

# High-pressure Synthesis and Structural, Electrical and Magnetic Properties of a New Filled Skutterudite $\text{TbFe}_4\text{P}_{12}$

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The new filled skutterudite  $\text{TbFe}_4\text{P}_{12}$  has been prepared at around 4 GPa and 1050 °C. Powder X-ray diffraction of  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$  and  $\text{Ru}$ ) has been studied with synchrotron radiation at ambient pressure. The crystal structures of both compounds were refined by Rietveld methods at ambient pressure. The positional parameters, bond lengths and bond angles have been obtained for  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$  and  $\text{Ru}$ ). The electrical and magnetic properties of  $\text{TbFe}_4\text{P}_{12}$  have been investigated at low temperatures. The susceptibility of this phosphide follows a Curie-Weiss behavior at higher temperatures. The linear slope of the  $\chi^{-1}$  vs.  $T$  curve from 15 to 300 K yields an effective magnetic moment of  $9.48 \mu_B$ . This value is close to the magnetic moment of the  $\text{Tb}^{3+}$  ion calculated from Hund's rule,  $9.72 \mu_B$ . The ferromagnetic transition of  $\text{TbFe}_4\text{P}_{12}$  was observed at around 10 K, and an electrical anomaly based on the magnetic ordering was detected. The relationship between the crystal structure and the physical properties of  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$  and  $\text{Ru}$ ) is discussed.

**Key words:** High-pressure Synthesis, Crystal Structure, Electrical and Magnetic Properties, Filled Skutterudite,  $\text{TbFe}_4\text{P}_{12}$

## Introduction

Ternary metal compounds with the general formula  $\text{LnT}_4\text{X}_{12}$  ( $\text{Ln} =$  lighter lanthanide,  $T = \text{Fe}$ ,  $\text{Ru}$  and  $\text{Os}$ ,  $\text{X} = \text{P}$ ,  $\text{As}$  and  $\text{Sb}$ ) crystallize with a skutterudite-type structure (cubic, space group:  $Im\bar{3}$ ) [1, 2]. These skutterudites with lighter lanthanides were frequently prepared by flux methods [1, 2]. However, we have prepared many skutterudite compounds with lighter lanthanides at high temperatures and high pressures [3]. These materials show interesting physical properties at low temperatures. Superconducting [4–6], semiconducting [7], metal-insulator transition [8–10], magnetic [11], heavy fermion [12], intermediate-valence [13, 14], and non-Fermi liquid behavior [15] have been observed in these materials. Further, skutterudite compounds exhibit remarkable thermoelectric properties [16, 17]. The physical properties of skutterudite compounds were reviewed by Sales [18].

We have prepared new filled skutterudites with heavy lanthanides (including Y),  $\text{LnT}_4\text{P}_{12}$  ( $\text{Ln} =$  heavy lanthanide,  $T = \text{Fe}$ ,  $\text{Ru}$  and  $\text{Os}$ ) at high temperatures

and high pressures [19–23]. The electrical and magnetic properties of these phosphides have been studied at low temperatures. Jeitschko *et al.* have synthesized a single crystal of  $\text{GdFe}_4\text{P}_{12}$  using the flux method [24]. This phosphide is a ferromagnet with a Curie temperature of 22 K. In contrast,  $\text{GdRu}_4\text{P}_{12}$  and  $\text{GdOs}_4\text{P}_{12}$  were prepared only at high pressure [20, 21]. The magnetic properties of both compounds show antiferromagnetic ordering at around 22 K for  $\text{GdRu}_4\text{P}_{12}$  [20] and a ferromagnetic transition at around 5 K for  $\text{GdOs}_4\text{P}_{12}$  [21]. The magnetic behavior of  $\text{GdRu}_4\text{P}_{12}$  differs from that of the Fe and Os compounds. The electrical and magnetic properties of  $\text{TbRu}_4\text{P}_{12}$  are similar to those of  $\text{GdRu}_4\text{P}_{12}$ .  $\text{TbRu}_4\text{P}_{12}$  shows an antiferromagnetic transition at around 22 K [20]. Powder neutron diffraction of this phosphide has been studied at low temperatures.  $\text{TbRu}_4\text{P}_{12}$  is the first filled skutterudite confirmed as an antiferromagnet by neutron diffraction [25]. The physical properties of  $\text{TbFe}_4\text{P}_{12}$  and  $\text{TbOs}_4\text{P}_{12}$  have not been investigated.

