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Crystal fields and exchange parameters in $LaAl_2$: Eu^{2+} and $LaAl_2$: Gd^{3+} single crystals

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Reported are 10- and 35-GHz ESR measurements on single crystals of $Gd_xLa_{1-x}Al_2$ and $Eu_xLa_{1-x}Al_2$, $x = 100-1000$ ppm. For the Gd alloys no effects of fine structure could be detected, which, under the prevalent experimental conditions implies $b_4 < 10$ G. In contrast the Eu alloys exhibit a large, $b_4 = +112$ G, $b_6 = -8$ G, crystal field, the largest in a metal to date and corresponding to an overall crystal-field splitting of 480 mK. This system is the first to show resolved fine structure *and* a bottleneck. A computer analysis using the full Barnes-Plefka theory shows excellent agreement between theory and experiment. As is usually the case, the exchange obtained from the *g* shift does not agree with that from the linewidth. We show that this cannot be explained in terms of the current "spherically symmetric partial-wave-expansion" approach but is reconcilable with the crystal-field split-band theory of Narath. Finally, we show that, including the ferromagnetic Kondo effect, our *g*-shift exchange parameter *is* consistent with the theoretical value of Harmon and Freeman for Gd^{3+} scaled to Eu^{2+}.

I. INTRODUCTION

Probably the most important goal of studies involving dilute magnetic alloys is a detailed understanding of the effective exchange, $-J\vec{S}\cdot\vec{s}$, interaction between the magnetic $3d$ or $4f$ and conduction electrons. Recently in connection with $4f$ magnetic ions, Huang *et al.*,[1] following Harmon and Freeman,[2] have pointed out that the dominant interaction, at a rare-earth site, is between the $4f$ shell and the $5d$ character of the conduction electrons. They assume a local model, the wave functions at the rare-earth site are atomiclike, and the host conduction electrons enter only through their hybridization with these rare-earth atomic orbitals. In terms of this model, these authors were able to explain the ESR data for some non-S-state $4f$ impurities in Al.[3] More recently Fert and Levy[4] have analyzed magnetic transport properties in dilute noble-metal alloys in terms of this same local model. Again this work is for non-S-state ions. The interaction for such ions, in the simplest model, is of the form $-a_0\vec{S}\cdot\vec{s}-a_1\vec{L}\cdot\vec{l}$ where $\vec{S}$ and $\vec{L}$ are the total spin and angular momentum operators for the magnetic $4f$ shell and where $\vec{s}$ and $\vec{l}$ refer to the same quantities associated with the $5d$ electrons. From atomic calculations or from the Harmon and Freeman[2] calculation for Gd metal, it is known that $a_0 \simeq 0.30$ eV and $a_1 \simeq 0.016$ eV. Fert and Levy[4] conclude that the "anisotropic" part, that is a_1, has the correct magnitude, while the "isotropic" part a_0 seems much too large. Very recently, Huang and Orbach[5] have attempted to explain this discrepancy in terms of spin-orbit splitting of the $5d$ electrons.

There are two unnecessary complications in the above studies. First, the observed exchange parameters are dependent (at least) upon the two parameters a_0 and a_1. This complication can be avoided by studying the S-state ions Gd^{3+} and Eu^{2+} for which the a_1 term is not involved. Second, probably the greatest uncertainty in such local models for rare-earth ions as dilute impurities in either Al or the noble metals is the nature of these $5d$ electrons. It seems well accepted that these form a semilocalized nonmagnetic Friedel-type "virtual bound state" (VBS). The sharp atomic $5d$ orbital is spread out in energy, forming what is generally assumed to be a Lorenzian VBS with a width Δ estimated to be about 2.5 eV for Al or 0.5 eV for the noble metals. However, such estimates must be treated with caution; there is little reliable experimental information. In order to cast some light on the size of the isotropic interaction $-a_0\vec{S}\cdot\vec{s}$, here we consider the dilute rare-earth compounds such as Eu^{2+} and Gd^{3+} doped into $LaAl_2$. Our results should be viewed in the context of other similar alloys such as Gd^{3+} and Eu^{2+} in La [fcc and double hcp (dhcp)]. Here the magnetic ion substitutes for a La atom. For the case of Gd^{3+}, the substituted ion is isoelectronic with La, at least as far as valence electrons are concerned, and one would expect that the local $5d$ density of states at the impurity site would be essentially identical to that relevant to the host La sites. To a lesser extent the same will be true for Eu^{2+} impurities; see Sec. III.

