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Pressure effect for metal–insulator transition in filled skutterudite $SmRu_4P_{12}$

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Abstract

We have measured the electrical resistance of the filled skutterudite $SmRu_4P_{12}$, which exhibits a metal–insulator (MI) transition at $T_{MI} = 16$ K, at high pressures up to 15 GPa. With increasing pressure, the semiconductor-like resistance was suppressed. We observed metallic behavior in the resistance above 3.5 GPa, while semiconductor-like increase of the resistance was observed below 2 K. Two characteristic anomalies below T_{MI}, a peak and a kink in the resistance curve, are observed at T_1 and T_2.

Keywords: Filled skutterudite; $SmRu_4P_{12}$; Metal–insulator transition; High pressure; Electrical resistance measurement

1. Introduction

Ternary metal pnictides with the general formula RT_4X_{12} (R = rare earths; T = Fe, Ru and Os; X = P, As and Sb) crystallize with a filled skutterudite-type structure [1,2]. Filled skutterudites have been the subject of interest due to their physical properties at low temperature, such as superconductivity, semiconductor-like behavior, magnetic ordering, heavy-fermion behavior and metal–insulator (MI) transition [3–7]. These novel physical properties may originate in the cooperation or competition between Fermi surface instability and the orbital degree of freedom coupling to a local distortion. Studying these compounds, which have the same structure and various physical properties can help lead to a systematic understanding of the origin of the strongly correlated electron systems.

$PrRu_4P_{12}$ and $SmRu_4P_{12}$ show a MI transition, which have the transition temperature $T_{MI} = 62$ and 18 K, respectively [6,7]. The origin of the MI transition of $PrRu_4P_{12}$ is neither due to magnetic ordering nor charge ordering, but due to a structural phase transition [6,8,9]. Under high pressure, the semiconductor-like electrical resistance of $PrRu_4P_{12}$ below T_{MI} was suppressed, and then a superconducting transition was observed above 12 GPa [10,11]. There is a significant difference between $PrRu_4P_{12}$ and $SmRu_4P_{12}$. $SmRu_4P_{12}$ clearly shows a magnetic anomaly at T_{MI} [7] in contrast to $PrRu_4P_{12}$. A double peak of specific heat was observed in magnetic fields [12]. The temperature derivative of the electrical resistivity $d\rho/dT$ and magnetization dM/dT exhibit two anomalies at the same temperatures as the peaks of specific heat, T_{MI} and lower temperature T^* [12,13]. The successive transition and B–T phase diagram are similar to those of CeB_6 [14], which show an antiferro-quadrupolar (AFQ) ordering. The magnetic entropy estimated at zero magnetic field reaches $R \ln 4$ below T_{MI} [12]. This suggests that the crystalline electric field ground state in cubic symmetry is a quartet, which has magnetic and orbital degrees of freedom. This ground state is different from one of $PrRu_4P_{12}$ with a doublet ground state.

The origin of MI transition in $SmRu_4P_{12}$ is considered to be due to structural change, such as $PrRu_4P_{12}$ [9], or AFQ ordering [12,13]. No phonon peaks appear below T_{MI} by infrared spectroscopy of $SmRu_4P_{12}$, suggesting that the MI transition is not driven by a structural change [15]. Elastic constants of $SmRu_4P_{12}$ show softening at T_{MI} [16]. This behavior is not consistent with the typical AFQ ordering, which is accompanied by hardening at T_Q, such as $PrFe_4P_{12}$

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[17]. From these facts, it is considered that the MI transition of $SmRu_4P_{12}$ is not due to an AFQ transition. The transition of $SmRu_4P_{12}$ at T_{MI} is needed to be reconsidered.

Ultrasonic measurements revealed that the value of bulk modulus of $SmRu_4P_{12}$ is 120 GPa [16], which is smaller than the value, 207 GPa of $PrRu_4P_{12}$ [10]. From these facts, we expect the larger pressure effect for the MI transition in $SmRu_4P_{12}$ than one for $PrRu_4P_{12}$.

To investigate, the MI transition of $SmRu_4P_{12}$ in the filled skutterudites, we performed the electrical resistance measurements at low temperature down to 0.1 K and at high pressures up to 15 GPa.

