Metal to insulator transition of filled skutterudite $PrRu_4P_{12}$ at low temperatures and high pressures

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Abstract

X-ray diffraction of a single crystal of $PrRu_4P_{12}$ has been studied at ambient pressure. $PrRu_4P_{12}$ has a filled skutterudite-type structure; space group: Im3, lattice constant: $a = 8.055(4)\,Å$, $Z = 2$, $D_{calc} = 5.826\,g/cm^3$. Positional parameters and interatomic distances in the phosphide were determined. By use of synchrotron radiation, powder X-ray diffraction patterns of $PrRu_4P_{12}$ were measured up to 50 GPa at room temperature. The lattice constant monotonically decreases with increasing pressure. The cell volume vs. pressure curve for $PrRu_4P_{12}$ is fitted with the Birch equation of state. The bulk modulus of the phosphide is $207 \pm 12\,GPa$. The resistivity of $PrRu_4P_{12}$ was measured as a function of temperature at high pressures. The metal to insulator transition is found at around 62 K under ambient pressure. The transition temperature (T_{MI}) rapidly increases with pressure at the rate of about 0.9 K/GPa up to 4.5 GPa. Above 6 GPa, T_{MI} abruptly decreases with increasing pressure. The semiconductor-like behavior below T_{MI} for $PrRu_4P_{12}$ is markedly suppressed at around 8 GPa. The metal to insulator transitions at low temperatures and high pressures are discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Ternary metal pnictides with a general formula LnT_4X_{12} (Ln = lanthanide; T = transition metal; X = pnicogen) crystallize with a filled skutterudite-type structure [1,2]. This structure is cubic, space group Im-3, $Z = 2$. Ln atoms locate at (0 0 0) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ of a cubic structure like BCC. The transition metal atoms (T) are in the center of a distorted octahedral environment of six pnicogen atoms. The skutterudite-type structure is characterized by formation of well-defined X_4^{4-} groups. The skutterudite compounds show interesting electrical and magnetic properties at low temperatures [3,4].

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We have found an interesting metal to insulator (MI) transition for $PrRu_4P_{12}$ at around 60 K under ambient pressure [5]. Anomalous behavior in the magnetic susceptibility is not observed at around 60 K. This suggests that the MI transition in $PrRu_4P_{12}$ is not caused by magnetic ordering [5]. PrL2-edge XANES measurements indicate that the valence state in the Pr atoms is trivalent down to 20 K [6]. Below the transition temperature (T_{MI}) an energy gap of $PrRu_4P_{12}$ is estimated to be about $100\,cm^{-1}$ from the optical reflection spectrum [7]. The Raman spectra of the phosphide are measured between 6 and 300 K; the $380\,cm^{-1}$ mode assigned to the vibration involving P atoms shows softening and broadening below the T_{MI} [8]. A slight jump in the thermal expansion coefficient is found at the T_{MI} [9]. The small anomaly in the specific heat appears at the T_{MI} [10]. Recently, using the electron diffraction technique, superlattice spots in the single crystal of $PrRu_4P_{12}$ are observed below the T_{MI} [11].

We have studied X-ray diffraction of a single crystal at ambient pressure and powder X-ray diffraction of $PrRu_4P_{12}$ up to 50 GPa at room temperature. The resistivity of $PrRu_4P_{12}$ has been measured at low temperatures and high pressures. In this report, the metal to insulator transition of $PrRu_4P_{12}$ at high pressure is discussed.

2. Experimental details

X-ray diffraction of a single crystal of $PrRu_4P_{12}$ was studied at room temperature (295 K). Intensity data were collected on a Rigaku automatic four-circle diffractometer using graphite-monochromated MoKα radiation. The structure was refined with a full-matrix least-squares program; space group: Im-3, lattice constant: $a = 8.055(4)$ Å, $Z = 2$, $D_{calc} = 5.826\,g/cm^3$, $F_{000} = 830.00$, $\mu(MoK\alpha) = 119.96$. The conventional residual (R) and the weighted residual (R_w) are 0.032 and 0.034, respectively. Single crystals of $PrRu_4P_{12}$ were grown by a Sn flux method. The mixtures with atomic ratio Pr:Ru:P:Sn = 1:4:20:50 were heated at 1000°C for a week and then cooled down slowly to 600°C at 2°C/h [11].