The high-pressure synthesis of  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$ ,  $\text{Ru}$  and  $\text{Os}$ ) was carried out at high temperatures. X-ray

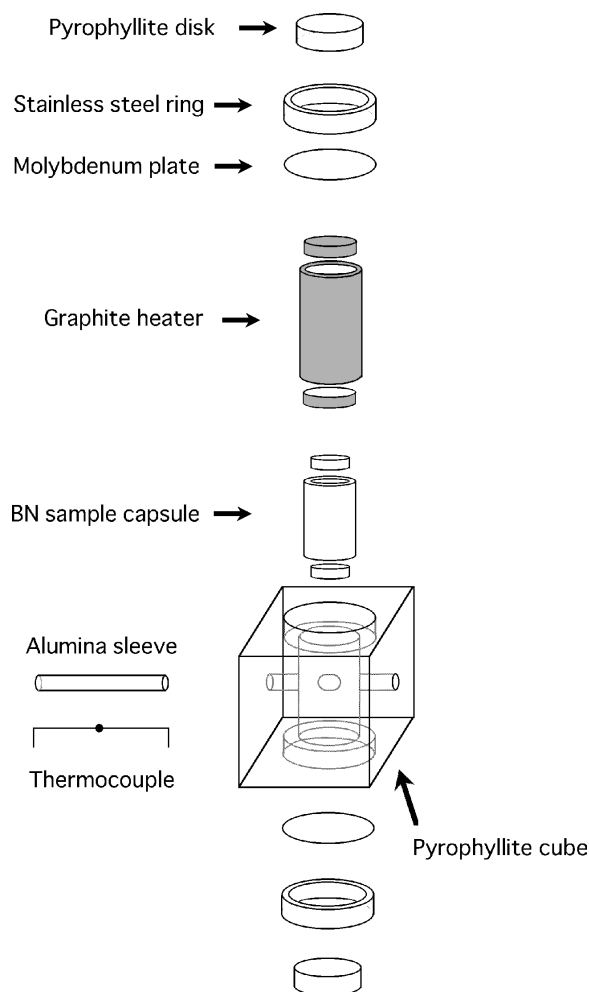


Fig. 1. Sample assembly for the high-pressure synthesis of filled skutterudite compounds.

powder diffraction of  $\text{TbFe}_4\text{P}_{12}$  and  $\text{TbRu}_4\text{P}_{12}$  with synchrotron radiation was studied at ambient pressure. The crystal structures of both compounds were refined with Rietveld methods. We report some results of the electrical resistivity and the magnetic susceptibility for  $\text{TbFe}_4\text{P}_{12}$ . In this report, the relationship between the crystal structures and the physical properties of  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$  and  $\text{Ru}$ ) is also discussed.

## Experimental Section

Using a wedge-type cubic-anvil high-pressure apparatus, many skutterudite compounds were prepared at high temperatures and high pressures. The upper and lower stages of the high-pressure apparatus consist of three anvils that slide on the wedge formed in shallow V-shaped grooves.

The anvil movement is completely synchronized by means of a wedge system. The anvils prepared from cemented tungsten carbide have a  $16 \times 16 \text{ mm}^2$  top-square face. The sample container made of pyrophyllite is formed into a cube of 21 mm edge length. Fig. 1 shows the sample assembly for the high-pressure synthesis of filled skutterudite compounds. This system is similar to that used for the preparation of ternary metal compounds [3]. Starting materials are put into a crucible made of boron nitride (BN). The crucible with a graphite heater is then inserted into the pyrophyllite cube. New filled skutterudites,  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$  and  $\text{Os}$ ) were prepared by reaction of stoichiometric amounts of metal and red phosphorus powder at around 4 GPa. The reaction temperatures were between 1050 and 1100 °C. High purity red phosphorus (> 99.99%) was used. Samples prepared were characterized by X-ray powder diffraction using  $\text{CuK}\alpha$  radiation and silicon as a standard.

Using synchrotron radiation, X-ray powder diffraction patterns of  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$  and  $\text{Ru}$ ) were measured with an imaging plate at r.t. The incident beam was monochromatized by Si(111) double crystals. The synchrotron radiation experiment with  $\lambda = 0.4126 \text{ \AA}$  was performed at the BL10XU in the SPring-8. The crystal structures of both skutterudites were refined with Rietveld methods using the program (RIETAN-2000) developed by Izumi [26].

