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Electrical and magnetic properties of new filled skutterudites LnFe$_4$P$_{12}$ (Ln = Ho, Er, Tm and Yb) and YRu$_4$P$_{12}$ with heavy lanthanide (including Y) prepared at high pressure

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Abstract

New filled skutterudites LnFe$_4$P$_{12}$ (Ln = Ho, Er, Tm and Yb) and YRu$_4$P$_{12}$ with
heavy lanthanide (including Y) have been prepared at high temperatures and
high pressures. Electrical and magnetic properties of these compounds have
been studied at low temperatures. The magnetic susceptibility of HoFe$_4$P$_{12}$ and
ErFe$_4$P$_{12}$ follows the Curie–Weiss behaviour at higher temperatures. The linear
slope of χ^{-1} versus T curves yields effective magnetic moments of 10.43 μ_B
for HoFe$_4$P$_{12}$ and 9.59 μ_B for ErFe$_4$P$_{12}$. These values are in good agreement
with magnetic moments of Ho^{3+} and Er^{3+} ions calculated from Hund's rule,
10.60 and 9.69 μ_B, respectively. HoFe$_4$P$_{12}$ shows a ferromagnetic transition
at around 5 K. TmFe$_4$P$_{12}$ and YbFe$_4$P$_{12}$ exhibit the paramagnetic behaviour
at low temperatures. The lattice constant of YbFe$_4$P$_{12}$ is 7.7877(5) Å, larger
than the value expected from the skutterudite compounds with the oxidation
state of +3. This compound may be in an intermediate valence state. YRu$_4$P$_{12}$
shows the superconducting transition at around 8.5 K. This compound is a new
superconductor. The T_c of YRu$_4$P$_{12}$ is higher than that of YFe$_4$P$_{12}$ and YOs$_4$P$_{12}$,
and is highest among the metal phosphides with a skutterudite-type structure.

1. Introduction

Filled skutterudites LnT$_4$X$_{12}$ (Ln = lighter lanthanide, T = Fe, Ru and Os, X = P, As
and Sb) with lighter lanthanide show interesting physical properties at low temperatures.
Superconducting [1–3], semiconducting [4], metal–insulator transition [5, 6], magnetic [7],
heavy-fermion [8], intermediate-valence [9] and non-Fermi-liquid behaviour [10] have
been observed in these materials. Further, skutterudite compounds exhibit remarkable

thermoelectric properties [11, 12]. These materials crystallize in a filled skutterudite-type structure (cubic, space group $Im\bar{3}$) [6, 13].

We have prepared new filled skutterudites with heavy lanthanide (including Y) at high temperatures and high pressures [14–16]. $GdRu_4P_{12}$ and $TbRu_4P_{12}$ are synthesized only at high pressure [14]. $GdRu_4P_{12}$ shows antiferromagnetic ordering at low temperatures. On the other hand, $GdFe_4P_{12}$ and $GdOs_4P_{12}$ show ferromagnetic transitions at around 22 and 5 K, respectively [16]. Similar behaviour is also observed for TbT_4P_{12} (T = Fe, Ru and Os) [17]. $DyFe_4P_{12}$ indicates a ferromagnetic ordering at around 10 K [15]. In contrast, $DyOs_4P_{12}$ does not show any magnetic transition down to 2 K [16]. However, there is a small electrical anomaly at around 5 K. YFe_4P_{12} and YOs_4P_{12} show the superconducting transition at around 7 and 3 K, respectively [15, 16, 18].

We have prepared new filled skutterudites $LnFe_4P_{12}$ (Ln = Ho, Er, Tm and Yb) and YRu_4P_{12} with heavy lanthanide (including Y) at high temperatures and high pressures, and have studied electrical and magnetic properties of these compounds at low temperatures. In this report, physical properties of new filled skutterudites prepared at high pressure are discussed.

