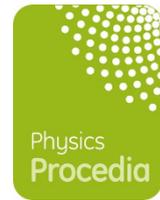


Pressure Dependence of Superconductivity in Filled-Skutterudite YOs₄P₁₂

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journal or publication title	Physics Procedia
volume	75
page range	200-205
year	2015
URL	http://hdl.handle.net/10258/00009043

doi: info:doi/10.1016/j.phpro.2015.12.025



Pressure Dependence of Superconductivity in Filled-Skutterudite $\text{YOs}_4\text{P}_{12}$

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Abstract

We have studied the magnetization on $\text{YOs}_4\text{P}_{12}$ under pressure up to ~ 4 GPa. Pure polycrystalline $\text{YOs}_4\text{P}_{12}$ was prepared by the high-pressure high-temperature method and was evaluated by the X-ray diffraction measurement. $\text{YOs}_4\text{P}_{12}$ shows superconducting transition at $T_{\text{SC}} \sim 3$ K at ambient pressure. We have investigated the pressure dependence of T_{SC} by means of DC magnetization measurements with incorporating opposed ceramic anvil pressure apparatus into MPMS. T_{SC} of $\text{YOs}_4\text{P}_{12}$ slightly decreases with pressure at a rate of $dT_{\text{SC}}/dP = -0.11$ K/GPa. This is quite contrary to the T_{SC} of related compounds $\text{YFe}_4\text{P}_{12}$, which rapidly increases with pressure at a rate of 1.0 K/GPa. The dT_{SC}/dP s relationship of $\text{YFe}_4\text{P}_{12}$ and $\text{YOs}_4\text{P}_{12}$ are similar with that of $\text{LaFe}_4\text{P}_{12}$ and $\text{LaOs}_4\text{P}_{12}$. T_{SC} of $\text{LaFe}_4\text{P}_{12}$ increases rapidly with pressure at a rate of $dT_{\text{SC}}/dP \sim 0.72$ K/GPa below 2 GPa and that of $\text{LaOs}_4\text{P}_{12}$ decreases gradually with pressure at a rate of -0.095 K/GPa. Considering these similarity, we can assume that the origin of dT_{SC}/dP of these compounds are the same and are attributed to the density of states at Fermi level and to the Hopfield parameter.

Keywords: $\text{YOs}_4\text{P}_{12}$, superconductivity, pressure, magnetization, ceramic anvil cell

1 Introduction

Ternary metallic pnictides with the general formula $\text{LnT}_4\text{X}_{12}$ (Ln =Lanthanide, T =Transition metal, X =Pnictogen) crystallize in a cubic structure with a space group $\text{Im-3}[1]$. These compounds, called filled skutterudite, show various physical properties by the choice of combination of elements. One of the prominent physical properties is superconductivity. So far, 19 filled-skutterudite compounds are reported to exhibit superconductivity at low temperatures. The temperature of the superconducting transition (T_{SC}) has varied depending on the compounds and the highest T_{SC} among filled-skutterudite superconductor is at 17 K on $\text{LaRh}_4\text{P}_{12}$ [2]. Almost all superconducting filled skutterudite compounds obey Bardeen-Cooper-Schrieffer (BCS) theory with a negative pressure dependence of T_{SC} (dT_{SC}/dP) due to the stiffness of lattice. Among filled skutterudites which have superconducting correlations,

