PHYSICAL REVIEW B **75**, 045107 (2007)

Multiband effects in the electron spin resonance of Gd^{3+} in the intermediate-valence compound $YbAl_3$ and its reference compound $LuAl_3$

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(Received 9 August 2006; published 5 January 2007)

Electron spin resonance (ESR) results of Gd^{3+} in $YbAl_3$ and $LuAl_3$ are analyzed using a multiband (f-, d-, and p-type) model of correlated conduction electrons. The need for a multiband analysis of our results is based on the following observations: (i) the Korringa rates $b \simeq 14$ Oe/K and $b \simeq 9$ Oe/K for Gd^{3+} for $YbAl_3$ and $LuAl_3$, respectively, are larger than those expected from the respective measured g shifts (Knight shift), and (ii) negative and positive g shifts $\Delta g \simeq -0.004$ and $\Delta g \simeq +0.003$ were observed for Gd^{3+} in $YbAl_3$ and $LuAl_3$, respectively. Specific heat and magnetic susceptibility measurements, in the samples studied by ESR, show that electron-electron correlations are present in both compounds.

DOI: 10.1103/PhysRevB.75.045107 PACS number(s): 71.27.+a, 76.30.Kg, 75.30.Mb, 71.20.Eh

I. INTRODUCTION

The rare earth trialuminides RAl_3 (R=rare earth) compounds have been extensively investigated due to their variety of interesting magnetic,[1–4] thermal,[5] transport,[6] and electronic physical properties.[7–10] In particular, $YbAl_3$ has been the focus of many detailed studies due to the intermediate-valence (IV) phenomena found in this compound similarly to that seen in CeNi, $CeSn_3$, and $YbAgCu_4$.[9,11–15]

In fact, the microscopic behavior of an IV system and the related duality and/or crossover between the localized and itinerant nature of the $4f$ electrons in a dense lattice is a classical subject of interest and still an unsolved problem in the physics of heavy-fermion (HF) systems.

The fundamental mechanism of this crossover involves the strength of the Kondo coupling between an f electron and the conduction electrons.[16] A reasonable understanding of the Kondo problem was achieved in the case of isolated Kondo impurities by the Anderson impurity model[17] (AIM), and despite the fact that many of these HF systems are concentrated stoichiometric systems, some of their physical properties, such as magnetic susceptibility and specific heat, qualitatively follow the predictions of the AIM.[18,19] On the other hand, other low-temperature physical properties of HF and IV systems are fundamentally different than those expected for the AIM such as a vanishing electrical resistivity and an optical conductivity consistent with renormalized band behavior.[18,20]

Although the problem of a lattice of Kondo impurities does not have a complete solution until now, many theories have been developed in terms of periodic Kondo impurities forming an Anderson lattice (AL).[21–23] A key issue for an AL is the role of lattice coherence, which can be thought of as dispersive or bandlike behavior of the $4f$ electrons or alternatively as correlations between the $4f$ electrons on different lattice sites. This contrasts the AL with the AIM where no such coherence is present.[19]

The simplicity of the $YbAl_3$ IV system which forms in cubic structure and grows in high-quality single crystals provides a unique opportunity to investigate the extension of the AIM to the physics of Kondo lattice compounds described by the AL models.[24]

As such, various recent experiments on high-quality single crystals of $YbAl_3$ have revealed the existence of a new low-energy temperature scale $T_{coh} \sim 30$–40 K for the onset of Fermi liquid coherence in addition to the Kondo temperature energy scale $T_K \sim 670$ K.[18] Furthermore, these experiments indicated slower crossover from the low-temperature Fermi liquid regime to the high-temperature local moment regime than that expected from the AIM. In fact the observed crossover seems to be more consistent with recent theories of the Anderson lattice model (ALM).[22,23]

However, to establish that the two energy scale effects observed for $YbAl_3$ and the crossover behavior predicted by the ALM are generic behavior for IV compounds, one needs to further explore details of the microscopic behavior of the Yb $4f$ electrons such as single-ion anisotropy and/or f-f electrons magnetic correlations that commonly have to be taken into account to understand the properties of IV (Ref. 25) or Kondo lattice materials.[26]

In this regard, further local experiments probing the temperature evolution and the microscopic interaction of $4f$ electrons in $YbAl_3$ may be very elucidating.

