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Preparation and electrical resistivity of $(Pu_{1-x}U_x)Sb$ and $(Pu_{1-x}Y_x)Sb$ single crystals

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Abstract

Single crystals of $(Pu_{1-x}U_x)Sb$ (with $x=0.25$, 0.5 and 0.75) and $(Pu_{1-x}Y_x)Sb$ (with $x=0.05$, 0.1, 0.4, 0.6, 0.75 and 0.85) were prepared by mineralization and encapsulated for resistivity measurements down to 1.5 K. Resistivity of $Pu_{0.75}U_{0.25}Sb$ shows two anomalies at 96 and 56 K suggesting two magnetic transitions, respectively, of antiferromagnetic and ferromagnetic type. $Pu_{0.5}U_{0.5}Sb$ displays a more complex behavior. A first transition is observed around 155 K, followed by a sharp maximum at 120 K and a second anomaly around 35 K. $Pu_{1-x}Y_xSb$ measured samples show a logarithmic increase of the resistivity with decreasing temperature, suggesting a Kondo behavior. For $x=0.4$ and 0.6 two magnetic transitions are deduced at 36/20 K and 24/7 K, respectively, and for $x=0.75$ only one transition is seen around 14 K. © 1998 Elsevier Science S.A.

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1. Introduction

Actinide monopnictides (with elements of group VA) and monochalcogenides (with elements of group VIA) are among the largest group of actinide materials being studied for more than 20 years (see, for reviews, Refs. [1–4]). Despite intensive efforts, the electronic structure of these materials remains elusive. To shed light on the electronic properties of these actinide rock salt compounds, studies of solid solutions have been started during the last decade (see, e.g. Refs. [1–5]). As far as transuranium compounds are concerned, PuSb is one of the most interesting and most studied. The magnetic properties are well known but not yet completely understood. Briefly, PuSb undergoes an antiferromagnetic transition, at around 85 K, of an incommensurate-type magnetic structure and displays, below 70 K, a second transition to a ferromagnetic type [1–4]. However, an understanding of the complex behavior of PuSb has been further complicated by variations in the transition temperatures as determined by the different measurements and the age of the sample studied, with T_C varying from 56 to 75 K and T_N from 76 to 85 K [6]. In the continuation of the investigation of this compound, we have prepared single crystals of $(Pu_{1-x}U_x)Sb$ and $(Pu_{1-x}Y_x)Sb$ solid solutions and measured their electrical resistivity.

2. Preparation of the samples

The starting polycrystalline materials, USb and YSb, were prepared by solid–vapor reaction in quartz ampoules, and PuSb by crushing single crystals formerly obtained by the mineralization technique described by Spirlet and Vogt [7]. Charges of 15–20 g of pelletized powders of stoichiometric amounts of the starting materials were encapsulated in a tungsten crucible by electron beam melting and then heated for several days (about 200 h) a few degrees below the estimated melting point of the compound. The temperature was then slowly decreased by steps of about 100°C, during 8 h, down to 1000°C and then cooled to room temperature according to the thermal inertia of our furnace. Large single crystals of $(Pu_{0.75}U_{0.25})Sb$, $(Pu_{0.5}U_{0.5})Sb$, $(Pu_{0.25}U_{0.75})Sb$, $(Pu_{0.95}Y_{0.05})Sb$, $(Pu_{0.9}Y_{0.1})Sb$, $(Pu_{0.6}Y_{0.4})Sb$, $(Pu_{0.4}Y_{0.6})Sb$, $(Pu_{0.25}Y_{0.75})Sb$ and $(Pu_{0.15}Y_{0.85})Sb$ were obtained. The samples were characterized by powder X-ray diffraction on crushed single crystals in a Debye–Scherrer camera (114.6 mm diameter) using the Cu Kβ radiation filtered by Ni. All

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Table 1
Lattice parameters, characteristic temperatures and fit parameters of the known electrical resistivity of $(Pu_{1-x}U_x)Sb$ and $(Pu_{1-x}Y_x)Sb$ compounds