2. Experimental procedure

By use of a wedge-type cubic-anvil high-pressure apparatus, many filled skutterudites with lighter lanthanide have been prepared at high temperatures and high pressures [2, 4, 5]. 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's movement is completely synchronized by means of a wedge system. The sample assembly for the preparation of filled skutterudites is similar to that used for the high-pressure synthesis of ternary metal compounds [19]. New filled skutterudites with heavy lanthanide (including Y), $LnFe_4P_{12}$ (Ln = Ho, Er, Tm and Yb) and YRu_4P_{12} were prepared by reaction of stoichiometric amounts of each metal and red phosphorus powders at around 4 GPa. The reaction temperatures were between 1000 and 1200 °C. These products were characterized by powder x-ray diffraction using Cu Kα radiation and silicon as a standard at ambient pressure. Figure 1 shows x-ray diffraction patterns of $HoFe_4P_{12}$ and $YbFe_4P_{12}$ at room temperature. These profiles were indexed in the filled skutterudite-type structure. When we prepared $HoFe_4P_{12}$ at high pressure, a small amount of FeP_2 was also produced. X-ray diffraction patterns of $ErFe_4P_{12}$, $TmFe_4P_{12}$ and YRu_4P_{12} are very similar to those of $HoFe_4P_{12}$ and $YbFe_4P_{12}$. Lattice constants of $LnFe_4P_{12}$ (Ln = Ho, Er, Tm and Yb) and YRu_4P_{12} are 7.7854(1), 7.7832(2), 7.7802(1), 7.7877(5) and 8.0298 (2) Å, respectively.

Copper or gold lead was attached to polycrystalline samples with silver paste, 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.

3. Results and discussion

We have systematically prepared new filled skutterudites with heavy lanthanide $LnFe_4P_{12}$ (Ln = lanthanide) at high pressures [15]. Recently, the good samples of $YbFe_4P_{12}$ have been obtained at high temperatures and high pressures. The lattice parameter of this compound is $a = 7.7877(5)$ Å. Figure 2 shows the relationship between the lattice constants and atomic numbers of lanthanide in $LnFe_4P_{12}$ (Ln = lanthanide). The lattice constant of these compounds basically decreases with increasing atomic number. However, some anomalies in this curve are observed for the Ce, Eu and Yb compounds. These may closely be related to the valence
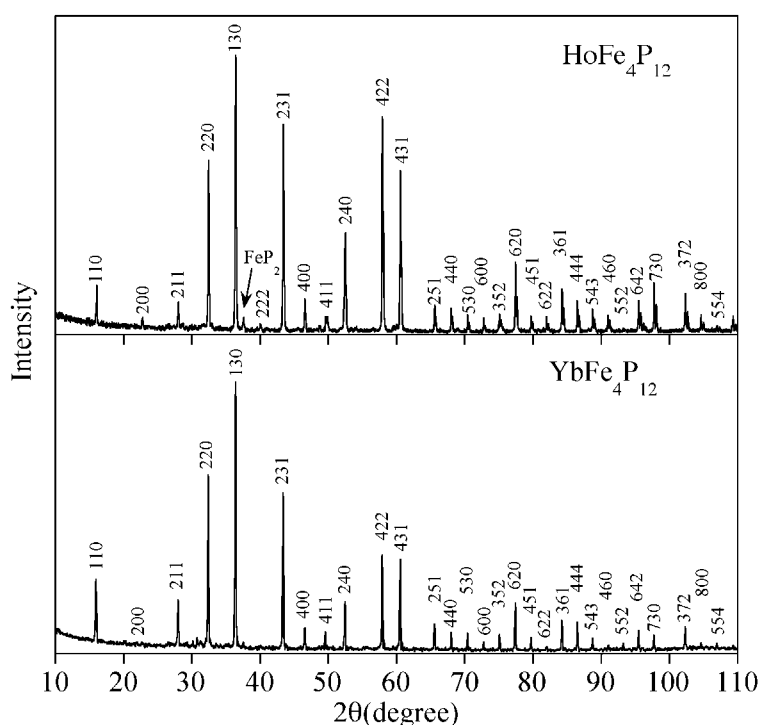
Figure 1. X-ray diffraction patterns of $HoFe_4P_{12}$ and $YbFe_4P_{12}$ at room temperature.

states in the materials. The oxidation states of CeT_4P_{12} [20–22] and EuT_4P_{12} (T = Fe, Ru and Os) [16, 23, 24] have already been discussed. The lattice constant of these Eu compounds is larger than that of skutterudites with trivalent ions. The magnetic behaviour of these compounds suggests that the Eu ions are divalent. The lattice constant of $YbFe_4P_{12}$ is larger than the value expected from some skutterudites with the oxidation state of +3. Thus, Yb ions in $YbFe_4P_{12}$ seem to be in a divalent or valence fluctuating state.

