

EPR linewidth of local magnetic moments diluted in Ce intermediate-valence compounds

Pablo A. Venegas

Departamento de Física, Faculdade de Ciências, UNESP, Campus Bauru, R. Engenheiro Luis Coube s/n, Bauru, São Paulo, Brazil

Gaston E. Barberis

Instituto de Física, Universidade Estadual de Campinas (UNICAMP), 13081 Campinas, São Paulo, Brazil

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Anomalous thermal behavior on the EPR linewidths has been observed for Gd impurities diluted in $Ce_x A_{1-x} B_n$ ($A = \text{La, Y}$, $B = \text{Ir, Os, Rh, Pd}$) intermediate-valence compounds. In this work we show that the exchange interaction between the local magnetic moments and the intermediate-valence host ions has an important contribution to the relaxation rates of the local moments. We calculated the relaxation, using the Redfield formalism and the ideas contained in the interconfigurational fluctuation model of Hirst. We show that the exchange interaction contribution has an exponential dependence on the excitation energy of the intermediate-valence ions.

I. INTRODUCTION

Ce intermetallic compounds have been extensively studied in the literature and many of them show anomalies typical of intermediate-valence (IV) alloys.¹ By doping Ce compounds with Gd^{3+} ions, their ESR spectra allow us to study locally the influence of the intermediate-valence Ce ions. In metals, the local moments ESR linewidth, ΔH , is expected to increase linearly with the temperature (Korringa²). In contrast, in $Ce_x A_{1-x} Pd_3$ ($A = \text{Ag, Y}$) and $Ce_x La_{1-x} Os_2$ the Gd ESR spectra show a nonlinear increase of ΔH in the temperature range $4.2 \leq T \leq 300$ K.³ At low temperatures the slope $d(\Delta H)/dT$ is smaller than in the isostructural non-IV compounds MPd_3 ($M = \text{Sc, Y, La}$),⁴ whereas at high temperatures the resonance line is strongly broadened and the slope asymptotically approaches the value measured in $LaPd_3$. The temperature dependence of ΔH becomes nonlinear and cannot be explained only by invoking the usual Korringa mechanism.

EPR studies in metallic hosts, which show interconfigurational fluctuations,⁵ suggest that the indirect exchange interaction between the local magnetic impurities and the Ce $4f$ electrons have an appreciable contribution to the linewidth of the magnetic impurities. The Ce interconfigurational fluctuations are transferred via the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction to the Gd site. These fluctuations generate an effective alternating magnetic field, which relaxes the Gd spins. A similar mechanism was also used for the interpretation of the NMR relaxation rates of noble metals with Kondo impurities,⁶⁻⁹ for perturbed angular correlation measurements of ^{140}Ce in $(La_{1-x} Y_x)Al_2$ alloys,¹⁰ and for Gd ESR on concentrated Van Vleck paramagnets.¹¹ We use this mechanism to explain the anomalous behavior of the linewidth of Gd diluted in the Ce intermediate valence compounds.

The Gd linewidth can be calculated with use of the ideas contained in the "interconfigurational fluctuation" model of Hirst.¹²⁻¹⁴ This model has been used to explain

various physical measurements and particularly magnetic susceptibility and Mössbauer studies in intermediate-valence compounds. In their approach the expectation value of the measured physical quantity (isomer shift, magnetic moment, etc.) is calculated by "averaging" over all possible $4f^n$ configurations. The occupation probability of the n configuration is usually expressed as $P_n(T) \propto \exp(-E_n/T_n)$ with $T_n = T + \Delta_n$.^{1,14,15} Here E_n and Δ_n are the energy and width of the $4f^n$ configuration. The quantity measured thus depends exponentially on the excitation energy, E_{ex} , defined as the energy required to delocalize a single electron from the $4f^n$ configuration (i.e., $E_{ex} = E_n - E_{n-1}$). Although this theoretical approach is phenomenological, it successfully explains most of the Europium Mössbauer spectra and susceptibility studies in mixed-valence compounds.^{16,17}

In this work we use this approach and the Redfield formalism¹⁸ to calculate the contribution of an excited configuration of the host Ce ions to the linewidth of the impurity spectra. We fit the experimental data and compare with other theoretical approaches.^{3,19}