only two compounds show positive dT_{SC}/dP . One is LaFe₄P₁₂ and the other is YFe₄P₁₂ [3, 4]. T_{SC} of LaFe₄P₁₂ increases with pressure at a rate of 0.71 K/GPa below 2GPa. The slope decreases with increasing pressure and T_{SC} seems to reach its maximum approximately at 7 GPa [5]. When Fe in LaFe₄P₁₂ is replaced by Ru or Os, the respective dT_{SC}/dP s becomes negative. T_{SC} of LaRu₄P₁₂ monotonically decreases with increasing pressure in rates of -0.07 K/GPa in the range of 0 ~2 GPa and -0.29 K/GPa in the range of 6~8 GPa. T_{SC} of LaOs₄P₁₂ monotonically decreases with increasing pressure at a rate of -0.095 K/GPa up to 1.8 GPa. At the first stage of this study, positive dT_{SC}/dP s is interpreted as the enhancement of T_{SC} due to the compression of the La metal. It is not to be denied that this conclusion is inconsistent by the appearance of positive dT_{SC}/dP s of YFe₄P₁₂ [4]. Y metal does not show superconductivity above 6 mK at ambient pressure and shows superconductivity only above 11 GPa [6]. According to band-structure calculations, $dT_{SC}/dP > 0$ for LaFe₄P₁₂ can be rationalized by the enhancement of the electronic density of states at Fermi level $D(E_F)$ and the Hopfield parameter η under pressure[7]. Meanwhile, $dT_{SC}/dP < 0$ for LaRu₄P₁₂ is attributed to the reduction of $D(E_F)$. As for YFe₄P₁₂, T_{SC} monotonically increases with pressure up to 8 GPa. The mechanism of dT_{SC}/dP for YFe₄P₁₂ is proposed to be the same as LaFe₄P₁₂ [4]. On the other hand, T_{SC} of YRu₄P₁₂ and YOs₄P₁₂ under pressure have not been investigated because of the difficulty of reproducibility of pure samples. YOs₄P₁₂ is one of filled skutterudite compounds, which shows superconductivity at $T_{SC} \sim 3$ K [8]. It can only be synthesized by the high-temperature and high-pressure method. The purpose of this study is to investigate the pressure dependence of T_{SC} of YOs₄P₁₂ and to reveal the origin of its dT_{SC}/dP .

	Lattice Constant (Å)	B ₀ (GPa) ^[9]	T _{SC} (K)	dT _{SC} /dP (K/GPa)
LaFe ₄ P ₁₂	7.8316	150	4.1	0.72 ^[3]
LaRu ₄ P ₁₂	8.0605	172	7.2	- 0.16 ^[3]
LaOs ₄ P ₁₂	8.0844	190	1.8	-0.095 ^[3]
YFe ₄ P ₁₂	7.7896	144	5.6	1 ^[4]
YRu ₄ P ₁₂	8.0298	183	8.5	-
YOs ₄ P ₁₂	8.0844	189	2.8	-0.11

Table 1: The sum of structural parameters and superconducting parameters of LnT_4P_{12} ($Ln=La, Y, T=Fe, Ru, Os$)

2 Experimental

We have synthesized YOs₄P₁₂ using the high-temperature and high-pressure method with a wedge type cubic anvil high pressure apparatus. The wedge-type cubic apparatus consists of the upper and lower stages with three anvils, respectively. The movement of the anvils is synchronized by a wedge system. The pressure from one axis gets converted to six faces. Starting material is 10% Y-rich stoichiometric rate, i.e., Y_{1.1}Os₄P₁₂, because Y can be easily oxidized and the amount of Y is likely to be underestimated when weighted. Each metal and red phosphorous powder were reacted at 4.5 GPa 1100°C for 30 min. The resulting sample was evaluated by X-ray diffraction method with Co K α radiation. We measured magnetization under pressure by incorporating an opposed anvil pressure cell into a commercial SQUID magnetometer MPMS (Quantum Design Inc.) [10]. Anvils of the pressure cell are made of non-composite ceramic (FCY20A) produced by the Fuji Die company, Japan. The outer and inner diameters, and the thickness of the NiCrAl gasket are 5.0, 0.5, and 0.5 mm, respectively. The pressure was evaluated from the superconducting transition temperature of Pb. Hydrostatic pressure is realized because the sample space was filled with glycerin as pressure medium, which will not solidify up to 6 GPa at room temperature. In order to get the accurate value of magnetization under pressure, we measured YOs₄P₁₂ with pressure cell and vacant pressure cell

separately. The signal of $\text{YOs}_4\text{P}_{12}$ was obtained by subtracting the induced voltage of the vacant pressure from that of $\text{YOs}_4\text{P}_{12}$ with pressure cell. The magnetization was calculated by fitting the subtracted data.