By use of synchrotron radiation, powder X-ray diffraction patterns of $PrRu_4P_{12}$ were measured with a diamond-anvil cell and an imaging plate up to 50 GPa at room temperature [12]. The incident beam was monochromatized with Si (1 1 1) double crystals to a wavelength of 0.6888 Å. The pressure in the diamond-cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby. A 4:1 methanol–ethanol solution was used as the pressure-transmitting fluid.

A high-pressure apparatus with a cubic-anvil device was used for the resistivity measurement of $PrRu_4P_{12}$ under hydrostatic conditions up to 8 GPa at low temperatures down to 4.2 K [13]. Polycrystals of $PrRu_4P_{12}$ were used for measurements of the resistivity and the powder X-ray diffraction. These samples were prepared at high temperatures and high pressures [5].

3. Results and discussion

Fig. 1 shows the crystal structure of $PrRu_4P_{12}$ determined from X-ray data of the single crystal. The resulting positional and thermal parameters are given in Table 1. The interatomic distances and angles are listed in Table 2. This structure is similar to that of $LaFe_4P_{12}$ that has already been determined from single crystal counter data by
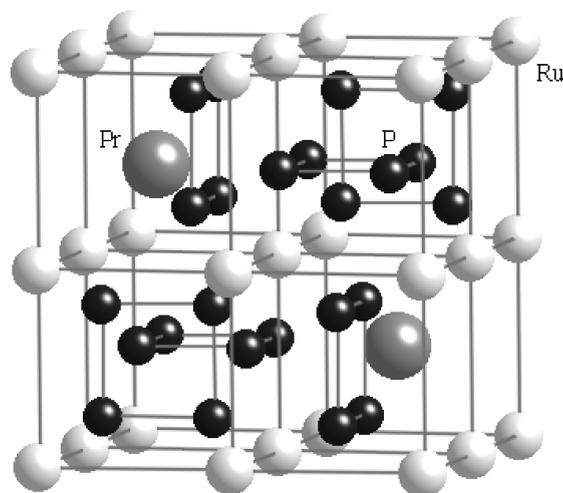
Fig. 1. Crystal structure of $PrRu_4P_{12}$. The Ru atom is taken as the origin (0 0 0).

Table 1
Positional and thermal parameters in $PrRu_4P_{12}$ at ambient pressure

$Im\bar{3}$	Pr 2(a)	Ru 8(c)	P 24(g)
x	0	0.2500	0
y	0	0.2500	0.3579
z	0	0.2500	0.1437
U_{11}	0.0074 (3)	0.0019 (3)	0.0051 (4)
U_{22}	U_{11}	U_{11}	0.0033 (4)
U_{33}	U_{11}	U_{11}	0.0035 (4)
B_{eq}	0.582 (4)	0.151 (4)	0.31 (2)

Table 2
Interatomic distances and angles in $PrRu_4P_{12}$ at ambient pressure

Interatomic distances (Å)		Interatomic angle (deg)	
Pr–P	3.107 (1) (12 ×)	Pr–P–Ru	78.04 (3)
Pr–Ru	3.488 (1) (8 ×)	Pr–P–P′	158.13 (2)
Ru–P	2.355 (1) (6 ×)	Pr–P–P″	68.13 (2)
P–P′	2.314 (2) (1 ×)	Ru–P–P′	111.67 (2)
P–P″	2.289 (2) (1 ×)	Ru–P–P″	111.33 (2)
		Ru–P–Ru	117.56 (5)
		P′–P–P″	90

Fig. 2. Powder X-ray diffraction patterns of $PrRu_4P_{12}$ at high pressures.

