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Magnetic-suseptibility measurements of a praseodymium Kondo system: $La_{1-x}Pr_xSn_3$ †

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The magnetic susceptibility of $La_{1-x}Pr_xSn_3$ compounds (x = 1.0, 0.7, 0.4, 0.2, 0.1, 0.05, 0.01, 0.0) has been measured between 2 and 300 K and the heat capacity of $PrSn_3$ and $LaSn_3$ between 20 and 300 K. It is shown that the magnetic susceptibility is anomalously reduced by the interaction with the conduction band showing the delocalization of the 4f shell of praseodymium.

I. INTRODUCTION

The compound $PrSn_3$ has the cubic $AuCu_3$-type structure. It orders antiferromagnetically at[1] 8.5 K and exhibits, in the paramagnetic domain, a resistivity minimum[2] which arises from a Kondo effect.[3] Praseodymium impurities produce an important decrease of the superconducting temperature of[4,5] $LaSn_3$ (dT_c/dx = 1.9 K/at.%), and the pressure effect on this transition temperature is large.[6]

II. SPECIFIC-HEAT MEASUREMENTS

We have studied, between 20 and 300 K, the heat capacity of $LaSn_3$ and $PrSn_3$ (Fig. 1). The samples used for the experiment were cylinders of about 25 g. Between 20 and 80 K, the heat capacities of the two compounds have the same value. Above 80 K, the heat capacity of $PrSn_3$ slightly exceeds that of $LaSn_3$.

In $PrSn_3$, the crystalline electric field splits the $J = 4$ ground multiplet of the praseodymium ion into four levels: Γ_1, Γ_3, Γ_4, and Γ_5. This specific-heat experiment gives two possibilities for the level scheme: the three first levels are inside an interval of 20 K and there is an excited state (Γ_5) at 300 K, or the total splitting Δ is smaller than 20 K and the difference between the heat capacities of $PrSn_3$ and $LaSn_3$ above 80 K does not arise from the population of an excited level.

III. MAGNETIC-SUSCEPTIBILITY MEASUREMENTS

A. Experimental

The purity of the lanthanum was 99.99% and the purity of the praseodymium 99.9%. The compounds were prepared in an induction furnace under helium atmosphere. The magnetic measurements have been performed with a translation balance between 2 and 300 K in a magnetic field of 1.7 kOe. The error bars are ±0.2 K on the temperature in the whole scale; the precision on the magnetic susceptibility is 1% with a minimum error of $\pm 0.3 \times 10^{-4}$ emu/mole.

B. Results

Samples of concentrations x = 1.0, 0.7, 0.4 (2), 0.2 (3), 0.1, 0.05 (3), 0.01, and 0.0 have been measured (Figs. 2–4). The numbers in brackets

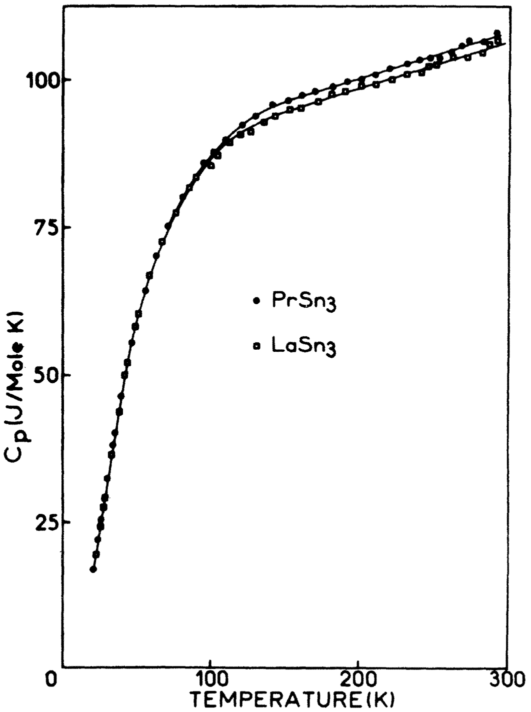

FIG. 1. Heat capacities of $PrSn_3$ and $LaSn_3$ vs temperature.

