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Superconductivity of the new skutterudite compound $La_xRh_4P_{12}$ prepared at high pressure

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Abstract

A new skutterudite compound $La_xRh_4P_{12}$ has been prepared at around 1100 °C and 4 GPa. This product was characterized by powder x-ray diffraction at ambient pressure. The x-ray diffraction profile of $La_xRh_4P_{12}$ is indexed to the filled skutterudite-type structure. The lattice constant of this sample is 8.0581(5) Å. The x value estimated from x-ray diffraction and electron probe microanalysis data is about 0.6. Electrical and magnetic properties of this compound have been studied at low temperatures. $La_xRh_4P_{12}$ showed a superconducting transition at around 17 K. This compound has the highest T_c among metal phosphides. The thermoelectric power of the new compound is negative, $S = -47\ \mu V\ K^{-1}$, at room temperature. The new superconducting material $La_xRh_4P_{12}$ is an n-type conductor.

1. Introduction

The superconductivity of various filled skutterudites has been studied at low temperatures. The ternary metal phosphides LaT_4P_{12} (T = Fe, Ru and Os) are superconductors with superconducting transition temperatures (T_cs) of 4.1, 7.2 and 1.8 K, respectively [1–3]. We have prepared new filled skutterudites with the element Y at high temperature and high pressure [4]. The compounds YT_4P_{12} (T = Fe, Ru and Os) show superconductivity at around 7, 8.5 and 3 K, respectively [5–7]. The T_cs of YT_4P_{12} are higher than those of the corresponding La compounds. The superconductivity of LaT_4X_{12} (T = Ru and Os; X = As and Sb) is observed at low temperatures [8–11]. $LaRu_4As_{12}$ has the highest T_c (10.3 K) among the skutterudite compounds. The interesting superconductivities of Pr-based skutterudites PrT_4X_{12} (T = Ru and Os; X = P, As and Sb) with f electrons have been investigated at low temperatures. $PrRu_4As_{12}$ shows a superconducting transition at around 2.4 K [8]. The pressure-induced superconductivity of $PrRu_4P_{12}$ is found at around 2 K and 14 GPa [12]. $PrOs_4Sb_{12}$ behaves as a heavy fermion superconductor at lower temperatures [13].

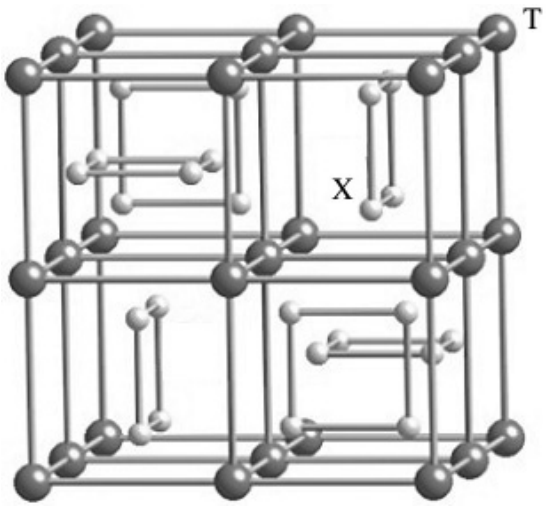

Figure 1. Crystal structure of a binary skutterudite compound with $CoAs_3$-type structure; T = Co, Rh and Ir, X = P, As and Sb.

Filled skutterudites LnT_4X_{12} (Ln = lanthanide; T = Fe, Ru and Os; X = P, As and Sb) crystallize in a skutterudite-type structure filled by lanthanide atoms [14]. This structure is cubic, with space group $Im\bar{3}$, $Z = 2$. Figure 1 shows the $CoAs_3$-type structure of binary skutterudite compounds with the general formula TX_3 (T = Co, Rh and Ir; X = P, As and Sb) [15]. There are two voids in the unit cells of these compounds. Metal atoms can be doped into these voids. Partially filled compounds $Ln_xCo_4P_{12}$ (Ln = lanthanide) are prepared by reaction of the elemental components in molten Sn at ambient pressure; the x value is below 0.25 [16]. Takizawa *et al* have synthesized new compounds $Sn_xCo_4Sb_{12}$ at high pressures; the x value increases with increasing pressure [17].

We have prepared the new skutterudite $La_xRh_4P_{12}$ at high temperature and high pressure. The electrical resistivity and magnetic susceptibility of this compound have been studied at low temperatures. Superconductivity of $La_xRh_4P_{12}$ is found at around 17 K.

