Pressure-induced metal-insulator transition in the filled skutterudite $PrFe_4P_{12}$

Hiroyuki Hidaka,[1] Ikuma Ando,[2] Hisashi Kotegawa,[1] Tatsuo C. Kobayashi,[1] Hisatomo Harima,[3] Miki Kobayashi,[4] Hitoshi Sugawara,[5] and Hideyuki Sato[4]
[1]*Department of Physics, Okayama University, Okayama 700-8530, Japan*
[2]*Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[3]*Department of Physics, Kobe University, Nada, Kobe 657-8501, Japan*
[4]*Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan*
[5]*Faculty of Integrated Arts and Sciences, Tokushima University, Tokushima 770-8502, Japan*
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We have studied the electrical resistivity of the filled skutterudite compound $PrFe_4P_{12}$ under high pressure. The antiferroquadrupolar ordering temperature T_Q decreases monotonically with increasing pressure up to 2.4 GPa. Above 2.4 GPa, we have found that a metal-insulator (M-I) transition appears. The insulating state is easily suppressed by a magnetic field. The observed Kondo effect and a field-induced heavy-fermion state at high pressure suggest that the quadrupolar interactions survive in the insulating region. The quadrupolar interactions might play an essential role in the M-I transition. $PrFe_4P_{12}$ is an unusual compound in that it shows a pressure-induced transition from a metal to an insulator.

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Filled skutterudite, with a general formula RT_4X_{12} (R= rare earth; T=Fe, Ru, and Os; X=P, As, and Sb), is one of the hot topics in condensed-matter physics. These compounds show a variety of electrical and magnetic properties depending on the components R, T, and X. These include ferromagnetism, antiferromagnetism, heavy-fermion (HF) states, superconductivity, and metal-insulator (M-I) transitions.[1–4] Among these compounds, some that are Pr based have attracted much attention. If the ground state of Pr^{3+} with a $4f^2$ contribution in the crystal electric field is the Γ_3 nonmagnetic doublet or the Γ_1 and Γ_4 quasiquartet, $4f^2$ will have an electric quadrupolar moment. The anomalous behavior in $PrOs_4Sb_{12}$ and $PrFe_4P_{12}$ suggests that these compounds could be candidates for this proposition. $PrOs_4Sb_{12}$ is a novel HF superconductor with a superconducting (SC) temperature T_c=1.85 K.[5] Two distinct SC phases, a breaking of time-reversal symmetry in the SC state, and a field-induced ordered phase above the upper critical field have been reported.[6–8] These properties are in contrast with other HF superconductors,[8] implying that this superconductivity is induced by an exotic mechanism through fluctuations of the quadrupolar moment.

On the other hand, $PrFe_4P_{12}$ shows an antiferroquadrupolar (AFQ) ordering at low temperature T. Its electrical resistivity ρ shows a Kondo behavior; that is, the T dependence of ρ depends on $-\ln T$ between 30 K and 100 K.[4] The absence of magnetic Bragg peaks in neutron scattering data and a negligible moment as estimated from the Pr nuclear Schottky contribution to the specific heat indicate that the ordered phase below T_Q=6.5 K is nonmagnetic in origin.[9,10] On the other hand, for neutron-diffraction measurements made in a magnetic field, antiferromagnetic Bragg reflections are observed.[11] A theoretical calculation[12] predicted a lattice distortion with $\mathbf{q}=(1,0,0)$ coupled with a nesting effect in the Fermi surface. This is confirmed by an x-ray-diffraction measurement.[13] Such an ordering is not observed in $LaFe_4P_{12}$. Recent NMR measurements showed the appearance of two P sites with different hyperfine fields below T_Q.[14] These results demonstrate that $4f$ electrons in Pr ions undergo AFQ ordering below T_Q.

