Pressure studies in filled skutterudite La$_{0.8}$Rh$_4$P$_{12}$

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Abstract. Filled skutterudite La$_x$Rh$_4$P$_{12}$ has the highest superconducting transition temperature ($T_c$) of 17 K [1]. An analysis of superconducting parameters of La$_x$Rh$_4$P$_{12}$ suggests that the relatively large the electron-phonon coupling constant $\lambda$ among the ternary filled skutterudite-type phosphides is one of the reasons why it has high $T_c$. In this study, high-pressure electrical resistively measurements for La$_{0.8}$Rh$_4$P$_{12}$ at $T_c = 13.6$ K using a piston cylinder device and a diamond anvil cell have been carried out up to 15 GPa. $T_c$ decreases with applying pressure at a rate of -0.5 K/GPa. High-pressure x-ray diffraction measurements have also been performed up to 5 GPa. The value of $B_0$ of 120 GPa is calculated from the x-ray data.

1. Introduction

The general chemical formula of the ternary filled skutterudite is MT$_4$X$_{12}$ (where M, T, and X are rare-earth and alkaline-earth metals, transition metals, and pnictides, respectively). This substance shows various physical properties, such as superconductivity, semiconductivity, metal-insulator transition, magnetic ordering, heavy fermion behavior, and so on. 14 filled skutterudite compounds have been reported to show superconductivity, so far. Among them, La$_x$Rh$_4$P$_{12}$ was reported to be the highest superconducting transition temperature ($T_c$) of 17 K [1]. The crystal structure of filled skutterudites MT$_4$P$_{12}$ is cubic, with space group Im-3. The M atoms locate at (000) and (1/2 1/2 1/2) of the cubic structure like bcc, and are adjacent twelve X atoms forming icosahedrons through strong covalent bond as shown in Figure 1. The atoms located at (1/4 1/4 1/4) are in the center of a distorted octahedral environment of six X atoms. The degree of hybridization of 4f electrons of rare-earth atoms in the icosahedron and p electron of networking pnictogen atom is thought to be one of the factors in showing fruitful variety of physical properties [1, 2].

In this paper, we report the pressure effects on superconducting properties of La$_x$Rh$_4$P$_{12}$ having the highest $T_c$ among the filled skutterudite compounds. The sample La$_{0.8}$Rh$_4$P$_{12}$ was prepared using a belt-type high-pressure apparatus [3]. Electrical resistivity measurements under high pressure have been carried out up to 3.0 GPa using a piston-cylinder device and up to 15 GPa using a diamond anvil cell (DAC). High-pressure x-ray diffraction measurements have also been performed using a multi-
2. Experimental procedure

The starting material, a powdered 1:4:12 molar mixture of La (nominal purity 99.9%), Rh (nominal purity 99.9%), and P (nominal purity 99.999%), was pressurized and heated to 9.4 GPa and 1473 K using a belt-type high-pressure apparatus. The chemical formula of the sample determined by electron probe microanalysis (EPMA) is \( \text{La}_{0.82}\text{Rh}_{3.9}\text{P}_{12.1} \). However, hereinafter, \( \text{La}_{0.8}\text{Rh}_{4}\text{P}_{12} \) denoted \( \text{La}_{0.82}\text{Rh}_{3.9}\text{P}_{12.1} \). Lattice constants have been determined by x-ray diffractometry to be 8.0785(2) Å; the density 5.59(7) g/cm\(^3\) [3].

High pressures are generated by the piston-cylinder apparatus up to 3.0 GPa in the temperature range of 4 - 300 K. A mixture of Fluronert (FC70:FC77=1:1) was used as a pressure transmitting medium. The size of rectangular sample is 1.41 mm in length, 0.93 mm in width and 0.30 mm in thickness. Electrical resistivity measurements were performed by a dc four-lead method. Gold wire as lead was attached to the sample using silver paste. The DAC is also used for the electrical resistivity measurements under higher pressures above 3 GPa. The cullet of diamonds in the DAC was \( \phi 0.6 \) mm in diameter. Rhenium plate with 0.2 mm in thickness was used for gasket. Powdered NaCl was used for the pressure transmitting medium. The electrical resistivity was measured by the dc four-lead method, in which Pt thin film was used as lead wire. Electrical insulation was realized by Al\(_2\)O\(_3\) powder which veils metallic gasket. The pressure in case of DAC was determined by a ruby fluorescence method using DPSS laser.

