Metal-Insulator Transition in $PrRu_4P_{12}$ with Skutterudite Structure

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The low temperature properties of $PrRu_4P_{12}$ and $PrOs_4P_{12}$ have been studied by means of electrical resistivity and magnetic susceptibility measurements. The resistivity of $PrRu_4P_{12}$ decreases with decreasing temperature from room temperature to about 60 K, but increases sharply with decreasing temperature below 60 K. A metal-insulator transition is found at around 60 K. The susceptibility of the phosphide shows no distinct anomaly at this temperature. No significant change in the powder x-ray diffraction pattern of $PrRu_4P_{12}$ is detected down to 10 K. The anomalous behavior may arise from a $4f$ instability of the Pr ion. [S0031-9007(97)04365-2]

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Ternary metal phosphides with general formula MT_4P_{12} (M = La through Eu, U, and Th, T = Fe, Ru, and Os) crystallize with the skutterudite structure filled by a lanthanide or actinide atom [1,2]. The MT_4P_{12} compounds have various physical properties at low temperature, such as superconductivity, semiconductivity, and magnetic order. $LaFe_4P_{12}$, $LaRu_4P_{12}$, and $LaOs_4P_{12}$ are metallic superconductors which have transition temperatures $T_C =$ 4.08, 7.02, and 1.83 K, respectively [3–5]. $CeFe_4P_{12}$, $CeRu_4P_{12}$, and UFe_4P_{12} show a semiconductorlike temperature dependence of the resistivity [6,7]. Furthermore, $CeFe_4P_{12}$ shows an almost temperature-independent magnetic susceptibility and a smaller lattice parameter than that expected for trivalent Ce [6]. These properties suggest that the Ce atoms are nearly tetravalent. The magnetic behavior of UFe_4P_{12} is very different from that of $CeFe_4P_{12}$. UFe_4P_{12} is ferromagnetic with a Curie temperature of 3.15 K and the magnetic properties suggest a $5f^2$ electron configuration for U (U^{4+}) [6,8]. It has been suggested that the semiconducting behavior of these compounds may relate to the tetravalent state of the Ce and U atoms because the rare earth ions are trivalent in other compounds, which are metallic [1]. On the other hand, it has also been suggested that this behavior may arise from strong hybridization of f electrons of the Ce and U atoms with the conduction electrons [6,8]. Recent band-structure calculations on $CeFe_4P_{12}$ and $CeFe_4Sb_{12}$ indicate that the Ce is near trivalent in both compounds, and these compounds possess a small band gap that arises from strong hybridization of Ce $4f$ states with both Fe $3d$ and pnicogen-p states [9].

The compound $PrFe_4P_{12}$ exhibits metallic conductivity and displays antiferromagnetic ordering below 6.2 K [5]. The magnetic properties of this compound would indicate a trivalent state for Pr [5]. These behaviors seem to be natural because the trivalent state is most stable for Pr-based compounds. Pr-based compounds are more rigid against attempts to drive them into instability than Ce- or Yb-based compounds because they are already two $4f$ electrons away from a more stable empty or closed $4f$ shell. However, $4f$ instabilities have been associated with Pr in dilute concentrations or under very high hydrostatic pressures. Pr metal undergoes a phase transition at 22 GPa with a large volume collapse [10]. The low temperature resistivity shows a qualitative change at pressures $P \geq$ 22 GPa [11]. This behavior may be taken as a signature for the destruction of the local $4f^2$ magnetic moments and demagnetization due to valence instability, Kondo-like mechanism, or formation of $4f$ bands by the direct overlap between the $4f$-electron wave function on different atoms. Although the trivalent oxidation state of Pr is most stable, the tetravalent state is accessible in a few compounds like the perovskite $APrO_3$ (where A is a divalent ion, e.g., Sr, Ba) [12]. An unstable $4f$ shell gives rise to very interesting properties: Kondo-like behavior was observed when Pr was substituted into Pd [13,14] and $LaSn_3$ [15,16]. Heavy-fermion phenomena were observed in $PrInAg_2$ [17].

In this Letter, we focus on $PrRu_4P_{12}$ and $PrOs_4P_{12}$ with a special interest in the $4f$ electron state in these Pr compounds, and report a metal-insulator (MI) transition in $PrRu_4P_{12}$ during temperature variation at ambient pressure for the first time. This transition could be due to a $4f$ instability of the Pr ion.

