Pressure Effect on the Structure and Superconducting Transition Temperature of Filled Skutterudites LaT4P12 (T=Fe, Ru)

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Pressure Effect on the Structure and Superconducting Transition Temperature of Filled Skutterudites LaT$_4$P$_{12}$ (T=Fe, Ru)
Pressure Effect on the Structure and Superconducting Transition Temperature of Filled Skutterudites \( \text{La}T_4\text{P}_{12} \) (\( T=\text{Fe, Ru} \))

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We studied the effect of pressure on the superconducting transition temperature \( T_{SC} \) of \( \text{La}T_4\text{P}_{12} \) (\( T=\text{Fe, Ru} \)) up to 8 GPa through electrical resistivity measurements in a cubic anvil apparatus. The \( T_{SC} \) of \( \text{LaFe}_4\text{P}_{12} \) was also determined through magnetization measurements up to 3.4 GPa with an opposed-anvil pressure cell. In \( \text{LaFe}_4\text{P}_{12} \), \( T_{SC} \) increases with pressure at a rate of 0.71 K/GPa from 0 GPa reaching its maximum at approximately 7 GPa. In contrast, the \( T_{SC} \) of \( \text{LaRu}_4\text{P}_{12} \) monotonically decreases with pressure. The decrease rate gradually increases from -0.07 to -0.29 K/GPa. The distinct pressure dependences of both \( T_{SC} \)’s cannot be explained solely from a structural point of view. We propose that the difference between the pressure dependence of \( T_{SC} \) for \( \text{LaFe}_4\text{P}_{12} \) and that for \( \text{LaRu}_4\text{P}_{12} \) can be attributed to the difference in the electronic density of states at the Fermi energy between these two compounds.

KEYWORDS: skutterudite, \( \text{LaFe}_4\text{P}_{12} \), \( \text{LaRu}_4\text{P}_{12} \), \( \text{La}T_4\text{P}_{12} \), superconductor, pressure, bulk modulus, density of states

1. Introduction

Ternary intermetallic compounds \( \text{Ln}T_4X_{12} \) (\( \text{Ln} = \text{Lanthanide, } T = \text{transition metal, } X = \text{pnictogens} \)) crystallize in the filled-skutterudite structure (space group \( \text{Im} \bar{3}, \text{No. 204} \)).\(^1\) Depending on the combination of elements, filled skutterudite compounds show various features. Filled skutterudite antimonids have attracted much attention owing to their improved thermoelectric properties.\(^2,3\) Filled skutterudite phosphides exhibit interesting physical phenomena: praseodymium-based materials exhibit metal-insulator (MI) transition,\(^4,5\) multipole ordering,\(^6\) and heavy-fermion behavior under magnetic fields;\(^7,8\) cerium compounds show Kondo semiconducting behavior;\(^9,10\) lanthanum compounds exhibit superconductivity.\(^11\) These interesting physical properties are believed to arise from the Fermi surface insta-
Nesting properties are observed in the Fermi surface of LaFe$_4$P$_{12}$ and LaRu$_4$P$_{12}$. Such nesting properties may be the origin of the MI transition in PrRu$_4$P$_{12}$. Among the various physical properties connected to this unique Fermi surface, in the present work, superconductivity is focused on. Thus far, 19 filled skutterudite compounds have been found to be superconductors. Among them, La$T_4$P$_{12}$ ($T$ = Fe, Ru, Os) have a distinct characteristic in terms of the pressure dependence of the superconducting transition temperature ($T_{SC}$). The $T_{SC}$’s of LaFe$_4$P$_{12}$, LaRu$_4$P$_{12}$, and LaOs$_4$P$_{12}$ at ambient pressures are 4.1, 7.2, and 1.8 K, respectively. In a previous high-pressure study up to 1.8 GPa, the $T_{SC}$ of LaFe$_4$P$_{12}$ was found to increase at a rate of 0.72 K/GPa, while those of LaRu$_4$P$_{12}$ and LaOs$_4$P$_{12}$ decrease gradually at rates of -0.16 and -0.095 K/GPa, respectively. DeLong and Meisner suggested that the pressure dependence of $T_{SC}$ can be explained by two competing contributions: the suppression of $T_{SC}$ due to the compression of the lattice (i.e., a decrease in volume), and the enhancement of $T_{SC}$ due to the effect of pressure on La itself. However, a mechanism relying only on the structure of the filled skutterudite is not completely consistent with all physical properties. One reason is that the Fermi surface properties of La$T_4$P$_{12}$, which lead to many intriguing physical properties, were not taken into account. $T_{SC}$ is also related to the density of states (DOS) at the Fermi surface. In order to verify the mechanism proposed by DeLong and Meisner and to clarify the origin of the distinct pressure dependence of $T_{SC}$, we investigated the pressure dependence of $T_{SC}$ in La$T_4$P$_{12}$ in an extended pressure range up to 8 GPa.