Therefore, the aim of this paper is to present a study of the electron spin resonance (ESR) of diluted Gd^{3+} in the IV $YbAl_3$ compound, as well as in the nonmagnetic isostructural

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$LuAl_3$, used as a reference compound. It has already been shown that the ESR technique can be very useful in the study of the microscopic electronic interactions in *f*-electron systems.[15,27,28]

We will show in this work that the ESR data of Gd^{3+} in RAl_3 (R=Yb, Lu) cannot be explained by the simple model of a single band of noncorrelated electrons. We argue that the contribution of the Yb $4f$-, Lu $5d$-, and Al $3p$-like electronic bands to the density of states at the Fermi level and electron-electron correlations are required to explain the data. This scenario is in general agreement with a recent band structure calculation[29] and suggests that reported values of the exchange interaction between the $4f$ electrons and the different conduction electrons bands may be relevant to construct more realistic models of the microscopic behavior of the $4f$ electrons in $YbAl_3$ and related IV systems.

II. EXPERIMENT

Single crystals of RAl_3 (R=Yb, Lu) were grown by the "self-flux" method with Al excess as described in Ref. 30. The magnetic susceptibility $\chi(T)$ was measured for $2 \leq T \leq 300$ K at a magnetic field of H=1 kOe in a Quantum Design magnetic properties measurement system (MPMS-5) superconducting quantum interference device (SQUID) RSO dc magnetometer. The specific heat $C(T)$ was obtained in a small-mass calorimeter system, Quantum Design PPMS-9 platform, which uses a quasiadiabatic thermal relaxation technique. The properties of our single crystals used in this work are very similar to those reported in Refs. 18 and 24. All ESR experiments were performed on a fine powder ($d \lesssim 38$ μm) for samples with Gd concentration ranging from 0.2% to 0.5% in a Bruker ELEXSYS X-band spectrometer (9.4 GHz) with a TE_{102} cavity coupled to a helium-gas-flux T-controller system for $4.2 \lesssim T \lesssim 300$ K. Powdered crystals were used in order to increase the ESR signal-to-noise ratio.

III. EXPERIMENTAL RESULTS

Figure 1 shows the magnetic susceptibility data for the $Yb_{1-x}Gd_xAl_3$ and $Lu_{1-x}Gd_xAl_3$ crystals used in the ESR experiments. The data for $YbAl_3$ are also included in this figure. The susceptibility data were corrected for the core diamagnetism of the compounds. Using the effective magnetic moments $\mu_{eff}=7.94\mu_B$ for Gd^{3+}, the Gd concentrations were estimated and their values are given in Table I. As previously reported,[18] two main features can be observed in the data for $YbAl_3$: a broad maximum at 127 K consistent with a Kondo temperature of $T_K \sim 500$ K and another low-T maximum at ~ 15 K consistent with a second energy scale of the order of $T_{coh} \sim 40$ K (see inset of Fig. 1) which was suggested to be associated with lattice coherence.[18,24] For the sample of $Yb_{0.997}Gd_{0.003}Al_3$ the broad maximum is now centered at ~ 114 K, a temperature slightly lower than that for $YbAl_3$, in contrast with the Lu substitution[24] which yields a shift of the broad maximum to higher T. The low-T maximum at ~ 15 K is either absent or prevented from being observed by the Gd^{3+} paramagnetic Curie tail.

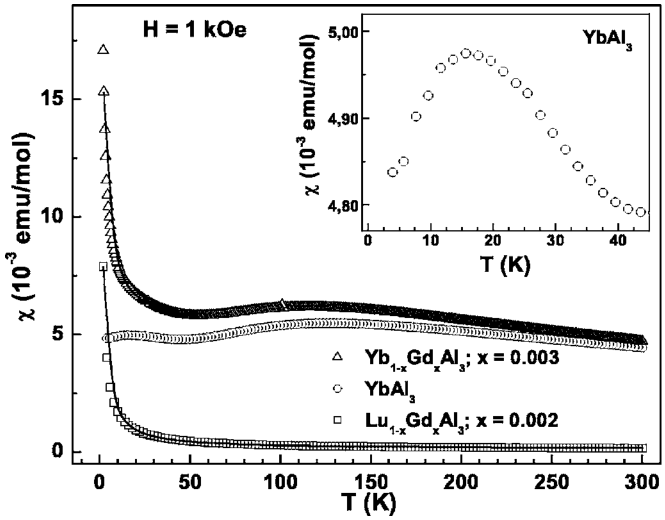

FIG. 1. Temperature dependence of the measured magnetic susceptibility $\chi(T)$ at H=1 kOe, for Gd^{3+} in $(Yb,Lu)_{1-x}Gd_xAl_3$. The solid lines are the Curie-Weiss fitting.