3 Results and Discussion

Figure 1 shows the X-ray diffraction pattern of $\text{YOs}_4\text{P}_{12}$. All distinct peaks can be assigned to the filled-skutterudite crystal structure. Peaks from impurity phases are within the level of noise, i.e., less than 1 %. Peaks that have a strong intensity (as indexed in Fig. 1) were picked up for calculation of the lattice parameter. The obtained lattice constant, $a = 8.0619 \text{ \AA}$, is in excellent agreement with that reported by K. Kihou *et al.*, $a = 8.0615(4) \text{ \AA}$ [8]. In other words, $\text{YOs}_4\text{P}_{12}$ prepared for this study is a pure sample without impurity phases and is consistent with a previous report.

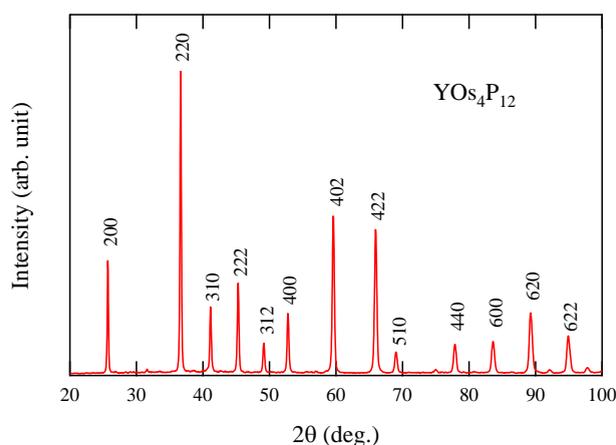


Fig. 1. X-ray diffraction pattern of $\text{YOs}_4\text{P}_{12}$. Only indexed peaks were used for calculation of lattice parameter

Figure 2 shows the temperature dependent magnetization divided by the field at $H=10 \text{ Oe}$. Distinct sharp drops due to superconductivity are observed at 2.8 K in both processes of field cooled (FC) and zero field cooled (ZFC). The temperature of T_{SC} is consistent to the previous report, in which the drop of resistivity contributing T_{SC} is observed at around 3 K [8]. The diamagnetic signal can be observed below the temperature at zero resistivity as for $\text{YFe}_4\text{P}_{12}$ [4]. The similar behavior is observed in this $\text{YOs}_4\text{P}_{12}$. With decreasing temperature the resistivity drops at 3 K to zero resistivity [8]. The diamagnetic signal in this study appears at 2.8 K, which is below the zero resistivity. We note that the process of ZFC is different from that of FC due to the pinning effect of a superconductor. While magnetic susceptibility (χ) at lowest temperature of FC is one-sevenths of that of ZFC on $\text{YFe}_4\text{P}_{12}$ [4], χ at lowest temperature of FC is two-thirds of that of ZFC on $\text{YOs}_4\text{P}_{12}$ in this study. The magnetization of $\text{YOs}_4\text{P}_{12}$ in this study shows smaller pinning effect than that of $\text{YFe}_4\text{P}_{12}$. The small pinning effect implies purity of the sample. In order to confirm the purity of $\text{YOs}_4\text{P}_{12}$, it is important to investigate residual resistivity. However, the sample synthesized in this study is too fragile to measure electrical resistivity. In order to investigate whether the residual resistivity has the same feature found for FC

and ZFC when comparing YO_4P_{12} and $\text{YFe}_4\text{P}_{12}$, synthesis of a sample with high degree of sintering is in progress.

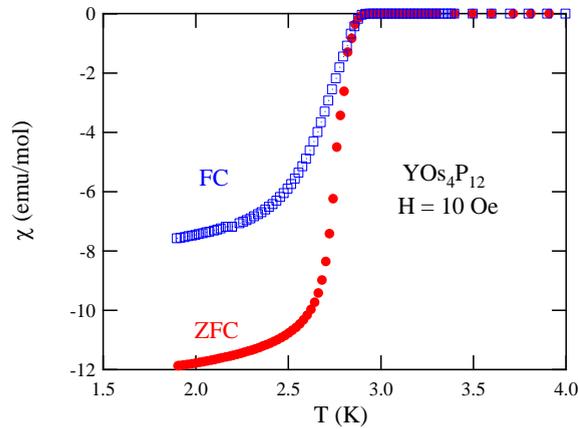


Fig. 2. Temperature dependence of χ under the field of $H = 10$ Oe with field cooled process (open square) and with zero field cooled process (closed circle).

