry and shift of the line positions relative to the central line are caused by second-order hyperfine effects. The central line ($I=0$) occurs at 916.3 Oe.

M_I	Experimental	Calculated
$\frac{1}{2}$	641.3 ± 5	643.1
$\frac{3}{2}$	696.3 ± 5	699.6
$\frac{5}{2}$	761.3 ± 5	762.4
$\frac{7}{2}$	831.3 ± 5	831.2
$-\frac{1}{2}$...	906.2
$-\frac{3}{2}$...	987.4
$-\frac{5}{2}$	1071.3 ± 5	1074.6
$-\frac{7}{2}$	1161.3 ± 5	1168.1

fit to the temperature dependence of the resonance linewidth. We find that $H_{\text{peak-to-peak}} = \alpha(c) + \beta T$, where α depends on the concentration c , and $\beta = 10.5 \pm 1.5$ Oe/deg does not. The actual value for $\alpha(c)$ is sensitively dependent on crystal preparation because of the strong sensitivity of the resonance g factor to strain. Local departures from cubic symmetry result in admixtures of higher-lying cubic field states into the ground Γ_7 doublet, leading to a distribution of g factors. In addition, Kohn-Vosko⁷ oscillations in the charge density of the Ag:Er solid solutions caused by the charge imbalance between the Ag host and the Er impurity of +2 would lead to a (concentration dependent) distribution of g factors. Whatever the source, a distribution of g values is verified to be the source of the residual width by linewidth measurements at 35 kMc for the 86-ppm sample. The observed linewidth fits a variation $\alpha' + \beta T$, where α' (86 ppm) = 39.4 ± 5 Oe. Compared to the X-band measurements displayed in Fig. 1 [α (86 ppm) = 15 ± 1.5 Oe], the ratio of residual widths, $\alpha'/\alpha = 2.6 \pm 0.5$ is in the vicinity, but less than, the ratio of experimental resonance frequencies, 3.9.

At the higher concentrations of Griffiths and Coles,² 2800 ppm, a residual width of 42 Oe was reported. This width, combined with the thermal contribution (their lowest reported temperature was 2.5°K) of 25 Oe, adds up to 67 Oe, a value quite comparable to the hyperfine splittings and probably sufficient to mask them. Our samples exhibited residual widths of 12.1, 15.5, and 15.0 (± 1.0) Oe at concentrations of 28, 65, and 86 ppm, respectively, which, when combined with the thermal width appropriate to 1.5°K of 15 Oe, gave much better resolution (see Fig. 1) and is the reason for our ability to resolve the hyperfine splitting at all. Of course, once one "knows" it is present, one can see it in more concentrated samples (e.g., see the 1500-ppm sample in Fig. 1).

At the higher concentrations, exchange narrowing via Ruderman-Kittel interactions between Er moments would tend to diminish both the strain and charge oscillation widths, as well as the hyperfine splitting. All these effects give ample reason for going to the limit of very dilute alloys where interaction effects can at least be regarded as small perturbations compared to the quantities of interest (e.g., the hyperfine interaction).

We argue that the observed Ag:Er resonance is not bottlenecked in the exchange sense.⁶ This conclusion is based on the difference in g values between the localized and conduction electron resonances, the small value for $\rho J \sim 0.012$ (derived from the value of β defined above⁸), where ρ is the conduction electron density of states and J is the effective localized conduction electron exchange

integral, and our experience with Mg:Er.⁸ In this latter alloy, the anisotropy of the resonance g factors and linewidths enables us to quantitatively determine the degree of bottleneck. We find that, by extrapolation of our results for Mg:Er to Ag:Er (e.g., ρJ is smaller by a factor of 0.58 for the Ag:Er system) no bottleneck exists by virtue of the large ratio between the Zeeman energy separation of localized and conduction electron resonances and the second-order exchange relaxation widths. The absence of a bottleneck enables us to analyze the line positions and widths of the Ag:Er almost trivially, as indeed we have done in Sec. I of this paper. Such is not the case, however, for the transition-metal alloys.

