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Anomalous properties in the low-carrier ordered phase of $PrRu_4P_{12}$: Consequence of hybridization between conduction and Pr 4*f* electrons

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The low-carrier ordered phase below the metal-non-metal transition temperature $T_{MI} \simeq 63$ K of $PrRu_4P_{12}$ is explored by probing magnetoresistance, magnetic susceptibility, thermoelectric power, and Hall effect on high-quality single crystals. All the measured properties exhibit the signature of decimation of the Fermi surface below T_{MI} and anomalous behaviors below 30 K including a large thermoelectric power ~ -200 $\mu V/K$ and a giant negative magnetoresistance (93% at ~ 0.4 K). The results indicate an additional structure below 30 K and a semimetal-like ground state. The observed anomalous behaviors are most likely associated with the role of *c*-*f* hybridization between conduction electrons and Pr 4*f* electrons, whose crystalline electric field level schemes show drastic change below T_{MI}.

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I. INTRODUCTION

The filled-skutterudite compounds $R\mathrm{Tr}_4\mathrm{Pn}_{12}$ (R=rare earth, Tr=Fe, Ru, and Os; and Pn=pnictogen) have attracted much attention for exhibiting unusual physical properties and their prospect in thermoelectric applications.[1–10] Particularly interesting are some Pr-based skutterudites,[11] which are unlike the Pr metal and ordinary Pr compounds that possess well-localized 4*f* electronic states. The exotic behaviors observed in these compounds are believed to be associated with strong electron correlation or *c*-*f* hybridization between conduction and Pr 4*f* electrons.[5–9,11] In this context, $PrRu_4P_{12}$ deserves further attention, since the mechanism of its exotic metal-insulator (M-I) transition[2] at $T_{MI} \simeq 60$ K and the ordered phase remain as mysterious puzzles, despite several studies.[2,12–17]

Multipole order cooperating with the Fermi-surface (FS) nesting resulting in the charge-density wave (CDW) has been suggested by a band-structure calculation as one possible mechanism of the M-I transition.[18] A structural transition below T_{MI} with the doubling of the unit cell and a change in space group from $Im\bar{3}$ above T_{MI} to $Pm\bar{3}$ below T_{MI} has been observed.[13] We have succeeded to measure the de Haas-van Alphen effect clarifying the FS topology in $LaRu_4P_{12}$ and found that its FS is similar to the theoretical FS of $PrRu_4P_{12}$ (Ref. 19) with the nesting instability. However, $LaRu_4P_{12}$ does not show any M-I transition, suggesting that the *c*-*f* hybridization between Pr 4*f* and conduction electrons is essential for the M-I transition in $PrRu_4P_{12}$.[19] The inelastic neutron-scattering (INS) experiment indicates the presence of strong *c*-*f* hybridization above T_{MI} while below T_{MI} the strength of hybridization reduces and Pr 4*f* electrons attain almost localized nature.[20] The INS results also suggest that the crystalline electric field (CEF) ground state is nonmagnetic Γ_1 singlet across T_{MI} both at the body center (Pr_1) and at the cubic corner (Pr_2) of the unit cell, while Pr_2 sites show an abrupt change to magnetic $\Gamma_4^{(2)}$ triplet below around 30 K keeping Pr_1 unchanged.[20,21] Recently, the M-I transition has been ascribed theoretically to an antiferro-hexadecapole order or scalar order without breaking the local symmetry at the Pr site.[22,23] However, a recent photoemission study claims that there is no notable change in *c*-*f* hybridization strength across the M-I transition.[24]

We have succeeded in growing high-quality single crystals of $PrRu_4P_{12}$ and its reference compound $LaRu_4P_{12}$, which has no 4*f* electron. In this paper, we report on the study of their transport and magnetic properties which documents the decimation of the Fermi surface below T_{MI} and anomalous behaviors at low temperatures in $PrRu_4P_{12}$. Indications of temperature-dependent carrier scattering from Pr sites and a direct coupling between 4*f* and conduction electrons have been observed in $PrRu_4P_{12}$.