2. Experimental Procedure

Polycrystalline La$T_4$P$_{12}$ ($T$ = Fe, Ru) was prepared at high temperature and high pressure using a wedge-type cubic anvil apparatus. Stoichiometric amounts of each metal and red phosphorus powder were reacted at 1050 °C under a pressure of 4.5 GPa for 0.5 h. The resulting sample was a cylinder of 2.5 mm diameter and 6 mm length. Single crystals of La$T_4$P$_{12}$ were also grown by a Sn flux method. The starting materials were La, Fe (or Ru), red P, and Sn mixed in an atomic ratio of 1:4:20:50, sealed in vacuum, heated to 1050 °C, and then cooled to 680 °C at a rate of 1 °C/h. Sn flux was removed by centrifugation, followed by etching in an aqueous solution of 6 mol/L HCl. The size of the resulting LaFe$_4$P$_{12}$ single crystals was up to 1.5 mm, while that of LaRu$_4$P$_{12}$ was less than 100 μm. The phase purity of the resulting compounds was identified by powder X-ray diffraction analysis. The impurity level was less than 1% for all the samples. In order to determine the bulk modulus of LaRu$_4$P$_{12}$, we also performed high-pressure powder X-ray diffraction measurements using synchrotron...
radiation with a wavelength $\lambda = 0.62 \, \text{Å}$ at BL-18C of the Photon Factory in Tsukuba, Japan. An imaging plate was used as the detector. The pressure was applied by a diamond anvil cell filled with a 4:1 mixture of methanol/ethanol as the pressure-transmitting medium. The applied pressure was determined by a ruby fluorescence method. Single-crystal LaFe$_4$P$_{12}$ and polycrystalline LaRu$_4$P$_{12}$ were used for resistivity and magnetization measurements. Magnetization under pressure was measured with a Magnetic Properties Measurement System (MPMS, Quantum Design Inc.). Pressure was applied using an opposed-anvil type ceramic pressure cell,\cite{18} where pressure was monitored by tracking the $T_{SC}$ of Sn. Electrical resistivity under pressure was measured with a cubic-anvil apparatus. Glycerin was used as the pressure medium in order to achieve hydrostatic conditions.

3. Results

Figure 1 shows the temperature dependences of the magnetization of LaFe$_4$P$_{12}$ measured at $H=10$ Oe after zero-field cooling at various pressures. A distinct drop upon cooling due to the Meissner effect of superconductivity is observed at $4.1 \, \text{K}$ at ambient pressure. $T_{SC}$ is defined by the onset of superconductivity, as indicated by the arrows. $T_{SC}$ increases monotonically with increasing pressure.

Figure 2 shows the temperature dependence of the resistivity of LaFe$_4$P$_{12}$ up to 8 GPa. A drop in resistivity caused by superconductivity is observed at $4.9 \, \text{K}$, followed by a zero resistivity at $4.5 \, \text{K}$ under 0 GPa. The sharpness of the drop in $\rho(T)$ is sensitive to the measurement conditions. The difference between the onset and offset of superconductivity is $\sim 0.5 \, \text{K}$ at $0$
Fig. 2. (Color online) Temperature dependences of electrical resistivity on LaFe$_4$P$_{12}$ at various pressures. The arrows indicate the midpoint of superconductivity.