Compound	Lattice parameter a (pm)	$T\rho_{max}$ [Ref.] (K)	T_N [Ref.] (K)	T_C [Ref.] (K)	$\rho_{300\ K}$ [Ref.] (μΩ cm)	A (μΩ cm K^{-2}) ($\rho=\rho_0+AT^2$)	b/a (1/ln K) ($\rho=a-b\cdot\ln T$)
PuSb	623.7(1)	103 [12]	82 [12]	59 [12]	675 [12]	0.0906 [12]	0.950 [8]
$Pu_{0.75}U_{0.25}Sb$	623.9(1)	134	96	56	750	0.102	0.044
$Pu_{0.5}U_{0.5}Sb$	622.3(1)	123/111	155/135	35/10	400	—	—
$Pu_{0.25}U_{0.75}Sb$	621.4(3)	—	—	—	—	—	—
USb	620.6(1)	140 [13]	215 [13]	—	600 [13]	T^4-type [13]	—
$Pu_{0.95}Y_{0.05}Sb$	624.2(1)	100 [8]	—	—	1710 [8]	T^2-type [8]	0.104 [8]
$Pu_{0.9}Y_{0.1}Sb$	624.0(1)	90 [8]	—	—	2080 [8]	T^2-type [8]	1.106 [8]
$Pu_{0.6}Y_{0.4}Sb$	621.8(1)	58	36	20	410	0.170	0.112
$Pu_{0.4}Y_{0.6}Sb$	620.2(3)	45	24	7	150	0.150	0.092
$Pu_{0.25}Y_{0.75}Sb$	619.3(2)	40	14	—	137	0.120	0.028
$Pu_{0.15}Y_{0.85}Sb$	615.2(1)	—	—	—	—	—	—
YSb	616.45 [9]	—	—	—	—	—	—

—, not measured or not indicated in the Ref.

samples were found to crystallize in the NaCl-type structure with the lattice parameters listed in Table 1.

3. Electrical resistivity measurements

Large single crystals (of about 4×2×1 mm^3) were encapsulated for electrical resistivity measurements using a technique developed at the CEN-Grenoble and described by Pleska [10]. No care was given to the orientation of the crystal. Measurements were performed down to 1.5 K with a conventional four-probe AC method [11].

3.1. $(Pu_{1-x}u_x)Sb$ solid solutions

In this section we present the resistivity curves obtained in the case of the study of the PuSb–USb system. We recall

