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LETTER TO THE EDITOR

Magnetic and transport properties of a new valence-fluctuating compound, CeRhP

T Sasakawa, T Suemitsu, J Kitagawa, O Sologub, P Salamakha and T Takabatake¹

Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

E-mail: takaba@hiroshima-u.ac.jp

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Abstract

We have synthesized CeRhP, aiming at breaking new ground as regards the CeRhPn (Pn = pnictogen) system. X-ray powder diffraction analysis shows that CeRhP crystallizes into the tetragonal LaPtSi-type structure. Both the magnetic susceptibility and thermopower exhibit a broad peak around 170 K, and the specific heat gives an electronic specific-heat coefficient of $30 \text{ mJ K}^{-2} \text{ mol}^{-1}$. These results indicate that CeRhP is a valence-fluctuating compound with a Kondo temperature of 400–500 K. The electrical resistivity shows a metallic behaviour, in contrast to the semimetal or semiconducting behaviour in CeRhSb and CeRhAs, with the orthorhombic ϵ -TiNiSi-type structure. This stresses the importance of the crystal symmetry to the gap formation in the CeRhPn series.

Cerium-based equiatomic pnictides CeRhPn (Pn = As, Sb and Bi) crystallize into the orthorhombic ϵ -TiNiSi-type structure (space group: $Pnma$) [1–3]. CeRhBi is a heavy-fermion metal with an electronic specific-heat coefficient $\gamma = 500 \text{ mJ K}^{-2} \text{ mol}^{-1}$, whereas both CeRhSb and CeRhAs are classified as so-called Kondo semiconductors where a pseudogap opens in a heavy-quasiparticle band around the Fermi level at low temperatures [1, 3, 4]. It has been predicted that the narrow gap in Kondo semiconductors causes huge thermopower at low temperatures [5]. In fact, the thermopower of CeRhSb and CeRhAs reaches as high as 80 and $138 \mu\text{V K}^{-1}$ at 20 and 35 K, respectively, and thus these compounds are highly attractive as thermoelectric materials [4, 6, 7]. The above-mentioned brief survey shows that CeRhPn (Pn = pnictogen) is a deeply interesting system, capable of presenting new exotic phenomena.

¹ Author to whom any correspondence should be addressed.

In Ce-based intermetallic compounds, it is well known that the reduction of the unit-cell volume strengthens hybridization between conduction-electron states and 4f-electron states (c–f hybridization). For the series of CeRhPn, in fact, specific-heat measurements have revealed that the c–f hybridization shows a progressive increase on going from Pn = Bi through Pn = Sb to Pn = As, along with the decrease in the unit-cell volume [1]. Therefore, the hybridization between the outer p-electron states of the Pn atoms and 4f-electron states of the Ce atoms must play an important role in the variety of physical properties in CeRhPn. Furthermore, the fact that the gap magnitude in CeRhAs is larger than in CeRhSb suggests that the strong c–f hybridization stabilizes the Kondo semiconducting state.

The above-mentioned trend in CeRhPn thus motivated us to synthesize CeRhP, the existence of which has not ever been reported as far as we know. If CeRhP exists and crystallizes into the ϵ -TiNiSi-type structure, then the c–f hybridization would be stronger than in CeRhAs. This may enable us to investigate how the strength of the c–f hybridization relates to the Kondo semiconducting state. Even if CeRhP crystallizes into another type of structure, it may exhibit exotic phenomena as mentioned above. Furthermore, it may help us to understand what crystal symmetry is requisite for the Kondo semiconducting state. In this letter, we will report on our success in synthesizing CeRhP and its magnetic and transport properties.

A polycrystalline sample was prepared through several procedures. An ingot of CeRh was prepared by arc melting of Ce and Rh under an Ar atmosphere. This ingot and pieces of P, in stoichiometric proportions, were sealed into a quartz tube and gradually heated to 800 °C in an electric furnace. The reactant was encapsulated in a molybdenum crucible by an arc welder under an Ar atmosphere, then heated to 1670 °C and slowly cooled in a furnace with a tungsten mesh heater. The synthesized sample was further annealed for two weeks at 600 °C. An optical metallograph detected the presence of small amounts of impurity phases (<1%). The composition of the main phase was determined as Ce:Rh:P = 1:1:1 by the electron-probe microanalysis (EPMA). The x-ray powder diffraction pattern indicates that the crystal structure is not of ϵ -TiNiSi type but of tetragonal LaPtSi type (space group: $I4_1md$). The lattice parameters were determined to be $a = 4.039$ Å and $c = 14.353$ Å.

