Exchange-relaxation narrowing of the fine structure of Gd in single crystals of Pd

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The magnetic-resonance spectrum of single crystal Pd:Gd (300 and 500 ppm) is reported at temperatures from 1.32 to 5.16 K. Fine structure appropriate to a cubic local environment is observed. The theory of Barnes and Zimmerman for fine-structure narrowing in dilute magnetic alloys is applied and a cubic crystalline field splitting parameter $b_4 = 29.6$ G extracted, in agreement with a previous report for a more concentrated sample (1300 ppm) by Devine $et\ al$. The theoretical spectrum does not exhibit structure in the vicinity of the field for resonance of the $M_s = 1/2 \leftrightarrow M_s = -1/2$ transition, whereas the experimental spectrum exhibits a peak at that position. The 1300-ppm sample reported by Divine $et\ al$. exhibits a substantially larger peak at this position (compared to the other fine-structure lines) than the 300-ppm sample, while the 500-ppm line is only slightly more intense than the 300-ppm sample. It is argued that long-range spin-spin interactions are responsible for the collapse of the fine structure of a fraction of the Gd spins to the $1/2 \leftrightarrow -1/2$ position, while the remainder of the Gd are isolated spins in the Pd matrix. The observed superposition of collapsed and isolated Gd spectra allows one to draw inferences about the spatial distribution of the spin-spin field at very low solute concentrations. In particular, the spin-spin interactions in Pd:Gd are consistent with a model wherein they are large within a sphere containing $\sim$200 Pd lattice sites, and negligible outside.

I. INTRODUCTION

We report the electron-magnetic-resonance spectrum of Pd:Gd (300 and 500 ppm) single-crystal dilute alloys in the liquid-helium (1.32 to 5.16 K) temperature range, for arbitrary magnetic field direction. A previous report presented single-crystal measurements at 1300, 650 and 200 ppm.[1] There, the spectrum was exhibited as a function of temperature only for the 1300-ppm sample, the others being too weak to follow over the full temperature range. A comparison of the spectra for various temperatures for the three samples (300, 500 and 1300 ppm) can be obtained from Figs. 1, 2, and 3 of this paper. In addition to the improved resolution at 300 and 500 ppm, a striking feature which differentiates these two from the 1300-ppm spectra is the magnitude of the structure at $\sim$ 3800 G. It is a small perturbation in the 300- and 500-ppm spectra, but dominates the 1300-ppm spectra at intermediate and high temperatures.

Recently, Barnes[2] and Plefka[3] have developed a theory for the narrowing of electron-spin-resonance fine structure via thermally induced conduction-localized electron exchange transitions in dilute magnetic alloys. Application was made to hexagonal hosts with uniaxial fine structure (Mg: Gd) by Zimmermann $et\ al$.[4] We have extended their work to cubic hosts, and attempted to fit the Pd:Gd spectra reported here as well as that in Ref. 1. As will be seen below, all of the features of Figs. 1 through 3 can be explained on the basis of this theory, with a single exception: the "$\frac{1}{2} \leftrightarrow -\frac{1}{2}$" feature is absent from the theoretical simula-

tion. It is argued in this paper that the true $\pm\frac{1}{2}$ transition line has been broadened and absorbed by exchange relaxation into the neighboring resolved fine-structure lines by virtue of the large spin-flip matrix elements for $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transitions. Measurements in the vicinity of the magnetic field angle of 29° with respect to the [001] axis in the (110) plane, where the fine structure collapses, yield values for the field for resonance, thermal broadening and residual linewidth, the only other variables in the problem. Therefore, the fitting procedure contains only a single adjustable parameter (the cubic-field splitting itself). Theoretical simulation spectra are exhibited in Figs. 4 through 6. The absence of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ line is evident, and its dependence on exchange relaxation vividly demonstrated in Fig. 6 where the spectrum at 1.32 °K is computed with and without exchange.

We interpret our results in the following manner. We suggest that the structure in Figs. 1 through 3 (apart from the feature at $\sim$ 3800 G) is resolved fine structure. Applying the theory of Barnes[2] we obtain a value for $b_4 = 29.6$ G (in the notation of Abragam and Bleaney[5]). The feature at $\sim$ 3800 G is attributed to Gd spins which experience strong exchange fields from "neighboring" Gd spins. We argue that this spin-spin interaction is statistical in the sense that it represents fluctuations in local concentrations in combination with a long-range spin-spin interaction.[6-9] Thus, the g factor for the "spurious" $\pm\frac{1}{2}$ signal lies at 1.788 ± 0.007, 1.788 ± 0.010, and 1.813 ± 0.007 for the 300-, 500-, and 1300-ppm samples, respectively, at $T = 1.3$, 1.35, and 1.55 °K. The center of gravity of the
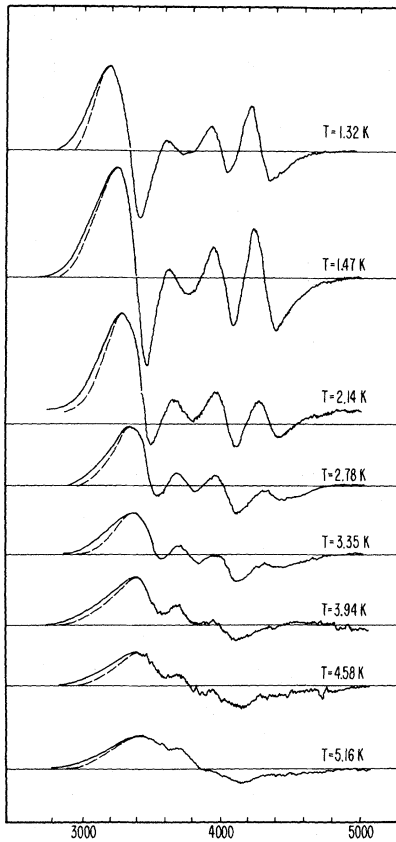
FIG. 1.   Measured Pd : Gd (300-ppm) spectra for dif-
ferent temperatures as a function of magnetic field along
the [001] direction. The intensity at 1.32 °K should be
multiplied by 1.6. The dashed lines are the estimated
Gd signal after subtracting the cavity background (with a
20% possible error).