II. EXPERIMENT

Single crystals of $PrRu_4P_{12}$ and $LaRu_4P_{12}$ were grown by the tin-flux method.[3] The raw materials were 4N (99.99% pure)-La, -Pr, -Ru, 6N-P, and 5N-Sn. The single crystalline nature has been checked by the back Laue x-ray scattering technique. X-ray powder-diffraction (XRD) experiment confirmed the filled-skutterudite structure and absence of any impurity phases. The results are also consistent with the calculation and the previous XRD report on the high-pressure grown polycrystal.[2] We have succeeded in observing the de Haas-van Alphen effect in $LaRu_4P_{12}$,[19] which indicates the high sample quality and also indirectly assures the high quality of $PrRu_4P_{12}$ single crystals grown by the same manner. Electrical resistivity, magnetoresistance, and Hall effect were measured by the standard dc four-probe method. All these measurements were performed in a top loading ^{3}He cryostat, which can be cooled down to ~ 0.3 K, equipped with a superconducting magnet capable of generating magnetic fields up to 16 T. The temperature dependence of the Hall effect was measured in a ^{3}He cryostat down to ~ 0.4 K under a magnetic field of 1.5 T generated by a dc current sweep magnet. The thermoelectric power data have been taken by the differential method using a Au-Fe (0.07%)-chromel thermocouple in a ^{4}He cryostat cooled down to ~ 1.5 K. The magnetic susceptibility was measured by a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

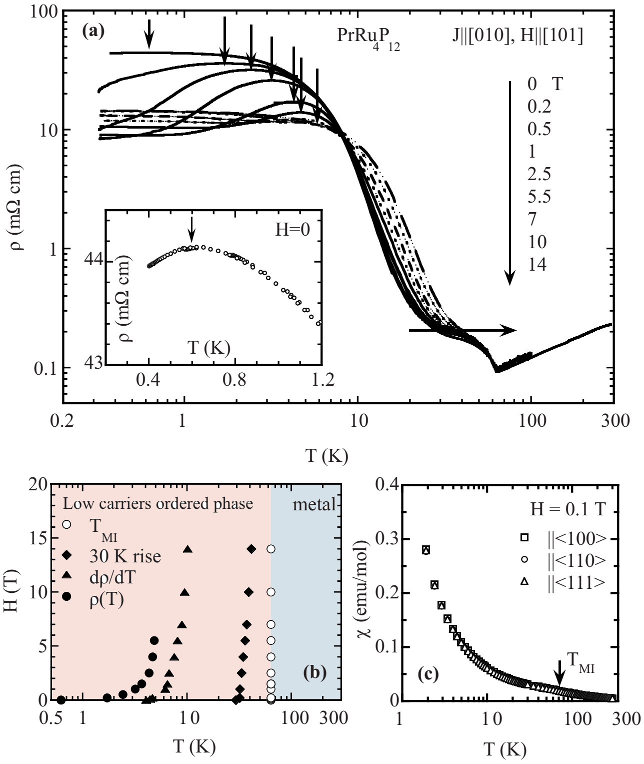

FIG. 1. (Color online) (a) Temperature dependence of electrical resistivity, $\rho(T)$, in $PrRu_4P_{12}$ under several magnetic fields. The short arrows indicate the shift in the position of the broad peak in $\rho(T)$ with increasing applied fields. The horizontal and the long vertical arrows indicate the shift in the $\rho(T)$ curves with increasing fields. The inset shows an expanded view of the faint peak around 0.6 K, as indicated by the short arrow, in $\rho(T)$ presented in the linear scales for $H=0$. (b) The phase diagram determined by the temperatures where the $\rho(T)$ shows peaks (filled circles), $d\rho(T)/dT$ shows negative peaks (filled triangles), ρ shows upturn below the shoulder around 30 K (filled diamonds), and the kink at T_{MI} in $\rho(T)$ (open circles) for different values of H. The shaded areas with two different colors/intensities distinguish the normal metallic state and the low-carrier ordered phase below T_{MI}. (c) Temperature dependence of magnetic susceptibility $\chi(T)$ in single crystalline $PrRu_4P_{12}$ for the fields along three different crystallographic directions.