Patterson and Fourier methods [1]. The skutterudite-type structure is characterized by formation of rectangular P_4^{4-} clusters. The P–P distances in $PrRu_4P_{12}$ are 2.289 Å along the shorter edge and 2.314 Å along the longer edge. These are rather shorter than the P–P distances (2.289 and 2.356 Å) in $LaFe_4P_{12}$ although the cell volume of $PrRu_4P_{12}$ is considerably larger than that of the iron compound. The Ru–P distance is shorter than the sum of atomic radius (1.34 Å) of Ru atom and the covalent radius (1.06 Å) of P atom. The Pr–P distance almost agrees with the sum of the atomic radius (1.82 Å) of the Pr atom and the atomic radius (1.28 Å) of the P atom. These distances in $PrRu_4P_{12}$ suggest metallic bond character. The X-ray diffraction of $PrRu_4P_{12}$ has been studied at low temperatures. The positional parameter of the phosphorus atom is insensitive to temperature. The ratio of lattice constant ($a_0 - a_T/a_0$; a_0—room temperature, a_T—low temperatures) of $PrRu_4P_{12}$ decreases with decreasing temperature

at the rate of -8.7×10^{-4}/K. This value is slightly smaller than the result of the linear thermal expansion measured by the three terminal capacitance method [9].

Fig. 2 shows powder X-ray diffraction patterns of $PrRu_4P_{12}$ with synchrotron radiation at high pressures and room temperature. The diffraction lines shift to the high angle region with increasing pressure. The width of the diffraction lines becomes broad at higher pressures. Fig. 3 shows the lattice constant vs. pressure curve for $PrRu_4P_{12}$ up to 50 GPa at room temperature. The structural anomaly in $PrRu_4P_{12}$ is not observed up to 50 GPa at room temperature. The ratio of the lattice constant ($a_0 - a_P/a_0$, a_0—ambient pressure, a_P—high pressures) decreases at the rate of -2.1×10^{-2}/GPa up to 4.5 GPa. Thus, the pressure dependence of the lattice constant is much larger than its temperature dependence. The pressure vs. volume curve for $PrRu_4P_{12}$ can be fitted by a Birch equation of state [14]. The bulk
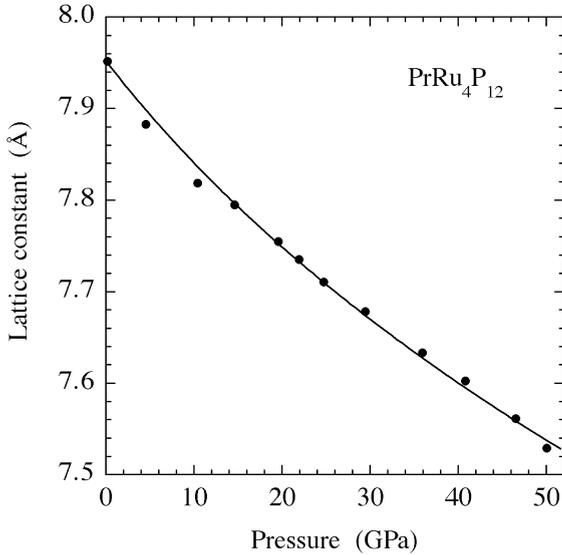
Fig. 3. Lattice constant vs. pressure curve for PrRu$_4$P$_{12}$.
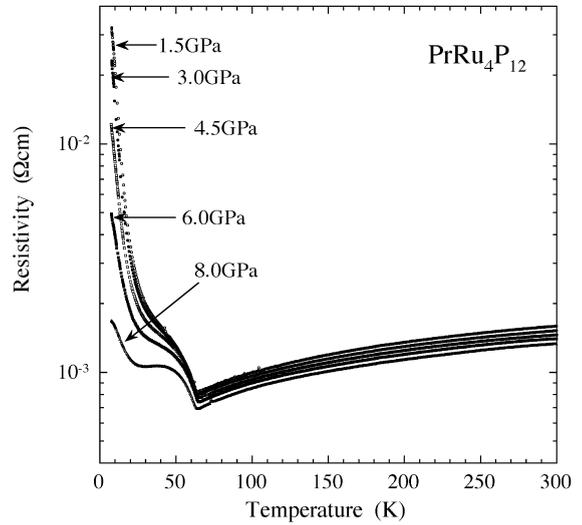
Fig. 4. Resistivity vs. temperature curves for PrRu$_4$P$_{12}$ at high pressures.

modulus obtained by a least-squares fit is 207 ± 12 GPa for PrRu$_4$P$_{12}$. This value is about 2.8 times that of PrP with a NaCl-type structure [12]. PrRu$_4$P$_{12}$ is a very hard material.

