ESR of Gd^{3+} in the Kondo-lattice compound $YbAgCu_4$ and its reference compounds $RAgCu_4$ (R=Y,Lu)

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Low-temperature ($T<30$ K) electron-spin-resonance (ESR) experiments of Gd^{3+} diluted in the Kondo-lattice compound $YbAgCu_4$ and its reference compounds $YAgCu_4$ and $LuAgCu_4$ are interpreted in terms of an enhanced density of states at the Fermi level for the Yb-based compound. The results of susceptibility and ESR (Korringa rate and g-shift) measurements show negligible electron-electron exchange enhancement for all the studied compounds. The exchange interaction between the Gd^{3+} local moment and the conduction electrons (c-e) is c-e wave vector dependent in all three compounds. [S0163-1829(97)01038-2]

I. INTRODUCTION

Hybridization between localized f-electron and conduction-electron (c-e) states have motivated experimentalists and theoreticians to study the phenomena involving strong electronic correlations.[1] The Ce- and Yb-based compounds are well suited for these studies. The $4f$ shell of Ce and Yb may contribute with an electron and a hole, respectively, to the conduction band, simplifying the theoretical analysis. The $YbAgCu_4$ compound of cubic $AuBe_5$ ($C15b, F43m$)-type structure,[2] is particularly appropriate because it has the following Kondo-type properties: (i) a relatively large linear coefficient of specific heat, $\gamma \approx 240$ mJ/mol K^2,[3,4] (ii) a temperature-dependent electrical resistivity characteristic of a Kondo-lattice system,[5] and (iii) a temperature-dependent magnetic susceptibility with a maximum at ≈ 35 K,[3] that can be described by the Bethe-ansatz solution of the Coqblin-Schrieffer Hamiltonian.[3,6,7] The relatively weak interaction between the Yb magnetic moments[3] makes electron-spin resonance (ESR) of diluted Gd^{3+} in $YbAgCu_4$ suitable to study the electronic properties of this compound. For comparison, the ESR of Gd^{3+} in the reference compounds of $YAgCu_4$ and $LuAgCu_4$ were measured. Complimentary susceptibility and specific-heat experiments were also performed.

In a recent paper we have studied the ESR of Gd^{3+} in the intermediate valence phase ($T \leqslant T_v \approx 50$ K) of $YbInCu_4$ and its reference compound $YInCu_4$.[8] Those results were interpreted in terms of an enhanced density of states at the Fermi level for the Yb-based compound. The aim of this work is to

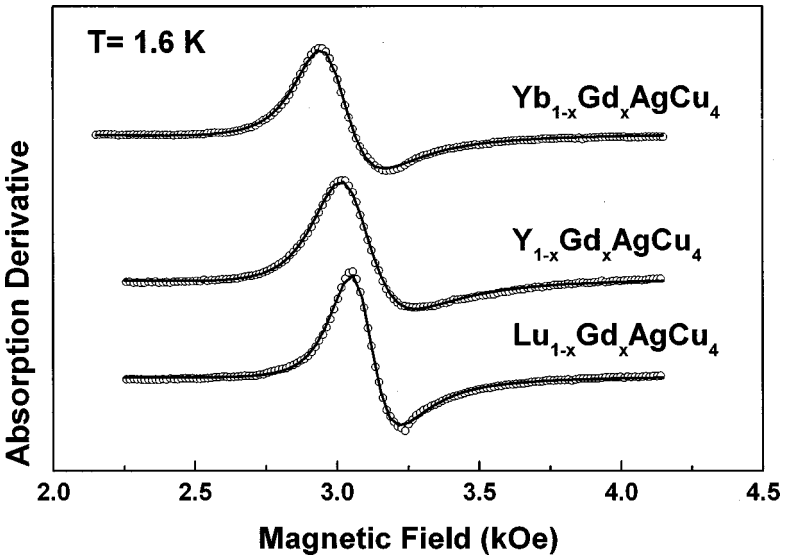

FIG. 1. Low temperature, $T=1.6$ K, ESR powder spectra for (a) 0.9(2)% of Gd^{3+} in $YbAgCu_4$, (b) 0.22(2)% of Gd^{3+} in $YAgCu_4$, and (c) 0.16(2)% of Gd^{3+} in $LuAgCu_4$. The solid lines are the best fit of the resonance to a Dyson line shape.