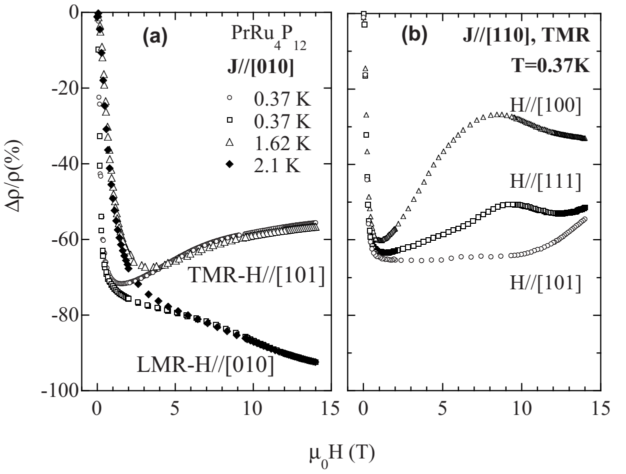

FIG. 2. (a) Field dependence of isothermal magnetoresistance in $PrRu_4P_{12}$ for both transverse (TMR) and longitudinal (LMR) geometries with the current $J\|[010]$. TMR for $J\|[110]$ are given in panel (b).

III. RESULTS

A. Electrical resistivity and magnetoresistance

Figure 1(a) shows the temperature (T) dependence of resistivity (ρ) in $PrRu_4P_{12}$ under the magnetic field (H) from 0 to 14 T. For $H=0$, ρ decreases with T like normal metals down to 63 K below which it increases with decreasing T showing a kink around 63 K that traces the so-called M-I transition. After showing a shoulder around 30 K ρ rapidly increases below ~ 10 K and then tends to saturate resulting a faint peak around 0.6 K as pointed by the inset. Overall $\rho(T)$ is similar to that of polycrystal grown under high pressure (Ref. 2). However, $\rho(\text{at } 1.5 \text{ K})/\rho(\text{at } 300 \text{ K})$ is one order higher than that in the polycrystal,[2] indicating the high quality of the present single crystals. No divergence in $\rho(T)$ and the decrease of resistivity with T below 0.6 K indicate the ground state of $PrRu_4P_{12}$ as a low-carrier semimetal rather than an insulator. There is no considerable effect of H up to 14 T on ρ across T_{MI} and on the values of T_{MI}, which is consistent with the high-field specific-heat measurement.[12] In contrast, the applied external magnetic field (H) causes a change in ρ below ~ 30 K followed by a suppression of ρ below ~ 10 K. The faint peak around 0.6 K at $H=0$ shifts to higher T with increasing H as indicated by the positions of the short arrows and then smears out above ~ 6 T. Figure 1(b) shows the H *vs* T phase diagram that gives the H dependence of the peaks of $\rho(T)$ and $d\rho(T)/dT$. The peak in $\rho(T)$, indicating this is not a simple insulator, may be caused by the strong correlation effect with the triplet CEF ground state of Pr. The triplet splits in applied fields due to Zeeman effect and the energy splitting of the triplet increases with fields. Therefore, the observed shift in the peak in $\rho(T)$ to higher temperatures in H is probably associated with the Zeeman splitting of the triplet. The drastic effect of H suggests that the magnetic state is changing below ~ 30 K in $PrRu_4P_{12}$. In contrast to a kink in $\rho(T)$, there is no distinct anomaly around T_{MI} in the temperature dependence of magnetic susceptibility, $\chi(T)$, as shown in Fig. 1(c), which is consistent with the results on the polycrystal,[2] suggesting a nonmagnetic origin of T_{MI}. The anisotropy in $\chi(T)$ measured under 0.1 T field applied along different crystallographic directions is small.