Ternary compounds $PrRu_4P_{12}$ and $PrOs_4P_{12}$ were prepared at high temperatures and high pressures using a wedge-type cubic-anvil high pressure apparatus [7,18]. The sample of MT_4P_{12} compound is usually synthesized by a Sn flux method [1,3–6,8,19]. However, we have used high-pressure synthesis in order to avoid contamination of a residual Sn flux, which may have an effect on conductivity [1,19]. These metal phosphides were prepared by reaction of stoichiometric amounts of metals and red phosphorus powder at around 4 GPa. The reaction temperatures were between 1000 and 1200 °C. The ruthenium powder was provided by Tanaka Kikinzoku Kogyo. The samples were characterized by power x-ray diffraction using CuKα_1 radiation and silicon as a standard. Figure 1 shows the x-ray diffraction pattern of $PrRu_4P_{12}$ prepared at high pressure. The crystal structure of $PrRu_4P_{12}$ is cubic with a lattice parameter of 8.0516 Å. $PrOs_4P_{12}$ is found to be isostructural to $PrRu_4P_{12}$ with a lattice parameter of 8.0794 Å. These values are consistent with the filled skutterudite structure reported by Jeitschko *et al.* [1].

Resistivity was measured with a standard dc four-probe method in the range of 1.7–300 K. The hydrostatic pressure was generated by using WC piston and CuBe cylinder device operating up to 1.6 GPa. A mixture of Fluorinert, FC70, and FC77 was used as the pressure-transmitting medium. The dc magnetic susceptibility and magnetization up to 5 T were measured in the range of 2–300 K with a Quantum Design MPMS SQUID magnetometer.

The electrical resistivity $\rho(T)$ normalized to room temperature vs temperature for $PrRu_4P_{12}$ is displayed in Fig. 2(a). $\rho(T)$ reveals a positive temperature dependence like typical metals between room temperature and about 60 K, however, $\rho(T)$ increases exponentially like semiconductors as the temperature is lowered below 60 K. We have found a metal-insulator (MI) transition in $PrRu_4P_{12}$ at around 60 K ($= T_{\mathrm{MI}}$). The MI transition temperature (T_{MI}) is determined from the minimum in resistivity. The value of ρ at 1.7 K reaches 20 times the value of ρ at 60 K. Figure 2(b) shows $\rho(T)$ of $PrRu_4P_{12}$ as a function of inverse temperature $1/T$. The data can be fit only over the limited temperature range $15\ \mathrm{K} < T < 40\ \mathrm{K}$ to an activation conduction form $\rho = \rho_0 \exp(\Delta E/k_B T)$, where ΔE is the activation energy and k_B is Boltzmann's constant. $\Delta E/k_B$ was 37 K derived from a best fit. The ground state of this compound could be insulating with a small energy gap. There was no hysteresis in the resistivity below T_{MI}. Therefore the transition could be second order, if this anomaly is a phase transition. $PrRu_4P_{12}$ was first studied by Meisner [3]. The author has inferred a possible ordering below 0.35 K in this compound. However, a transport measurement of this compound has not been reported.

The electrical resistivity $\rho(T)$ normalized to room temperature vs temperature data for isostructural $PrOs_4P_{12}$ are displayed in Fig. 3. In contrast to be behavior of $PrRu_4P_{12}$, $\rho(T)$ reveals a positive temperature dependence at all temperatures. The resistivity is not sensitive to temperature between 100 and 300 K. Below 70 K, $\rho(T)$ drops steeply like Pr metal [11] or many Kondo lattice Ce compounds. Furthermore, a bend in the $\rho(T)$ curve is visible at around 7 K, as shown in the inset of Fig. 3.

The magnetic susceptibility χ and the reciprocal magnetic susceptibility χ^{-1} is plotted vs temperature between 2 and 300 K for $PrRu_4P_{12}$ in Fig. 4. Magnetic susceptibility shows no distinct anomaly at $T_{\mathrm{MI}} = 60$ K in spite of the drastic change in resistivity. This suggests that the anomaly is not associated with any magnetic phase transition. A Curie-Weiss temperature dependence of the susceptibility is observed at higher temperatures. The linear slope of χ^{-1} vs T from 150 to 300 K yields an effective magnetic moment of $3.84\mu_B$, which is greater than $3.58\mu_B$ calculated for a Hund's-rule ground state of Pr^{3+}. This suggests that Pr is trivalent at high temperature, and the discrepancy may arise from a positive ferromagnetic exchange polarization of the conduction electrons. The Curie-Weiss temperature is -7 K. At lower temperatures the magnetic susceptibility deviates from the Curie-Weiss behavior extrapolated from high temperatures. As can be seen