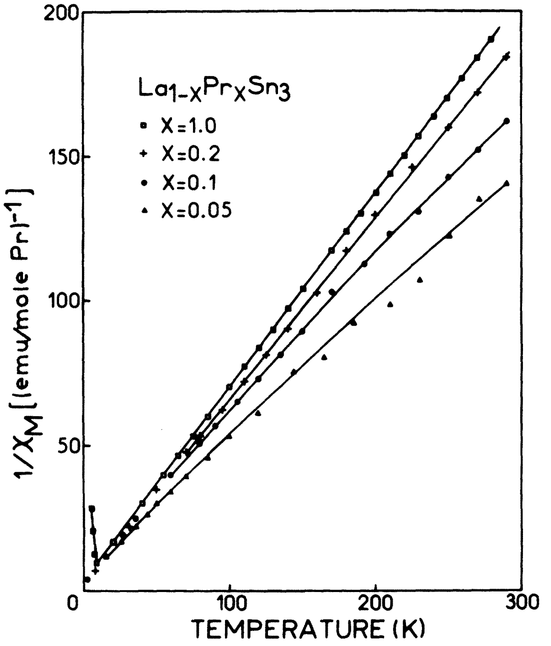

FIG. 2. High-temperature reciprocal susceptibilities of $La_{1-x}Pr_xSn_3$ compounds.

are the numbers of samples of a given concentration effectively measured; the discrepancies between two samples of a given concentration (coming from the same or different ingots) were always within the experimental error bars. In the following, we describe our results in the paramagnetic domain exclusively.

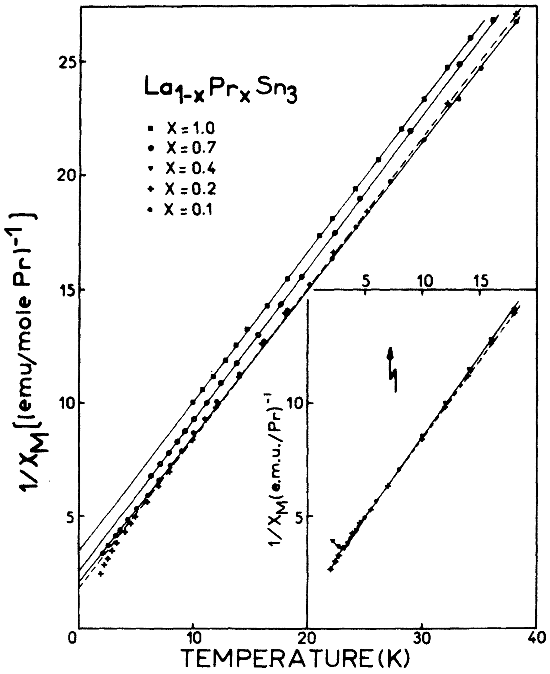

FIG. 3. Low-temperature reciprocal susceptibilities of $La_{1-x}Pr_xSn_3$ compounds.

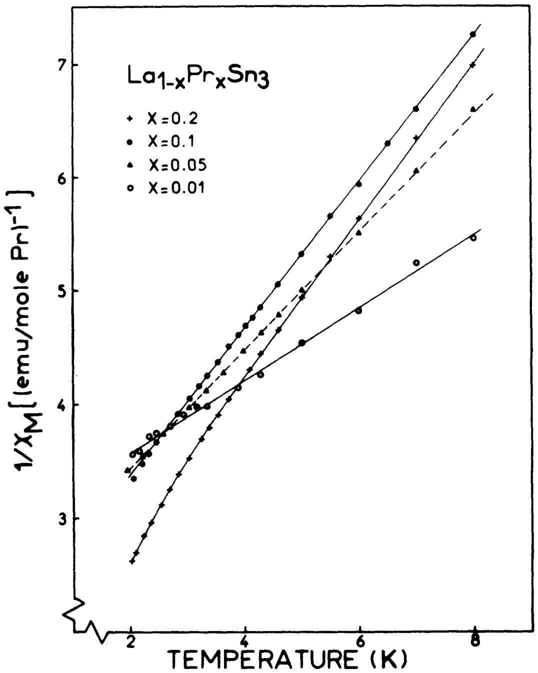

FIG. 4. Low-temperature reciprocal susceptibilities of $La_{1-x}Pr_xSn_3$ compounds.

