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The electrical resistance of PuSb under high pressure

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Abstract

A new experimental set-up with a Bridgman-type high pressure cell in a closed containment allows resistance measurements on highly radioactive materials. We present results of high pressure, low temperature studies on PuSb single crystals in the pressure range to 25 GPa and at temperatures between 1.3 K and 300 K. As pressure on PuSb is increased, its Néel temperature and the transition temperature to the ferromagnetic ground state are increased. In the pressure range from 10 to 15 GPa, we observed a strong decrease in the resistance associated with the crystallographic phase transition from the B1 (NaCl) to the B2 (CsCl) structure. The high pressure phase appears to be non-magnetic.

1. Introduction

The magnetic properties of the light actinide compounds are strongly influenced by the degree of itinerancy of the 5f electrons. The localized or itinerant behaviour depending on the actinide–actinide distance is well displayed in the Hill plots [1]. Localized 5f electrons and magnetism are mainly found in compounds in which the actinide–actinide distance is larger than the Hill limit. Unfortunately, Hill plots take only direct 5f electron overlap into account and therefore exceptions occur whenever other mechanisms of band formation involving 5f electrons (*i.e.* hybridization) with ligand electrons become important. One difficulty in discussing the Hill plots is that a change in the actinide–actinide distance is usually accompanied by a change in the chemical composition also in comparing different compounds. High pressure experiments are therefore attractive for studying the influence of the actinide–actinide distance, as the composition is kept invariant.

Because of their radiotoxicity, handling of the transuranium elements is difficult and restricted to specially equipped laboratories. At the Institute for Transuranium Elements in Karlsruhe, Germany, we constructed an experimental set-up to measure the electrical resistance under high pressure. A glove-box allows the preparation and loading of radioactive samples in a Bridgman-type high pressure cell. We present here a study of PuSb, a substance whose complicated magnetic phase diagram has already been the subject of several investigations at ambient pressure.

2. Experimental details

The measurements were performed in a liquid helium bath cryostat. By pumping on the bath, temperatures down to 1.3 K were accessible. The press is of the opposed anvil type. The anvils are fabricated of sintered diamonds with a flat surface 2 mm in diameter, which allowed pressures up to 28 GPa to be attained. The press and the high pressure cell have been described elsewhere [2, 3]. The temperature was measured with a Pt100 platinum resistor between 300 K and 50 K, and with a calibrated Ge resistor below 50 K. The pressure was determined from the superconducting transition temperature of a small Pb foil placed next to the sample, using the calibration table of Bireckoven and Wittig [4]. The sample's resistance, as well as that of the Pb, were measured by a four-probe d.c. method. The preparation of PuSb single crystals has been described elsewhere [5]. The samples were flat plates cleaved perpendicular to the [100] axis of a PuSb single crystal.

3. Results

We measured the resistance of PuSb in the temperature range from 300 K to 1.3 K at pressures up

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to 25 GPa. Figure 1 shows that the temperature dependence of the resistance at the lowest pressures is in good agreement with the ambient pressure resistivity curve given by Blaise *et al.* [6]. With increasing pressure, the maximum of the resistance is shifted to higher temperatures and the decrease in the resistance with increasing temperature becomes less pronounced (Fig. 1). As seen from Fig. 2 the temperature derivative of the resistance features two maxima in agreement with the ambient pressure behaviour. The maximum (or