Figure 2 shows the specific heat for the $YbAl_3$ and $LuAl_3$ compounds in the temperature range of $2 \lesssim T \lesssim 300$ K. The magnetic contribution to the heat capacity of $YbAl_3$ divided by T, C_m/T, obtained by subtracting the contribution of the nonmagnetic $LuAl_3$, is presented in the inset on the right side of Fig. 2. The electronic specific heat coefficients for both compounds are obtained from the fitting of the corresponding data to $C/T=\gamma+\beta T^2$—i.e., taking into consideration the electronic and lattice contributions. Linear T^2 fitting of the data below 5 K (see inset on the left side of Fig. 2) yields values for γ and β given in Table I. These values are in good agreement with the values found in the literature.[18,24] Notice that the phonon contribution (β) to the specific heat is identical in both compounds.

Figure 3 shows the ESR X-band powder spectra of Gd^{3+} in $Yb_{0.997}Gd_{0.003}Al_3$ and $Lu_{0.998}Gd_{0.002}Al_3$ at T=4.2 K. The ESR spectrum consists of a single Dysonian resonance with $A/B \approx 2.2(2)$. This line shape is characteristic of localized magnetic moments in a metallic host with a skin depth smaller than the size of the used particles. The g values and linewidths were obtained from the fitting of the resonances to the appropriate admixture of absorption and dispersion Lorentzian derivatives.[31] The solid lines are the best fit to the observed resonances and the obtained g values are presented in Table I. Within the accuracy of the measurements, the g values were T and Gd concentration independent (not shown).

Figure 4 presents the T dependence of the ESR linewidth for Gd^{3+} in $Yb_{0.997}Gd_{0.003}Al_3$ and $Lu_{0.998}Gd_{0.002}Al_3$. For both samples the width increases linearly with T. The linear dependence of the line width was fitted to the expression $\Delta H = a+bT$. The values for a and b are presented in Table I. Within the accuracy of the measurements, the b parameters were independent of the Gd concentration (not shown).

The absence of any feature in the ESR data (linewidth and g value) indicated that the effects responsible for the susceptibility anomaly at T, 15 K (see Fig. 1), believed to be due to a lattice coherence,[18,24] either are absent for the Gd-doped

TABLE I. Experimental parameters for Gd^{3+} diluted in $YbAl_3$ and $LuAl_3$.

Gd^{3+} in	g	Δg	a [Oe]	b [Oe/K]	x	γ [mJ/(mol K^2)]	β [mJ/(mol K^4)]
$YbAl_3$	1.989(2)	−0.004(3)	17(2)	14.0(5)	0.003	45(1)	0.11(1)
$LuAl_3$	1.996(1)	+0.003(2)	26(3)	9.0(5)	0.002	3.7(1)	0.11(1)

samples or they do not renormalize the interaction between the localized Gd^{3+} $4f$- and conduction-electron spins.

IV. ANALYSIS AND DISCUSSION

The exchange interaction $J_{fs}S\text{-}s$ between a localized $4f$-electron spin (S) on the solute atom of Gd^{3+} and the conduction electron (ce) spin (s) of the host metal yields an ESR g shift (Knight shift) (Ref. 32) and a thermal broadening of the linewidth (Korringa rate) (Ref. 33), given, respectively, by

$$\Delta g = J_{fs}\eta_F \tag{1}$$

and

$$b = \frac{d(\Delta H)}{dT} = \frac{\pi k_B}{g\mu_B} J_{fs}^2 \eta_F^2, \tag{2}$$

where J_{fs} is the effective exchange parameter in the absence of ce momentum transfer, $q=|\mathbf{k}_{out}-\mathbf{k}_{in}|$, i.e., $\langle J_{fs}(q)\rangle_F = J_{fs}$,[34] η_F is the "bare" density of states for one spin direction at the Fermi surface, k_B is the Boltzmann constant, μ_B is the Bohr magneton, and g is the Gd^{3+} g value.

