Anomalous properties in the low-carrier ordered phase of PrRu$_4$P$_{12}$: Consequence of hybridization between conduction and Pr 4f electrons

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The low-carrier ordered phase below the metal-non-metal transition temperature $T_{MI} \simeq 63$ K of PrRu$_4$P$_{12}$ is explored by probing magneto-resistance, 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 $\sim 200 \mu V/K$ and a giant negative magnetoresistance (93% at $\sim 0.4$ 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 novel role of c-f hybridization between conduction electrons and Pr 4f electrons, whose crystalline electric field level schemes show drastic change below $T_{MI}$.

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I. INTRODUCTION

The filled-skutterudite compounds RTr$_4$P$_{12}$ ($R=$ rare earth, Tr= Fe, Ru, Os; and Pn=pnictogen) have attracted much attention for exhibiting unusual physical properties and their prospect in thermo-electric applications. Particularly interesting are some Pr-based skutterudites, which are unlike the Pr metal and ordinary Pr compounds that possess well-localized 4f 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 4f electrons. In this context, PrRu$_4$P$_{12}$ deserves further attention, since the mechanism of its exotic metal-insulator (M-I) transition at $T_{MI} \simeq 60$ K and the ordered phase remain as mysterious puzzles, despite several studies.

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. A structural transition below $T_{MI}$ with the doubling of the unit cell and a change in space group from $Pn\overline{3}$ above $T_{MI}$ to $Pm\overline{3}$ below $T_{MI}$ has been observed. We have succeeded in measuring the de Haas-van Alphen (dHvA) effect clarifying the FS topology in LaRu$_4$P$_{12}$ and found that its FS is similar to the theoretical FS of PrRu$_4$P$_{12}$ (Ref. 19) with the nesting instability. However, LaRu$_4$P$_{12}$ does not show any M-I transition, suggesting that the c-f hybridization between Pr 4f and conduction electrons is essential for the M-I transition in PrRu$_4$P$_{12}$. 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 4f electrons attain almost localized nature. The INS results also suggest that the crystalline electric field (CEF) ground state is nonmagnetic $\Gamma_1$ 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 $\Gamma_1^{(2)}$ triplet below around 30 K keeping Pr$_1$ uncharged. 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. However, a recent photoemission study claims that there is no notable change in c-f hybridization strength across the M-I transition.

We have succeeded in growing high-quality single crystals of PrRu$_4$P$_{12}$ and its reference compound LaRu$_4$P$_{12}$, which has no 4f-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$_4$P$_{12}$. Indications of temperature-dependent carrier scattering from Pr-sites and a direct coupling between 4f and conduction electrons have been observed in PrRu$_4$P$_{12}$.

II. EXPERIMENT

Single crystals of PrRu$_4$P$_{12}$ and LaRu$_4$P$_{12}$ were grown by the tin-flux method. 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. We have succeeded in observing the de Haas-van Alphen effect in LaRu$_4$P$_{12}$ which indicates the high sample quality and also indirectly assures the high quality of PrRu$_4$P$_{12}$ 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 $\sim 0.3$ K, equipped with a superconducting magnet capable of generating magnetic fields up to 16 T. The tem-
temperature dependence of the Hall effect was measured in a $^3$He cryostat down to $\sim 0.4$ 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 $^3$He cryostat cooled down to $\sim 1.5$ K. The magnetic susceptibility was measured by a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

### III. RESULTS

#### A. Electrical resistivity and magnetoresistance

Figure 1(a) shows the temperature ($T$) dependence of resistivity ($\rho$) in PrRu$_4$P$_{12}$ under the magnetic field ($H$) from 0 to 14 T. For $H = 0$, $\rho$ 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 $\rho$ rapidly increases below $\sim 10$ K and then tends to saturate resulting a faint peak around 0.6 K as pointed by the arrow in the inset. Overall $\rho(T)$ is similar to that of polycrystal grown under high pressure (Ref. [2]). However, $\rho$(at 1.5 K)/$\rho$(at 300 K) is one order higher than that in the polycrystal, 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$_4$P$_{12}$ as a low carrier semimetal rather than an insulator. There is no considerable effect of $H$ up to 14 T on $\rho$ across $T_{MI}$ and on the values of $T_{MI}$, which is consistent with the high field specific heat measurement.\(^2\) In contrast, the applied external magnetic field ($H$) causes a change in $\rho$ below $\sim 30$ K followed by a suppression of $\rho$ below $\sim 10$ 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 $\sim 6$ 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 $\sim 30$ K in PrRu$_4$P$_{12}$. 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 polycrystals suggesting a non magnetic 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$_4$P$_{12}$. Surprisingly, $\rho$ 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$_4$P$_{12}$ is positive\(^2\) and increases almost linearly with $H$, indicating that the negative GMR in PrRu$_4$P$_{12}$ 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 sharp increase at $\sim 0.5$ T, although...
no magnetic order was detected down to 60 mK. 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 $\sim 150$ mK; the molar entropy of $(Rln3)/2$ at 10 K is consistent with the triplet CEF ground state for one of the two Pr-sites. Despite the little anisotropy in $M(H)$ at high fields 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 $H$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(a) Field dependence of isothermal magnetoresistance in PrRu$_4$P$_{12}$ for both transverse (TMR) and longitudinal (LMR) geometries with the current $J \parallel [010]$. TMR for $J \parallel [110]$ are given in panel (b).}
\end{figure}

