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Superconductivity of new filled skutterudite YFe_4P_{12} prepared at high pressure

I Shirotani[1], Y Shimaya[1], K Kihou[1], C Sekine[1], N Takeda[2], M Ishikawa[2] and T Yagi[2]

[1] Muroran Institute of Technology, 27-1, Mizumoto, Muroran-shi 050-8585, Japan
[2] Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwa-no-ha, Kashiwa-shi, Chiba 277-8581, Japan

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Abstract
A new filled skutterudite YFe_4P_{12} has been prepared at high temperatures and high pressures. The electrical resistivity and dc magnetic susceptibility of this compound were measured at low temperatures. The superconductivity in YFe_4P_{12} is observed at around 7 K. This phosphide is a new superconductor. The specific heat of YFe_4P_{12} has been studied between 2 and 20 K. The specific heat fitted to the expression $C = \gamma T + \beta T^3$, by a least squares analysis, yielded the values $\gamma = 27.2$ mJ mol^{-1} K^{-2} and $\beta = 0.195$ mJ mol^{-1} K^{-4}. The Debye temperature (Θ_D) is found to be 553 K. The electronic density of the states at the Fermi energy for YFe_4P_{12} is 0.45 state eV^{-1}/atom.

1. Introduction

Ternary metal pnictides with the general formula LnT_4X_{12} (Ln = lanthanide; T = Fe, Ru and Os; X = pnicogen) crystallize in a skutterudite ($CoAs_3$-type) structure filled by lanthanide atoms [1]. These filled skutterudites show an interesting superconductivity at low temperatures. One of the most striking features of filled skutterudites is the occurrence of the superconductivity in $LaFe_4P_{12}$ with the ferromagnetic element Fe [2]. The ternary metal phosphides LaT_4P_{12} (T = Fe, Ru and Os) are superconductors with the superconducting transition temperatures (T_cs) = 4.1, 7.2 and 1.8 K, respectively [2–4]. The superconductivity in $LaRu_4X_{12}$ (X = As and Sb) is observed at around 10.3 and 2.8 K, respectively [5, 6]. The T_c of $LaRu_4As_{12}$ is highest among the skutterudite compounds. The compound $PrRu_4As_{12}$ is the specially interesting superconductor with a T_c of 2.4 K [5] because the superconductivity in $PrRu_4P_{12}$ [7] is not observed down to 2 K. $PrOs_4Sb_{12}$, which is a heavy fermion compound, shows the anomalous superconductivity below 1.8 K [8]. We have prepared a new filled skutterudite YFe_4P_{12} at high temperatures and high pressures, and have found the superconducting transition at around 7 K. In this paper the physical property in this new superconductor with the ferromagnetic element Fe is discussed.

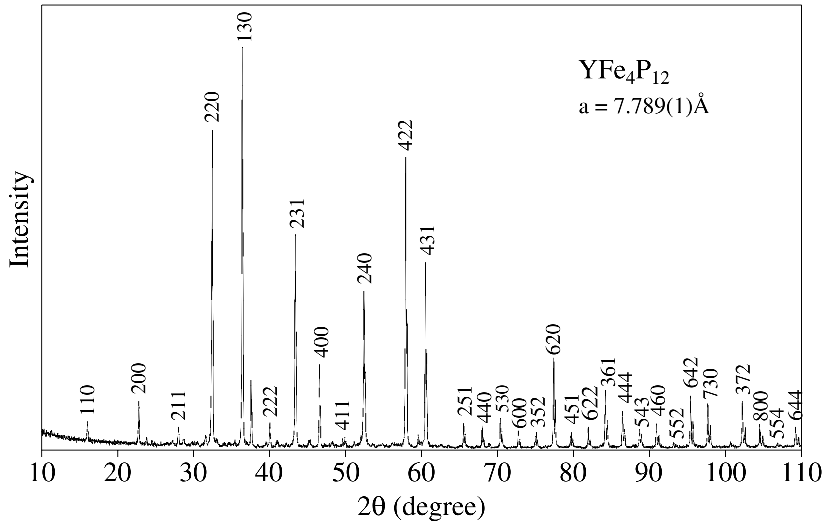

Figure 1. X-ray diffraction pattern of YFe_4P_{12} prepared at around 1050 °C and 4 GPa.