Equations (1) and (2) are normally used in the analysis of the ESR data for highly diluted rare-earth magnetic moments in intermetallic compounds with appreciable residual resistivity—i.e., large ce spin-flip scattering (absence of "bottleneck" and "dynamic" effects).[35] In our case the ESR parameters were found to be independent of the concentration. Thus, we can assume that these systems are in the unbottleneck regime.[35] Combining the above equations we can write

$$b = \frac{d(\Delta H)}{dT} = \frac{\pi k_B}{g\mu_B}(\Delta g)^2. \tag{3}$$

Using the g value of Gd^{3+} in insulators as 1.993(1) (Ref. 36) and the measured g values (see Table I) we have estimated the g shifts $\Delta g^{Yb} \simeq -4(3)\times 10^{-3}$ and $\Delta g^{Lu} \simeq 3(2)\times 10^{-3}$ for the Gd^{3+} resonance in $YbAl_3$ and $LuAl_3$, respectively. For these g shifts and $\pi k_B/g\mu_B = 2.34\times 10^4$ Oe/K, Eq. (3) predicts a thermal broadening much smaller ($b \lesssim 0.4$ Oe/K) than those measured for $YbAl_3$ and $LuAl_3$, see Table I). Therefore, we conclude that the approximations made in Eqs. (1) and (2) are not adequate for either compound. Besides, in spite of their large error bars, the sign of the g shifts are opposite in both compounds. It is in general accepted that in these cases the q dependence of the exchange interaction may be ignored and one can assume that $\langle J_{fs}(q)\rangle_F = J_{fs}$.[27,34] However, the contribution from different ce bands and ce correlations must be taken into consideration in the analysis of the ESR data.[37–39] This is because the contribution to the total g shift, coming from the exchange interaction with ce in different bands, may have opposite signs. For instance, it is positive for s- or d-ce at the Gd site (atomic-type) and negative for p- and f-ce at the Al and Yb

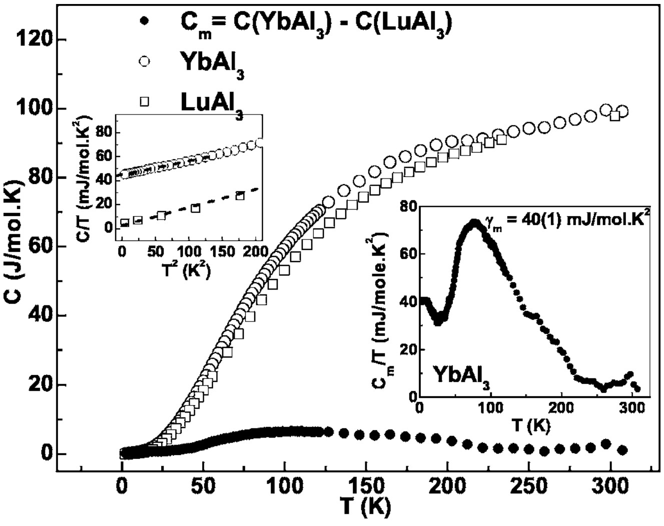

FIG. 2. Specific heat C as a function of T for (Yb,Lu)Al_3. The inset on the right side shows the magnetic contribution to the heat capacity of $YbAl_3$, C_m/T. The inset on the left side presents the low-T C/T data for both compounds.

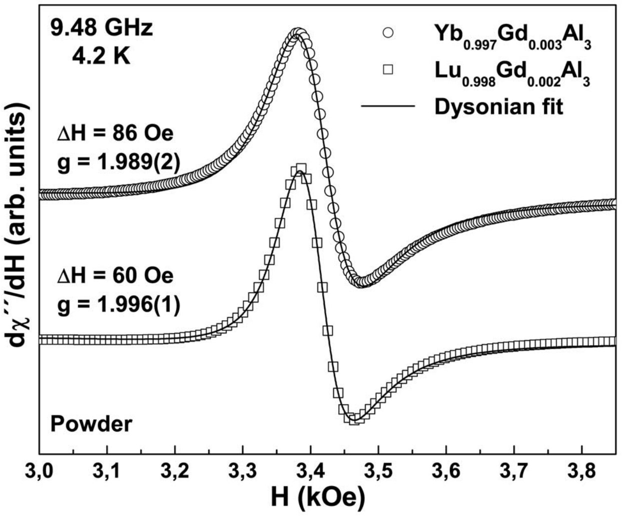

FIG. 3. X-band ESR powder spectra of Gd^{3+} in $Yb_{0.997}Gd_{0.003}Al_3$ and $Lu_{0.998}Gd_{0.002}Al_3$ at T=4.2 K. The solid lines are best fit to a Dysonian line shape.

