Thermoelectric properties of strongly correlated compounds AnPd$_3$ (An = Pu, Np)

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INTRODUCTION

In order to advance the fundamental understanding of their thermo-physical properties actinide materials, so important in nuclear energy applications, all aspects of the so-called $5f$-electron challenge need to be tackled [1, 2]. Actinides are characterized by the coexistence of localized and itinerant (delocalized) $5f$-states near the Fermi energy. This dual nature of the $5f$-states leads to many exotic phenomena that are observed in these strongly correlated materials, spanning magnetic ordering, heavy-fermion ground state, unconventional superconductivity, and/or "non-Fermi liquid" state (see Refs. [3, 4, 5, 6, 7, 8]). The special transport properties of the strongly correlated electron systems are related to the formation, near the Fermi level, of a narrow band with lsrge density of states. Therefore, the Seebeck coefficient in these materials, being proportional to the density of states at the Fermi level, often reaches large values and shows characteristic temperature dependence [9, 10]. Exceptionally enhanced thermopower values have been reported for compounds like CePd$_3$ (~120 μV/K around 150 K [11]) and YbAl$_3$ (~-90 μV/K at about 250 K [12]), which are archetypal intermediate valent compounds. Despite intensive theoretical and experimental efforts the electronic structure of their $5f$-electron counterparts is still not well understood. UPd$_3$ crystalizes in the hexagonal crystal structure and shows four phase transitions below 7.8 K, attributed to a succession of antiferroquadrupolar orderings of the uranium ions localized on the quasi-cubic sites of the $d$hcp structure [13, 14]. Depending on a heat treatment, NpPd$_3$ crystallizes in hexagonal (TiNi$_3$-type) and cubic AuCu$_3$-type of structures [15, 16]. The hexagonal NpPd$_3$ (^{hex}NpPd$_3$) exhibits two transitions at 30 and 10 K. It has been suggested that the low temperature transition might be due to ordinary antiferromagnetic ordering while the high temperature one might be caused by a quadrupolar order [17]. The cubic NpPd$_3$ (^{cub}NpPd$_3$) orders antiferromagnetically below 52 K and the magnetic and transport measurements suggests that the transition is first order [16]. PuPd$_3$ crystalizes in the cubic structure and shows an antiferromagnetic order below 24 K [16, 18, 19, 20].

To explore the influence of electronic correlations on the thermoelectric properties in the AnPd$_3$ system, here we present the Seebeck coefficient measurements of NpPd$_3$ and PuPd$_3$ intermetallics. We show that the electrical resistivity shows characteristic behavior of systems with Kondo interactions. The magnitude and overall temperature dependence of the thermoelectric power of NpPd$_3$ and PuPd$_3$ are typical for $4f$- and $5f$-electron strongly correlated materials. For ^{cub}NpPd$_3$ a

sharp transition and change of sign in $S(T)$ at the Néel temperature indicate a first order nature of the magnetic transition, probably accompanied by a large change in the Fermi surface topology. We have also estimated power factor (S^2/ρ) of these materials. It is shown to be relatively high, although much smaller than observed in CePd$_3$.

RESULTS AND DISCUSSION

Polycrystalline samples of NpPd$_3$ and PuPd$_3$ were prepared by arc melting stoichiometric amounts of the elemental components in a Zr-gettered argon atmosphere. The samples were examined by x-ray powder diffraction and the phase composition was determined by energy dispersive x-ray analysis with a Philips XL40 scanning electron microscope. The crystal structure was shown to be a cubic (^{cub}NpPd$_3$ and PuPd$_3$) with the AuCu$_3$- or hexagonal TiNi$_3$-type of structure (^{hex}NpPd$_3$) with lattice parameters similar to the those reported in literature [16, 18, 19]. Electrical resistance was measured from 2-300 K using the ACT option in a Quantum Design Physical Property Measurement System (PPMS). Four platinum wires were attached on a bar shaped polycrystalline sample using silver paint for a standard resistivity measurement. The thermoelectric power was measured using a custom-made device in the temperature range of 2-300 K using HFC copper as a reference material. Figure 1 shows PuPd$_3$ sample, which was used for the measurements. Due to the radioactivity of Np and Pu, all operations were performed in a nitrogen inert atmosphere glove-box and a special encapsulation procedure
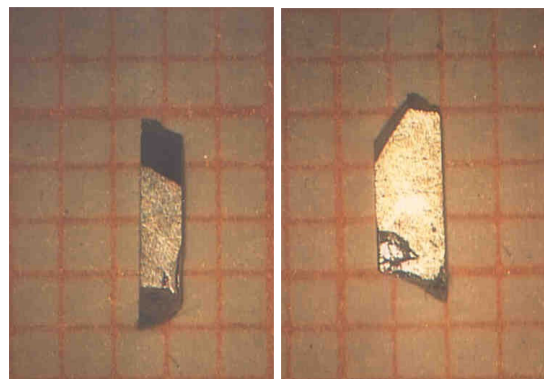