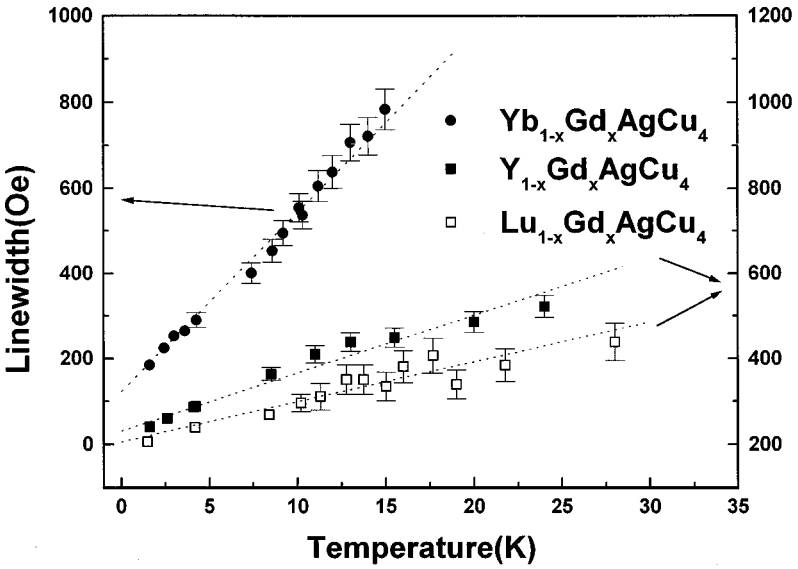

FIG. 2. Temperature dependence of the ESR linewidth for 0.9(2)% of Gd^{3+} in $YbAgCu_4$, 0.22(2)% of Gd^{3+} in $YAgCu_4$, and 0.16(2)% of Gd^{3+} in $LuAgCu_4$. The dashed lines are the best fit to $\Delta H = a + bT$. a and b are given in Table I.

study, also via ESR of Gd^{3+} impurities, the electronic properties of the Kondo-lattice compound $YbAgCu_4$ and compare it with the intermediate valence compound $YbInCu_4$.

II. EXPERIMENT

Single crystals of $R_{1-x}Gd_xAgCu_4$ (R=Yb,Y,Lu; $0.0008 \leqslant x \leqslant 0.009$ nominal) were grown from a flux of excess AgCu by the method described elsewhere.[9] The crystals were of cubiclike shape with typical sizes of $4\times3\times1$ mm^3. The room-temperature lattice parameters were measured in x-ray powder-diffraction experiments. The ESR experiments have been carried out in a Varian E-line X-band spectrometer, using a liquid-helium tail dewar (1.6–4.15 K) and a helium gas flux (7–30 K) adapted to a room-temperature TE_{102} cavity. For the high-temperature ESR measurements, powdered crystals were used in order to increase the ESR signal-to-noise ratio. The susceptibility measurements have been taken in a Quantum Design dc superconducting quantum interference device magnetometer. Specific-heat measurements were performed in a small-mass calorimeter system that employs a quasiadiabatic thermal relaxation technique.[10] Undoped samples have been used for these measurements and the masses ranged from 45 to 145 mg.

III. EXPERIMENTAL RESULTS

Figure 1 shows the ESR powder spectra of Gd^{3+} diluted in $YbAgCu_4$, $YAgCu_4$, and $LuAgCu_4$ measured at $T = 1.6$ K. Typical Dysonian line shapes[11] with $A/B \approx 2.2(2)$ were observed. These line shapes are characteristic of localized magnetic moments in a metallic host with a skin depth smaller than the size of the sample particles. The g value and linewidth were obtained from the fitting of the resonances to the appropriate admixture of absorption and dispersion.[12] The solid lines, in Fig. 1, are the best fit to the observed resonances.