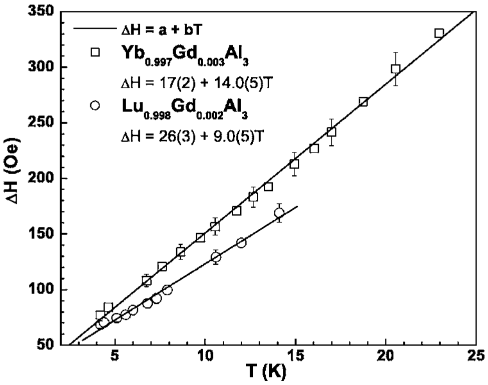

FIG. 4. Temperature dependence of the ESR linewidth for ~0.2% of Gd^{3+} in $YbAl_3$ and $LuAl_3$. The solid lines are the best fit to $\Delta H = a + bT$. Values of the parameters a and b are given in Table I.

sites (covalent type), whereas their contribution to the thermal broadening of the linewidth (Korringa rate) is always positive. From the low-T $C/T = \gamma + \beta T^2$ data of Fig. 2 we have extracted the electronic contribution to the specific heat for $YbAl_3$ and $LuAl_3$ (see Table I). In a free *ce* gas model, the Sommerfeld coefficient is given by $\gamma = (2/3)\pi^2 k_B^2 \eta_F$. Hence, we estimate a total density of states at the Fermi level of $\eta_F = 9.5(2)$ states/(eV mol spin) and $\eta_F \simeq 0.79(2)$ states/(eV mol spin) for $YbAl_3$ and $LuAl_3$, respectively (see Table II). We should mention that the density of states at the Fermi level obtained from a recent band structure calculation by Lee *et al.*[29] gives smaller values than those extracted from our specific heat measurements, mainly for the Yb-based compound. Using our values for the density of states and the free *ce* spin susceptibility, $\chi_0 = 2\mu_B^2 \eta_F$, we estimate $\chi_0 \simeq 6.2(2) \times 10^{-4}$ emu/mol and $\chi_0 \simeq 0.50(2) \times 10^{-4}$ emu/mol for the Yb- and Lu-based compounds, respectively. These values are much smaller than their respective high-T susceptibility of $\simeq 44 \times 10^{-4}$ emu/mol and $\simeq 1.5 \times 10^{-4}$ emu/mol (already corrected by the compound core diamagnetism; see Fig. 1). These results suggest that the *ce* spin susceptibility is enhanced by an electron-electron exchange interaction in both compounds and the Stoner factor due to *ce* correlations must be taken into consideration in the analysis of our ESR results.

Analysis of Gd^{3+} in $LuAl_3$: In the absence of q dependence of the exchange interactions $[\langle J_{f,dp}(q)\rangle_F = J_{f,dp}]$, but in the presence of (i) electron-electron exchange enhancement of the *ce* spin susceptibility and (ii) contributions from two *ce* bands [Lu (Gd) d-like and Al p-like] Eqs. (1) and (2) became

$$\Delta g^{Lu} = \Delta g_{fd} + \Delta g_{fp} = \left[\frac{J_{fd}\eta_{Fd}}{(1-\alpha_d)} - \frac{J_{fp}\eta_{Fp}}{(1-\alpha_p)} \right] \tag{4}$$

and

$$b^{Lu} = \frac{\pi k_B}{g\mu_B}\left[F_d \Delta g_{fd}^2 K(\alpha_d) + F_p \Delta g_{fp}^2 K(\alpha_p)\right] \tag{5}$$

$$= \frac{\pi k_B}{g\mu_B}\left[F_d \frac{J_{fd}^2 \eta_{Fd}^2}{(1-\alpha_d)^2} K(\alpha_d) + F_p \frac{J_{fp}^2 \eta_{Fp}^2}{(1-\alpha_p)^2} K(\alpha_p) \right], \tag{6}$$