The magnetic susceptibility of the sample of 200 mg in weight was measured by using a quantum design magnetometer in a field of 1 T for both zero-field-cooled (ZFC) and field-cooled (FC) processes between 2 and 300 K. The specific-heat measurement was performed by a semi-adiabatic heat-pulse method between 0.6 and 70 K. For a bar-shaped sample of 2 mm in length, the electrical resistivity and thermopower were measured, respectively, by a conventional four-probe dc method and a differential method with a temperature gradient of 0.05–0.3 K.

Figure 1 represents the temperature dependence of the magnetic susceptibility χ . At around 170 K ($=T_{\chi_{max}}$), χ shows a broad maximum which is typical of valence-fluctuating compounds. An upturn below 60 K probably originates from magnetic impurity phases. Irreversible behaviour of χ in the ZFC and FC processes is observed below 12 K. This irreversibility can be ascribed to the magnetic ordering of the impurity phase CeP, which has a complex magnetic phase diagram [8]. Between 15 and 50 K, $\chi(T)$ is well reproduced by the following equation (see the solid curve in figure 1):

$$\chi = \chi_0 + \frac{C_{imp}}{T + \Theta_{imp}}. \quad (1)$$

The first term represents a temperature-independent Pauli paramagnetism in CeRhP and the second one a Curie–Weiss contribution from the magnetic impurities. The χ_0 thus obtained is 1.30×10^{-3} emu mol⁻¹, C_{imp} is 1.97×10^{-2} emu K mol⁻¹ and Θ_{imp} is 7.33 K. The Kondo temperature T_K can be extracted from the χ_0 -value by the use of the exact solution of the

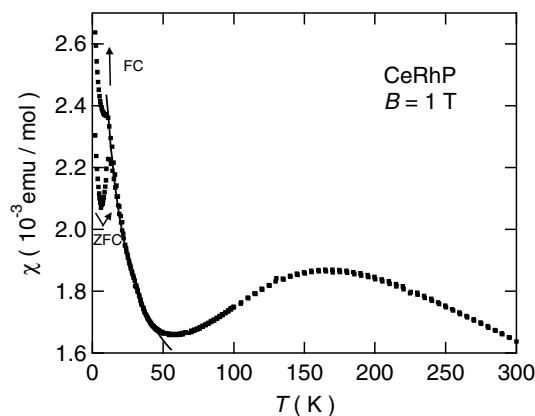


Figure 1. The temperature dependence of the magnetic susceptibility of CeRhP measured in the ZFC and FC processes under a magnetic field of 1 T. The solid curve represents the fit by equation (1).

Coqblin–Schrieffer model which explains various physical properties of valence-fluctuating compounds [9]. The relation between χ_0 and T_K is given by

$$\chi_0 = \frac{(g\mu_B)^2 J(J+1)\omega_v}{3k_B T_K}, \quad \omega_v = \frac{\exp(1+c-3/2\nu)}{2\pi\Gamma(1+1/\nu)}, \quad (2)$$

where ω_v means the generalized Wilson number, ν is $2J+1$ (J : the total angular momentum), c the Euler constant, g the Landé g -factor, μ_B the Bohr magneton and $\Gamma(\nu)$ the gamma function [9, 10]. If all of the degeneracy associated with the $J = 5/2$ multiplet of Ce^{3+} ion participates in the Kondo effect, T_K is estimated to be 400 K, by substituting $J = 5/2$ in equation (2). From this T_K -value, it is expected that $\chi(T)$ possesses a broad peak at 165 K ($T_K = 2.4T_{\chi_{max}}$) [9, 10], which is in agreement with the experimental value of 170 K.