Copper or gold leads were attached to polycrystalline samples with silver filled by epoxy, and four-lead electrical resistance measurements were performed at low temperatures. The *dc* magnetic susceptibility was measured in the range of 1.8–300 K with a Quantum Design SQUID magnetometer.

## Results and Discussion

### High-pressure synthesis of new filled skutterudites, $\text{LnT}_4\text{P}_{12}$ ( $\text{Ln} = \text{lanthanide}$ , $T = \text{Fe}$ , $\text{Ru}$ and $\text{Os}$ )

We have systematically prepared filled skutterudite phosphides,  $\text{LnT}_4\text{P}_{12}$  ( $\text{Ln} = \text{lanthanide}$  and  $\text{Y}$ ,  $T = \text{Fe}$ ,  $\text{Ru}$  and  $\text{Os}$ ) at high temperatures and high pressures. The high-pressure synthesis of  $\text{TbT}_4\text{P}_{12}$  ( $T = \text{Fe}$ ,  $\text{Ru}$  and  $\text{Os}$ ) was also carried out at high temperatures. Fig. 2 shows the relationship between lattice constants and atomic numbers of lanthanides (including  $\text{Y}$ ) in  $\text{LnT}_4\text{P}_{12}$ . The black circles designate the new skutterudites prepared by us. The lattice constant of these phosphides basically decreases with increasing atomic number of  $\text{Ln}$  according to lanthanide contraction. However, some anomalies in these curves are observed for the  $\text{Ce}$ ,  $\text{Eu}$  and  $\text{Yb}$  compounds. These may be closely related to the valence states in the materials. The oxidation states of  $\text{CeT}_4\text{P}_{12}$  ( $T =$

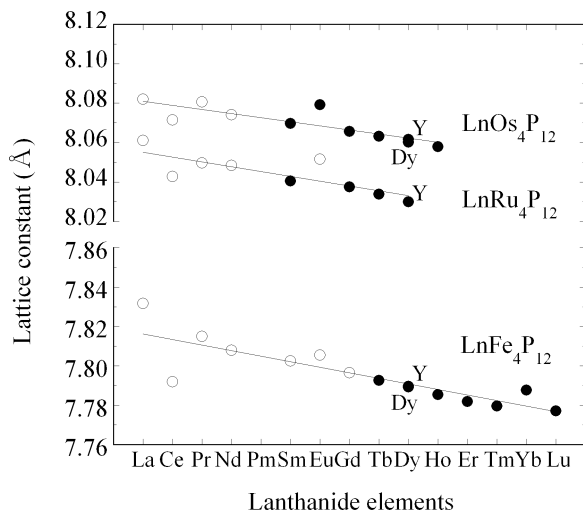


Fig. 2. Relationship between lattice constants and atomic numbers of the lanthanides (including Y) in  $\text{LnT}_4\text{P}_{12}$ . The black circles designate new filled skutterudites prepared by us. The lattice constants of  $\text{YT}_4\text{P}_{12}$  agree closely with those of  $\text{DyT}_4\text{P}_{12}$ . These are shown by the symbol Y in the figure.  $\text{DyRu}_4\text{P}_{12}$  has not been synthesized.

Fe, Ru and Os) [27–29],  $\text{EuT}_4\text{P}_{12}$  [21,30,31] and  $\text{YbFe}_4\text{P}_{12}$  [14,23] have already been discussed.

The electrical and magnetic properties of new skutterudites with heavy lanthanides have been studied at low temperatures [19–23]. These results are summarized.  $\text{GdFe}_4\text{P}_{12}$  and  $\text{GdOs}_4\text{P}_{12}$  behave as ferromagnets with Curie temperatures of 22 K and 5 K, respectively. In contrast,  $\text{GdRu}_4\text{P}_{12}$  shows antiferromagnetic ordering at around 22 K.  $\text{DyFe}_4\text{P}_{12}$  indicates ferromagnetic behavior at around 10 K. On the other hand,  $\text{DyOs}_4\text{P}_{12}$  does not show a magnetic transition down to 2 K. However, there is a small electrical anomaly at