X-ray diffraction measurements at high pressures were performed in the beam line of the TRISTAN accumulation ring (AR-NE5) at High Energy Accelerator Research Organization (KEK) [4]. High pressures were applied by the multi-anvil high-pressure apparatus MAX80 [5]. WC anvils with square flat-surface size of 6 mm \( \times \) 6 mm were used. A powdered sample was loaded in the h-BN capsule and it was set in the center of a boron-epoxy pressure-transmitting medium. The pressure was evaluated from the lattice constant of a NaCl internal pressure marker [6]. X-ray diffraction patterns were measured by an energy-dispersive method using synchrotron radiation from the bending magnet. Lattice constants were obtained by the least-squares fitting of the indexed pattern.
3. Results and discussion

Figure 2 (a) and (b) show the electrical resistivity versus temperature curves for La$_{0.8}$Rh$_4$P$_{12}$ using the piston-cylinder apparatus and using the DAC, respectively. $T_c$ was determined by the temperature at which the resistivity loss was observed due to superconducting transition. From these results, it is observed that $T_c$ shows slight decrease up to 2.5 GPa and a pronounced decrease above 3.0 GPa up to 15.4 GPa, with increasing pressure. The superconducting state is destroyed more rapidly in the pressure region above 3.0 GPa, where the DAC was used. The pressure dependence of $T_c$ is shown in Figure 3. The value of $dT_c/dP$ is estimated to be -0.3 K/GPa below 2.5 GPa and -0.5 K/GPa above 3.0 GPa. $T_c$ extrapolated to ambient pressure was estimated to be 13.6 K.

![Figure 2](image1.png)

(a) The electrical resistivity versus temperature curves and (b) the electrical resistance versus temperature curves for La$_{0.8}$Rh$_4$P$_{12}$.

![Figure 3](image2.png)

Figure 3. The pressure dependence of $T_c$. The value of $dT_c/dP$ is estimated to be -0.3 K/GPa in the range of pressure using the piston-cylinder apparatus and -0.5 K/GPa in the range of pressure using the DAC.

Figure 4 (a) and (b) show the normalized lattice constant and volume as a function of pressure, respectively. In Figure 4, it is observed that the lattice constant and the volume show approximately
linear compression. A bulk modulus $B_0$ calculated by the Birch equation was 118.79 GPa [7]. On the other hand, the bulk modulus $B_0$ calculated by the Murnaghan-Birch equation was 125.97 GPa ($B_0'$ = 7.9294) [7].

$T_c$’s, lattice constants, and bulk moduli of several superconducting filled skutterudites are summarized in Table 1 [8, 9]. While the lattice constants of La$_{0.8}$Rh$_4$P$_{12}$, LaRu$_4$P$_{12}$, and PrRu$_4$P$_{12}$ were close to each other, LaRu$_4$Sb$_{12}$ and PrRu$_4$Sb$_{12}$ have the larger lattice constants than others listed in Table 1. Because an ionic size of Sb is larger than P, the lattice constant of LaRu$_4$Sb$_{12}$ is larger than LaRu$_4$P$_{12}$, and LaRu$_4$Sb$_{12}$ shows the smaller bulk modulus. In case of LaRu$_4$X$_{12}$ series shown in Table 1, LaRu$_4$As$_{12}$ has the highest $T_c$. LaOs$_4$X$_{12}$ series have the same tendency about $T_c$ [1]. From our results $d\ln T_c/dP$ is calculated to be $-0.02 \sim -0.03$ GPa$^{-1}$. In case of LaRu$_4$P$_{12}$, $d\ln T_c/dP$ is $-0.02$ GPa$^{-1}$, which is similar to one of La$_{0.8}$Rh$_4$P$_{12}$. Then there might be some similarities between La$_{0.8}$Rh$_4$P$_{12}$ and LaRu$_4$P$_{12}$ if considering that the superconductivity is related to the volume of these compounds somehow. Thus, if LaRh$_4$As$_{12}$ is synthesized, it could have the highest $T_c$ among the filled skutterudites, because it is inferred that the negative pressure effect on La$_{0.8}$Rh$_4$P$_{12}$ enhances the $T_c$. As a next step, we will perform the high pressure experiments of other filled skutterudites compounds to

Table 1. $T_c$’s, lattice constants, bulk moduli and the pressure dependence of $T_c$ of several superconducting filled skutterudites are summarized.

| Compound       | $T_c$ (K) | Lattice constant a (Å) | Bulk moduli $B_0$ (GPa) | $dT_c/dP$ (K/GPa) |
|----------------|-----------|------------------------|-------------------------|-------------------|
| La$_{0.8}$Rh$_4$P$_{12}$ | 13.6       | 8.0785                 | 125.97                  | $-0.3 \sim -0.5$  |
| La$_4$Rh$_4$P$_{12}$        | 17         | 8.0581                 | -                       | -                 |
| LaRu$_4$P$_{12}$            | 7.2        | 8.0605                 | 172                     | -0.16             |
| LaRu$_4$As$_{12}$           | 10.3       | 8.5081                 | -                       | -0.4              |
| LaRu$_4$Sb$_{12}$           | 3.58       | 9.2781                 | 98                      | -                 |
| PrRu$_4$P$_{12}$ (14.7GPa)  | 2          | 8.0516                 | 207                     | -                 |
| PrRu$_4$Sb$_{12}$           | 1.1        | 9.2648                 | 111                     | -0.21             |

Figure 4. (a) The normalized lattice constant and (b) volume as a function of pressure. Run1 and Run2 are the first and the second run, respectively. The solid lines represent fitted data by the Murnaghan-Birch equation.
examine the correlation between the $T_c$ and the volume. The magnetic measurements under high pressure will also be carried out to clarify the pressure effect on the superconductivity in filled skutterudites.

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