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Superconducting properties of filled skutterudite $La_{0.8}Rh_4P_{12}$

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The superconducting properties of filled skutterudite $La_{0.8}Rh_4P_{12}$ synthesized at 9.4 GPa and 1473 K using a belt-type apparatus were investigated by measuring the magnetization, electrical resistivity, and specific heat. Filled skutterudite $La_{0.8}Rh_4P_{12}$ is a type-II superconducting material with a critical temperature for the superconducting transition, T_C, of 14.9 K. The upper critical field $H_{C2}(0)$ and Ginzburg-Landau coherent length $\xi(0)$ were determined to be 167(1) kOe and 4.41(1) nm, respectively. The electronic heat-capacity coefficient γ_n and the Debye temperature Θ_D were 25.1(8) mJ/mol K^2 and 459(12) K, respectively. Using T_C and Θ_D, the electron-phonon coupling constant λ was estimated to be approximately 0.7, suggesting that $La_{0.8}Rh_4P_{12}$ is an intermediately coupled superconducting material.

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Filled skutterudites, with a general chemical formula of MT_4X_{12} (where M, T, and X are rare-earth and alkaline-earth metals, transition metals, and pnictides, respectively), show a variety of physical properties, such as superconductivity,[1] semiconductivity,[2] ferromagnetism,[1] and antiferromagnetism,[3] when the combinations of M, T, and X are changed. So far, 14 filled skutterudites have been reported as superconducting materials.[1,4–15] Among them, $La_xRh_4P_{12}$, which was reported by Shirotani *et al.* in 2005, has the highest critical temperature for the superconducting transition, T_C (17 K).[15] Details of the superconducting properties of $La_xRh_4P_{12}$, however, have not been reported.

In this paper, we report the superconducting properties of $La_{0.8}Rh_4P_{12}$ synthesized at 9.4 GPa and 1473 K, using a belt-type high-pressure apparatus, based on the results of measurements of the dc magnetization, electrical resistivity, and specific heat.

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.[16] For this synthesis, we modified the sample assembly described in Ref. 16; i.e., we used a hexagonal BN instead of Pt for the sample capsule and sintered TiC instead of graphite for the electrodes. The chemical compositions and lattice constant were determined by electron probe microanalysis (EPMA) and powder x-ray diffractometry, respectively. The electrical resistivity and specific heat were measured using the physical properties measurement system (Quantum Design Co.), and the dc magnetization was measured using the magnetic properties measurement system (Quantum Design Co.).

The results of EPMA indicate that the sample consists of three phases: $La_xRh_4P_{12}$, Rh_3P_2, and LaP_yO_z ($y\sim1$, $z\sim1$), and that $La_xRh_4P_{12}$ is the main phase in the sample. The chemical compositions of $La_xRh_4P_{12}$ were determined to be 4.8(5) at. % La, 23.2(1) at. % Rh, and 72.0(5) at. % P. The corresponding x, chemical formula, and molecular weight are 0.82(8), $La_{0.82}Rh_{3.9}P_{12.1}$, and 888(12) g, respectively. We hereinafter denote $La_{0.82}Rh_{3.9}P_{12.1}$ as $La_{0.8}Rh_4P_{12}$. Figure 1 shows the x-ray diffraction pattern of the sample together with a calculated pattern assuming that $LaRh_4P_{12}$ has a lattice constant of 8.078 Å and internal parameters that are the same as those of $La_{0.2}Co_4P_{12}$.[17] This pattern also indicates that $La_{0.8}Rh_4P_{12}$ is the main phase, which is consistent with the result of EPMA. The lattice constant was determined to be 8.0785(5) Å; the density, 5.59(7) g/cm^3.