The work on the totality of the above-mentioned systems has been extensive[6–9] (see Table I). The depression of the superconducting transition temperature for all the six systems is known. From ESR experiments on both ions in polycrystalline $LaAl_2$ and fcc La, the sign of the effective exchange interaction as well as the relaxation rate have been determined. More recently the third-order contribution in the exchange scattering rate in the resistivity (the ferromagnetic Kondo anomaly) as well as the negative magnetic resistence have been investigated.[10] De Haas-van Alphen (dHvA) data on $LaAl_2$ and YAl_2 also exist.[11]

The principal purpose of this paper is to introduce new experimental data on the systems $Eu_x^{2+}\,La_{1-x}Al_2$ and $Gd_x^{3+}\,La_{1-x}Al_2$ (Sec. II). The significant difference between the present and earlier work on the same systems is that our measurements were made upon single-crystal samples. The most striking new result is the very large *S*-state crystal cubic field parameter for the Eu^{2+} alloys $b_4 = +112 \pm 4$ G. The Gd^{3+} alloys showed no crystal-field effects, implying $b_4 < 10$ G. By a detailed analysis of the Eu^{2+} results, using the now well-established Barnes[12]-Plefka[13] relaxation theory, we have also been able to deduce the sixth-order parameter $b_6 = -8 \pm 2$ G. This is only the second time[14] that it has proved possible to determine such a parameter for a metallic system. The problem of *S*-state crystal electric fields (CEF) in metals represents an interesting field of study in its own right. Clearly the *S*-state crystal fields are a high-order perturbation-theory contribution and are small compared to the CEF for non-*S*-state ions. This smallness should perhaps be seen as an advantage for a study of the various contributions given by the conduction electrons. The situation is similar to the analysis of hyperfine fields. The core-polarization field (for Eu^{2+}, Gd^{3+}, or Fe^{3+}) is small compared to the ordinary angular momentum contribution. This core polarization is also difficult to calculate from first principles. Notwithstanding this, a study[15] of different host materials has given enormous insight into the influence of the conduction electrons. These *S*-state fields have recently been discussed by Barnes, Baberschke, and Hardiman.[16] They point out that in certain metals the *S*-state crystal fields are anomalously large. The *S*-state field b_4 must always be quoted in the perspective of the fundamental crystal field A_4^0. In the traditional insulator theory[17] the former is a derivative of the latter, and comes about because of admixture to excited *LS* states (the same admixture which leads to a small renormalization of the ionic *g* factor; see, for example, Abragam and Bleaney[17(b)]). Such a theory leads to a value for the ratio $R = (b_4^0 / A_4^0 \langle r^4 \rangle)$. A *large* value for such a ratio in an *insulator* is $R = 2 \times 10^{-5}$ relevant to Gd^{3+} in CaF_2. The corresponding value for Eu^{2+} in the *metal* $LaAl_2$ is $R = -2.6 \times 10^{-4}$, a full order of magnitude larger. The above authors examined[16] the role of covalency; this effect depends upon the interconfigurational energy E_-. That is the difference between the energy of the Eu^{2+} configuration, schematically $(Xe)4f^7 5d^x 6s^{2-x}$ and the adjacent Eu^{3+} configuration, $(Xe)4f^6 5d^{1+x} 6s^{2-x}$. It was claimed that the above anomalously large *R* might be explained by covalency if this interconfigurational energy $E_- \simeq 1$ eV. Since this time the energy E_- has been measured using the x-ray-photoemission-spectroscopy (XPS) technique by Schneider and Laubschat.[18] They find $E_- = 1.0 \pm 0.1$ eV. This, together with the ESR results presented here, therefore leads considerable support to this covalency model. In Sec. III we consider the question of the isotropic part of the exchange $-a_0 \vec{S} \cdot \vec{s}$, and concentrate on our new detailed Eu^{2+} results. Fert and Levy[4] suggested that there must exist some unspecified (screening) process which greatly reduces this isotropic exchange parameter a_0 but leaves the anisotropic part alone. We wish to point out that such a screening process of the isotropic part is already known; namely, the ferromagnetic-Kondo $(J > 0)$ effect. In Sec. III we show that the observed $\Delta g = 0.06$ at helium temperatures *is* consistent with a "bare" exchange of $a_0 = 300$ meV, a density of $\rho \sim 1$ states/eV spin and a *d*-band width of order 5 eV.

TABLE I. Various experimental exchange parameters for Gd and Eu in La and $LaAl_2$: $\Delta g_{\max} = \rho J_1, g\mu_B b_k = \pi \hbar^{-1} \rho^2 J_2^2 k$, and the T_c depression is given by $k(dT_c/dc) = \frac{3}{16}\pi\rho \tilde{J}_2^2 S(S+1)c$, with *c* the concentration of impurities.