1. $x = 1.0, 0.7, 0.4$ (Figs. 2 and 3)

The Néel and paramagnetic Curie temperatures of these compounds are given in the Table I. Above 10 K, they exhibit a perfect Curie-Weiss behavior with a Curie constant $C = 1.5$ lower than the free tripositive ion value ($C = 1.6$), in agreement with the result of Tsuchida *et al.*[1] The reciprocal susceptibility of these compounds may be written approximately as

$$1/\chi_M = T/1.5 + nx\,,$$

where $n \simeq 3.5$ is a molecular-field coefficient taking into account the antiferromagnetic interactions. Thus the crystal-field effect on the magnetic susceptibility is weak. The solution given by the specific-heat measurements with an excited level

TABLE I. Néel and paramagnetic Curie temperatures of $La_{1-x}Pr_xSn_3$ compounds.

x	T_N	Θ_p
1.0	8.5	−5.2
0.7	6.1	−4
0.4	3.1	−3.1

at 300 K has to be rejected: it would lead, in particular, to a crystal-field contribution to the paramagnetic Curie temperature $\theta_p = -12$ K, higher than the experimental value ($\theta_p \simeq -5$ K). The second solution ($\Delta < 20$ K) confirms the susceptibility results and is in approximate agreement with the result of McCallum *et al.*[4]

2. *Concentration range $x \leqslant 0.2$ (Figs. 2-4)*

The susceptibility of $LaSn_3$ is paramagnetic between 2 and 300 K. It takes in particular, under 50 K, a constant value $\chi_M = (3.2 \pm 0.3)\times 10^{-4}$ emu/mole, in agreement with the result of Welsh *et al.*[7]

In the high-temperature region, the measured Curie constant of the Pr dilute alloys (Fig. 2) increases with decreasing praseodymium concentration, owing to the matrix contribution. At low temperature, very anomalously, the susceptibility per praseodymium ion decreases with the concentration (Figs. 3 and 4) whereas it should increase since the global interactions are antiferromagnetic. Up to 2 K, we did not observe any Van Vleck paramagnetism, contrary to McCallum *et al.*[4] However, resistivity measurements[3] have shown that the ground state is nonmagnetic and that there is an excited level 3 or 4 K higher.

IV. DISCUSSION

The reduction of the Curie constant of the more concentrated compounds is an indication of a conduction electron polarization antiparallel to the localized moment. The strong low-temperature reduction of the magnetic susceptibility of the more dilute alloys is another indication of a Kondo effect in the $La_{1-x}Pr_xSn_3$ solid solutions. In particular, an antiferromagnetic exchange-induced transition of these dilute alloys, in the temperature range of the experiments, is totally excluded since the $x = 0.4$ compound orders only at 3.1 K.

When the interaction Γ between the conduction band and $4f$ electrons is negative, as it is the case in $PrSn_3$,[8] the usual Hamiltonian $\mathcal{H} = -\Gamma(g-1)\vec{J}\cdot\vec{s}$ does not predict a Kondo effect in the light-rare-earth compounds. In order to explain the Kondo effect in the cerium alloys, Coqblin and Schrieffer[9] have derived a Hamiltonian which takes into account the spin and orbit exchange scattering. The wave function $|k,M\rangle$ of a conduction electron concerned in the resonant scattering mechanism with a $J = \frac{5}{2}$ ion is given as a function of the partial waves $|k, l, m, \sigma\rangle$, where $l = 3$, m is the z component of the angular momentum and σ is the spin:

$$|k,M\rangle = \alpha_M |k, 3, M+\tfrac{1}{2}, -\tfrac{1}{2}\rangle + \beta_M |k, 3, M-\tfrac{1}{2}, \tfrac{1}{2}\rangle,$$

where $\alpha_M = [\frac{1}{14}(7+2M)]^{1/2}$ and $\beta_M = [\frac{1}{14}(7-2M)]^{1/2}$. When we calculate $|k, \frac{5}{2}\rangle \ldots |k, -\frac{5}{2}\rangle$, we observe that the coupling of the orbital momentum m and the spin σ of the partial wave is predominantly antiparallel; for instance

$$|k, \tfrac{5}{2}\rangle = (\tfrac{12}{14})^{1/2} \, |k, 3, 3, -\tfrac{1}{2}\rangle + (\tfrac{2}{14})^{1/2} \, |k, 3, 2, \tfrac{1}{2}\rangle \, .$$

The Clebsch-Gordan coefficients of the partial waves of the conduction electrons concerned in the resonant scattering mechanism with a light-rare-earth ion are identical to those determined for a cerium ion since, for the light-rare-earth ion, the orbital momentum and the spin of the $4f$ electrons are antiparallel as for cerium.

Thus in the light-rare-earth alloys, the total $4f$ momentum and the total conduction-electron momentum are antiparallel when Γ is negative and a Kondo effect is possible.

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