where J_{fd} is the exchange parameter (atomic type) between the Gd^{3+} localized $4f$-electron spin and $5d$-conduction-electron spin at the Gd^{3+} site, J_{fp} the exchange parameter (covalent type) between the Gd^{3+} localized $4f$-electron spin and $3p$-conduction-electron spin at the Al site, η_{Fd} and η_{Fp} the density of states at the Fermi level for $5d$ and $3p$ conduction electrons, respectively, $K(\alpha_d)$ and $K(\alpha_p)$ the reduction factors of the Korringa relaxation for core polarization, and $F_d = 1/5$ and $F_p = 1/3$ factors associated with the orbital degeneracy of the unsplit (no crystal-field effects) $5d$ and $3p$ bands at the Fermi level, respectively.[40,41]

It is known that in the presence of such *ce* correlations the spin susceptibility of the host metal, χ_e, can be approximated by[37,38]

$$\chi_e = \frac{2\mu_B^2 \eta_{Fd}}{(1-\alpha_d)} + \frac{2\mu_B^2 \eta_{Fp}}{(1-\alpha_p)}, \tag{7}$$

where $\alpha_{d,p}$ accounts for the electron-electron exchange enhancement and $(1-\alpha_{d,p})^{-1}$ for the corresponding Stoner factors. According to a recent band structure calculation by Lee *et al.*,[29] the occupied Yb s, Lu s, and Al s states are small for $YbAl_3$ and $LuAl_3$ and, therefore, will not be considered in our analysis. Furthermore, in each compound these authors showed that the partial densities of d and p states at the Fermi level are about the same, and also, they are similar in both compounds.[29] Thus, we will consider $\eta_{Fd} \simeq \eta_{Fp}$ in both compounds. We shall also assume that the Stoner factors for the d and p electrons are about the same in both compounds. Hence, an upper limit for $\alpha_d \simeq \alpha_p = \alpha_{d,p}$ may be estimated assuming that the T-independent (high-T) part of the susceptibility, 1.5×10^{-4} emu/mol of Fig. 1 (already corrected by the $LuAl_3$ core diamagnetism $\chi_{dia} = -0.87 \times 10^{-4}$ emu/mol), corresponds to the enhanced *ce* spin susceptibility of the compound, χ_e. Then, for $LuAl_3$, taking $\eta_{Fd} \simeq \eta_{Fp} = \eta_{Fd,p}$

TABLE II. Derived parameters for Gd^{3+} diluted in $YbAl_3$ and $LuAl_3$.

Gd^{3+} in	$\eta(E_F)$ [state/(eV mol spin)]	α α_f $\alpha_{d,p}$	$K(\alpha)$ $K(\alpha_f)$ $K(\alpha_{d,p})$	J_{fd} [meV]	J_{fp} [meV]	J_{ff} [meV]
$YbAl_3$	9.5(2)	0.87(1)	0.14(2)	37(3)	34(2)	1.6(2)
$LuAl_3$	0.79(2)	0.67(1)	0.40(2)	37(3)	34(2)	

$\simeq \eta_F/2 \simeq 0.395$ states/(eV mol spin) in Eq. (7), we estimate $\alpha_{d,p} \simeq 0.67(1)$ and, from Refs. 38 and 42, the corresponding value for $K(\alpha_{d,p}) \simeq 0.40(2)$ (see Table II).

Taking into account the above considerations, we can now extract the exchange parameters for Gd^{3+} in the reference compound of LuAl_3. In terms of the exchange parameters J_{fd} and J_{fp}, Eqs. (4) and (6) for the g shift and Korringa relation may be rewritten as

$$\Delta g^{Lu} \frac{(1-\alpha_{d,p})}{\eta_{Fd,p}} = [J_{fd} - J_{fp}] \tag{8}$$

and

$$b^{Lu} \frac{g\mu_B}{\pi k_B} \frac{(1-\alpha_{d,p})^2}{\eta_{Fd,p}^2 K(\alpha_{d,p})} = \left[\left(\frac{1}{5}\right) J_{fd}^2 + \left(\frac{1}{3}\right) J_{fp}^2\right]. \tag{9}$$

Solving these equations for J_{fd} and J_{fp} and using the known parameters on the left-hand side of these equations we find, within the accuracy of our experiments, $J_{fd} \simeq 37(3)$ meV and $J_{fp} \simeq 34(2)$ meV (see Table II). Note that the negative contribution to the total g shift from the covalent fp-exchange interaction was already taken into account in Eqs. (4) and (8) and that the slightly larger value of J_{fd}, as compared with that of J_{fp}, allows for the small positive value measured for Δg^{Lu}.