2. Experimental procedure

By use of a wedge-type cubic-anvil high-pressure apparatus, various skutterudite compounds have been prepared at high temperatures and high pressures [2–9]. 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 skutterudite compounds is similar to that used for the high-pressure synthesis of ternary metal compounds [18]. The new skutterudite compound $La_xRh_4P_{12}$ was prepared by reaction of each metal and red phosphorus powders at around 4 GPa and 1100 °C. The retention time was 1.5 h under these conditions. This product was characterized by powder x-ray diffraction using Cu Kα radiation and silicon as a standard at ambient pressure. Figure 2 shows x-ray diffraction of $La_xRh_4P_{12}$ prepared at around 4 GPa and 1100 °C. This profile was indexed to the filled skutterudite-type structure. The lattice constant of the sample is $a = 8.0581(5)$ Å. There are small amounts of LaP and RhP_2 produced at high pressure. These materials do not show superconductivity above 1.5 K. The x value estimated from x-ray diffraction and electron probe microanalysis (EPMA) data is about 0.6. Two voids in the unit cell are about 60% occupied by La atoms at 4 GPa.

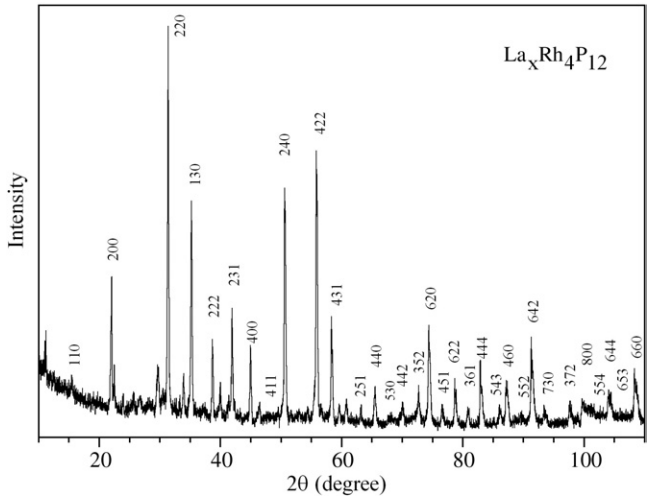

Figure 2. X-ray diffraction of $La_xRh_4P_{12}$ prepared at around 4 GPa and 1100 °C.

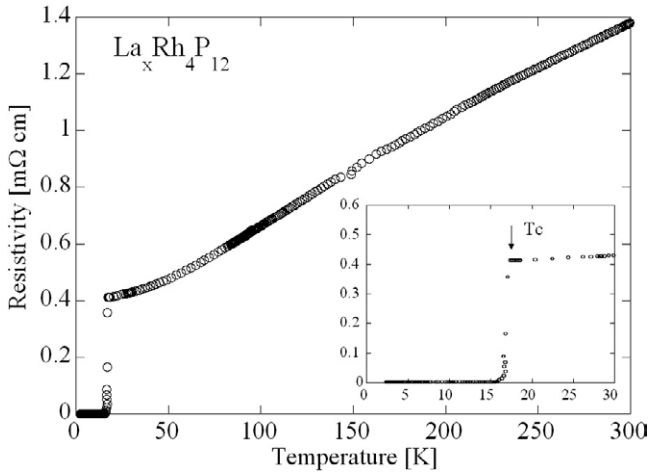

Figure 3. Electrical resistivity of $La_xRh_4P_{12}$ at low temperatures.

A copper or gold lead was attached to each polycrystalline sample 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

Figure 3 shows the resistivity versus temperature curves for $La_xRh_4P_{12}$. A binary skutterudite compound RhP_3 has the $CoAs_3$-type structure [15]. There are two voids in the unit cell of the compound. La atoms are doped into RhP_3 at high pressure. The lattice constant of $La_xRh_4P_{12}$ prepared at around 4 GPa and 1100 °C is $a = 8.0581$ Å. This value is much larger than the lattice parameter ($a = 7.996$ Å) of RhP_3. As mentioned above, the two voids in the unit cell

