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RESISTIVITY MINIMUM IN Pd : Pr DILUTE ALLOYS

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Résumé. — Nous avons mesuré la résistivité électrique de quelques alliages Pd$_{1-x}$Pr$_x$ ($x = 0.02$ et 0.03) entre 1.5 et 300 K. Des minima de résistivité ont été observés vers 20 K. En dessous de ces minima, la résistivité électrique varie linéairement avec log$_{10}$ $T$ mais avec un changement de pente vers 4 K. Dans des composés cubiques de praséodyme, un tel minimum résultant d’un effet du champ cristallin peut être observé quand le triplet $J_3$ est le niveau fondamental. Cependant, l’accord entre les valeurs calculées avec la formule de Hirst qui tient compte du champ cristallin et les résultats expérimentaux est très mauvais. A titre de comparaison, nous avons mesuré la résistivité électrique de composés dilués Pd : Sm et Pd : Tm et des composés définis PrPd$_3$ et SmPd$_3$ qui ne présentent pas de minimum de résistivité. Nous avons également mesuré la susceptibilité magnétique du composé Pd$_{0.98}$Pr$_{0.02}$.

Abstract. — The electrical resistivity of some Pd$_{1-x}$Pr$_x$ ($x = 0.02$ and 0.03) alloys has been measured between 1.5 and 300 K. Resistivity minima have been observed around 20 K. Below the minimum, the resistivity varies linearly with log$_{10}$ $T$ but there is a slope change at about 4 K. In praseodymium cubic compounds, such a resistivity minimum resulting from a crystal field effect may be observed when the $J_3$ triplet is the ground state. However, the agreement between the values calculated with Hirst’s formula, which takes into account the crystal field and the experimental values is very bad. For comparison, we have measured the electrical resistivity of Pd : Sm and Pd : Tm dilute compounds which exhibit no resistivity minimum, in the same way as PrPd$_3$ and SmPd$_3$. We have also measured the magnetic susceptibility of the compound Pd$_{0.98}$Pr$_{0.02}$.

1. Introduction. — So far, a Kondo effect, due to the praseodymium ion has been observed in two systems : Zr$_{1-x}$Pr$_x$B$_{12}$ ($x \approx 0.01$) [1] and La$_{1-x}$Pr$_x$Sn$_3$ (0.1 $\leq x \leq 1$) [2, 3]. From the decrease of the superconducting transition temperature, Fisk and Matthias [1] deduce that cerium, as impurity in ZrB$_{12}$, is non magnetic. This is also the case for cerium in the definite compound CeSn$_3$ [4]. Thus, one may think that the occurrence of a Kondo phenomenon due to the praseodymium ion is favoured when the cerium ion, placed in the same matrix, is non magnetic. This is also the case for cerium in the definite compound CeSn$_3$ [4]. Thus, one may think that the occurrence of a Kondo phenomenon due to the praseodymium ion is favoured when the cerium ion, placed in the same matrix, is non magnetic. Susceptibility measurements [5, 6] show that the cerium, as impurity in palladium, is non magnetic and no resistivity minimum is observed for this compound between 1.5 and 25 K [6]. In order to observe a Kondo effect, a large density of states at the Fermi level is also favourable. For these reasons, we have chosen to study the Pd : Pr dilute alloys.

2. Experiment. — The purity of the palladium and of the praseodymium were respectively 99.99 % and 99.9 %. The Pd$_{0.97}$X$_{0.03}$ (X = Pr, Sm, Tm) alloys have been melted on a water-cooled copper floating boat with an induction technique and very rapidly quenched. The compounds Pd$_{0.98}$Pr$_{0.02}$, Pd$_{0.98}$Lu$_{0.02}$, PrPd$_3$ and SmPd$_3$ have been melted in an induction furnace in alumina crucibles. Samples of approximate dimensions 1.5 $\times$ 1.5 $\times$ 15 mm$^3$ have been cut by spark erosion. X-ray measurements on the dilute Pd : X alloys showed a f.c.c. structure with a parameter close to the lattice constant of the palladium.

The electrical resistivity measurements have been performed between 1.5 and 300 K by a classical A.C. four probe technique. Electrical contacts were made by very sharp-pointed brass screws. The relative precision of the measurements is $10^{-3}$ and the absolute precision, including the uncertainties of sample dimen-
sions, is about 2%. The error bars on the temperature are ±0.2 K.

We have also performed susceptibility measurements on two compounds: Pd₀.₉₈Pr₀.₀₂ and Pd₀.₉₈Lu₀.₀₂. The sensitivity of the translation balance is 10⁻⁹ c.m.u. and the relative precision of the measurements between two different compounds of the same shape is 10⁻³.