Analysis of Gd^{3+} in YbAl_3: It is evident from the low-T C/T specific heat data of Fig. 2 and the band structure calculation by Lee *et al.*[29] that in the Yb-based compound there is a large extra contribution to the density of states at the Fermi level coming from the existence of f-like electrons. We may estimate this contribution taking the difference between the density of states at the Fermi level of the Yb- and Lu-based compounds, obtained from the Sommerfeld coefficients of the specific heat data. We found $\eta_{Ff} = 8.71$ states/(eV mole spin). In the presence of *ce* correlations the f-electron spin susceptibility χ_f can be approximated by[39,38]

$$\chi_f = \frac{2\mu_B^2 \eta_{Ff}}{(1-\alpha_f)}, \tag{10}$$

where α_f accounts for the f-electron-electron exchange enhancement and $(1-\alpha_f)^{-1}$ for the corresponding Stoner factor. The f-electron spin susceptibility $\chi_f = 42.5 \times 10^{-4}$ emu/mol can be obtained from the difference between the T-independent (high-T) part of the susceptibility, 44.0×10^{-4} emu/mol of Fig. 1 (already corrected by the YbAl_3 core diamagnetism $\chi_{dia} = -0.86 \times 10^{-4}$ emu/mol) and the corresponding value for LuAl_3 of 1.5×10^{-4} emu/mol (see above). Using $\eta_{Ff} = 8.71$ states/(eV mol spin) and $\chi_f = 42.5 \times 10^{-4}$ emu/mol in Eq. (10), we estimate $\alpha_f \simeq 0.87(1)$ and from Refs. 38 and 42 the corresponding value for $K(\alpha_f) \simeq 0.14(2)$ (see Table II). It is interesting to note that, as expected, the estimated value for the electron-electron correlation of the f-like electrons, $\alpha_f \simeq 0.87(1)$, is found to be larger than that of the d- and p-like electrons, $\alpha_{d,p} \simeq 0.67$.

In the absence of q dependence of the exchange interactions ($\langle J_{f,dp}(q)\rangle_F = J_{f,dp}$), but in the presence of (i) electron-electron exchange enhancement of the *ce* spin susceptibility and (ii) contributions from three *ce* bands [Lu (Gd) $5d$-like, Al $3p$-like, and Yb $4f$-like], Eqs. (1) and (2) become

$$\Delta g^{Yb} = \Delta g_{fd} + \Delta g_{fp} + \Delta g_{ff} = \left[\frac{J_{fd}\eta_{Fd}}{(1-\alpha_d)} - \frac{J_{fp}\eta_{Fp}}{(1-\alpha_p)} - \frac{J_{ff}\eta_{Ff}}{(1-\alpha_f)}\right] \tag{11}$$

and

$$b^{Yb} = \frac{\pi k_B}{g\mu_B}[F_d \Delta g_{fd}^2 K(\alpha_d) + F_p \Delta g_{fp}^2 K(\alpha_p) + F_f \Delta g_{ff}^2 K(\alpha_f)] \tag{12}$$

$$= \frac{\pi k_B}{g\mu_B}\left[F_d \frac{J_{fd}^2 \eta_{Fd}^2}{(1-\alpha_d)^2} K(\alpha_d) + F_p \frac{J_{fp}^2 \eta_{Fp}^2}{(1-\alpha_p)^2} K(\alpha_p) + F_f \frac{J_{ff}^2 \eta_{Fp}^2}{(1-\alpha_f)^2} K(\alpha_f)\right], \tag{13}$$

where the symbols are identical to those used in Eqs. (4) and (6) and have the same meaning as those for LuAl_3. J_{ff} is the exchange interaction (covalent type) between the Gd^{3+}-localized $4f$-electron spin and f-conduction-electron spin at the Yb site, η_{Ff} is the density of states at the Fermi level for the f conduction electrons, $K(\alpha_f)$ is the reduction factor of the Korringa relaxation for core polarization, and $F_f = 1/7$ is associated with the orbital degeneracy of the unsplit (no crystal-field effects) f band at the Fermi level.[40,41]

