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# Electron paramagnetic resonance of Gd<sup>3+</sup> in platinum<sup>\*</sup>

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We have observed the electron paramagnetic resonance (EPR) of  $Gd^{3+}$  in both polycrystalline and single-crystal samples of dilute Pt:Gd alloys. The polycrystalline samples display a single resonance line whose thermal broadening is concentration dependent. Fully resolved fine structure appropriate to  $Gd^{3+}$  in a cubic environment is obtained from the single-crystal samples. From these results a value for  $b_4^0$  of +86 G is deduced, a value some three times larger than that found to date in any other cubic pure metals. It is shown conclusively that the experimental spectra from the single-crystal samples consist of the resolved single-ion fine-structure spectrum and an additional "cluster" line with the same g value as the single-ion spectrum. For most directions in the {110} plane excellent agreement is obtained between the single-ion spectra and those simulated using the Barnes-Plefka motional-narrowing theory. The existence and behavior of the "cluster" line is qualitatively explained in terms of a cross-relaxation process. Finally it is shown that the excitation energy  $E_{\pm}$  for the process  $4f^7 \rightarrow 4f^8$  as involved in EPR is not the same as measured by optical experiments such as x-ray photoemission spectroscopy. A theory which describes this is capable of explaining the experimental exchange and crystal-field parameters.

## I. INTRODUCTION

The electron paramagnetic resonance (EPR) finestructure spectrum of  $Gd^{3+}$  as dilute impurity in a number of insulators is well known and has been extensively studied.<sup>1</sup> The spin Hamiltonian used to describe such fine structure in cubic environment is

$$H = g \mu_{\beta} \vec{H} \cdot \vec{S} + \frac{1}{60} b_{4}^{0} O_{4} + \frac{1}{1260} b_{6}^{0} O_{6} \quad , \tag{1}$$

where  $O_4$  and  $O_6$  are the fourth- and the sixth-degree operators appropriate to a cubic environment<sup>2</sup> and  $b_0^4$ and  $b_0^6$  are the experimentally determined splitting parameters. The overall separation of the seven fine-structure lines for any given orientation of the magnetic field with respect to the crystalline axes is in a first approximation proportional to  $b_0^4$  (for S state ions the effects of the sixth-order term is invariably much smaller than that of the fourth).

Over the past several years there has been a steadily increasing number of reports of resolved fine structure in the EPR of  $Gd^{3+}$  dissolved as an impurity in both metals<sup>3</sup> and intermetallic compounds.<sup>4</sup> Studies in these metallic hosts have been complicated by the somewhat larger resonance linewidths when compared to insulators, and by the partial (or complete) narrowing of the fine-structure spectra caused by the conduction-electron induced single-ion hopping. This narrowing can be well handled using the Barnes-Plefka (BP) theory.<sup>5</sup>

Briefly stated, if a magnetic ion is in the state  $|S_z\rangle$ 

it can relax, via the mutual spin flip with a conduction electron, only to either  $|S_z - 1\rangle$  or  $|S_z + 1\rangle$ . Similarly  $|S_z + 1\rangle$  can relax only to  $|S_z\rangle$  or  $|S_z + 2\rangle$ . This implies a transfer of the dynamic magnetization, associated with the  $S_z = S_z + 1$  transition, to and from that associated with the two adjacent transitions  $S_z - 1 \rightleftharpoons S_z$  and  $S_z + 1 \leftrightharpoons S_z + 2$ . Such "hopping," if it occurs sufficiently frequently, can lead to a collapse or "narrowing" of the fine-structure resonance spectrum in a fashion somewhat analogous to the motional narrowing of NMR (nuclear magnetic resonance) in liquids except that the present relaxation process will eventually broaden the narrowed line. The relevant local moment Korringa relaxation rate is proportional to temperature, at least for temperatures greater than the Zeeman energy. Hence, the rate of hopping, and therefore the degree of collapse of the fine structure, changes as a function of temperature.

This single-ion hopping theory was first used<sup>6</sup> to explain the experimental spectra of Mg:Gd, a bottlenecked system. Its validity in the isothermal (unbottlenecked) limit has since been convincingly demonstrated by its application to a number of systems; perhaps the most striking example is the work of Urban *et al.*<sup>7</sup> on LaSb:Gd. This single-ion conduction-electron narrowing of the fine structure is thus distinct from the process that leads to the narrowing of the hyperfine structure<sup>8</sup> and which only occurs in the bottlenecked regime. Such bottleneck narrowing can occur, but is always qualitatively insignificant compared to the single-ion process.

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In addition to the above mechanisms, narrowing of both the fine and hyperfine structures can be caused by direct or indirect ion-ion exchange. Such effects have been well studied in insulators, especially exchange narrowing of the dipolar broadening. In metals such exchange can arise at relatively large ion-ion distances via the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. The EPR spectra of the metallic system Pd:Gd<sup>3</sup> shows an extra resonance line which has been interpreted<sup>3</sup> as the collapsed fine structure of interacting Gd-Gd ions. This has been referred to as the "cluster" resonance. However, due to the long range of the RKKY interaction, particularly in the very strongly exchange enhanced Pd host, the interacting Gd ions need not necessarily be in a true metallurgical cluster (i.e., nearest neighbors); they may simply be relatively closely spaced pairs, etc., occurring due to statistical fluctuations in the ion-ion separation.

We report in this paper our EPR measurements on the Pt:Gd system, in polycrystalline and single-crystal forms at both X- (9 GHz) and Q- (35 GHz) band frequencies. From the well resolved fine structure which we observe at low temperature, we find a very large value for  $b_4^0$ . This, together with the rather low value of the Korringa broadening exhibited by this system, allows us to explore in some detail the match between our experiments and the BP theory. With the introduction of some new phenomenological parameters, excellent agreement is found with the "single ion" part of the spectra. As in the Pd:Gd experiments<sup>3</sup> we also find an additional "cluster" resonance line in the spectrum. However, there are rather serious discrepancies between the behavior of this extra line and that expected from a simple Gd:Gd exchange model.<sup>3</sup> In particular, we find that in some of our plate single-crystal samples the relative intensity of the cluster line depends on both the crystallographic and geometric orientation of the sample with respect to the measuring field. Also, for some crystal orientations the cluster line disappears when measured at low temperatures and at Q band. We propose here a cross-relaxation model for the cluster line which will at least qualitatively account for the observed behavior.

We feel that several of the results obtained from the analysis of the "single-ion" spectra are worthy of special note. We confirm (from the g shift) that like Pd:Gd the exchange constant is negative, and also find, again as in Pd:Gd, that the g-shift exchange constant is very much larger than that obtained from the thermal broadening of the resonance lines. We have attempted an analysis of the exchange constants in terms of interatomic covalent mixing. The measured  $b_4^0$  is the largest found in a pure metal to date and somewhat larger than comparable Gd<sup>3+</sup> insulator values. On the other hand, recent Pt:Er (i.e., non-S-state) measurements<sup>9</sup> indicate that the fundamen-

tal crystal field  $A_4^0 \langle r^4 \rangle$  in Pt is more than an order of magnitude smaller than in comparable insulators. The resulting large ratio  $R = (b_4^0 / A_4^0 \langle r^4 \rangle)$  thus does not appear to be compatible with current insulator theory for S-state ion crystal fields, and has led to speculation that a new covalent mixing process might be important in metals.<sup>10</sup> The relatively narrow lines (for a metal) have enabled us to make the first determination of the sixth-order parameter  $b_6^0$  in such a system. Also for the first time we have been able to show quite conclusively that there exists an extra process for the residual width in systems with resolved fine structure, namely, a spread in the fourth-order parameter  $b_4^0$ -about 10% in Pt:Gd. It is not possible to tell if such variations are spatial or temporal; although we tend to favor the former explanation. Finally, our theoretical fit to the BP theory shows the importance of correctly accounting for the effect of the internal molecular fields. The modified theory,<sup>11</sup> which accounts properly for such fields, not the original theory,<sup>5</sup> gives agreement with the experimental phenomena.

### **II. EXPERIMENTAL TECHNIQUES**

Master alloys with nominal concentration of 5000 ppm (atomic) were prepared by arc melting 99.9999% platinum wire (obtained from Johnson Matthey) and 99.9% gadolinium foils (from Goodfellows Metals) under 0.5 atm of 99.9999% argon. Less concentrated alloys were then prepared by successive dilution. From the arc melted ingots grain samples were obtained by filing with a tungsten carbide file. To obtain single crystals the ingots were first cold rolled to 0.3 mm foil-these foils were then annealed at  $\sim$  1350 °C for 12–14 h under 99.9999% argon at 1 atm. After this annealing the foils were strained about 4% by pulling and then reannealed under the same conditions as before, except that during the second annealing the temperature was raised slowly from 1000 to 1400 °C; this stage taking typically 5 h. The samples were then maintained at 1400 °C for up to 12 h and finally slowly cooled to ambient. The single crystals resulting from this primary recrystallization technique were up to 6 mm in linear dimension and usually had a {110} plane perpendicular to the plate. These plate crystals were then cut from the foil by electroerosion. The nominal concentrations for a selection of the grain samples were checked by spectroscopic analysis. The single-crystal concentration was checked on several samples by susceptibility measurements. In all cases the nominal and deduced concentrations agreed to better than 15%. The observed phenomena are not strongly dependent upon the concentration, hence such modest discrepancies in the concentration are not important.

The EPR spectra were measured using convention-



FIG. 1. Evolution of the X-band half-height linewidth with temperature for powdered Pt:Gd samples of various concentrations. The values deduced for the thermal broadening rate, b, and the zero temperature residual linewidth,  $a_b$  are given in the insert.

al Varian X- and Q-band reflection spectrometers having base temperatures of 1.1 and 1.6 K, respectively. In the X-band apparatus the cavity is always maintained at room temperature. The grain samples were mounted in quartz (suprasil) tubes while the single crystals were mounted in PTFE (polytetrafluoroethylene) holders. For the latter, the magnetic field could be rotated in the  $\{110\}$  plane of the sample.

# **III. EXPERIMENTAL RESULTS**

The only previous work on Pt:Gd is that of Davidov *et al.*<sup>12</sup> who reported only a g value measured at 4.2 K on grain samples. In this section we report our measurements on grain and single-crystal samples at X and Q band.