field for resonance of the fine-structure lines
corresponds to g factors of 1.788 ± 0.007, 1.788
± 0.01, and 1.785 ± 0.007, respectively (at the
same temperatures). The work of Cottet and
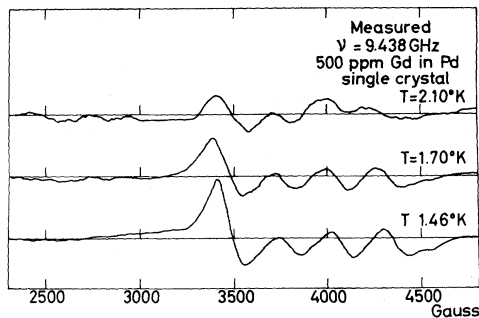Peter,[10] and Cottet,[11] would yield $g = 1.780 \pm 0.005$

FIG. 2.   Measured Pd : Gd (500-ppm) spectra for dif-
ferent temperatures as a function of magnetic field along
the [001] direction. The dashed lines are the estimated
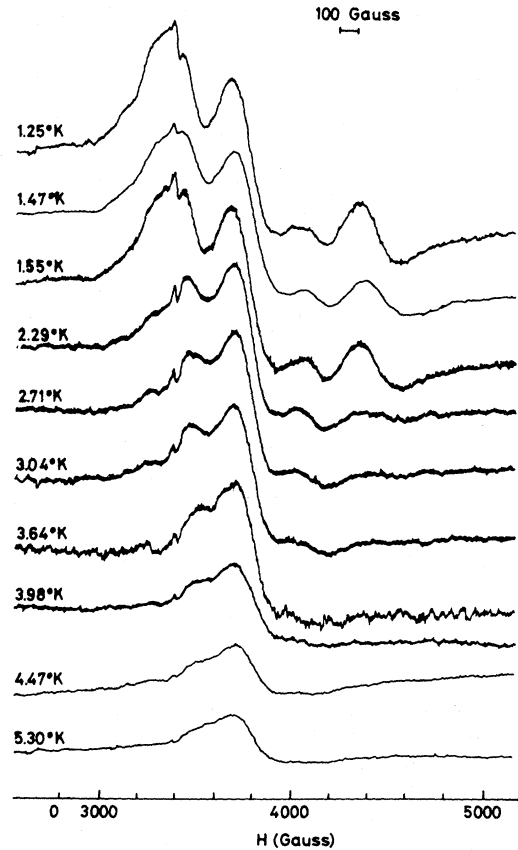Gd signal after subtracting the cavity background.

FIG. 3.   Measured Pd : Gd (1300-ppm) spectra for dif-
ferent temperatures as a function of magnetic field along
the [001] direction, from Ref. 1.

for Gd concentrations less than 2000 ppm in Pd.[12]
This leads us to the conclusion that sizeable local
fluctuations in concentration are present. Cottet
and Peter[10] demonstrate the concentration depen-
dence of the resonance g factor, so that the posi-
tion of the $\pm \frac{1}{2}$ line in the 1300-ppm sample would
correspond to an effective concentration of ~ 7000
ppm. This seems metallurgically puzzling, but
not inconsistent with the recent work of Beck and
Claus.[13] The less concentrated ($c \gtrsim 500$ ppm) sam-
ples exhibit no apparent g-factor difference be-
tween the $\pm \frac{1}{2}$ feature and the fine-structure center
of gravity.

The only explanation for such behavior, and the
simultaneous presence of isolated Gd fine-struc-
ture spectra, is a peculiar long-range dependence
of the spin-spin indirect-exchange coupling. Also,
the superposition of spectra indicates that few if
any of the Gd spins experience an intermediate en-
vironment. Because of the lack of a g-factor shift
at low concentrations, as would be the case in the
presence of large local concentrations, one is
therefore led to surmise a long-range polarization
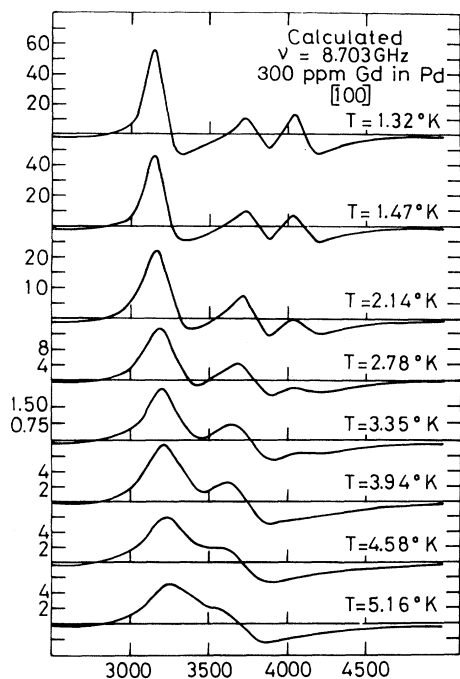with a sharp falloff of the spin-spin indirect-ex-