GPa; it is ~0.2 K from 2 to 7 GPa. Since the sample measured at 0 GPa is the same as that measured under pressure, the difference can probably be attributed to the measuring apparatus. The resistivity drop broadens slightly at 8 GPa. The difference between the onset and offset of superconductivity is ~0.5 K and may be attributed to the change in the hydrostatic conditions. Although the pressure medium, i.e., glycerin, produces good hydrostatic conditions even above 5 GPa, the hydrostatic pressure conditions may deteriorate gradually at over 6 GPa, at which point glycerin solidifies. We define $T_{SC}$ as the temperature midway between the onset and offset of superconductivity.

Figure 3 shows the temperature dependence of resistivity for LaRu$_4$P$_{12}$ up to 8 GPa. A drop in resistivity caused by superconductivity is observed, followed by a zero resistivity. We define $T_{SC}$ in the same way as mentioned previously for resistivity measurements. $T_{SC}$ decreases with increasing pressure. We note that the $\rho$ for LaRu$_4$P$_{12}$ in the normal conducting state is nearly a thousand times higher than that for LaFe$_4$P$_{12}$. This increase can be attributed to the difference in sample quality because LaFe$_4$P$_{12}$ was measured in single-crystal form, while LaRu$_4$P$_{12}$ was measured in polycrystalline form. The residual resistivity ratio (RRR) of LaFe$_4$P$_{12}$ is 560, while that of LaRu$_4$P$_{12}$ is 7.

Figure 4 shows the pressure dependence of $T_{SC}$. The $T_{SC}$ of LaRu$_4$P$_{12}$ decreases monotonically with increasing pressure. The pressure coefficient $dT_{SC}/dP$ slightly increases from -0.07(5) K/GPa in the range of 0 to 2 GPa to -0.29(0) K/GPa from 6 to 8 GPa. Although the $dT_{SC}/dP$ obtained in this study is slightly different from that of -0.16 K/GPa at 1.8 GPa found
Fig. 3. (Color online) Temperature dependences of resistivity for LaRu$_4$P$_{12}$ up to 8 GPa. The arrows indicate the midpoint of superconductivity.

Fig. 4. (Color online) Pressure dependence of $T_{SC}$ for LaFe$_4$P$_{12}$ investigated by magnetization (closed triangle) and resistivity (closed circle) measurements. Corresponding measurements for LaRu$_4$P$_{12}$ (open circle) are also shown. The dashed-dotted line and dashed line are guide lines of the pressure dependences of the $T_{SC}$’s of LaFe$_4$P$_{12}$ and LaRu$_4$P$_{12}$, respectively. Previously reported values for LaFe$_4$P$_{12}$ (open diamond) and LaRu$_4$P$_{12}$ (closed diamond) are also plotted. The solid line indicates the $T_{SC}$ of LaFe$_4$P$_{12}$ at ambient pressure.

in a previous study, the gradual decrease in $T_{SC}$ with pressure found here is consistent with the results of previous studies. In contrast, the $T_{SC}$ of LaFe$_4$P$_{12}$ increases rapidly with increasing pressure. Below 2 GPa, the $dT_{SC}/dT$ for LaFe$_4$P$_{12}$ as determined from magnetization measurements is 1.04 K/GPa and that from electrical resistivity is 0.71 K/GPa. This rapid increase is consistent with the value of 0.72 K/GPa in a previous report. The slight dif-
difference in $dT_{SC}/dP$ can probably be attributed to the difference in hydrostatic pressure conditions. The cubic anvil pressure cell for electrical resistivity measurements can achieve a better hydrostatic pressure condition than the opposed-anvil type cell used for magnetization measurements. The $dT_{SC}/dP$ determined from magnetization measurements is well reproducible with a difference of less than 2% in two separated runs. Above 2 GPa, $dT_{SC}/dP$ gradually decreases with pressure, and $T_{SC}$ seems to reach its maximum of approximately 7 GPa.

