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## Exchange narrowing effects in the EPR linewidth of Gd diluted in Ce compounds

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Anomalous thermal behavior on the EPR linewidths of Gd impurities diluted in Ce compounds has been observed. In metals, the local magnetic moment EPR linewidth,  $\Delta H$ , is expected to increase linearly with the temperature. In contrast, in  $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$  the Gd EPR spectra show a nonlinear increase. In this work, the mechanisms that are responsible for the thermal behavior of the EPR lines in  $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$  are examined. We show that the exchange interaction between the local magnetic moments and the conduction electrons are responsible for the narrowing of the spectra at low temperatures. At high temperatures, the contribution to the linewidth of the exchange interaction between the local magnetic moments and the Ce ions has an exponential dependence on the excitation energy of the intermediate valent ions. A complete fitting of the EPR spectra for powdered samples is obtained. © 1998 American Institute of Physics. [S0021-8979(98)39911-9]

### I. INTRODUCTION

During the last two decades Ce compounds have been extensively studied and many of them show anomalies typical of intermediate valence systems.<sup>1</sup> Electron paramagnetic resonance (EPR) spectra of magnetic ions diluted in Ce compounds allow us to study locally the influence of the intermediate valent Ce ions. In normal metals, the thermal behavior of the local moments EPR linewidth,  $\Delta H$ , is linear and described by the Korringa mechanism.<sup>2</sup> In contrast, in  $\text{Ce}_x\text{A}_{1-x}\text{Pd}_3$  (A=Ag, Y) and  $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$  the Gd spectra shows a nonlinear increase of  $\Delta H$  in the temperature range  $4.2 < T < 300$  K, and a strong dependence on the Ce concentration.<sup>3,4</sup> At low temperatures ( $T$ ) the slope  $d(\Delta H)/dT$  is smaller than in the isostructural non-IV compounds  $\text{MPd}_3$  (M=Sc, Y, La)<sup>5</sup> and  $\text{LaOs}_2$ ,<sup>4</sup> however, at high temperatures the resonance line is strongly broadened and the slope asymptotically approaches the value measured on them. Then, to describe this abnormal behavior of linewidth other mechanisms different from the Korringa are necessary.

It was demonstrated<sup>6</sup> that at high temperatures, the indirect exchange interaction between the local magnetic and the Ce 4*f* electrons has an appreciable contribution to the linewidth of the magnetic impurities at high temperature. The Ce interconfigurational fluctuations are transferred via the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction to the Gd site as an effective alternating magnetic field, which relaxes the Gd spins. However, this mechanism is not sufficient to describe the low temperature behavior of the Gd linewidth. It is well known<sup>7,8</sup> that the Gd EPR spectra shows a resolved fine structure at low  $T$ , which is narrowed due to

the exchange interaction between local magnetic moments and conduction electron when the temperature is increased. Then, for the correct description of the thermal behavior of the Gd spectra it is necessary to include not only the intermediate valence effects but also the narrowing mechanism. The goal of this work is to calculate the EPR spectra of Gd diluted in  $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$  including the both mechanisms.

### II. THEORETICAL ANALYSIS

To obtain the EPR absorption, the transverse dynamic susceptibility of the local magnetic moments coupled to the conduction electrons is necessary. The susceptibility, including the crystal field interaction, can be obtained using the projector formalism in the Liouville space.<sup>9</sup> Normally the EPR experiments are performed at a concentration that the conduction electrons static susceptibility is much smaller than those of the local moments, then, in this approximation, the susceptibility for the system in the nonbottleneck regime can be written as follows

$$\chi^+(\omega) \approx 1 - \omega_0 \left[ \sum_{M, M'} P_M(\Omega^{-1})_{M, M'} \right], \quad (1)$$

where  $\Omega_{M, M'}^{-1}$  is the transition matrix, the quantum numbers  $M$  and  $M'$  describe the various Zeeman states ( $M, M' = -S, -S+1, \dots, S-1$ ) associated to the  $S=7/2$  Gd spin and  $P_M$  are transition probabilities associated to the  $M \leftrightarrow M+1$  transition and can be written as:

$$P_M = C_M \exp^{M\hbar\omega_0/kT} / \sum_M C_{M'} \exp^{M'\hbar\omega_0/kT}, \quad (2)$$

where  $C_M = S(S+1) - M(M+1)$  and  $k$  is the Boltzmann constant. The elements of the transition matrix for  $kT$  large compared to  $\hbar\omega_0$  are expressed by the formula

