

# DIFFERENT EFFECT OF CERIUM AND GADOLINIUM IMPURITIES ON THE PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF LANTHANUM\*

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The different effect of cerium and gadolinium impurities on the pressure dependence of the superconducting transition temperature of lanthanum is due to different electronic structures of the rare-earth impurity. The ionic model explains the properties of gadolinium alloys, while the resonant scattering theory explains those of cerium alloys.

The superconducting transition temperature  $T_c$  for solid solutions of cerium and gadolinium in lanthanum has been recently measured as a function of pressure.<sup>1</sup> The plot of  $T_c$  versus the impurity concentration  $c$  at different pressures gives straight lines (at least for small concentration) shown in Fig. 1. Their slope is almost independent of the pressure in La:Gd ( $dT_c/dc = -400^\circ\text{K}$ ), while it is strongly varying with pressure in La:Ce:  $dT_c/dc = -170^\circ\text{K}$  at normal pressure,  $-240^\circ\text{K}$  at 5 kbar, and  $-320^\circ\text{K}$  at 10 kbar.

Moreover, the La:Ce alloys show a resistivity minimum at very low temperatures, while the La:Gd alloys do not show it.<sup>2</sup>

The theoretical explanation of these experiments comes from the model recently developed for rare-earth metals and alloys<sup>3</sup> and from the Schrieffer-Wolff transformation.<sup>4</sup> If one writes the interaction Hamiltonian between the localized spins  $\tilde{S}$  on impurity sites and the spins of conduction electrons  $\tilde{s}$ ,

$$H = -J\tilde{S} \cdot \tilde{s}, \quad (1)$$

there are in fact two mechanisms contributing to the value of  $J$ : (1) There always exists the normal exchange-scattering mechanism.<sup>5</sup> It gives a positive and almost pressure-independent value  $J_1$  for  $J$ .<sup>1</sup> (2) Moreover, when the energy level of  $4f$  electrons coming from the rare-earth impurity is close enough to the Fermi level, there is an important mixing between localized  $4f$  electrons and conduction electrons. The interaction (1) is produced by a mechanism of resonant scattering of the conduction electrons by the localized potential of the  $4f$  electrons. Here we call  $E$  the distance between the  $4f$  energy level and the Fermi level and  $V_{kf}$  the matrix element of mixing between localized  $4f$  electrons and conduction electrons. Schrieffer and Wolff<sup>4</sup> have shown that, in the limit of small  $V_{kf}$  and large Coulomb repulsion integral  $U$ , the resonant scattering mechanism leads to an interaction given

by (1) with a value  $J_2$  for  $J$ :

$$J_2 = -2V_{kf}^2/E. \quad (2)$$

The second-order (in  $V_{kf}$ ) formula (2) is valid when  $U$  is much larger than  $E$  and when  $E$  is not too small compared with  $V_{kf}$ . This expression is approximately still valid for cerium impurities, because  $V_{kf}$  is of the order of some hundredths of an eV,  $U$  of the order of several eV, and the  $4f$  level lies some hundredths of an eV to  $\frac{1}{10}$  eV below the Fermi level.<sup>3</sup>

The expression (1) is very appropriate for the study of the superconducting transition temperature in rare-earth alloys, but causes some concern for the study of the Kondo effect. A complete study of the Kondo effect in rare-earth alloys has been recently done by use of the Schrieffer-Wolff transformation and will be reported elsewhere,<sup>6</sup> but this work does not change the main physical conclusions of the present paper.