In Fig. 2, the dc magnetization M measured in zero-field cooling (ZFC) and field cooling (FC) at an applied field of 20.0 Oe is shown as a function of the temperature. The sample has a rectangular parallelepiped shape with dimensions of $2.69\times0.77\times0.542$ mm^3, and the magnetic field was applied parallel to the longest axis direction. The left inset shows an expanded view at temperatures ranging from 12 to 18 K, revealing a Meissner effect at temperatures below 14.9 K. This effect suggests that $La_{0.8}Rh_4P_{12}$ is a superconducting material with a T_C of 14.9 K, as confirmed by electrical resistivity measurements. The magnetic shielding fraction in ZFC and the flux exclusion in FC at 2.0 K were evaluated to be 89% and 1.6% of the theoretical value of the perfect magnetism, respectively, showing that superconductivity is a bulk effect. The right inset is a plot of the magnetization measured at 10 K after ZFC versus the applied mag-

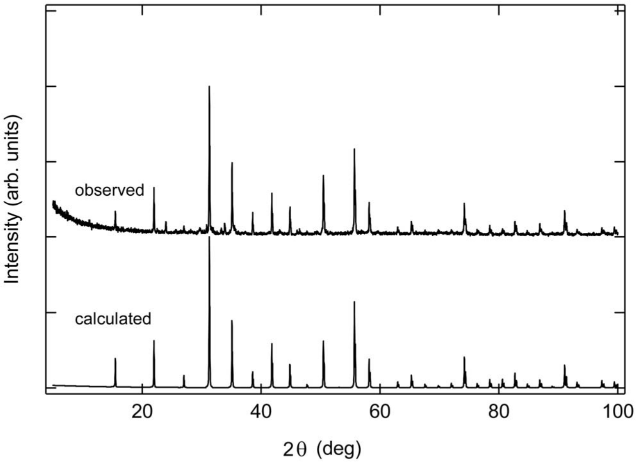

FIG. 1. X-ray diffraction pattern of the sample together with the calculated pattern of $LaRh_4P_{12}$ (Cu $K\alpha$).

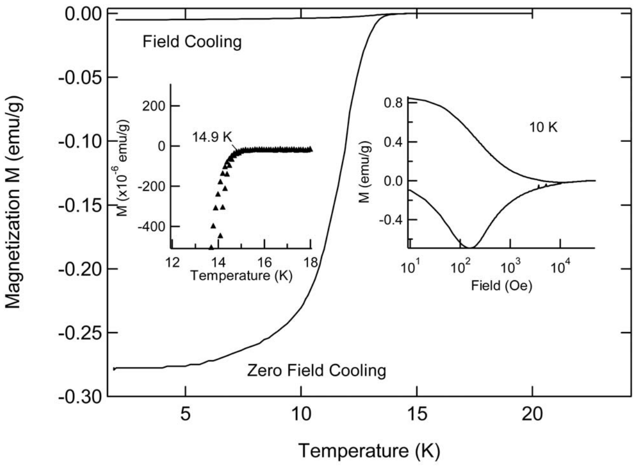

FIG. 2. Magnetization M in an applied magnetic field of 20 Oe as a function of the temperature. The left inset shows an expanded view of the magnetization near T_C. The right inset is the magnetization at 10 K as a function of the magnetic field.

netic field, which demonstrates that $La_{0.84}Rh_4P_{12}$ is a type-II superconductor. A lower critical field H_{C1} determined from the initial deviation from linearity was approximately 70 Oe at 2 K. The temperature dependence of H_{C1} is being investigated in detail.

