

expected to occur if the core fraction increased with pressure. The only effect apparent is that the central parabola becomes broader with pressure, as one would expect on the basis of the increased mean density of valence electrons. The statistical reliability of the data does not justify using them as a test of free-electron theory in this connection.

We are planning to check the entirely unexpected line-shape results using a Ge(Li) spectrometer of much improved resolution and efficiency. The implication of the present results, namely that the core fraction is independent of pressure, is so difficult to accept that we have refrained from comparing our measured annihilation rates with theory.

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Resolved "Fine Structure" in the Magnetic Resonance of a Localized Moment in a Metal*

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The first observation of the resolved fine-structure splitting of a localized moment in a metal is reported in the EPR spectrum of single-crystal dilute Au:Gd alloys. A theory of line narrowing of fine-structure lines from spin-spin couplings and localized-conduction electron exchange is developed. The narrowing distorts the observed resonance line shape, and is essential to the extraction of the fine-structure splitting parameter: $b_4 = -20 \pm 1$ G.

We report the first observation of a resolved crystal-field splitting in the electron paramagnetic resonance (EPR) of a localized moment in a metal. Dilute Au:Gd single crystals were used for our measurements. For low temperatures and specific angles, the spectrum exhibits two resolved resonance lines. At other angles, where only one line is resolved, a strong angular variation in linewidth is observed. We attribute the former behavior to resolved, the latter to unresolved, fine structure. Dynamic effects, originating with a Gd spin-spin interaction arising from the Ruderman-Kittel-Kasuya-Yosida indirect exchange, and the Gd conduction-electron relaxation strongly affect the form of the spectrum. The distortion of the line shape (substantial narrowing) can be described by a population-weighted difference in stochastic transition matrices, arising from these interactions, appropriate to fine-structure resonance splittings. The concentration, temperature,

and angular variation of the spectrum enable us to extract the functional behavior, and explicit values, for the transition rates, as well as the value for the fine-structure splitting parameter. We fit the spectrum by a fourth-order crystal-field parameter $b_4 = -20 \pm 1$ G, and by an isotropic g factor $g = 2.05 \pm 0.01$.

Electron-spin-resonance measurements were performed on single-crystal Au:Gd samples, grown in the form of cylinders, with nominal Gd concentrations of 1000, 300, and 150 ppm. Complementary measurements were performed on powder samples with nominal Gd concentrations of 1000, 500, 150, 75, and 35 ppm. The measurements were conducted at 3 and 0.8 cm wavelength, and as a function of angle and temperature in the liquid-He range. The magnetic field was rotated in a plane perpendicular to the cylinder axis. The spectra at 3 cm exhibit the following features:

(1) At 4.2°K a "single" line is observed for

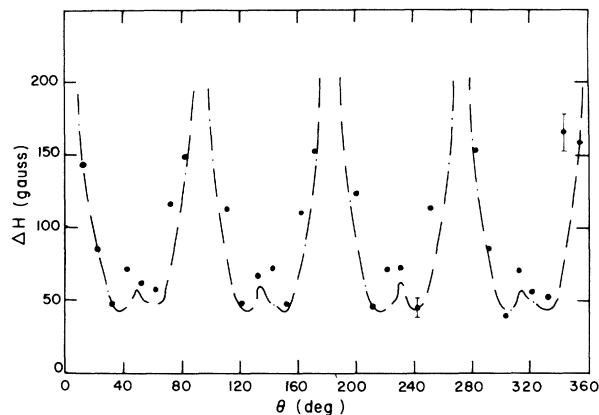


FIG. 1. The angular variation of the magnetic resonance linewidth (half-width at half-power) for single-crystal Au:Gd (300 ppm) at a frequency of 8.7 GHz at 1.4°K. The broken lines are the spin-spin narrowed theoretical fit; the solid circles are the experimental results.

all values of angle. The linewidth exhibits an appreciable angular variation. Similar changes are also obtained at 1.4°K (Fig. 1), except for certain angles where the magnetic field is approximately in the [100] direction. At this position, a resolved structure consisting of two peaks is observed [Fig. 2(a)]. The values of the angles at which the spectra exhibit this behavior are identical to those at which maxima in the linewidths are observed at 4.2°K.

(2) At 1.4°K, the resonance position of the "single" line exhibits an angular variation of 30 ± 5 G. This variation is slightly reduced at 4.2°K. The field for resonance at the angle (θ_{\min}) appropriate to minimum linewidth yields a g value of 2.05 ± 0.01 . The same g value also obtains for powdered samples of Au:Gd for all the concentrations measured.