### A. Grain samples: X band

The grain samples all display a single distorted Dysonian line having a g value of  $1.94 \pm 0.01$ , in agreement with the previous work. The behavior of the linewidths with temperature and concentration are shown in Fig. 1.

The thermal broadening appears linear, as expected, but its small value, circa 2 G  $K^{-1}$ , and its increase



FIG. 2. Two low-temperature X-band EPR spectra  $(d\chi''/dH)$  for a PtGd 1300 ppm single-crystal plate with the measuring field parallel to the [001]  $(\theta = 0^{\circ})$  and [111]  $(\theta = 55^{\circ})$  directions. The spectra contain a background contribution around 3.3 kG (see Fig. 4 for an example). The expected fields for resonance of the seven Gd<sup>3+</sup> transitions, calculated to second order in  $b_4^0$ , have been superimposed on the figure. The position of the cluster line referred to in the text is also marked.

with decreasing concentration is sometimes indicative of bottleneck behavior. However, the coexistence of a bottleneck and a large, constant, negative g shift needs a somewhat contorted explanation.

### B. Single-crystal samples: X band

The X-band EPR spectra on the single-crystal samples at the lowest temperature shows an almost completely resolved fine structure appropriate to Gd<sup>3+</sup> in cubic environment. In Fig. 2 we show representative spectra from a 1300 ppm single crystal at 1.2 K and with the magnetic field parallel to the [001] and [111] directions. These have been superimposed on the expected angular dependence in the {110} plane of the fields for resonance for the seven transitions of  $Gd^{3+}$  in the absence of any narrowing. As can be seen the agreement is reasonable, thus affirming the local cubic site symmetry of the Gd<sup>3+</sup> ion. The degree of resolution of the spectrum, particularly in the [001] direction, is due to the very large value of  $b_4^0$ (almost 90 G) and to the rather low thermal broadening of the lines. When  $\theta$ , the angle between the magnetic field and [001], is in the vicinity of 30° the spectrum collapses to a single line. We shall discuss this behavior at some length in later sections. For the moment we note that the measured thermal broadening of the single line at the collapsed angle for this sample was  $2.0 \pm 0.3$  G K<sup>-1</sup> between 20 and 40 K. Figure 3 shows the evolution of the spectrum in the [001] direction on reducing the temperature from 4.2 to 1.2 K. The increase in intensity with decreasing temperature of the highest-field line allows us to assign the transitions and hence unambiguously determine the sign of  $b_4^0$  to be positive. Below about 2 K, the  $-\frac{1}{2} \rightleftharpoons -\frac{3}{2}$  and  $-\frac{3}{2} \leftrightarrows -\frac{5}{2}$  pair of transitions become resolved, whereas the corresponding high-field pair do not. The approximation often used<sup>3</sup> of calculating the resonance fields in cubic symmetry to first order only in  $b_4^0$  leads to a symmetric distribution of the resonance lines about the isotropic central line. As can be seen from Figs. 1 and 2, with such a large value of  $b_4^0$  the second-order terms become significant; the central line is not isotropic and in the [001] direction the separations of the  $-\frac{1}{2} \rightleftharpoons -\frac{3}{2}$ ,  $-\frac{3}{2} \rightleftharpoons -\frac{5}{2}$ , and the  $+\frac{1}{2} \rightleftharpoons +\frac{3}{2}$ ,  $+\frac{3}{2}$  $\rightleftharpoons +\frac{5}{2}$  pairs are not equal. The primary effect of a small sixth-order term,  $b_6^0$ , is to change each pair separation equally in the [001] direction with negative  $b_6^0$  increasing the separation.

As a comparison of the two directions exhibited in Fig. 2 shows the central peak in the [001] direction is in fact composed of two lines: the  $-\frac{1}{2} \rightleftharpoons +\frac{1}{2}$  line and what is found to be an isotropic cluster line. We have marked the position of this isotropic resonance by a vertical line. Careful measurements have been



FIG. 3. Evolution of the X-band fine-structure spectrum with temperature in the [001] direction for the *Pt*Gd 1300 ppm single-crystal plate.

made to correctly determine the origin of the central peak. In Fig. 4 we show the spectra at  $\theta = 17^{\circ}$  and 44° and the corresponding background signal at the same temperature, the experimental conditions being strictly the same, save for the presence of the sample. The isotropic cluster and  $\pm \frac{1}{2}$  lines are well separated and can be clearly identified. The cluster signal thus originated from the sample and has an isotropic gvalue of  $1.94 \pm 0.01$ . That this g factor is the same as for the single-ion fine-structure spectrum is perhaps the strongest evidence that this signal is from  $Gd^{3+}$  in Pt and not from, say, some surface contamination. We shall discuss the possible origin of this extra resonance together with the behavior of the X-band spectra around the crossing angle, after we have discussed the Q-band results and the parametrization of the single-ion spectra.

# C. Single-crystal samples: Q band

Figure 5 shows the spectra obtained from the 1300 ppm crystal at Q band (35 GHz) between 1.6 and 5.3



FIG. 4. Low-temperature X-band spectra for the  $P_I$ Gd 1300 ppm single-crystal plate at  $\theta = 17^\circ$  and 44° together with the background signals under the same measurement conditions: The extra line in the center of the spectra comes from the sample.

K with the magnetic field in the [001] and  $\theta = 44^{\circ}$  directions.

The positions of the outer lines of the spectra, again away from the crossing angle, is as expected after the preliminary analysis of the X-band results. For the same ratio of  $h\nu/kT$  (i.e., degree of depopulation,  $\nu$  being the measurement frequency), the spectra at the two frequencies are very similar, the linewidths being larger at Q band due to both the higher temperature and an increase of about 100 G in the residual widths. Comparison of the spectra in the [001] direction at 5.3 K at Q band with that at 1.43 K at X band in Fig. 3 illustrates this. At the lowest temperatures for both the [001] and  $\theta = 44^{\circ}$  directions only the  $-\frac{1}{2} \rightleftharpoons -\frac{3}{2}$ ,  $-\frac{3}{2} \oiint -\frac{5}{2}$  pair and the  $-\frac{7}{2} \leftrightharpoons -\frac{5}{2}$  transitions are easily identified, as expected from depopulation of the higher levels. There also appears to be a weak and broad resonance in the center of the spectra (at the  $+\frac{1}{2} \rightleftharpoons -\frac{1}{2}$  position), but there is no evidence of the extra line identified at Xband for the same sample. However, on increasing the temperature in either of these directions (or any other direction away from the crossing angle at 30° and around 90°) a resonance appears at the same g



FIG. 5. *Q*-band spectra for the *Pt*Gd 1300 ppm singlecrystal plate for various temperatures at  $\theta = 0^{\circ}$  ([001]) and 44°. Note the absence of any narrow line in the center of the two lowest-temperature spectra.

value as the extra line seen at X band. We note that the width of this line is about three times broader than the extra line at X band but that its width at around 5 K is at least a factor of 2 narrower than the central line at 1.6 K which we attribute to the  $+\frac{1}{2} = -\frac{1}{2}$ transition. For this reason it is not possible that at Q band we have misidentified the  $\pm \frac{1}{2}$  as the extra line. (It is clear that at 5 K the center line must contain a contribution from the repopulated  $\pm \frac{1}{2}$  line, but this will be even broader than at 1.6 K.)

# IV. PARAMETRIZATION OF THE SINGLE-ION SPECTRA: PROCEDURES

In this section we shall deal with the fitting of the single-ion spectra to the theory. We use "single-ion" spectra here to mean the usual seven transitions of  $Gd^{3+}$  as shown in Fig. 2. We exclude for the moment any discussion of the extra resonance. Hence, we initially will look at directions away from the crossing angle. Having established the parameters

which give the best fit to the experimental data for these directions, we shall then compare the predictions of the theory and the experimental results around the crossing angles in the next section. We have obtained the Gd<sup>3+</sup> energy levels from Lacroix's formulas<sup>13</sup> and then taken into account the effects of the dynamics using the modified theory of Barnes.<sup>11</sup> This modified theory must be used for the following reason. Our samples show no signs of magnetic ordering down to our base temperature, about 1 K, while the original Barnes theory,<sup>5</sup> with the exchange constant deduced from the g shift, would predict observable magnetic correlation effects as a precursor of ferromagnetic ordering. However, this original theory, and other earlier calculations including implicitly the original theory of Hasegawa,<sup>14</sup> are inadequate in that they use a certain continuum approximation. In the modified theory this problem is overcome by introducing an extra molecular field seen by the local moments, i.e., one replaces the usual field

$$(\vec{H} + \lambda \vec{M}_e) \tag{2}$$

by

$$(\vec{H} + \lambda \vec{M}_e + \alpha \vec{M}_s) , \qquad (3)$$

where  $\vec{H}$ ,  $\vec{M}_e$ , and  $\vec{M}_s$  are, respectively, the external field, the conduction electron, and the local momentum magnetizations, and where  $\lambda$  is the usual and  $\alpha$  a new molecular-field constant. With this, the magnetic ordering temperature  $\theta$  is given by

$$(\theta/k_BT) = (\lambda^2 \chi_e^0 + \alpha) \chi_s^0 = \lambda^2 \chi_s^0 \sum_{R_{ij}, i \neq j} F(R_{ij}) \quad , \qquad (4)$$

where  $F(R_{ij})$  is a suitably normalized RKKY function; i.e.,  $\alpha$  is defined so that the extreme right-hand expression is simply the usual molecular-field expression for the magnetic ordering temperature. In the absence of any evidence for magnetic ordering, or a realistic theory for  $F(R_{ij})$ , we simply choose  $\alpha$  such that  $\theta$  is zero.

In the initial version of the simulation program the input parameters are the four experimental variables, temperature, frequency, orientation, and concentration, and what we shall term the fitting parameters; namely, the g shift, Korringa (magnetic ionconduction electron) rate  $\delta_{se}$ , a single residual linewidth, the crystal-field parameters  $b_4^0$  and  $b_6^0$ , and the electron-lattice relaxation rate,  $\delta_{el}$ , which determines the degree of bottleneck. The g shift and Korringa rate are taken into account via, respectively, the products  $[J_1\rho(E_F)]$  and  $[J_2\rho(E_F)]^2$  where  $J_1$  and  $J_2$ represent the two different determinations of the exchange integral. Our technique was to fit first in the [001] direction at 1.2 K and X band, and then compare the results of the simulations for other directions and temperatures at both X and Q band. In principle, values for the first three fitting parameters

can be obtained from the high-temperature collapsed line behavior and these we used as a starting point.