Figures 2(a) and 2(b) show the field dependence of several isothermal magnetoresistance $\Delta\rho=[\rho(H)-\rho(H=0)]/\rho(H=0)$ in both transverse and longitudinal geometries in $PrRu_4P_{12}$. Surprisingly, ρ sharply drops resulting in a negative giant ($\sim 70\%$) magnetoresistance (GMR) under $H \leq 0.5$ T in both geometries among which the longitudinal magnetoresistance (LMR) attains a value as high as $\sim 93\%$ in 14 T at 0.37 K. In contrast, transverse magnetoresistance (TMR) in $LaRu_4P_{12}$ is positive[19] and increases almost linearly with H, indicating that the negative GMR in $PrRu_4P_{12}$ is associated with the $4f$-electron state. Magnetic field dependence of magnetization $M(H)$ at 60 mK, measured on the same single crystal on which $\chi(T)$ data were taken, shows a

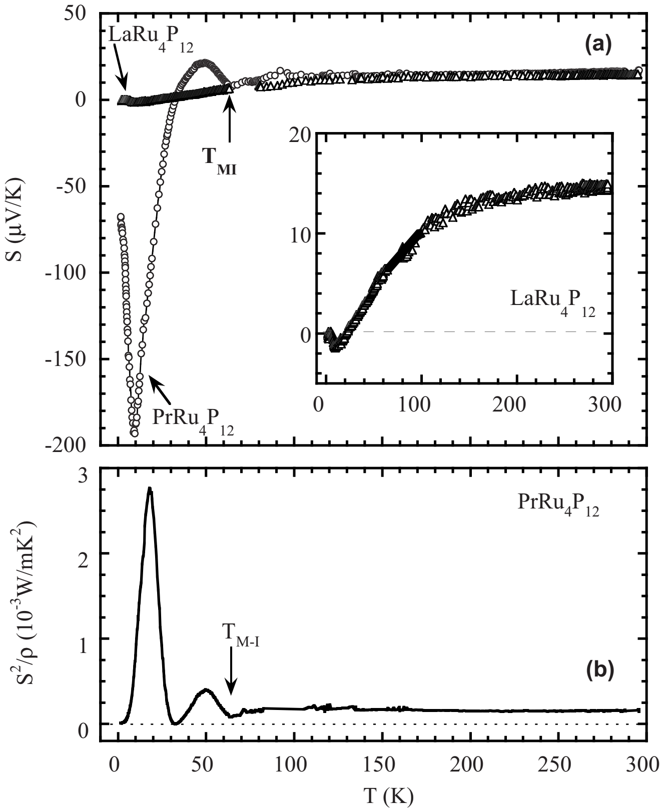

FIG. 3. Temperature dependence of thermoelectric power $S(T)$ in $PrRu_4P_{12}$ and $LaRu_4P_{12}$. Data were taken on arrays of more than one single crystal due to size constraints. The inset shows $S(T)$ in $LaRu_4P_{12}$ in an expanded y-axis view. (b) The temperature dependence of thermoelectric power factor S^2/ρ in $PrRu_4P_{12}$.

sharp increase at ~0.5 T, although no magnetic order was detected down to 60 mK.[25] The sharp increase in $M(H)$ was ascribed to the contribution from the CEF triplet ground state of the 50% Pr ions. Our recent specific-heat measurement confirms no magnetic order down to ≃150 mK; the molar entropy of $(R\ln 3)/2$ at 10 K is consistent with the triplet CEF ground state for one of the two Pr sites.[26] Despite the little anisotropy in $M(H)$ at high fields[25] and in $\chi(T)$, magnetoresistance is, interestingly, anisotropic at higher fields. There may be two components in the magnetoresistance; one is isotropic and dominating in low fields, while the other is anisotropic electronic response, possibly related with CEF, which is playing a role at higher H.