The specific heat C of CeRhP in figure 2 monotonically increases without showing any phase transition on heating up to 70 K. The inset of figure 2 represents the C/T versus T^2 plot, where a faint peak appears at around 6 K. Since the entropy release associated with the anomaly is three orders of magnitude smaller than $R \ln 2$, it is ascribed to a magnetic ordering of the cerium oxide in the sample. The origin of the upturn below 1.7 K is not yet clear. The linear extrapolation of the C/T versus T^2 plot from below 8 K to $T = 0$ K gives $\gamma = 30 \text{ mJ K}^{-2} \text{ mol}^{-1}$. The Debye temperature $\Theta_D = 210$ K is obtained from the slope of the linear line. Using the γ - and χ_0 -values, the Wilson ratio $R_W = \gamma/\chi_0$ is calculated as 2.3, which is close to 2.0, the value expected for the strongly correlated electron system. The exact solution of the Coqblin–Schrieffer model connects the γ -value with T_K via the following equation [9, 10]:

$$\gamma = \frac{\omega_v(\nu-1)\pi^2 k_B}{3\nu T_K}. \quad (3)$$

From the γ -value, T_K is estimated to be 490 K, in accordance with $T_K = 400$ K estimated from χ_0 .

The temperature dependence of the electrical resistivity is shown in figure 3(a). As temperature decreases, $\rho(T)$ decreases with a steep slope below 150 K. The residual resistivity ratio $\rho(300 \text{ K})/\rho(1.5 \text{ K})$ is 38.8 with the residual resistivity ρ_0 of $8.0 \mu\Omega \text{ cm}$, signalling the high quality of the present sample. It should be stressed that the metallic behaviour of CeRhP is highly contrasted with the semimetal or semiconducting ones for CeRhSb and

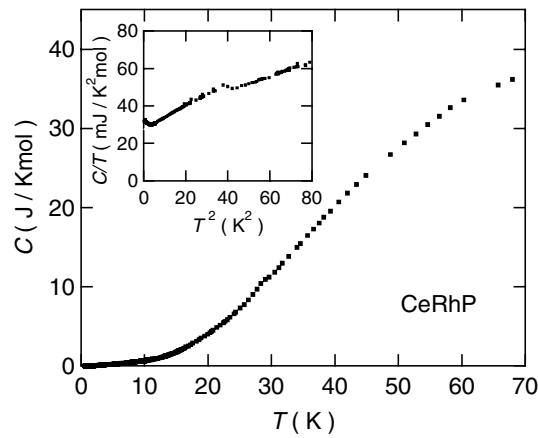


Figure 2. The temperature dependence of the specific heat of CeRhP. The inset shows the C/T versus T^2 plot.

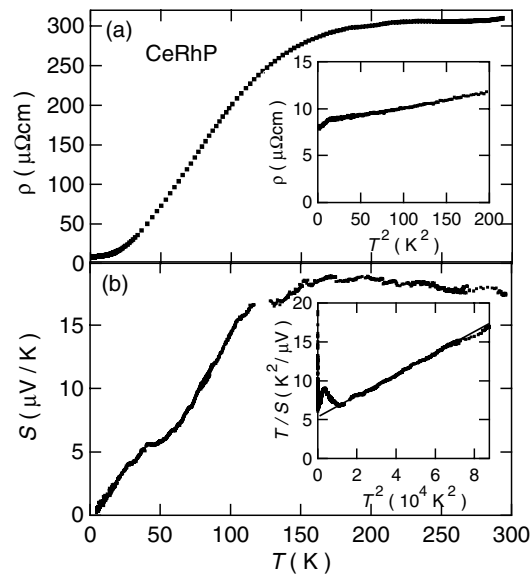


Figure 3. (a) The temperature dependence of the electrical resistivity of CeRhP. The inset shows the ρ versus T^2 plot. (b) The temperature dependence of the thermopower of CeRhP. The inset displays the T/S versus T^2 plot. The solid curve represents the thermopower calculated using equation (4).