around 5 K.  $\text{YT}_4\text{P}_{12}$  ( $T = \text{Fe, Ru and Os}$ ) show a superconducting transition at around 7, 8.5 and 3 K, respectively [22,23]. The  $T_c$ 's of these three Y phosphides are higher than those of the corresponding La compounds. The magnetic susceptibilities of  $\text{HoFe}_4\text{P}_{12}$  and  $\text{ErFe}_4\text{P}_{12}$  follow the Curie-Weiss behavior at higher temperatures. The linear slope of  $\chi^{-1}$  vs.  $T$  curves yield effective magnetic moments of  $10.43 \mu_B$  for  $\text{HoFe}_4\text{P}_{12}$  and  $9.59 \mu_B$  for  $\text{ErFe}_4\text{P}_{12}$ . These values are in good agreement with the magnetic moments of  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  ions calculated from Hund's rule, 10.60 and  $9.69 \mu_B$ , respectively.  $\text{HoFe}_4\text{P}_{12}$  shows a ferromagnetic transition at around 5 K.

$\text{TmFe}_4\text{P}_{12}$  and  $\text{YbFe}_4\text{P}_{12}$  exhibit paramagnetic behavior. The linear slope of the  $\chi^{-1}$  vs.  $T$  curve for  $\text{TmFe}_4\text{P}_{12}$  yields an effective magnetic moment of  $6.58 \mu_B$ . The effective magnetic moment obtained from the  $\chi^{-1}$  vs.  $T$  curve is  $3.58 \mu_B$  for  $\text{YbFe}_4\text{P}_{12}$ . The magnetic moment of  $\text{Yb}^{3+}$  ion calculated from Hund's rule is  $4.54 \mu_B$ . These results suggest that the Yb compound may have an intermediate valence between +2 and +3 [14,23]. The valence state of this compound is very interesting. The resistivity of  $\text{YbFe}_4\text{P}_{12}$  decreases monotonously with decreasing temperature, but slowly increases from 50 K down to 2 K. The resistivity minimum is found at around 50 K.

#### Crystal structure of $\text{TbT}_4\text{P}_{12}$ ( $T = \text{Fe and Ru}$ )

We have already refined the crystal structures of some filled skutterudites on powder X-ray diffraction data with Rietveld methods [7,14]. Filled skutterudites,  $\text{LnT}_4\text{P}_{12}$  ( $\text{Ln} = \text{lanthanide}$ ;  $T = \text{Fe, Ru and Os}$ ), crystallize in the  $\text{CoAs}_3$ -type structure filled by lanthanide atoms (cubic, space group:  $Im\bar{3}$ ) [1,2,7,14].

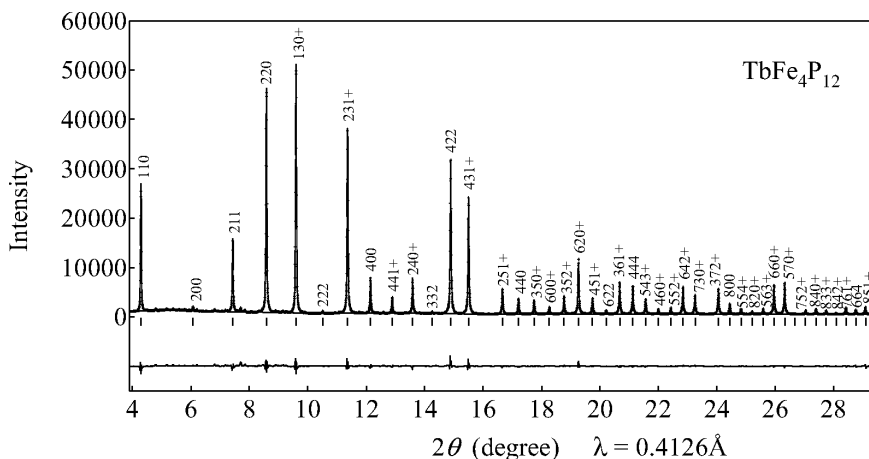


Fig. 3. Observed X-ray diffraction pattern, calculated profile and respective differences for  $\text{TbFe}_4\text{P}_{12}$ .