B. Thermoelectric power

Figure 3(a) shows a temperature dependence of thermoelectric power $S(T)$ in $PrRu_4P_{12}$ and $LaRu_4P_{12}$. At the room temperature (RT) the equal value of $S\sim 15$ μV/K in both compounds indicates similar electronic states at the vicinity of the Fermi level E_F. The large absolute value of S compared to that of the simple metals may be ascribable to the large contribution from the 4d bands of Ru and/or 5p bands of P near the Fermi level.[19] In $LaRu_4P_{12}$, S is positive at RT and it gradually decreases with temperature (see the inset). There is no anomaly in $S(T)$ around 60 K while S changes sign below ~20 K. This type of temperature dependence might be due to a combination of diffusion and phonon-drag contribution. After showing a minimum around ~10 K, S goes sharply to zero below 7 K due to superconductivity.[19] In $PrRu_4P_{12}$, S shows a similar temperature dependence down to ~65 K below which it increases across T_{MI} tracing the M-I transition, indicating a change in the Fermi surface. After showing a maximum at ~50 K S changes sign below ~30 K and then exhibits a minimum at ~10 K with a dramatically large negative value of ~−200 μV/K. Such a large negative value of S was also reported in $PrFe_4P_{12}$ in its ordered state below 6.5 K,[27] where the low-carrier density was confirmed. In many correlated metals, the absolute value of the dimensionless ratio $q=SN_Ae/T\gamma$ (where γ is the linear coefficient of the electronic specific heat, e is the elementary charge, and N_A is the Avogadro number) is of the order of unity.[28] The slope of thermopower below 1.8 K is large ($S/T\simeq -43$ μV/K^2 at 1.6 K) in $PrRu_4P_{12}$. Following a similar assumption to Ref. 27 and assuming a value of $\gamma\sim 0.1$ J/K^2 mol in $PrRu_4P_{12}$, since a precise value of γ at low T is not yet determined,[26] one can get a value of $q\simeq -43$ at 1.6 K in $PrRu_4P_{12}$. This value is of similar order to $q\simeq -53$ at ~0.1 K in $PrFe_4P_{12}$,[27] suggesting a presence of large correlation in the nonmetallic state of $PrRu_4P_{12}$. In order to interpret the $S(T)$ behavior in $PrRu_4P_{12}$, one should consider the diffusion thermopower represented by an energy derivative of conductivity $\sigma(\varepsilon)$ as $S=-(\pi^2k_B^2T/3e\sigma)[d\sigma(\varepsilon)/d\varepsilon]_{\varepsilon_F}$,[29] where $d\sigma(\varepsilon)/d\varepsilon$ depends on carrier numbers and scattering probability. In the high-mobility semiconductor a large value of S could be expected at low T where the carrier numbers are small. In $PrRu_4P_{12}$, both the increase in S across T_{MI} and the main contribution to the large negative value of S at low T may be ascribable to this reason, indicating the change in the Fermi surfaces below T_{MI}. The large negative peak in $S(T)$, suggesting a presence of strong correlation, is often ascribed to the growth of magnetic correlation and/or Kondo effect. Such a large S might be of technological importance as potential thermoelectric material at this low-temperature range. Figure 3(b) shows the thermoelectric power factor S^2/ρ, which defines the electrical performance of the thermoelectric material, in $PrRu_4P_{12}$. The value of S^2/ρ increases across T_{MI} tracing the M-I transition while it shows a peak around 50 K followed by a steep increase below ~30 K leading to a peak around this temperature and finally it decreases to zero. The maximum value of $S^2/\rho\sim 2.8$ mW/mK^{-2} around 30 K is promising as a thermoelectric material. One can compare this value at 30 K with that of $Bi_{86}Sb_{14}$ alloy,[30] which is known for a good thermoelectric material.