II. THE MODEL

The spin Hamiltonian describing the Ce ions in the n configuration can be written

$$H = H_{cf} + H_z, \quad (1)$$

where the crystal-field Hamiltonian for Ce is

$$H_{cf} = \sum_l [B_4 O_4(\mathbf{J}^{(l)}) + B_6 O_6(\mathbf{J}^{(l)})] \quad (2)$$

with $O_4(\mathbf{J}^{(l)})$ and $O_6(\mathbf{J}^{(l)})$ the cubic combinations of Stevens' equivalent operators of the fourth and sixth degree, respectively, B_4 and B_6 are the crystalline-field parameters of the fourth and sixth degree, respectively, and $\mathbf{J}^{(l)}$ is the total angular momentum of the l th Ce ion. The Zeeman Hamiltonian for Ce is

$$H_z = g_J \mu_B \sum_l \mathbf{H} \cdot \mathbf{J}^{(l)}, \quad (3)$$

where μ_B is the Bohr magneton, g_J is the Landé factor, and \mathbf{H} is the external magnetic field.

The Gd Hamiltonian can be written as

$$H' = H'_{cf} + H'_z + H_{ex} . \quad (4)$$

Here H'_{cf} and H'_z are defined in a similar form as H_{cf} and H_z , with the obvious substitution of $\mathbf{J}^{(l)}$ by the spin of the Gd, \mathbf{S} . The Gd impurity interacts with the neighboring host Ce ions via exchange interaction:

$$H_{ex} = -(g_J - 1) \mathcal{J} \sum_{l=1}^{z_0} \mathbf{S} \cdot \mathbf{J}^{(l)} , \quad (5)$$

where \mathcal{J} is the exchange intergal between the two ions and z_0 is the number of Ce neighbor ions of each impurity. For simplicity, however, we have considered only the first Ce neighbors. We calculate the relaxation rate of the impurity if it does not create a perturbation of the Ce host Hamiltonian.

III. THE LINEWIDTH

In our metallic host the impurity ESR linewidth calculations must consider the energy transfer between the impurity spin \mathbf{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 altering 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, ω_0 , 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 systems." On the other hand, the static magnetic field splits the Gd resonance in $2S = 7$ fine-structure lines, which are well resolved at low temperatures.²⁰ In the present case, for simplicity, we assume that the fine structure is collapsed and suppose the Gd with an effective spin $S = \frac{1}{2}$. With these assumptions the impurity linewidth can be expressed as

$$\Delta H = a + bT + \Delta_{IF} , \quad (6)$$

where a is the residual linewidth, b is the usual Korringa contribution originating from the impurity-conduction-electron exchange interaction, and Δ_{IF} is the impurity linewidth due to the exchange interaction with the Ce host ions. The last contribution arises from the RKKY coupling between the Ce and Gd ions, which transfers the Ce fluctuations to the Gd site.

The ESR relaxation of an impurity due to (stable) excited configurations of the host ions can be calculated using the Bloch-Redfield-Wangsness formalism,¹⁸ in analogy with impurity relaxation in Van-Vleck compounds.¹¹ Then the relaxation rate can be written as

$$\Delta H = \frac{\pi}{2\hbar^2} [\mathcal{J}(g_J - 1)]^2 [k_{yy}(\omega_0) + k_{xx}(\omega_0) + 2k_{zz}(0)] , \quad (7)$$

where ω_0 is the impurity resonance frequency. $k_{qq}(\omega)$ ($q = x, y, z$) is the Fourier transform of the spectral functions defined as

$$k_{qq}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\langle \sum_{k=1}^{z_0} \delta J_q^{(k)}(t) \sum_{k=1}^{z_0} \delta J_q^{(k)} \right\rangle e^{i\omega t} dt . \quad (8)$$

Here $\langle \rangle$ denotes a thermal average and $\delta J_q^{(k)}$ the fluctuation in the q component of the total angular momentum of Ce due to the interconfigurational fluctuations, defined as

$$\delta J_q^{(k)} = J_q^{(k)} - \langle J_q^{(k)} \rangle . \quad (9)$$

In the absence of pair correlations, i.e., terms like $\langle \delta J_q^{(i)}(t) \delta J_q^{(j)} \rangle$ with $i \neq j$, Eq. (8) is reduced to the form

$$k_{qq} = z_0 K_{qq}(\omega) \quad (10)$$

with $K_{qq}(\omega)$ defined as

$$K_{qq}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \delta J_q(t) \delta J_q \rangle e^{i\omega t} dt . \quad (11)$$