		$\Delta T_c/\Delta C$ (K/at.%)	b_k (G/K)	$\Delta g_{\max}$
Gd	$LaAl_2$	4.0(2)[a]	60(10)[a,b]	+0.11(11)[a,b]
Eu		2.5(3)[a]	31(5)[a]	+0.07(1)[a]
Gd	La (fcc)	4.0(2)[c]	75(7)[c,a]	+0.12(1)[c,a]
Eu		2.1(3)[d]	. . .	+0.12(1)[d,a]
Gd	La (dbcp)	4.4[e]	. . .	. . .
Eu		2.3[e]	. . .	. . .

[a] Reference 7.
[b] Reference 8.
[c] Reference 6.
[d] Reference 6(b).
[e] Reference 9.

Finally on the more technical level, (ESR in metals) our experiments represent the first observation of resolved fine structure, or for that matter any kind of structure, in the *bottlenecked regime*. Such a possibility was predicted in the original theoretical papers of Barnes[12] and Plefka.[13] The similar situation for hyperfine structure was predicted earlier by Barnes *et al.*[19] Our experiments therefore complement those for the nonbottleneck case[20] and represent the first complete experimental test of the full Barnes-Plefka theory including this bottleneck effect; agreement is excellent.

II. EXPERIMENTAL RESULTS AND THEORETICAL INTERPRETATION

The single crystals of the cubic Laves phase doped with Eu or Gd were grown from the melt. An induction furnace with tungsten crucibles or the levitation technique were used. Depending on the impurity concentration, the residual resistivity ratio was between 10 and 100. The concentration of Eu^{2+} or Gd^{3+} was determined from the saturation magnetization. The width of the superconducting transition for the 400- or 1100-ppm Eu^{2+} samples was narrower than 0.1 K. For all samples we could observe dHvA oscillations (for higher concentrations only the low-frequency branch[11]).

The skin depth for 10 GHz is in the order of 1 μm. For 35 GHz small pieces of 3–5 mm have been used. Experimentally we got the best ESR signals with a "natural" cleaved surface. Spark cutting or etching produced a disturbed signal or washed out the Eu. XPS measurements on our samples proved that there was no Eu^{3+} in the samples; however, a small Eu-oxide signal was observed. To get the same ESR sensitivity at 10 GHz, very large ($\sim$25 times) crystals would be necessary. We were not able to grow those large pieces with the same homogeneity.

ESR experiments have been performed at 10 and 35 GHz for Eu- and Gd-doped samples with concentrations between 100 and 1000 ppm. Fully resolved fine structure was observed for Eu. The Gd spectra yield only a single-line spectrum; no angular dependence of the field for resonance or the linewidth could be detected. We conclude that $b_4^{\mathrm{Gd}} < b_4^{\mathrm{Eu}}$; a rough estimate yields $b_4^{\mathrm{Gd}} \lesssim 10$ G. Because of the metallurgical problems and previously published X-band data, we focus in this paper on the analysis of the Eu^{2+} Q-band data. Figure 1 shows the experimental spectrum for different crystal orientations. Figure 2 shows the field for resonance over the full angular dependence in the {110} plane for a 420- and 1100-ppm sample. As a first step in the analysis, we calculated H_{res} in second-order perturbation theory. At $T = 1.25$ K and 35 GHz only the lower-lying levels are populated. The full line and experimental points in Fig. 2 show rough agreement; however, the experimental line intensities as well as the change of the line shape for different orientations make it evident that a proper analysis can only be done using the full dynamic theory. The dashed lines in Fig. 1 show this fit, which is in excellent agreement with the experiments. The value of the parameters used