Figure 3 shows dc magnetic susceptibility and inverse susceptibility of $HoFe_4P_{12}$ measured in a magnetic field of 1 tesla (T) at low temperatures. The susceptibility of this phosphide follows a Curie–Weiss behaviour at higher temperatures. The linear slope of the χ^{-1} versus T curve from 10 to 300 K yields an effective magnetic moment of 10.43 μ_B. This value is close to the magnetic moment of Ho^{3+} ion calculated from Hund's rule, 10.60 μ_B. The positive Weiss constant and the sudden increase of susceptibility in $HoFe_4P_{12}$ shows the ferromagnetic transition at around 5 K. The magnetization versus applied magnetic field curves for $HoFe_4P_{12}$ at 2 and 15 K are inserted in figure 3. The magnetization of this phosphide abruptly increases in the low field region and saturates in the higher field region at 2 K. These magnetic features in $HoFe_4P_{12}$ are due to the occurrence of the ferromagnetic ordering at around 5 K. There is a small amount of FeP_2 in the diffraction pattern of $HoFe_4P_{12}$. As FeP_2 is a nonmagnetic compound, this phosphide does not affect the magnetic property of the Ho compound. Figure 4 shows the electrical resistivity of $HoFe_4P_{12}$ at low temperatures. The resistivity decreases with decreasing temperature down to 5 K. An electrical anomaly based on the magnetic ordering in $HoFe_4P_{12}$ is observed at around 5 K.

Figure 5 shows the temperature dependence of dc magnetic susceptibility and inverse susceptibility of $ErFe_4P_{12}$ measured in a magnetic field of 1 T. The susceptibility of $ErFe_4P_{12}$
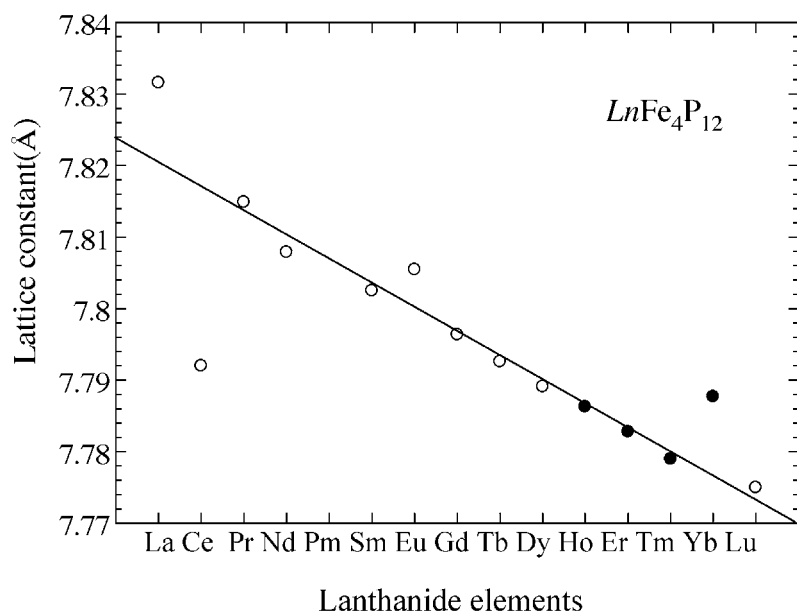
Figure 2. Relationship between lattice constants and atomic numbers of lanthanide in $LnFe_4P_{12}$ (Ln = lanthanide). We have studied physical properties of the filled skutterudites shown by a black circle.

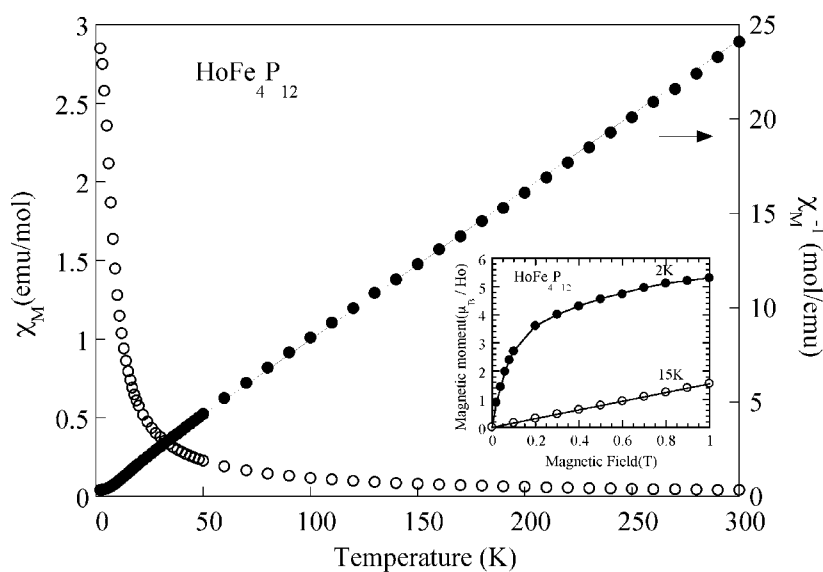**Figure 3.** Temperature dependence of dc magnetic susceptibility and inverse susceptibility of $HoFe_4P_{12}$ measured in a magnetic field of 1 tesla (T). Inset: magnetic moment versus magnetic field curves at 2 and 15 K.