Table 1. Positional parameters of TbFe<sub>4</sub>P<sub>12</sub> ( $a = 7.79242(1)$  Å,  $R_{wp} = 4.0\%$ ,  $R_I = 2.5\%$ ,  $S = 1.5$ ) and TbRu<sub>4</sub>P<sub>12</sub> ( $a = 8.0368(7)$  Å,  $R_{wp} = 2.0\%$ ,  $R_I = 4.2\%$ ,  $S = 2.2$ ).

	Tb	Fe (Ru)	P
$Im\bar{3}$	2(a)	8(c)	24(g)
TbFe <sub>4</sub> P <sub>12</sub> :			
$x$	0	1/4	0
$y$	0	1/4	0.3529(1)
$z$	0	1/4	0.1488(1)
$B$ (Å <sup>2</sup> )	1.06(3)	0.61(4)	0.60(4)
TbRu <sub>4</sub> P <sub>12</sub> :			
$x$	0	1/4	0
$y$	0	1/4	0.3594(4)
$z$	0	1/4	0.1423(4)
$B$ (Å <sup>2</sup> )	0.96(3)	0.28(4)	0.85(3)

Table 2. Bond lengths and bond angles for TbT<sub>4</sub>P<sub>12</sub> ( $T = \text{Fe}$  and Ru).

	TbFe <sub>4</sub> P <sub>12</sub>	TbRu <sub>4</sub> P <sub>12</sub>
$a$ (Å)	7.7824	8.0368
Tb-P (Å)	2.984	3.105
Tb-T (Å)	3.3742	3.4774
T-P (Å)	2.2494	2.356
P-P' (Å)	2.293	2.257
P-P'' (Å)	2.309	2.286
Tb-P-T (°)	78.92	77.77
Tb-P-P' (°)	67.14	68.40
Tb-P-P'' (°)	157.14	157.40
T-P-P' (°)	110.52	111.53
T-P-P'' (°)	110.88	111.90
T-P-T' (°)	120.00	116.80

$Ln$  atoms are located at (000) and (1/2 1/2 1/2) in the cubic structure. Transition metal atoms ( $T$ ) are in the center of distorted octahedra of six phosphorus atoms. The skutterudite-type structure is characterized by formation of well-defined  $P_4^{4-}$  groups.

Powder X-ray diffraction of TbT<sub>4</sub>P<sub>12</sub> ( $T = \text{Fe}$  and Ru) has been studied in detail with synchrotron radiation at ambient pressure. The crystal structures of both compounds were studied with Rietveld methods. The entire profiles of X-ray diffraction in TbT<sub>4</sub>P<sub>12</sub> ( $T = \text{Fe}$  and Ru) have been fitted to the calculated patterns. Fig. 3 shows the observed X-ray diffraction pattern, the calculated profile and the respective differences for TbFe<sub>4</sub>P<sub>12</sub>. The agreement between both profiles is good. The structure of TbFe<sub>4</sub>P<sub>12</sub> was refined to  $R_{wp} = 4.0\%$ . Similar results were also obtained for TbRu<sub>4</sub>P<sub>12</sub>. The positional parameters in TbT<sub>4</sub>P<sub>12</sub> ( $T = \text{Fe}$  and Ru) obtained by the Rietveld analysis are given in Table 1. Bond lengths and bond angles of both compounds are summarized in Table 2. The skutterudite-

Table 3.  $Ln$ - $Ln$  distances and magnetic properties of  $LnT_4P_{12}$  ( $Ln = \text{Gd}$  and Tb;  $T = \text{Fe}$ , Ru and Os).

	magnetic property	$T_c$ (K)	$Ln$ - $Ln$ distance (Å)
GdFe <sub>4</sub> P <sub>12</sub>	ferro	22	6.752 [21]
GdRu <sub>4</sub> P <sub>12</sub>	antiferro	22	6.960 [20]
GdOs <sub>4</sub> P <sub>12</sub>	ferro	5	6.984 [21]
TbFe <sub>4</sub> P <sub>12</sub>	ferro	10	6.748 [present work]
TbRu <sub>4</sub> P <sub>12</sub>	antiferro	20	6.956 [20]
TbOs <sub>4</sub> P <sub>12</sub>	—	—	6.983 [present work]