Figure 2 gives the temperature dependence of the linewidth for the three compounds. The linear dependence of the linewidth was fitted to the expression $\Delta H = a + bT$. Within the accuracy of the measurements, the g values have been found to be temperature independent. The a, b, and g parameters were, within our experimental error and used concentrations, independent of the Gd concentration. Their values are shown in Table I. In single crystals the Gd^{3+} resonance did not show crystal-field features, i.e., fine structure and/or anisotropic linewidth.

Figure 3 shows the magnetic susceptibility, corrected for the compound core diamagnetism, for some of the samples used in our ESR experiments. From the low-temperature tails ($T < 20$ K) the Gd concentrations were estimated and their values are given in Table I. For $T > 20$ K, the temperature dependence of the susceptibility of the $Yb_{1-x}Gd_xAgCu_4$ samples presents similar features to that found in undoped $YbAgCu_4$.[3]

Figure 4 shows the specific heat for the $RAgCu_4$ (R=Yb,Y,Lu) crystals in the temperature range of $2\text{ K} < T < 20$ K. The low-temperature C/T data increase linearly with T^2 as seen in the inset of Fig. 4. The fitting parameters, γ and β, obtained from these data are given in Table I. Notice that our values for γ and β in $YbAgCu_4$ are significantly different from those found by others.[3,4] This probably has to do with the high purity of our crystals.[9] The density of states,

TABLE I. Experimental parameters for Gd:$RAgCu_4$ (R=Yb,Y,Lu).

	a Å	g	a Oe	b Oe/K	c %	γ mJ/mol K^2	β mJ/mol K^4
Yb(Gd)$AgCu_4$	7.08(1)	2.17(1)	123(15)	42(3)	0.17(2)	207(6)	0.63(6)
Y(Gd)$AgCu_4$	7.20(1)	2.10(1)	227(9)	15(1)	0.22(2)	11.4(2)	0.46(2)
Lu(Gd)$AgCu_4$	7.10(1)	2.09(1)	180(12)	11(1)	0.16(2)	10.0(2)	0.68(2)

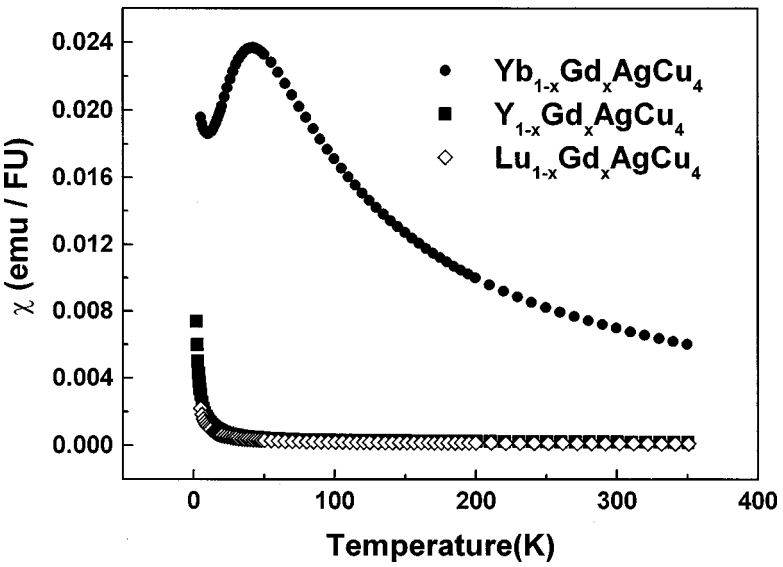

FIG. 3. Temperature dependence of the magnetic susceptibility, measured at 5 kOe, for 0.17% of Gd^{3+} in $YbAgCu_4$, 0.22% of Gd^{3+} in $YAgCu_4$, and 0.16% of Gd^{3+} in $LuAgCu_4$.

$\eta(E_F)$, and the Debye temperatures, θ_D, extracted from these parameters are given in Table II.

