First Observation of a Kondo Effect from Praseodymium Excited Crystal-Field Levels in $La_{1-x}Pr_xSn_3$ Compounds*

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The electrical resistivity of $La_{1-x}Pr_xSn_3$ compounds ($x=0.0$, 0.1, 0.2, 0.4, and 1.0) has been measured between 1 and 300 K. A resistivity minimum is observed, which arises from a Kondo effect due to excited crystal-field levels of the praseodymium ion, the ground state being nonmagnetic. The plot of $\rho(La_{1-x}Pr_xSn_3)-\rho(LaSn_3)$ versus $\ln T$ is approximately linear above 25 K.

The compounds RSn_3, where R is a rare earth, have been extensively studied. $LaSn_3$ is a superconductor with a critical temperature $T_c=6.45$ K[1]; its resistivity has been measured[2,3] and its band structure theoretically determined.[4,5] $CeSn_3$ becomes nonmagnetic at low temperature.[6] The compounds (Pr, Nd, Sm, Gd)Sn_3 order antiferromagnetically.[7,8] In the paramagnetic domain, the electrical resistivity of $PrSn_3$ exhibits a minimum[3]; another fact suggested that a Kondo effect could exist in the $La_{1-x}Pr_xSn_3$ compounds: Praseodymium impurities produce an important decrease of the critical temperature of $LaSn_3$ ($dT_c/dx=-1.9$ K/at.%),[9,10] but they have a much smaller effect in the similar compounds $LaPb_3$ and $LaTl_3$ ($dT_c/dx=-0.17$ and -0.1 K/at.%, respectively).[1] Similarly, a resistivity minimum associated with a strong depression of T_c has been found in the Kondo system $Zr_{1-x}Pr_xB_{12}$.[11]

In order to understand the resistivity minimum observed in $PrSn_3$, susceptibility measurements on $La_{1-x}Pr_xSn_3$ compounds and specific-heat measurements of $LaSn_3$ and $PrSn_3$ were performed.[12] These experiments indicated that, in the $La_{1-x}Pr_xSn_3$ compounds, the interaction between the conduction band and the $4f$ electrons strongly reduces the magnetic susceptibility and that the crystal-field splitting Δ is smaller than 20 K. This value of Δ is in rough agreement with the recent result of McCallum *et al.*[9] Finally, we have performed resistivity measurements.

Samples of approximate dimensions $0.2\times0.2\times1.5$ cm^3 were cut by spark erosion from polycrystalline ingots of concentrations $x=0.0$, 0.1, 0.2, 0.4, and 1.0. The measurements were performed between 1 and 300 K by a standard four-probe technique described elsewhere.[13] As we had relatively important uncertainties in the geometrical dimensions of the samples, we have adjusted their room-temperature resistivities so as to obtain a linear variation of these values with the praseodymium concentration. Such a normalization is only a first approximation because it is in violation of Nordheim's rule (which predicts a nonlinear variation of the nonmagnetic impurity contribution). It supposes also that the phonon contribution is the same for all the compounds. However, our results are not modified qualitatively by the different possible approximations. We have also measured the resistivity of the compound $La_{0.9}Gd_{0.1}Sn_3$.

Our results are presented in Figs. 1 and 2. For $LaSn_3$ and $PrSn_3$, they are in agreement with previously reported measurements.[3] At temperatures below 20 K, the phonon resistivity of $LaSn_3$ is proportional to $T^{3.3}$, a result comparable with the T^4 variation obtained by Grobman[2] and by Stalinski, Kletowski, and Henkie.[3] The resistivity of all the praseodymium compounds exhibits a maximum and a minimum; their temperatures are given in Table I. The compound $La_{0.9}Gd_{0.1}Sn_3$ did not show any minimum. The differences $\Delta\rho=\rho(La_{1-x}Pr_xSn_3)-\rho(LaSn_3)$, plotted in Fig. 3, decrease roughly linearly versus $\ln T$ above 25 K.

$PrSn_3$ and $La_{0.6}Pr_{0.4}Sn_3$ order antiferromagnetically at 8.5 and 3.1 K, respectively.[12] Their resistivities increase very sharply at their Néel temperatures. On the contrary, Fig. 2 shows that the $x=0.2$ compound is still paramagnetic

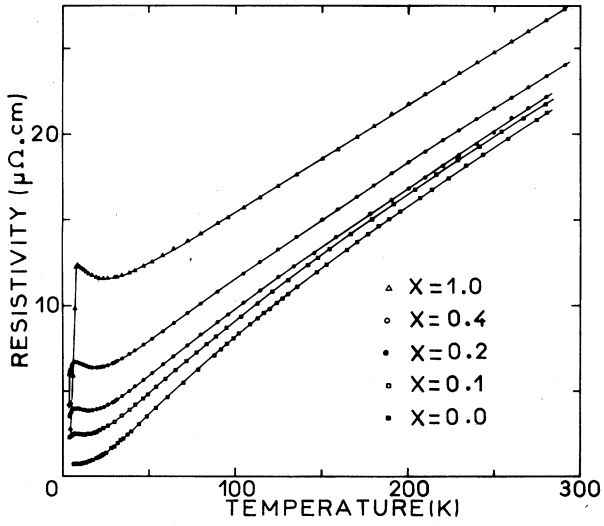

FIG. 1. Electrical resistivity of the compounds $La_{1-x}Pr_xSn_3$ versus temperature.

at 1 K. Its small resistivity at this temperature is evidence that the ground state is nonmagnetic and the rapid increase of this resistivity between 1 and 4 K indicates that there are excited states 3 or 4 K higher. The resistivity increase of the $x=0.4$ compound at T_N is very sharp because the disappearance of order and the population of excited states occur at the same temperature.