III. TRANSITION-METAL ALLOYS

It is now appropriate to ask why, even in very dilute (as low as 9-ppm Cu:Mn⁹) transition-metal alloys, the hyperfine splitting has not been seen. These alloys have the intrinsic property of similar (on the scale of exchange relaxation widths $1/T_{ds}$ and $1/T_{sd}$, as defined by Hasegawa⁶) conduction and localized electron g values, and an exchange magnetic-resonance bottleneck obtains. The effect of the bottleneck on the hyperfine splitting of the magnetic-resonance line was first sketched by Langreth *et al.*¹⁰ We have rederived and extended their results to arbitrary g values and examined an additional limit which may be of some practical interest. The basic expansion parameter in their theory when a strong bottleneck is present [$|\omega_s - \omega_e| < 1/T_{sd}$ and $\Delta_{el} < \hbar/T_{sd}$, where ω_s and ω_e are the localized and conduction electron Zeeman frequencies, and $1/T_{sd}$ and Δ_{eL} the Overhauser¹¹ (second-order exchange) linewidth and spin-lattice relaxation width, respectively, for the conduction electron] is $\omega_{HF} T_{ds}$, where ω_{HF} is the hyperfine-splitting frequency and T_{ds} the second-order "bare" (in the

sense of unbottlenecked) exchange linewidth for the localized spin. When $\omega_{HF} T_{ds} \ll 1$, no first-order hyperfine splitting occurs in the bottleneck resonance.¹⁰ An additional linewidth obtains equal in magnitude to $\omega_{HF}^2 T_{ds}$, but only of the order of 1 G for Cu:Mn (where $\omega_{HF} \sim 35$ Oe and $1/T_{ds} \sim 1000$ Oe.) We have found another limit which, while still applicable to the bottlenecked regime, will allow the hyperfine splitting to be observed. In the limit that $\omega_{HF} T_{ds} \gg 1$, additional (spurious for zero hyperfine field) roots combine with the narrow bottlenecked root to yield $2I+1$ roots of equal intensity, split by the full hyperfine splitting, and each processing a width $(2I)/[(2I+1)T_{ds}]$. Because T_{ds} is linearly dependent on $1/T$, a system with sufficiently modest s - d exchange interaction might, over a convenient temperature range, pass from the $\omega_{HF} T_{ds}$ large to small region, and these predictions could be quantitatively checked. It does not seem possible for the former region to obtain in the transition-metal alloy series since $1/TT_{ds} \sim 1000$ Oe/deg and $\omega_{HF} \sim 50$ Oe at best. However, the S -state rare earths seem excellent candidates.

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¹Subsequent to our observations, made in reflection, the hyperfine splitting of Ag:Er was observed in transmission by B. L. Gehman and S. Schultz (private communication).

²D. Griffiths and B. R. Coles, Phys. Rev. Letters **16**, 1093 (1966); L. L. Hirst, G. Williams, D. Griffiths, and B. R. Coles, J. Appl. Phys. **39**, 844 (1968). A more recent g value reported for Ag:Er is 6.85 ± 0.04 [B. R. Coles (private communication)].

³M. Abraham, A. Weeks, G. W. Clark, and C. B. Finch, Phys. Rev. **137**, A138 (1965).

⁴N. Bloembergen, J. Appl. Phys. **23**, 1379 (1952).

⁵G. Feher and A. F. Kip, Phys. Rev. **98**, 377 (1955); F. J. Dyson, *ibid.* **98**, 349 (1955).

⁶H. Hasegawa, Progr. Theoret. Phys. (Kyoto) **21**, 483 (1959); H. Cottet, P. Donze, J. Dupraz, B.

Giovannini, and M. Peter, Z. Angew. Phys. **24**, 249 (1968); J. Dupraz, B. Giovannini, R. Orbach, J. D. Riley, and J. Zitkova, in *Proceedings of the International Symposium on Electron and Nuclear Magnetic Resonance*, Monash University, 1969 (Plenum, New York, 1970), p. 197.

⁷W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

⁸C. R. Burr and R. Orbach, Phys. Rev. Letters **19**, 1133 (1967); R. Chui and J. D. Riley (unpublished).