The value of  $b_4^0$  can be quite accurately determined from the position of the  $-\frac{5}{2} \rightleftharpoons -\frac{7}{2}$  line. The factors governing the splitting of the  $-\frac{1}{2} \leftrightharpoons -\frac{3}{2}$ ,  $-\frac{3}{2} \leftrightharpoons -\frac{5}{2}$ pair are rather involved. The observed separation is greater than that expected from consideration of the  $b_{\rm A}^{0}$  term alone and any narrowing will cause the two lines to come together. As we mentioned above, the effect of a  $b_6^0$  term is to increase (or to decrease) the separations of both the low-field and the high-field pair. The value of  $b_6^0$  sufficient to reproduce the observed low-field splitting (in the [001] direction), however, predicts a splitting of the high-field pair which is not observed. In view of the low thermal broadening and its concentration dependence in the powdered samples we have investigated the effect that the degree of bottleneck has on the simulated spectrum. It turns out that the degree of bottleneck in this system can have a profound effect on the separation and relative intensities of the  $-\frac{1}{2} = -\frac{3}{2}, -\frac{3}{2} = -\frac{5}{2}$  pair at sufficiently low temperatures where the strength of the narrowing process is weak. This is particularly clear in the [001] direction where the separation of that pair is maximum.

The explanation of this bottleneck effect lies in one of two types of narrowing processes which can operate in this system. One, the hopping processes already mentioned, is of the conventional motional narrowing type, and it arises here from the Korringa relaxation process. However, the one operating on the  $-\frac{1}{2} \rightleftharpoons -\frac{3}{2}$ ,  $-\frac{3}{2} \oiint -\frac{5}{2}$  pair is not of this type; it arises from the effect of internal molecular fields. While the former process causes the two lines to be pulled together and to finally merge without large transfers of intensity, the latter forces the lines to separate with one line gaining all the intensity and staying near the central position. Since this latter type of process does not appear to have been discussed in the literature, we briefly explain its origin in Appendix A.

We should perhaps also specify more clearly what we mean by a bottleneck in this context. Roughly speaking, if the electron-ion back relaxation rate  $\delta_{es} \ll \delta_{el}$  the system is nonbottlenecked or in the isothermal regime. When the inverse inequality is satisfied the system is said to be bottlenecked. It has been shown that in the presence of fine structure there are two types of bottleneck regimes.<sup>5,11</sup> First, when the Korringa rate is sufficiently large, the fine structure is narrowed and, to a first approximation, the situation is as it would be without structure. The thermal broadening is drastically reduced and the Knight shift is not effective. The second regime, and the one relevant here, is when narrowing does not occur. Then, qualitatively there is little difference between this bottlenecked regime and the nonbottlenecked one. Quantitatively, the thermal broadening and Knight shift are reduced a little, but more important, the dynamic narrowing effects described above come into play. In simulation studies such as those described here, where the concentration is known and the Korringa rate determined otherwise, the electron-lattice rate  $\delta_{el}$  is the only free parameter with which to vary the degree of bottleneck. This will be referred to as the bottleneck parameter.

The effect of the degree of bottleneck is illustrated in Fig. 6. The simulated spectra are shown for the



FIG. 6. Three low-temperature X-band theoretical spectra [(a), (b), (c)] together with the experiment (d). The calculated spectra correspond to the modified BP hopping theory. The line positions have been calculated to first order only in  $b_4^0$ , also the residual linewidth is the same for all transitions. The values of  $\delta_{el}$ , the electron-lattice rate, used in the calculated spectra are: (a)  $2 \times 10^{14} \text{ s}^{-1}$ , (b)  $2 \times 10^{11} \text{ s}^{-1}$ , and (c)  $2 \times 10^7 \text{ s}^{-1}$ . Hence, turning on the bottleneck strongly affects the  $-\frac{1}{2} \pm -\frac{3}{2}$ ,  $-\frac{3}{2} \pm -\frac{5}{2}$  pair (see explanations in the text).

[001] direction, with the energy levels calculated to first order in  $b_4^0$  only, hence the splitting of the highand low-field pairs should be equal. This is indeed the case for the isothermal nonbottlenecked limit [spectrum (a), Fig. 6]. Upon turning on the bottleneck [spectra (b) and (c)], the high-field pair are relatively unaffected, but at low field the  $-\frac{1}{2} \rightleftharpoons -\frac{3}{2}$  line increases in intensity and moves to lower field (higher g value) while, because of the interplay of various effects, the  $-\frac{3}{2} \oiint -\frac{5}{2}$  line stays in roughly the same place but loses almost all its intensity. As the bottleneck is slowly applied, the lines first separate and then their relative intensities change rapidly.

A comparison of the theoretical simulations in Fig. 6 with the experimental spectra shown in the same figure indicates that while the intensities of the different lines can be made reasonably correct (apart from the central line) the linewidths and hence peak heights are not. Conventional wisdom dictates that the linewidth of each line should be of the form

$$\Delta H_{S_z = S_z + 1} = \Delta H_{\text{residual}} + A_{S_z} T \quad , \tag{5}$$

where  $A_{S_z}T$  represents the Korringa broadening; it is proportional to  $[S(S+1) - S_z(S_z+1)]$ . The source of  $\Delta H_{\text{residual}}$  is far from clear but as explained elsewhere<sup>11</sup> for a system with resolved fine structure it may be due to a distribution of internal fields, in which case it should be roughly the same for each line in the fine-structure spectrum. An internal field distribution amounts to a g-factor distribution and hence this residual width would be expected to increase linearly with measuring field. It is possible, if not particularly satisfying, to incorporate phenomenologically a residual linewidth for each individual line and for each orientation. Instead of this, we have found empirically a more satisfactory explanation, namely, that a spread in the  $b_4^0$  parameter gives a very good fit to the experimental data.<sup>15</sup> One may appreciate that, if there is a (Lorentzian) distribution in the  $b_4^0$  parameter, the effect is a residual width which increases linearly with the distance of a given line from the center of the spectrum. We note that this effect is independent of the measurement field (ignoring second-order crystal-field effects).

To return to the fitting procedure, a value of the  $\epsilon$  parameter which corresponds to the spread in  $b_4^0$  is obtained by writing the width, for example, of the  $-\frac{7}{2} \Longrightarrow -\frac{5}{2}$  transition as

$$\Delta H_{\rm res}\left(-\frac{7}{2} \leftrightarrows -\frac{5}{2}\right) = \Delta H_{\rm res}^0$$
$$+ \epsilon \left|E\left(-\frac{5}{2}\right) - E\left(-\frac{7}{2}\right) - h\omega_0\right| \qquad (6)$$











FIG. 7. (a), (b) Comparison of the calculated (upper) and experimental (lower) X-band spectra for PtGd 1300 ppm single crystal for various values of  $\theta$  at the lowest temperature.

In the [001] direction, this corresponds to

$$\Delta H_{\rm res}(-\frac{7}{2} \leftrightarrows -\frac{5}{2}) \simeq \Delta H_{\rm res}^0 + 20b_4^0 \epsilon \quad . \tag{7}$$

Here  $\Delta H_{\rm res}^0$  represents the field dependent, g-factor distribution discussed above. The value of  $\epsilon$  obtained by comparing the result of Eq. (7) and experiment is then taken to be orientation, temperature, and field independent. The factors governing the separation and relative intensities of the low-field pair in the [001] direction are then  $b_4^0$ , which is already determined, a negative  $b_6^0$  term producing a separation, the Korringa rate which governs simultaneously the individual line broadening and the hopping (narrowing) processes, and the bottleneck parameter  $\delta_{el}$ . We first used the crossing angle Korringa rate and then did a two parameter fit on the separation and intensities with  $b_6^0$  and the bottleneck parameter. We note that there is only one solution. The results of

such a fit and the predictions for other directions are shown in Fig. 7: The agreement between theory and experiment is quite good at the lowest temperature for the angle shown.

However, on attempting to reproduce the sequence in temperature shown in Fig. 3, we find that the low-field pair do not narrow sufficiently quickly; it becomes clear that the Korringa rate measured at the crossing angle is too small. In principle the real Korringa rate can be determined from the broadening of any of the individual lines. Since the  $\frac{5}{2} \rightleftharpoons \frac{7}{2}$  line is too weak, the  $-\frac{1}{2} \rightleftharpoons \frac{1}{2}$  line is always close to the ex-tra resonance, and the  $\frac{1}{2} \leftrightharpoons \frac{3}{2}$ ,  $\frac{3}{2} \leftrightharpoons \frac{5}{2}$  pair are never resolved, the only candidates are the  $-\frac{1}{2} \leftrightharpoons -\frac{3}{2}$  line at around  $\theta = 17^{\circ}$  and the  $-\frac{5}{2} \rightleftharpoons -\frac{7}{2}$  at [001]. However, a reliable measurement of the thermal broadening is impossible due to the large residual width and

rapidly decreasing intensity of these lines. We therefore increased the Korringa rate to reproduce the observed collapse of the low field ([001]) pair, while readjusting slightly the values of  $b_6^0$  and the bottleneck to keep the fit good at the lowest temperature. We also used the hopping between the  $\pm \frac{1}{2}$  and  $-\frac{3}{2} \Longrightarrow -\frac{5}{2}, -\frac{5}{2} \leftrightarrows -\frac{7}{2}$  pair of transitions at around  $\theta = 40^{\circ}$  to confirm the value of the Korringa rate. Figure 8 shows the final results of the X-band simulation, Fig. 9 those for Q band. All the parameters in the latter have exactly the same values as at Xband save the residual width  $\Delta H_{res}^0$ . Table I lists these final values. We note that the Korringa rate is a factor of 2 higher than that measured at the collapsed angle. The *Q*-band residual width is about a factor of 3 larger than at X band, supporting the idea of an internal field distribution. Hence, after incorporating the bottleneck and spread in  $b_4^0$ , we have good agreement between theory and experiment for the single-ion spectrum away from the crossing angles.