Assuming that the contribution of d and p conduction electrons to the g shift and Korringa rate in YbAl_3 and in its reference compound of LuAl_3 are the same, Eqs. (11) and (13) may be reduced to

$$\Delta g^{Yb} = \Delta g^{Lu} - \frac{J_{ff}\eta_{Ff}}{(1-\alpha_f)} \tag{14}$$

and

$$b^{Yb} = b^{Lu} + \frac{\pi k_B}{g\mu_B}\left[F_f \frac{J_{ff}^2 \eta_{Ff}^2}{(1-\alpha_f)^2} K(\alpha_f)\right]. \tag{15}$$

Using the experimental data for the g shifts and thermal broadening of the linewidths, b, for both compounds (see Table I) and the values for η_{Ff}, α_f, $K(\alpha_f)$, and F_f given above, we extract the exchange parameter (covalent type) between the Gd^{3+} localized $4f$-electron spin and f-conduction-electron spin at the Yb site, $J_{ff} \simeq 0.1$ meV and $J_{ff} \simeq 1.6(2)$ meV from Eqs. (14) and (15), respectively. Due to the higher data accuracy for the thermal broadening of the linewidth, we feel more confident with the value of $J_{ff} \simeq 1.6(2)$ meV for the exchange parameter (see Table II). Note that the negative contribution to the total g shift from the covalent ff-exchange interaction was already taken into account in Eqs. (11) and (14) and that despite the small value for J_{ff}, as compared with those of J_{fd} and J_{fp} (see above), the large value of η_{Ff} allows for the small negative value measured for Δg^{Yb}.

V. CONCLUSIONS

The ESR experimental results of Gd^{3+} in YbAl$_3$ and LuAl$_3$ were analyzed within a framework of a multiband model of f, d, and p bands including electron-electron exchange correlations. The f band was associated with the 4f electrons at the Yb site, the d band with the Lu 5d electrons at the Gd site, and the p band with the 3p electrons at the Al site. The large density of states at the Fermi level in the YbAl$_3$ compound due to the Yb 4f electrons, among other physical properties,[18,24] characterizes it as an IV system. However, the Gd^{3+} ESR results yield a Korringa rate comparable with the corresponding value of the reference compound LuAl$_3$, indicating that the Yb 4f electrons do not play an important role in the relaxation process of the Gd^{3+} impurities. This is, presumably, in consequence that the ESR probes, at the Gd^{3+} site, the local density of states at the Fermi level via the exchange parameter J_{ff}, which we found to be very small in this compound due to the small overlap between the highly localized 4f electrons of the Gd^{3+} with the 4f *ce* of Yb that remains partly localized at the Yb site.[43–46] Nevertheless, despite the small value found for J_{ff} it is large enough to produce a g shift opposite to that found in LuAl$_3$. Our analysis allowed us to estimate the values for the exchange parameters involved in the mechanism of the exchange interaction between the Gd^{3+}-localized 4f-electron spin and the *ce* spin in the various bands. Nonetheless, these values have to be taken with care in view of the various assumptions and approximations made.

In both systems the bottleneck and dynamic effects were not observed.[35] This is consistent with the multiband scenario used for the analysis of our ESR data, since fast spin-lattice relaxation rates due to the spin-orbit coupling are expected via the mechanism of exchange interaction between the Gd^{3+}-localized 4f-electron spin with the host f, d, and p *ce* spin.[39,47] The exchange interaction between the Gd^{3+}-localized 4f-electron spin and the *ce* spin was found to be wave vector independent ($\langle J_{f,dp}(q)\rangle_F = J_{f,dp}$) for both compounds.[34]

The multiple-band scenario of YbAl$_3$ and reported values of the exchange interaction between the 4f electrons and the different conduction-electron bands may be relevant to construct more realistic models of the microscopic behavior of the 4f electrons in YbAl$_3$ or related IV systems.

ACKNOWLEDGMENTS

This work was supported by FAPESP (SP-Brazil) Grants Nos. 04/08798-2, 03/09861-7, and 00/08649-6 and CNPq (Brazil) Grants Nos. 307668/03, 04/08798-2, and 304466/20003-4. Work at LANL was performed under the auspices of the U.S. DOE.

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