(3) The temperature dependence of the linewidth was measured both for single-crystal and powdered samples. In the single crystal at θ_{\min} , a nearly linear increase of the linewidth with temperature was observed, varying roughly as $a + bT$. The value of a decreases with decreasing concentration. The value of b was found to be approximately the same for both the powdered sample and the single crystal (at θ_{\min}) for the same Gd concentration. For the lowest Gd concentration measured (35 ppm), $b = 8 \pm 1$ G/deg. The value of a was found to be larger for powdered samples than for single crystals (for the same Gd concentration). The results are tabulated in Table I.

In the 0.8-cm experiments, the measured

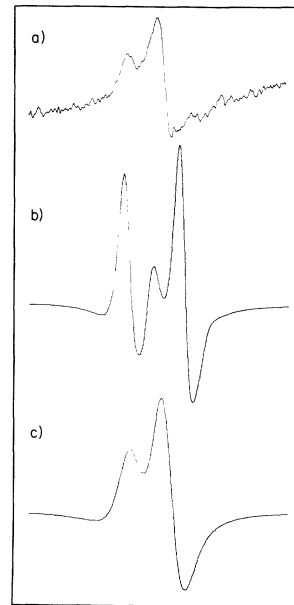


FIG. 2. (a) The magnetic resonance spectrum of Au:Gd (300 ppm) observed experimentally at 1.4°K, with the magnetic field approximately along the [100] direction (maximum fine-structure separation). The full magnetic field sweep used in this and the spectra below is 2.5 kG with the center field set at 3.0 kG. (b) The theoretical fine-structure spectrum for Au:Gd with the magnetic field along the [100] direction, including the Boltzmann population factor for each level, the associated transition probability, the residual width, and the mixing and broadening associated with the conduction-localized electron exchange coupling. The spin-spin coupling has not yet been included. (c) The theoretical fine-structure spectrum for Au:Gd as in (b), but including the effects of spin-spin coupling (see text).

linewidth is much broader than at 3 cm. The signal-to-noise ratio is thereby much poorer than at 3 cm, and we are unable to analyze our data quantitatively. However, we do observe

TABLE I. The linewidth of Au:Gd at low Gd concentration increases roughly as $a + bT$. Values of a and b , in gauss, are listed for the various low-concentration samples measured.

Concentration (ppm)	a	b	Form of sample
150	17 ± 3	6 ± 1	Single crystal
300	44 ± 5	7 ± 2	Single crystal
35	44 ± 3	8 ± 1	Powder
75	66 ± 3	7 ± 1	Powder
150	66 ± 5	7 ± 2	Powder
500	79 ± 5	6 ± 2	Powder

an appropriate angular variation of linewidth expected in the presence of fine structure, as discussed below.

An interpretation of the angular dependence of the linewidth can be given in terms of crystal-field splitting of the Gd $^8S_{7/2}$ state with consequent "fine structure" in the magnetic resonance spectrum. The $^8S_{7/2}$ in a cubic crystalline field splits into a doublet Γ_6 , doublet Γ_7 , and quartet Γ_8 . The energy levels in the presence of both the crystalline and external magnetic field have been calculated by many authors,^{1,2} and the fine-structure spectrum is expected to exhibit seven lines. The field for resonance is given by

$$\begin{aligned} H(\pm \frac{5}{2} \rightarrow \pm \frac{7}{2}) &= H_0 \mp (20b_4/g\beta)(1 - 5\varphi), \\ H(\pm \frac{3}{2} \rightarrow \pm \frac{5}{2}) &= H_0 \pm (10b_4/g\beta)(1 - 5\varphi), \\ H(\pm \frac{1}{2} \rightarrow \pm \frac{3}{2}) &= H_0 \pm (12b_4/g\beta)(1 - 5\varphi), \\ H(\frac{1}{2} \rightarrow -\frac{1}{2}) &= H_0, \end{aligned} \quad (1)$$

where $\varphi = l^2m^2 + m^2n^2 + n^2l^2$, with l , m , and n the direction cosines between the magnetic field and the cubic axes, and b_4 the fourth-order crystal-field parameter.³ We neglect terms of the sixth order (as in nonmetals, they are expected to be much smaller).

It is clearly seen from (1) that all the fine-structure lines collapse into a single line centered at H_0 at an angle where $\varphi = \frac{1}{5}$. This angle corresponds to the "minimum" linewidth angle θ_{\min} in our observed spectra. We take, therefore, this minimum linewidth to be the width of each of the fine-structure lines. It is composed of a residual and a "Korringa" part. The latter (see below) will mix as well as broaden each of the fine-structure lines. Figure 2(b) exhibits the theoretical line shape in the [100] direction for all the fine-structure lines, taking into account the Boltzmann population factors as well as the relevant transition probabilities. The shape of each of the lines was assumed to be metallic, with an A/B ratio of 2.5 (this is the value of A/B found at θ_{\min}).