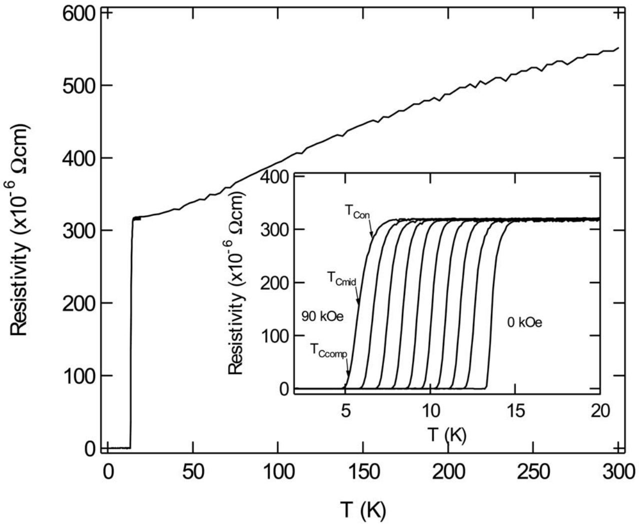

FIG. 3. Electrical resistivity as a function of the temperature. The inset is the electrical resistivity in various magnetic fields from 0 to 90 kOe in steps of 10 kOe (right to left) as a function of the temperature. The symbols T_{Con}, T_{Cmid}, and T_{Ccomp} in the figure represent the temperature in which the value of ρ reaches 90%, 50%, and 10%, respectively, of that at 15.3 K at 0 kOe.

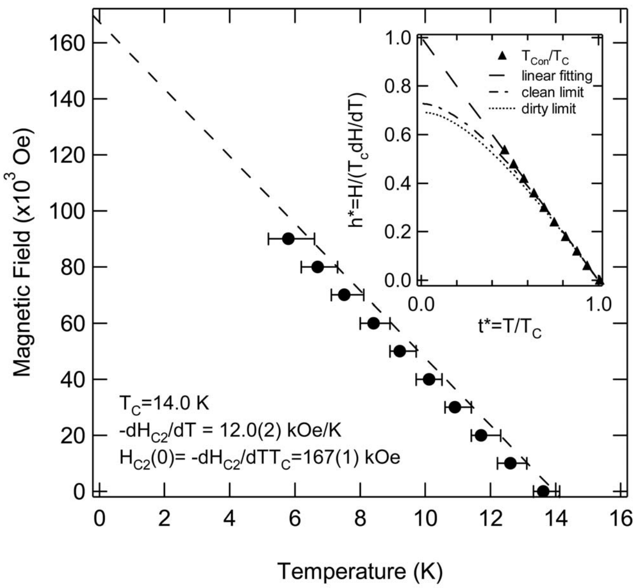

FIG. 4. Magnetic field–temperature phase diagram deduced from the electrical resistivity data. T_{Cmid} is represented by solid circles, and T_{Con} and T_{Ccomp} are indicated by vertical bars. The broken line is a linear fitting of T_{Con}. $H_{C2}(0)$ was estimated from T_{Con} using a linear fitting. The inset shows the reduced magnetic field $h^*=H/(dH/dT)T_C$ as a function of reduced temperature $t^*=T_{Con}/T_C$. The dashed-dotted and dotted lines show h^* calculated by a pair-breaking model in the clean limit and in the dirty limit, respectively (Ref. 18). The broken line is a linear fitting.

Figure 3 is a plot of the electrical resistivity ρ versus the temperature. The sample has a rectangular parallelepiped shape 2.45 mm in length, 0.91 mm in width, and 0.43 mm in thickness. The value of ρ is 3.173×10^{-4} Ω cm at 15.3 K and 5.482×10^{-4} Ω cm at 300 K. The residual resistivity ratio, $\rho_{300\ K}/\rho_{15.3\ K}$, is 1.75. ρ shows a small decrease at 15.2 K and a pronounced decrease at 14.5 K. The width of the transition ΔT (90%–10%) is 0.8 K. These results confirm that $La_{0.8}Rh_4P_{12}$ is a superconducting material with a T_C of 14.9 K, as suggested by the magnetization measurements. This value of T_C is approximately 2 K lower than that reported in Ref. 15, which may be attributed to the difference in the La concentrations of the samples. The inset shows ρ for temperatures ranging from 2 to 20 K in field cooling at various magnetic fields. The symbols T_{Con}, T_{Cmid}, and T_{Ccomp} represent the temperatures at which the value of ρ reached 90%, 50%, and 10% of that at 15.3 K at 0 kOe, respectively. Superconductivity was suppressed by the magnetic fields, which were applied parallel to the length direction.