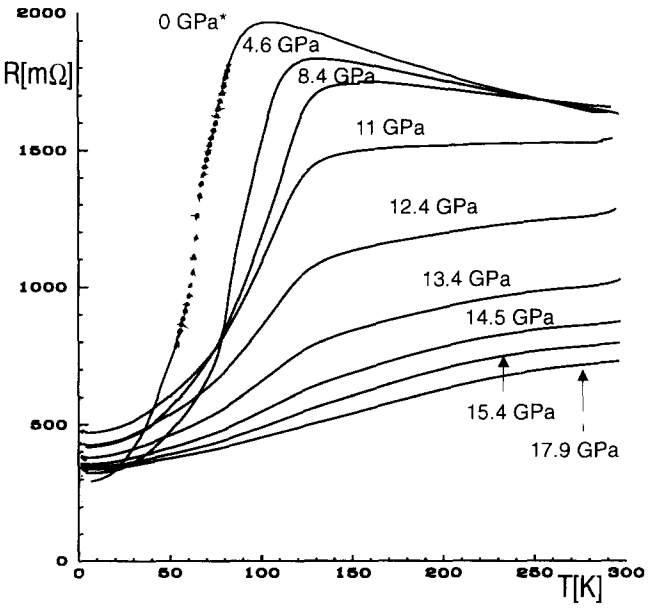

Fig. 1. The electrical resistance of PuSb at selected pressures up to 18 GPa. The zero pressure curve represents rescaled data from Blaise *et al.* [6].

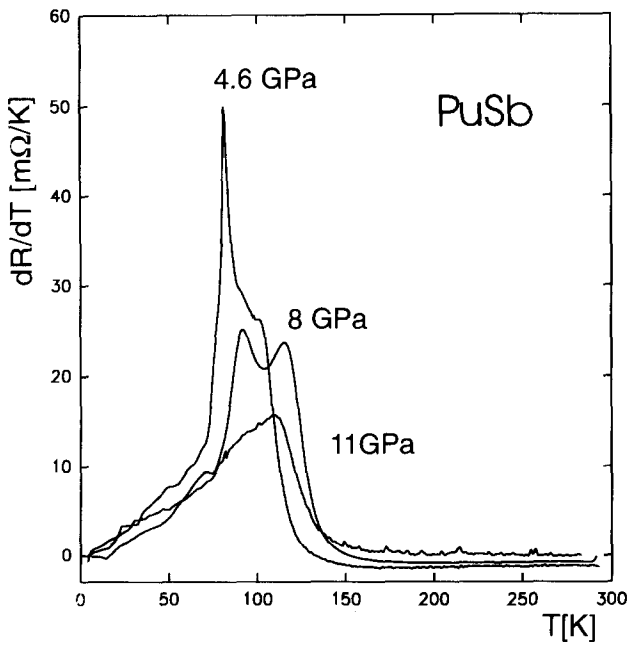

Fig. 2. Typical dR/dT curves of PuSb at selected pressures.

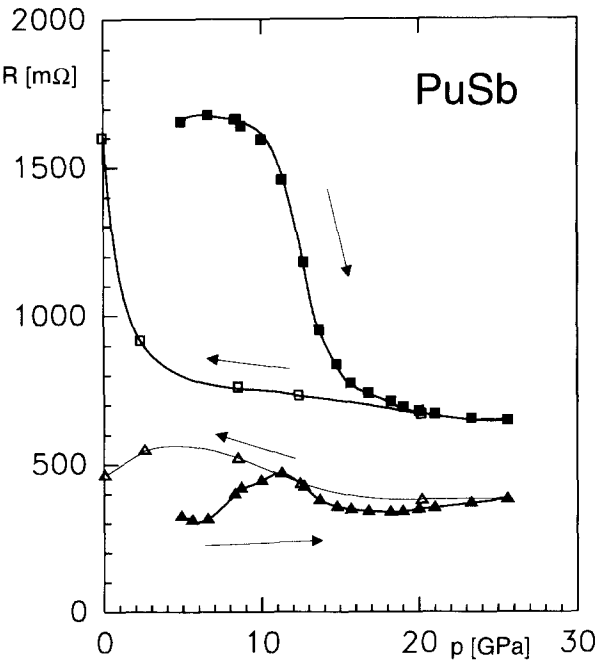

Fig. 3. The resistance of PuSb *vs.* pressure at 273 K (■, □) and 4.2 K (▲, △) for increasing (■, ▲) and decreasing (□, △) pressure.

shoulder) at higher temperatures indicates the Néel temperature, which increases from 82 K to 112 K at 8 GPa. The low temperature peak is associated with the temperature of the transition from the incommensurate antiferromagnetic phase to the ferromagnetic ground state, which increases from 65 K to 80 K. Above 8 GPa this phase transition disappeared.

