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E. P. R. CONDUCTION-ELECTRON RELAXATION BY CERIUM AND GADOLINIUM IMPURITIES IN $LaAl_2$ [1]

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ABSTRACT

The conduction-electron relaxation by Cerium impurities is computed by use of the effective exchange Hamiltonian which takes into account both combined spin and orbit exchange scattering and crystalline field effects, which finally can account for recent *EPR* measurements of *Gd* in $LaAl_2$ with Cerium impurities.

RÉSUMÉ

La relaxation des électrons de conduction par les impuretés de Cérium est calculée en utilisant l'Hamiltonien effectif d'échange qui tient compte à la fois de la diffusion d'échange de spin et d'orbite et des effets de champ cristallin, ce qui finalement peut rendre compte des récentes mesures de *RPE* du *Gd* dans le $LaAl_2$ avec des impuretés de Cérium.

Recent electron-spin-resonance measurements of Gadolinium in $LaAl_2Gd$ alloys [1] alone or with Cerium impurities [2] have allowed to determine the conduction electron-relaxation rates due to *G*d and *Ce* in $LaAl_2$. It has been shown that the spin-flip relaxation rate of the conduction electrons due to *Gd* and *Ce* in $LaAl_2$ increases roughly linearly with impurity concentration and is equal at low temperatures to $(1 \pm 0.6) \times 10^7$ sec $^{-1}$/ppm for *Gd* [1] and $(7 \pm 3) \times 10^7$ sec $^{-1}$/ppm for *Ce* [2].

The superconducting temperature and the resistivity of $LaAl_2Gd$ and $LaAl_2Ce$ have been measured at normal and high pressure [3, 4]. The $LaAl_2Gd$ alloy has

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no Kondo effect, a pressure-independent superconducting temperature and is described by the ionic model. On the opposite, the $LaAl_2Ce$ alloy presents both a Kondo effect and a large pressure dependence of the superconducting temperature; it can thus be described by a model taking into account both the resonant scattering due to the proximity of the $4f$ level to the Fermi level and the crystalline field of the Cerium impurity [4, 5].

The purpose of this letter is to present a simple explanation for the spin-flip relaxation rate due to Cerium and Gadolinium. There are two mechanisms responsible for spin-flip scattering of conduction electrons by impurities in metals: either the spin-orbit coupling on the impurity site or the conduction electron-impurity spin exchange interaction. The first mechanism studied by Yafet [6] has been used for explaining the spin-flip relaxation of conduction electrons by non magnetic transition impurities or by magnetic ones with only a spin magnetic moment. But this model is definitively not valid for cerium impurities which have spin and orbital contributions to the magnetic moment.

The spin-flip scattering of Gadolinium is due alone to the exchange interaction mechanism and is computed by used of the classical ionic Hamiltonian:

$$H = -2J \vec{s}\,\vec{S} \tag{1}$$

On the opposite, both mechanisms are important in Cerium; moreover the spin-flip scattering is important because the $4f$ level is close to the Fermi level, as previously recognized [2]. These effects can be described by the previously derived effective exchange Hamiltonian which describes the resonant scattering mechanism and takes into account both combined spin and orbit exchange scattering and the crystalline field effect of cerium impurity [5]. For a Cerium atom, the large spin-orbit coupling leads to a ground state of total angular momentum $j = 5/2$, which is then split by the crystalline field. In cubic $LaAl_2$, the crystalline field gives a doublet ground state Γ_7 and a quartet excited state Γ_8 [4]. We follow the notations of reference [5]. If we call M the eigenvalue of a $4f$ eigenfunction in presence of crystalline field, E_M (< 0) its energy compared to the Fermi energy, c_M^+ the creation operator for a localized $4f$ electron of z-component M and c_{kM}^+ the creation operator for a conduction-electron partial wave function of wavenumber k, $j = 5/2$ and z-component M, the effective exchange Hamiltonian is [5]:

$$H = -\sum_{\substack{kk' \\ MM'}} J_{MM'}\, c_{k'M'}^+ c_{kM} (c_M^+ c_{M'} - \delta_{MM'} \langle n_M \rangle) + \sum_{kk'M} \mathcal{V}\, c_{k'M}^+ c_{kM} \tag{2}$$

$$J_{MM'} = \frac{|V_{kf}|^2}{2} \left(\frac{1}{E_M} + \frac{1}{E_{M'}} \right) \tag{3}$$

where $\mathcal{V}$, taken here as independent of M, gives the direct scattering and V_{kf} is the mixing parameter between conduction and $4f$ electrons.