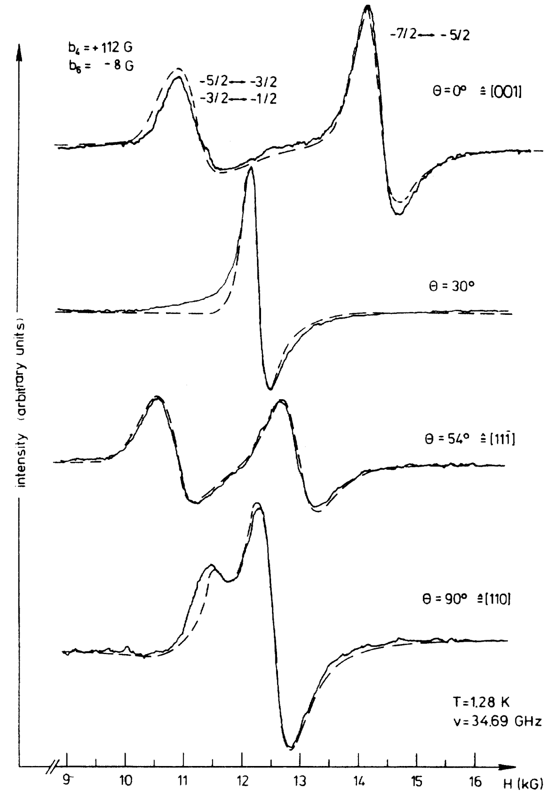

FIG. 1. Experimental fine-structure spectrum of 1100 ppm Eu in $LaAl_2$ single crystal for different orientations, θ being the angle between applied field H and cubic crystal axis. The dashed line shows a computer fit applying the Barnes theory (Sec. II) and the fit parameter in Table II.

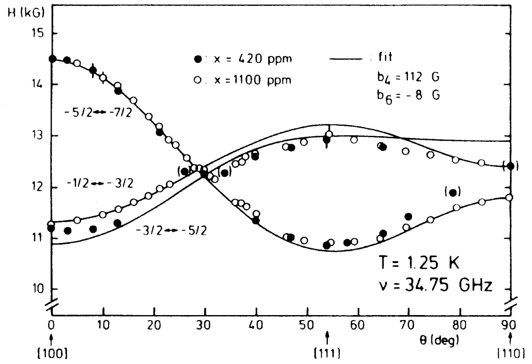

FIG. 2. The resonance field is given for two concentrations of 400 ppm ○ 1100 ppm ●, respectively, and its full angular variation in the {10$\bar{1}$} plane. The solid line is a fine-structure fit for $S = \frac{7}{2}$ including second-order perturbation theory but leaving out the effect of the conduction electrons. This simple fit yields already rough agreement with the experiment. For some points (●) the determination of H_{res} is not meaningful because the line shape deviates very strong from a Dysonian.

in the theoretical fit are displayed in Table II. Before going through the fitting procedure, let us point out which parameters are expected to be sensitive to single-crystal or polycrystalline hosts and which are independent. The exchange coupling is believed to be independent of host imperfections. Here the g shift $\Delta g = \rho J$ and the Korringa rate $(\pi \rho^2 J_2^2 kT)$ should and *do* agree, within errors, with the published value for the polycrystalline samples. The spin-orbit coupling of the conduction electrons—the relaxation rate of the conducting electrons to the thermal bath δ_{el}—will strongly depend on host imperfections; it would be expected to be smaller in single crystals and our single crystals are indeed somewhat more strongly bottlenecked than polycrystalline samples of the same concentration. Despite the relatively large number of parameters involved, it remains the case that the fitting procedure is really quite rigorous. The parameters are determined by the experimetal data in the following manner. The principal crystal-field parameter $b_4 = +112$ G is accurately determined by the overall splitting in the [001] direction and confirmed by the near-perfect agreement of the full angular dependence of the $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ transition (Fig. 2). The crossplay between this and the other fit parameters is only a few percent. The linewidth exchange J_2 determines the Korringa rate of thermal broadening, which in turn can be determined by the rate of increase of linewidth with temperature in the [001] direction. The residual width a accounts for that part of the linewidth which does not increase with temperature. There is no crossplay between these two widths. However, there is a *weak* interplay ($\sim 20\%$) between the degree of bottleneck and the observed Korringa broadening for the direction [001]. The degree of bottleneck is determined by the *effective* rate of Korringa broadening at the collapsed angle near 30°. Here the situation is as it would be without fine structure; the thermal broadening is reduced from 100% to zero by turning on the bottleneck, that is, by varying the electron-lattice rate δ_{el}. The [001] Korringa broadening must be readjusted slightly for crossplay. Finally J_1, the exchange parameter which determines the g shift, is varied to give the correct field for resonance at the collapsed angle. There is some crossplay between J_1 and the degree of bottleneck, but the whole procedure of adjusting J_2, J_1, and the bottleneck is strongly convergent. Somewhat as a bonus we found evidence in the spectrum for a finite value of b_6. Figure 3 shows the effect that varying b_6 has upon the spectrum for the directions [001], [111], and [110]. While there is virtually no effect on the [001] direction, which, as we have indicated above, determines our principal parameters, the fit is considerably improved, particularly for the [110] direction by including the b_6 value indicated in the table. We found no concrete evidence for a spread in the b_4 parameter, as was found necessary to fit the data for the dilute alloys Pt:Gd.[14] The theory used is that of Barnes as modified to include internal fields correctly.[6(b)] We set the Curie-Weiss θ of the latter paper equal to zero, indicating the absence of a significant average internal field.