B. Thermoelectric power

Figure 2(a) shows a temperature dependence of thermoelectric power $S(T)$ in PrRu$_4$P$_{12}$ and LaRu$_4$P$_{12}$. At the room temperature (RT) the equal value of $S \sim 15\mu$ V/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. In LaRu$_4$P$_{12}$, $S$ 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 $\sim 20$ K. This type of temperature dependence might be due to a combination of diffusion and phonon drag contribution. After showing a minimum around $\sim 10$ K, $S$ goes sharply to zero below 7 K due to superconductivity. In PrRu$_4$P$_{12}$, $S$ shows a similar temperature dependence down to $\sim 65$ 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 $\sim 50$ K $S$ changes sign below $\sim 30$ K and then exhibits a minimum at $\sim 10$ K with a dramatically large negative value of $\sim -200\mu$ V/K. Such a large negative value of $S$ was also reported in PrFe$_4$P$_{12}$ in its ordered state below 6.5 K where the low carrier density was confirmed. In many correlated metals, the absolute value of the dimensionless ratio $q = S N_A e / T \gamma$ (where $\gamma$ 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. The slope of thermopower below 1.8 K is large ($S/T \sim -43\mu$ V/K$^2$ at 1.6 K) in PrRu$_4$P$_{12}$. Following a similar assumption to Ref. 27 and assuming a value of $\gamma \sim 0.1 J/K^2$ mol in PrRu$_4$P$_{12}$, since a precise value of $\gamma$ at low $T$ is not yet determined, one can get a value of $q \sim -43$ at 1.6 K in PrRu$_4$P$_{12}$. This value is of similar order to $q \sim -53$ at $\sim 0.1$ K in PrFe$_4$P$_{12}$ suggesting a presence of large correlation in the non-metallic state of PrRu$_4$P$_{12}$. In order to interpret the $S(T)$ behavior in PrRu$_4$P$_{12}$, one should consider the diffusion thermopower represented by an energy derivative of conductivity $\sigma(\epsilon)$ as $S = -(\pi^2 k_B^2 T/3e\sigma)d\sigma(\epsilon)/d\epsilon |_{\epsilon_F}$, where $d\sigma(\epsilon)/d\epsilon$ 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$_4$P$_{12}$, 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 2(b) shows the thermoelectric power factor $S^2/\rho$, which defines the electrical performance of the thermoelectric material, in PrRu$_4$P$_{12}$. The value of $S^2/\rho$ increases across $T_{MI}$ tracing the M-I transition, while it shows a peak around 50 K followed by a steep increase below $\sim 30$ 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$_2$Te$_3$ alloy, which is known for a good thermoelectric material.

C. Hall effect

Figure 3(a) shows the temperature dependence of the Hall coefficient $R_H(T)$, where the room temperature (RT) values of $R_H \sim 4 \times 10^{-10}$ and $3.2 \times 10^{-10} m^3/C$ yield a carrier concentration of $\sim 1.6 \times 10^{28}$ and $\sim 1.9 \times 10^{28} / m^3$ for PrRu$_4$P$_{12}$ and LaRu$_4$P$_{12}$, 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$_4$P$_{12}$, $R_H$ shows a weak $T$
dependence with a minimum around 155 K and a broad peak around \( \sim 30 \) 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. Below \( \sim 5 \) K, \( R_H \) increases and then goes sharply to zero due to superconductivity below \( T_c \sim 4 \) K (at 1.5 T) as indicated by the arrow in the inset. In PrRu\(_4\)P\(_{12}\), \( R_H \) 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 \( \sim 30 \) 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 \( \sim 5 \) K, \( R_H \) increases and then goes sharply to zero due to superconductivity below \( T_c \sim 4 \) K (at 1.5 T) as indicated by the arrow in the inset. The increase in \( R_H \) with decreasing \( T \) leads to a maximum around \( \sim 30 \) 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 sites obtains \( \Gamma^2_1 \) ground state, while the other retains \( \Gamma_1 \) ground state. Such a minimum in \( R_H(T) \) is sometimes ascribed to the growth of antiferromagnetic correlations and/or Kondo effect. Figure 3(b) shows the Hall mobility \( \mu_H = R_H/\rho \) at 1.5 T. In a simple one-band picture, \( \mu_H \) is directly proportional to the quasi-particle life time and independent of carrier density. Across \( T_{MI} \), \( \mu_H \) 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 non-metallic ordered state.
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 $\rho$. The observation of broad and sharp peaks above and below $T_{MI}$, respectively, in the inelastic neutron scattering (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\(^{22}\) which is triggered by an interaction with $f$-electrons, unlike the conventional CDW 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 $a_{\sigma}$ conduction band, which is contributed mainly by pnictogen $p$ orbits, and the $4f$ states\(^{23}\) 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 (DOS). The suppression of the gap increases the carrier density reducing the values of $\rho$ in a region of intermediate temperatures below $T_{MI}$. Below the level-crossing temperature, $\rho$ shows an upturn again, although it remains finite even at the lowest temperature, indicating a low-carrier semi-metallic ground state. A large residual resistivity $\rho_0$ 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 $\rho_0$ is likely to be originated by the latter mechanism, since $\rho$ is very sensitive to $H$ only below 10 K; in particular, $\rho_0$ is drastically decreased by a small field $(\leq 1 \text{ T})$. 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 a small exchange interaction of the form $H_{ex} = J_{ex} S_c S_f$, 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 $(\leq 10 \text{K})$ resistivity is influenced by the applied magnetic fields. The absence of any magnetic order even down to 20 mK has been confirmed by the $\mu$SR measurement\(^{24}\).
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 4$f$-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 PrRu$_4$P$_{12}$. The phase transition below 63 K might be due to an antiferrohexadecapole 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 thermopower $\sim -200\mu$V/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 4$f$ electrons, resulting in a change in CEF ground state of the Pr$_2$ sites at the cubic corner from $\Gamma_1$ to $\Gamma_4^{(2)}$.

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