C. Hall effect

Figure 4(a) shows the temperature dependence of the Hall coefficient $R_H(T)$, where the RT values of $R_H\simeq 4\times 10^{-10}$ and 3.2×10^{-10} m^3/C yield a carrier concentration of ~1.6 $\times 10^{28}$ and ~1.9×10^{28}/m^3 for $PrRu_4P_{12}$ and $LaRu_4P_{12}$, respectively. These similar values of R_H at RT indicate the similar electronic states in both compounds, as also indicated by the $S(T)$ behavior. In $LaRu_4P_{12}$, R_H shows a weak T de-

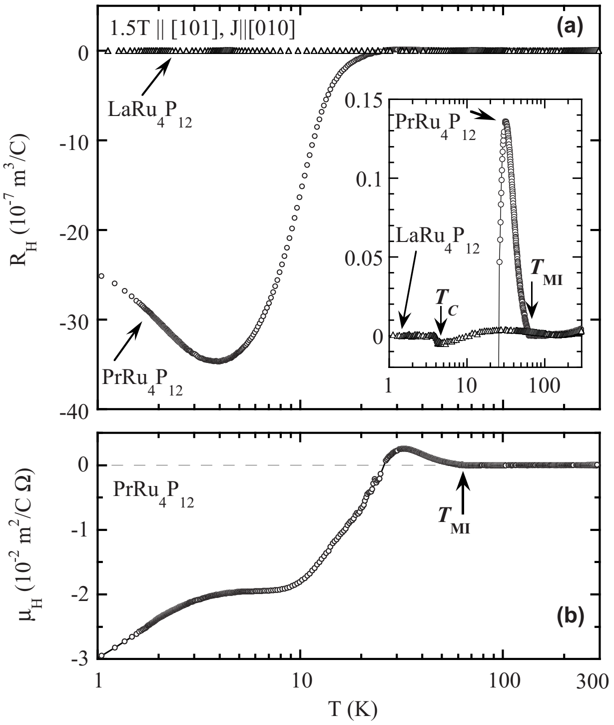

FIG. 4. (a) Temperature dependence of Hall coefficient R_H in $PrRu_4P_{12}$ and $LaRu_4P_{12}$ for $J \parallel [010]$ and $H = 1.5$ T$\parallel$[101]. The inset shows an expanded vertical axis of the plot. (b) The temperature dependence of Hall mobility μ_H for the same geometry in $PrRu_4P_{12}$.

pendence with a minimum around 155 K and a broad peak around ∼30 K followed by a sign change below 11 K (see the inset), this complex temperature dependence might be due to the temperature dependence of anisotropy in the relaxation time.[31] Below ∼5 K, R_H increases and then goes sharply to zero due to superconductivity below $T_c \simeq 4$ K (at 1.5 T) as indicated by the arrow in the inset. In $PrRu_4P_{12}$, R_H shows an increase across T_{MI} (clearly visible in the inset) tracing the M-I transition, which indicate a change in the electronic state. The increase in R_H with decreasing T leads to a maximum around ∼30 K below which R_H drops rapidly to change sign to negative and then shows a minimum around 4 K. Note that $\rho(T)$ also increases below 30 K and shows a peak around 4 K at 1.5 T [see Fig. 1(a)]. Below 30 K one of the Pr sties obtains $\Gamma_4^{(2)}$ ground state while the other retains Γ_1 ground state.[20] Such a minimum in $R_H(T)$ is sometimes ascribed to the growth of antiferromagnetic correlations and/or Kondo effect. Figure 4(b) shows the Hall mobility $\mu_H = R_H/\rho$ at 1.5 T. In a simple one-band picture, μ_H is directly proportional to the quasiparticle lifetime and independent of carrier density. Across T_{MI}, μ_H increases tracing the M-I transition and then rapidly drops below 30 K. It changes sign from positive to negative below 26 K and then saturates below 10 K followed by a further drop around 4 K. The Hall conductivity behavior indicates an existence of temperature-dependent carriers scattering from Pr sites in the nonmetallic ordered state.