Figure 3 shows the temperature dependent magnetic susceptibility up to 3.9 GPa with ZFC process. Since the weight of the sample for the measurement under pressure is too small to get the accurate value of χ , χ was calibrated by the data at ambient pressure. A distinct sharp drop due to the Meissner effect of superconductivity is observed at every pressure. We note that $\chi(T)$ at temperatures slightly above the reduction due to the Meissner effect faintly increases with decreasing temperature which cannot be seen in χ at ambient pressure. Although the pressure might cause this behavior, the signal in the normal state is too small to discuss this behavior.

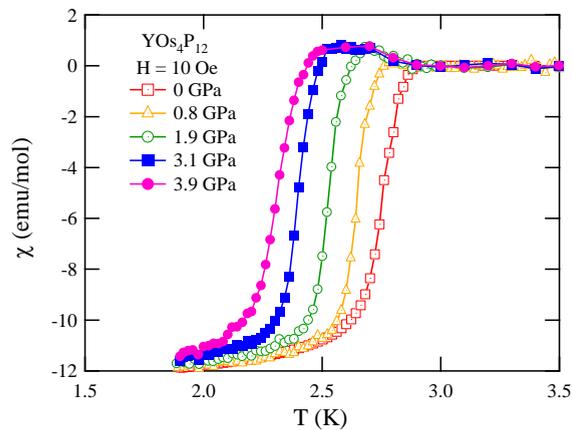


Fig. 3. Temperature dependence of magnetic susceptibility (χ - T) with zero field cooled process at 0 GPa (open square), 0.8 GPa (open triangle), 1.9 GPa (open circle), 3.1 GPa (closed square), and 3.9 GPa (closed circle).

Figure 4 shows the temperature derivative of the magnetic susceptibility. Peaks are observed, corresponding to the middle point between the onset and offset of superconductivity. We thus define the peak of $d\chi/dT(T)$ as T_{SC} . T_{SC} monotonically decreases by applying pressure.

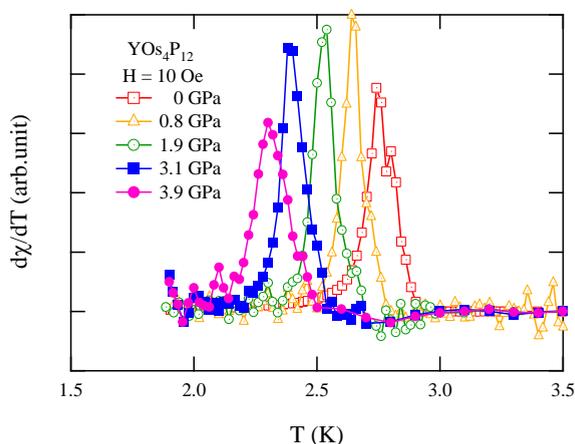


Fig. 4. Temperature derivative of magnetic susceptibility $d\chi/dT$ against temperature under pressure.

Figure 5 shows the shift of superconducting temperature ($\Delta T_{SC}(P) = T_{SC}(P) - T_{SC}(0)$) as a function of pressure of YOs₄P₁₂. In addition, ΔT_{SC} of related compounds LnT₄P₁₂ (Ln= La, Y, T=Fe, Ru, Os) except YRu₄P₁₂ are also shown. T_{SC} of YOs₄P₁₂ monotonically decreases with pressure at a rate of -0.11 K/GPa. As can be seen from the graph, ΔT_{SC} of LaRu₄P₁₂ and LaOs₄P₁₂ and YOs₄P₁₂ decreases with pressure at almost the same rate.

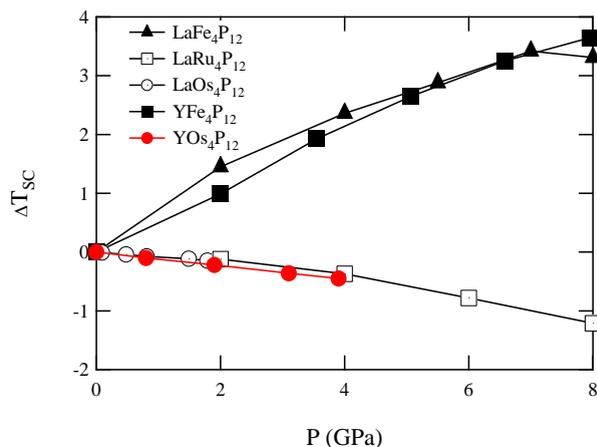


Fig. 5. Pressure dependence of ΔT_{SC} on LaFe₄P₁₂[5](closed triangle), LaRu₄P₁₂[5] (open square), LaOs₄P₁₂[3] (open circle) YFe₄P₁₂[4](closed square), YOs₄P₁₂(closed circle).