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$$\begin{aligned} \Omega_{M,M'} = & (\hbar \omega_0 / g \mu_B - H - H_M) \delta_{M,M'} - i \Delta H_{res} \delta_{M,M'} \\ & - i \frac{1}{2} b C_{M'} (2 \delta_{M,M'} - \delta_{M,M'} \\ & - \delta_{M,M'+1} - \delta_{M,M'-1}), \end{aligned} \quad (3)$$

where  $\omega_0$  is the microwave frequency,  $H$  is the variable external magnetic field,  $\Delta H_{res}$  is the temperature independent residual linewidth of the various fine structure lines,  $b$  is the Korringa parameter,  $\mu_B$  is the Bohr magneton, and  $H_M$  is the resonance field of the Gd  $M \rightarrow M+1$  transition. As we can see, the transition matrix is a tridiagonal matrix where the diagonal elements contain the linewidth of each resonance line and the resonance field. The upper and lower diagonals terms represent the fluctuation rates of the local moment between two consecutives resonance frequencies.

In a cubic environment the fine structure spectra is given by

$$\begin{aligned} H(\pm \frac{7}{2} \leftrightarrow \pm \frac{5}{2}) &= H_0 \mp (1 - 5 \phi) b_4, \\ H(\pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}) &= H_0 \pm (1 - 5 \phi) b_4, \\ H(\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}) &= H_0 \pm (1 - 5 \phi) b_4, \\ H(+ \frac{1}{2} \leftrightarrow - \frac{1}{2}) &= H_0, \end{aligned} \quad (4)$$

where  $b_4$  is the crystal field parameter for the Gd ion,  $\phi$  is given by

$$\phi = \sin^2 \theta \cos^2 \theta + \sin^4 \theta \cos^2 \varphi \sin^2 \theta \quad (5)$$

and  $\theta$  and  $\varphi$  are spherical coordinates of the applied magnetic field  $H$  with respect to the axes of the crystal.

As it was shown previously,<sup>7,8</sup> for the LaSb:Gd and CePd<sub>3</sub>:Gd, the spin-spin interaction between Gd ions has an important role in the calculation of the resonance spectra. In both cases was found that when the spin-spin interaction is not taken into account the narrowing in the theoretical spectra occurs at higher temperatures than in the experiment, the transition  $1/2 \leftrightarrow 1/2$  does not appear in the theoretical spectra in the intermediate temperature range, however, it appears in the experiment, and the experimental linewidth of the single line at high temperatures is smaller than the calculated one. The discrepancies between theory and experiment can be overcome by introducing this interaction. Unfortunately, no theoretical calculation which takes spin-spin interaction into account exists at present. We shall introduce the spin-spin interaction in a phenomenological way.<sup>7,8</sup> This can be done by adding to the transition matrix elements the term:

$$\Omega_{M,M'}^{ex} = i \frac{H_{ex}}{P_M} (1 - \delta_{M,M'}) - i \frac{6H_{ex}}{P_M} \delta_{M,M'}, \quad (6)$$

where  $H_{ex}$  is the exchange-field parameter. The transition matrix has some properties that must be satisfied for this additional term. First,  $P_M \text{Im}(\Omega_{M,M'})$  are the elements of a negative-definite symmetric matrix. This guarantees a positive energy absorption. Second, as the total spin commutes with the exchange Hamiltonian, the relation  $\sum_M \Omega_{M,M'} = 0$  must hold. Since these two requirements are satisfied, we can believe that the additional term for the transition matrix describes the main effects of the spin-spin interaction. Because of the random distribution of the Gd ions, it is realistic to assume a distribution of  $H_{ex}$ . For the present calculations we