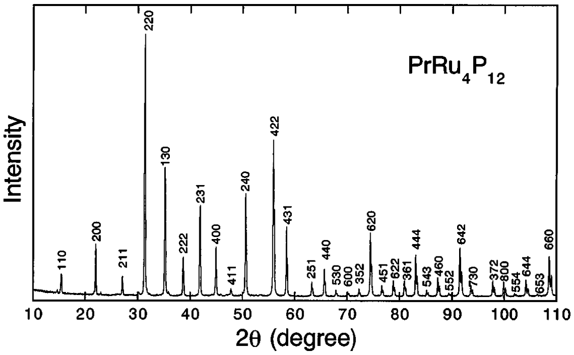

FIG. 1. X-ray diffraction profile of $PrRu_4P_{12}$ prepared at around 1100 °C and 4 GPa.

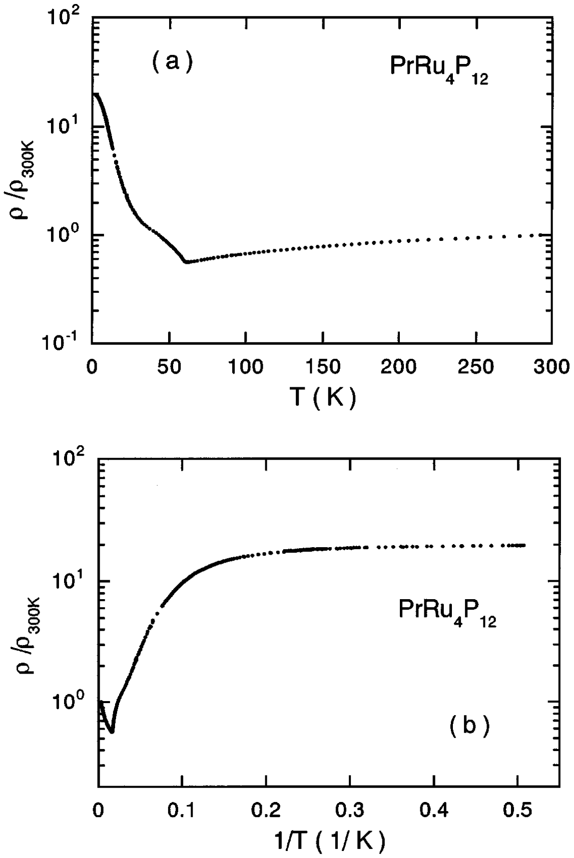

FIG. 2. (a) Normalized electrical resistivity $\rho/\rho_{300\ \mathrm{K}}$ vs temperature for $PrRu_4P_{12}$ (b) $\rho/\rho_{300\ \mathrm{K}}$ of $PrRu_4P_{12}$ as a function of inverse temperature $1/T$.

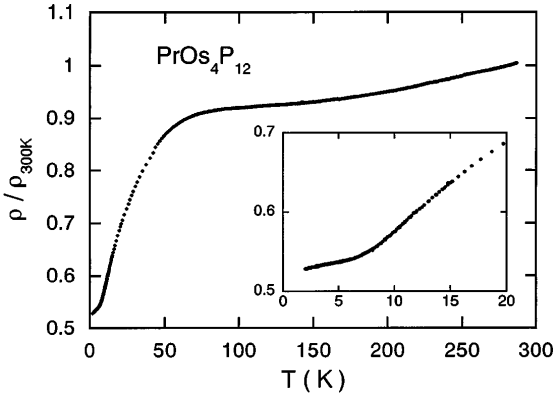

FIG. 3. Normalized electrical resistivity $\rho/\rho_{300\ \mathrm{K}}$ vs temperature for $\mathrm{PrOs_4P_{12}}$. The inset shows an enlarged view below 20 K.

in Fig. 4, the reciprocal susceptibility starts to level off below 60 K, and the slope gradually becomes steep as the temperature is lowered. The isostructual compound $\mathrm{PrFe_4P_{12}}$ shows antiferromagnetic ordering at 6.2 K [5]. The effective magnetic moment for $\mathrm{PrFe_4P_{12}}$ is $3.62\mu_B$ above 80 K, which is very close to $3.58\mu_B$ calculated for Pr^{3+}. The effective moment below 40 K is $\mu_{\mathrm{eff}} \sim 3.18\mu_B$. Because of the difference between these values of μ_{eff} the importance of crystalline electric field (CEF) is stressed [5].