In the pressure range from 10 to 15 GPa the electrical resistance at the higher temperatures decreases strongly, as shown by the isobars at 11 GPa–14.5 GPa in Fig. 1. The resistance at 4.2 K has a maximum at 12 GPa, almost coinciding with the pressure where the resistance at 273 K decreases most steeply (Fig. 3). In the same pressure range the maximum in dR/dT related to the Néel temperature disappears. The temperature dependence of the resistance above 15 GPa shows no sign of magnetic ordering, most obviously displayed in the resistance at 25 GPa (Fig. 4). On release of pressure, the resistance at 273 K increases slightly (Fig. 3). Below 2.5 GPa, it increased sharply to the ambient pressure value (Fig. 3).

4. Discussion

The high pressure behaviour of PuSb determined by our resistance measurements is dominated by the pronounced changes found above 8 GPa. These changes might be related to a crystallographic phase transformation, as will be discussed later.

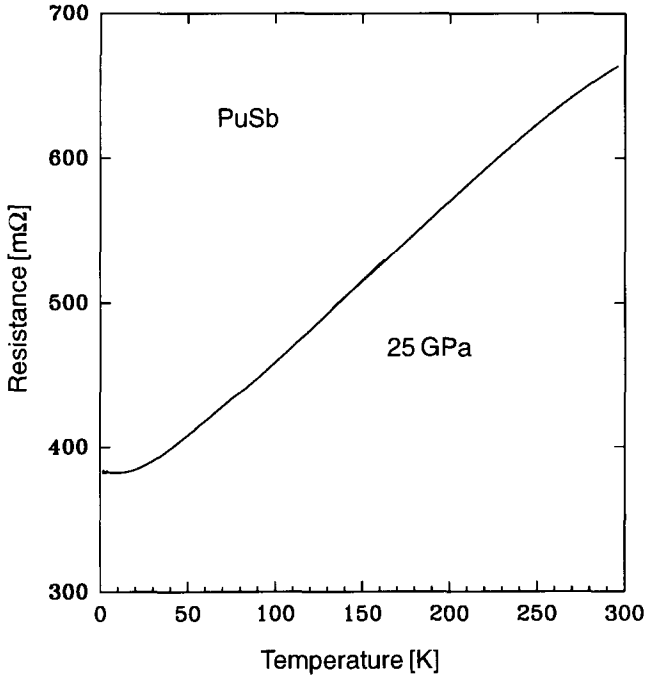

Fig. 4. The resistance of PuSb at 25 GPa.

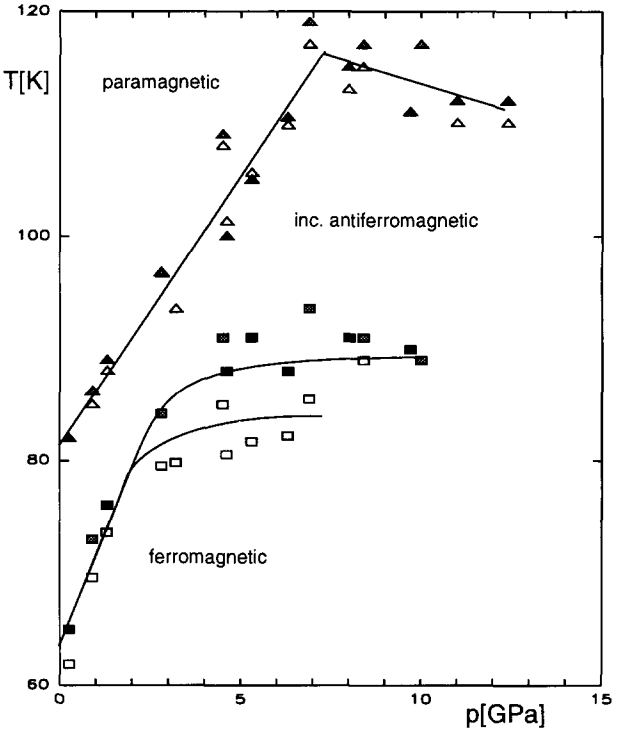

Fig. 5. Magnetic phase diagram of PuSb, derived from measurement of the electrical resistance as a function of pressure and temperature: Néel temperature T_N (▲, △) and transition temperature T_{IC} (■, □) for increasing (▲, ■) and decreasing (△, □) temperature.