Fig. 4 shows the electrical resistivity vs. temperature curves for PrRu$_4$P$_{12}$ at high pressures. The resistivity decreases with increasing pressure up to 8 GPa under hydrostatic conditions. When the temperature dependence of the resistivity of the phosphide is measured at constant pressures, the MI transitions are observed at low temperatures and high pressures. The semiconductor-like behavior below the T_{MI} in PrRu$_4$P$_{12}$ is markedly suppressed at around 8 GPa. Fig. 5 shows the effect of pressure on T_{MI} for PrRu$_4$P$_{12}$. T_{MI} rapidly increases with pressure at the rate of about 0.9 K/GPa up to 4.5 GPa. Above 6 GPa, T_{MI} abruptly decreases with increasing pressure.

PrRu$_4$P$_{12}$ shows the MI transition at around 62 K under ambient pressure. This anomalous behavior does not arise from magnetic ordering and valence fluctuations based on the f electrons in Pr [5,6]. A λ-like second order-type anomaly in the specific heat appears at T_{MI}; this does not depend on the magnetic field at least up to 12 T [10]. Superlattice spots in the single crystal of PrRu$_4$P$_{12}$ are observed below the T_{MI}; this may arise from
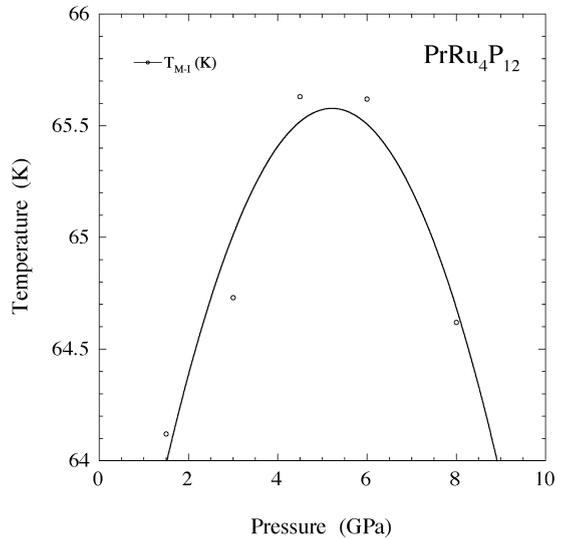
Fig. 5. T_{MI} plotted as a function of pressure for PrRu$_4$P$_{12}$.

the opening of a band gap due to a nesting of the Fermi surface [11]. The appearance of the super-lattice structure provides two possible origins of the MI transition, a charge density wave (CDW) transition or antiferro-quadrupolar (AFQ) ordering. Matsuhira et al. suggest that the MI transition in PrRu$_4$P$_{12}$ is due to the CDW transition rather

than the AFQ transition from the detailed study of the electronic specific heat [15].

We have studied the magnetic susceptibility and electrical resistivity of the alloys $La_{1-x}Pr_xRu_4P_{12}$ diluted by La atom [16]. As the lattice constant in the alloys increases with increasing La concentration, the average Pr–Pr distances increase. T_{MI} of the alloys shifts to lower temperatures with increasing La concentration.

The lattice constant of $PrRu_4P_{12}$ decreases from 8.057 Å at ambient pressure to 7.887 Å at 4.5 GPa. Thus, the distance between the nearest Pr atoms decreases from 6.98 Å at ambient pressure to 6.82 Å at 4.5 GPa. The increase of inter-site interactions between Pr atoms drives up T_{MI}. This tendency is consistent with the result of the alloys $La_{1-x}Pr_xRu_4P_{12}$. However, T_{MI} surprisingly decreases with increasing pressure above 4.5 GPa although the Pr–Pr distances shorten successively with pressure. The resistivity of $PrRu_4P_{12}$ below T_{MI} is remarkably suppressed at around 8 GPa. The f-electrons in $PrRu_4P_{12}$ may easily be itinerant in the crystal at higher pressures. Thus, these results suggest that the MI transition in $PrRu_4P_{12}$ may disappear at very high pressures. As $PrRu_4As_{12}$ shows superconductivity at around 2.4 K [17], $PrRu_4P_{12}$ may behave as a superconductor at very high pressures.

Acknowledgements

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