2. Experiment

Using a wedge-type cubic-anvil high-pressure apparatus, YFe_4P_{12} was prepared at high temperatures and high pressures. The sample assembly for the preparation of the filled skutterudite is similar to that used for the synthesis of black phosphorus [9]. YFe_4P_{12} was prepared by reaction of stoichiometric amounts of each metal and red phosphorus powders at around 1050 °C and 4 GPa. The samples were characterized by powder x-ray diffraction using Cu Kα radiation and silicon as a standard. Figure 1 shows the x-ray diffraction pattern of YFe_4P_{12}. Many diffraction lines of the compound are assigned by the index of the cubic skutterudite structure. The lattice constant of the phosphide is $a = 7.789(1)$ Å. A small amount of FeP_2 is produced at high pressure, but this compound does not show superconductivity down to 2 K. Copper or gold leads were attached to polycrystalline samples with silver-epoxy, and four-points electrical resistivity 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. The specific heat measurement for YFe_4P_{12} was performed in the temperature range between 2 and 20 K.

3. Results

Figure 2 shows the resistivity versus temperature curve for YFe_4P_{12} at low temperatures. The resistivity decreases with decreasing temperature, and drops sharply at around 7 K. Figure 3 shows the temperature dependence of the dc magnetic susceptibility measured in an applied magnetic field of 5 Oe for YFe_4P_{12}. The sample cooled in zero field shows a magnetic shielding equal to approximately 100% of that expected for perfect diamagnetism. The existence of hysteresis between zero-field cooling (ZFC) and field cooling (FC) indicates that the phosphide is a type II superconductor. YFe_4P_{12} is a new superconductor with the ferromagnetic element Fe. Figure 4 shows the result of the specific heat measurement of YFe_4P_{12} at low temperatures. The heat capacity C can be fitted to the expression $C = \gamma T + \beta T^3$ by a least-squares analysis, which yields the value $\gamma = 27.2$ mJ mol^{-1} K^{-2} and $\beta = 0.195$ mJ mol^{-1} K^{-4}, the latter

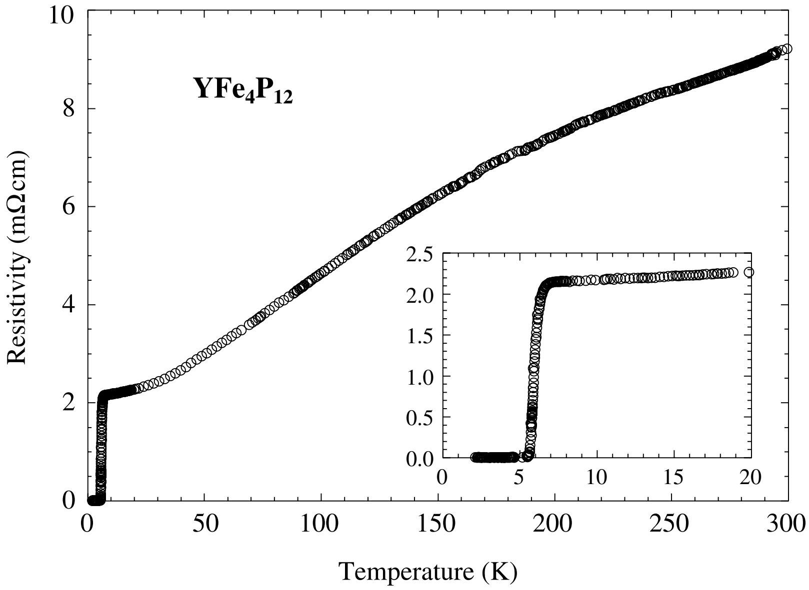

Figure 2. Electrical resistivity of YFe_4P_{12} at low temperatures.

