Crystal-field effects on the superconducting transition temperature of $LaSn_3$:Pr, $LaPb_3$:Pr, and $LaTl_3$:Pr

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The crystal-field effects on the superconducting transition temperature of matrix LaX_3 (X = Sn, Pb, Tl) containing praseodymium impurities are examined. Using the theory of Fulde, we have taken into account all the crystal-field levels of the impurity. Exchange integrals Γ are evaluated from the depression of the superconducting transition temperature T_c in $La_{1-n}Pr_nX_3$ solutions. The large value of Γ found in $La_{1-n}Pr_nSn_3$ is in agreement with the observation of a Kondo effect in these compounds.

INTRODUCTION

Fulde and co-workers[1-4] have calculated the superconducting transition temperature T_c of a matrix containing rare-earth impurities with crystal-field-split energy levels. In particular, they consider a two-level system $|i\rangle$ and $|j\rangle$ with energies E_i and E_j ($\delta = E_j - E_i$). They suppose that the system has no magnetic moment in the ground state and that there is a nondiagonal Van Vleck term connecting the two levels as follows:

$$M_{ij}^2 = |\langle i|\vec{J}|j\rangle|^2 .$$

For instance, in the case of a cubic symmetry,

$$M_{ij}^2 = 3|\langle i|J_z|j\rangle|^2 .$$

The variation of T_c with the impurity concentration n is given by the following formula, in this case of inelastic exchange scattering[1]:

$$\ln(T_c/T_{c0}) + \Psi(\tfrac{1}{2}+\rho) - \Psi(\tfrac{1}{2}) = 0 \qquad (1)$$

where ρ is the pair-breaking parameter

$$\rho = \frac{1}{4\pi k_B T_c}\left(\frac{1}{\tau_{ij}}\right) y\left(\frac{\delta}{T_c}\right)$$

and

$$1/\tau_{ij} = \tfrac{1}{2}\pi n N(E_F)\Gamma^2(g-1)^2 M_{ij}^2 ,$$

$N(E_F)$ is the density of states of the condition band at the Fermi level for one spin direction, Γ is the interaction between conduction and $4f$ electrons ($\mathcal{H} = -\Gamma\,\vec{s}\,\vec{S}$), and $y(\delta/T_c)$ is a function calculated by Fulde *et al.*[2] (Fig. 1).

Taking into account all the levels (magnetic and nonmagnetic, that is, elastic and inelastic exchange scattering), we have used for ρ the following expression

$$\rho = \frac{n N(E_F)(g-1)^2\Gamma^2}{4\pi k_B T_c} F(T_c) , \qquad (2)$$

where

$$F(T_c) = \frac{1}{Z}\sum_{i,j}^{i\neq j}\left[M_{ii}^2 + 0.5\,M_{ij}^2\, y\left(\frac{E_{ij}}{T_c}\right)\right] \times \exp\left(-\frac{E_i}{T_c}\right) ;$$

and where

$$Z = \sum_i \exp\left(-\frac{E_i}{T_c}\right) \quad \text{and} \quad E_{ij} = |E_i - E_j| .$$

In the absence of a crystal field,

$$F(T_c) = \frac{1}{2J+1}\sum_{i,j}^{i\neq j}(M_{ii}^2 + M_{ij}^2) = J(J+1)$$

and Eqs. (1) and (2) give the result of Abrikosov and Gor'kov.[5] With crystal-field-split levels and for small concentrations, we get the formula

$$\left.\frac{dT_c}{dn}\right|_{T_{c0}} = -\frac{\pi^2}{8k_B} N(E_F)\Gamma^2(g-1)^2 F(T_{c0}) \qquad (3)$$

instead of the classical formula

$$\left.\frac{dT_c}{dn}\right|_{T_{c0}} = -\frac{\pi^2}{8k_B} N(E_F)\Gamma^2(g-1)^2 J(J+1) .$$

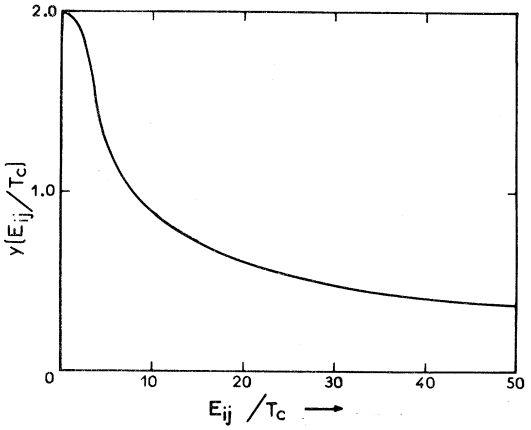

FIG. 1. $y(E_{ij}/T_c)$ vs E_{ij}/T_c for inelastic exchange scattering calculated by Fulde and Peschel (Ref. 4).

TABLE I. Superconducting transition temperature (T_c) of $La_{1-n}Pr_nSn_3$ compounds.

n	T_c
0.0	6.45
0.005	5.5
0.009	4.73
0.0106	4.46

We have used the fact that $\Psi'(\frac{1}{2}) = \frac{1}{2}\pi^2$.

