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Transport properties and the metal–insulator transition of $PrRu_4P_{12}$ single crystal

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Abstract
We report the first successful growth of a high-quality single crystal by the flux method, and the measurement of its electrical resistivity and magnetoresistance (MR), for the filled skutterudite $PrRu_4P_{12}$, which exhibits a metal–insulator (M–I) transition below $T_{MI} \simeq 63$ K. In zero magnetic field, the resistivity increases from that of the metallic state below 63 K, mirroring the M–I transition, shows a shoulder at around 30 K with a further increase beyond it, and then slowly decreases, showing a faint peak at around 0.6 K. In magnetic fields, the resistivity decreases drastically at low temperatures, i.e., a large negative MR appears, and the peak shifts to higher temperatures, although the field effect is only slight above 7 K.

1. Introduction

The filled-skutterudite compounds RT_4Pn_{12} (R = rare earth; T = Fe, Ru, Os; and Pn = pnictogen) have attracted much attention on the basis of both their novel physical properties (e.g., the metal–insulator (M–I) transition [1], heavy-fermion (HF) and anomalous nonmagnetic (probably quadrupolar) ordering [2–4], and HF superconductivity [5–7]) and their thermoelectric applications. Among the Pr-based compounds, $PrFe_4P_{12}$ shows an anomalous nonmagnetic phase transition below $T_A = 6.5$ K [2, 3] and heavy-fermion behaviour [4]. $PrOs_4Sb_{12}$ shows HF superconductivity below $T_C = 1.85$ K [5] and a field-induced ordered phase [6]. $PrRu_4P_{12}$ is reported to show a M–I transition at $T_{MI} = 60$ K [1]. The origin of the M–I transition and the ground state in $PrRu_4P_{12}$ still remain controversial despite intensive investigations [1, 8–10]. A structural phase transition has been found below T_{MI} from a superlattice structure in the electron diffraction results [8]. Curnoe *et al* argued that an antiferroquadrupolar ordering could be associated with this M–I transition [9]. A band structure calculation suggests that the nesting of the Fermi surface with $\boldsymbol{q} = (1, 0, 0)$ leading to the formation of a charge density wave could be the origin of the M–I transition [10]. To obtain a better understanding of the remaining problems concerning $PrRu_4P_{12}$, we have grown high-quality single crystals. In this paper we report the preliminary results for ρ and the MR of a single crystal of $PrRu_4P_{12}$.

2. Experiment

Single crystals of $PrRu_4P_{12}$ were grown by a tin-flux method which is basically the same as that described by Torikachvili *et al* [11] for other skutterudites. The raw materials were 3N (99.9% pure) Pr, 4N Ru, 6N P, and 5N Sn. The single-crystalline nature was confirmed by the back-reflection Laue technique. The electrical resistivity and magnetoresistance were measured by the standard dc four-probe method using a computer-controlled current source and a nanovoltmeter (Keithley 182). The magnetic fields (H) were generated by a 1.5 T normal magnet.

3. Results

Figure 1(a) shows the temperature dependence (0.4–300 K) of the electrical resistivity $\rho(T)$ in zero field and an applied magnetic field of 1.5 T. In zero field, $\rho(T)$ shows typical metallic behaviour, i.e., slowly decreases with temperature down to 63 K. Below 63 K, ρ starts to increase, showing a minimum at $T_{MI} \simeq 63$ K, the M–I transition point. Below T_{MI}, ρ shows a broad shoulder around 30 K followed by a sharp increase. Although these behaviours are qualitatively similar to those reported for a high-pressure-grown polycrystal in [1], $\rho_{1.7\,K}/\rho_{60\,K} \sim 200$ for the present sample, while this ratio is only ∼20 in [1], indicating the high quality of the single crystal. Note that, using the same flux method, we grew single crystals of $LaRu_4P_{12}$ with the residual resistivity ratio ∼700, and succeeded in detecting de Haas–van alphen oscillations [12]. The inset shows the best fit of the ρ (on a logarithmic scale) versus $1/T$ plot for $PrRu_4P_{12}$ to a semiconducting-like 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. The best fit over the range 12 K $< T <$ 22 K yields $\Delta E/k_B \simeq 58$ K, which is larger than the value 37 K derived from a similar fit over the range 15 K $< T <$ 40 K by Sekine *et al* [1]. On further lowering T, ρ slowly decreases, showing a faint maximum at $T_{max} \sim 0.6$ K (see figure 1(b)), which is in contrast to the increase of ρ with decreasing temperature seen in ordinary semiconductors. In a magnetic field $H = 1.5$ T, ρ at higher T and that at T_{MI} change little within the experimental accuracy (see figure 1(a)); however, it decreases at low T below 7 K and a pronounced peak appears at around $T_{max} \sim 3.7$ K (see figure 1(b)). In a field of 1.5 T, a peak at $T_{max} \sim 1.2$ K in the specific heat C_{4f} versus T was reported by Sekine *et al* [9], which was attributable to either a possible magnetic order below 0.35 K, suggested by Meisner [13], or a Schottky anomaly caused by very closely spaced crystalline-electric-field (CEF) levels.