A comparison of Figs. 2(a) and 2(b) indicates the necessity of introducing a narrowing mechanism into our theoretical model. It is important to recognize that the Korringa interaction does result in the collapse of some of the fine-structure lines, but it is not an adjustable parameter. Its magnitude is determined by the temperature dependence of the linewidth at θ_{\min} , and

we have used this value in generating Fig. 2(b). We hypothesize that spin-spin couplings, somewhat smaller than the cubic crystalline field splitting, exist in Au:Gd. Loram, Whall, and Ford⁴ have made a detailed analysis of such interactions in dilute Au:Mn alloys, obtaining very much larger values for the mean square fields than would result from simple local-exchange models (nearly two orders of magnitude). Scaling their results by the square of the respective exchange integrals, and allowing for the difference in concentrations according to Fig. 4 of Ref. 4, we obtain a root mean square field of 250 G for Au:Gd at 300 ppm. Our analysis below yields a value approximately one tenth of this extrapolation. It is interesting to note that systematics of this sort have been predicted by Caroli.⁵ He shows that for virtual bound states lying close to the Fermi level (Au:Mn?) a spin-spin coupling two orders of magnitude larger than predicted by a simple local-exchange model would result. Such an enhancement would be absent for rare earths where the occupied $4f$ levels lie well below the Fermi energy (e.g., Gd). Loram, Whall, and Ford,⁴ however, attribute the enhancement to the wave-vector dependence of the localized-conduction electron exchange coupling.

The computation of the exchange narrowing of fine structure at temperatures of the order of the Zeeman splittings has not apparently been previously published. It differs substantially from Mössbauer calculations because the "effective field" the electronic spin "sees" is a function of the M_s state in which it finds itself instantaneously. We have taken over the cross-relaxation model of Blume,⁶ developed for the temperature dependence of the Mössbauer line shape for ferric hemin, and altered it to apply to the case of fine structure in the presence of spin-spin and localized-conduction electron exchange coupling. We shall merely sketch our method here—a full exposition will be published elsewhere. One notes that the rf perturbation of the spin is given by $\mathcal{H}' = -\frac{1}{2}\gamma\hbar H_1[S_+e^{-i\omega t} + S_-e^{i\omega t}]$, where H_1 is the applied rf field of frequency ω , and γ the gyromagnetic ratio. A spin in a given m_s state will emit and absorb photons at frequencies which differ by the fine-structure shifts of the adjacent $m_s \pm 1$ levels. Hence, a stochastic model of fine-structure narrowing must differentiate between the two processes. We construct two transition matrices, appropriate to rf photon absorption and emission, with matrix ele-

ments of the form

$$C \sum_{m_s'', m_s'''} |\langle m_s | S^{\pm} | m_s' \rangle|^2 |\langle m_s'' | S^{\pm} | m_s''' \rangle|^2 n_{m_s'''}$$

associated with the transition frequency appropriate to $m_s = m_s'$. The form of these elements is similar to those of Blume,⁵ except that here overlapping lines allow for m_s'' and m_s''' different from m_s and m_s' . The coefficient C is a constant, and $n_{m_s'''}$ is the fractional Boltzmann population of the m_s''' Zeeman level. We also include spin-flip and frequency-modulation terms, arising from the localized-conduction electron exchange scattering. The theoretical result, for $C=2$ G, is exhibited in Fig. 2(c). The quantity $CS(S+1)$, according to cross-relaxation theory,⁷ is of the order of the root mean square spin-spin field. The value obtained here is an order of magnitude smaller than that extrapolated from Au:Mn, in qualitative agreement with the predictions of Caroli.⁵ The use of a single value for C is in error—one should rather average the appropriate spectra over a distribution of spin-spin couplings. This may explain some of the small differences in features between the observed and the calculated spectra. The theoretical model also yields a field for resonance having an angular variation of 35 G, in reasonable agreement with the experimental results.

The crystalline field parameter $b_4 = -20$ G in Au:Gd is identical in sign to that found for Gd in the nonmetallic hosts CaF_2 ¹ and ThO_2 ⁸ (eight coordination number) and CaO (six coordination number).⁹ The magnitude, however, is half that found for Gd^{+3} in ThO_2 and CaF_2 but two times that found for CaO. Although the origin of crystal-field splitting of Gd^{+3} in the various hosts (metals and nonmetals alike!) is not completely understood, it is worthwhile to point out that the sign of b_4 for all rare-earth resonances (Er, Dy, Gd) measured in the noble metals (twelve coordination) is negative. The same parameter is also negative for identical ions in CaF_2 and ThO_2 (eight coordination number).