The AFQ-ordered state in $PrFe_4P_{12}$ is suppressed by applying a field of $H_Q\sim 5.5$ T, where the HF state appears.[15,16] In electrical resistivity measurements, $\rho(T)$ has a dependence of the form ρ_0+AT^2, with large values of A=3–15 $\mu\Omega$ cm/K^2 for magnetic fields between 4 and 10 T.[17] The specific-heat measurement at 6 T shows an enormous electronic specific-heat coefficient γ of 1.2 J/K^2 mol.[16] The large values of γ and the constant A, measured with the same field, are consistent with the Kadowaki-Woods relation.[17] In addition, the huge cyclotron mass ($m_c^*=81m_0$) determined by the de Haas–van Alphen (dHvA) measurement is direct evidence of the HF state.[16] It is suggested that the Kondo effect, the AFQ order, and the heavy mass in a strong field result from the quadrupolar interactions.

In the present study, we have carried out electrical resistivity measurements at high pressure and found a pressure-induced transition from metal to insulator. In contrast, most compounds showing a M-I transition, such as SmB_6 (Ref. 18) and $PrRu_4P_{12}$,[19] change from insulator to metal as a result of applying pressure: the inverse of this study.

Single crystals were grown by the tin-flux method as described in Ref. 2. The high quality of the present sample was ensured by the successful observation of the dHvA effect on samples grown in the same manner.[16] The electrical resistivity for $J//H//[100]$ was measured by a conventional four-probe method. Pressure was applied by an indenter cell with daphne oil 7373 as the pressure-transmitting medium. The resistivity at room temperature was normalized to the value of the previous work,[4] because of the uncertainty in the absolute value obtainedby using a tiny sample in the pressure cell. The pressure value was determined by T_c of lead.

The temperature dependence of the electrical resistivity $\rho(T)$ under pressure is shown in Figs. 1(a) and 1(b). At the ambient pressure, $\rho(T)$ obeys a logarithmic T dependence

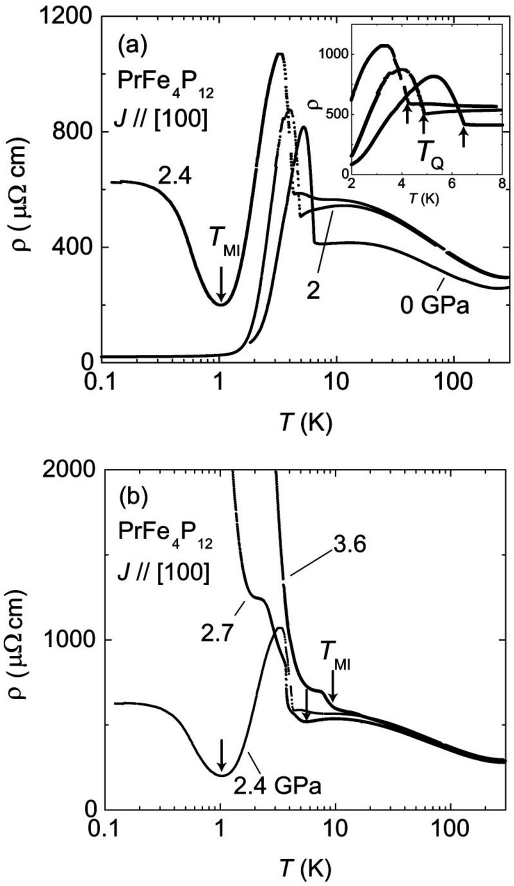

FIG. 1. T dependence of the electrical resistivity under pressure. (a) $P \leqslant 2.4$ GPa: The inset shows an enlarged view between 2 K and 8 K. The AFQ-ordering temperature T_Q decreases gradually with increasing pressure. At 2.4 GPa, a M-I transition appears below T_Q. (b) $P \geqslant 2.4$ GPa: T_{MI} increases with increasing pressure. We cannot observe any anomaly for T_Q above 2.7 GPa owing to the insulating behavior.

between 30 K and 100 K, and shows a sharp upturn at $T_Q = 6.5$ K due to the AFQ order. This behavior agrees with the data reported previously.[4] The anomaly at the AFQ transition continues up to $P = 2.4$ GPa, and is accompanied by a gradual decrease of T_Q.