Figure 2 shows the magnetic field dependence of ρ at $T = 0.45$ K. ρ decreases drastically with increasing H, i.e., a large negative MR appears, and then tends to saturate within the measured field (1.5 T) limit. At 1.5 T, ρ drops to 14% of its zero-field value. Sekine *et al* suggested the non-Kramers doublet Γ_3 as a possible ground state. Our very recent specific heat measurement suggests no magnetic order down to 0.15 K and the CEF ground state is most probably a singlet, and above ∼1 K there exists another CEF level [14]. Considering these facts, so large a negative MR at low temperatures is anomalous. It is not yet clear whether the two levels mentioned above are slightly split Γ_3 levels or not. At the present stage, we can only speculate that the large negative MR might arise from the field-induced suppression of the quadrupole degree of freedom and stabilization of the magnetic degree of freedom associated with the two levels mentioned above. Determination of the actual CEF level scheme would be necessary for a better understanding of the underlying mechanism.

4. Summary

We succeeded in growing high-quality single crystals of $PrRu_4P_{12}$ by the flux method for the first time. We found that an applied magnetic field generates a large negative MR at low

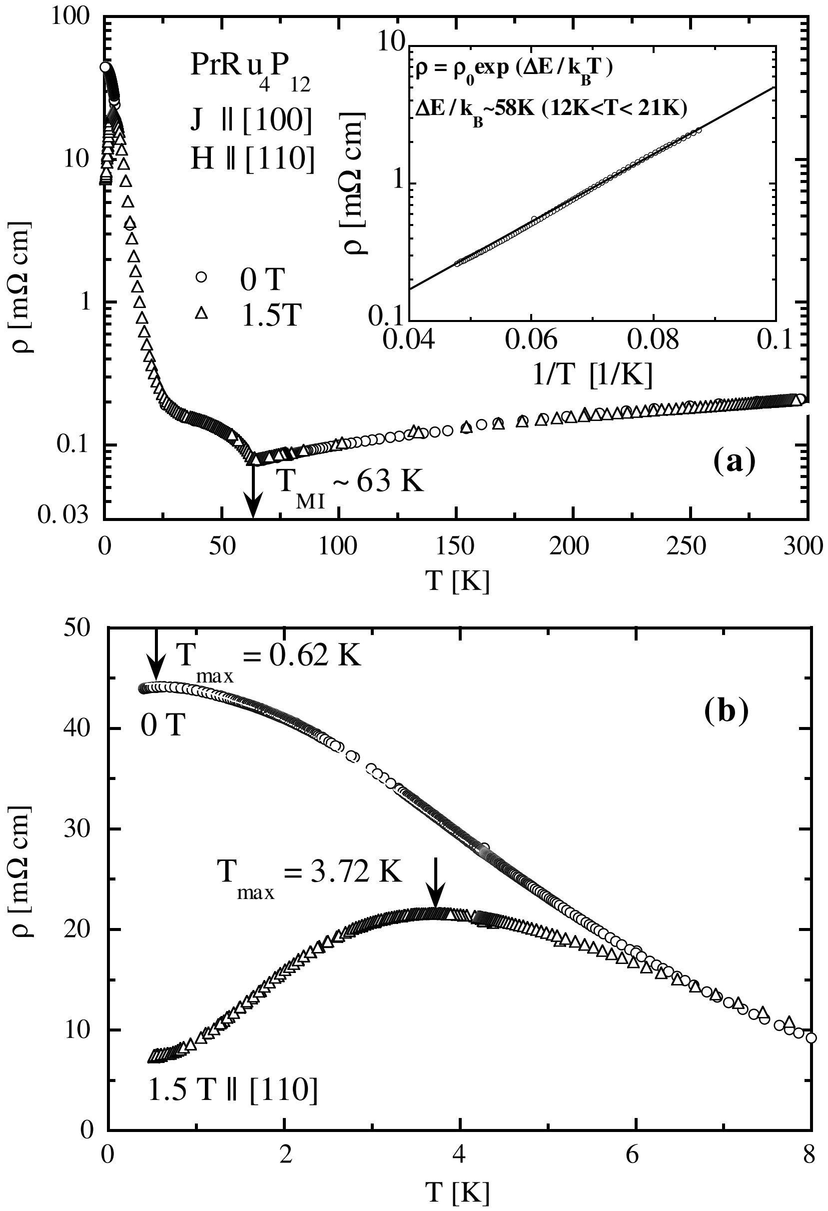

Figure 1. (a) The temperature dependence of the electrical resistivity $\rho(T)$, plotted with a logarithmic vertical axis, in a $PrRu_4P_{12}$ single crystal under $H = 0$ and 1.5 T applied perpendicular to the current. The inset shows the best fit to $\rho = \rho_0 \exp(\Delta E/k_B T)$. (b) An expanded view of $\rho(T)$ at low temperatures with a linear vertical axis.

temperatures, although the field has little effect on the M–I transition temperature. A faint peak is observed in $\rho(T)$ around 0.6 K in zero field which shifts to higher temperatures with increasing field. Considering the localized character of Pr 4f electrons and the absence of magnetic order down to 0.15 K, the observation of a large negative MR adds further interest to exploring the actual CEF ground state as well as the origin of the M–I transition; such investigations are in progress.

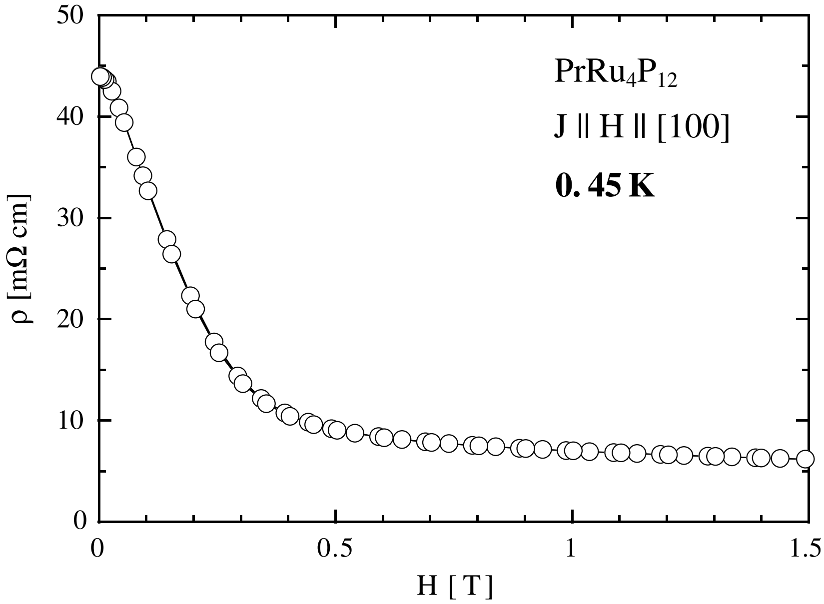

Figure 2. The magnetic field dependence of the resistivity $\rho(H)$ for a $PrRu_4P_{12}$ single crystal in the longitudinal $(J \parallel H)$ geometry. The solid curve is a guide to the eyes.

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