⁹S. Schultz, M. R. Shanabargar, and P. M. Platzman, Phys. Rev. Letters **19**, 749 (1967); **19**, 1271(E) (1967). More details are available from the thesis of M. R. Shanabargar, University of California, San Diego (unpublished).

¹⁰D. C. Langreth, D. L. Cowan, and J. W. Wilkins, Solid State Commun. **6**, 131 (1968).

¹¹A. Overhauser, Phys. Rev. **89**, 689 (1953).

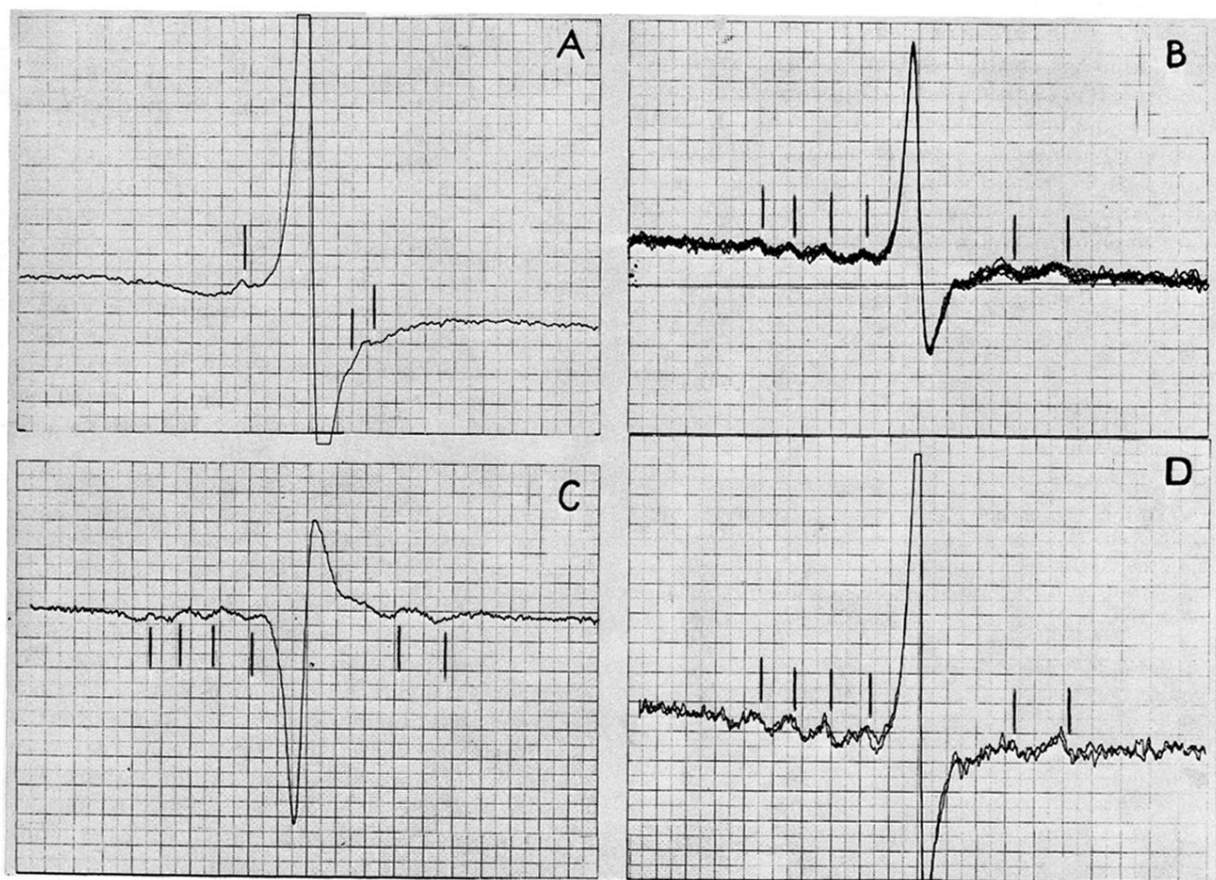


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