We observe a sharp increase of $\rho(T)$ below T_Q at 2.4 GPa, suggesting that the ground state changes from metallic to insulating. As shown in Fig. 1(b), where ρ starts to increase rapidly, T_{MI} moves to higher temperatures with increasing pressure. We do not observe any anomaly corresponding to T_Q above 2.7 GPa, because it is obscured by the sharp increase in $\rho(T)$ due to the M-I transition. We observe that $\rho \propto -\ln T$, which is indicative of the Kondo effect, and can evenbe observed above 2.4 GPa.

Figures 2(a) and 2(b) show $\rho(T)$ measured for several magnetic fields along the crystal axis [100] at pressures of 2.7 GPa and 3.3 GPa. For zero field, ρ_0 reaches 3.2×10^4 $\mu\Omega$ cm at 2.7 GPa and 2.4×10^5 $\mu\Omega$ cm at 3.3 GPa. This value of ρ_0 of 3.3 GPa is one order of magnitude larger than $\rho_0 \sim 4.4 \times 10^4$ $\mu\Omega$ cm for $PrRu_4P_{12}$, which also exhibits a M-I transition.[3,20] By applying the field, the insulating behavior is drastically suppressed, and finally ρ_0 reaches a

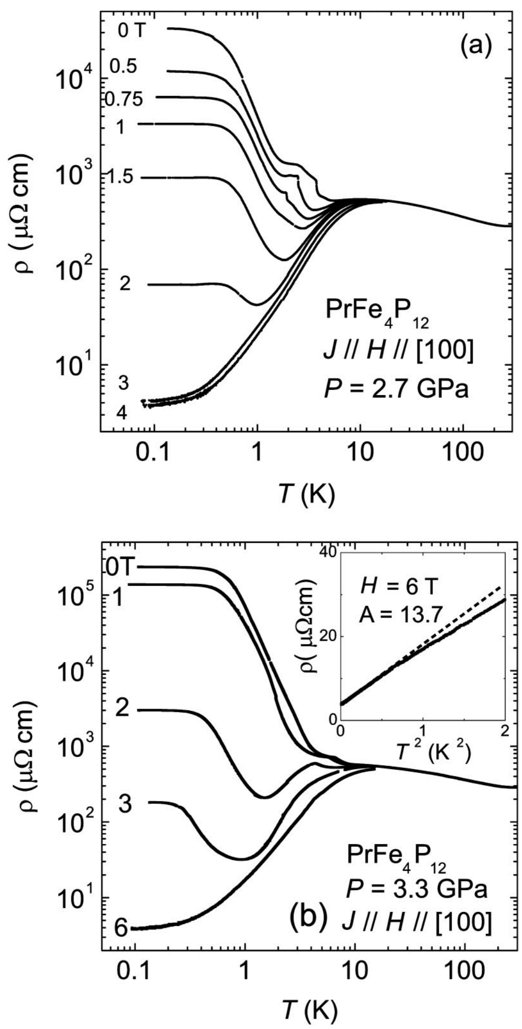

FIG. 2. T dependence of the electrical resistivity for several magnetic fields at (a) 2.7 GPa and (b) 3.3 GPa. The insulating behavior is suppressed by applying the field, and finally $\rho(T)$ shows metallic behavior. The inset in (b) shows the Fermi-liquid behavior obeying a form $\rho(T) = \rho_0 + AT^2$, with $A = 13.7$ $\mu\Omega$ cm/K^2 below ~ 1 K.

value of ~ 4 $\mu\Omega$ cm for all pressures. When T_{MI} disappears, the resistivity at low T becomes similar to Fermi-liquid (FL) behavior. In fact, at 3.3 GPa with a field of 6 T, $\rho(T)$ obeys $\rho(T) = \rho_0 + AT^2$ below ~ 1 K, as shown in the inset of Fig. 2(b). The estimated value of $A = 13.7$ $\mu\Omega$ cm/K^2 is comparable to $A = 3-15$ $\mu\Omega$ cm/K^2 at ambient pressure.[17] This large value of A suggests that the HF state in a field is realized at high pressure.