In general, the two mechanisms described here

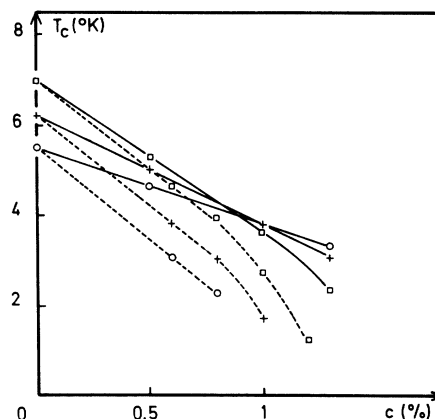


FIG. 1. Superconducting transition temperature versus impurity concentration at different pressures (after T. F. Smith). Dashed curve, La:Gd alloys; solid curve, La:Ce alloys. Circles, normal pressure; plus signs, 5-kbar pressure; squares, 10-kbar pressure.

contribute to the value of  $J$ :

$$J = J_1 + J_2. \quad (3)$$

The difference of behavior between La:Gd and La:Ce alloys is explained by the following argument:

(1) In La:Gd alloys, the gadolinium impurities behave as ions and the resonant scattering mechanism is negligible.  $J$ , equal to  $J_1$ , is positive and pressure independent. Its positive value is checked by the absence of a resistivity minimum at low temperatures.

(2) In La:Ce alloys, a  $4f$  level is close to the Fermi level and the resonant scattering mechanism is more important than the normal exchange-scattering mechanism. The total  $J$  value is negative, which is checked by the presence of a resistivity minimum at low temperatures. Moreover, the Fermi level decreases and the  $4f$  energy level does not change, when the pressure is applied.<sup>3</sup>  $E$  decreases and  $|J|$  increases with the pressure.

The variation of the superconducting temperature with the concentration  $c$  of magnetic impurities is given by<sup>7</sup>

$$\frac{dT_c}{dc} = -\frac{\pi^2}{8} \frac{n(E_F)}{k_B} S(S+1)J^2, \quad (4)$$

where  $n(E_F)$  is the density of states at the Fermi level of the conduction band for one spin direction.

The value of the density of states of the conduction band for pure lanthanum, deduced from specific heat data,<sup>8</sup> is  $n(E_F) = 2.4$  states/eV atom. In fact, the conduction band is composed of both a  $6s$  band and a narrow  $5d$  band. Band calculations on yttrium,<sup>9</sup> which is similar to lanthanum, have shown that the  $d$  electrons contribute greatly to the total density of states. Furthermore, both  $6s$  and  $5d$  electrons participate to the superconductivity mechanism, but with different densities of states and different effective masses. One can surmise that the density of states coming into the formula (4) is certainly lowered from the 2.4 states/eV atom value. However, it is not possible to compute it exactly, in the absence of both a two-band calculation for superconductivity and also precise data on the band structure of lanthanum. So here we take two limiting cases: The first value is the total density of states  $n(E_F) = 2.4$  states/eV atom, which gives a lower limit for  $|J|$ . The second value is a typical free-electron density of states  $n(E_F) = 0.5$  states/eV

atom, which gives an upper limit for  $|J|$ .

Here, we have made the reasonable assumption of keeping  $n(E_F)$  constant with pressure. In fact, the relative variation of  $n(E_F)$ , as well as the relative variation of the value  $J_{Gd}$  of  $J$  for La:Gd alloys, is negligible compared with the relative variation of the value  $J_{Ce}$  of  $J$  for La:Ce alloys. So, the approximation of taking  $n(E_F)$  constant with pressure is consistent with the preceding theoretical analysis. A study of the pressure dependence of the normal and superconducting properties of pure lanthanum is actually in progress and will be reported elsewhere.<sup>10</sup>

The calculation, by use of the expression (4), gives the following results: (1) For La:Gd alloys,  $J_{Gd}$  is constant with pressure, as expected, and of the order of 1/20 eV, in good agreement with previous calculations.<sup>5</sup> (2) For La:Ce alloys,  $J_{Ce}$  is negative and of the order of 0.1–0.2 eV. This anomalously large value  $J$  for cerium impurities is in good agreement with all the preceding calculations on rare-earth alloys.<sup>2,11</sup> In order to determine the position  $E$  of the  $4f$  level in La:Ce alloys and its variation  $dE$  between the normal pressure and 10 kbar, we take  $J_1$  equal to the constant value  $J_{Gd}$  and we express  $E$  as a function of the Hartree-Fock half-width  $\Delta$  of the virtual bound state<sup>3</sup>:

$$\Delta = \pi n(E_F) V_{kf}^2. \quad (5)$$

Thus, the position of the  $4f$  level is

$$\frac{E}{\Delta} = \frac{2}{n(E_F)|J_2|}. \quad (6)$$

Table I gives the different values of  $J$ ,  $E$ , and  $dE$ , taking the half-width  $\Delta = 0.02$  eV.<sup>3</sup> The values found for  $E$ , of the order of 0.05–0.1 eV, and  $dE$ , of the order of some 0.01 eV, are of just the same order of magnitude as previously obtained values for cerium.<sup>3</sup>

Thus, the simple argument developed here gives a fairly good explanation of the difference of behavior between La:Ce and La:Gd alloys. It is not possible to extrapolate the calculation to higher pressures, because the second-order calculation in  $V_{kf}$  of the Schrieffer-Wolff transformation is no longer valid, when  $E$  becomes very small.

However, we can suggest that these experiments should be continued at higher pressures in La:Ce alloys, in order to observe the disappearance of magnetism and the Kondo effect and also a completely different behavior of  $T_c$ . Another

Table I. Values (in eV) of the exchange integral  $J$  for La:Ce and La:Gd alloys, of the position  $E$  of the  $4f$  level, and its variation  $dE$  under a 10 kbar pressure in La:Ce alloys. Calculations are done with two densities of states,  $n(E_F)=2.4$  and  $0.5$  states/eV atom, and with a half-width  $\Delta=0.02$  eV. (Between brackets the pressures  $p$  are expressed in kbar.)

	$J_{\text{Gd}}=J_1$ (eV)	$J_{\text{Ce}}(p=0)$ (eV)	$J_{\text{Ce}}(p=10)$ (eV)	$E(p=0)$ (eV)	$E(p=10)$ (eV)	$dE=E(p=0)-E(p=10)$ (eV)
$n(E_F)=2.4$ states/eV atom	0.03	-0.08	-0.11	0.05	0.04	0.01
$n(E_F)=0.5$ states/eV atom	0.06	-0.18	-0.24	0.11	0.085	0.025

similar system, the Y:Ce alloys,<sup>11</sup> which are not superconductors, would also be very interesting to study at very high pressures. Both La:Ce and Y:Ce alloys show a Kondo effect and are good candidates to study experimentally the transition from magnetism to nonmagnetism at very high pressures when  $E$  becomes zero. This study would relate directly to all the recent theoretical developments on the Kondo effect.

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## OBSERVATION OF A THERMODYNAMIC DISTINCTION BETWEEN BRILLOUIN ZONE CENTER AND BOUNDARY EXCITON STATES IN $\text{MnF}_2$

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The shape of the intrinsic-emission magnon sideband is well described assuming a wave-vector representation but with zero dispersion for the exciton. An observed difference in the decay rates of the intrinsic-emission zero-magnon line and magnon sideband implies that the zone-center and zone-boundary excitons are distinct thermodynamic states. Thus, the exciton wave-vector states are, at least approximately, eigenstates.

A number of recent papers have been concerned with the properties of the optically excited states of  $\text{MnF}_2$ ,<sup>1</sup> particularly those states belonging to the lowest  $^4T_1$ . These transitions have been classified as zero-magnon lines and magnon sidebands, both of which are zero-phonon lines, as well as broad phonon sidebands which are not relevant to this communication. In order to cal-

culate the shapes of the magnon sidebands,<sup>2-5</sup> a Frenkel exciton representation has been assumed for these excited states wherein the zero-magnon lines correspond to the creation (in absorption) or the annihilation (in emission) of excitons near the center of the Brillouin zone ( $\vec{k}=0$ ), while the sideband peaks correspond to the creation or annihilation of an exciton with the simul-