follows the Curie–Weiss behaviour at high temperatures. The linear slope of the χ^{-1} versus T curve from 10 to 300 K yields an effective magnetic moment of 9.59 μ_B. This value is in good agreement with the magnetic moment of the Er^{3+} ion calculated from Hund's rule, 9.69 μ_B.
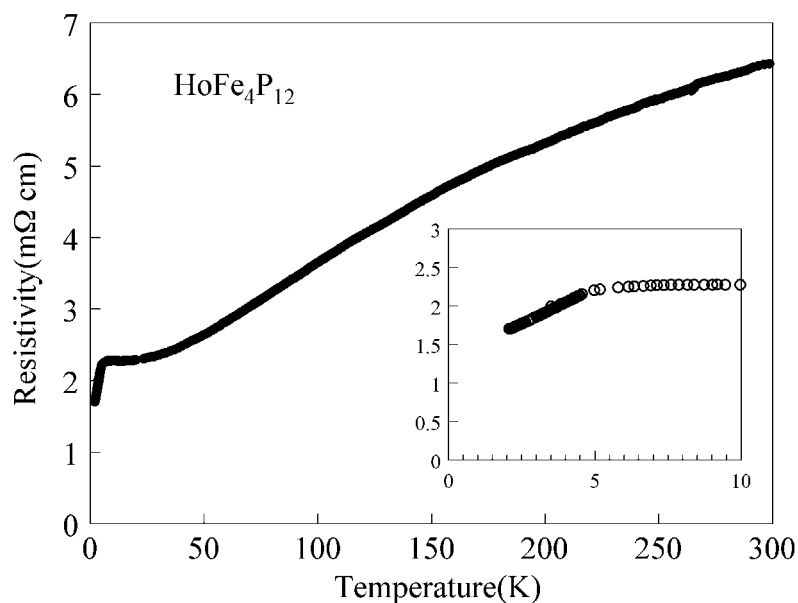
Figure 4. Electrical resistivity versus temperature curves for HoFe$_4$P$_{12}$.

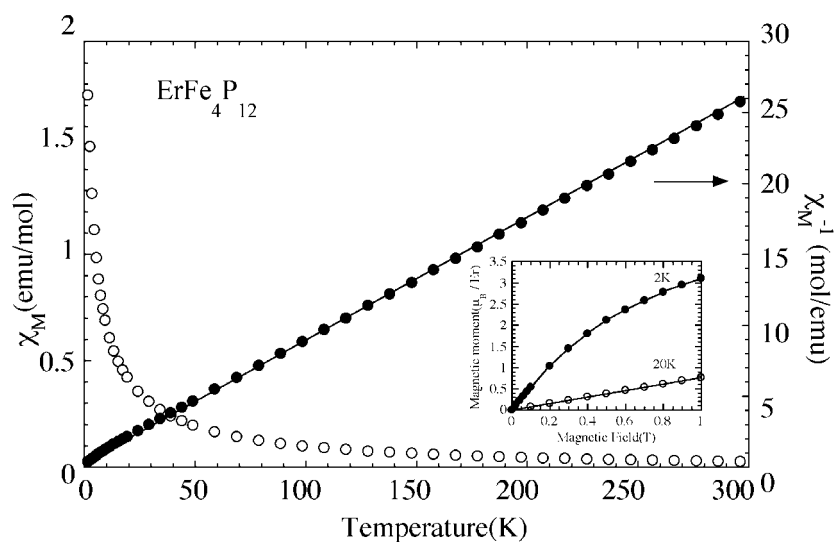**Figure 5.** Magnetic susceptibility and inverse susceptibility of ErFe$_4$P$_{12}$ measured in a magnetic field of 1 T at low temperatures. Inset: magnetic moment versus magnetic field curves at 2 and 20 K.