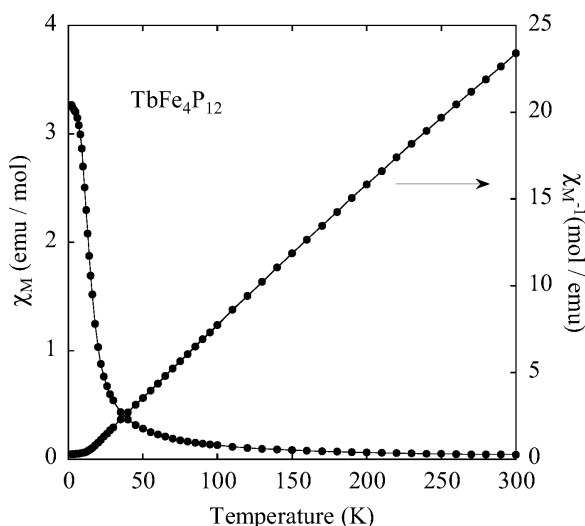


Fig. 4. Magnetic susceptibility and inverse susceptibility of TbFe<sub>4</sub>P<sub>12</sub> measured in a magnetic field of 1 tesla (T) at low temperatures.

type structure is characterized by formation of rectangular  $P_4^{4-}$  clusters. The P-P distances in TbFe<sub>4</sub>P<sub>12</sub> are 2.293 Å along the shorter edge and 2.319 Å along the longer edge. On the other hand, the P-P distances in TbRu<sub>4</sub>P<sub>12</sub> are 2.257 and 2.286 Å. The ratio of these P-P distances is 0.989 for TbFe<sub>4</sub>P<sub>12</sub> and 0.987 for TbRu<sub>4</sub>P<sub>12</sub>. The shape of the  $P_4^{4-}$  units in TbFe<sub>4</sub>P<sub>12</sub> is closer to a square compared with that of TbRu<sub>4</sub>P<sub>12</sub>. The equivalent isotropic displacement parameter ( $B_{eq}$ ) of Tb in TbFe<sub>4</sub>P<sub>12</sub> is 1.06 Å<sup>2</sup>. The corresponding value for TbRu<sub>4</sub>P<sub>12</sub> is 0.958. We have reported that the  $B_{eq}$  value of YbFe<sub>4</sub>P<sub>12</sub> is 1.20 [14]. The  $B_{eq}$  values in several filled skutterudites with heavy lanthanide are thus larger than those of lighter lanthanides. These large values of  $B_{eq}$  may be due to the rattling effect.

#### Electrical and magnetic properties of TbFe<sub>4</sub>P<sub>12</sub>

Fig. 4 shows dc magnetic susceptibility and inverse susceptibility of TbFe<sub>4</sub>P<sub>12</sub> measured in a magnetic

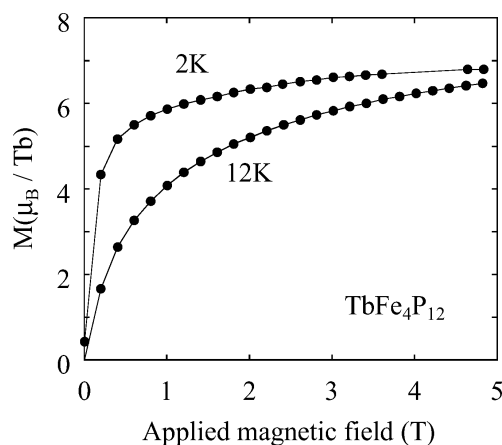


Fig. 5. Magnetic moment *versus* applied magnetic field curves for TbFe<sub>4</sub>P<sub>12</sub> at 2 K and 12 K.

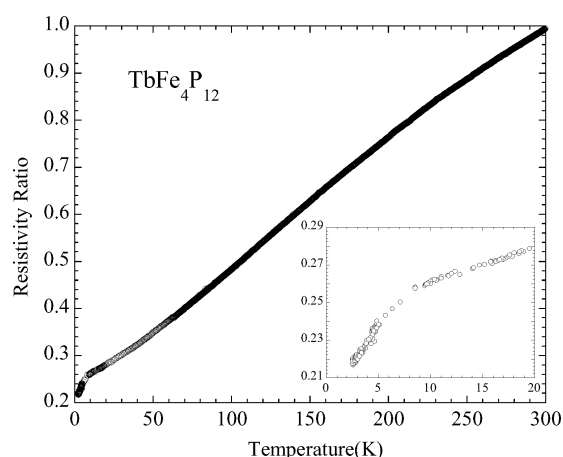


Fig. 6. Electrical resistivity of TbFe<sub>4</sub>P<sub>12</sub> at low temperatures.

