Extremely Large Magnetoresistance and Anisotropic Transport in Multipolar Kondo System PrTi$_2$Al$_{20}$

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Multipolar Kondo systems offer unprecedented opportunities to design astonishing quantum phases and functionalities beyond spin-only descriptions. A model material platform of this kind is the cubic heavy-fermion system PrTi$_2$Al$_{20}$ ($\text{Tr} = \text{Ti}$, V), which hosts a nonmagnetic crystal-electric-field (CEF) ground state and substantial Kondo entanglement of the local quadrupolar and octopolar moments with the conduction electron sea. Here, we explore magnetoresistance (MR) and Hall effect of PrTi$_2$Al$_{20}$ that develops ferroquadrupolar (FQ) order below $T_Q \sim 2$ K and compare its behavior with that of the non-4$f$ analog, LaTi$_2$Al$_{20}$. In the FQ ordered phase, PrTi$_2$Al$_{20}$ displays extremely large magnetoresistance (XMR) of $\sim 10^\%$. The unsaturated, quasi-linear field ($B$) dependence of the XMR violates Kohler’s scaling and defies description based on carrier compensation alone. By comparing the MR and the Hall effect observed in PrTi$_2$Al$_{20}$ and LaTi$_2$Al$_{20}$, we conclude that the open-orbit topology on the electron-type Fermi surface (FS) sheet is key for the observed XMR. The low-temperature MR and the Hall resistivity in PrTi$_2$Al$_{20}$ display pronounced anisotropy in the [111] and [001] magnetic fields, which is absent in LaTi$_2$Al$_{20}$, suggesting that the transport anisotropy ties in with the anisotropic magnetic-field response of the quadrupolar order parameter.

The quest for material platforms exhibiting large magnetotransport has pushed progress in both fundamental science and technological applications. The outstanding examples, such as giant magnetoresistance in magnetic multilayers, are typically engendered by the interplay of the spin structure with charge transport. Recent studies uncover XMR in nonmagnetic metals and semimetals, some featuring novel topological band structure, such as Dirac or Weyl nodes. Nevertheless, a universal understanding of the mechanism behind the observed XMR is lacking. Aside from the spin and charge degrees of freedom, electron orbitals are a critical ingredient for creating new quantum phases and functionalities in strongly correlated systems. Since the electronic band structure finds its root in the interplay between orbitals and the crystal lattice, the ordering and fluctuations of orbitals are expected to yield remarkable effects on transport properties. In 3$d$ transition metal compounds, however, the spin, orbital, and charge degrees of freedom are inextricably intertwined, thus hindering a clear understanding of how orbital ordering and fluctuations tie in with novel transport phenomena. In contrast, cubic 4$f$ rare-earth materials may host a nonmagnetic crystal-electric-field (CEF) ground state with high-rank multipolar moments, offering a route to materialize novel transport phenomena of a purely orbital origin.

The multipolar Kondo system PrTi$_2$Al$_{20}$ provides a suitable stage for investigating orbital ordering and its ties to exotic electronic transport. In this system, the cubic $T_d$ symmetry of the Pr site stabilizes a non-Kramers $\Gamma_3$ doublet ground state that carries quadrupolar and octupolar, but no magnetic dipolar moment. This nonmagnetic ground-state doublet is well separated from the first-excited magnetic triplet by a CEF gap of $\Delta\text{CEF} \sim 60$ K, and thus governs the low-temperature properties of the system. A ferroquadrupolar (FQ) order with the order parameter $O_{20}$ ($3J_z^2 - J^2$, $3J_y^2 - J^2$, and $3J_z^2 - J^2$) develops below $T_Q \sim 2$ K at zero-magnetic field, with a superconducting transition inside the FQ phase. Moreover, the cage-like local structure maximizes the number of Al ions surrounding the Pr 4$f$ moments, leading to substantial Kondo entanglement of the multipolar moments with the conduction ($c$) electrons and formation of heavy quasiparticles, as experimentally confirmed by various experimental probes. Pressure tuning of PrTi$_2$Al$_{20}$ results in a rich phase diagram featuring strongly enhanced superconducting transition temperature $T_c$ and quasiparticle effective mass $m^*$ on approaching the FQ phase boundary and robust non-Fermi-liquid (NFL) behavior over a wide parameter range.

The multipolar Kondo effect and quantum critical fluctuations originating from the orbital degrees of freedom are essential in generating the observed exotic superconductivity and NFL state.