Table I summarizes the experimental parameters obtained in this work for the $R\mathrm{AgCu}_4$ (R=Yb,Y,Lu) compounds.

IV. ANALYSIS AND DISCUSSION

The exchange interaction, $J_{\mathrm{fs}}\mathbf{S}\cdot\mathbf{s}$, between a localized $4f$ electron spin ($\mathbf{S}$) on a solute atom (Gd^{3+}) and the free c-e's spin ($\mathbf{s}$) of the host metal, results in a g shift (Knight shift)[13] and in a thermal line broadening (Korringa relaxation)[14] of the ESR spectra. Conduction electron-electron exchange enhancement[15,16] and $\mathbf{q}$-dependent exchange interaction, $J_{\mathrm{fs}}(\mathbf{q})$,[17] are often used in the analysis of the ESR data.[8] $J_{\mathrm{fs}}(\mathbf{q})$ is the Fourier transform of the spatially varying exchange coupling. In this case, and when ''bottleneck'' and ''dynamic'' effects are not present, the g shift (Δg) and Korringa rate (b) can be written as[18]

$$\Delta g = J_{\mathrm{fs}}(\mathbf{0})\,\frac{\eta(E_F)}{1-\alpha}, \tag{1}$$

and

$$b = \frac{d(\Delta H)}{dT} = \frac{\pi k}{g\mu_B}\,\langle J_{\mathrm{fs}}^2(\mathbf{q})\rangle\,\eta^2(E_F)\,\frac{K(\alpha)}{(1-\alpha)^2}, \tag{2}$$

where $J_{\mathrm{fs}}(\mathbf{0})$ and $\langle J_{\mathrm{fs}}^2(\mathbf{q})\rangle$ are the effective exchange parameters between the Gd^{3+} local moment and the c-e in the presence of c-e momentum transfer.[17] Under this assumption the Gd^{3+} g shift probes the c-e polarization ($\mathbf{q}=0$) and the Korringa rate the c-e momentum transfer ($0\leqslant\mathbf{q}\leqslant 2k_F$) averaged over the Fermi surface.[17] $(1-\alpha)^{-1}$ and $K(\alpha)$ are the Stoner and the Korringa enhancement factors, respectively, due to the electron-electron (e-e) exchange interaction.[8,19,20] $\eta(E_F)$ is the ''bare'' density of states for one spin direction at the Fermi level, k is the Boltzmann constant, μ_B is the Bohr magneton, and g is the Gd^{3+} g value.

Equations (1) and (2) are appropriated for the analysis of ESR data of highly diluted rare earths in metallic hosts with appreciable c-e spin-flip scattering, i.e., *unbottleneck* regime. We found in this work that the ESR parameters do not de-

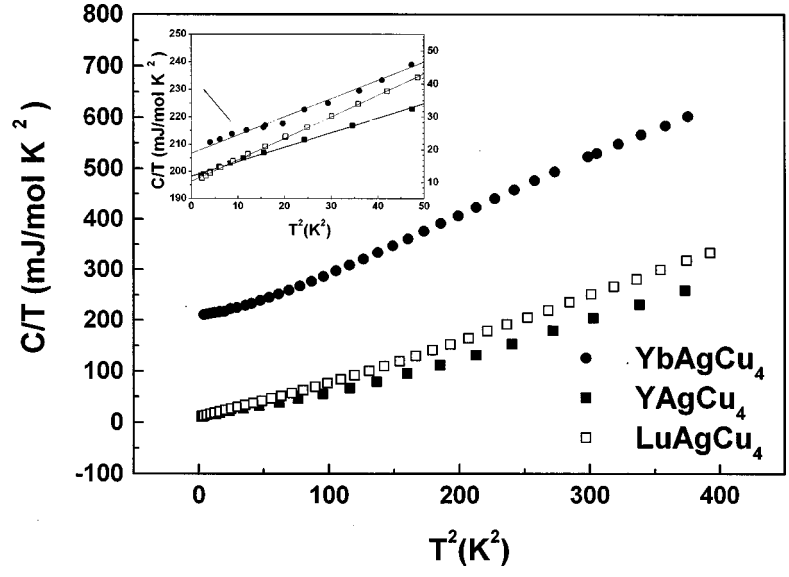

FIG. 4. Specific heat (C/T) as a function of T^2 for $R\mathrm{AgCu}_4$ (R=Yb,Y,Lu) compounds. The inset shows the low-temperature T^2 dependence of C/T. The solid line is the best fit to $C/T=\gamma+\beta T^2$. γ and β are given in Table I.

