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Pressure Effect on the Structure and Superconducting Transition Temperature of Filled Skutterudites LaT_4P$_{12}$ (T=Fe, Ru)

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We studied the effect of pressure on the superconducting transition temperature T_{SC} of LaT_4P$_{12}$ (T=Fe, Ru) up to 8 GPa through electrical resistivity measurements in a cubic anvil apparatus. The T_{SC} of LaFe$_4$P$_{12}$ was also determined through magnetization measurements up to 3.4 GPa with an opposed-anvil pressure cell. In LaFe$_4$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 LaRu$_4$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 LaFe$_4$P$_{12}$ and that for LaRu$_4$P$_{12}$ can be attributed to the difference in the electronic density of states at the Fermi energy between these two compounds.

KEYWORDS: skutterudite, LaFe$_4$P$_{12}$, LaRu$_4$P$_{12}$, LaT_4P$_{12}$, superconductor, pressure, bulk modulus, density of states

1. Introduction

Ternary intermetallic compounds LnT_4X_{12} (*Ln*=Lanthanide, T=transition metal, X=pnictogens) crystallize in the filled-skutterudite structure (space group $Im\bar{3}$, 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-

bility.[12] Nesting properties are observed in the Fermi surface of $LaFe_4P_{12}$[13] and $LaRu_4P_{12}$.[14] Such nesting properties may be the origin of the MI transition in $PrRu_4P_{12}$.[15,16] 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, LaT_4P_{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 $LaFe_4P_{12}$, $LaRu_4P_{12}$, and $LaOs_4P_{12}$ at ambient pressures are 4.1, 7.2, and 1.8 K, respectively.[11,17] In a previous high-pressure study up to 1.8 GPa,[17] the T_{SC} of $LaFe_4P_{12}$ was found to increase at a rate of 0.72 K/GPa, while those of $LaRu_4P_{12}$ and $LaOs_4P_{12}$ decrease gradually at rates of -0.16 and -0.095 K/GPa, respectively. DeLong and Meisner[17] 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 LaT_4P_{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[17] and to clarify the origin of the distinct pressure dependence of T_{SC}, we investigated the pressure dependence of T_{SC} in LaT_4P_{12} in an extended pressure range up to 8 GPa.

2. Experimental Procedure

Polycrystalline LaT_4P_{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 LaT_4P_{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 $LaFe_4P_{12}$ single crystals was up to 1.5 mm, while that of $LaRu_4P_{12}$ 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 $LaRu_4P_{12}$, we also performed high-pressure powder X-ray diffraction measurements using synchrotron
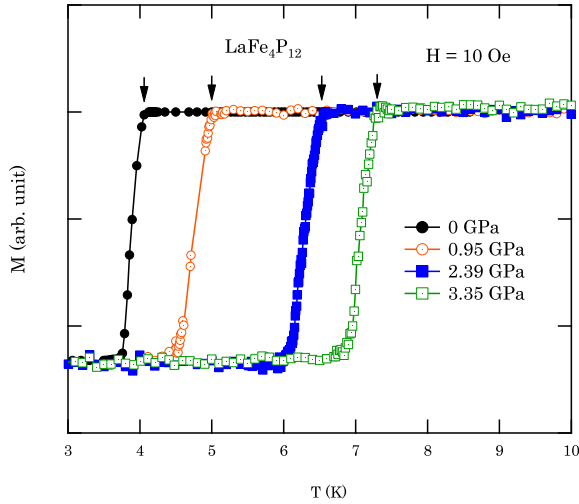
Fig. 1. (Color online) Temperature dependences of magnetization of $LaFe_4P_{12}$ measured at H=10 Oe after zero-field cooling under various pressures. The arrows indicate the onset of the superconductivity.

radiation with a wavelength $\lambda = 0.62$ 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 $LaFe_4P_{12}$ and polycrystalline $LaRu_4P_{12}$ 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,[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 $LaFe_4P_{12}$ 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 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 $LaFe_4P_{12}$ up to 8 GPa. A drop in resistivity caused by superconductivity is observed at 4.9 K, followed by a zero resistivity at 4.5 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 ~0.5 K at 0
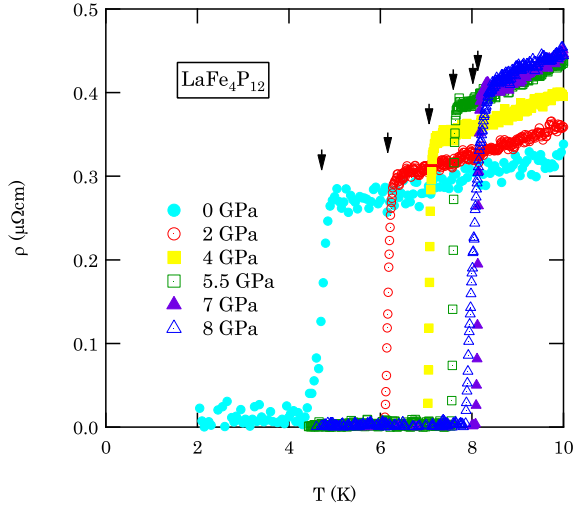
Fig. 2. (Color online) Temperature dependences of electrical resistivity on $LaFe_4P_{12}$ at various pressures. The arrows indicate the midpoint of superconductivity.