In order to verify that the resistivity minimum does not result from a temperature-dependent spin-disorder resistivity due to the scattering from the crystal-electric-field levels of the praseodymium ion, we have calculated this contribution for twenty different sets of the crystal-field parameters W and X, with a total crystal-field splitting of 20 K, using the formula of Rao and Wallace.[14] The increase of resistivity between 10 and 50 K is about 15% but we did not observe any minimum.

Moreover, susceptibility measurements[15] show that the $x=0.1$ compound does not order up to 0.05 K. Thus, the resistivity minimum observed for this compound does not arise from a short-range-order phenomenon.

These results indicate that the behavior of these compounds is characteristic of a Kondo system: In this case, for noninteracting impurities, T_{min} should be proportional to $x^{1/n}$, where n is the power of the temperature in the low-temperature phonon resistivity of the matrix. We find that T_{min} increases as $x^{1/n}$ with $n=3.4 \pm 0.4$; thus the correlation with the $T^{3.3}$ or T^4 variation found for $LaSn_3$ below 20 K is very satisfactory. The temperature of the resistivity maximum is practically the same ($T_{max} \simeq 7.5$ K) for all the compounds (except $PrSn_3$ which orders at 8.5 K) because this maximum arises from the competition between the logarithmical decrease and the temperature-dependent spin-disorder resistivity, both effects depending on the praseodymium concentration. As the crystal-field splitting is very small, the observed logarithmical variation is in good agreement with that calculated by Cornut and Coqblin[16] for cerium compounds. In the present case, however, the ground state is nonmagnetic and the Kondo effect originates from excited levels (Γ_4 and Γ_5).

In $PrSn_3$, NMR measurements[17] have shown

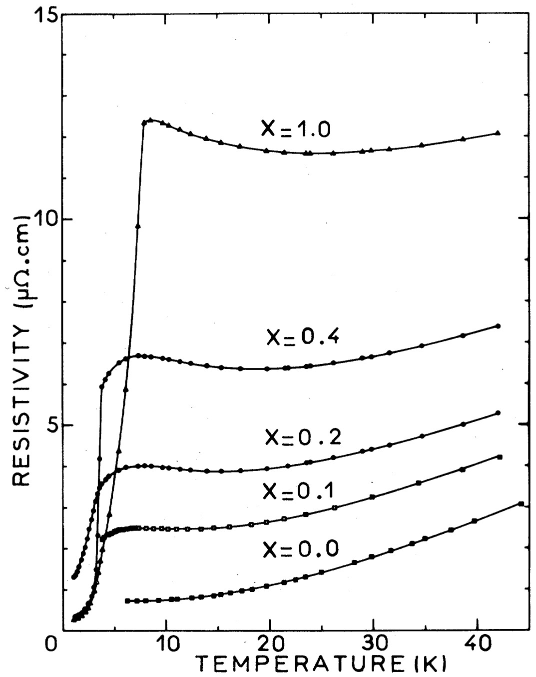

FIG. 2. Low-temperature electrical resistivity of the compounds $La_{1-x}Pr_xSn_3$ versus temperature.

TABLE I. Temperatures of the resistivity maxima and minima of the $La_{1-x}Pr_xSn_3$ compounds.

x	T_{min} (K)	T_{max} (K)
1.0	24.5	8.5
0.4	19	7.3
0.2	15.5	7.5
0.1	12	7.5

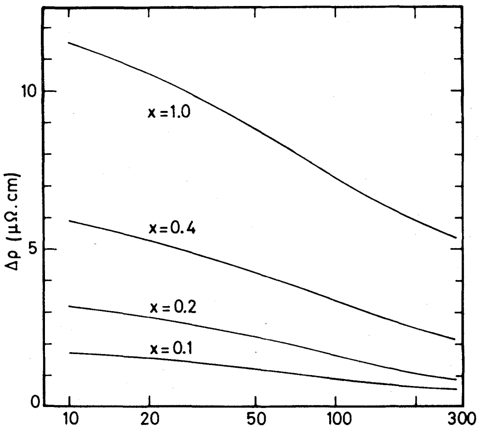

FIG. 3. Plot of $\Delta\rho = \rho(La_{1-x}Pr_xSn_3) - \rho(LaSn_3)$ versus $\ln T$.

that the interaction between the conduction band and $4f$ electrons is negative ($\Gamma = -0.2$ eV). In this case, the usual Hamiltonian $\mathcal{H} = -\Gamma(g-1)\vec{J}\cdot\vec{s}$ does not predict a Kondo effect in the first-rare-earth-series compounds. For the case of cerium, an effective Hamiltonian, which does not have this inconvenience, has been derived by Coqblin and Schrieffer.[18] It takes into account spin and orbit exchange scattering. From this theory, it appears that the spin and the orbital momenta of the conduction electrons concerned in the resonant scattering mechanism with a first-rare-earth-series ion are predominantly antiparallel.[12] Thus, the total rare-earth momentum and the total conduction-electron momentum are antiparallel when Γ is negative and a Kondo effect is possible.

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