3. Resistivity measurements. — Praseodymium is soluble in palladium up to a concentration x = 0.02 [7]. The compound Pd₀.₉₈Pr₀.₀₂, melted in an alumina crucible and cooled down relatively slowly, was found by resistivity or susceptibility measurements to be homogeneous within 12%. For rapidly quenched alloys, the limit of solubility of the praseodymium reaches 4% [7]. The compound Pd₀.₉₇Pr₀.₀₃, very rapidly quenched, was quite inhomogeneous owing to the large temperature gradient during the melt. Indeed, five samples were cut in this ingot and showed very different resistivities (Fig. 1).

All these compounds exhibit a resistivity minimum ranging from 15 to 24 K (Figs. 1 and 2) except the sample 5 (Fig. 1) which has a residual resistivity close to the palladium value and thus a very small Pr concentration.

The resistivity versus T at low temperature of all these compounds varies approximately linearly (Figs. 1 and 2). Plotted versus log₁₀ T (Fig. 3), the differences Δρ = ρ(sample i) − ρ(Pd), vary linearly versus log₁₀ T but there is a slope change at 4 K. This result is also valid for the homogeneous Pd₀.₉₈Pr₀.₀₂ alloy. For all these compounds, after subtraction of the resistivity of sample 5, the resistivity minimum is at about 25 K and the depth of the minimum is about 6%. Therefore, sample 5 might be considered to be the correct matrix resistivity. In this case, when plotting Δρ versus log₁₀ T, the slope change at 4 K would be slightly increased.
By contrast, the compounds Pd_{0.97}Sm_{0.03} and Pd_{0.97}Tm_{0.03}, which have been prepared with the same technique as the Pd_{0.97}Pr_{0.03} alloys, do not exhibit any resistivity minimum (Fig. 4) in a similar way to PrPd_{3} and SmPd_{3}.

All these results show without ambiguity that the resistivity minimum of the Pd : Pr alloys is a genuine property of the system.

4. Discussion. — From the low temperature resistivity behaviour of the Pd : Pr dilute alloys, we may expect that the ground state is the \( \Gamma_{5} \) triplet (or that it is quite close to the lowest level). We have then tried to explain the observed resistivity minimum by a crystal field effect. Indeed, in Pr cubic compounds, a resistivity minimum may be observed but only when the \( \Gamma_{5} \) triplet is the ground state. The temperature dependent spin disorder resistivity due to the scattering of the conduction electrons by the crystal field levels has been calculated by Hirst [8]. It can be written

\[
\rho = \rho_{\text{ex}} \operatorname{tr} (PQ^{\text{ex}})
\]

where the trace is taken over the \( 2 J + 1 \) crystal field states \( |i\rangle \) whose energies are \( E_{i} \). The matrices \( P \) and \( Q^{\text{ex}} \) are:

\[
P_{ij} = \frac{\exp(-E_{i}/k_{B}T)}{\sum_{k} \exp(-E_{k}/k_{B}T)} \left( E_{i} - E_{j} \right) / k_{B}T
\]

and

\[
Q_{ii}^{\text{ex}} = \left| \langle i | J_{z} | j \rangle \right|^{2} + \frac{1}{2} \left| \langle i | J^{+} | j \rangle \right|^{2} + \frac{1}{2} \left| \langle i | J^{-} | j \rangle \right|^{2}
\]

where \( k_{B} \) is the Boltzmann constant and \( \rho_{\text{ex}} \) is a constant which depends on the 4f-conduction electron interaction strength.

We have then attempted to explain the low temperature resistivity curves, trying a large number of crystalline electric field (CEF) parameters with the \( \Gamma_{5} \) triplet as ground state. The agreement between calculated (Fig. 5) and experimental values is very poor. As there is a large density of d states at the Fermi level, it is probably necessary to take into account aspherical Coulomb scattering [9, 10] as suggested by Guertin et al. [6]. It is then useful to determine the CEF parameters. In the dilute Pd : Er alloys, these parameters have been obtained by Murani et al. [11] by neutron spectroscopy. They have found, using the classical notations of Lea et al. [12],

\[
W = -0.17 \text{ K} \quad \text{and} \quad x = 0.47
\]

and

\[
W(1 - |x|) = A_{6} \gamma \langle r^{6} \rangle F_{6}
\]

and \( A_{6} = 2.74 \) has been calculated by Freeman and Watson [13]. With these CEF parameters, the ground state is the \( \Gamma_{5} \) triplet, in agreement with the resistivity measurements. With the close values,

\[
W = -4.3 \text{ K} \quad \text{and} \quad x = -0.7365
\]
it is possible to explain qualitatively the curves of figure 3 in terms of a Kondo effect. In fact, between 1.5 and 4 K the spin disorder resistivity, calculated with these parameters, increases rapidly (see the dashed curve of figure 5) and then there is a plateau, which might explain the slope change at 4 K of the resistivity curves of figure 3. Above 15 K, the resistivity increases again rapidly which might lead to the observed resistivity minima, the decreasing logarithmic resistivity term being compensated by the increase of the spin disorder resistivity. Of course, these values of $W$ and $x$ would be only approximate. We may then remark that, with these CEF parameters, the ground state is the doublet $\Gamma_3$, the triplet $\Gamma_5$ being situated 0.2 K higher. However, our measurements, made above 1.5 K, cannot give evidence of this fact.