To illustrate the very real effect of the bottleneck in Fig. 4, we show the *theoretical* spectrum for the angles $\theta = 0°$ and 30° with and without the bottleneck and also with the (large) degree of bottleneck indicated by the experiment. Clearly the effect is signifi-

TABLE II. Fit parameters for the computer-simulated ESR spectra. See dashed line in Fig. 1. Most of the parameters do not affect each other in the fitting procedure—for details see Sec. II.

Impurity spin	$S = \frac{7}{2}$
Impurity g value	$g_i = 1.993$
Cond. electr. g value	$g_e = 2$
Exchange g shift	$J_1 = 0.04$ eV
Exchange linewidth	$J_2 = 0.024$ eV
Density of states at the Fermi energy	$\rho = 1.5$ states eV spin
Electron-lattice rate	$\delta_{el} = 1 \times 10^{11}$ sec^{-1}
Overhauser rate	$\delta_{ei} = 0.53 \times 10^{11}$ sec^{-1}/1000 ppm
Residual linewidth	$a = 150$ G
Temperature	$T = 1.28$ K
CEF parameter	$b_4 = +112$ G $b_6 = -8$ G
Ordering temperature	$T_{\text{ord}} = 0$

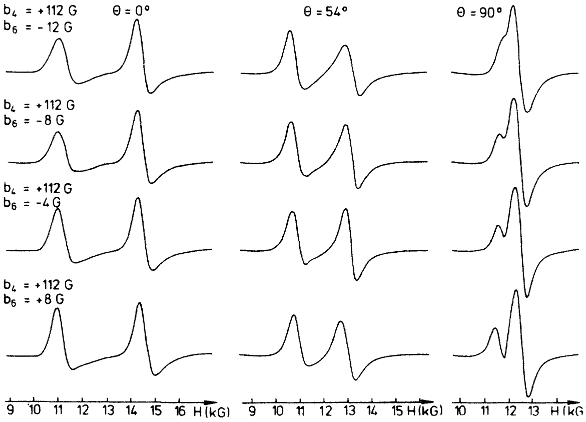

FIG. 3. Theoretical computer simulation of the resonance spectrum for $\mathrm{Eu}_x\mathrm{La}_{1-x}\mathrm{Al}_2 (x = 0.0011)$, to show the effect of sixth-order crystal-field parameter b_6. For $\theta = 90°$ and a comparison with Fig. 1 b_6 was determined to be -8 G. $T = 1.28$ K and $\nu = 34.75$ GHz.

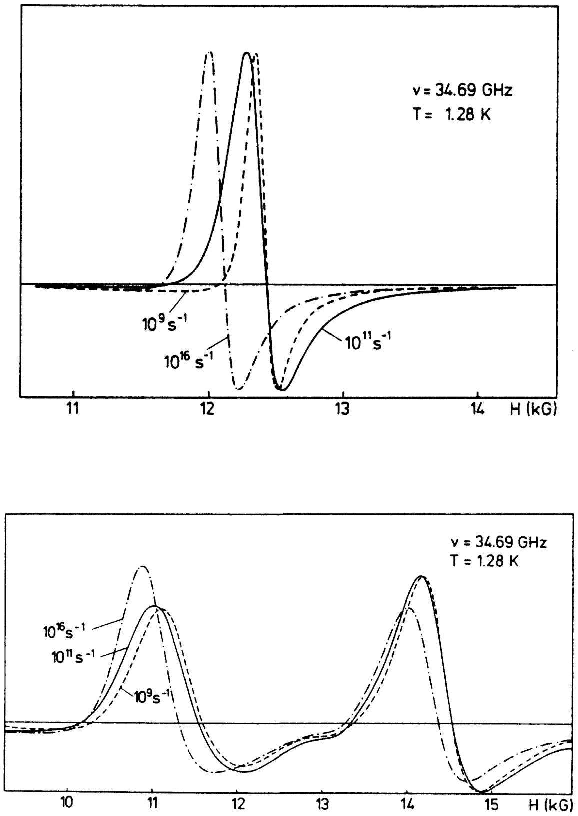

FIG. 4. The fit shows the different effect of bottleneck on the resonance at the collapsed angle $\theta = 30^\circ$ and for the [100] direction. $\delta_{el} = 10^{16}$ sec^{-1} and 10^9 sec^{-1}, respectively, correspond to the isothermal limit and the extreme bottleneck. The solid line ($\delta_{el} = 10^{11}$ sec^{-1}), is equivalent to the dashed one in Fig. 1. The effective g value for this line equals to 2.02.

cant. The full Knight shift and the total Korringa rate are suppressed by the bottleneck at the collapsed angle ($\theta = 30^\circ$), while only a fraction of the Knight shift and Korringa rate cancel for the $\theta = 0^\circ$ resolved structure.