4. Discussion

Before discussing the pressure dependence of $T_{SC}$, we explain the relation between LaFe$_4$P$_{12}$ and LaRu$_4$P$_{12}$. Fe and Ru are in the same group in the periodic table and the radius of the Fe ion is smaller than that of the Ru ion. Thus, substituting Fe for Ru in LaRu$_4$P$_{12}$ causes a decrease in volume due to chemical pressure. To clarify the relation between LaFe$_4$P$_{12}$ and LaRu$_4$P$_{12}$ from a structural point of view, we applied physical pressure on LaRu$_4$P$_{12}$. Figure 5 shows the pressure dependence of the unit-cell volume of LaRu$_4$P$_{12}$, obtained from a synchrotron X-ray study at a pressure of up to 10 GPa. The dotted line indicates a fit to the Birch-Murnaghan equation of state:  

$$P = \frac{3}{2}B_0 \left\{ \left( \frac{V}{V_0} \right)^2 - \left( \frac{V}{V_0} \right)^\frac{5}{3} \right\} \left[ 1 + \frac{3}{4} \left( B'_0 - 4 \right) \left( \frac{V}{V_0} \right)^2 - 1 \right],$$

(1)

where $P$ is the pressure, $V$ is the volume, $V_0$ is the volume at 0 GPa, $B_0$ is the bulk modulus, and $B'_0$ is the first derivative of $B_0$. The fitted line is obtained from the data below 10 GPa.
Table I. Lattice parameters and bulk moduli of $LaT_4P_{12}$ ($T$=Fe, Ru).

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<th>LaRu$<em>4$P$</em>{12}$</th>
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<td>a (Å)</td>
<td>7.8311</td>
<td>8.05645</td>
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<tr>
<td>V ($Å^3$)</td>
<td>480.251</td>
<td>522.9151</td>
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<tr>
<td>$B_0$ (GPa)</td>
<td>150$^{23)}$</td>
<td>170</td>
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We obtained a $B_0$ of 170 GPa for our sample, which is consistent with the value of 172 GPa observed in a previous study.$^{21,22}$ Table I shows the lattice constants and unit-cell volumes at ambient pressure in addition to the bulk moduli of $LaT_4P_{12}$ ($T$= Fe, Ru). From Table I, the unit-cell volume of LaFe$_4$P$_{12}$ is 91.8% of that of LaRu$_4$P$_{12}$. In Fig. 5, the solid line indicates 91.8% of the unit-cell volume of LaRu$_4$P$_{12}$ at ambient pressure, corresponding to the volume of LaFe$_4$P$_{12}$. Extrapolating the fit to the Birch-Murnaghan equation of state indicates that $V/V_0$ will reach 0.918 at 17.5 GPa, as indicated by the arrow in Fig. 5. Thus, the structure of LaFe$_4$P$_{12}$ at ambient pressure corresponds to that of LaRu$_4$P$_{12}$ at 17.5 GPa.

We discuss the difference in the pressure dependence of $T_{SC}$ between LaFe$_4$P$_{12}$ and LaRu$_4$P$_{12}$. DeLong and Meisner proposed that the pressure dependence of $T_{SC}$ can be attributed to the crystal structure.$^{17}$ Their arguments are reproduced here. When the 12 P cage structure around La is too small for La atoms as in LaFe$_4$P$_{12}$, pressure acts directly on the La site. In this situation, $T_{SC}$ increases with pressure because the $T_{SC}$ of La increases with pressure. When the cage structure is too large for LaRu$_4$P$_{12}$, pressure does not affect La atoms. In this situation, $T_{SC}$ decreases with pressure owing to the contraction of the skutterudite structure. However, this idea is questionable for the following two reasons. (1) If the pressure dependence of $T_{SC}$ is attributed solely to the crystal structure, the contraction of LaRu$_4$P$_{12}$ with pressure should lead to similar properties to LaFe$_4$P$_{12}$. In Fig. 4, the dashed line is the guide line of the pressure dependence of $T_{SC}$ of LaRu$_4$P$_{12}$ below 8 GPa. If this guide line is extrapolated to 10 GPa, it reaches 4.7 K at 9.5 GPa. LaFe$_4$P$_{12}$ has a $T_{SC}$ of 4.7 K at ambient pressure. Thus, LaRu$_4$P$_{12}$ has the same unit-cell volume as LaFe$_4$P$_{12}$ at 17.5 GPa, but has the same $T_{SC}$ as LaFe$_4$P$_{12}$ at 9.5 GPa. The difference between these pressures suggests that $T_{SC}$ should not be attributed solely to the structure. (2) The $T_{SC}$ of La increases up to 20 GPa.$^{24}$ If this increase in $T_{SC}$ can be attributed to the superconductivity associated with the La atom only, the $T_{SC}$ of LaFe$_4$P$_{12}$ should also increase with pressure up to at least 20 GPa. In contrast, our results in Fig. 4 reveal that the $T_{SC}$ of LaFe$_4$P$_{12}$ actually reaches its maximum at approximately 7 GPa.
Here, we suggest that the origin of the pressure dependence of $T_{SC}$ is associated with the DOS at the FL. $^{139}$La, $^{31}$P-NMR studies revealed that LaFe$_4$P$_{12}$ can be classified as a spin-singlet s-wave superconductor with a weak-electron-phonon-coupling parameter of $\lambda = 0.2^{25,26}$ and a superconducting gap of $2\Delta/(k_B T_{SC}) = 3.8^{26}$. In weakly coupled superconductors, $T_{SC}$ is related to the density of the state at the Fermi energy $N(E_F)$ through the relation