Given the distribution of ion-ion interactions in a dilute alloy, and if the "cluster" line truly arises from the narrowing effect of such interactions, then the intensity of the "extra" line relative to the single-ion spectrum should be a function of the overall splitting and therefore of the angle; such an effect *is* observed. In Fig. 10 we have shown both the X-band experimental spectra and those predicted by the theory near the crossing angle using the values given in Table I, i.e., for  $\theta$  from 26° to 33°. It is possible that the experimentally determined directions have a

TABLE I. Final values of the parameters used in the fitting procedure for Pt:Gd. Parameters not listed here are sample temperature, impurity concentration, and crystal orientation. The g-factor value taken for the free ion  $Gd^{3+}$   $g_i = 1.991$  and for the conduction electrons  $g_e = 2.000$ . Note that these are the g factors without exchange corrections.

. 2	X band	Q band	
	86 G	as X band	
$b_{\ell}^{0}$	-2.6 G	as X band	
- 0 V	~9 GHz	~ 35 GHz	
$\Delta H_{\rm res}^0$	55 G	~170 G	
E	0.083	as X band	
$J_1$	-0.026(eV)	as X band	
$ J_2 $	0.0044 (eV) <sup>a</sup>	as X band	
Tord	0 K	as X band	
δ	$5 \times 10^{10} \text{ s}^{-1}$	as X band	
ρ	1.38 states/eV spin <sup>a</sup>	as X band	

<sup>a</sup>These values would predict a thermal broadening of 3.6  $G K^{-1}$  for the collapsed (crossing angle) single-ion spectrum.

systematic error of  $\pm 1^\circ$ , this being the accuracy with which the crystal orientation in the field is known. However, these spectra were taken in succession and the error in their relative orientations is less than  $\pm \frac{1}{4}^{\circ}$ . For ease of comparison, a vertical line corresponding to g = 1.94 has been drawn through each set of spectra. This g value corresponds to the peak of both the observed single line between 27° and 32° and that of the extra line observed superimposed on the resolved single-ion spectra (see, for example, Fig. 7,  $\theta = 17^{\circ}$ ). The theory predicts that a rather complicated spectrum at circa 27° and 32° should reduce to one strong line at  $29^{\circ}$  and  $30^{\circ}$  which is shifted from g = 1.94 by about 215 G. In contrast, the experimental spectrum is constant in position (at g = 1.94) from 27° to 32°. We also note that the shape of the (sin-



FIG. 8. Comparison between the calculated (lower at each temperature) and experimental (upper) X-band spectra in the [001] direction for the *Pt*Gd 1300 ppm single crystal as a function of increasing temperature.



FIG. 9. Calculated Q-band spectra for the PtGd 1300 ppm single crystal in the [001] and  $\theta = 44^{\circ}$  directions at various temperatures. The parameters used in the calculation are those listed in Table I. Agreement with the experimental data shown in Fig. 5 is quite good except for the cluster line which is not included in the theory.

gle) experimental line at  $30^{\circ}$  deviates significantly from the expected metallic lineshape.<sup>16</sup>

We suppose again that the observed spectra have three components, the single-ion spectra, the background, and the extra cluster resonance. The form and intensity of the cluster resonance can be estimated by subtracting from the observed spectra, first the background and then a variable amount of single-ion spectra. Around the collapsed angle this latter amount has to be estimated mainly from the behavior of the low-field shoulder of the observed line. If such a decomposition is valid, then it becomes obvious that as one approaches the 30° position, intensity is being lost by the single-ion spectra and gained by the cluster resonance. We estimate the ratio (cluster intensity:single-ion intensity) to be



FIG. 10. Comparison between the calculated (left-hand groups) and experimental (right-hand group) X-band spectra for the PtGd 1300 ppm single crystal at the lowest temperature around the crossing angle ( $\theta \simeq 30^{\circ}$ ).

about 1.9 for  $\theta = 44^\circ$ . At  $\theta = 29^\circ$ , however, the ratio is 6:4—the effect is dramatic.

# V. EXTRA OR CLUSTER RESONANCE

Having been able to separate and clearly identify the cluster line we were interested to obtain further information upon its origin. It would be logical to study its concentration dependence; however, in view of the difficulty we had in making single-crystal samples of Pt:Gd this did not prove possible. On the other hand, by chance one 3000 ppm single-crystal plate had an orientation in which equivalent crystalline axes did not have the same orientation with respect to the plate and this permitted us to study what we believe is a strain dependence of the cluster intensity. Figure 11 illustrates the actual relative orientations. From this we can delineate two angular zones, one on either side of [001], each of which contains equivalent crystallographic directions but which have different orientations with respect to the plane of the plate. We label these the parallel and perpendicular zones. As Fig. 11 clearly shows, there is a striking difference between the spectra taken in the two zones. In the parallel sector, the intensity of the cluster line appears to have been reduced beyond detection. (Note that the Dewar background has been subtracted off in this figure.) Further comparison of the theoretical simulation with the experimental spectra around the crossing angle in the parallel zone actually works quite well; the anomalously fast collapsing of the fine structure around the crossing angle is very much reduced, when compared to the behavior in the perpendicular sector, or the behavior in the 1300 ppm sample. It is pertinent to the following discussion to notice here that the residual linewidth



FIG. 11. Two low-temperature X-band spectra for the PtGd 3000 ppm single crystal for two equivalent crystalline directions ( $\theta = 44^{\circ}$ ) which have different geometric orientations with respect to the plate sample. The insert shows the geometry. The plane of the sample is at right angles to that of the paper. Note both the larger linewidths and the greater cluster line intensity at g = 1.94 for the perpendicular direction. The background signal from the Dewar (see Fig. 4) has been subtracted from these spectra.

 $\Delta H_{res}^0$  is appreciably larger in the perpendicular zone than in the parallel one; the spread in  $b_4^0$  does not, however, appear to change. We also recall that our crystal samples were made by primary recrystallization and that any residual strain is almost certain to be either in the sample plane or perpendicular to it.

Although no previous works have observed such a variety of phenomena associated with it, the cluster line is by no means unique to Pt:Gd. In fact, the appearance of a cluster line appears to be the rule rather than the exception. Such lines have been observed in such contrasting metallic systems as  $Pd:Gd^3$  and LaSb:Gd.<sup>4</sup>

The cluster line in Pd:Gd is in many ways similar to the one found here. For example, it also appears to vanish upon lowering the temperature at Q band,<sup>17</sup> and its intensity is apparently a function of concentration and/or metallurgy. Moret *et al.*<sup>18</sup> state that the linewidth changes by some 40% as a function of angle, although this is not clearly evident from their published data. Whether or not the line is displaced to the first moment position is also unclear.

In LaSb:Gd the very low density of states, amongst other things, gives a very small Korringa rate and hence rate of narrowing with increasing temperature. It was therefore possible to study this system<sup>4</sup> over the wide temperature range from 1.7 to 300 K. Here again, at Q band, the cluster line appears only at higher temperatures, but on a differrent scale. While the cluster has appeared in both Pt:Gd and Pd:Gd by 5 K, it is not clearly evident in LaSb:Gd until a temperature some ten times higher. No anisotropy in the cluster was noted by these authors.

On the theoretical level, while both Barnes<sup>11</sup> and Moret et al.<sup>18</sup> have outlined a theory which incorporates the cluster line into the single-ion spectrum, it is clear from the known theory for pairs as applied to insulators, that such theories are too naive. The spin-spin interaction within small spin clusters is not sufficient to narrow the fine structure to a single narrow line; one must still account for the BP narrowing. Even a more refined theory doing this cannot account easily for the existence of a cluster resonance in such varied metallic systems. The internal fields required are simply too large to be reconciled with the known values of the exchange constant; this is particularly evident for a system like LaSb where the exchange constants and/or density of states is so small. We now believe that the cluster line arises from cross relaxation. The possible importance of cross relaxation in the context of EPR in metals was first pointed out some time ago by Chock et al.<sup>3</sup> but has since been ignored. Their theory, however, needs some embellishment. Our aim here is not to reproduce the observed spectrum but rather outline a theory which allows an understanding of the observed phenomena. As a starting point we use the very general formula (and notation) of Barnes and

Zitkova-Wilcox<sup>19</sup> for the Korringa rate

$$\frac{1}{T_{se}} = \frac{1}{2} \left( \frac{J}{N} \right)^{2} \left[ \left[ (e^{\beta\omega} - 1)^{-1} - (e^{-\beta\omega} - 1)^{-1} \right] \operatorname{Im} \left( \sum_{q} \left[ \chi_{e}^{\pm}(q, \omega + is) \right] \right) + \left[ (e^{\beta(\omega - \omega_{s})} - 1)^{-1} - (e^{-\beta(\omega - \omega_{s})} - 1)^{-1} \right] \operatorname{Im} \left( \sum_{q} \left[ \chi_{e}^{z}(q, \omega - \omega_{s} + is) \right] \right) \right].$$
(8)

Here  $\mu_{\beta} = 1$  in the definition of the X, thus for the imaginary parts

$$(1/N^2) \sum_{q} \chi_e^{\pm} = (1/N^2) \sum_{q} \chi_e^{\pm}$$
$$= (1/N^2) \sum_{q} \chi_e^z = -i2\rho^2 \omega$$

and with  $kT > \omega$  the above gives the usual result  $(1/T_{se}) = 4\pi (\rho J)^2 kT$ . The present interest is in calculating  $(1/T_{se})$ , which in turn dictates the degree of narrowing, this using a formula for the  $\chi_e$  which includes multi-impurity cross-relaxation effects. One observes that, for example,

$$\frac{1}{N^2} \sum_{q} \chi_e^{\pm}(q, \omega) \equiv \frac{1}{N^2} \chi_e^{\pm}(\vec{R} = 0, \omega)$$
$$= \left(\frac{1}{N^2} \chi_e^{\pm}(\vec{R} = 0, \omega)\right)^0$$
$$+ J^2 \sum_{i \neq j} [F(R_{ij})]^2 \chi_j^{\pm}(\omega) \quad , \quad (9)$$

where the first term on the right corresponds to the above, zero concentration value and where  $J^2F(R_{ij})$  is the RKKY interaction energy  $H = -\sum_{i \neq j} 2J^2F(R_{ij}) \vec{S}_i \cdot \vec{S}_j$ . The impurity in question is at the origin and it is assumed that  $g_e = g_s = 2$ in this calculation. The above can be derived by evaluating the self-energies indicated in Fig. 12, but can also be understood on an intuitive basis. Near



FIG. 12. The self-energy which produces impurityimpurity cross relaxation. The labels *i* and *j* refer to different impurity sites. This Feynman diagram formalism is described in Ref. 19.

the impurity resonance frequency  $\omega \simeq \omega_s$  the imaginary part of  $\chi_s^z$  will be small and might be ignored. One has then an extra homogeneous rate

$$\frac{1}{T_{ss}} = \sum_{j} \left( \frac{kT}{\omega} \right) [J^2 F(R_{ij})]^2 \operatorname{Im}[\chi_j^{\pm}(\omega + is)] \quad (10)$$

which, since  $\chi_j^{\pm}(\omega)$  is the dynamic impurity susceptibility, is strongly frequency dependent. In fact  $\operatorname{Im}[\chi_j^{\pm}(\omega+is)]$  is nothing but the contribution of the *j*th impurity to the absorptive part of the EPR signal. Thus in general the evaluation of the EPR signal becomes a self-consistency problem. In addition, it is evident that the statistical fluctuations in the value of the sum in Eq. (10) will be all important in explaining the appearance of a cluster line.