The magnetization of ErFe$_4$P$_{12}$ linearly increases with increasing magnetic field at 20 K, and considerably increases in the low field region but does not saturate up to 1 T at 2 K.

Figure 6 shows the dc magnetic susceptibility and inverse susceptibility of TmFe$_4$P$_{12}$ measured in a magnetic field of 1 T at low temperatures. The susceptibility of TmFe$_4$P$_{12}$ follows the Curie–Weiss law at higher temperatures. The linear slope of the χ^{-1} versus T curve from 100 to 300 K yields an effective magnetic moment of 6.58 μ_B. The magnetic moments
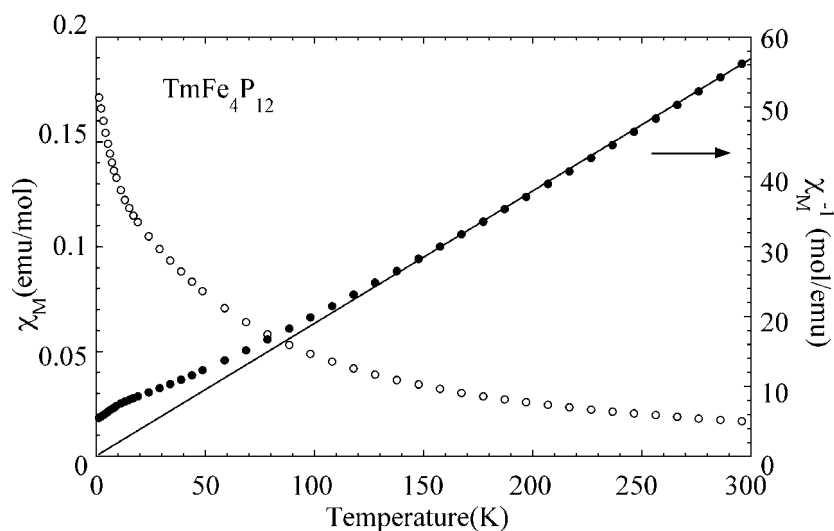
Figure 6. Magnetic susceptibility and inverse susceptibility versus temperature curves for TmFe$_4$P$_{12}$ measured in a magnetic field of 1 T.
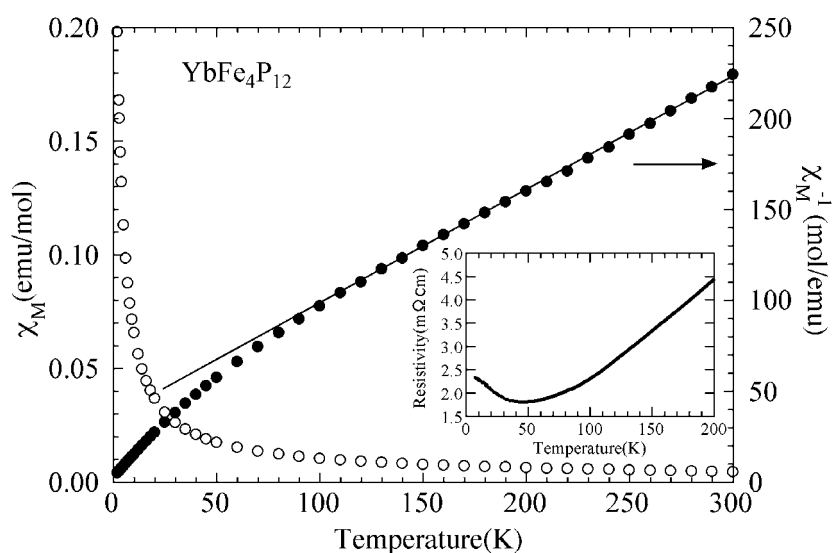

Figure 7. Magnetic susceptibility and inverse susceptibility of YbFe$_4$P$_{12}$ measured in a magnetic field of 1 T at low temperatures. Inset: resistivity versus temperature curve.

of Tm^{2+} and Tm^{3+} ions calculated from Hund's rule are 4.54 μ_B and 7.57 μ_B, respectively. The magnetization of TmFe$_4$P$_{12}$ linearly increases with increasing magnetic field at 2, 10 and 20 K. The phosphide indicates the paramagnetic behaviour at low temperatures.