FIG. 4. Calculated Pd : Gd (300-ppm) spectra for different temperatures as a function of magnetic field along the [001] direction. The parameters used appear on the graph. Notice the change in vertical scale for many of the temperatures.

change interaction at about six lattice constants. This concept is in remarkable agreement with the conclusions of Peter *et al.*,[14] Giovannini *et al.*,[6] Low and Holden,[7] Schrieffer,[8] and Clogston.[9]

In the next section, the experimental procedures are outlined. The exchange-relaxation line-narrow-
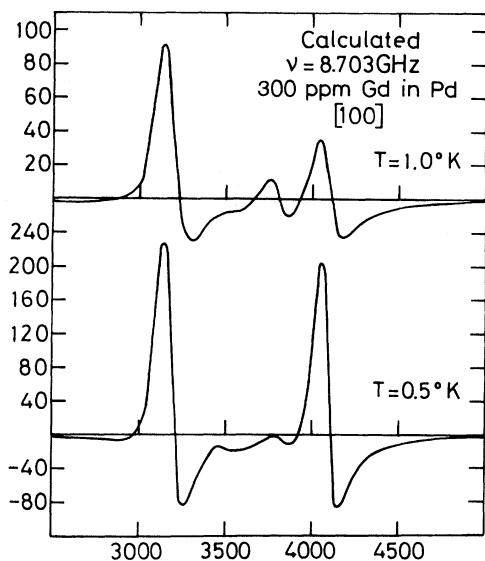

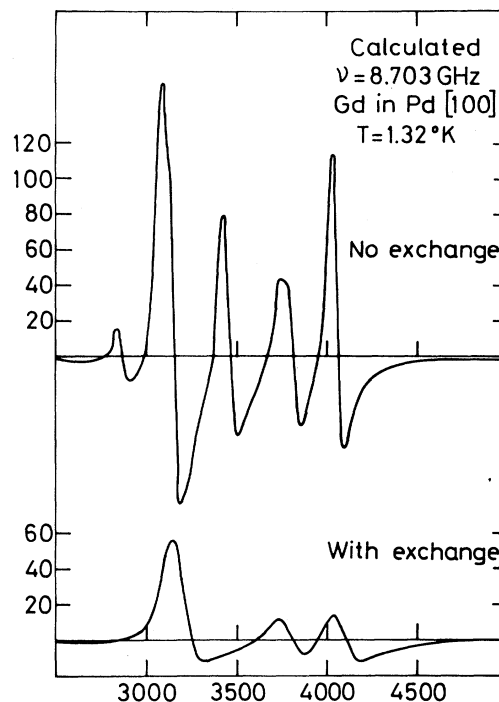FIG. 5. Continuation of Fig. 4 to lower temperatures.

FIG. 6. Calculated Pd : Gd (300-ppm) spectra at T = 1.32 °K (same as in Fig. 4) calculated with (upper) and without (lower) exchange. The positions of the seven fine-structure lines are clear, as is the absence of the $\pm \frac{1}{2}$ line when the exchange is "turned on".

ing theory is applied to our results in Sec. III. A discussion is given concerning the discrepancy between the values obtained in Ref. 1 for the exchange constant between the localized and conduction electron spin deduced from the Pd : Gd g-shift, and from the temperature-dependent linewidth. Section IV summarizes our work and remarks on future possibilities.

II. EXPERIMENTAL TECHNIQUES

The experimental results reported in this work (and previously[1]) were obtained from single crystal 300 and 500 (and 200, 650, and 1300) ppm Pd : Gd alloys. The 1300-ppm sample was purchased from Koch-Light and Co., while the remaining samples were prepared in the following manner. The requisite amounts of Gd were arc melted together with 99.999% pure Pd to produce alloy boules of the required concentrations. The arc melting process was repeated several times for each sample to ensure homogeneity of alloying. Weight losses were carefully controlled during this process, and any samples showing severe loss were rejected. After cleaning, the samples were heavily cold worked by rolling the boules (approximately 4 mm in thickness) into foils 0.2
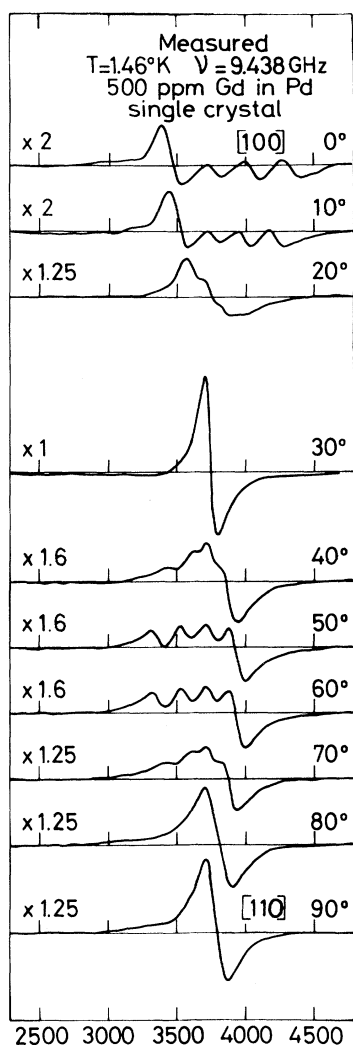
FIG. 7. Measured Pd : Gd (500-ppm) spectra at 1.46 °K as a function of magnetic field angle with the [001] direction, in the (110) plane. The dashed lines are the estimated Gd signal, after subtracting the cavity background.