Figure 4 is a magnetic field–temperature diagram deduced from the electrical resistivity measurements. The circles show T_{Cmid}, and the vertical bars show T_{Con} and T_{Ccomp}. We determined dH/dT and T_C to be $-12.0(2)$ kOe/K and 14.0 K from a linear fitting of the H-T_{Con} plot (broken line), respectively. The inset shows a reduced magnetic field h^* as a function of the reduced temperature t^*, where $h^*=H/(dH/dT)T_C$ and $t^*=T_{Con}/T_C$. The broken line shows a linear fitting of h^* against t^*. The dashed-dotted and dotted lines show h^* calculated by a pair-breaking model in the clean limit and in the dirty limit,[18] respectively. h^* has a linear t^* dependence and deviates from the calculated curve when t^* is lower than approximately 0.6 for h^* in the clean limit and approximately 0.7 for that in the dirty limit. We, therefore, determined $H_{C2}(0)$ to be 167(1) kOe from linear fitting. This value of $H_{C2}(0)$ is approximately two-thirds of the Pauli limiting field H_P (258 kOe), defined as $H_P=18.4T_C$ (kOe),[19,20] which indicates an absence of Pauli lim-

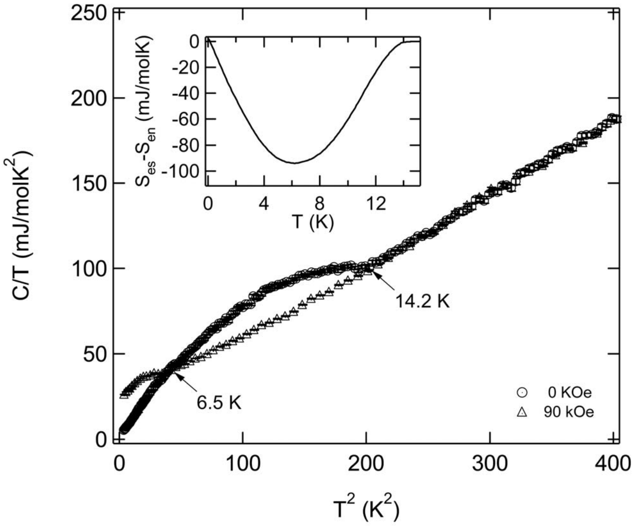

FIG. 5. Specific heat divided by the temperature C/T at 0 and 90 kOe as a function of the squared temperature. The inset shows the difference in entropy between the normal and superconducting states, $S_{\mathrm{es}}-S_{\mathrm{en}}$, as a function of the temperature.

iting in $La_{0.8}Rh_4P_{12}$. The Ginzburg-Landau coherent length $\xi(0)$ was determined to be 4.44(1) nm using the formula $H_{C2}(0)=\mathbf{\Phi}_0/2\pi\xi(0)^2$, where $\mathbf{\Phi}_0$ is the flux quantum.[21] The electron mean free path l was estimated to be $7.8\times10^{-2}[S/S_F]^{-1}$ nm from the equation $l=1.27\times10^4[\rho(n^{2/3}S/S_F)]^{-1}$, where ρ, n, S, and S_F are the resistivity at 15.3 K (in Ω cm), the conduction electron density (in cm^{-3}), the Fermi surface (in cm^{-2}), and the Fermi surface of an electron gas of density n, respectively.[22] We calculated n to be 2.568×10^{23} cm^{-3} from the density, the chemical compositions, and the number of valence electrons of La, Rh, and P, i.e., 3, 9, and 5, respectively. Since the values of S/S_F are 0.35 for Nb_3Sn and 0.5 for V_3Si,[22] we assumed the value of S/S_F in $La_{0.8}Rh_4P_{12}$ to be between 0.1 and 1.0, leading to a value of l between 0.078 and 0.78 nm. This value of l is smaller than $\xi(0)$, which indicates that the sample is a dirty material.