Figure 5 shows the field dependence of Hall resistivity $\rho_H(H)$ in $PrRu_4P_{12}$ and $LaRu_4P_{12}$ at several constant temperatures. In both compounds, the sign of ρ_H is negative up to 14 T, although the absolute value is several orders higher in $PrRu_4P_{12}$. There is a clear change in slope in $\rho_H(H)$ at $H \sim 0.2$ T in $PrRu_4P_{12}$ (see the inset), where ρ drops to 70% as shown in Fig. 2(a) and M also increases sharply.[25] Tentatively considering the concept of anomalous Hall effect, i.e., $\rho_H(H) = R_0 H + R_S M$, our analysis shows that the anomalous part $R_S M$ can neither be explained by the skew scattering ($\propto \rho M$) nor by the side jump scattering ($\propto \rho^2 M$) contribution (not shown here). At higher fields the absolute value of ρ_H increases almost linearly with H up to 6 T and shows a broad peak around 11 T. Taking into account the absence of anomaly in $M(H)$ around this field range,[25] this peak indicates an interesting field-induced change in electronic state.

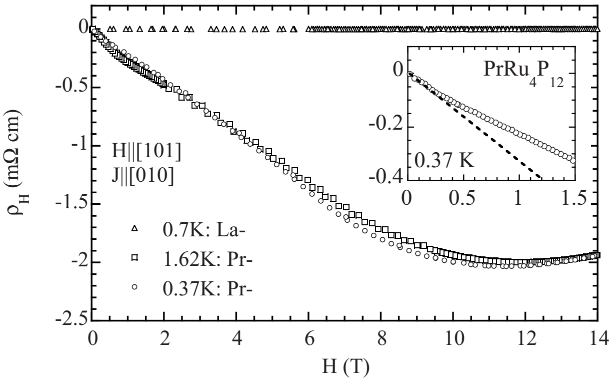

FIG. 5. Field dependence of isothermal Hall resistivity (ρ_H) in (Pr-,La-)Ru_4P_{12}. The inset shows the expanded view of ρ_H at the low H region in $PrRu_4P_{12}$, where the dotted line indicates a change in slope.

IV. DISCUSSION

According to the results presented in this paper, the anomalies across T_{MI} in the electric and thermoelectric transport indicate that most of the Fermi surface vanishes below T_{MI}, leading to an increase in ρ. The observation of broad and sharp peaks above and below T_{MI}, respectively, in the INS measurement suggests that the 4f electrons shift from itinerant above T_{MI} to rather localized state below T_{MI}.[20] Considering these facts, the phase transition at T_{MI} could be a hexadecapole (or higher multipole and scalar) order as argued in the theoretical model,[22] where no breaking of the local symmetry and existence of strong c-f hybridization have been predicted. The CDW of the conduction electron associated with this order is an unconventional one,[32] which is triggered by an interaction with f electrons, unlike the conventional CDW, that is, stabilized by the cooperation between the Fermi-surface instability and the electron-phonon interaction. The anisotropy in the single crystal has been found very small in the ordered phase, which is compatible with the hexadecapole model. However, the resistivity shows shoulder at intermediate temperatures below T_{MI}. In order to understand this with the other anomalous behaviors observed in the ordered phase the INS results, suggesting a change in the strength of hybridization and the CEF level crossing as described in Sec. I, should be taken into account. The c-f