mm thick. The foils were then cleaned and heated to 1520 °C in alumina crucibles, under an argon atmosphere. After several hours at 1520 °C, the furnace was cooled and the samples removed. Generally, the foils, approximately 3 cm square, contained two or more very large single crystals grown during the process of recrystallization. Occasionally, the entire foil was found to be a complete single crystal. The required single crystal was cut from the foil using electroerosion. Concentration determination was made where possible by chemical analysis, and by measurement of the susceptibility of samples composed of remnants of the recrystallized foils. An estimated concentration accuracy of 50 ppm applies to each

sample.

Standard X-band Varian superheterodyne and E-line spectrometers, operating at 9.5 GHz, were used to make the EPR measurements, the magnetic field being calibrated using a proton resonance magnetometer. The sample orientation in the microwave cavity was adjusted so that the plane of rotation of the static magnetic field coincided with a (110) plane of the sample. Low temperatures were obtained using a liquid helium cryostat in which the area around the sample and cavity was either filled with He exchange gas, or else He was liquified in the cavity space and the temperature lowered by pumping. In this manner, temperatures as low as 1.3 °K were easily obtained. The temperature of the sample was measured using a germanium resistance thermometer mounted on the microwave cavity directly behind the sample.

The experimental results for the external field directed along the [001] direction are exhibited in Figs 1–3 for Gd concentrations of 300, 500, and 1300 ppm, respectively. The angular dependence of the 500 ppm spectrum is exhibited in Fig. 7.

III. APPLICATION OF THE EXCHANGE-RELAXATION LINE-NARROWING THEORY

The magnetic-resonance study of Devine et al.[1] was the first to resolve the fine structure of Pd : Gd alloys. Their spectra for 1300 ppm (Fig. 3 here) exhibit four distinct lines at $T = 1.25$ °K. These were assigned to the fine-structure transitions $-\frac{5}{2} \leftrightarrow -\frac{3}{2}$, $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$; $-\frac{1}{2} \leftrightarrow \frac{1}{2}$; $\frac{3}{2} \leftrightarrow \frac{5}{2}$, $\frac{1}{2} \leftrightarrow \frac{3}{2}$; and $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$. The paired transitions were seen as overlapping lines, and the $\frac{7}{2} \leftrightarrow \frac{5}{2}$ transition was hardly detected because of low thermal population. The spectra were fitted to an appropriate cubic field splitting by superposing properly assymetric lines[15] at appropriate field positions with appropriate relative intensities. The fit at 1.25 °K was excellent, but at higher temperature failed significantly. According to Ref. 1, "we find satisfactory agreement only if we take a temperature-dependent ion-ion exchange coupling term together with an added central resonance line. The results of such calculations are thus, for us, not presently explicative of our results."

In this section, we apply the exchange-relaxation line-narrowing theory of Barnes[2] to the low-concentration (300 and 500 ppm) Pd : Gd spectrum. The observed spectra will be matched over the full temperature range and as well over the full angular range for the magnetic field in a (110) plane. An "explanation" for the anomalous central $(\pm\frac{1}{2})$ resonance line (which, as noted by Devine et al.,[1] does appear to vary in relative strength with concentration) will be given.

The resolved lines in Figs. 1 and 2 allow for the extraction of the cubic fine-structure parameter b_4 (b_6 appears to be negligible here[16]). Fortunately, Pd:Gd does not appear to be "bottlenecked," so that at sufficiently low temperature the fine structure can be clearly resolved. We adapt the fitting procedure of Zimmermann *et al.*[4] for axial hosts to the cubic case by substituting the appropriate fields for resonance for the various cubic-field-shifted Zeeman levels. The fine structure collapses when the external magnetic field makes an angle of 29° with respect to the [001] direction in a (110) plane. This allows for an accurate measurement of the g shift, thermal broadening, and residual width of the "isolated" Gd spins at low Gd concentrations, where the $\pm\frac{1}{2}$ line intensity arising from interacting spins is small compared to the collapsed line intensity of the noninteracting spins. The field for resonance of the 300-ppm sample (at the crossing angle) was appropriate to $g = 1.792 \pm 0.008$, in slight disagreement with Ref. 1 which quotes 1.806 for the 200-ppm sample. The thermal broadening was found to equal 9.3 ± 0.4 G/K for the 300-ppm sample, well within the error limits of Ref. 1, and the residual width was best approximated by 50 G for the 300-ppm and 70 G for the 500-ppm sample.