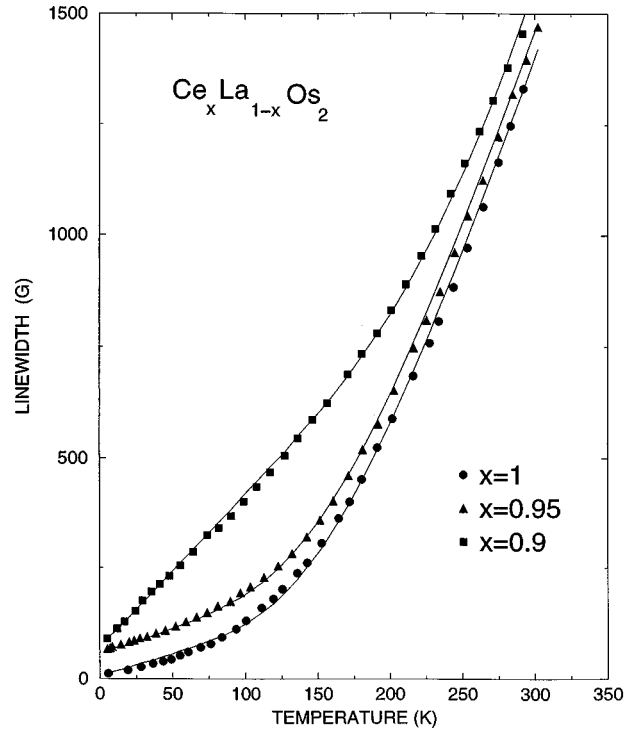


FIG. 1. Temperature dependence of the Gd linewidth for selected values of concentration  $x$  in  $Ce_xLa_{1-x}Os_2$ . The full lines represent the theoretical results. The residual linewidths are not realistic and the data has been shifted to avoid curve overlap.

use a slightly modified Lorentzian distribution for the exchange field with a maximum at  $H_{ex} = 0$ . The mean exchange field amounts to about 95 G and the distribution function was cut off at 1500 G.

### III. THE LINEWIDTH

In our metallic host the impurity EPR linewidth calculations must consider the energy transfer between the impurity spin  $S$ , the spin of the host rare earth ions (Ce), the spins of the conduction electrons as well as the lattice, in the presence of static external magnetic field and a small alternating field. In the present work we shall assume that the system is in the unbottlenecked regime, i.e., the conduction electrons and the host magnetic ions are in equilibrium with the lattice. In addition we shall assume that the transverse susceptibility associated with the impurity at the impurity resonance frequency is much larger than those of the other spin systems at the same frequency. In this limit one can consider only the transverse magnetization,  $M_x$ , of the impurities and neglect the interaction of the rf field with the magnetic host ions and the conduction electrons. In other words, the magnetic host ions and the conduction electrons are “passive dissipative

TABLE I. Obtained parameters  $b, b_4, A, E_{ex}$  that fit the linewidth thermal behavior for Gd diluted in  $Ce_xLa_{1-x}Os_2$ .  $E_{ex}$  (expt.) is the experimental value of  $E_{ex}$  to be taken as a comparison.

$x$	$b[G/K]$	$b_4[G]$	$A[G]$	$E_{ex}$ (theor.)	$E_{ex}$ (expt.)
1.0	1.07	4.8	10 200	670	500
0.95	1.32	10.6	10 150	684	
0.9	3.5	9.0	9800	1243	

systems.’’ With these assumptions the impurity linewidth can be expressed as:

$$\Delta H = \Delta H_{res} + bT + \Delta_{IF}, \quad (7)$$

where  $\Delta H_{res}$  is the residual linewidth,  $b$  is the usual Korringa contribution, originated from the impurity-conduction-electron exchange interaction, and  $\Delta_{IF}$  is the impurity linewidth due to the exchange interaction with the Ce host ions.<sup>6</sup> The last contribution arises from the RKKY coupling between the Ce and Gd ions, which transfers the Ce fluctuations to the Gd site. Ce ions fluctuate between the  $4f^0$  and the  $4f^1$  configurations. If we assume the  $4f^0$  configuration as the ground state (with  $J_z=0$ ), the contribution of the excited  $4f^1$  configuration to the impurity linewidth can be written as:

$$\Delta_{IF} = A e^{-E_{ex}/T}, \quad (8)$$

where  $E_{ex}$  is the energy required to delocalize a single electron from the Ce  $4f^1$  configuration and  $A$  is an adjustable parameter defined in Ref. 6.