More detailed considerations show that in the presence of a cluster line the traditional relaxation diagram, Fig. 13(a), becomes modified as in Fig. 13(b). Perhaps the most important point is that  $(1/T_{ss})$ transfers spin between the two impurity subsystems and does not alter the "true" Korringa rate  $(1/T_{se})$ which transfers spin from the impurity to the conduction electrons. We emphasize this because the derivation of Eq. (10) from Eq. (9) would appear to imply the contrary.

As stated above, the formation of the cluster itself is, at least in part, a self-consistent problem. Consider the two spin problem. There are two important questions to ask. First, how large a RKKY interaction  $J^2F(R_{ij})$  is required in order that cross relaxation will produce a single line? Second, is this relaxation process more efficient than the straightforward exchange narrowing effect suggested by previous authors? The self-consistent problem has the following nature: Consider that relaxation *is* sufficient to cause narrowing-calculate the resulting  $(1/T_{ss}^c)$  within the cluster—then see how large an internal field is needed to be consistent with the starting assumption. The criterion for complete narrowing for cubic splitting without a bottleneck is

$$|9(1/T_{ss}^{e} + 1/T_{se}) + iF'| > 2[\langle (\Delta \omega)^{2} \rangle]^{1/2} \simeq 24b_{4}^{0} \quad .$$
(11)

The term iF' is included to indicate the effect of spin-spin field; we return to this below. The quantity  $\langle (\Delta \omega)^2 \rangle$  is the susceptibility weighted second mo-



FIG. 13. (a),(b) A comparison of the usual and modified relaxation diagrams. The latter indicates the relaxation paths possible when a cluster resonance exists. The cross relaxation of the cluster to and from the local moments depends upon the relative susceptibilities; the rate  $(1/T_{ss})$  is therefore only indicative.

ment of the fine-structure spectrum. The dynamic susceptibility, in the narrowed situation, is of the form

$$\chi_j^{\pm}(\omega) = \frac{(g_s)^2 S(S+1)}{3kT} \left( 1 + \frac{\omega}{\omega_s + i\Delta - \omega} \right) , \qquad (12)$$

where  $\Delta$  is the total width for a given temperature. In the region of resonance and for  $kT \gg \omega_s$ 

$$(1/T_{ss}^{c}) = 21 \{ [J^{2}F(R_{ii})]^{2}/\Delta \} \equiv 21(F^{2}/\Delta) \quad , \quad (13)$$

where  $(1/T_{ss}^c)$ ,  $\Delta$ , and the interaction  $F = J^2 F(R_{ij})$  might all be measured in field units. The self-consistency criterion is therefore

$$9(F^2/\Delta) > 24b_4^0 \quad . \tag{14}$$

From experiment we estimate for X band  $\Delta = 50$  G which via Eq. (14) implies a spin-spin field F larger than 70 G; a quite modest field. Magnetic fields of this order are consistent with spin-glass temperatures known for other rare-earth systems.<sup>20</sup> We note that the rms rather than average field is involved.

How does the above field compare with that required for simple exchange narrowing? As discussed elsewhere<sup>11</sup> the maximum F' which can enter Eq. (11) is given by the previous definition  $F' = J^2 F(R_{ij})$ . Thus, as observed by Baberschke and Von Spalden,<sup>21</sup> internal fields of several thousand gauss are required to produce a cluster line by such internal exchange field narrowing. Clearly cross relaxation is much more efficient, and we conclude that the cluster line corresponds to spins which see an average rms internal field of order 100 G. Notice though that we have yet to account for cluster single-ion interactions. A given spin might also be narrowed by this interaction if the relevant field and  $\chi_i^{\pm}(\omega_s)$ , the single-ion spectral density at the cluster resonant field (i.e., the center of the spectrum), is sufficiently large.

Before going on to discuss the observed cluster

phenomena in terms of these processes we make two observations which lend support to the hypothesis that the cluster is due to cross relaxation. One is that clusters have never been observed in hyperfine spectra; simple exchange narrowing would be equally effective here (give or take differences in exchange couplings). The other is that the Pt:Gd cluster, and probably the others, do not follow the (shifted) first moment of the crystal-field Hamiltonian; this is in accord with the BP motional narrowing theory but requires a tenuous explanation in terms of exchange narrowing.

To recapitulate, three parameters are important in determining the strength of the cluster line observed: (i) the single-ion spectral density at the cluster resonant field, (ii) the effective  $b_4^0$  in Eq. (11) which depends on the crystal orientation, and (iii) the cluster width  $\Delta$  entering in Eq. (12). How do we now explain our observed cluster phenomena? First we take the behavior as a function of angle. As the crystal is turned towards the crossing angle the effective  $b_4^0$  decreases, the criterion for narrowing becomes easier to satisfy, and the cluster grows smoothly. Very close to the crossing angle the spectral density of the single-ion spectrum at the cluster increases very rapidly, the cluster single-ion interaction becomes important, and a rapid growth of the cluster occurs. Variations in the single-ion residual width,  $\Delta H_{\rm res}^0$ , can also change the single-ion intensity at the cluster position. For our 3000 ppm sample the  $\Delta H_{\rm res}^0$ is different for equivalent crystalline orientations, due, we believe, to a preferential strain broadening (see Fig. 11). The greater residual width in the perpendicular sector, particularly of the  $\pm \frac{1}{2}$  line, increases the single impurity intensity at the cluster line and therefore the strength of the latter. Thus, the differences between the parallel and perpendicular sector in the 3000 ppm sample, and between this and the 1300 ppm sample, can be explained in terms of

preferential strain broadening and concentration effects both related to the single-ion residual width.

The disappearance of the cluster for low temperatures at Q band can be explained in a similar way. First the Q-band residual width is about three times larger than at X band, making a cluster resonance more difficult to form. Further, the single-ion spectral density at the cluster position is much smaller because only the  $-\frac{7}{2} \rightleftharpoons -\frac{5}{2}$  and  $-\frac{5}{2} \rightleftharpoons -\frac{3}{2}$  transitions are populated. The net effect is evidently too small. As the temperature increases the single-ion intensity at the cluster increases rapidly (the  $\pm \frac{1}{2}$  line is repopulated) while  $\Delta$  is still dominated by the residual width. Finally the single-ion  $(1/T_{se})$  processes also increase and a cluster resonance forms. This is somewhat reminiscent of the arguments of Urban *et al.*<sup>4</sup> in connection with LaSb:Gd.

Whether the cluster has an angle dependent width depends upon the degree of narrowing within the cluster and therefore might or might not be present.

#### VI. DISCUSSION

The principal questions we shall discuss are the origins of the negative exchange parameter  $J_1$ , the ratio  $(J_2/J_1)$ , the large  $b_4^0$  parameter, the modulation of  $b_4^0$ , the field dependent residual width, and the reduced Korringa rate for the collapsed or powder line.

First we take the question of the exchange parameters  $J_1$  and  $J_2$ , determined, respectively, by the g shift and the Korringa rate and/or degree of narrowing. Our present results should be viewed in the perspective of other recent measurements of the exchange parameters in elemental metals. In Table II we show the exchange parameters  $J_1$  obtained using the simple formula  $(\Delta g/g) = \rho J_1$  where  $\rho$  is the "bare" density of states indicated for each element in the table; specifically, we do *not* include any enhancement factors. We wish to make two observations about this table. First, we note that the exchange parameters for the noble metals Ag and Au are almost an order of magnitude larger than those from the III B column metals, starting with Sc. Second, if we compare La and Pt, we find that they are in some respects very similar; they both have large, comparable, d density of states at the Fermi level, their low-temperature susceptibility is similar, implying that they are both modestly enhanced by the electron-electron interaction, and indeed the magnitude of their exchange parameters,  $J_1$ , are similar. However, the signs of  $J_1$  are opposite in these two metals.

Before considering further the above observations, we first wish to emphasize a relatively elementary fact concerning the importance of the Kondo effect, for either sign of the effective exchange. The Kondo effect, in the EPR context, for  $T > T_K$ , has been considered by Barnes<sup>22</sup> and Baberschke *et al.*<sup>4</sup> They show that the usual analysis suffices if the effective exchange constant  $J_1$  is interpreted in terms of the standard formula for the effective exchange

$$2\rho J_1 = [(1/2\rho J_0) - \ln(kT/D)]^{-1} .$$
(15)

With a relatively small D = 5 eV, and in the helium temperature range,  $T \simeq 1$  K, one has  $\ln(D/kT) \simeq 11$ . It is therefore inconsistent to analyze a value of  $|2\rho J_1| \sim 0.1$  without accounting for the Kondo effect. Invariably, this is the order of magnitude of the measured g shifts,  $\Delta g = 2\rho J_1$ , and hence the Kondo effect must be accounted for. One might also note that this  $\ln(kT/D)$  term also implies a maximum positive g shift of order + 0.1, however large the density of states might be.

One can understand the difference in  $J_1$  between the III B Sc group and the noble metals in terms of the local density-of-states model recently employed by Liu and Orbach<sup>23</sup> and by Fert and Levy.<sup>24</sup> In order to satisfy the Friedel sum rule and remain neutral, the Gd impurity in a noble metal is expected to have a 5d screening charge localized in a nonmagnet-

TABLE II. Representative exchange parameters calculated with the bare density of states,  $\rho$ , given in the table. In particular, no host electron-electron interaction enhancement effects have been included.