As noted in Ref. 1, the g shift and linewidth yield values for the exchange coupling between the localized and conduction electrons of $J(g$ value) $= -0.016 \pm 0.005$ eV and $|J$(linewidth)$| = 0.003 \pm 0.0005$ eV, respectively. The effect of exchange enhancement was included by Devine *et al.*,[1] but they only took into account s waves (delta function spatial interaction). If one generalizes the exchange to a finite range, one can expand in partial waves and define[17]:

$$J(\vec{q}) = \sum_L (2L+1) J^{(L)} P_L(\cos\theta) , \qquad (1)$$

where θ is the angle between incoming and outgoing conduction-electron wave vectors. Clearly, (1) assumes a spherical Fermi surface[18] (otherwise, J is not a function of the difference of incoming and outgoing wave vectors, but rather depends on their individual magnitudes), and such is hardly the case for Pd metal. Any accurate analysis must treat the full $J(\vec{k}, \vec{k}')$ character of the exchange.[19] However, if one pushes ahead with a partial wave analysis, one runs into the following difficulty:

Given (1), one can define values for the g shift and linewidth exchange as follows[17,20]:

$$J(g \text{ shift}) = \frac{\sum_L (2L+1) J^{(L)}}{1 - U\chi(1)} ; \qquad (2a)$$

$$J^2(\text{linewidth}) = \sum_{L,L'} (2L+1)(2L'+1) J^{(L)} J^{(L')}$$

$$\times \left\langle \frac{P_L(\cos\theta) P_{L'}(\cos\theta)}{[1 - U\chi(\cos\theta)]^2} \right\rangle. \qquad (2b)$$

Here, U is the conduction-electron–conduction-electron Coulomb repulsion, $\chi(\cos\theta)$ is the wave-vector-dependent static susceptibility where $\cos\theta$ is defined after (1), and the brackets indicte $\frac{1}{2}$ the integral over $\cos\theta$ from -1 to $+1$. For Pd, Duclo *et al.*[21] give $U\chi(1) \equiv \alpha = 0.86$. The integrals in (2b) have been kindly computed for us by R. E. Walstedt for values of α at or near 0.86, and for partial waves from s to f character. If one now examines (2), using the values for $J(g$ value) and $|J$(linewidth)$|$ given above, one quickly recognizes that the experimental g shift is too large for the accompanying line width. For example, consider the limiting partial waves, s and f (it is unlikely that higher partial waves could contribute significantly). Using Walker and Walstedt's values for the integrals in (2b), we obtain the following relations:

$$J^{(0)} + 7J^{(3)} = -0.016 \pm 0.005 \text{ eV},$$

$$0.302(J^{(0)})^2 + 2.52(J^{(3)})^2 + 2(0.0837) J^{(0)} J^{(3)}$$

$$= (2.7 \pm 0.97) \times 10^{-6} \text{ eV}^2. \qquad (3)$$

It is easy to show that there is no solution to (3). Indeed, the maximum ratio possible (for $\alpha = 0.86$) for $|J(g$ value)$/J$(linewidth)$| = 4.41$. The experimental values on the right-hand side of (3), give a minimum ratio of 5.74 at the extremes of the error limits. Thus, no solution is possible, and a full wave-vector-dependent formulation is required. It is somewhat fortunate that J(linewidth) should be so small. Indeed, if it were within the limits of a partial wave analysis, the entire fine structure would be collapsed even at 1 °K. The ability to observe the fine structure at all in Pd: Gd thus depends on the nonspherical character of the Fermi surface. This may explain why cubic fine structure is observed in so few cases,[22] and never as well resolved as in Pd: Gd to date.

Once the g shift and linewidth are determined, it is a straightforward procedure to obtain the exchange narrowed fine-structure spectrum. The g-shift value for J not only determines the central position of the spectrum, but also affects the magnitude of the third-order terms in the fine-structure matrix.[2] These terms arise from the fact that exchange relaxation is to the instantaneous local field,[23] the latter being the vector sum of the external static and rf fields, and the internal exchange field. Thus, the exchange-relaxation term for the localized spin is

$$-\delta_{ie}[\vec{M}_i - \chi_i(\vec{H} + \lambda\vec{M}_e)] + (g_i/g_e)\delta_{ei}[\vec{M}_e - \chi_e(\vec{H} + \lambda\vec{M}_i)] ,$$
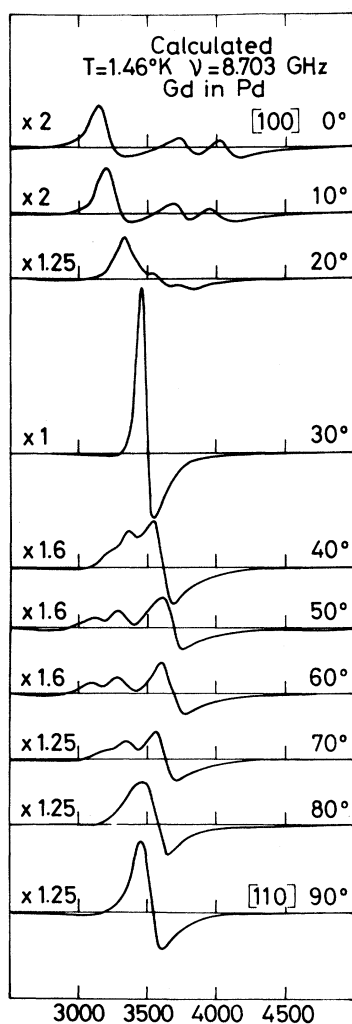
FIG. 8. The calculated Pd:Gd (500-ppm) spectra at 1.46°K as a function of magnetic-field angle with the [001] direction, in the (110) plane. Note that the frequency differs from that used for Fig. 7, so that the calculated spectra are not centered at 3800 G as are those of Fig. 7.

where δ_{ie}, δ_{ei} are proportional to $[J(\text{linewidth})]^2$, and $\lambda = J(g \text{ shift})/g_i g_e$. Interchange of i and e yields the equivalent expression for the conduction-electron exchange relaxation term. Making these modifications in Ref. 4, a best fit was achieved for $b_4 = 29.6$ G. This value is within the error limits of Ref. 1.