We compute the spin-flip relaxation rate $\delta = \frac{1}{T_1}$ for the Hamiltonian (2) only at low temperatures, i.e. when the only occupied state is the ground state of energy E_0 and of degeneracy λ_0. The relaxation rate is given by [7]:

$$\delta = \frac{1}{T_1} = \frac{2\pi}{\hbar} c\, \rho(E_F) \sum_{\sigma} \overline{|\langle k\sigma \mid H \mid k' - \sigma \rangle|^2} \tag{4}$$

where we average for both localized and conduction electrons of opposite spins. $\rho(E_F)$ is the density of states of the conduction band for one spin direction. For the Hamiltonian (2), δ is given by:

$$\delta = \frac{1}{T_1} = \frac{2\pi c}{\hbar} \rho(E_F)\, J_{00}^2\, A_{00} \tag{5}$$

$$A_{00} = \frac{\lambda_0^2 - 1}{(2j+1)\,\lambda_0} - \frac{\lambda_0}{2(2j+1)} + \frac{2\sum_{M_0} \alpha_{M_0}^4}{\lambda_0^2 (2j+1)} \tag{6}$$

$$\alpha_{M_0}^2 = \frac{7 + 2M_0}{14} \tag{7}$$

The sum over M_0 in (6) is made over the M_0 values of the ground state. J_{00} is the exchange integral corresponding to the ground state.

We give in table 1 the A_{00} values corresponding to the case of Cerium: the ground states are either in hexagonal symmetry the doublets $\pm 1/2$, $\pm 3/2$, $\pm 5/2$ or in cubic symmetry the doublet Γ_7 and the quartet Γ_8.

TABLE 1

The A_{00} values for the different possible ground states of Cerium in cubic and hexagonal symmetry.

Symmetry	hexagonal			cubic	
ground state	$\pm 1/2$	$\pm 3/2$	$\pm 5/2$	Γ_7	Γ_8
A_{00}	0.126	0.133	0.146	0.127	0.316

In the case of Gadolinium, the spin-flip relaxation rate is computed by (1) and is given by:

$$\delta = \frac{1}{T_1} = \frac{4\pi c}{3\hbar} \rho(E_F)\, J^2\, S(S+1) \tag{8}$$

Then we compute the exchange integrals for *Ce* and *Gd* obtained respectively by [5] and [8] in order to fit the experimental values of δ. In $LaAl_2Ce$ alloys, the ground state is the Γ_7 doublet and the Γ_8 state lies around 100-200 K above Γ_7 [4], so that the low temperatures formula [5] is appropriate to describe the present E. P. R. measurements. The density of states $\rho(E_F)$ is estimated from specific heat measurements on $LaAl_2$ (8) and is taken here equal to: $\rho(E_F) = 0.78$ st./ev. at. for one spin direction. In (5), A_{00} corresponds to the Γ_7 value and in (8), $S = 7/2$. Table 2 gives the deduced values of J for *Gd* and J_{00} for the Γ_7 state of *Ce*.

TABLE 2

The J_{00} values for Cerium and the J values for Gadolinium in $LaAl_2$ deduced either from EPR or from superconducting temperature measurements.

	For *Ce* : J_{00} (in *eV*)	For *Gd* : J (in *eV*)
From *EPR*	0.27	0.013
From $\frac{dT_c}{dc}$	0.15	0.025

We can compare these values of the exchange integrals to those deduced from the measurements of the decrease dT_c/dc of the superconducting temperature T_c with the concentration c of *Ce* or *Gd* impurities in $LaAl_2$ [3]. For $LaAl_2Ce$ alloys, we can easily derive:

$$\frac{dTc}{dc} = -\frac{\pi^2}{2}\frac{\rho(E_F)}{k_B} J_{00}^2 \frac{\lambda_0^2 - 1}{(2j+1)\lambda_0} \tag{9}$$

and for $LaAl_2Gd$ alloys:

$$\frac{dT_c}{dc} = -\frac{\pi^2}{2}\frac{\rho(E_F)}{k_B} J^2 S(S+1) \tag{10}$$

Using the experimental values of $\frac{dT_c}{dc}$ derived by Maple *et al.* [3], we obtain the J and J_{00} values reported in table 2.

The values of table 2 deduced from E. P. R. agree relatively well with those obtained from superconductivity. So, while the spin-flip relaxation rate of Gadolinium is described by the exchange scattering mechanism, the spin-flip relaxation of Cerium is quite well accounted for by the Hamiltonian (2). This Hamiltonian,

which is very different from the Hamiltonian (1), contains the spin and orbit exchange scattering and the crystalline field effect for a cerium impurity with the $4f$ level close to the Fermi level. An interesting remark to do is that the Hamiltonian (2) gives a non zero $1/T_1$ value for all the ground states listed in table 1, while for example the Hamiltonian (1) would have given a zero $1/T_1$ value for the two $\pm$ 3/2 and $\pm$ 5/2 ground states; from this point of view also, the Hamiltonian (2) is more appropriate for describing the spin-flip relaxation due to Cerium.

The preceeding calculation in the low temperature limit and in the Born approximation can be extended by including the excited states of the crystalline field effect to describe the higher temperatures domain and by computing the third order terms in J to derive the influence of the Kondo effect on the conduction-electron relaxation due to cerium impurities as for the resistivity [5], but no experimental data are presently available on these subjects. We can finally suggest to measure the relaxation rates at high pressures to see the variation of T_1 for cerium impurities.

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