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,[19] 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 $LaRu_4P_{12}$ 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 ρ for $LaRu_4P_{12}$ in the normal conducting state is nearly a thousand times higher than that for $LaFe_4P_{12}$. This increase can be attributed to the difference in sample quality because $LaFe_4P_{12}$ was measured in single-crystal form, while $LaRu_4P_{12}$ was measured in polycrystalline form. The residual resistivity ratio (RRR) of $LaFe_4P_{12}$ is 560, while that of $LaRu_4P_{12}$ is 7.

Figure 4 shows the pressure dependence of T_{SC}. The T_{SC} of $LaRu_4P_{12}$ 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
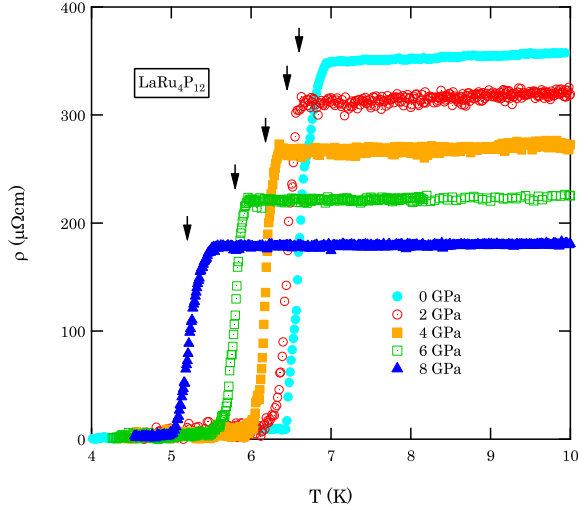
Fig. 3. (Color online) Temperature dependences of resistivity for $LaRu_4P_{12}$ up to 8 GPa. The arrows indicate the midpoint of superconductivity.

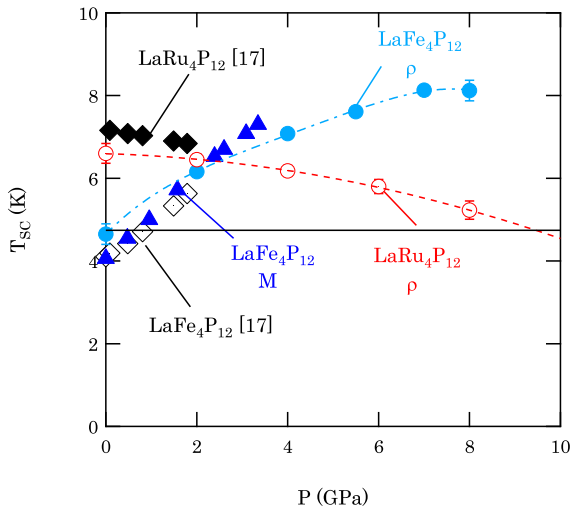**Fig. 4.** (Color online) Pressure dependence of T_{SC} for $LaFe_4P_{12}$ investigated by magnetization (closed triangle) and resistivity (closed circle) measurements. Corresponding measurements for $LaRu_4P_{12}$ (open circle) are also shown. The dashed-dotted line and dashed line are guide lines of the pressure dependences of the T_{SC}'s of $LaFe_4P_{12}$ and $LaRu_4P_{12}$, respectively. Previously reported values for $LaFe_4P_{12}$ (open diamond) and $LaRu_4P_{12}$ (closed diamond) are also plotted.[17] The solid line indicates the T_{SC} of $LaFe_4P_{12}$ at ambient pressure.