The experimental spectra are displayed in Figs. 1-3, (the dashed line follows after subtraction of cavity background), while the theoretical spectra for the [001] magnetic-field direction are exhibited in Fig. 4 for various temperatures. In order to exhibit the strong effect of population differences amongst the various M_s levels, as well as the thermal width, the derivative spectra for $T = 0.5$

and 1 °K are plotted in Fig. 5. An enormous change in relative line intensity is predicted, indicating the importance of lower temperature measurements when feasible.

Overall, the agreement between experiment (Figs. 1-3) and theory (Fig. 4) is excellent, with one glaring exception. The observed line at ~ 3800 G, at the field for resonance of the $\pm\frac{1}{2}$ transition, is absent from the theoretical spectra. To obtain a feeling for the adequacy of the fitting procedure, Fig. 6 compares the $T = 1.32$ °K theoretical spectrum for vanishing exchange with that using the values for exchange which led to Fig. 4. Figure 7 displays the angular dependence of the 500-ppm spectra at 1.46 °K, while Fig. 8 exhibits the theoretical simulation. Again, the agreement is excellent, except in the vicinity of 3800 G. Close inspection of Figs. 7 and 8 will show that superposition of an additional line of Norberg shape[15] at 3800 G on the theoretical spectra, Fig. 8, would generate curves very similar to the experimental spectra, Fig. 7, keeping the total oscillator strength of the additional line fixed (but allowing its width to vary—see below).

The absence of the $\pm\frac{1}{2}$ line from the theoretical spectra is connected with the large $\Delta M_s = \pm 1$ spin-flip matrix elements for small M_s levels. The proximity of the $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$ line (immediately to lower field) and the $\frac{1}{2} \leftrightarrow \frac{3}{2}$ line (immediately to higher field) "sap" strength from the $\pm\frac{1}{2}$ line as the temperature is raised. For δ_{ie} as large as it is in Pd:Gd above 1 °K, the $\pm\frac{1}{2}$ line simply disappears. It should be noticed that the $\frac{3}{2} \leftrightarrow \frac{5}{2}, \frac{1}{2} \leftrightarrow \frac{3}{2}$ line at ~ 4000 G moves towards the spectrum center with increasing temperature, while the $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ line (on the extreme high-field side, at roughly 4300 G) simply broadens and diminishes in amplitude. This is caused by the fact that the latter can only "communicate" with the $-\frac{5}{2} \leftrightarrow -\frac{3}{2}$ line which lies at the opposite (low-field) end of the spectrum. The smaller $\Delta M_s = \pm 1$ spin-flip matrix elements appropriate to large M_s levels also diminishes the frequency pulling effect of the $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ line. All in all, the fit appears quite satisfactory, apart from the apparent presence of the $\pm\frac{1}{2}$ line in the experimental spectra.

We offer the following explanation. A glance at Figs. 1 and 2 (the 300- and 500-ppm spectra) and Fig. 3 (the 1300-ppm spectra) indicates a difference in intensity of the $\pm\frac{1}{2}$ line (at ~ 3800 G) relative to the remainder of the spectrum. The 1300-ppm spectra is entirely dominated by this line at high temperatures, while the 300-ppm spectra is only slightly influenced by it. The 500-ppm spectra conforms more closely to the latter than to the former. The theoretical simulation contains no hint of the line at any temperature apart from some very small structure at 0.5 °K.

We account for the presence of this additional line by proposing a large indirect-exchange spin-spin interaction (exchange enhanced[6]) between nearby Gd sites in the Pd matrix. This isotropic coupling, comparable to the fine-structure splitting, splits the resonance line into a multitude of components. As the strength of the spin-spin coupling varies over the interaction range, only the central line remains at the $\pm\frac{1}{2}$ line position. In order to obtain a super position of "isolated" and collapsed "interacting" spin spectra, the range of the coupling must be long, cutting off rather sharply at the edge of the sphere of influence. The strength of the coupling can be estimated from the angular dependence of the collapsed line width. We shall show below that it would correspond to (approximately) a -0.2% conduction electron polarization over a volume enclosing ~ 200 lattice sites. Other explanations may also explain the observed behavior. In our view, this one appears reasonable and is certainly consistent with the observed data.

The details are as follows. Let a site at the origin be occupied by a Gd spin. The probability that no other site is occupied within a volume containing 200 lattice sites (i.e., probability of isolated spin spectra) is[24]

$$P_{\text{iso}} = (1-c)^{200} \sim e^{-200c} . \tag{4}$$

At 1300 ppm, $P_{\text{iso}} \cong 0.77$, which is approximately correct according to the lower-temperature curves of Fig. 3. In addition, the field for resonance for the center of gravity of the isolated fine-structure lines corresponds to $g = 1.785 \pm 0.007$. The inter-acting collapsed line is centered at $g = 1.813 \pm 0.007$, corresponding to an effective concentration between 0.6 and 0.8 at.%, according to Cottet and Peter.[10] These concentrations correspond to average interaction distances appropriate to volumes of influence containing between 125 to 167 lattice sites. It is well known that rare earths diminish the Pd host susceptibility by virtue of the electrons they contribute to the conduction band. This in turn diminishes the host susceptibility and thence the g shift. Thus, within a charge density sphere of influence, a decrease in the g shift should result. The effective volume for this effect is smaller than that which we hypothesize for the spin-spin interaction, and is a reflection of the fact that exchange enhances the range of the latter but de-enhances the range of the former. The observed relatively long range for the charge-density fluctuations is probably connected with the small k_F associated with the radius of the Pd Fermi-surface cylinders.[25] Our picture of the 1300-ppm sample $\pm\frac{1}{2}$ line is therefore one of spins interacting via indirect exchange, with most of the interacting spins lying within a (smaller) charge-density volume of influence resulting in a diminu-tion of the g shift of the collapsed line.