The resonance absorption  $P$  is calculated using the relation  $P = [\text{Re}(\chi^+(\omega)) - \text{Im}(\chi^+(\omega))]$ . To obtain the EPR linewidth of the powdered samples we have to integrate the absorption over all directions of the magnetic field.

#### IV. RESULTS AND DISCUSSION

Using the results above we calculate the total linewidth of the Gd resonance. Figure 1 shows the calculated and experimental linewidth of a  $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$  powdered sample, as a function of temperature for selected concentrations of Ce. The residual linewidth is sample dependent and it was not considered in the plot. To fit the data we adjust the parameters  $b$ ,  $b_4$ ,  $A$ , and  $E_{ex}$  using the Monte Carlo simulated annealing. With this technique it is possible to obtain more accurate results than previous calculations with conventional methods.<sup>6-8</sup> Comparing our theoretical results with the experimental data we can see that in all of the cases we got an excellent fit. According to our model, at low  $T$  the main contribution to the linewidth is originated in the usual Korringa mechanism and the exchange narrowing effects. At high temperatures the population of the excited Ce  $4f^1$  configuration is increased, and the exponential contribution given by  $\Delta_{IF}$  is the most important. The parameters used to fit the experimental data are shown in Table I. The analysis *a priori* of the exchange narrowing effects in this system is not easy because there do not exist a single crystal spectra to obtain by a direct measure the crystal field parameter, however, if we look for the spectra of  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Os}_2$  in Fig. 1(a) of Ref. 4 we can see clearly that the Dysonian type line does not fit the experimental result. The experimental spectra shows the typical broadening at low  $T$  due to the fine structure contribution, and these effects tend to be more important in higher Ce concentrations.<sup>8</sup> If we compare the exchange narrowing effects for the present case with that in  $\text{CePd}_3$  (Ref. 8) certainly the exchange narrowing effects are less important in the former one, due to the smaller crystal field parameter. Otherwise, its contribution is more important at lower temperatures than in  $\text{CePd}_3$  because the higher Korringa parameter values collapse the spectra at lower tempera-

tures. It is necessary to point out that the minimization results show clearly a nonzero value for the crystal field parameter which reflects the importance of this mechanism. On the other hand, looking for the intermediate valence mechanism, the effect of the Ce concentration at high temperature seems clear. The increase in the excitation energy value when the Ce concentration is reduced agree with the interconfigurational fluctuation model.<sup>10-13</sup> This model predicts an increasing on the excitation energy when we cross from the intermediate valence to the magnetic regime. On the other hand, the  $A$  value depends on the strength of the Ce fluctuation spectra and we can expect an increase with the Ce concentration. The small values of  $b$  obtained for high Ce concentrations (when compared with those of  $\text{LaOs}_2$ ) agree with the experimental results of Ref. 4 at low  $T$ , with the prediction of the ‘‘hybridization hole’’ model<sup>3</sup> for Gd diluted in  $\text{CePd}_3$  powdered sample and with that obtained in Ref. 8 for the monocrystalline spectra of the same compound. This result agrees also with that obtained by Hirst<sup>12</sup> for low  $T$ , but not with the result obtained in Ref. 14, which predicts a higher value for  $b$ . However, the thermal behavior of the linewidth obtained by the latter authors agrees, at least qualitatively, with that obtained here. It is important to observe that in contrast to the hybridization hole model, here we have supposed a constant density of states as in a normal metal. The nonlinear contribution to the linewidth, at high  $T$ , according with the present model, is originated in the exchange interaction of the magnetic impurities with the Ce ions.

In conclusion, our calculations using the intermediate valence and exchange narrowing mechanism permit a quantitative description of the thermal behavior of Gd linewidths. Note that the values obtained for the excitation energy are, within the experimental error, close to that founded by Sereni *et al.*<sup>15</sup> The agreement with experimental results supports our interpretation.

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