$$T_{SC} \sim 1.14\theta_D \exp \left(\frac{-1}{N(E_F)V}\right),$$

(2)

where $\theta_D$ is the Debye temperature and $V$ is the potential energy of phonon-electron interaction. $T_{SC}$ is more sensitive to $N(E_F)V$ than to $\theta_D$. The $N(E_F)V$s of LaFe$_4$P$_{12}$ and LaRu$_4$P$_{12}$ seem similar because these compounds are isostructural and Fe and Ru are of the same family, as mentioned above. However, their $N(E_F)$s may exhibit a distinct response to pressure. Although the calculated energy band structure for LaRu$_4$P$_{12}$ shows that the FL is situated in a large peak at the DOS,$^{27}$ a sub-millielectronvolt resolution photoemission spectroscopy (PES) study could not detect such a structure.$^{28}$ From the PES study, the DOS decreases with increasing energy around the FL. On the other hand, the FL of LaFe$_4$P$_{12}$ is slightly below the local maximum calculated total density of states for the 48th band.$^{13}$ These findings can explain why the $dT_{SC}/dP$ of LaFe$_4$P$_{12}$ is much higher than that of LaRu$_4$P$_{12}$. If the local maximum of the DOS and the Fermi level approach each other with pressure application, $N(E_F)$ and $T_{SC}$ should rapidly increase. From our results, the $T_{SC}$ of LaFe$_4$P$_{12}$ peaks above 7 GPa. This suggests that the Fermi level is located at the local maximum of the DOS at approximately 7 GPa. In order to verify our assumption, theoretical or experimental study of the Fermi surface under pressure is needed.

5. Conclusions

We have studied the pressure dependence of the $T_{SC}$ of La$T_4$P$_{12}$ ($T$ = Fe, Ru) up to 8 GPa. Our present study extends the scope of previous works by measuring the pressure dependence of $T_{SC}$ up to 8 GPa. The pressure dependence of $T_{SC}$ for LaFe$_4$P$_{12}$ is confirmed by resistivity and magnetization measurements. The $T_{SC}$ of LaRu$_4$P$_{12}$ decreases monotonically at rates of 0.07 - 0.29 K/GPa. In contrast, the $T_{SC}$ of LaFe$_4$P$_{12}$ increases at rates of 0.71 - 1.04 K/GPa below 2 GPa. The rate of increase of $T_{SC}$ with pressure for LaFe$_4$P$_{12}$ gradually decreases and $T_{SC}$ seems to reach its maximum at approximately 7 GPa. We suggest that the difference in the pressure dependence of $T_{SC}$ between LaRu$_4$P$_{12}$ and LaFe$_4$P$_{12}$ can be attributed to the difference in the response of the electronic DOS at the Fermi level to pressure.
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References