Figure 3(a) shows ρ vs $1/T$ at a pressure of 2.7 GPa. By fitting these data to an activation form $\rho = C \exp(E_g/k_B T)$, where E_g is the activation energy, we can estimate a value for E_g/k_B. At zero field, the data in the narrow temperature range of $0.7\ \mathrm{K} < T < 1.7$ K give $E_g/k_B \sim 2.8$ K. At both 3.3 GPa and 3.6 GPa, almost the same value of $E_g/k_B \sim 10$ K is estimated at zero field. Figure 3(b) shows the field dependence of the energy gap at 2.7 GPa. By applying the field, E_g/k_B decreases, and finally the metallic behavior is realized. From the field dependence of ρ at 100 mK (shown in the inset), the

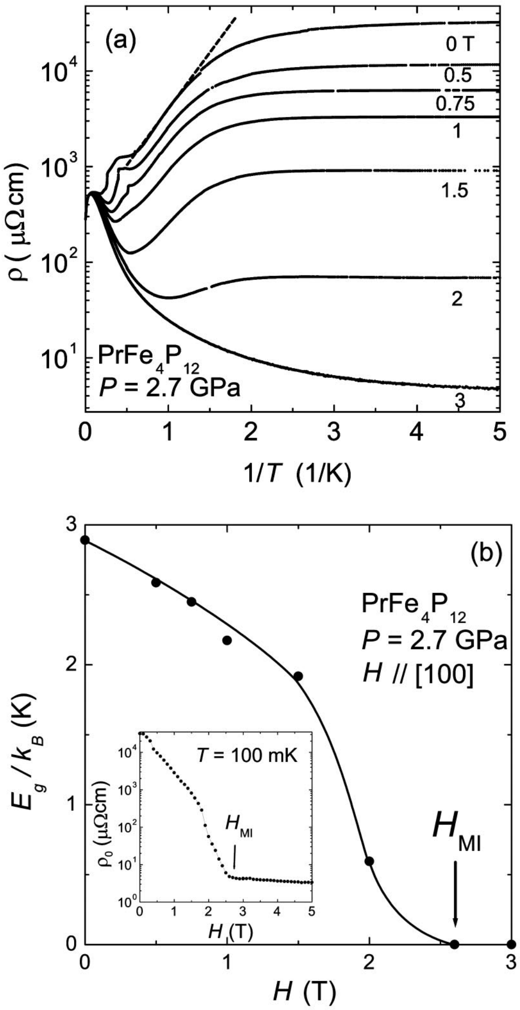

FIG. 3. (a) ρ vs $1/T$ at 2.7 GPa under several magnetic fields. The dotted line indicates $\rho = C\exp(E_g/k_BT)$. The insulating behavior clearly disappears at 3 T. (b) The magnetic field dependence of E_g/k_B and the residual resistivity ρ_o (inset) at 2.7 GPa.

critical field for the *M-I* transition (H_{MI}) at 2.7 GPa is determined to be 2.6 T. As shown in Fig. 2(b), H_{MI} at 3.3 GPa is larger than that at 2.7 GPa.

Figure 4 shows the pressure-temperature (P-T) phase diagram, and the pressure dependence of E_g/k_B (inset). In the P-T phase diagram, T_Q decreases gradually up to a pressure of 2.4 GPa. At 2.4 GPa, the insulating state appears abruptly below T_Q. Above 2.4 GPa, T_{MI} increases rapidly and reaches $\sim$9.4 K at 3.6 GPa. It is not clear whether the boundary between metal and insulator is the thermodynamic phase transition or not. We cannot determine the pressure dependence of T_Q above 2.4 GPa owing to the *M-I* transition. The inset shows that E_g/k_B increases with increasing T_{MI}.

The ground state in $PrFe_4P_{12}$ changes from metal to insulator with increasing pressure. This is not the case for most compounds showing the *M-I* transition. $PrRu_4P_{12}$ shows the *M-I* transition at $T_{MI} = 62$ K at ambient pressure:[3] this is caused by a charge density wave (CDW). This insulating state is suppressed by applying a pressure of 12 GPa.[19] Typical Kondo insulators such as SmB_6 and CeNiSn show insulating behavior at ambient pressure, and the hybridization gaps are suppressed by pressures of 4 GPa and 2.4 GPa, respectively.[18,21] $PrFe_4P_{12}$ is unusual in that the transition from metal to insulator results by increasing the pressure.