Figure 7 shows the temperature dependence of the resistivity ratio ($\rho/\rho_{273\,K}$) of ErFe$_4$P$_{12}$ and TmFe$_4$P$_{12}$. The resistivity of ErFe$_4$P$_{12}$ decreases monotonically with decreasing temperature down to 12 K. Below this temperature, the resistivity slowly increases with decreasing temperature. The magnetic anomaly is not observed at around 12 K. The resistivity of TmFe$_4$P$_{12}$ decreases linearly with decreasing temperature down to 10 K.
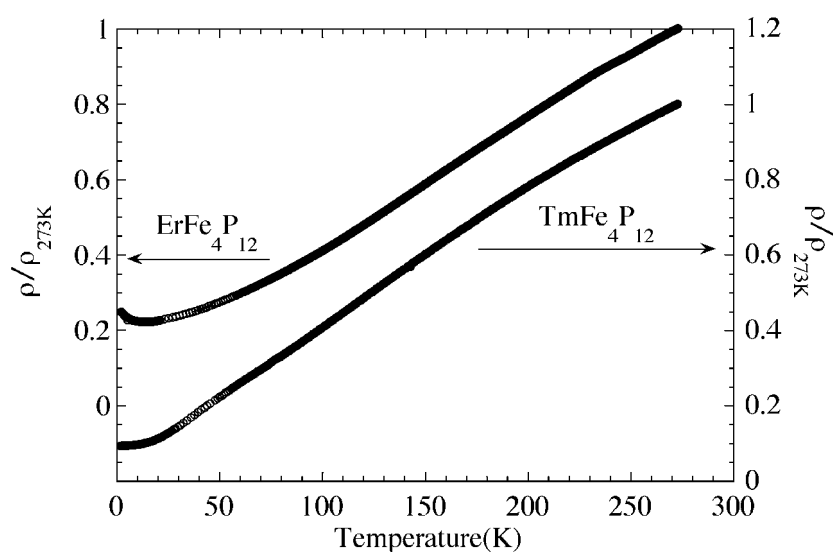
Figure 8. Resistivity ratio ($\rho/\rho_{273\ K}$) versus temperature curves for ErFe$_4$P$_{12}$ and TmFe$_4$P$_{12}$.

As shown in figure 2, there is an overhang of the lattice constant for YbFe$_4$P$_{12}$ in the lattice constant versus atomic number curve. The lattice constant of YbFe$_4$P$_{12}$ is larger than that of HoFe$_4$P$_{12}$ with the oxidation state of +3. Figure 8 shows dc magnetic susceptibility and inverse susceptibility of YbFe$_4$P$_{12}$ measured in a magnetic field of 1 T at low temperatures. The susceptibility of YbFe$_4$P$_{12}$ follows the Curie–Weiss behaviour at higher temperatures. The linear slope of the χ^{-1} versus T curve from 70 to 300 K yields an effective magnetic moment of 3.58 μ_B. The magnetic moment of Yb^{3+} ion calculated from Hund's rule is 4.54 μ_B. These results suggest that the Yb compound has an intermediate valence between +2 and +3. The magnetization of YbFe$_4$P$_{12}$ linearly increases with increasing magnetic field up to 1 T at 2 and 20 K. This compound exhibits the paramagnetic behaviour at low temperatures. The resistivity versus temperature curve for YbFe$_4$P$_{12}$ is inserted in figure 8. The resistivity of this phosphide decreases monotonically with decreasing temperature, but slowly increases from 45 K down to 2 K. The resistivity minimum is found at around 45 K.

The lattice parameter of YbFe$_4$Sb$_{12}$ is a = 9.158 Å, significantly larger than in Ln = La–Sm, and indicates a tendency towards divalent behaviour of Yb. The electrical resistivity, magnetic susceptibility and specific heat of this compound have been studied at low temperatures. Dilley *et al* suggest that Yb ions in YbFe$_4$Sb$_{12}$ have the intermediate valence between +2 and +3 [9]. Recently, the valence state of this compound has been reviewed in detail by Berardan *et al* [25].