In the present case, the Ce interconfigurational fluctuation frequency, $\Delta\omega$, is much greater than the impurity resonance frequency, ω_0 . Physically for our model it means that for a very short correlation time, the spectral density of the fluctuating field is "white" to the frequencies far above the resonance frequency. So that if we view the problem from a rotating frame (that is one where the magnetization is rotating at the Larmor frequency), the x , y , and z directions are equivalent and the effects of the external magnetic field in the fluctuation spectra can be neglected. In this case we have that

$$K_{xx}(\omega_0) \cong K_{xx}(0) ; K_{yy}(\omega_0) \cong K_{yy}(0) \quad (12)$$

and for cubic symmetry

$$K_{xx}(0) = K_{yy}(0) = K_{zz}(0) . \quad (13)$$

With these assumptions the calculation of spectral functions (see Ref. 11) leads to the following expression for the linewidth:

$$\Delta_{IF} = \frac{2\pi}{\hbar^2} [\mathcal{J}(g_J - 1)]^2 z_0 F(0) \sum_{n\alpha} p_n |\langle n\alpha | J_z | n\alpha \rangle|^2 , \quad (14)$$

where $|n\alpha\rangle$ and E_n are the eigenvectors and eigenvalues of H , $F(0)$ a frequency distribution function due to the finite width of the Ce $4f^n$ states, and $p_n = \exp(-E_n/T)/Z$, with $Z = \sum_n \exp(-E_n/T)$.

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

$$\Delta_{IF} = A e^{-E_{ex}/T} , \quad (15)$$

where

$$A = (2\pi/\hbar^2) [\mathcal{J}(g_J - 1)]^2 z_0 F(0) |\langle 1\alpha | J_z | 1\alpha \rangle|^2$$

and E_{ex} is the excitation energy required to delocalize a single electron from the Ce $4f^1$ configuration.

IV. RESULTS AND DISCUSSION

Using the expression obtained in Eq. (15) we can calculate the total linewidth of the Gd resonance, given by Eq. (7). Figures 1 and 2 plot the calculated linewidth as a function of the temperature for selected cases of $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$ and $\text{Ce}_x\text{Y}_{1-x}\text{Pd}_3$ powered samples. The residual linewidth, which is sample dependent, is not considered in the plots (see figure captions). To fit the data we adjust the parameters b , A , and E_{ex} , where b represents the “apparent” Korringa parameter. This is done so because we are not considering the exchange narrowing effect of the fine structure of Gd at low T .²¹ As stated previously, here we assume an effective spin $S = \frac{1}{2}$ for the magnetic ion. Rigorously, the linewidth calculations have to consider the contribution of the fine structure associated with the spin $S = \frac{7}{2}$ of Gd. However, the exchange narrowing effect collapses the spectra in a single line, which can be treated by an $S = \frac{1}{2}$ effective spin. This collapse, at low T , is more evident for big values of b and the resonance is well described by this effective spin. For the cases where b is small and the fine-structure contribution, not considered here, is important we use an apparent Korringa parameter, associated to the $S = \frac{1}{2}$ effective spin. An example of the last case is the Gd diluted in CePd_3 resonance. Comparing our theoretical results with the experimental data we can see that in most of the cases we got an excellent fit. The same calculations have been made for $\text{Ce}(\text{Pd}_{1-x}\text{Ag}_x)_3$ and $\text{Ce}(\text{Pd}_{1-x}\text{Rh}_x)_3$ with similar results. According to our model, at low T the main contribution to the linewidth is originated in the usual Korringa mechanism. At high temperature the population of the excited Ce $4f^1$ configuration is in-