EVALUATION OF EXCHANGE INTEGRALS IN (La, Pr)X_3 COMPOUNDS

The compounds $LaSn_3$, $LaPb_3$, $LaTl_3$ are superconductors[6,7] with critical temperatures of 6.45 K, 4.05 K, and 1.5 K respectively. Lethuillier and Chaussy[8] have determined the crystal-field parameters of the three compounds $PrSn_3$, $PrPb_3$, and $PrTl_3$. For $PrSn_3$, the total splitting is most probably smaller than 20 K and $F(T_{c0}) \simeq 20$. For $PrPb_3$, in the notation of Lea *et al.*,[9] $W = -0.65$ K, $x = 0.6$, and $F(T_{c0}) = 15$. For $PrTl_3$, $W = 1.6$ K, $x = -0.9$, and $F(T_{c0}) = 5.6$. Bucher *et al.*[7] have studied the superconducting transition temperature of the compounds $La_{1-n}Pr_nPb_3$ and $La_{1-n}Pr_nTl_3$; they find, respectively,

$$\left.\frac{dT_c}{dn}\right|_{T_{c0}} = -17 \text{ K} \quad \text{and} \quad \left.\frac{dT_c}{dn}\right|_{T_{c0}} = -10 \text{ K}.$$

We have studied the critical temperature of three alloys $La_{1-n}Pr_nSn_3$ (Table I) by the appearance of diamagnetism at the transition, and for these alloys we have found a much more rapid decrease of T_c:

$$\left.\frac{dT_c}{dn}\right|_{T_{c0}} = -190 \text{ K}.$$

The values of the densities of states are available from specific-heat measurements.[7] We have used for their evaluation (Table II) the strong-coupling model of McMillan.[10] Using the Eq. (3), we have determined the exchange integrals in these (La, Pr)X_3 solutions (Table II).

TABLE II. Evaluation of exchange integrals in the (La, Pr)X_3 solutions.

	(La, Pr)Sn_3	(La, Pr)Pb_3	(La, Pr)Tl_3
$F(T_{c0})$	20	15	5.6
$\left.\frac{dT_c}{dn}\right\|_{T_{c0}}$	−190	−17	−10
$n(E_F)$ (states/eV/at. for one spin direction)	0.33	0.40	0.47
$\lvert\Gamma\rvert$ (eV)	0.22	0.07	0.08

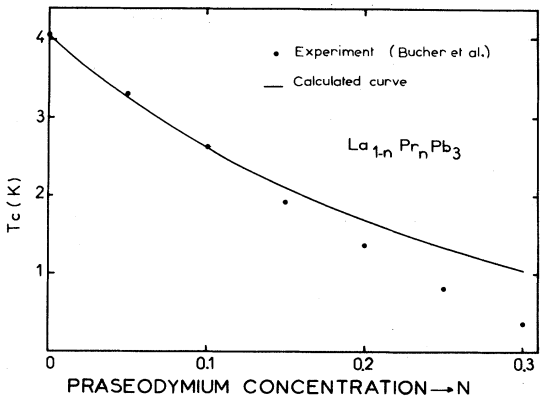

FIG. 2. Superconducting transition temperature vs praseodymium concentration in $La_{1-n}Pr_nPb_3$ compounds.

Thus the very striking difference between the decrease of the critical temperatures of the systems (La, Pr)Pb_3 and (La, Pr)Sn_3 (Ref. 7) is not ascribed to crystal-field effects but to a very important conduction band—4*f* electrons interaction in (La, Pr)Sn_3. The value of $|\Gamma|$ so determined is in good agreement with that ($\Gamma = -0.2$ eV) determined by NMR measurements.[11] This large negative value of Γ is confirmed by the observation of a resistivity minimum in the $La_{1-n}Pr_nSn_3$ compounds due to a Kondo effect.[12] In the solutions $La_{1-n}Pr_nRu_2$, an important decrease of T_c with n has been observed[13]:

$$\left.\frac{dT_c}{dn}\right|_{T_{c0}} = -110 \text{ K}$$

as in $La_{1-n}Pr_nSn_3$, and, very curiously, $CeRu_2$ is nonmagnetic at low temperature[14] as in $CeSn_3$.[15]

In these praseodymium compounds, the 4*f* levels are probably close to the conduction band: this gives rise to a large negative exchange integral due to interband mixing.[16]

We have reported (Fig. 2) the variation of the critical temperatures of the $La_{1-n}Pr_nPb_3$ compounds, experimentally determined by Bucher *et al.*[7] and by the calculated curve using Eqs. (1) and (2). The agreement is not very good. Perhaps interband mixing[17] could account for the nearly linear experimental curve, but we think that aspherical Coulomb scattering[2,17] increases the curvature of the calculated curve, reducing the agreement.

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[1]P. Fulde and H. E. Hoenig, Solid State Commun. 8, 341 (1970).
[2]P. Fulde, L. L. Hirst, and A. Luther, Z. Phys. 230, 155 (1970).
[3]J. Keller and P. Fulde, J. Low Temp. Phys. 4, 289 (1971).
[4]P. Fulde and I. Peschel, Adv. Phys. 21, 1 (1972).
[5]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 39, 1781(1960)[Sov. Phys.-JETP 12, 1243 (1961)].
[6]A. M. Toxen, R. J. Gambino, and N. R. Stemple, Bull. Am. Phys. Soc. 12, 57 (1967).
[7]E. Bucher, K. Andres, J. P. Maita, and G. W. Hull, Helv. Phys. Acta 41, 723 (1968).
[8]P. Lethuillier and J. Chaussy (unpublished).
[9]K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).
[10]W. L. McMillan, Phys. Rev. 167, 331 (1968).
[11]F. Borsa, R. G. Barnes, and R. A. Reese, Phys. Status Solidi 19, 359 (1967).
[12]P. Lethuillier and P. Haen (unpublished).
[13]B. Hillenbrand and M. Wilhelm, Phys. Lett. A 40, 387 (1972).
[14]B. Hillenbrand, K. Schuster, and M. Wilhelm, Z. Naturforsch. 26a, 1684 (1971).
[15]R. Tournier, J. Chaussy, and P. Lethuillier (unpublished).
[16]R. E. Watson, S. Koide, M. Peter, and A. J. Freeman, Phys. Rev. 139, A167 (1965).
[17]H. Capellmann, J. Phys. Chem. Solids 32, 2439 (1971).