TABLE II. Extracted parameters for Gd:RAgCu$_4$ (R=Yb,Y,Lu).

	$\eta(E_F)$ states/eV mol spin	θ_D K	$J_{fs}(\mathbf{0})$ meV	$\langle J_{fs}^2(\mathbf{q})\rangle^{1/2}$ meV	$K(\alpha)$	α
Yb(Gd)AgCu$_4$	44(2)	≈264	4.0(3)	0.9(2)	0.9(4)	0.1(4)
Y(Gd)AgCu$_4$	2.42(4)	≈294	44(5)	11(1)	≈1	≈0
Lu(Gd)AgCu$_4$	2.12(4)	≈257	45(5)	10(1)	≈1	≈0

pend on the Gd^{3+} concentration. Hence, it is expected that the following relation would hold:[8,18]

$$b=\frac{d(\Delta H)}{dT}=\frac{\pi k}{g\mu_B}\frac{\langle J_{fs}^2(\mathbf{q})\rangle}{J_{fs}^2(\mathbf{0})}(\Delta g)^2K(\alpha). \tag{3}$$

In our analysis the contribution from different c-e bands can be neglected, because the measured thermal broadening of the linewidths is much smaller than that expected from the measured g shifts.[21,22]

The electronic contribution to the heat capacity of these compounds yields to the γ values shown in Table I. In a free c-e gas model $\gamma=(2/3)\pi^2k^2\eta(E_F)$. Thus, the density of states at the Fermi level, $\eta(E_F)$ can be estimated for the Y- and Lu-based samples (see Table II). From the density of states, the electronic spin susceptibility, $\chi_e=2\mu_B^2\eta(E_F)$, can be evaluated. The values calculated are 0.15×10^{-3} and 0.13×10^{-3} emu/FU for the Y- and Lu-based, respectively. These results are in good agreement with their susceptibility measured at high temperatures (Pauli susceptibility), once corrected for the core diamagnetism (see Fig. 3). Hence, one can assume that e-e exchange enhancement is not important in these compounds, i.e., $\alpha\approx0$ and $K(\alpha)\approx1$.[19,20]

The exchange parameters between the Gd^{3+} local moment and the c-e in RAgCu$_4$ (R=Y,Lu) were estimated using Eq. (3), where we used the g value of Gd^{3+} in insulators as a reference, 1.993(2),[23] $\pi k/g\mu_B=2.34\times10^4$ Oe/K, and the values of Δg, b, and $\eta(E_F)$ listed in Tables I and II. Table II summarizes the obtained values. Notice that the ratio, $\langle J_{fs}^2(\mathbf{q})\rangle^{1/2}/J_{fs}(\mathbf{0})$, is nearly the same for these isomorphous compounds.