The magnetic susceptibility χ and the reciprocal magnetic susceptibility χ^{-1} is plotted vs temperature between 2 and 300 K for $\mathrm{PrOs_4P_{12}}$ in Fig. 5. A Curie-Weiss behavior is observed down to low temperature. Effective magnetic moment for $\mathrm{PrOs_4P_{12}}$ is $3.63\mu_B$, which is very close to $3.58\mu_B$ calculated for Pr^{3+}. The Weiss temperature is -17 K for $\mathrm{PrOs_4P_{12}}$. The magnetic properties of $\mathrm{PrOs_4P_{12}}$ are similar to those of $\mathrm{PrFe_4P_{12}}$. Although CEF effects would also be important in these Pr compounds, the deviation from Curie-Weiss behavior at low temperature in $\mathrm{PrRu_4P_{12}}$ is much larger than that of $\mathrm{PrFe_4P_{12}}$ and $\mathrm{PrOs_4P_{12}}$. This anomalous behavior of $\mathrm{PrRu_4P_{12}}$ may be related to the MI transition.

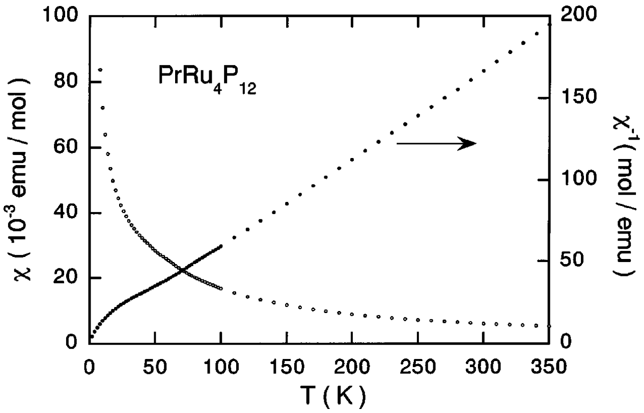

FIG. 4. Magnetic susceptibility χ and inverse magnetic susceptibility χ^{-1} vs temperature for $\mathrm{PrRu_4P_{12}}$.

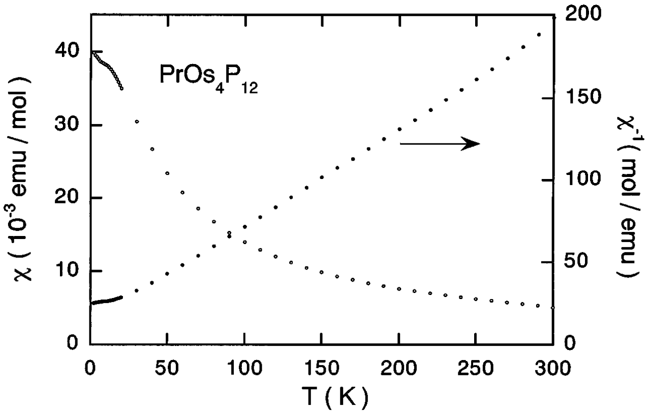

FIG. 5. Magnetic susceptibility χ and inverse magnetic susceptibility χ^{-1} vs temperature for $\mathrm{PrOs_4P_{12}}$.

Magnetization measurements were performed on $\mathrm{PrRu_4P_{12}}$ and $\mathrm{PrOs_4P_{12}}$ (Fig. 6). The magnetization curve for $\mathrm{PrRu_4P_{12}}$ at 2 K yielded a saturation value at $5T$ of $1.1\mu_B/\mathrm{Pr}$, much less than the Pr^{3+} free-ion value of $3.2\mu_B/\mathrm{Pr}$. The magnetization curve for $\mathrm{PrOs_4P_{12}}$ at 2 K shows a linear increase and the value at $5T$ is $0.33\mu_B/\mathrm{Pr}$, which is much less than the value of $\mathrm{PrRu_4P_{12}}$. These behaviors suggest that the CEF ground state is a nonmagnetic Γ_1 or Γ_3. The field dependence and nonsaturation are due to the polarization of a nonmagnetic ground state by mixing in some of the higher-lying CEF states with increasing field [20]. Such an effect would also be consistent with the absence of magnetic ordering, at least above 1 K.

Further, we have studied the x-ray diffraction of $\mathrm{PrRu_4P_{12}}$ at low temperatures and the pressure dependence of resistivity on $\mathrm{PrRu_4P_{12}}$ to characterize the MI transition. No significant change in the x-ray powder-diffraction pattern of $\mathrm{PrRu_4P_{12}}$ was detected down to 10 K (not shown). Thus, the anomalies observed in the $\rho(T)$ data are not due to a crystallographic phase transformation.