On the other hand, magnetotransport phenomena in PrTi$_2$Al$_{20}$ have not been explored. A giant anisotropic magnetoresistance ratio (AMR) of about 20% is recently reported in the sister compound PrV$_2$Al$_{20}$ under a [001] magnetic field, similar to that observed in the nematic order in iron-based superconductors. This AMR is believed to be driven by quadrupolar (i.e., orbital) rearrangement and the accompanied Fermi surface (FS) change, which opens intriguing...
ing prospects of exotic magnetotransport stemming from the interplay of FS properties with the FQ order in PrT$_2$Al$_2$O$_7$. However, investigations into the FS properties of PrT$_2$Al$_2$O$_7$ ($T^* = Ti, V$) are particularly challenging. Density functional theory (DFT) calculation of the FS is obscured by the large number of atoms in one unit cell and the strong electronic correlation. Experimentally, a recent de-Haas-van Alphen (dHvA) study on PrT$_2$Al$_2$O$_7$ and LaT$_2$Al$_2$O$_7$ reveals a complex FS comprising multiple electron and hole sheets in both materials. The resolved FS sheets in PrT$_2$Al$_2$O$_7$ shows similar geometry as those in LaT$_2$Al$_2$O$_7$, while some electron FS sheets in PrT$_2$Al$_2$O$_7$ have enhanced cyclotron effective mass $\sim 8 - 10 m_0$, indicating their sensitivity to the $c$-$f$ hybridization effect. Moreover, NMR magnetization and specific heat measurements indicate that an applied magnetic field of about 2 T along certain orientations induces a discontinuous switching of the FQ order parameter, likely accompanied by a change in the $c$-$f$ hybridization which may cause the reconstruction of FS. This possible field-induced FS reconstruction due to changes in FQ ordering structure remains an open question; quantum oscillations are observed only for $B \gtrsim 2$ T, thus offering no evidence for the potential low-field FS changes. MR and Hall effect are effective alternatives for probing FS properties; comparing their behavior in PrT$_2$Al$_2$O$_7$ and LaT$_2$Al$_2$O$_7$ may yield more profound insights into the interplay of FS and electrical transport properties with multipolar ordering and fluctuations.

In this letter, we report transverse MR and Hall effect $\rho_{4f}$ in high-quality single-crystal PrT$_2$Al$_2$O$_7$ and its non-4$f$ analog LaT$_2$Al$_2$O$_7$. Comparing the observed features for these two materials reveals that open orbits on the electron-type FS sheets are essential for inducing the three orders-of-magnitude increase of transverse MR across the FQ transition in PrT$_2$Al$_2$O$_7$. Moreover, the MR and Hall effect in PrT$_2$Al$_2$O$_7$ develop strong anisotropy on approaching the FQ phase, intimately linked to the sharply distinct behavior of quadrupolar order and fluctuations in different magnetic field orientations. The details about material synthesis and experimental methods are in the Supplementary Materials.

Figure 1 shows the temperature $T$ dependence of the zero-field resistivity $\rho$ for PrT$_2$Al$_2$O$_7$ and LaT$_2$Al$_2$O$_7$. The zero-field Pr-$4f$ electron contribution to the resistivity, $\rho_{4f}(T)$, is obtained by subtracting the resistivity curve of the isostructural, non-$4f$ analog LaT$_2$Al$_2$O$_7$ from the raw data of PrT$_2$Al$_2$O$_7$. In the high-$T$ regime of $T \lesssim 60$ K, $\rho_{4f}(T)$ shows a logarithmic increase in cooling and reaches a broad peak at $T \sim \Delta_{CEF}$. The behavior of $\rho_{4f}(T)$ in this $T$-regime is governed by the magnetic Kondo effect arising from the excited magnetic triplet. Below $\Delta_{CEF} \sim 60$ K, the excited triplet states become less relevant, leading to competing multipolar and magnetic Kondo effects. As a result, $\rho_{4f}(T)$ settles into a Fermi-liquid (FL) regime with $\sim T^2$ behavior for $7 \leq T \lesssim 17$ K, rather than exhibiting the $\sim T^{1/2}$ non-Fermi liquid behavior expected for a quadrupolar Kondo lattice (Fig. 1, inset). The $T^2$ coefficient $A$ is about 200 times the value found in LaT$_2$Al$_2$O$_7$, consistent with heavy fermion formation reported by previous specific heat and dHvA experiment. The sharp exponential decay of $\rho_{4f}(T)$ below $T_Q \sim 2$ K marks the entry into the FQ ordered state with ceased quadrupolar-fluctuation scattering. We note that $\rho(T)$ deviates from the $T^2$ dependence and shows upward convex curvature $\rho \sim T^n$ ($n \lesssim 1$) for $T_Q < T \lesssim 7$ K. This behavior can be attributed to a crossover from the FL state driven by competing magnetic and quadrupolar Kondo effects to a non-Fermi-liquid (NFL) state stemming from the quadrupolar Kondo effect, as predicted by numerical renormalization group calculations. Previous specific heat measurements reveal an entropy release in the same temperature range, supporting this scenario. In the close neighborhood of $T_Q$, critical quadrupolar fluctuations associated with the FQ transition might also influence the behavior of $\rho(T)$, while their effects are unlikely to persist up to as high as 7K. The overall behavior of $\rho_{4f}(T)$ is consistent with the previous report.