2. Experimental

The single crystal of $SmRu_4P_{12}$ was synthesized by Sn-flux method. The electrical resistance measurements of $SmRu_4P_{12}$ were carried out by an ac four-probe method at temperatures down to 0.1 K and at quasi-hydrostatic pressures up to 15 GPa. We used a diamond-anvil cell (DAC) made of non-magnetic Be–Cu alloy as a high-pressure apparatus. For electrical resistance measurements, the Be–Cu metal gasket was covered with a thin c-BN layer for electrical insulation. The pressure chamber has a cylindrical shape with about 0.1 mm length and 0.3 mm in diameter, which is the hole of the insulated gasket. The sample was cut into a rectangular shape of 0.2 mm × 0.1 mm × 0.05 mm and attached with four gold wires (10 μm in diameter) as electrodes. The chamber was filled with NaCl as a pressure-transmitting medium. The absolute value of the electrical resistivity was not determined due to the small size of the sample. The pressure was applied at room temperature and calibrated at 77 K by a standard ruby fluorescence method. The DAC was assembled on the mixing chamber of a $^3He/^4He$ dilution refrigerator and cooled down to 0.1 K.

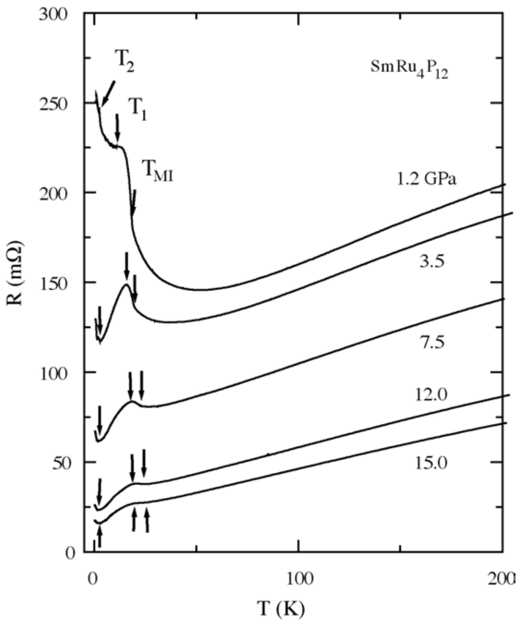

Fig. 1. Temperature dependences of electrical resistance of $SmRu_4P_{12}$ under several pressures. The arrows show T_{MI}, T_1 and T_2.

3. Results

The temperature dependence of the electrical resistance, $R(T)$, at several pressures is shown in Fig. 1. The resistance markedly decreases with increasing pressure, however, it is considered that the measured R may include the contact resistance between sample and electrodes, therefore this decrease is not intrinsic. At 1.2 GPa, $R(T)$ shows a minimum at around 50 K and increases at lower temperature. These behaviors may be due to the Kondo effect [7]. With increasing pressure, the temperature of the minimum of $R(T)$ decreased. The R below T_{MI} was remarkably suppressed, and a broad peak and a bend of R were observed above 3.5 GPa as shown with arrows in Fig. 1. We defined the characteristic temperatures as T_1 and T_2 at the temperatures which the anomalies of $R(T)$ were observed. Between T_1 and T_2, $R(T)$ above 3.5 GPa showed metallic behavior. Below T_2, R markedly increased like a semiconductor. The increase of R below T_2 is suppressed with pressure.

Fig. 2 shows the temperature dependence of the normalized electrical resistance, $R/R_{50\,K}$ below 50 K and at pressures of 3.5 and 11.5 GPa. The anomaly of the R at T_{MI} is broadened and T_{MI} increases at higher pressure. The peak of the R just below T_{MI} is suppressed with pressure. At 11.5 GPa, the minimum of $R(T)$ is not observed. At 15 GPa, the maximum of $R(T)$ below T_{MI} is not observed, as shown in the inset of Fig. 2, therefore T_1 is not able to be determined.

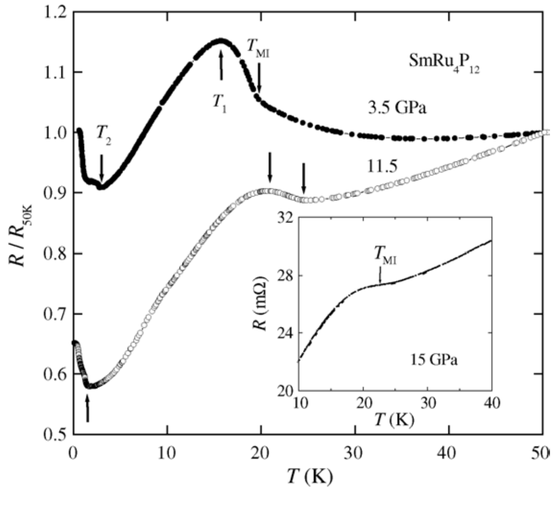

Fig. 2. Temperature dependence of the normalized resistance, $R/R_{50\,K}$ at the pressures 3.5 and 11.5 GPa. The inset shows the $R(T)$ curve around T_{MI} at a pressure of 15 GPa.