Fig. 1. The polycrystalline samples of PuPd$_3$ that have been used for the thermoelectric measurements.
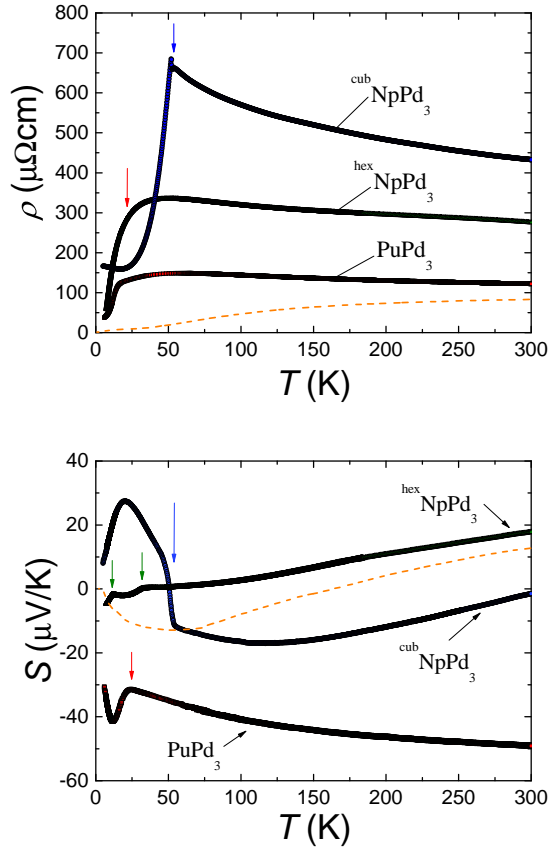
Fig. 2. (a) The temperature dependence of the electrical resistivity of PuPd$_3$ (red squares), hexagonal NpPd$_3$ (green triangles), and cubic NpPd$_3$ (blue circles); (b) the temperature dependence of the thermoelectric power of the AnPd$_3$ samples. For comparison we have also included the electrical resistivity (i||[0001]) and thermoelectric power (ΔT||[0001]) of UPd$_3$ single crystal (data has been taken from Ref.[21]). Arrows mark the temperatures of the phase transitions (see text).

was used in order to avoid any contamination risk.

Figure 2a shows the temperature dependence of the electrical resistivity of the compounds studied. In agreement with previous studies [16, 17, 20] the magnitude and the temperature dependence of the electrical resistivity is typical for $4f$- and $5f$-electron strongly correlated materials [8]. With lowering temperature the electrical resistivity grows and shows ln(T) behavior, characteristic of dense Kondo systems [22]. The sharp anomaly at 52 K in ^{cub}NpPd$_3$ corresponds with the magnetic ordering in this material. The ρT dependence of PuPd$_3$ exhibits a kink at T_N=24 K. In the case of ^{hex}NpPd$_3$, the electrical resistivity starts to drop below 30 K but no clear anomalies are observed neither at 30 nor 10 K. For comparison we have also included in the figure the temperature dependence of the electrical resistivity of UPd$_3$ single crystal [21]. As can be seen the ρT shows typical behavior of metallic systems, in agreement with localized nature of $5f$-electrons in this

material.