The transverse MR of PrT$_2$Al$_2$O$_7$ measured under $B \parallel [111]$ and $B \parallel [001]$ are shown in Fig. 2(a), (c) and (d). We first focus on the behavior observed for $B \parallel [111]$. In the high-$T$ regime dominated by the magnetic Kondo effect, the MR exhibits quadratic field dependence $\Delta_{MR} \propto B^2$ (Fig. 2(a), inset and Fig. S1(a)). Once the multipolar Kondo effect kicks in below $\Delta_{CEF} \sim 60$ K, the MR develops a crossover from the low-field $B^2$ behavior to a quasi-linear field dependence (Fig. 2(a)); the crossover shifts to a lower field on cooling. Below $T_Q \sim 2$ K, the window of $B^2$ behavior completely vanishes, and unsaturated quasi-linear MR persists up to 16 T. Remarkably, the magnitude of MR undergoes three orders of magnitude enhancement across the FQ transition, reaching $\sim 10^3 \mu\Omega$ at 0.1 K (Fig. 2(a)); this value falls in the typical range $10^3 - 10^8 \mu\Omega$ of extremely large magnetoresistance (XMR).
The MR observed for $B \parallel [001]$ is nearly identical to that for $B \parallel [111]$ for $T \geq 10$ K (Fig. 2(c)). Below $T_Q$, XMR on the order of $\sim 10^{3\%}$ also emerges for $B \parallel [001]$, but with clear anisotropy compared with $B \parallel [111]$ (Fig. 2(a), main panel), which will be discussed in detail later.

Though XMR is extensively explored in topological and two-dimensional materials, it has not yet been reported in a pure orbital ordered phase. Thus, identifying the mechanism behind the observed XMR in PrTi$_2$Al$_{20}$ may help widen the scope of XMR studies. To explore the mechanism behind the observed XMR, we make a comparison with the magnetotransport behavior in non-4$f$ analog LaTi$_2$Al$_{20}$. As shown in Fig. 2(b) and Fig. S1(b), for both $B \parallel [111]$ and $B \parallel [001]$, the MR of LaTi$_2$Al$_{20}$ follows $B^2$ behavior up to 9 T for $T \geq 200$ K and develops a crossover from $B^2$ to nearly $B$-linear dependence on cooling; unsaturated XMR on the order of $10^{3\%}$ takes place in the FL state below 20 K (see Fig. 1, inset for the FL fit). Owing to the lack of 4$f$ multipolar moments in LaTi$_2$Al$_{20}$, this close resemblance suggests that the XMR arises from some common characteristics of the two materials that are insensitive to the presence of multipolar moments and their long-range FQ order at the low-$T$ limit. Moreover, the $c$-$f$ hybridization tends to decline sharply in the FQ ordered state, evident from the previous specific heat measurements showing that the residual entropy associated with the quadrupolar Kondo effect is released in the FQ ordered state, as well as the gapped behavior (i.e., exponential decay) of $\rho(T)$ (Fig. 1) and specific heat below the FQ transition temperature $T_Q^{18}$. Thus, it appears unlikely that the interaction between multipolar moments and conduction electrons plays a major role in producing the XMR in the FQ ordered state of PrTi$_2$Al$_{20}$.