	$2J_1$ (eV)		$2J_1$ (eV)		$2J_1$ (eV)
$\frac{\text{Sc}}{\rho \simeq 1.0}$	0.150				
$\begin{array}{c} Y\\ \rho \simeq 1.0 \end{array}$	0.150	$Pd \\ \rho = 1.62$	-0.123	$Ag \\ \rho = 0.135$	0.741
La (Lu) $\rho \simeq 1.0$	0.118 (0.108)	$\begin{array}{c} \text{Pt} \\ \rho = 1.38 \end{array}$	-0.052	$Au \\ \rho = 0.154$	0.260

ic virtual bound state (VBS) with a width of perhaps  $\frac{1}{4} - \frac{1}{2}$  eV. Assuming that there is about one electron in this 5d VBS implies a local 5d density of states of  $\rho_{5d} \sim 1$  st/eV spin. Using this  $\rho_{5d}$  (instead of the host  $\rho$ ) to extract  $J_1$ , results in reasonable agreement with the III B results. However, this still leaves the problem of explaining the small size of  $J_1$ , circa 100 meV. The calculations of Harmon and Freeman<sup>25</sup> give for the above 4f - 5d interaction  $-a_0 \vec{S} \cdot \vec{S}$  with  $a_0 \sim 350$  meV. A comparison with the observed band splitting of Gd metal indicates that this value may be up to, but not more than, a factor of 2 too large. This still leaves a discrepancy between the calculated and observed EPR values. However, if we now use the naive Kondo formula (15) with  $2J_0 = 350 \text{ meV}, \rho = 1 \text{ state/eV spin, and } D = 5 \text{ eV},$ then, at helium temperatures, we obtain  $J_1 \cong 70$  meV, which is consistent with observation.

We now address the question of the negative effective exchange constant in Pd and Pt. Various previous suggestions have been summarized by Taylor and Coles.<sup>26</sup> The processes of Coles *et al.*<sup>27</sup> or Davidov *et al.*<sup>28</sup> would apply equally to Pt and Pd or Sc, Y, La, and Lu. Viewing the ensemble of the available data, the creation of a local 5*d* moment, as suggested by Campbell,<sup>29</sup> is unlikely and anyway is not consistent with the resolved  $S = \frac{7}{2}$  crystal-field splitting in Pt and Pd (the 4*f* and 5*d* moments would be held parallel and the effective spin would differ from  $S = \frac{7}{2}$ ).

The obvious difference between a Pt-type and a La-type host is that in the former the Fermi level lies in a peak near the top of the 5d band, while in the latter the peak is near the bottom. As a consequence, the impurity 5d electrons will hybridize differently with the d electrons of the host. Clearly the potential for these electrons in La:Gd alloys will differ very little on the impurity site from that in the host. One would expect a local density of states on the Gd site to be essentially identical to that in the host. In particular, one will have the local density of states,  $\rho_{5d}$ , ~1 st/eV spin. In the context of Pt:Gd alloys, it is useful to consider the band-structure calculations of Kübler<sup>30</sup> for the analogous CsCl structure intermetallic compound ScRu. In this compound the Fermi surface lies in a (rather small) peak at the top of the Ru d band. Through hybridization, the top of this band repels the 5d band of the Sc and, because of a "hybridization hole," the Sc 5d density of states at the Fermi surface is very small. Translated to Pt:Gd, the schematic situation might look something like Fig. 14. In ScRu, despite the fact that the principal part of the Sc d band lies well above the Fermi surface, the tail below the Fermi surface contains about one and one-half electrons, the same number of 5d electrons as in Sc metal itself. Thus the 5dscreening of the Gd<sup>3+</sup> charge in Pt:Gd<sup>3+</sup> might be expected to remain very much effective. We see the



FIG. 14. The schematic density of states as imagined for Pt:Gd alloys (see text).

significant difference between La:Gd and Pt:Gd allovs as being the difference in the local density of states on the impurity site. While there is a large local 5ddensity of states  $\rho_{5d} \sim 1$  st/eV spin in the former alloys, in the latter we expect  $\rho_{5d}$  (and other components of the density of states) to be an order of magnitude smaller. This strongly suggests to us that in Pt:Gd all intra-atomic exchange processes are very strongly reduced and that the negative exchange constant is associated with an interatomic process as suggested by Davidov et al.<sup>28</sup> However, we differ from these authors in attributing the source of the process; they suggest direct exchange is responsible. It is perhaps pertinent to recall at this point the experiments of Peter et al.<sup>31</sup> on Pd alloys. The values of the negative exchange that these authors found are very much bigger at the beginning and end of the rare-earth series than at the center. Such behavior is the hallmark of a covalency process. We would therefore favor interatomic covalent mixing as the source of the negative exchange in Pt and Pd, etc. In Sc, etc., this process will be swamped by the intraatomic 4f-5d exchange.

We must, however, ask how the covalency can be so large. Indeed, Coles et al.<sup>27</sup> argue that the extreme stability of the 4f shell for  $Gd^{3+}$  precludes such processes. We believe that, while the 4f shell is indeed stable, certain 4f-conduction-electron mixing matrix elements  $V_{\vec{k}f}$  are quite large. Perhaps the most striking evidence for small mixing elements comes from rare-earth band calculations in which the 4f electrons have been included; such 4f bandwidths are typically  $5 \times 10^{-2}$  eV. This value, however, does not lead to a particularly small estimate for the maximum  $V_{fd} \sim 0.25$  eV for interatomic f-d mixing.<sup>10</sup> An even larger value results when one recalls that such calculated 4f widths are for bands placed well below the Fermi surface. It is a well-known trend that, say, d-band widths decrease rapidly as one crosses the periodic table; Sc has a bandwidth about three times that of Cu.<sup>32</sup> A similar but much stronger tendency must occur for 4f electrons. In the band calculation of Switendick<sup>33</sup> for LaAl<sub>2</sub> the 4f-band width is about 1.5 eV, here the band is approximately 3 eV above the Fermi surface. The reason is simple: the 4f VBS is contained by the centrifugal barrier, the nearer the VBS is to the top of this barrier the easier is tunneling through the barrier, and therefore the larger become the  $V_{\vec{k}f}$  matrix elements. Now in Gd metal the majority spin band lies at an energy  $E_{-} = 8.3$  eV below the Fermi surface and will, from the above, be quite narrow  $(V_{\vec{k}f})$ small). However,  $E_{+} \simeq 3.2$  eV; the minority band lies well above the Fermi surface implying that the corresponding  $V_{kf}^{\pm}$  matrix elements can be considerably larger. We suggest that  $V_{kf}^{\pm} \sim \frac{1}{3}$  eV for f-s or f-d would be a conservative estimate. This corresponds to a magnetic alloy VBS width of  $\Delta^+ = 2\pi\rho V^2$  $\sim 0.09$  eV in the noble metals (twice the traditional VBS width, see Ref. 34). The negative exchange constant from this source is therefore  $2J_0 = -(2V^2/$  $E_{+}$ ) = -0.07 eV. However, this is without either the Kondo effect or cancellation effects due to the residual intra-atomic direct exchange. We take  $2\rho J_0 = 0.042$  as a rough estimate of the latter. Then Eq. (15) becomes

$$2\rho J_1 = \left[ \left( 2\rho J_0 - 2\rho V^2 / E_+ \right)^{-1} - \ln \left( kT / D \right) \right]^{-1} .$$
 (16)

With  $\rho = 1.5$  st/eV spin, the above gives  $2\rho J_1 = \Delta g \approx -0.2$  in agreement with the data for Pd:Gd. Playing with the numbers quickly shows that the cancellation between  $2\rho J_0$  and  $(2\rho V^2/E_+)$  is all important and that agreement with Pt:Gd is easily obtained with a slightly larger value of  $2\rho J_0 = 0.057$  ( $\rho = 1.38$  state/eV spin). We thus conclude that the observed negative exchange parameters in Pt:Gd and Pd:Gd are easily explained in terms of interatomic covalent mixing, and that the difference between these and alloys of Sc, Y, La, and Lu is the absence or presence of an appreciable 5d density of states at the Gd site. Fur-

ther, it is important in both types of system to account for the Kondo effect.

Finally, in connection with the exchange, the small Korringa ratio  $(J_2/J_1)^2 = 0.016$  also supports the idea of interatomic process. Ignoring enhancement effects, as one should for a covalency process,<sup>35</sup> and using a standard "polynomial" expansion,<sup>36</sup> would suggest a minimum  $(J_2/J_1)^2 = \frac{1}{7} = 0.14$ . While such an expansion is probably reasonably rapidly convergent for intra-atomic processes, it will not be so for interatomic processes. One would have

$$V_{kf}V_{k+q}^* \sim e^{i\vec{q}\cdot\vec{a}}$$
$$\sim \sum_{l} (2l+1)i^{l}J_{l}(qa)F_{l}(\cos\theta)$$

where the  $\vec{a}$  are the translation vectors of the lattice. In the integrals for the Korringa rate (or the definition of  $J_2$ ) this series cannot be expected to be rapidly convergent; the oscillatory nature of the  $J_l(qa)$  as a function of q can be invoked to explain the small Korringa ratio  $(J_2/J_1)^2$ .

Turning now to the crystal field, the observed value  $b_4^0 = 86$  G for Pt:Gd is almost three times larger than for Gd in any other elemental metal,<sup>3</sup> and larger than any such splitting in an insulator. The origin of the  $b_4^0$  parameter for S states in metals has recently been discussed at some length by Barnes, Baberschke, and Hardiman.<sup>10</sup> They analyze the ratio  $R = (b_4^0/A_4^0 \langle r^4 \rangle)$  and conclude that in metals such as Pt and Pd this ratio is anomalously large and that it apparently cannot be explained by the insulator theory. In fact R is about a factor of 10 larger than comparable ratios in insulators. It is suggested that this large ratio in Pt and Pd also owe their origin to interatomic covalent mixing. In their notation

$$b_{4}^{0} = \sum_{\pm} \frac{10}{63} \left( \frac{\zeta}{E_{\pm}} \right)^{4} \left[ A_{\pm} (A_{4}^{0} \langle r^{4} \rangle)_{\text{CEC}} - \frac{1}{4b_{\pm}} (A_{4}^{0} \langle r^{4} \rangle)_{\text{cov}}^{\pm} \right]^{4} .$$
(17)

Without going into the details, it is perhaps clear that the controlling factor in determining  $b_4^0$  is the ratio  $(\zeta/E_{\pm})^4$ ,  $\zeta$  is the spin-orbit coupling parameter (=0.2 eV).