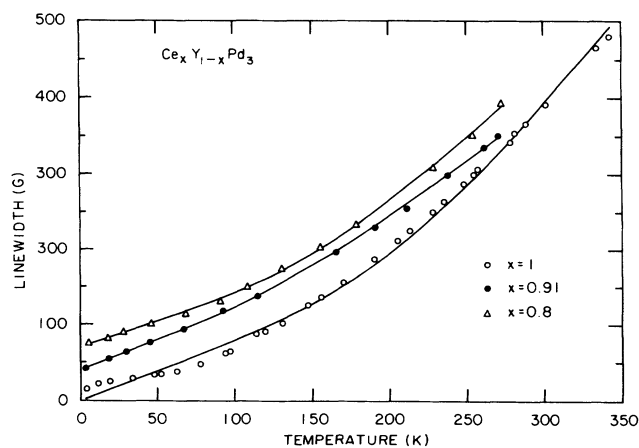


FIG. 1. Temperature dependence of the linewidth for different values of the concentration x in $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$. The full lines are the plot of the theoretical expression [Eq. (6)]. The fitting parameters can be found in Table I(a). The residual linewidths are not realistic, for the data was shifted in order to avoid superimposed curves.

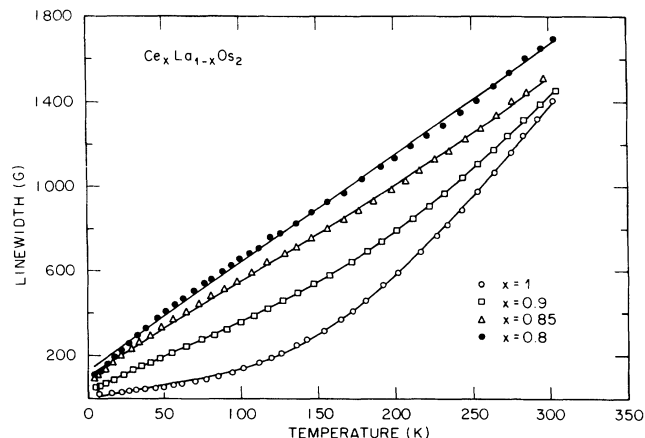


FIG. 2. Same as Fig. 1 for $\text{Ce}_x\text{Y}_{1-x}\text{Pd}_3$.

creased, and the exponential contribution given by Δ_{IF} is the most important. The parameters used to fit the experimental data are shown in Table I.

Looking at the values of the fitting parameters the effect of the Ce concentration seems clear. The increase in the excitation energy value when the Ce concentration is reduced agree with the interconfigurational fluctuation model.¹²⁻¹⁴ The model predicts an increase of the excitation energy when we cross from the intermediate valence to the magnetic regime. This is the case, for example, when we go from CeOs_2 to LaOs_2 . 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 value of b obtained for high Ce concentrations, at low T , agree with the prediction of the “hybridization hole” model³ for Gd diluted in the CePd_3 powered sample and with that obtained by us²¹ for the monocrystalline spectra of the sample compound. This result agrees also with that obtained by Hirst,²² for low T , but not with the result obtained in Ref. 19, which predicts a higher value for b . However, the thermal behavior of the linewidth obtained by the latter authors agree, at least qualitatively, with that obtained here.

TABLE I. Obtained values of the parameters b , a , and E_{ex} that fit Eq. (6) for diluted Gd. The last column shows the experimental value of E_{ex} published in Ref. 23, to be taken as a comparison.

x	b [G/K]	A [G]	E_{ex} (theor.)	E_{ex} (expt.)
(a) $\text{Ce}_x\text{La}_{1-x}\text{Os}_2$				
1	1.27	9547	672	500
0.95	1.31	9580	678	
0.9	3.28	7364	849	
0.85	4.5	3112	1132	
0.8	5.18	94	1681	
(b) $\text{Ce}_x\text{Y}_{1-x}\text{Pd}_3$				
1	0.54	1543	576	360
0.91	0.69	1170	609	
0.8	0.76	642	517	

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, according to the present model, is originated in the exchange interaction of the magnetic impurities with the Ce ions. Our calculations, regarding the hybridization hole model, permit a quantitative description of the linewidth, but using a lesser number of adjustable parameters. In the other hand, is necessary to point out that for small values of x , where the Δ_{IF} value is small in comparison with the Korringa contribution, the numerical simulation of ΔH leads to unexpected small values of E_{ex} . However, as we can clearly see in the $Ce_xLa_{1-x}Os_2$ case, b asymptotically approaches the

$LaOs_2$ b value when x goes to 0.

Note that the values obtained for the excitation energy are, within the experimental error, close to that founded by Sereni, Olcese, and Rizzuto.²³ This agreement with experimental results supports this interpretation.

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