The spatial distribution cannot be purely random, for according to the above numbers only $\sim 60\%$ of the *interacting* spins would be within the charge-density interaction volume. Thus, there may be a tendency towards clustering when the local concentration exceeds the average value of 1300 ppm (in excess of 0.5% according to our volume-of-spin-influence estimate). This behavior may be connected with the fact that the 1300-ppm sample (see Section II) was prepared by zone-refining, whereas the more dilute samples (300 and 500 ppm) were prepared by the recrystallization method. The former has a greater tendency towards clustering (in the sense of Beck[13]) than the latter.

Finally, Peter *et al.*[14] examined the ratio of g shift to linewidth caused by additional rare-earth impurities in Pd:Gd. The radius of the sphere of influence was estimated to equal 14 Å, equivalent to an interaction volume of ~ 800 sites, rather larger than our result of 200 sites.

As the temperature is raised, the resolved fine-structure lines reduce in intensity relative to the collapsed $\pm\frac{1}{2}$ line. This may be caused by differing rf susceptibilities of the two species, the latter containing a substantial Weiss constant which reduces its temperature variation at low temperatures. Indeed, the low-temperature single-crystal linewidth at the collapsed angle,[1] and of powders[10] at concentrations such that the cluster resonance dominates, exhibit an upturn in the linewidth as the temperature is lowered in the He range. This is generally assigned to interaction effects.

As the concentration is lowered to 500 and 300 ppm, the P_{iso} reaches 0.90 and 0.94, again in qualitative agreements with Figs. 2 and 1, respectively. At these concentrations, the relative probability of finding Gd impurities within the charge-density volume of influence, as compared to the spin-interaction volume of influence, is of course the same as at 1300 ppm. However, the probability of exceeding 0.5 local at.% concentration is so small that clustering appears to be absent, and no detectable difference in g shift could be found for the collapsed lines as compared to the center of gravities of the fine-structure spectra.

We can estimate the strength of the spin-spin coupling using the angular dependence of the width of the collapsed line in the (110) plane (Fig. 7). It can be seen that it narrows considerably, from ~ 100 G in the [001] direction to less than 60 G near the [111] direction (near 55°). We superpose a line with a Norberg shape on the theoretical spectra (Fig. 8) at the position of the $\pm\frac{1}{2}$ line, and allow its width to vary as $[(\Delta H)^2/H_{\text{ex}}] + a$. Here, a is a constant (50 G). ΔH is the difference in the extreme field positions of the fine structure, and H_{ex}

is to be fitted. Keeping the oscillator strength constant, one is able to (very approximately) reproduce the experimental spectra of Fig. 7 with H_{ex} corresponding to an interaction strength of 1 cm^{-1}. This interaction strength must reflect the conduction-electron polarization in the vicinity of the interacting Gd spins. Thus,

$$1 \text{ cm}^{-1} = \mathcal{J}(g \text{ shift}) \vec{S} \cdot \langle \vec{s} \rangle. \qquad (5)$$

Using the measured value for $\mathcal{J}(g$ shift), we find $\langle \vec{s} \rangle = 0.2\%$. Using the spin volume of influence of 200, this means an antiferromagnetic conduction-electron polarization of $0.4\mu_B$. This is a little smaller than that found by Crangle,[26] but exceeds the more recent value (zero) extracted by Guertin et al.[27] (but see Taylor and Coles[28]). We must emphasize that this result is very approximate, and essentially assumes that the indirect-exchange coupling is constant over the volume of influence. Detailed examination of Fig. 7 leads us to this conclusion, but we can only state with assurance that the data is consistent with our interpretation. Independent measurements (e.g., neutron diffraction) are required to substantiate our model.

IV. DISCUSSION

By extending the exchange-relaxation narrowing theory of Barnes[2] and Zimmermann et al.[4] to cubic hosts, and using parameters deduced from experiment, we are able to reproduce, for the greater part, the explicit shape of the observed fine-structure spectrum, its collapse with increasing temperature, and its detailed angular dependence. In both dilute (e.g., 300-ppm) and concentrated (e.g., 1300-ppm) samples, the intensity of the $\pm \frac{1}{2}$ transition is larger than expected theoretically, the effect being more pronounced the higher

the concentration. Our data are consistent with a model of an indirect exchange spin-spin interaction extending over a volume of influence containing 200 lattice sites, and dropping off sharply beyond this range. A perturbation analysis leads to an estimate of a -0.2% conduction-electron polarization within this volume. To account for the behavior of the collapsed line in the 1300-ppm sample, we must introduce concentration clustering.

Finally, a word should be said about the spin-spin interaction in dilute magnetic alloys. Previous analyses[29] have in the main adopted an Ising (or effective-field) model. It is clear that such an approach is insufficient for EPR studies. The spin-spin interaction leads to fine-structure narrowing by virtue of the dynamic spin flips associated with the *transverse* components of the spin operators. An Ising-like model would result only in a broadening of the EPR line. Thus, interaction narrowing of fine-structure offers a mechanism for extraction of the dynamic spin-spin interaction distribution in a dilute alloy. Further studies, both experimental and theoretical, are clearly called for.