In the pressure region from 0 to 2 GPa, dT_{SC}/dP of YOs₄P₁₂, LaRu₄P₁₂, and LaOs₄P₁₂ are -0.11, -0.07, and -0.095 K/GPa, respectively. As it can be seen in table 1, the bulk modulus is not much different in these three compounds. Thus it would not be controversial to assume that the origin of dT_{SC}/dP for these three compounds is the same. J. G. Cheng et al. proposed that the difference of dT_{SC}/dP of YFe₄P₁₂ and YRu₄P₁₂ is attributed to the density of states at Fermi level and the Hopfield parameter η from the band calculation [4]. The same mechanism is proposed to the difference of

dT_{SC}/dP on LaFe₄P₁₂ and LaRu₄P₁₂ [7]. From the similarity of dT_{SC}/dP of YOs₄P₁₂, LaRu₄P₁₂, and LaOs₄P₁₂, we propose that dT_{SC}/dP of YOs₄P₁₂ has the same mechanism, i.e., the reduction of $D(\epsilon_F)$ and η .

We will describe the model of the electronic density of states ($D(\epsilon)$) of LaOs₄P₁₂ and YOs₄P₁₂, the band calculation of which have not been reported. The Fermi level (FL) of YRu₄P₁₂ at 0 GPa is just at the peak of $D(\epsilon)$ and that of LaRu₄P₁₂ is near the peak of $D(\epsilon)$. On the other hand, FL of YFe₄P₁₂ and LaFe₄P₁₂ is above a peak of $D(\epsilon)$. That is why T_{SC} of YRu₄P₁₂ (8.5 K) is higher than T_{SC} of YFe₄P₁₂ (5.6 K) and that of LaRu₄P₁₂ (7.2 K) is higher than that of LaFe₄P₁₂ (4.1 K). In the case of LaOs₄P₁₂ (T_{SC} ~1.8 K) and YOs₄P₁₂ (T_{SC} ~2.8 K), T_{SC} is lower than that of LaFe₄P₁₂ and YFe₄P₁₂, respectively. Thus, the FL of LaOs₄P₁₂ and YOs₄P₁₂ cannot be at the peak of $D(\epsilon)$. Considering the peak of $D(\epsilon)$ moves to high energy region at 8 GPa in the band calculation of LnT_4P_{12} (Ln =La, Y, T =Ru, Os)[4,7], the FL of LaOs₄P₁₂ and YOs₄P₁₂ should be below a maximum of $D(\epsilon)$ and $D(\epsilon)$ probably shifts to higher energy by applying pressure. That is why T_{SC} of YOs₄P₁₂ is lower than YFe₄P₁₂ and dT_{SC}/dP of YOs₄P₁₂ has a negative value. The same model can be applied to the case of LaOs₄P₁₂ and LaFe₄P₁₂. To confirm this model, however, band calculations of YOs₄P₁₂ and LaOs₄P₁₂ are desired.

4 Summary

We have investigated the pressure dependence of T_{SC} of YOs₄P₁₂ up to 4 GPa. T_{SC} of YOs₄P₁₂ slightly decreases with pressure by about -0.11 K/GPa. It is quite contrary to T_{SC} of YFe₄P₁₂, which rapidly increases at a rate of 1.0 K/GPa. There are similar relationships between LaFe₄P₁₂ and LaOs₄P₁₂, because dT_{SC}/dP of LaFe₄P₁₂ is 0.72 K/GPa and that of LaOs₄P₁₂ is -0.095 K/GPa. Thus we propose the origin of dT_{SC}/dP of these compounds is the same and is attributed to distinct features of the density of states at Fermi level and the Hopfield parameter.

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