Figure 5 further demonstrates this point; shown are the *experimental* thermal broadening for $\theta = 0$ and 30°. For the collapsed $\theta = 30^\circ$ case the bottleneck reduces the thermal broadening (21 G/K) from its unbottlenecked value (31 G/K). While the $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ line of the resolved structure has a thermal broadening some seven times the *unbottlenecked* value. These multiplication factors for the thermal broadening for the resolved spectra are in agreement with theory[12,13] and have been investigated in the nonbottlenecked limit by Urban *et al.*[20]

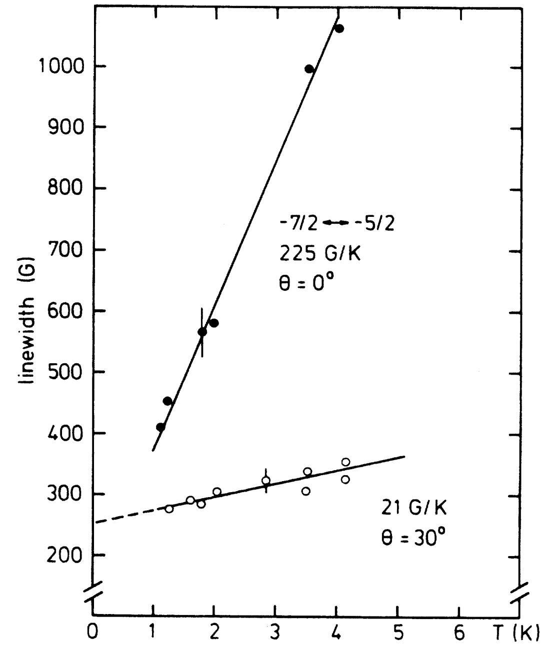

FIG. 5. For the 1100-ppm sample the different effect of bottleneck manifested in the thermal broadening. For $\theta = 30^\circ$ the thermal broadening equals 21 G/K, whereas the isothermal Korringa rate equals $b_K = 31$ G/K. The $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ transition yields for the thermal broadening 225 G/K. (225/7) ≈ 32 G/K is in rough agreement with b_K.

III. EXCHANGE PARAMETERS

The analysis of the conduction electron to local moment exchange presented here differs in three significant ways from that usually encountered in the ESR context. First, we argue that the density of states used in the simulations presented in the last section is not necessarily the same as should be used to extract what might be reasonably called the fundamental exchange parameter(s). Second, we use the present data to show that the by now almost standard "spherically symmetric partial-wave expansion" is not appropriate to *d*-band metals in general and the present alloys in particular. Third, we emphasize the importance of the ferromagnetic Kondo effect in the understanding of the size of the observed low-temperature exchange. Including this effect brings about reasonable agreement between experiment and the calculated exchange of Harmon and Freeman.[2]

First, the question of the relevant density of states. Following Refs. 7 and 8, the specific heat leads to a value $\rho = 1.5$ states / eV spin formula unit for the "bare" density of states. This is the sum of the local density of states for one La and two Al and, provided the concentration is specified as the fraction of La atoms substituted, this is the usual, and correct, density of states to use in the Barnes-Plefka theory, that is if conduction-electron enhancement effects are not important. The enhancement factor $(1-a)^{-1}$ for $LaAl_2$ is 2.3 (Ref. 8) or ≈ 2.0 (Ref. 7) depending upon the detail of the analysis; thus a value of $\rho \simeq 3$ would be more appropriate. In view of the uncertainties in this enhancement factor, we preferred to perform our simulation work using the value $\rho \simeq 1.5$, as indicated in Table II. The only important effect a change would have, for our relatively high concentrations, is to *reduce* the values of J_1 and J_2 but not their ratio. Specifically, J_1 and J_2 would be divided by $(1-a)^{-1}$. However, we wish to emphasize that the exchange parameters deduced by either of the above procedures are not the fundamental ones, only the products (ρJ_1) and (ρJ_2) have real significance.