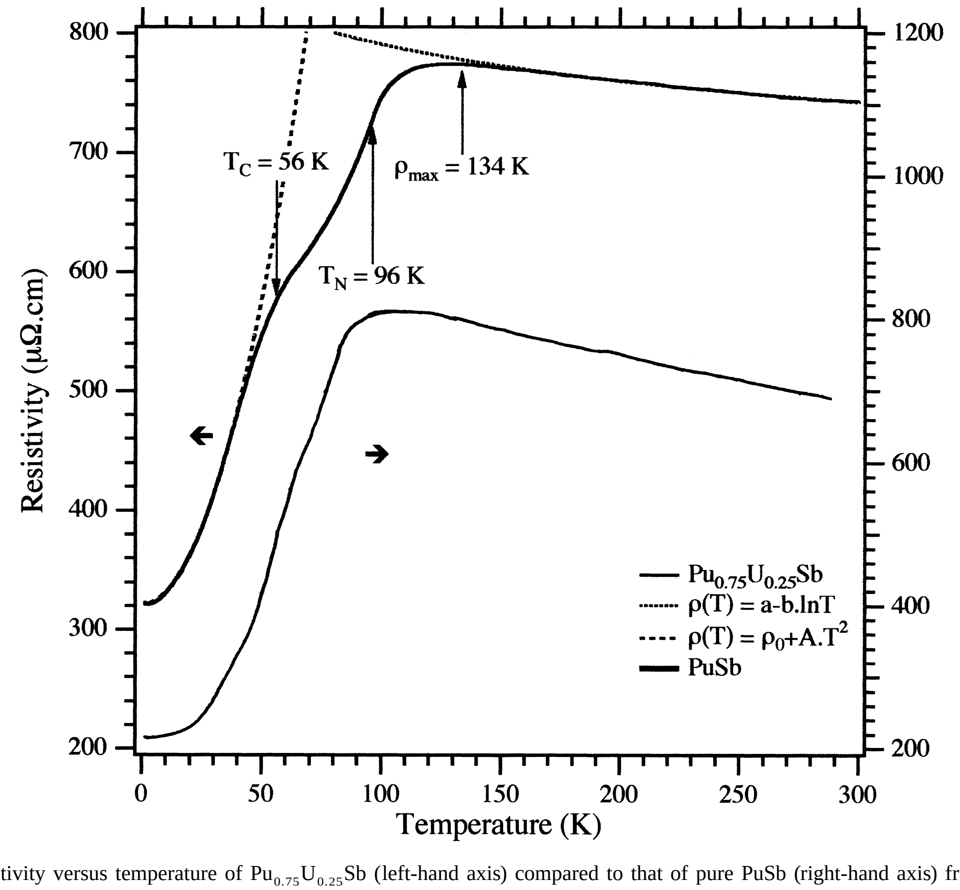

Fig. 1. Electrical resistivity versus temperature of $Pu_{0.75}U_{0.25}Sb$ (left-hand axis) compared to that of pure PuSb (right-hand axis) from Ref. [12]. Dashed lines represent the fits of the equations given in the inset with characteristics parameters given in Table 1.

first some typical features observed in the resistivity of the pure compounds.

The resistivity of the pure PuSb was already extensively described by Thérond [12]. According to the known magnetic properties of PuSb, three zones are distinguishable. The ferromagnetic zone, below 60 K, is characterized by a quadratic variation of the resistivity as a function of the temperature (at least between 15 and 51 K). The incommensurate zone, between 60 and 80 K (or more precisely between T_C and T_N), is characterized by a linear increase of the resistivity versus the temperature, and the paramagnetic zone marked by a large maximum around 103 K and a logarithmic decrease over 110 K assigned to a Kondo-type behavior.

The resistivity of pure USb, presented by Schoenes et al. [13], is characterized by a very large and broad maximum centered at 140 K with a value of more than 1000 μΩ cm typical for a semimetal, the Neel temperature appears as a maximum in $d\rho/dT$ at 215 K, and up to 45 K a T^4 behavior is observed. The appearance of the huge maximum around 140 K was interpreted as the signature of the triple-k type I antiferromagnetic structure (see, e.g. Ref. [3]).

Our resistivity curve obtained for $Pu_{0.75}U_{0.25}Sb$ is displayed in Fig. 1, we enclose a reproduction of the pure PuSb curve shown in Ref. [12] for comparison. The resistivity of the two compounds displays essentially the same features. In $Pu_{0.75}U_{0.25}Sb$ two clear anomalies are presented around 56 and 96 K. By analogy to pure PuSb, we may understand these anomalies as the appearance of a ferromagnetic transition around 56 K and an antiferromagnetic transition around 96 K. Up to 40 K a quadratic variation of the $\rho_0+A\cdot T^2$ type, with $\rho_0=321$ μΩ cm and $A=0.102$ μΩ cm K^{-2} (compared to 0.0906 μΩ cm K^{-2} for PuSb [12]), fits very well the experimental data and is attributed to electron–phonon scattering phenomena in a ferromagnet. In contrast to PuSb, no clear linear variation of the resistivity is observed between T_C and T_N, a T^4-law would eventually satisfy the experimental data. In the paramagnetic state, we observe a broad maximum around 130 K, which could be attributed to a variation of the resistivity due to crystal field effects or due to coherent phenomena in the Kondo lattice before ordering. Over 150 K, a logarithmic decrease of the resistivity as a function of the temperature is seen, which could be fitted with an $a-b\cdot\ln T$ type law, with $a=994$ μΩ cm and $b=44.2$ μΩ cm/ln K, suggesting a Kondo-type behavior at higher temperature.