When treating the Kondo effect within the Anderson model<sup>36</sup> it turns out that this amounts to a renormalization of both the  $V_{\vec{k}f}$  and the energy  $E_+$ . Since the latter energy determines the covalent contribution to  $b_4^0$ , according to Eq. (17), it is important to estimate the size of this effect. One finds that

$$E_{+}^{R} = E_{+} - \rho V^{2} \ln(kT/D) \quad . \tag{18}$$

Compared with Eq. (16) there is a factor of 2 different in the  $\ln(kT/D)$  term but no cancellation effect with atomic exchange effects. With the above parameters  $E_+$  is reduced from 3.2 to 1.2 eV, an enormous renormalization effect. In terms of the Feynman diagram formalism of Ref. 37, Eq. (17) comes from evaluating the diagrams shown in Fig. 15(a) while the Kondo effect comes from summing the series which is indicated by Fig. 15(b). Part of this series amounts to a dressing of the 4*f* propagator, and it is found that the integrals which lead to Eq. (17) are now no longer simple to evaluate. It is, however, reasonable to estimate the effect of the above renormalization by replacing  $E_+$  in Eq. (17) by  $E_+^R$  given by Eq. (18). As was discussed by Barnes *et al.*<sup>10</sup> the observed  $b_+^0$  corresponds to an  $E_+^R = 1$ eV, in reasonable agreement with the foregoing analysis of the exchange constant.

Herbst et al. 38 have recently pointed out that,



FIG. 15. (a) Self-energy diagrams which generate the covalent contribution to  $b_4^0$ ; here the notation is that of Ref. 37. (b) Diagrams indicative of those which generate the Kondo divergence. The first illustrated diagram is the beginning of a series which renormalizes  $E_+$ , as discussed in the text, while the second begins a series which renormalizes  $V_{kf}^+$ .

whereas x-ray photoemission spectroscopy (XPS) on valence fluctuation compounds yields a value for, say,  $E_{\pm}$  on the order of 3.5 eV, the smooth temperature dependence of the magnetic susceptibility would indicate  $E_{\pm}$  energies about two orders of magnitude smaller. The Kondo renormalization represented by Eq. (18) might go at least part of the way to explain the discrepancy: the renormalization is appropriate to EPR and to magnetic susceptibility measurements, but it will not affect the XPS measurements.

We have shown that in order to satisfactorily explain the residual widths of the various EPR transitions we must have a modulation of about 8% in the  $b_4^0$  parameter. Such modulation might be temporal or spatial. Any discussion of this is mainly preempted by a lack of detailed understanding of the origin of  $b_4^0$ itself. However, one can say it is not due to a mosaic pattern in our single crystal, or to local distortions in the crystal axes: both of these lead to a width which is minimum at turning points, e.g., for H parallel to the [100] direction. It could be due to local expansion and contraction of the lattice parameters, a consequence of dislocations, etc., distribution in local charge density of the conduction electrons, or, if the covalent idea for  $b_4^0$  is correct, due to local variations in the parameters  $E_{\pm}$  or  $V_{\vec{k}f}$ , which, in the Anderson model, determine the electronic structure of the impurity. It might also be recalled that Sjöstrand and Seidel<sup>39</sup> have demonstrated a similar spread of about 3% in the hyperfine coupling constant, A, in the system Au:<sup>167</sup>Er. In this system the  $\Gamma_7$  ground state is weakly admixed with the first  $\Gamma_8$  excited state, and such an admixture modifies the hyperfine constant and g factor. The separation  $E(\Gamma_8) - E(\Gamma_7)$  is determined by the crystal field and is of the order 10 to 20 K.<sup>39,40</sup> Modulation of this separation would alter the admixture and hence modulate the hyperfine constant A. Their experiments are therefore indirect evidence for the same effect as we observe here.

The question of the origin of a field dependent residual width for S states is interesting. Since the Gd:Gd exchange interaction commutes with the total Gd magnetization, the internal field distribution cannot lead to a width in the absence of fine structure. However, as pointed out elsewhere,<sup>11</sup> in the presence of structure such a field distribution can lead to a residual width, and this is most probably the origin of the width,  $\Delta H_{res}^0$ , for the single-ion part of the spectrum. The behavior of the collapsed angle residual width is confused by the presence of the cluster and will not, for this reason, be discussed.

The reduced Korringa rate observed at the collapsed angle and in powder samples probably arises because the observed line is a concentration dependent mixture of the cluster and a slightly bottlenecked single-ion spectrum.

#### VII. CONCLUSIONS

The S-state crystal-field parameter  $b_4^0$  for Pt:Gd is large and positive, the sign being in agreement with the other elemental cubic metals measured to date.<sup>3</sup> The low-temperature experimental spectrum exhibits resolved structure which collapses as a function of the angle the magnetic field makes with the crystal axes. The experiment and Barnes-Plefka theory<sup>5</sup> are in excellent agreement for the "single-ion" spectrum. However, as with most other alloys which exhibit fine structure, there exists an extra "cluster" resonance. Because of the large second-order effects in  $b_4^0$ , it is possible in this alloy to separate the  $\pm \frac{1}{2}$ transition from the cluster resonance. The general behavior of the cluster resonance is consistent with a cross-relaxation model proposed here. We find strong evidence for a modulation (probably from site to site) in the crystal-field parameter  $b_4^0$ , this to be distinguished from a random strain model<sup>15</sup> which does not fit the data. There is also evidence for a weak bottleneck in this system.

The experimentally determined exchange  $J_1$  and  $J_2$ and crystal-field  $b_4^0$  parameters, viewed in the context of other metallic systems, are analyzed in terms of a theory which emphasizes interatomic covalent mixing and, in particular, the importance of Kondo renormalization.

Recently Herbst *et al.*<sup>38</sup> have brought to notice an apparent difference between the interconfigurational excitation energies  $E_{\pm}$  as deduced from susceptibility and XPS measurements. We have shown here that there is a renormalization of the  $E_{\pm}$  which is relevant to EPR *and* the first but not the second type of

aforementioned experiment (following the formalism of Refs. 34, 36, and 37).

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## APPENDIX A

Here we wish to outline a calculation illustrating the origin of the molecular-field narrowing process which acts at low temperature on the  $\pm \frac{5}{2} \rightleftharpoons \pm \frac{3}{2}$ ,  $\pm \frac{3}{2} \rightleftharpoons \pm \frac{1}{2}$  pairs. The discussion has two stages. First we reduce the equations of the BP theory to a pair of coupled equations for these two transitions; this shows why the minus but not the plus pair of transitions are affected. The resulting equations are quadratic and their solution shows why the lines move apart and transfer intensity rather than pulling together, as they would if motional narrowing were operating.

One starts with the linearized equations of the modified BP theory

$$\frac{d}{dt}M_{S_{z}} = \left(-i\left(\omega_{S_{z}} + \lambda X_{e}\omega_{s} + \alpha X_{s}\omega_{s}\right) - \frac{1}{T_{st}} - \frac{1}{T_{se}}\right) \left[M_{S_{z}} - \chi_{S_{z}}^{0} \left(h_{rf} + \lambda M_{e} + \alpha \sum_{S_{z}'} M_{S_{z}'}\right)\right] - \left(\frac{1}{T_{S_{z}^{-1}}} + \frac{1}{T_{S_{z}^{-1}}}\right) M_{S_{z}} + \frac{1}{T_{S_{z}^{-1}}}M_{S_{z}^{-1}} + \frac{1}{T_{S_{z}^{-1}}}M_{S_{z}^{-1}} + \left(\frac{g_{s}}{g_{e}}\right) \frac{1}{T_{eS_{z}}} \left[M_{e} - \chi_{e}^{0} \left[h_{rf} + \lambda \sum_{S_{z}'} M_{S_{z}'}\right]\right]$$
(A1a)

$$\frac{d}{dt}M_e = \left(-i\left(\omega_e + \lambda\chi_s\omega_e\right) - \frac{1}{T_{es}} - \frac{1}{T_{el}}\right) \left[M_e - \chi_e^0 \left[h_{rf} + \lambda\sum_{S'_z} M_{S'_z}\right]\right] + \left(\frac{g_e}{g_s}\right) \frac{1}{T_{se}} \sum_{S'_z} \left[M_{S_z} - \chi_{S_z}^0 \left[h_{rf} + \lambda M_e + \alpha\sum_{S'_z} M_{S'_z}\right]\right] \right]$$

These equations are simplified by several steps:

(i) The conduction-electron magnetization is removed using a standard trick,<sup>5</sup> valid if  $g_e = g_s$  and  $\chi_s^0 \gg \chi_e^0$ .

(ii) Since at the low temperatures of interest the  $-\frac{5}{2} \rightleftharpoons -\frac{3}{2}$  and  $-\frac{3}{2} \rightleftharpoons -\frac{1}{2}$  pair of lines are resolved, it is implied that the single-ion motional narrowing or hopping process is relatively ineffective. Hence, for the sake of a simple demonstration we drop the off-

diagonal relaxation terms (i.e., the off diagonal  $1/T_{S_{\star}}^{S_{z}} \pm 1$  rates).

(iii) We drop the bottleneck induced *motional* process proportional to  $1/T_{se}$ ; this is always small compared to the already neglected terms (ii).

This leaves a coupling between the magnetization  $M_{S_z}$  which is due to the molecular fields and is proportional to the Knight shift  $\lambda \chi_e^0 \omega_s$ :

$$\frac{d}{dt}M_{S_z} \approx \left[-i\left(\omega_{S_z} + \lambda \chi_e^0 \omega_s\right) - \Delta_{S_z}\right]\left(M_{S_z} - \chi_{S_z}^0 h_{\rm ff}\right) + i\lambda \chi_e^0 \omega_s \left(\frac{\chi_{S_z}^0}{\chi_s^0}\right) B \sum_{S_z'} M_{S_z'} , \qquad (A2)$$

where the width  $\Delta_{S_z}$  of the transition  $S_z = S_z + 1$  associated with  $M_{S_z}$  is given, to within relatively small corrections, by Eq. (5).