in a previous study,[17] the gradual decrease in T_{SC} with pressure found here is consistent with the results of previous studies. In contrast, the T_{SC} of $LaFe_4P_{12}$ increases rapidly with increasing pressure. Below 2 GPa, the dT_{SC}/dP for $LaFe_4P_{12}$ 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.[17] The slight dif-
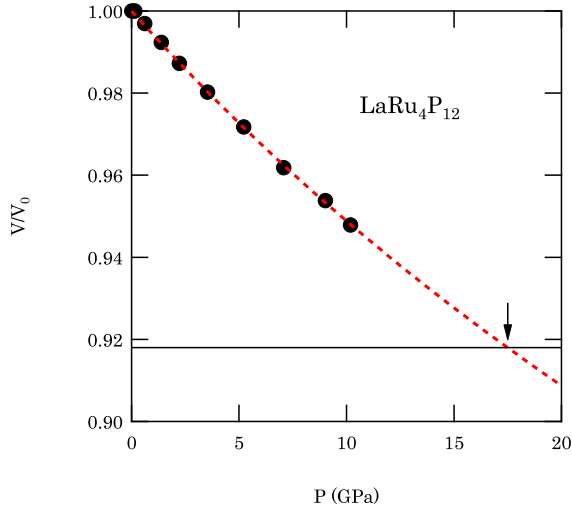
Fig. 5. (Color online) Pressure dependence of volume on $LaRu_4P_{12}$ normalized at ambient pressure. The dotted line indicates the fit to the Birch-Murnaghan equation of state. See text for details. The solid line corresponds to the volume of $LaFe_4P_{12}$ at ambient pressure.

ference 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 $LaFe_4P_{12}$ and $LaRu_4P_{12}$. 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 $LaRu_4P_{12}$ causes a decrease in volume due to chemical pressure. To clarify the relation between $LaFe_4P_{12}$ and $LaRu_4P_{12}$ from a structural point of view, we applied physical pressure on $LaRu_4P_{12}$. Figure 5 shows the pressure dependence of the unit-cell volume of $LaRu_4P_{12}$, 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:[20]

$$P = \frac{3}{2}B_0\left\{\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}}\right\}\left[1 + \frac{3}{4}\left(B_0' - 4\right)\left\{\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right\}\right], \tag{1}$$

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).

	$LaFe_4P_{12}$	$LaRu_4P_{12}$
a (Å)	7.8311	8.05645
V (Å³)	480.251	522.9151
B_0 (GPa)	150[23]	170

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 $LaFe_4P_{12}$ is 91.8% of that of $LaRu_4P_{12}$. In Fig. 5, the solid line indicates 91.8% of the unit-cell volume of $LaRu_4P_{12}$ at ambient pressure, corresponding to the volume of $LaFe_4P_{12}$. 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 $LaFe_4P_{12}$ at ambient pressure corresponds to that of $LaRu_4P_{12}$ at 17.5 GPa.

We discuss the difference in the pressure dependence of T_{SC} between $LaFe_4P_{12}$ and $LaRu_4P_{12}$. 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 $LaFe_4P_{12}$, 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 $LaRu_4P_{12}$, 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 $LaRu_4P_{12}$ with pressure should lead to similar properties to $LaFe_4P_{12}$. In Fig. 4, the dashed line is the guide line of the pressure dependence of T_{SC} of $LaRu_4P_{12}$ below 8 GPa. If this guide line is extrapolated to 10 GPa, it reaches 4.7 K at 9.5 GPa. $LaFe_4P_{12}$ has a T_{SC} of 4.7 K at ambient pressure. Thus, $LaRu_4P_{12}$ has the same unit-cell volume as $LaFe_4P_{12}$ at 17.5 GPa, but has the same T_{SC} as $LaFe_4P_{12}$ 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 $LaFe_4P_{12}$ should also increase with pressure up to at least 20 GPa. In contrast, our results in Fig. 4 reveal that the T_{SC} of $LaFe_4P_{12}$ 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 $LaFe_4P_{12}$ 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

$$T_{SC} \sim 1.14\theta_D \exp\left[\frac{-1}{N(E_F)V}\right], \tag{2}$$

where θ_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 θ_D. The $N(E_F)V$s of $LaFe_4P_{12}$ and $LaRu_4P_{12}$ 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 $LaRu_4P_{12}$ 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 $LaFe_4P_{12}$ 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 $LaFe_4P_{12}$ is much higher than that of $LaRu_4P_{12}$. 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 $LaFe_4P_{12}$ 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 LaT_4P_{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 $LaFe_4P_{12}$ is confirmed by resistivity and magnetization measurements. The T_{SC} of $LaRu_4P_{12}$ decreases monotonically at rates of 0.07 - 0.29 K/GPa. In contrast, the T_{SC} of $LaFe_4P_{12}$ increases at rates of 0.71 - 1.04 K/GPa below 2 GPa. The rate of increase of T_{SC} with pressure for $LaFe_4P_{12}$ 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 $LaRu_4P_{12}$ and $LaFe_4P_{12}$ can be attributed to the difference in the response of the electronic DOS at the Fermi level to pressure.

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