Figure 5 shows the specific heat divided by the temperature C/T measured at magnetic fields (field cooling) of 0 and 90 kOe as a function of the squared temperature T^2. An anomaly attributed to the superconducting transition was observed at 14.2 K for 0 kOe and 6.8 K for 90 kOe, which is consistent with the resistivity data. The obtained parameters γ_n, β, and δ were 25.1(8) $\mathrm{mJ/mol\,K^2}$ 0.338(9) $\mathrm{mJ/mol\,K^4}$, and $1.7(2)\times10^{-4}$ $\mathrm{mJ/mol\,K^6}$ respectively, by fitting the C/T data at 90 kOe and temperatures ranging from 6.8 to 19.9 K with $\gamma_n+\beta T^2+\delta T^4$. The Debye temperature, Θ_D, was calculated to be 459(12) K from the value of β. We calculated the electronic specific heat of the superconducting state C_{es} by subtracting the phonon specific heat $C_{\mathrm{ph}}=\beta T^3+\delta T^5$ from C(0 kOe). After extrapolating C_{es}(0 kOe) to 0 K, the difference in entropy between the normal and superconducting states, $S_{\mathrm{es}}-S_{\mathrm{en}}$, was calculated by integrating $(C_{\mathrm{es}}-\gamma_n)/T$ from 15 K to the lower temperatures, as shown in the inset. The entropy difference goes to zero when the temperature goes to zero, which confirms the thermodynamic consistency

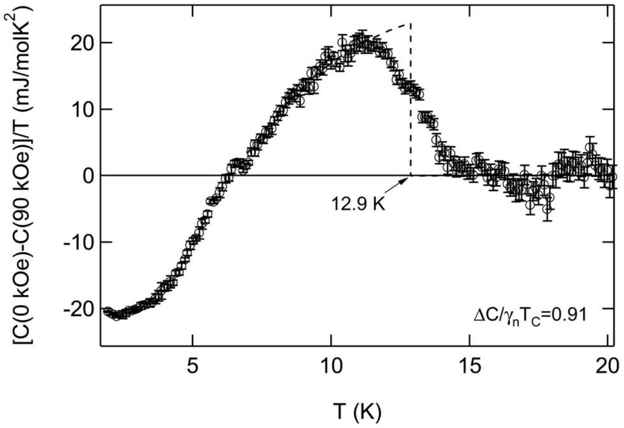

FIG. 6. Specific-heat difference between 90 and 0 kOe divided by the temperature $[C(90\ \mathrm{kOe})-C(0\ \mathrm{kOe})]/T$ as a function of the temperature.

of the fitting. The value of γ_n in the dirty limit also can be estimated from the values of dH_{C2}/dT and ρ using the following relation: $-(dH_{C2}/dT)=4.48\times10^4\gamma_n\rho$, where the units of dH_{C2}/dT, γ_n, and ρ are Oe K^{-1} erg cm^{-3} K^{-2}, and Ω cm, respectively.[22] The value of γ_n obtained from the above relation is 13.6 $\mathrm{mJ/mol\,K^2}$ when the values of ρ at 15.3 K (3.173×10^{-4} Ω cm) and dH/dT (12.0 kOe K^{-1}) are used. The values of γ_n from the specific-heat measurements are 1.8 times larger than those obtained from dH_{C2}/dT and ρ. One of the plausible explanations for this discrepancy is impurity phases contained in the sample. The existence of impurity phases is expected to change the value of ρ more sensitively than that of C. Since the oxide LaP_yO_z is contained in the sample, the ρ of the sample is anticipated to be larger than the ρ of $La_{0.8}Rh_4P_{12}$ itself. As a result, γ_n is obtained from dH_{C2}/dT, and ρ becomes smaller than that obtained by specific-heat measurements because γ_n is in inverse proportion to ρ in the equation.