The Seebeck coefficient is a sensitive probe of density of states relative to the Fermi level [23], it can therefore be used as a tool to characterize the electronic structure of materials, especially strongly correlated systems [24, 10, 9]. The temperature dependence of the thermoelectric power of NpPd$_3$ and PuPd$_3$ is shown in Fig.2b. The overall shape and magnitude of the $S(T)$ are typical of Kondo lattices (see Refs. [24, 25, 26] and references therein). At room temperature the magnitude of the thermopower is strongly enhanced and has a value of about -50 μV/K for PuPd$_3$ and 20 μV/K for ^{cub}NpPd$_3$. These values of S are one order of magnitude larger than the values observed in simple metals such as copper or silver [23]. The strongly enhanced value of the Seebeck coefficient indicates that $5f$ electrons participate in the bonding and are present at the Fermi energy. Furthermore, the negative sign of thermopower in the cubic materials indicate that electrons might dominate thermal and electrical conduction (and conversely for hexagonal materials). For ^{cub}NpPd$_3$ the thermopower shows a rapid change at T_N, consistent with first order type of the magnetic transition. Furthermore, at the transition, the Seebeck coefficient changes sign from negative to positive. This sharp transition of thermoelectric power together with the change of sign suggests that electronic structure of ^{cub}NpPd$_3$ is strongly reconstructed at the Néel temperature. Also PuPd$_3$ shows an anomaly at T_N=24 K, although not so sharp as ^{cub}NpPd$_3$. Interestingly, for ^{hex}NpPd$_3$ two clear phase transitions can be observed at 10 and 30 K in agreement with the heat capacity studies. For comparison, we have also included the thermopower results for UPd$_3$ single crystal. As can be seen, the overall magnitude and temperature dependence of $S(T)$ are consistent with localized nature of $5f$-electrons in this materials.

High values of the thermopower and relatively small magnitude of the electrical resistivity lead to enhanced power factor (a measure of the thermoelectric potential) of about 16 μWcm^{-1}K^{-2} for PuPd$_3$ at low temperatures. Even though
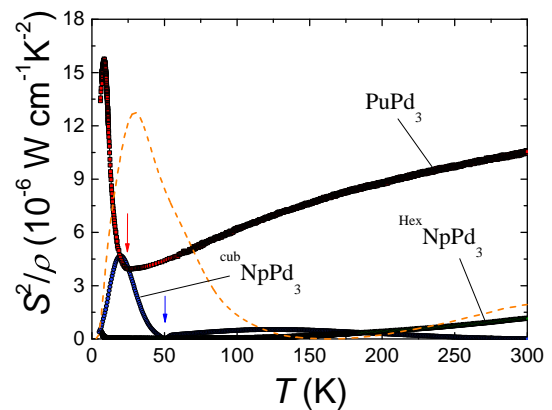

Fig. 3. The temperature dependence of the power factor (defined as $S^2\rho^{-1}$(T)) obtained for the AnPd$_3$ samples. The dashed line shows results for UPd$_3$ (see text). Arrows mark temperatures of the phase transitions.

the power factors are relatively large in $PuPd_3$ and UPd_3, the thermoelectric characteristics of the $5f$-electron materials are smaller than those derived for the Ce-based phases. For instance, in the case of valence fluctuator $CePd_3$ the power factor is as high as $90\,\mu Wcm^{-1}K^{-2}$ [27].

SUMMARY AND CONCLUSIONS

To summarize, we present, for the first time, the thermoelectric properties of $NpPd_3$ and $PuPd_3$ compounds. We show that the Seebeck coefficient of these materials is enhanced and its magnitude and temperature dependence are characteristic of dense Kondo systems in which $5f$-states are present in the vicinity of the Fermi level. The electrical resistivity also shows characteristic behavior of Kondo lattices in these materials. For $^{cub}NpPd_3$ a sharp transition in electrical resistivity and thermopower together with a change of sign of $S(T)$ at the Néel temperature, indicate a first order nature of the magnetic transition. This transition is probably accompanied by a large Fermi-surface reconstruction. Further studies, however, are required to better understand the electronic structure of $^{cub}NpPd_3$ and other $An Pd_3$ phases. We have also estimated power factor (S^2/ρ) of the samples studied. We find out that it is relatively large, although much smaller than observed in rare-earth-based $RE Pd_3$ phases, especially $CePd_3$.

ACKNOWLEDGMENTS

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