In the case of $Pu_{0.5}U_{0.5}Sb$, the resistivity measurements performed first with decreasing temperature down to 1.5 K, then with increasing temperature, display a remarkable hysteresis phenomenon. Between 5 and 190 K, the two curves present the same general fingerprints but are shifted, respectively, to each other by about 15 K (Fig. 2). Outside

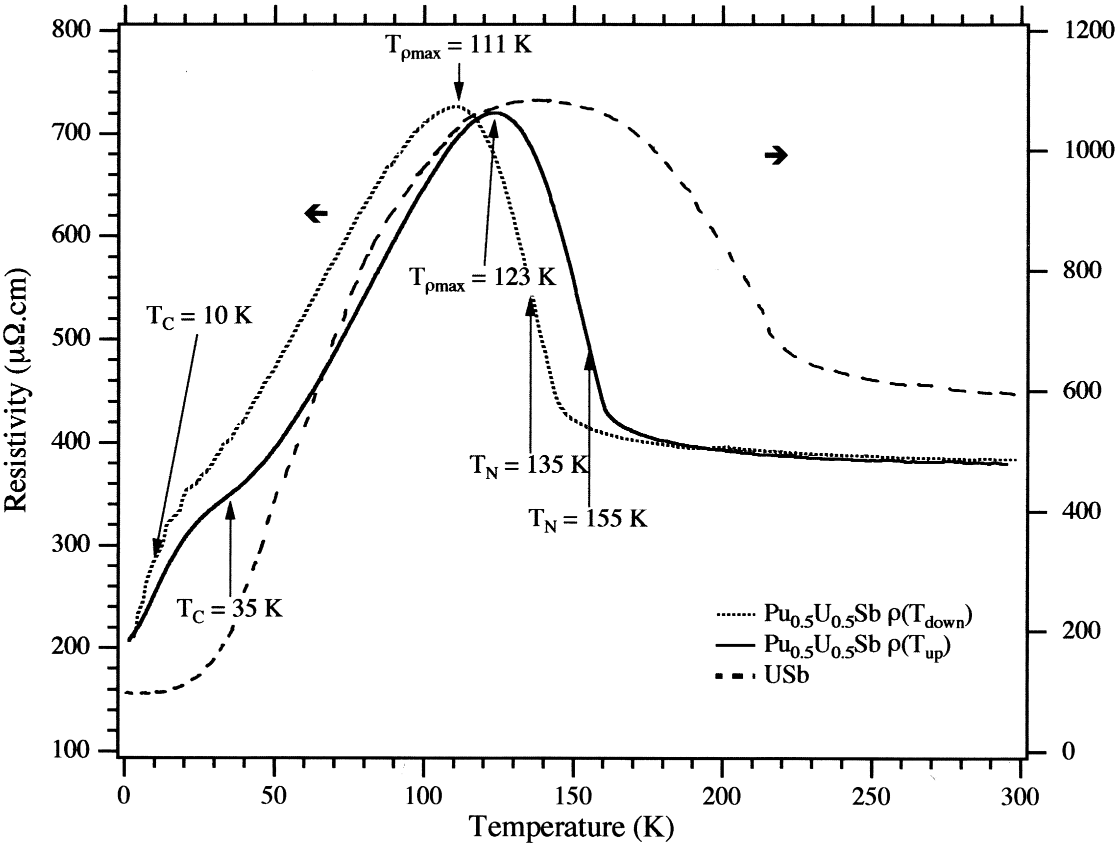

Fig. 2. Electrical resistivity versus temperature of $Pu_{0.5}U_{0.5}Sb$ (left-hand axis) compared to that of pure USb (right-hand axis) from Ref. [13].