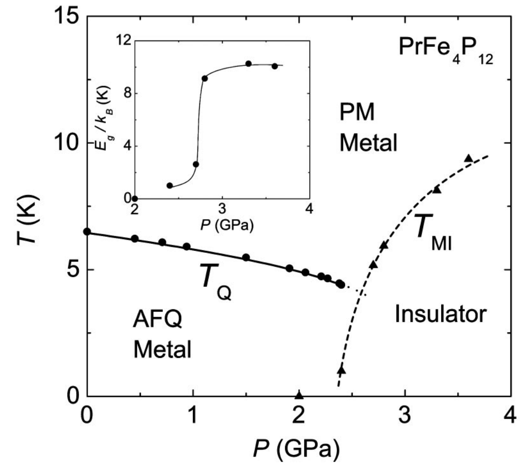

FIG. 4. The pressure-temperature phase diagram and the pressure dependence of E_g/k_B (inset). The ground state in $PrFe_4P_{12}$ changes from the AFQ metallic state to the insulating state at 2.4 GPa.

For high pressures, $PrFe_4P_{12}$ still shows the Kondo behavior for $\rho(T)$, indicating that the valency of the Pr ion is nearly unchanged at 3+. A filled skutterudite compound with Pr^{3+} is an uncompensated metal and it could not be an insulator within the same primitive unit cell of PrT_4X_{12}. To be the insulator, it requires a doubled unit cell. In the case of $PrRu_4P_{12}$ with Pr^{3+}, the origin of the *M-I* transition is the CDW connected to a nesting of the Fermi surface as predicted by a band calculation and confirmed by a precise x-ray-diffraction measurement.[22–24] The x-ray-diffraction measurement revealed a structural phase transition that doubles the unit cell.[25] It is this doubled unit cell and the removal of whole carriers due to the nesting effect that make it possible for the compound to be an insulator. On the other hand, the band calculation indicates that $PrFe_4P_{12}$ also has good nesting properties in the main conduction band as does $PrRu_4P_{12}$, but it has an extra holelike band crossing the Fermi surface, which prevents a perfect nesting effect.[26] If this extra holelike band disappears as a pressure effect, the *M-I* transition originating from the CDW or the AFQ ordering might occur. Regarding the possibility of the CDW: the *M-I* transition in $PrFe_4P_{12}$ shows a strong-field dependence, which contrasts with the case of $PrRu_4P_{12}$. The T_{MI} in $PrRu_4P_{12}$ shows a quite weak-field dependence of electrical resistivity up to a field of 14 T, and a quite weak-field dependence of specific-heat measurements up to 12 T.[27,28] This suggests that the *M-I* transition in $PrFe_4P_{12}$ may not be caused by the simple CDW. In $PrFe_4P_{12}$, the $-\ln T$ dependence on $\rho(T)$ and the field-induced HF state suggest that the quadrupolar interactions survive even in the insulating region. In addition, the values of T_{MI} and H_{MI} are close to those of T_Q and H_Q, respectively. In this context, the quadrupolar interactions might play an essential role in the *M-I* transition. It is important to clarify whether an AFQ-ordering state coexists with the insulating state or not. Further experiments, such as NMR, Hall effect, and x-ray diffraction, are needed to clarify this, and are in progress.

In summary, we studied the electrical resistivity of $PrFe_4P_{12}$ at high pressure. At 2.4 GPa, the *M-I* transition appears abruptly, and T_{MI} moves to higher temperatures with increasing pressure. The insulating state is easily suppressed by a magnetic field. The Kondo behavior at high temperature and the field-induced FL behavior with a large value of A imply that the quadrupolar interactions survive in the insulating region. This suggests that the *M-I* transition might be related to the quadrupolar interactions. The *M-I* transition at high pressure for $PrFe_4P_{12}$ contrasts with that for typical Kondo insulators and $PrRu_4P_{12}$. $PrFe_4P_{12}$ is an unusual compound as it shows a transition from metal to insulator as a result of increasing pressure.

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