The important points to note in relation to the discussion of Sec. IV are (i) that the coupling between the  $M_{S_2}$  is determined by the degree of bottleneck through B where

$$B = \left(1 - \frac{(1/T_{el})^2}{(1/T_{el} + 1/T_{es})^2 + (\lambda \chi_s \omega_e)^2}\right) , \quad (A3)$$

i.e., B = 1 for a strongly bottlenecked system and zero in the complete absence of a bottleneck; the bottlenecked "turns on" the process; (ii) that the coupling is proportional to the susceptibility, or intensity of the transitions coupled. Thus, because the levels associated with  $-\frac{5}{2} = -\frac{3}{2}$ ,  $-\frac{3}{2} = -\frac{1}{2}$  transitions are more strongly populated than the positive pair, only the former transitions are affected by this process. Disregarding all other transitions but the negative pair, and keeping only essentials, we reduce the above to the following:

$$(\omega_1 + i\Delta + \delta - \omega)M_1 - \delta M_2 = Sh_{\rm rf} , \qquad (A4a)$$

$$(\omega_2 + i\Delta + \delta - \omega)M_2 - \delta M_1 = Sh_{\rm rf}$$
 (A4b)

This reduction amounts to assuming that the widths and intensities of the two lines are, for practical purposes, equal. The quantity  $\delta$  is the bottleneck dependent, Knight-shift proportional, coupling term derived above. The general roots of this are trivial to evaluate. There are two regimes, one is narrowed with  $\delta >> |\omega_1 - \omega_2|$ . In this case one root has most of the intensity and sits near the average of  $\omega_1$  and  $\omega_2$ ; it is unshifted by  $\delta$ . The second, corresponding to our case, is unnarrowed with  $\delta << |\omega_1 - \omega_2|$ , then

- \*A preliminary report of this work has been published in Crystal Field Effects in Metals and Alloys, edited by A. Furrer (Plenum, New York, 1977), p. 71.
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- <sup>1</sup>For a review of crystal-field parameters in insulators, see A. H. Buckmaster and Y. H. Shing, Phys. Status Solidi A <u>12</u>, 325 (1972).
- <sup>2</sup>A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).
- <sup>3</sup>Pd: R. A. B. Devine, D. Shaltiel, J. M. Moret, J. Ortelli, W. Zingg, and M. Peter, Solid State Commun. <u>11</u>, 525 (1972). Au: E. P. Chock, R. Chui, D. Davidov, R. Orbach, D. Shaltiel, and L. J. Tao, Phys. Rev. Lett. <u>27</u>, 582 (1972). Ag: S. Oseroff, B. Gehman, S. Schultz, and C. Rettori, Phys. Rev. Lett. <u>10</u>, 679 (1975). Mg: P. H. Zimmerman, D. Davidòv, R. Orbach, L. J. Tao, and J. Zitkova, Phys. Rev. B <u>6</u>, 2783 (1972). Sc: M. B. Salamon, Phys. Rev. Lett. <u>26</u>, 704 (1971); J. Nagel and K. Baberschke, in *Crystal Field Effects in Metals and Alloys*, edited by A. Furrer (Plenum, New York, 1977), p. 66. Y: B.

the roots are

$$\omega_2 + i\Delta + \delta - \frac{\delta^2}{\omega_1 - \omega_2} \tag{A5a}$$

and

$$\omega_1 + i\Delta + \delta + \frac{\delta^2}{\omega_1 - \omega_2}$$
, (A5b)

which have, respectively, strengths of

$$S\left(1+\frac{\delta}{\omega_1-\omega_2}\right) \tag{A6a}$$

and

$$S\left(1-\frac{\delta}{\omega_1-\omega_2}\right) . \tag{A6b}$$

The roots separate with increasing  $\delta^2$  and are also shifted by an amount  $\delta$  relative to the narrowed regime. With  $\delta$  positive the first root gains intensity from the second. Since  $\delta$  is proportional to *B*, this process depends upon the degree bottleneck. Finally, the other motional or relaxation narrowing processes result in similar equations, except there  $\delta$  is imaginary. The change  $\delta \rightarrow i \delta$  in Eqs. (A5) illustrates correctly that in this case the lines draw together. Thus, mathematically, the difference between the two types of narrowing is simply a matter of whether the terms coupling the equations of motion are real or imaginary. Coupling arising from relaxation gives one type, those due to internal molecular fields, the other.

Elschner and G. Weimann, Solid State Commun. <u>9</u>, 1935 (1971). Lu: K. Baberschke and J. Nagel, Phys. Rev. B <u>13</u>, 2793 (1976).

- <sup>4</sup>YAs, YSb, YBi, LaSb, LaBi-all with Gd<sup>3+</sup> impurity: For references see P. Urban and D. Seipler, J. Phys. F <u>7</u>, 1589 (1977). LaAl<sub>2</sub>:Gd and LaAl<sub>2</sub>:Eu. K. Baberschke, S. E. Barnes, and B. Bachor, J. Appl. Phys. <u>49</u>, 1451 (1978); K. Baberschke, B. Bachor, and S. E. Barnes, Phys. Rev. B <u>21</u>, 2666 (1980).
- <sup>5</sup>S. E. Barnes, Ph.D. thesis (University of California, Los Angeles, 1972) (unpublished). See also: P. H. Zimmerman *et al.* of Ref. 3; S. E. Barnes, Phys. Rev. B <u>9</u>, 4789 (1974); T. Plefka, Phys. Status Solidi B <u>51</u>, 113 (1972); <u>55</u>, 129 (1973).

<sup>6</sup>Mg:Gd. See Ref. 3.

- <sup>7</sup>LaSb:Gd. See Ref. 4.
- <sup>8</sup>S. E. Barnes, J. Dupraz, and R. Orbach, J. Appl. Phys. <u>42</u>, 1659 (1971); erratum <u>42</u>, 5908 (1971).
- <sup>9</sup>J. Pellisson, M. Hardiman, and A. Treyvaud (unpublished). <sup>10</sup>S. E. Barnes, K. Baberschke, and M. Hardiman, Phys.
- Rev. B <u>18</u>, 2409 (1978).
- <sup>11</sup>S. E. Barnes, J. Phys. F <u>4</u>, 1535 (1974).
- <sup>12</sup>Pt:Gd. D. Davidov, R. Orbach, C. Rettori, D. Shaltiel, L.

J. Tao, and B. Ricks, Solid State Commun. <u>10</u>, 451 (1972).

- <sup>13</sup>R. Lacroix, Helv. Phys. Acta <u>30</u>, 354 (1957).
- <sup>14</sup>H. Hasegawa, Prog. Theor. Phys. <u>21</u>, 483 (1959).
- <sup>15</sup>A spread in  $b_4^0$  is not equivalent to a random strain model; such a theory gives a minimum in the linewidth for the direction [001]—this is not compatible with our experimental results. See, for example, Ref. 2, p. 207.
- <sup>16</sup>M. Peter, J. Appl. Phys. <u>32</u>, 3385 (1961).
- <sup>17</sup>D. Shaltiel, K. Baberschke, J. Nagel, and G. Koopmann, Phys. Rev. B <u>16</u>, 3262 (1977).
- <sup>18</sup>J. M. Moret, R. Orbach, M. Peter, D. Shaltiel, J. T. Suss, W. Zingg, R. A. B. Devine, and P. H. Zimmermann, Phys. Rev. B 11, 2002 (1975).
- <sup>19</sup>S. E. Barnes and J. Zitkova-Wilcox, Phys. Rev. B <u>7</u>, 2163 (1973).
- <sup>20</sup>C. D. Bredl, F. Steglich, H. V. Löhneysen, and K. Matho, J. Phys. (Paris) <u>39</u>, C6-925 (1978).
- <sup>21</sup>K. Baberschke and Y. Von Spalden, Phys. Rev. B <u>19</u>, 5933 (1979).
- <sup>22</sup>S. E. Barnes, J. Phys. F <u>6</u>, 1713 (1976).
- <sup>23</sup>N. L. Huang Liu and R. Orbach, Phys. Rev. B <u>17</u>, 3701 (1978).
- <sup>24</sup>A. Fert and P. M. Levy, Phys. Rev. B 16, 5052 (1977).
- <sup>25</sup>B. N. Harmon and A: J. Freeman, Phys. Rev. B <u>10</u>, 4849 (1974).
- <sup>26</sup>R. H. Taylor and B. R. Coles, J. Phys. F <u>4</u>, 303 (1974).

- <sup>27</sup>B. R. Coles, D. Griffiths, R. J. Lowin, and R. H. Taylor, J. Phys. C <u>3</u>, L121 (1970).
- <sup>28</sup>D. Davidov, R. Orbach, C. Rettori, D. Shaltiel, L. H. Tao, and B. Ricks, Phys. Lett. A <u>40</u>, 269 (1972); Solid State Commun. 10, 451 (1972).
- <sup>29</sup>I. Campbell, J. Phys. F <u>21</u>, 47 (1972).
- <sup>30</sup>J. Kübler, J. Phys. F <u>8</u>, 2301 (1978).
- <sup>31</sup>M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. Lett. <u>9</u>, 50 (1962).
- <sup>32</sup>O. K. Andersen, Physica (Utrecht) <u>91B</u>, 317 (1977).
- <sup>33</sup>A. C. Switendick, in *Proceedings of the 10th Rare Earth Conference, Carefree, Arizona, 1973,* edited by C. J. Kevane and T. Moeller (National Technical Information Services, Springfield, Va., 1973), p. 235.
- <sup>34</sup>S. E. Barnes, J. Phys. F <u>6</u>, 115 (1976).
- <sup>35</sup>D. Davidov, K. Maki, R. Orbach, C. Rettori, and E. P. Chock, Solid State Commun. <u>12</u>, 621 (1973).
- <sup>36</sup>S. E. Barnes (unpublished).
- <sup>37</sup>S. E. Barnes, J. Phys. (Paris) <u>39</u>, C6-828 (1978).
- <sup>38</sup>J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B <u>17</u>, 3089 (1978).
- <sup>39</sup>M. E. Sjöstrand and G. Seidel, Phys. Rev. <u>11</u>, 3292 (1975).
- <sup>40</sup>D. Davidov, C. Rettori, A. Dixon, K. Baberschke, E. P. Chock, and R. Orbach, Phys. Rev. B <u>8</u>, 3563 (1973).