Figure 9 shows the resistivity versus temperature curve for YRu$_4$P$_{12}$. The resistivity decreases with decreasing temperature, and drops sharply at around 8.5 K. The dc susceptibility is exhibited in the inset of the figure 9. The sample cooled in zero field shows a magnetic shielding expected for perfect diamagnetism. The existence of hysteresis between zero-field cooling (ZFC) and field cooling (FC) indicates that the phosphide is the type II superconductor. YRu$_4$P$_{12}$ is a new superconductor with the superconducting transition temperature (T_c) of 8.5 K.

Figure 10 shows the T_c versus lattice constant curves for YT$_4$P$_{12}$ and LaT$_4$P$_{12}$ (T = Fe, Ru and Os). The superconductivity of YFe$_4$P$_{12}$ and YOs$_4$P$_{12}$ was found at around 7 and 3 K,
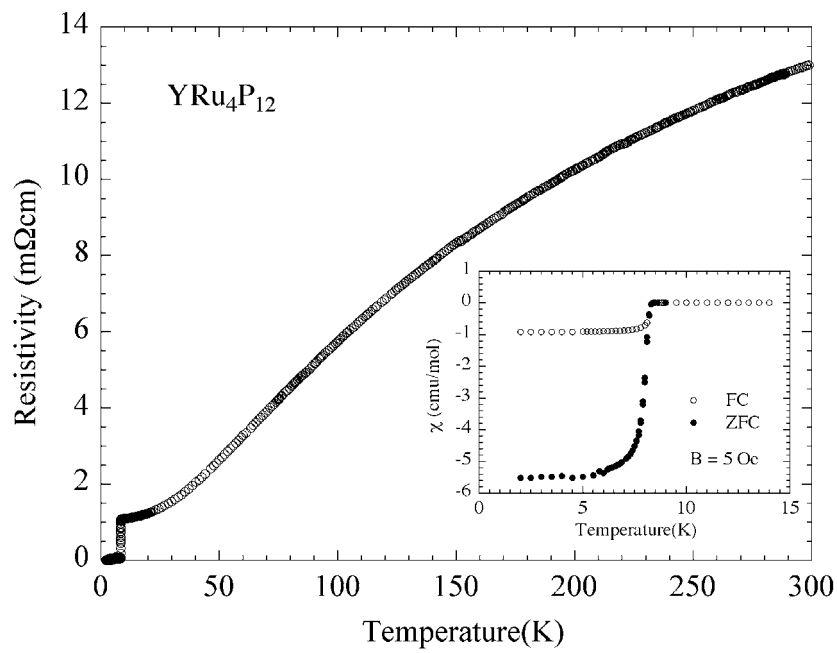
Figure 9. Resistivity versus temperature curve for YRu$_4$P$_{12}$. Inset: temperature dependence of dc susceptibility.
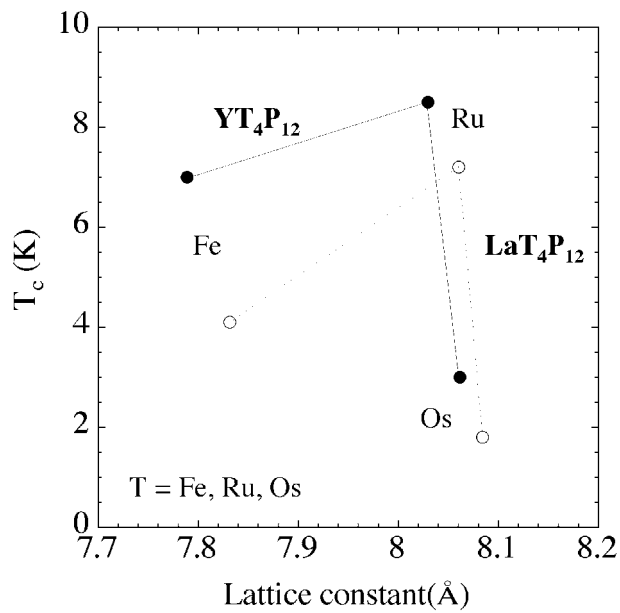

Figure 10. T_c versus lattice constant curves for YT$_4$P$_{12}$ and LaT$_4$P$_{12}$ (T = Fe, Ru and Os): black circle, Y compounds; open circle, La compounds.

respectively [15, 16, 18]. The T_c of YRu$_4$P$_{12}$ is higher than that of these Fe and Os compounds. Filled skutterudites LaT$_4$P$_{12}$ (T = Fe, Ru and Os) are superconductors with T_cs = 4.1, 7.2 and