For the analysis of the Gd^{3+} ESR data in YbAgCu$_4$, we assume that the ratio, $\langle J_{fs}^2(\mathbf{q})\rangle/J_{fs}^2(\mathbf{0})\approx0.056(4)$, is the same for YbAgCu$_4$ and RAgCu$_4$ (R=Y,Lu) compounds. Using for YbAgCu$_4$ $\Delta g=0.18(1)$ and $b=42(2)$ Oe/K from Table I, we calculated $K(\alpha)\approx0.9(4)$ from Eq. (3). From Refs. 19 and 20 this value corresponds to $\alpha\approx0.1(4)$, i.e., for YbAgCu$_4$, the e-e exchange enhancement is also negligible. There is still not a model that includes the e-e exchange interaction for the analysis of the ESR, magnetic susceptibility, and specific-heat data in Kondo-lattice systems.[24] Hence, at the moment it is not possible to compare the Stoner factor obtained from ESR and that from transport measurements.[25] Thus, the best we can do is to use $\eta(E_F)=43(2)$ states/eV mol spin, $\alpha\approx0.1(4)$ (see Table II), and Eqs. (1) and (2) to estimate the exchange parameters, $J_{fs}(\mathbf{0})$ and $\langle J_{fs}^2(\mathbf{q})\rangle^{1/2}$, between Gd^{3+} and the c-e in YbAgCu$_4$. Those values are given in Table II.

The exchange parameters, $J_{fs}(\mathbf{0})$ and $\langle J_{fs}^2(\mathbf{q})\rangle^{1/2}$ calculated for YbAgCu$_4$, are both about ten times smaller than their respective values for the Y- and Lu-based compounds. This may suggest a much higher c-e localization for the Yb than for the Y- and Lu-based compounds. That is consistent with the large density of states associated with a ''narrow'' $4f$ band at the Fermi level of the Kondo-lattice compound YbAgCu$_4$. But a smaller positive exchange parameter, $J_{fs}(\mathbf{0})$, may also suggest a larger covalent (interband mixing) contribution to the exchange parameter in the Yb-based compound.[17,26] However, due to the oversimplified model used to extract the density of states, $\eta(E_F)$, the values for $J_{fs}(\mathbf{0})$ and $\langle J_{fs}^2(\mathbf{q})\rangle^{1/2}$ obtained for YbAgCu$_4$ should be taken with extra caution. Collective effects may enhance the density of states,[27] $\eta(E_F)$. Thus, our values represent just a lower limit for the exchange parameters.

V. CONCLUSIONS

The large density of states at the Fermi level for the Kondo-lattice compound YbAgCu$_4$, characteristic of highly correlated electron systems, results in a larger g shift and Korringa rate of the Gd^{3+} resonance when compared with the corresponding values of its reference compounds RAgCu$_4$ (R=Y,Lu). The exchange interaction between the localized magnetic moment of Gd^{3+} and the c-e is wave-vector dependent, $J_{fs}(\mathbf{q})$, for all three isomorphic compounds. The exchange parameter, $J_{fs}(\mathbf{0})$, is found to be positive for all of them. As YbAgCu$_4$ is a Kondo-lattice system, an antiferromagnetic exchange interaction is expected between the localized magnetic moment of Yb^{3+} and the c-e. Hence, we conclude that the exchange interaction with the c-e is atomiclike for Gd^{3+} and covalentlike for Yb^{3+}.[17]

There is an interesting observation to be made from the results of our previous measurements in the intermediate-valent compound YbInCu$_4$ (Ref. 8) and the present measurements in the Kondo-lattice compound YbAgCu$_4$. Both compounds belong to the class of highly correlated electron systems with relatively large γ values, 50(5) and 207(6) mJ/mol K^2 for YbInCu$_4$ and YbAgCu$_4$, respectively. For YbInCu$_4$ our results suggested a large electron-electron exchange interaction. Instead, for YbAgCu$_4$ this interaction, within the accuracy of our experiments, seems to be negligible. If so Coqblin-Schrieffer's model for magnetic impurities dissolved in a free c-e metal,[6,7] could be a good description for the magnetic susceptibility, $\chi(T)$, of YbAgCu$_4$.[3]

Finally, as in our earlier work,[8] the present results show that ESR experiments of Gd^{3+} diluted in metallic hosts with large electronic effective masses may be used to probe the high density of states at the Fermi level of these compounds. However, we should mention that ESR failed to observe this

property in other strongly correlated electron systems.[28–31] Therefore, a model that takes into account the large electronic effective mass, c-e localization, impurity perturbation of the local density of states, and e-e interactions is needed for a realistic analysis of the ESR results.

ACKNOWLEDGMENTS

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