In the low pressure region up to 8 GPa three properties derived from our results call for an explanation. First, there is a strong increase in the Néel temperature from 82 K to 112 K at 8 GPa (Figs. 2 and 5); second, there is the shift in the maximum of the resistance to higher temperatures (Fig. 1); third, there is the weakening of the "Kondo"-like resistance decrease at higher temperatures (Fig. 1). All these features are very reminiscent of the high pressure behaviour of UTe [7]. In UTe, suppression of the Kondo behaviour with pressure leads to a strong increase in the Curie temperature. We propose that the increase in the ordering temperature in PuSb can be understood in the same way.

The magnetic properties of PuSb have been inferred from previous magnetization [8] and neutron diffraction [9] experiments. Cooper *et al.* [8] interpreted the magnetic behaviour of PuSb using a theory for band-hybridization-mediated interaction in moderately delocalized systems. The transition from the incommensurate antiferromagnetic phase to the ferromagnetic ground state is thought to be first order. The observed hysteresis of this transition at higher pressures (Fig. 5) indicates a first-order phase transition.

Above 10 GPa the 273 K resistance of PuSb decreases rapidly to a value of about 40% at 15 GPa (Fig. 3). On releasing pressure the resistance only returns to the original value at pressures below 2.5 GPa. The resistance at 4.2 K has a pronounced maximum at 12 GPa (Fig. 3) which is also shifted to lower pressure during the release of the pressure. This hysteretic behaviour of the resistance is reminiscent of that reported from high pressure X-ray diffraction [10]. According to those investigations, PuSb undergoes a crystallographic phase transition from the NaCl structure type to the CsCl structure type at a pressure between 17 GPa and 20 GPa. The high pressure phase (CsCl structure) remains metastable with decreasing pressure down to 2 GPa. This feature, together with the maximum in the 4.2 K resistance around 12.5 GPa, which can then be explained by the formation of lattice defects (*e.g.* grain boundaries) during the phase transition, supports our interpretation that the profound changes in the resistance between 10 GPa and 15 GPa are caused by the crystallographic phase transition.

The temperature dependence of the resistance at the highest pressures is exponential at temperatures below 20 K and, quite remarkably, almost linear at higher temperatures (Fig. 4). Hence, an indication for magnetic ordering could not be detected. During the crystallographic phase transition the plutonium–plutonium distance decreases from 417 pm to 366 pm, and the metal's coordination number changes from 6 to 8. The value of 366 pm for the Pu–Pu distance is still above the Hill limit for plutonium (330–340 pm) [1], but the decrease of the Pu–Pu distance might increase the degree of the 5f electrons at the phase transition by means of increased 5f–5f overlap, and/or 5f–6d hybridization, and could lead to the absence of magnetic ordering in the high pressure phase. Although

the transition from the NaCl to the CsCl structure occurs in many cases where 5f electrons are not involved, these electrons may be influenced by such a transition. We believe that, in the special case of PuSb at high pressures, the 5f electrons can be delocalized.

5. Conclusion

Our results of the electrical resistance under high pressure of PuSb may well be a conclusive example for demonstrating how this kind of investigation can contribute to the understanding of the physical properties of transuranium metals and compounds. The magnetic ordering temperatures, obtained from the temperature dependence of the resistance at high pressures, allow us to suggest a magnetic phase diagram for PuSb as shown in Fig. 5. The similarity in the pressure dependence of the Néel temperature to previous results for UTe is emphasized. The crystallographic phase transition from the NaCl structure to the CsCl structure leads to a strong decrease in the resistance. The high pressure phase exhibits no anomaly in its electrical resistance and hence no sign of magnetic ordering. We propose that 5f delocalization occurs during the phase transition.

Acknowledgments

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