1.8 K, respectively [2, 26]. The T_c values of YT_4P_{12} are higher than those of the corresponding La compounds. YRu_4P_{12} has the highest T_c among the metal phosphides with the skutterudite-type structure. The T_c values of YRu_4P_{12} and $LaRu_4P_{12}$ are higher than those of the Fe and Os compounds. We have already studied x-ray diffraction of LnT_4X_{12} (Ln = La, Ce and Pr; T = Fe, Ru and Os; X = P and Sb) at high pressures, and obtained their bulk moduli [20]. The bulk modulus of the Ru compounds is larger than the Fe and Os compounds. Thus, we suggest that the T_c of YT_4P_{12} and LaT_4P_{12} may be closely related to the bulk modulus.

Acknowledgments

References

[1] Shirotani I, Uchiumi T, Ohno T, Sekine C, Nakazawa Y, Kanoda K, Todo S and Yagi T 1997 *Phys. Rev.* B **56** 7866
[2] Uchiumi T, Shirotani I, Sekine C, Todo S, Yagi T, Nakazawa Y and Kanoda K 1999 *J. Phys. Chem. Solids* **60** 689
[3] Bauer E D, Frederick N A, Ho P C, Zapf V S and Maple M B 2002 *Phys. Rev.* B **65** 100506
[4] Shirotani I, Uchiumi T, Sekine C, Kimura S and Hamaya N 1999 *J. Solid State Chem.* **142** 146
[5] Sekine C, Uchiumi T, Shirotani I and Yagi T 1997 *Phys. Rev. Lett.* **79** 3218
[6] Shirotani I, Hayashi J, Adachi T, Sekine C, Kawakami T, Nakanishi T, Takahashi H, Tang J, Matsushita A and Matsumoto T 2002 *Physica* B **322** 408
[7] Danebrock M E, Christroph B, Evers H and Jeitschko W 1996 *J. Phys. Chem. Solids* **57** 381
[8] Bauer E D, Slebarski A, Freeman E J, Sirvent C and Maple M B 2001 *J. Phys.: Condens. Matter* **13** 4495
[9] Dilley N R, Freeman E J, Bauer E D and Maple M B 1998 *Phys. Rev.* B **58** 6287
[10] Takeda N and Ishikawa M 2001 *J. Phys.: Condens. Matter* **13** 5971
[11] Sales B C, Mandrus D and Williams R K 1996 *Science* **272** 1325
[12] Sekine C, Akita K, Yanase N, Shirotani I, Inagawa I and Lee C-H 2001 *Japan. J. Appl. Phys.* **40** 3326
[13] Jeitschko W and Braun D 1977 *Acta Crystallogr.* B **33** 3401
[14] Sekine C, Uchiumi T, Shirotani I, Matsuhira K, Sakakibara T, Goto T and Yagi T 2000 *Phys. Rev.* B **62** 11581
[15] Shirotani I, Shimaya Y, Kihou K, Sekine C and Yagi T 2003 *J. Solid State Chem.* **174** 32
[16] Kihou K, Shirotani I, Shimaya Y, Sekine C and Yagi T 2004 *Mater. Res. Bull.* **39** 317
[17] Kihou K, Sekine C, Shirotani I, Lee C-H, Hijiri K and Takeda K 2005 *Physica* B at press
[18] Shirotani I, Shimaya Y, Kihou K, Sekine C, Takeda N, Ishikawa M and Yagi T 2003 *J. Phys.: Condens. Matter* **15** S2201
[19] Shirotani I 2003 *Bull. Chem. Soc. Japan* **76** 1291
[20] Shirotani I, Noro T, Hayashi J, Sekine C, Giri R and Kikegawa T 2004 *J. Phys.: Condens. Matter* **16** 7853
[21] Jung D, Whangbo M-H and Alvarez S 1990 *Inorg. Chem.* **29** 2252
[22] Nordstrom L and Singh D J 1996 *Phys. Rev.* B **53** 1103
[23] Sekine C, Inoue M, Inaba T and Shirotani I 2000 *Physica* B **281/282** 308
[24] Grandjean F, Gerard A, Braun D J and Jettschko W 1984 *J. Phys. Chem. Solids* **45** 877
[25] Berardan D, Godart C, Alleno E, Berger St and Bauer E 2003 *J. Alloys Compounds* **351** 18
[26] DeLong L E and Meisner G P 1985 *Solid State Commun.* **53** 119