this temperature range the measured resistivity values coincide. This observation could not be explained by an experimental artefact and, moreover, was reproducible. At the present stage only resistivity measurements were performed on this compound and, therefore, do not allow a direct explanation of this phenomenon. Apart of the hysteresis mentioned above, the variation of the resistivity versus the temperature is very similar to that of USb, redrawn in Fig. 2 (from Ref. [13]). It is characterized by a large and broad maximum centered at 123 K (for T up) or 111 K (for T down) which could be related to the signature of a triple-k antiferromagnetic structure, the Neel temperature appears as a maximum in $d\rho/dT$ at 155 K (T up) or 135 K (T down). However, a second anomaly is seen around 35 K (T up) or 10 K (T down). This second anomaly recalls the one observed for pure PuSb or $Pu_{0.75}U_{0.25}Sb$, and may suggest that $Pu_{0.5}U_{0.5}Sb$ undergoes a second transition at low temperature in a ferromagnetic state. Finally at low temperature no T^2- or T^4-type behavior is observed. In fact, a linear increase of ρ with T, of the type encountered in non-Fermi liquid systems, seems to describe better the experimental data.

3.2. $(Pu_{1-x}y_x)$Sb solid solutions

By diluting PuSb with nonmagnetic YSb it is intended to decrease the exchange forces, and one should by using this method be able to approach the localized state and get unambiguous evidence on the underlying crystal-field interactions being almost unaffected by diluting effects. Amanowicz [8] reported resistivity measurements on $Pu_{0.95}Y_{0.05}Sb$ and $Pu_{0.9}Y_{0.1}Sb$. In both compounds a logarithmic decrease of the resistivity with the temperature was observed above 130 K and suggested a Kondo behavior. The increase of the slope b of the $a-b\cdot\ln T$ type law, as a function of the Y concentration (x), indicated a reduction of the Kondo temperature by increasing x. At low temperature (between 15 and 50 K) the data could be adjusted according to a $\rho_0+A\cdot T^2$ type law, with A being proportional to x. No information on possible ordering transition were reported.

In Fig. 3 we present the resistivity curves obtained for our samples $(Pu_{0.6}Y_{0.4})Sb$, $(Pu_{0.4}Y_{0.6})Sb$ and $(Pu_{0.25}Y_{0.75})Sb$. For a better overview of these results we choose to present them in the form of the resistivity ratio