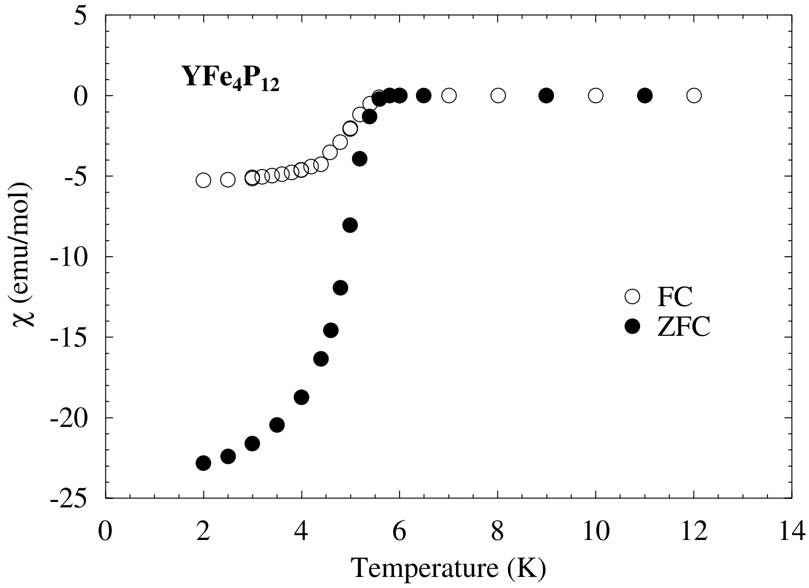

Figure 3. Magnetic susceptibility measured in an applied magnetic field of 5 Oe for YFe_4P_{12} at low temperatures.

value corresponding to the Debye temperature $\Theta_D = 553$ K. Since the specific heat jump ΔC is 200 mJ mol^{-1} K^{-1} at T_c(=5.5 K), $\Delta C/\gamma T_c$ is 1.33. This value almost agrees with 1.43 of BCS theory. In the normal state, $T > T_c$ the coefficient γ is related to the electronic density

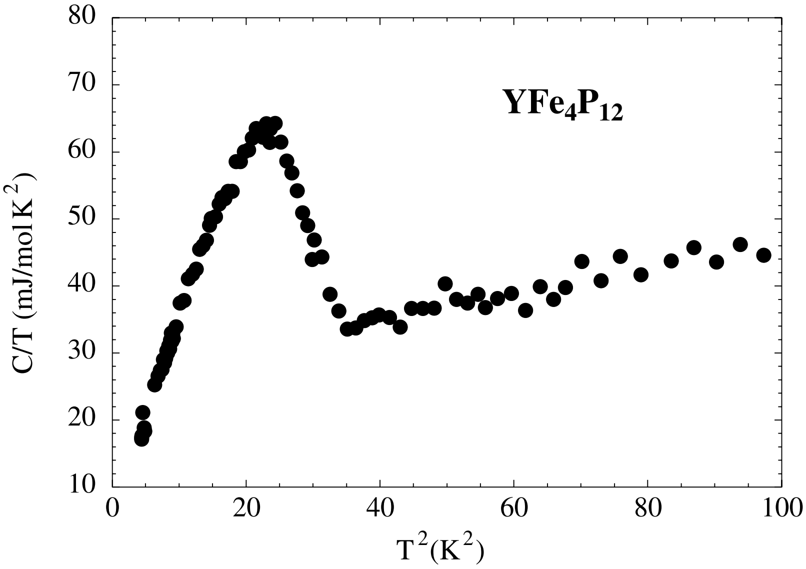

Figure 4. Low temperature specific heat of YFe_4P_{12}.

of state at Fermi energy, $N(0)$:

$$\gamma = \frac{\pi^2}{3} n N_0 k_B^2 N(0)(1 + \lambda) \tag{1}$$

where n is the number of atoms per formula unit, N_0 is Avogadro's number, k_B is the Boltzmann constant and λ is the electron–phonon coupling parameter given by McMillan [10]. The coefficient β is related to the Debye temperature by the following equation:

$$\beta = \frac{12}{5} \pi^4 n N_0 k_B / \Theta_D^3. \tag{2}$$

In order to derive $N(0)$, McMillan's formula for λ may be used:

$$\lambda = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_c)}{(1 - 0.62\mu^*) \ln(\Theta_D/1.45T_c) - 1.04} \tag{3}$$

where μ^* is taken to be 0.1 [11, 12]. The values of λ and $N(0)$ are 0.50 and 0.45 states eV^{-1}/atom for YFe_4P_{12}. The T_c^{onset} (7 K) of YFe_4P_{12} is about 3 K higher than that (4.1 K) of $LaFe_4P_{12}$ [1]. However, the density of state at Fermi energy for YFe_4P_{12} is lower than that of $LaFe_4P_{12}$ [11]. One of the most striking features of filled skutterudites is the occurrence of superconductivity in $LaFe_4P_{12}$ and YFe_4P_{12} with the ferromagnetic element Fe. Recently, Shimizu *et al* have reported that iron behaves as a superconductor below 2 K at pressures between 15 and 30 GPa [13]. The superconducting transitions in $M_2Fe_3Si_5$ (M = Sc, Y and Lu) were observed at around 2–6 K [14]. YFe_4P_{12} has the highest T_c among those materials containing the ferromagnetic element Fe.

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