The fundamental exchange parameters as calculated by Harmon and Freeman[2] for Gd metal are between the $4f$ shell and the $l=1,2$, or 3 partial-wave components of the conduction-electron states. It is therefore the partial densities of states at the impurity site which are important. In substitutional alloys of the present kind, this will be more or less related to the local density of states at the La site; this is elaborated on below. There are now two band calculations for $LaAl_2$. Switendick[21] has calculated both the partial and total density of states; unfortunately the calculated value of the total is a factor of 2 smaller than the specific-heat value. Very recently Hasegawa and Yansee[22] have repeated the calculation using a self-consistent augmented-plane-wave method; now the total density of states is somewhat too large; dominant at the Fermi surface is La $5d$ in character. Equally unfortunate, the latter authors do not give the partial density of states. Taken together, these two calculations suggest that the error lies in the calculated La $5d$ density; we propose the following: Following Switendick[21] the local Al density is s-p-like and has a value $\rho_{Al}=0.26\pm0.05$ states /eV Al spin. Since these will be nearly-free electrons and therefore relatively insensitive to potential constructs, etc., and since this corresponds well to the value for di- or trivalent metals in general and the density $\rho=0.21$ for Al metal itself in particular, we treat this figure as reliable, whence the local density of states on the La site is $\rho_{La}=0.98$ states /eV La spin which we would now like to divide between s and d character. The (f_0) band calculation[21] attributes 14% to be s-like; i.e., $\rho_{s\,La}=0.14$, with the rest nearly all d-like, $\rho_{d\,La}=0.84$. For $LaAl_2$:Gd one might then argue that in view of the likeness of all of the calculated band structures for the trivalent rare earths, the local impurity density of states would be the same as that on the La host sites. Clearly such an argument is no longer exact when divalent Eu is substituted for a La. This notwithstanding, the densities will not be very different. We reason as follows: The d band in Eu metal is only a little higher $(\sim \frac{1}{4}\text{eV})$ than in the trivalent metals and hybridization will tend to level out the difference. We rather arbitrarily reduce the local density of states by 20% on the Eu site and give the result the same amount as an error: $\rho_{d\,Eu}=0.67\pm0.17$ and $\rho_{s\,Eu}=0.11\pm0.03$. However, of all of the uncertainties in the above, the least is in the nature of local La, Gd, or Eu density of states. The calculations for $LaAl_2$ agree with those for the rare-earth metals[2] and other comparable intermetallics,[23] with the conclusion that roughly 80% of the local density of states is of d character; this is important in connection with the conduction-electron degeneracy.

Before proceeding to discuss the size of the exchange parameters deduced with the above partial density of states, let us first turn to this question of conduction-electron degeneracy. There are available two ways to account for degeneracy, the first being the spherically symmetric partial-wave expansion.[24] This consists of writing

$$J(k,k')=\sum_L(2L+1)J_LP_L(\cos\theta_{kk'}) \quad ,$$

where $\theta_{kk'}$ is the angle between k and k'. The subscript L is associated with the Lth angular momentum component of the conduction-electron density about the center of impurity site. If one says, as is almost the case here, that this density is wholly d-like, then only the term $L=2$ is present, and, following Ref. 24 the degeneracy factor $d=(J_1/J_2)^2=2L+1=5$. Alternatively the degeneracy of the d bands might be handled in the fashion described by Narath.[25] In cubic symmetry angular momentum is not a good quantum number. Rather than angular momentum components, the wave functions are characterized by the cubic group representations Γ_3 and Γ_5. The Γ_3 wave functions are doubly, while those of the Γ_5 are triply degenerate. Only in the absence of cubic splitting are all five of the Γ_3 and Γ_5 wave functions degenerate. Thus, rather than a fixed degeneracy $d=5$, d electrons should be associated with a variable degeneracy varying between 2 and 5. As Blandin[26] has pointed out, the Kondo effect, to be introduced into the analysis below, does not change this degeneracy factor, at least in the model upon which the spherically symmetric partial-wave analysis is based. Thus we might use in an estimate of d the "bare" exchange given by Harmon and Freeman[2]: $\simeq 300$ meV for $l=2$, $\simeq 180$ meV for $l=1$, and $\simeq 120$ meV for $l=0$. From the partial-wave expansion one finds $d=5.8$; adding a small *positive* $l=0$ or 1 contribution actually makes the agreement worse. Only a very much larger $l=0$ or 1 contribution would bring about agreement with experiment. If, however, we allow for the cubic splitting of the Γ_3 and Γ_5 and include a $l=0$ contribution using the above decomposition of the density of states, one deduces that the d states at the Fermi surface are of predominately Γ_3

character (90%) with only a small Γ_5 component (10%). However, in view of the crudeness of our decomposition of the density of states and experimental errors, a considerable variation in the above can be admitted, including a second solution with dominant Γ_5 character (see curve of Ref. 25). While our analysis is inconclusive about the actual Γ_3 or Γ_5 nature of the Fermi-level states, we feel that it *does* demonstrate the general invalidity of the spherically symmetric partial-wave expansions in the context of *d*-band metals.