Note added in proof. After submission of this paper, D. E. Dugdale [J. Phys. C **7**, 3758(1974)] published an account of this theory. His conclusions are similar to those of this work. He applied his method, limited to large numbers of interacting spins, to the case of $S = 1$ with uniaxial fine structure. The limitation to large numbers makes its applicability to Pd : Gd somewhat questionable, but its conclusions for $S = 1$ if extrapolated to $S = \frac{7}{2}$ in the presence of cubic fine-structure splittings would substantiate the arguments presented in this work. A quantitative application to Pd : Gd would appear to be in order.

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[1]R. A. B. Devine, D. Shaltiel, J. -M. Moret, J. Ortelli, W. Zingg, and M. Peter, Sol. State Commun. **11**, 525 (1972).
[2]S. E. Barnes, Phys. Rev. B **9**, 4789 (1974).
[3]T. Plefka, Phys. Stat. Sol. B **51**, K113 (1972).
[4]P. H. Zimmermann, D. Davidov, R. Orbach, L. J. Tao, and J. Zitkova, Phys. Rev. B **6**, 2783 (1972).
[5]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford U.P., Oxford, England, 1970), p. 149.
[6]B. Giovannini, M. Peter, and J. R. Schrieffer, Phys. Rev. Lett. **12**, 736 (1964).
[7]G. G. Low and T. M. Holden, Proc. Phys. Soc. (Lond.) **89**, 119 (1966).
[8]J. R. Schrieffer, Phys. Rev. Lett. **19**, 644 (1967).
[9]A. M. Clogston, Phys. Rev. Lett. **19**, 583 (1967).
[10]H. Cottet and M. Peter, Sol. State Commun. **8**, 1601 (1970).

[11]H. Cottet, Ph.D. Thesis, University of Geneva, 1971 (unpublished).

[12]H. Cottet and M. Peter (Refs. 10 & 11) worked with powders, so any fine-structure transitions not exchange narrowed would be averaged out. Hence, their measurements are a direct measure of the field for resonance for only the $\pm\frac{1}{2}$ transition.

[13]P. A. Beck, J. Less Comm. Met. **28**, 193 (1972); H. Claus, Phys. Rev. B **5**, 1134 (1972).

[14]M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. Lett. **9**, 50 (1962).

[15]R. E. Norberg, Phys. Rev. **86**, 745 (1952); F. J. Dyson, Phys. Rev. **98**, 349 (1955); G. Feher and A. F. Kip, Phys. Rev. **98**, 377 (1955). The authors are indebted to Professor C. P. Slichter for pointing out to us the work of Professor R. E. Norberg on Pd:H in which the effect of skin effect on line shape was first calculated.

[16]Measurements in the (111) plane showed only a 50-G change in width as the angle was varied, and almost no change in resonance field. This variation is of the same order as our residual width, and hence does not significantly affect our analysis.

[17]D. Davidov, K. Maki, R. Orbach, C. Rettori, and E. P. Chock, Sol. State Commun. **12**, 621 (1973).

[18]R. E. Watson, *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p. 413.

[19]R. E. Watson, A. J. Freeman, and S. Koide, Phys. Rev. **186**, 625 (1969).

[20]L. R. Walker and R. E. Walstedt, Phys. Rev. B (to be published).

[21]R. Duclo, S. Foner, and A. Narath, J. Appl. Phys. **40**, 1206 (1969).

[22]E. P. Chock, R. Chui, D. Davidov, R. Orbach, D. Shaltiel, and L. J. Tao, Phys. Rev. Lett. **27**, 582 (1971).

[23]S. E. Barnes and J. Zitkova, Phys. Rev. B **7**, 2163 (1973).

[24]R. H. Silsbee (private communication).

[25]A. J. Freeman, J. O. Dimmock, and A. M. Furdyna, J. Appl. Phys. **37**, 1256 (1965); O. K. Andersen and A. R. Mackintosh, Sol. State Commun. **6**, 285 (1968).

[26]J. Crangle, Phys. Rev. Lett. **13**, 569 (1964).

[27]R. P. Guertin, H. C. Praddaude, S. Foner, E. J. McNiff Jr., and B. Barsoumian, Phys. Rev. B **7**, 274 (1973).

[28]R. H. Taylor and B. R. Coles, J. Phys. F. (G.B.) **4**, 303 (1974). In this informative paper on the ESR of Pd:Gd the authors point out that Crangle (Ref. 26) finds a 20% reduction in the moment of Pd:Gd from the free-spin value, D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter [Phys. Rev. **135**, 1346 (1964)] find a 22% reduction, and H. J. Schaller, R. S. Craig, and W. E. Wallace [J. Solid St. Chem. **5**, 338 (1972)] an 18% reduction. Only Guertin *et al.* (Ref. 27) find no change from the free-spin value.

[29]W. Marshall, Phys. Rev. **118**, 1519 (1960); M. W. Klein and R. Brout, Phys. Rev. **132**, 2412 (1963); S. Liu, Phys. Rev. **157**, 411 (1967); M. W. Klein, Phys. Rev. **173**, 552 (1968); M. W. Klein and L. Shen, Phys. Rev. B **5**, 1174 (1972).