Finally, deviations from Matthiessen’s rule [14] might also give a contribution to the anomalous low temperature variation of the resistivity of the Pd : Pr dilute alloys.

In order to understand these results better, we performed susceptibility measurements.

5. Susceptibility measurements. — The magnetic susceptibility of two Pd$_{0.96}$Pr$_{0.02}$ samples (1 and 2), cut in the same ingot, has been measured between 4 and 300 K. At 4 K, the susceptibility of the sample 1 slightly exceeds that of sample 2 (by 12 %) (Fig. 6).

![Fig. 6. Reciprocal susceptibilities of two compounds Pd$_{0.96}$Pr$_{0.02}$ versus temperature after correction for the Pd$_{0.98}$Lu$_{0.02}$ matrix susceptibility.](image)

indicating that the Pr concentration of these two samples differs by about 12 %; indeed at this temperature, the matrix susceptibility is weak (about 13 % of the Pr susceptibility). At room temperature, the susceptibility of our palladium is:

$$\chi = 0.581 \times 10^{-3} \text{ e.m.u./Mole}$$

$$= 1.003 \chi (\text{sample 1}) = 0.986 \chi (\text{sample 2})$$

Quite clearly, it is not correct to subtract the susceptibility of the palladium so as to obtain the Pr contribution since this would lead, at room temperature, to $\chi_{\text{Pr}} \simeq 10^{-3}$ e.m.u./Mole or smaller values whereas one should find $\chi_{\text{Pr}} \simeq 5 \times 10^{-3}$ e.m.u./Mole. The best matrix contribution to subtract would be the susceptibility of a Pd$_{0.98}$La$_{0.02}$ compound. However, lanthanum is soluble in palladium only when the alloy is cooled very rapidly [7]. In this case, the alloy will be as inhomogeneous as our Pd$_{0.97}$Pr$_{0.03}$ compound. It is then, necessary to consider that the correct matrix is Pd$_{0.98}$Lu$_{0.02}$ as was used by Shaltiel et al. [5]. For this compound, our measurements are in agreement with those of Guertin et al. [6]. The corrected reciprocal susceptibilities are shown in figure 6. We may now comment that sample 2, which has a smaller Pr concentration than sample 1, has a larger susceptibility at room temperature. This is easy to explain : if we consider that the Pr concentration of sample 1 is exactly 2 %, then that of sample 2 will be about 1.8 % so that the matrix susceptibility to subtract will be that of Pd$_{0.98}$Lu$_{0.02}$.

At room temperature, this variation of the matrix contribution with the Lu concentration may be estimated from the work of Guertin et al. [6] to be $2 \times 10^{-5}$ e.m.u./Mole, the Pd : Lu susceptibility decreasing when the Lu concentration increases. Thus, for the sample 2, a larger matrix susceptibility should be subtracted.

After correction for the matrix contribution the low temperature Curie constants are respectively 1.35 and 1.4, whereas the theoretical Curie constant of Pr$^{3+}$ is 1.6. This shows that the $\Gamma_5$ triplet is the ground state (or that it is quite close to the ground state). The high temperature Curie constant of the two samples, measured between 100 and 200 K is $C = 2.5$, showing that the Pr concentration of our samples is slightly larger than 2 %. Indeed, in this temperature region, since the matrix susceptibility has the same order of magnitude as the Pr susceptibility, a small change in the Pr concentration will lead to a large variation of the Curie constant. With the parameters which may explain a possible Kondo effect : $W = -4.3$ K, $x = -0.736$ 5, the low temperature calculated Curie constant is $C \simeq 1.2$, in good agreement with the experimental values since the Pr concentration of our samples slightly exceeds 2 %.

6. Conclusion. — At present, it is not possible to say if the resistivity minimum observed in the Pd$_{1-x}$Pr$_x$ compounds arises from a Kondo effect or from a crystal field effect including aspherical Coulomb
scattering. For these compounds, susceptibility measurements give rather poor indications about the crystal field level scheme and neutron spectroscopy would not probably be efficient owing to the small Pr moment and the weak Pr concentration. Low temperature resistivity measurements might lead to the correct interpretation.

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