field of 1 tesla (T) at low temperatures. The susceptibility of this phosphide follows a Curie-Weiss behavior at higher temperatures. The linear slope of the  $\chi^{-1}$  vs.  $T$  curve from 15 to 300 K yields an effective magnetic moment of  $9.48 \mu_B$ . This value is close to the magnetic moment of Tb<sup>3+</sup> ion calculated from Hund's rule,  $9.72 \mu_B$ . The positive Weiss constant and the sudden increase of susceptibility of TbFe<sub>4</sub>P<sub>12</sub> suggest a ferromagnetic transition at around 10 K. Fig. 5 shows the magnetic moment *versus* applied magnetic field curves for TbFe<sub>4</sub>P<sub>12</sub> at 2 K and 12 K. The magnetization of TbFe<sub>4</sub>P<sub>12</sub> abruptly increases in the low field region and saturates in the higher field region at 2 K. These mag-

netic features of TbFe<sub>4</sub>P<sub>12</sub> are due to the occurrence of ferromagnetic ordering at around 10 K. Fig. 6 shows the electrical resistivity of TbFe<sub>4</sub>P<sub>12</sub> at low temperatures. The resistivity decreases with decreasing temperature down to 10 K. The electrical anomaly based on the magnetic ordering in TbFe<sub>4</sub>P<sub>12</sub> is observed at around 10 K.

The  $Ln$ - $Ln$  distances and magnetic properties of  $LnT_4P_{12}$  ( $Ln = Gd$  and  $Tb$ ;  $T = Fe, Ru$  and  $Os$ ) are summarized in Table 3. GdFe<sub>4</sub>P<sub>12</sub> behaves as a ferromagnet with a Curie temperature of 22 K [24]. GdRu<sub>4</sub>P<sub>12</sub> shows antiferromagnetic ordering at around 22 K [20]. GdOs<sub>4</sub>P<sub>12</sub> shows a ferromagnetic transition at around 5 K [21]. A similar magnetic behavior is also observed for TbT<sub>4</sub>P<sub>12</sub> ( $T = Fe$  and  $Ru$ ). The ferromagnetic transition of TbFe<sub>4</sub>P<sub>12</sub> occurs at around 10 K though  $T_c$  is lower by 12 K than that of GdFe<sub>4</sub>P<sub>12</sub>. On the other hand, TbRu<sub>4</sub>P<sub>12</sub> shows an antiferromagnetic transition at around 22 K. The magnetic properties of the Ru phosphide differ from those of the Fe and Os compounds. The Gd-Gd distances in GdFe<sub>4</sub>P<sub>12</sub> are the shortest among the Fe, Ru and Os compounds. GdOs<sub>4</sub>P<sub>12</sub> has the longest Gd-Gd distance. Ferromagnetic transitions are found for both compounds, GdFe<sub>4</sub>P<sub>12</sub> and GdOs<sub>4</sub>P<sub>12</sub>. In contrast, GdRu<sub>4</sub>P<sub>12</sub> with an intermediate Gd-Gd distance shows an antiferromagnetic transition. The Tb-Tb distances in TbT<sub>4</sub>P<sub>12</sub> are close to the Gd-Gd distances in GdT<sub>4</sub>P<sub>12</sub>. Thus, the direct magnetic interaction between  $Ln$  atoms must be very small since the  $Ln$ - $Ln$  distances are very long. The magnetic features of  $LnT_4P_{12}$  do not depend only on the  $Ln$ - $Ln$  distances. As shown in Table 2, the bond angles for TbFe<sub>4</sub>P<sub>12</sub> are considerably different from those of TbRu<sub>4</sub>P<sub>12</sub>. Especially, the  $T$ -P- $T'$  angles are very different for both compounds. Thus, these may be closely related to the magnetic behavior in the skutterudite compounds. The magnetic properties of  $LnT_4P_{12}$  ( $Ln = Gd$  and  $Tb$ ;  $T = Fe, Ru$  and  $Os$ ) must arise from the interactions between the  $Ln$ , P and  $T$  (Fe, Ru and Os) atoms.

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