In Fig. 6, the difference in C/T between 0 and 90 kOe, $[C(0\ \mathrm{kOe})-C(90\ \mathrm{kOe})]/T$, is shown as a function of the temperature. The dashed line represents an entropy-conserving construction assuming that $C_{\mathrm{es}}=A\exp(-b/k_BT)$, where k_B is Boltzmann's constant. The transition to the superconducting state with an entropy-conserving construction gives $\Delta C(T_C)/T_C=22.9(6)$ $\mathrm{mJ/mol\,K^2}$ and $T_C=12.9$ K. The ratio of the specific-heat jump at T_C to γ_n, $\Delta C(T_C)/\gamma_nT_C$, is calculated to be 0.91, which is smaller than the value of the BCS theory (1.43).[21] The electron-phonon coupling constant λ was calculated to be approximately 0.7 from the semiempirical formula proposed by McMillan: $\lambda=[1.04+\mu^*\ln(\Theta_D/1.45T_C)]/[(1-0.62\mu^*)\ln(\Theta_D/1.45T_C)-1.04]$,[23] where $\mu^*=0.1$, $\Theta_D=459$ K, and $T_C=12.9$ K, which suggests that $La_{0.82}Rh_{3.9}P_{12.1}$ is an intermediately coupled superconductor.

Table I contains a list of the superconducting parameters of $La_{0.8}Rh_4P_{12}$ together with those of $LaRu_4P_{12}$, $LaFe_4P_{12}$, and YFe_4P_{12}, which have relatively high T_C values among the ternary filled skutterudite-type phosphides and reported superconducting parameters.[6,10,24] The electronic density of states $N(0)$ was calculated from the relation γ_n

TABLE I. Superconducting parameters of $La_{0.8}Rh_4P_{12}$, $LaRu_4P_{12}$ (Ref. 6), YFe_4P_{12} (Ref. 10), and $LaFe_4P_{12}$ (Ref. 24).

	$La_{0.8}Rh_4P_{12}$	$LaRu_4P_{12}$	YFe_4P_{12}	$LaFe_4P_{12}$
T_C (K)	14.9	7.2	7	4.1
H_{C2} (kOe)	167(1)	36.5		
ξ (nm)	4.41(1)	9.5		
γ_n (mJ/mol K^2)	25.1(8)	26	27.2	57
Θ_D (K)	459(12)	446	553	580
$N(0)$ (states/eV atom)	0.37(1)	0.42	0.45	0.98
λ	0.7	0.57	0.5	0.45

$=\pi^2 n_{\mathrm{atom}} N_0 k_B^2 N(0)(1+\lambda)/3$, where n_{atom} is the number of atoms per formula unit and N_0 is Avogadro's number.[21] The value of λ in the three materials was calculated using the above-mentioned equation. $La_{0.8}Rh_4P_{12}$ has a higher H_{C2} than $LaRu_4P_{12}$, which is consistent with the higher T_C of $La_{0.8}Rh_4P_{12}$ because H_{C2} is proportional to T_C.[19] It is worth noting that $La_{0.8}Rh_4P_{12}$ has the largest λ among the four skutterudites. The largest λ in $La_{0.8}Rh_4P_{12}$ plausibly explains why $La_{0.8}Rh_4P_{12}$ has the highest T_C among the four. The McMillan equation modified by Allen and Dynes is known to be a better approximation and to be applicable to larger values of λ.[25] In order to use the modified McMillan equation, information on the phonon density of states (a logarithmic average frequency of phonon) is required, but no information is available. The original McMillan equation is known to be reliable when $\lambda < 1$, and the difference between the original and modified equations is approximately 10% in this λ region. Since the value of λ obtained here is smaller than 1, the results showing that $La_{0.8}Rh_4P_{12}$ has the largest λ among the four do not change significantly even when the modified equation is used to obtain λ.

In summary, $La_{0.8}Rh_4P_{12}$ was synthesized at 9.4 GPa and 1473 K using a belt-type apparatus. The measurements of the electrical resistivity, magnetization, and specific heat revealed that $La_{0.8}Rh_4P_{12}$ is an intermediately coupled type-II superconducting material with a T_C of 14.9 K and H_{C2} of 167(1) kOe. A comparison of superconducting parameters between $La_{0.8}Rh_4P_{12}$ and the other three skutterudites suggests that the relatively large λ in $La_{0.8}Rh_4P_{12}$ is a plausible explanation for the fact that $La_{0.8}Rh_4P_{12}$ has the highest T_C among the ternary filled skutterudite-type phosphides.

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