CeRhAs. In the inset of figure 3(a), we show the ρ versus T^2 plot. A small inflection at 3.3 K would not be indicating intrinsic nature for CeRhP, because neither χ nor C shows any anomaly at 3.3 K. Below 10 K, $\rho(T)$ can be described by $\rho_0 + AT^2$ with $A = 1.4 \times 10^{-3} \mu\Omega \text{ cm K}^{-2}$, where the second term arises from an electron–electron scattering. The Fermi-liquid theory suggests that A/γ^2 in strongly correlated electron systems adopts a universal value of $1.0 \times 10^{-5} \mu\Omega \text{ cm K}^{-2}/(\text{mJ K}^{-2} \text{ mol}^{-1})^2$ [11]. The value of A/γ^2 of $1.5 \times 10^{-5} \mu\Omega \text{ cm K}^{-2}/(\text{mJ K}^{-2} \text{ mol}^{-1})^2$ for CeRhP is in good agreement with the universal value, which means that the Fermi-liquid state is realized in CeRhP at low temperatures.

Figure 3(b) displays the temperature dependence of the thermopower $S(T)$. The positive sign of $S(T)$ implies that the dominant carriers are holes. $S(T)$ passes through a broad maximum of $18 \mu\text{V K}^{-1}$ around $T_{Smax} = 170 \text{ K}$, and goes to zero with decreasing temperature. This is the typical behaviour of the valence-fluctuating Ce compounds [12]. The T_{Smax} -value and the above-mentioned T_K -value satisfy the relation $T_{Smax} \sim T_K/3$, which is derived from the single-impurity Anderson model [13]. For a metallic system, S is usually represented by the summation of the diffusion term S_d and the phonon drag one S_g . Assuming a Lorentzian form for a heavy-quasiparticle band around the Fermi level, Mott's equation for S_d is modified as follows [14]:

$$S_d = \frac{UT}{V^2 + T^2}, \quad U = \frac{2(\epsilon_0 - \epsilon_F)}{|e|}, \quad V^2 = 3 \frac{(\epsilon_0 - \epsilon_F)^2 + W^2}{\pi^2 k_B^2}, \quad (4)$$

where ϵ_0 is the peak position, ϵ_F the Fermi energy, e the electronic charge and W the width of the Lorentzian band. The fit of equation (4) to the data above 110 K is shown by the solid curve in the T/S versus T^2 plot (figure 3(b) inset). The fit gives the values 3.7 and 31 meV for $(\epsilon_0 - \epsilon_F)$ and W , respectively. These values are close to those of the typical valence-fluctuating compound CeNi_2 [14]. A shoulder at 45 K in $S(T)$ might be the contribution of S_g , since S_g has a maximum at a temperature of $0.1\text{--}0.3\Theta_D$ in a sample characterized by low residual resistivity [15].

Contrary to our expectation, the present study revealed that CeRhP does not crystallize into the ϵ -TiNiSi-type structure and exhibits no exotic phenomena. It is however meaningful to discuss prerequisites for the Kondo semiconductor from the viewpoint of the c - f hybridization and the crystal structure as mentioned in the introduction. The strength of the c - f hybridization in CeRhP can be placed between those in CeRhSb and CeRhAs judging from their T_K -values (400–500 K for CeRhP, 360 K for CeRhSb and 1200 K for CeRhAs). In this sense, CeRhP satisfies one of the requirements for realizing the Kondo semiconducting state. Nevertheless, the band structure of the LaPtSi-type crystal structure may lead to a metallic valence-fluctuating state instead of the Kondo semiconducting state. This conjecture is based on the fact that only compounds with the ϵ -TiNiSi-type structure have been reported as Kondo semiconductors, except the cubic compounds such as $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and YbB_{12} [16, 17]. The present study of CeRhP thus brings out the uniqueness of the ϵ -TiNiSi-type structure.

In summary, we have reported a set of measurements of the magnetic susceptibility, specific heat, electrical resistivity and thermopower for the newly found compound CeRhP. The combined results indicate that CeRhP is a valence-fluctuating compound with $T_K = 400\text{--}500 \text{ K}$ and shows Fermi-liquid behaviour at low temperatures. The c - f hybridization would be strong enough to stimulate the development of a pseudogap as in CeRhSb and CeRhAs. Nevertheless, CeRhP is a good metal, probably because its crystal structure is not of ϵ -TiNiSi type but of LaPtSi type. We have encountered a good opportunity in this study to get a grasp of the conditions necessary to stabilize the Kondo semiconducting state. It is concluded that not only the strength of the c - f hybridization but also the crystal structure are decisive prerequisites at least in the CeRhPn system.

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