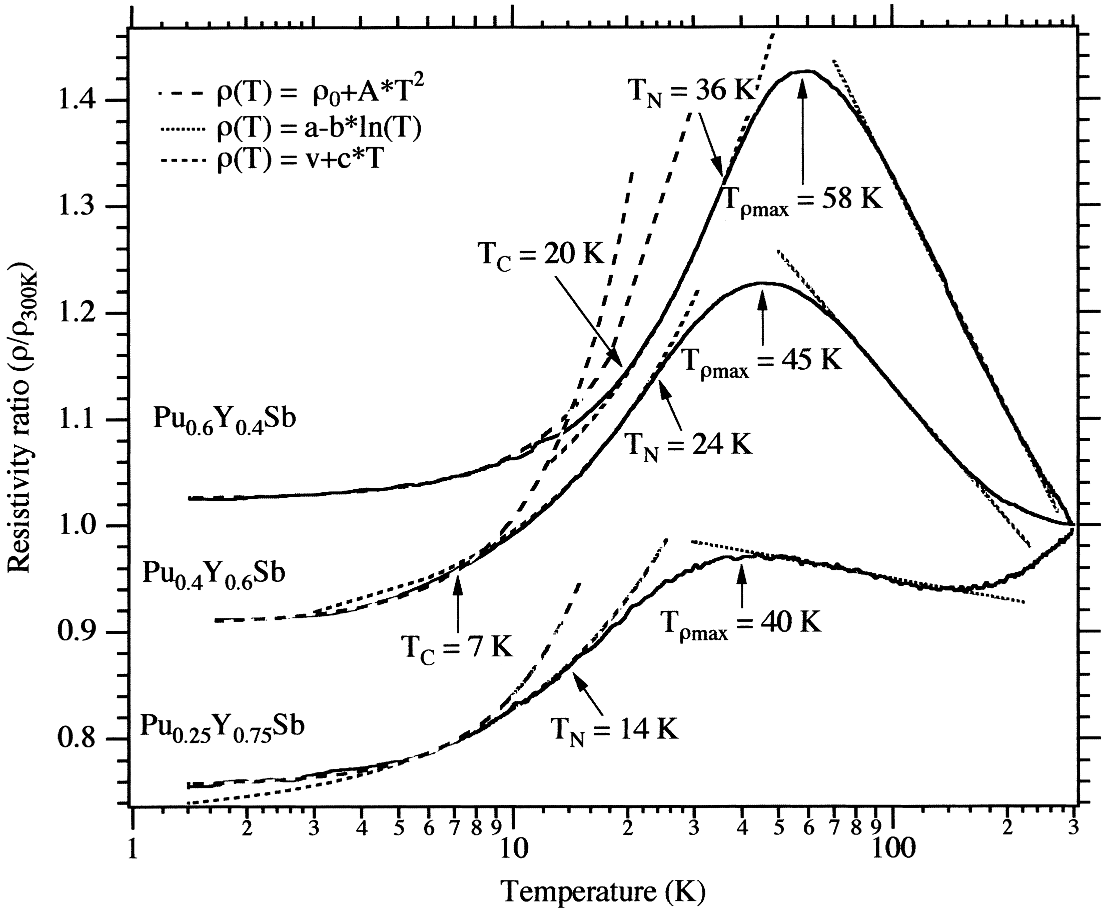

Fig. 3. Electrical resistivity versus a logarithmic scale of temperature of $Pu_{1-x}Y_xSb$ single crystals. Dashed lines represents the fits of the equations given in inset with characteristics parameters given in Table 1.

$\rho/\rho_{300\ \mathrm{K}}$ versus a logarithmic scale of temperature. The three new compounds display the same features. At low temperature, a quadratic variation of the resistivity fits well the experimental points. Then, as the temperature increases, a linear variation is observed. By analogy with the pure PuSb compound (see Section 3.1 and Ref. [12]) we attributed the lower and upper limit of this linear zone to magnetic transition of ferromagnetic and antiferromagnetic type, respectively. The transition temperatures so deduced are in good agreement with those obtained by Vogt et al. [14] in recent preliminary results of magnetic susceptibility measurements on the same systems. In the paramagnetic state, the resistivities go through a broad maximum, which may be related to crystal field effects, the magnetic ions being well diluted in our systems. Over this maximum, the logarithmic decrease of the resistivity may be understood as a Kondo behavior. At higher temperatures, the curves deviate from a Kondo-type comportment. This can be related to the relative enhancement of the phonon contribution with regard to the magnon contribution. This is in a sense corroborated by the fact that this effect increases with the dilution of the Pu magnetic ions and by the relatively low value of the resistivity measured at room temperature (see Table 1). We may suggest that below $x=0.4$, the system approaches the ideal case of localized state.

4. Conclusions

Single crystals of $(\mathrm{Pu}_{1-x}\mathrm{U}_x)\mathrm{Sb}$ and $(\mathrm{Pu}_{1-x}\mathrm{Y}_x)\mathrm{Sb}$ solid solutions were produced and characterized. In order to provide a first characterization of their physical properties we have investigated their electrical resistivity. On the limited basis of these results alone and by analogy with related systems, we have proposed a first scheme of their magnetic properties and extracted some characteristic parameters listed for summary in Table 1. Further experiments, such as magnetic susceptibility and magnetization, as well as neutron and X-ray magnetic scattering (on $(\mathrm{Pu}_{1-x}\mathrm{U}_x)\mathrm{Sb}$), on these newly obtained systems are planned in a near future.

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