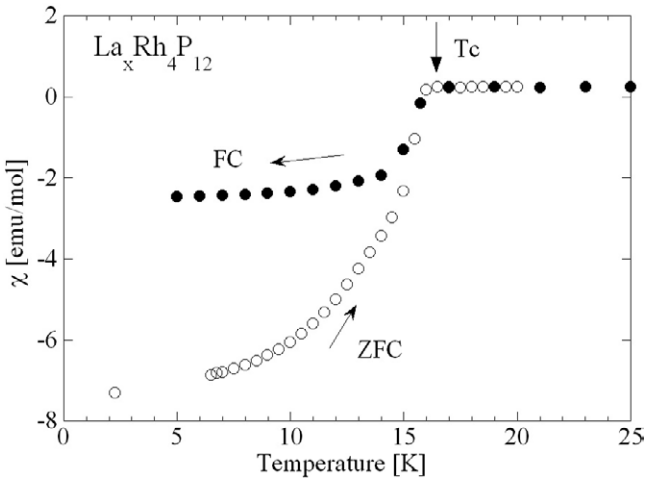

Figure 4. Susceptibility measured in an applied magnetic field of 5 Oe for $La_xRh_4P_{12}$ at low temperatures.

Table 1. T_cs and lattice constants of various skutterudite superconductors.

	Lattice constant (Å)	T_c (K)
$La_xRh_4P_{12}$	8.0581	17
YFe_4P_{12}	7.789	7
YRu_4P_{12}	8.0298	8.5
YOs_4P_{12}	8.0615	3
$LaFe_4P_{12}$	7.8316	4.1
$LaRu_4P_{12}$	8.0605	7.2
$LaOs_4P_{12}$	8.0844	1.8
$LaRu_4As_{12}$	8.5081	10.3
$LaOs_4As_{12}$	8.5437	3.2
$LaRu_4Sb_{12}$	9.2781	3.58
$LaOs_4Sb_{12}$	9.3029	0.74
$PrRu_4P_{12}$	8.0516	2 (14.7 GPa)
$PrRu_4As_{12}$	8.4963	2.4
$PrRu_4Sb_{12}$	9.2648	1.1
$PrOs_4Sb_{12}$	9.3031	1.85

are about 60% occupied by La atoms at 4 GPa. The resistivity of $La_xRh_4P_{12}$ decreases with decreasing temperature, and drops sharply at around 17 K. This sample shows the highest T_c obtained by us. Figure 4 shows the temperature dependence of the dc susceptibility measured in an applied magnetic field of 5 Oe for $La_xRh_4P_{12}$. The sample cooled in zero field shows large magnetic shielding at low temperatures. The existence of hysteresis between zero-field cooling (ZFC) and field cooling (FC) indicates that the phosphide is a type II superconductor.

The superconductivity of filled skutterudites LaT_4X_{12} (T = Fe, Ru and Os; X = P, As and Sb) has been studied at low temperatures. $La_xRh_4P_{12}$ is a new superconductor with a T_c of 17 K. The T_cs and lattice constants of these skutterudites are summarized in table 1. The lattice constant (=8.0605 Å) of $LaRu_4P_{12}$ is close to that of $La_xRh_4P_{12}$. Superconductivity of the Ru compound is observed at around 7.2 K. The T_c of $La_xRh_4P_{12}$ is about 10 K higher than that of $LaRu_4P_{12}$. The electronic density of the states at the Fermi energy (D_F) and

the electron–phonon coupling parameter (λ) of $LaRu_4P_{12}$ are 0.42 states/eV atom and 0.57, respectively [3]. $LaRu_4As_{12}$ has the high T_c of 10.3 K. The values of D_F and λ for this arsenide are larger than those of $LaRu_4P_{12}$ [3, 8]. Since the T_c of $La_xRh_4P_{12}$ is much higher than that of $LaRu_4As_{12}$, the larger values for D_F and λ of $La_xRh_4P_{12}$ are to be expected. We have already reported that MoRuP and MoNiP have the highest T_c (15.5 K) among the metal phosphides [18, 19]. The T_c of $La_xRh_4P_{12}$ (17 K) is higher than those of both Mo phosphides.

The Seebeck coefficient of $La_xRh_4P_{12}$ has been measured at temperatures between 100 and 400 K. The thermoelectric power of the compound is negative, $S = -47\ \mu V\ K^{-1}$, at room temperature. The absolute value of S increases linearly with increasing temperature. Ordinary filled skutterudites have positive Seebeck and Hall coefficients and behave as p-type conductors. In contrast, $La_xRh_4P_{12}$ is an n-type conductor with the skutterudite structure. The electronic band structure of this compound is very interesting.

Acknowledgments

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