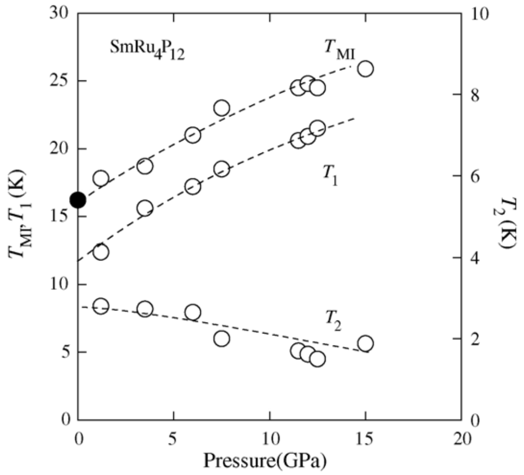

Fig. 3. Pressure dependence of $T_{\rm MI}$, T_1 and T_2. (●) Shows $T_{\rm MI}$ at ambient pressure from ref. [7]. The dashed lines show guides to eyes.

4. Discussions

The pressure dependence of $T_{\rm MI}$, T_1 and T_2 are shown in Fig. 3. $T_{\rm MI}$ increases with 60% at 15 GPa, in contrast to the case of PrRu$_4$P$_{12}$ in which the change in $T_{\rm MI}$ was less than 10% [10,11]. The pressure effect on the MI transition of SmRu$_4$P$_{12}$ is larger than that of PrRu$_4$P$_{12}$. T_2 gradually decreases with increasing pressure. We expect that T_2 decreases and becomes 0 K at higher pressure than 15 GPa, and then SmRu$_4$P$_{12}$ shows a new phase transition, such as superconductivity like PrRu$_4$P$_{12}$.

A similar behavior of $R(T)$ just below $T_{\rm MI}$ of SmRu$_4$P$_{12}$ was also observed in GdRu$_4$P$_{12}$ and TbRu$_4$P$_{12}$, which exhibit antiferromagnetic ordering at $T_{\rm N} = 22$ and 20 K, respectively [4]. The origin of a sharp increase of the resistivity just below $T_{\rm N}$ in the Gd and Tb compounds may be due to nesting of the Fermi surface [4]. It is expected that PrRu$_4$P$_{12}$, SmRu$_4$P$_{12}$, GdRu$_4$P$_{12}$ and TbRu$_4$P$_{12}$ have almost the same Fermi surface because valence fluctuations are very weak [12]. In the case of PrRu$_4$P$_{12}$, it is considered that a local distortion plays a role in the MI transition [18,19]. A similar change is considered in the MI transition of SmRu$_4$P$_{12}$. The local distortion of SmRu$_4$P$_{12}$ may be suppressed under the high pressure, therefore similar behavior in GdRu$_4$P$_{12}$ and TbRu$_4$P$_{12}$ is observed.

The origin of the anomaly at T_2 is unclear. The increment of the R below T_2 was suppressed with pressure, however it was still observed at a pressure of 15 GPa. T_2 slightly decreases with pressure. These behaviors are similar to the MI transition in PrRu$_4$P$_{12}$. $T_{\rm MI}$ of PrRu$_4$P$_{12}$ slightly decreases above 6 GPa, however the semiconductor-like resistance below $T_{\rm MI}$ is suppressed [10,11]. Does the MI transition occur not at $T_{\rm MI}$, but at T_2, or at both temperatures? Further characterizations of the anomaly at T_2, such as optical and specific heat measurement, are required.

In summary, we have measured the temperature dependence of the electrical resistance of SmRu$_4$P$_{12}$ at pressures up to 15 GPa and at temperatures down to 0.1 K. Above 3.5 GPa, a maximum and a kink are observed at the temperatures T_1 and T_2, respectively. In a temperature range between T_1 and T_2, the $R(T)$ shows a typical metallic behavior. Below T_2, an increase of the R was observed, and the R is suppressed with increasing pressure. At higher pressure, the increase of R may disappear, then SmRu$_4$P$_{12}$ shows typical metallic behavior at low temperature.

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