The resistivity of $\mathrm{PrRu_4P_{12}}$ has been measured at high pressures. The high pressure apparatus used here

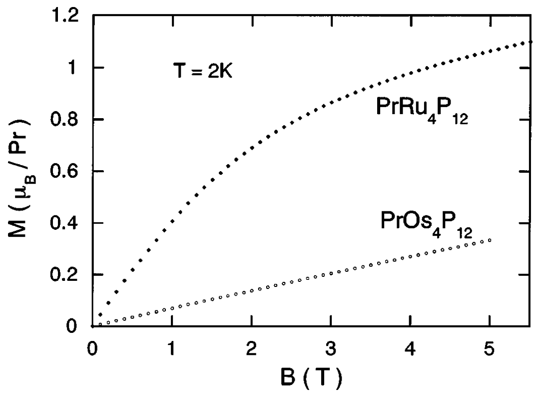

FIG. 6. Magnetization curves for $\mathrm{PrRu_4P_{12}}$ and $\mathrm{PrOs_4P_{12}}$ at 2 K.

is basically similar to that designed by Swenson [21]. The load is always kept constant by controlling the oil pressure of the hydraulic press, so there is no pressure change on both the cooling and heating temperature processes. Figure 7 shows the temperature dependence of resistivity $\rho(T)$ for $PrRu_4P_{12}$, normalized to room temperature, at temperatures near T_{MI}, and at various hydrostatic pressures up to 1.6 GPa. The onset of the MI transition temperature (T_{MI}) is determined from the minimum in resistivity. T_{MI} is shown in the inset of Fig. 7 as a function of pressure. T_{MI} increases with increasing pressure in almost linear fashion up to 1.6 GPa at the rate of $dT_{MI}/dP = 0.6$ K/GPa.

The MI transition $PrRu_4P_{12}$ is not due to a crystallographic transformation, nor a magnetic phase transition. This transition also seems not to be explained by a transition from Pr^{3+} at high temperature to Pr^{4+} at low temperature, because we have not observed a significant volume anomaly near the MI transition, which would be expected in this case. Isostructural $PrFe_4P_{12}$ and $PrOs_4P_{12}$ show metallic behavior and only $PrRu_4P_{12}$ shows a MI transition. The reason may be that the Pr ion is in a special environment due to the Ru-P sublattice. Although the origin of this MI transition is unclear, hybridization between $4f$ electron of Pr and $4d$ band of Ru seems to be important for gap formation. This argument is strengthened because the insulating phase is stabilized by pressure as mentioned above. Valence mixing is probably important in this system, at least in terms of the d-shell valence of Ru [22]. The problem is to prove that this valence mixing is driving of $4f$ instability, which is associated with the MI transition. This problem may also be closely related to that of semiconducting behavior in $CeFe_4P_{12}$, $CeRu_4P_{12}$, and URu_4P_{12}.

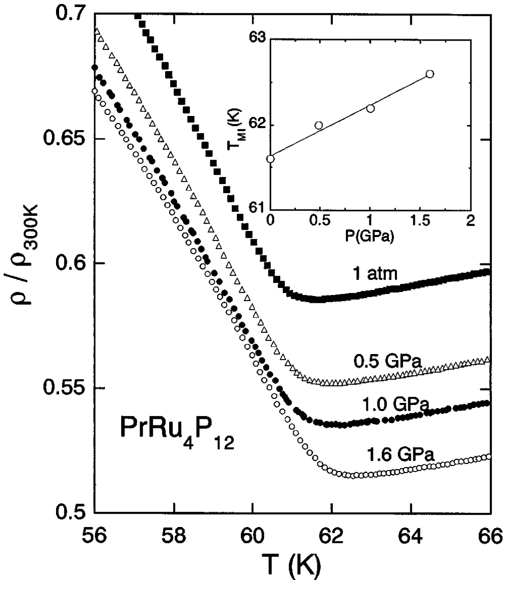

FIG. 7. Normalized electrical resistivity $\rho/\rho_{300\,K}$ of $PrRu_4P_{12}$ as a function of temperature at pressures ranging from 1 atm to 1.6 GPa.

In summary, the transport properties of the compounds $PrRu_4P_{12}$ and $PrOs_4P_{12}$ are reported for the first time. The magnetic behavior of these materials could be explained in terms of a nonmagnetic CEF ground state for Pr^{3+}. We have discovered a MI transition in $PrRu_4P_{12}$ at around 60 K. This transition could be due to a $4f$ instability of the Pr ion.

Further experiments are needed to fully characterize the MI transition in this compound. More detailed measurements of the transport properties of this material, such as the magnetoresistance of the Hall effect experiments, are required.

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