It should be mentioned here that first- and second-moment calculations, similar to that performed previously for the unresolved fine structure in Mg:Gd,¹⁰ are also in agreement with our experimental results. The slope of the linewidth versus temperature, b , "increases" with decreasing concentration. This effect can be attributed to either the existence of a bottleneck in the magnetic resonance, or (we suggest) to

the fact that, in samples with "large" Gd concentrations (large residual width), simple additivity of the residual and thermal widths is not a good approximation. The former does not seem appropriate here, for addition of 2 and 1% Pt impurities into Au:Gd increases appreciably the value of a , and decreases b . This is opposite to the change expected if a bottleneck were present. If we take the magnitude of the exchange interaction between the localized moment and the conduction electrons to be the same in Au:Gd as in (nonbottlenecked) Au:Er,¹¹ a value for b obtains equal to the observed value of 8 G/°K at the lowest Gd concentrations. This is further evidence for the absence of a bottleneck, and leads us to attribute the apparent concentration dependence of b to the second origin given above.

Finally, we should like to mention that the origin of the g shift in Au:Gd does not appear explicable in terms of a simple exchange polarization model. The value of J required to fit the linewidth ($J = +0.1$ eV) would yield a g shift much smaller (+0.02) than the observed (+0.05) value. We currently have no explanation for this discrepancy.

In conclusion, we have observed for the first time a resolved "fine structure" in the EPR of a localized moment in a metal. We have demonstrated the existence of dynamic effects which result in line shapes quite different from those found in nonmetals, and we have developed a model which seems capable of explaining our results. And, we have extracted a value for the crystal field $b_4 = -20$ G.

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Localized Versus Itinerant Description of Ferromagnetism in Iron*

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Temperature-dependent hyperfine-field studies of *FeSi* and *FeMn* alloys show that ferromagnetism in iron is a result of long-range exchange interactions, coupling largely localized magnetic moments. This long-range exchange is probably due to the partially itinerant character of the *3d* electrons.

Studies of hyperfine fields in dilute iron-based alloys at temperatures low compared to the Curie temperature have yielded a considerable amount of information about the spin-density distribution in these alloys. For simple dilutents one can also obtain information about the spin-density distribution in the pure metal, which may lead to a better understanding of the origin of ferromagnetism in iron.

Mössbauer-effect and nuclear-magnetic-resonance spectra of iron alloys consist of a distribution of overlapping peaks which can be attributed to absorbing nuclei having various numbers of impurities in the neighboring shells. An impurity can effect the hyperfine field at neighboring nuclei in several distinct ways: (a) polarization effects produced by the magnetic moment of the impurity causing spin-density oscillations; (b) changes in the magnetic moment of *3d* character on atoms surrounding the impurity. These changes can occur both in the localized magnetic moment if present or in the spin-density distributions of the itinerant *3d* electrons. (c) By changing the effective exchange coupling strength of the localized moments of neighboring ions, the temperature dependence of the localized moments and thus the hyperfine field at atoms surrounding the impurity will change.

Until now most of the studies of hyperfine fields in ferromagnetic alloys have been concentrated in the low-temperature range. From these measurements one obtains information about mecha-

nisms (a) and (b). Although various models have been used in attempts to explain these experimental results, it seems quite unlikely that one will be able to determine the relative importance of mechanisms (a) and (b). This is especially so since the more basic problems like the origin of ferromagnetism in iron and the nature of the magnetic moments are as yet unsolved. The most important question really is, "Should the magnetic properties of iron be described using a localized-moment picture or should one use the band description as in the Stoner model?" Perhaps when these problems are solved one will be able to understand the hyperfine fields at low temperatures. A study of the localized versus band description of iron can be done through mechanism (c). To our knowledge the only iron-based alloys on which a detailed temperature-dependent study has been done are the *FeMn* alloys.¹ For these alloys the temperature dependence of the Mn^{55} hyperfine field as well as that of Fe^{57} in some of the configurations² can be described reasonably well with molecular field theory^{2,3} assuming localized moments of $(2-3)\mu_B$ and $2.2\mu_B$ for the Mn and Fe atoms, respectively. In the molecular field theory used, only nearest-neighbor exchange interactions are assumed to be important. Although the localized-moment model cannot explain the results in detail, it does give a good qualitative description of the temperature dependences of the various hyperfine fields. It should be noted that if iron were a pure Stoner ferromagnet, the hy-