The final subject to be discussed in this section is the ferromagnetic Kondo effect. We wish to make a connection between the experimental *g* shift $\Delta g = 0.06$ and the theoretical values for $4f$-$5d$ exchange calculated by Harmon and Freeman[2] for Gd^{3+} metal, scaled to Eu^{2+} following Legvold *et al.*[9]; the value is $a_0 = (0.73)(300) = 220$ meV. Including a similar scaling factor for the *s* exchange and using the above density of states yields $\Delta g_{\text{bare}} = 0.16$, a value some $2\frac{1}{2}$ times too large. At first sight this does not seem too bad since Harmon and Freeman also found that this calculated value was a factor of 2 too large. Simply to state that our experiments also indicate that the exchange is too large by a factor of roughly 2 would be naive for two reasons. First Fert and Levy[4] find that the anisotropic parts of the exchange calculated on essentially the same basis *are* in agreement with experiment, and second it is simply wrong to ignore the antiscreening effect contained in the ferromagnetic Kondo Hamiltonian. As shown by Ref. 12(c), the Kondo effect can be included in ESR theory simply by defining a temperature-dependent effective exchange

$$\rho J_1(T) = \frac{1}{1/\rho a_0 - \ln(kT/D)} \equiv \left[\ln \frac{T_k}{T} \right]^{-1} ;$$

$$T_k \equiv D\, e^{(1/\rho J)} ,$$

where this definition of T_k enables the same formulas to be used for both the ferro- and antiferromagnetic cases. The alternative $T_k' \equiv D \exp(-1/|\rho J|)$ is perhaps more significant; this is the temperature at which $\rho J_1(T)$ has one-half its high-temperature value. As is well known, $J_1(T)$ scales to zero at absolute zero; at intermediate temperatures it has a value given by the above. With the numbers $a_0 = 220$ meV, $\rho = 0.78$ states /eV spin (the *total* Eu density of states for simplicity) and $D = 5$ eV, one has $T_k = 20 \times 10^6$ K or $T_k' = 170$ K, which at liquid-helium temperatures ($T = 1$ K) gives $\rho J_1 = \Delta g = 0.06$, in agreement with experiment. It is interesting to make the equivalent calculation for Gd metal, in which presumably one must replace kT by the spin splitting $\Delta \simeq 0.5$ eV. This gives (with $a_0 = 300$ meV, $\rho = 1$, and $D = 5$ eV) $J_1 = 177$ meV; i.e., the Kondo effect is capable of explaining the factor of roughly 2 differences between the observed and calculated values in both dilute alloys *and* Gd metal. We are not suggesting that the above figures should be taken too seriously; the above calculation ignores degeneracy and detailed band-structure effects, not to mention conduction-electron enhancement (in the context of the latter, the comparison between experiment and theory for Gd metal[2] would indicate that either it is not important or already included in canceling errors). The intention is simply to indicate the physical nature of the "screening" process which is capable of reducing appreciably the bare value of the exchange; in the ESR context at least this does not seem to have been previously appreciated.

IV. CONCLUSION

The *S*-state ion Eu^{2+} substituted for La in the intermetalic compound $LaAl_2$ exhibits a large positive crystal-field parameter $b_4 = 112$ G. The sixth-order parameter $b_6 = -8$ G has also been determined. In agreement with polycrystalline measurements, the exchange is positive, with a *g* shift $\Delta g = \rho J_1 = 0.06$ appropriate to the nonbottlenecked limit. The exchange parameter deduced from the linewidth is somewhat smaller, corresponding to an effective conduction-electron degeneracy $d = (J_1/J_2)^2 \simeq 3$. We show that the cubic split-band model of Narath,[25] but not the "partial-wave-expansion"[24] method, is capable of explaining this result.

These *Q*-band measurements have been performed on high-quality single crystals and are the first to our knowledge to show no extra or "cluster" line. This absence of a cluster line together with the fact that our system is bottlenecked permits what is probably the most stringent test to date of the Barnes-Plefka motional narrowing theory; the agreement between experiment and theory is excellent.

In the analysis of the exchange parameter J_1, we have emphasized the importance of a local-density-of-states model, and have pointed out the importance of the ferromagnetic Kondo effect. When this is accounted for, the calculated bare $a_0 \simeq 220$ meV *is* compatible with an observed exchange $J_1 = 77$ meV, the latter deduced with a total local density of states $\rho_{\text{Eu}} = 0.78$ states /eV Eu spin.

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