hybridization between the a_u conduction band, which is contributed mainly by pnictogen p orbits, and the $4f$ states,[33] combined with the formation of charge-density modulation with the wave vector $q=(1,0,0)$ due to Fermi-surface nesting, has been ascribed to play the major role in the modification of the CEF level schemes, i.e., CEF level crossing in the low-temperature region.[21] The positive-valence Ru-ion displacement closer to Pr_1 and further from Pr_2, resulting in the larger and smaller point-charge Coulomb potentials for the Pr $4f$ electrons, respectively, also contributes in the CEF splitting, however this contribution is only a little because of its small magnitude of the order of 10^{-3}. The c-f hybridization effect is treated as the perturbation involving two channels of intermediate states of $4f^1$ with the creation of an electron in the vacant states and $4f^3$ with a hole in the filled states.[21] It is demonstrated that the $4f^3$ process pulls down the $\Gamma_4^{(2)}$ triplet and the $4f^1$ process works in an opposite way. Above T_{MI}, the contributions of both the $4f^1$ and $4f^3$ processes are comparable, so that the total effect on the CEF splitting may not be sufficient to pull down $\Gamma_4^{(2)}$ to a much lower energy level. With decreasing temperature below T_{MI}, the Fermi surface starts to vanish and the $4f$ electrons shift to a rather localized state leading to the different CEF schemes between Pr_1 and Pr_2.[21] The contribution of the $4f^3$ process becomes larger than that of the $4f^1$ process at Pr_2 and the contributions of both processes remain comparable at Pr_1.

This CEF level crossing could be responsible for the observed anomalies around 30 K in all measured properties. The level occupancy of the CEF singlet and triplet is expected to be fluctuating at least around and above the level crossing temperature. These (orbital) fluctuations give rise to scattering of conduction electrons and smears the gap edge of the conduction-electron density of states. The suppression of the gap increases the carrier density reducing the values of ρ in a region of intermediate temperatures below T_{MI}. Below the level-crossing temperature, ρ shows an upturn again, although it remains finite even at the lowest temperature, indicating a low-carrier semimetallic ground state. A large residual resistivity ρ_0 at $T\sim 0$ usually originates from randomness since theoretically periodic lattice without randomness should give $\rho_0\sim 0$ or infinite value. Randomness can be arisen from impurity/vacancy or random splitting of the triplet in one of the sublattices. The present large ρ_0 is likely to be originated by the latter mechanism since ρ is very sensitive to H only below 10 K, in particular, ρ_0 is drastically decreased by a small field (≤ 1 T). Therefore, the scattering of conduction electrons from random split triplets is suppressed due to the uniform alignment of the triplet. The above arguments implicitly assumes an small exchange interaction of the form $H_{ex}=J_{ex}S_cS_f$, where J_{ex} is the exchange constant corresponding to the so-called on-site Kondo coupling, S_c is the conduction-electron spin, and S_f is the $4f$-electron spin populated at the triplet $\Gamma_4^{(2)}$. Formally, if S_f is random, conduction electron has to move in a random (magnetic) potential. On the other hand, the potential becomes uniform when all S_f align along one direction. The value of J_{ex}, accounting the hybridization between p state of the cage ions and f state at the center, is expected to be of the order of 1 K, since only the low-temperature (≤ 10 K) resistivity is influenced by the applied magnetic fields. The absence of any magnetic order even down to 20 mK has been confirmed by the μSR measurement.[34] Thus, the obtained effect of magnetic fields, particularly GMR at low T, observed only in Pr compound, could be arisen due to the suppression of the Kondo scattering of the charge carriers from the $4f$ electrons. Finally, under high magnetic fields the transverse magnetoresistance is anisotropic and the Hall resistivity shows a broad peak despite no anomaly and little anisotropy in the magnetization at high fields. These facts indicate a magnetic field induced change in electronic state, the detail of which would be interesting for further investigation.

V. SUMMARY

In summary, we have investigated the transport and magnetic properties in single-crystalline $\mathrm{PrRu_4P_{12}}$. The phase transition below 63 K might be due to an antiferro-hexadecapole order, where a dominant c-f hybridization plays an essential role. An additional structure has been recognized below 30 K exhibiting the anomalous behaviors, e.g., highly temperature-dependent carrier scattering, giant negative magnetoresistance, large themopower ~ -200 μV/K, etc., without showing any magnetic order. Judging from the resistivity behavior, the ground state emerges as a low-carrier semimetal. These anomalous behaviors are most likely associated with the c-f hybridization between the remaining charge carriers and Pr $4f$ electrons, resulting in a change in CEF ground state of the Pr_2 sites at the cubic corner from Γ_1 to $\Gamma_4^{(2)}$.

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