Electron-hole compensation and ultrahigh carrier mobility (in the range of $10^9$ cm$^2$/Vs) are the two most common mechanisms that generate XMR$^{18}$. These are often realized in semimetals featuring small Fermi pockets and low density of states (DOS) near the Fermi level$^{24,25}$. However, both PrTi$_2$Al$_{20}$ and LaTi$_2$Al$_{20}$ are metallic systems with sizable FS sheets and DOS near the Fermi level, unlikely to reach the ultrahigh mobility as in the semimetal cases. Moreover, carrier compensation or high mobility alone typically yields unsaturated, quadratic MR $\sim B^2$, inconsistent with the observed quasi-linear field dependence shown in Fig. 2. Exceptions may occur for topological Dirac and Weyl semimetals, in which the linear band dispersion can lead to unsaturated linear-in-$B$ MR$^{24,25}$, while this situation does not apply to the band structures of PrTi$_2$Al$_{20}$ or LaTi$_2$Al$_{20}$. Thus, carrier compensation or high mobility is insufficient to explain the nonsaturating linear XMR observed here; another factor is at play for its generation.

Given that PrTi$_2$Al$_{20}$ has no spin degrees of freedom in its CEF ground state and shows no trace of charge order at low-$T$$^{12,13,24}$, we can also rule out spin fluctuations and charge density waves as possible mechanisms for the observed XMR. We then turn to the FS properties given that the previous dHvA study suggests similar FS geometry for PrTi$_2$Al$_{20}$ and LaTi$_2$Al$_{20}$. In particular, we consider the possibility of enhanced MR due to open-orbit FS topology$^{29,41}$.

The previously reported FS of LaTi$_2$Al$_{20}$ comprises a large jungle-gym-like electron sheet (96th band), with cubic symmetry and "necks" along the eight symmetrically equivalent (111) axes$^{27}$ bearing similarity with the well-studied FS of copper$^{23,31}$. Such "necks" in the FS can induce open orbits for the FS cross section in a certain range of magnetic field, leading to complex field angle dependence of the XMR. In the copper case, when $B \parallel \langle 001 \rangle$, the MR value is at a minimum with a convex upward curvature. As $B$ rotates from $\langle 001 \rangle$ to $\langle 110 \rangle$, the MR can exhibit unsaturated, quasi-linear field dependence for some intermediate angles (such as $B \parallel \langle 111 \rangle$) before reaching a maximum with quadratic field dependence$^{28,29}$. Thus, the open-orbit FS topology well accounts for the quasi-linear XMR and its anisotropy between $B \parallel [111]$ and $B \parallel [001]$ at the low-$T$ limit. The similar MR behavior observed in PrTi$_2$Al$_{20}$ and LaTi$_2$Al$_{20}$ at the low-$T$ limit suggests that such open-orbit FS topology persists even with $c$-$f$ hybridization and the long-range FQ order, serving as a key driver of the nonsaturating, linear XMR in PrTi$_2$Al$_{20}$.

We note that quantum oscillations emerge in MR and Hall effect below $\sim 1$ K in PrTi$_2$Al$_{20}$ (see details in the Supplementary Materials and Fig. S7). The observable quantum oscillations indicate that the system fulfills the high-field limit.
in the FQ ordered state, namely, $\omega_c \tau \gtrsim 2\pi$, where $\omega_c$ is the cyclotron frequency, and $\tau$ is the scattering time. Under this condition, the carriers can traverse a complete cyclotron orbit before being scattered, allowing the open-orbit FS geometry to be reflected in the magnetotransport, consistent with the presence of open-orbit-induced linear XMR within the FQ state. Moreover, the crossover in MR from $B^2$ to $B$-linear behavior on cooling leads to a violation of ordinary and extended Kohler’s rules (Supplementary Materials and Fig. S2). Violation of the Kohler’s rule is typically associated with changes in the anisotropy pattern of the scattering time $\tau(k)$ on the FS, as reported in cuprates and iron-based superconductors.24,25

This scenario is again in line with more carriers moving along the open-orbit trajectories on the FS as inelastic and orbital-fluctuation-induced scatterings cease in the low-$T$ FQ state.

Interestingly, the MR of PrTi$_2$Al$_2$0 is nearly isotropic at high $T$s but becomes strongly anisotropic on approaching the FQ order (Figs. 2(c) and (d)): For $T_Q \lesssim T < 10$ K, the MR increases monotonically under $B \parallel [111]$, whereas forming a broad maximum and then declines at higher fields under $B \parallel [001]$. Within the FQ order, the MR curve displays a kink around $B = 2$ T $\parallel [001]$ (Fig. 2(a)), whereas this anomaly is absent for $B \parallel [111]$; the difference in magnitude reaches nearly two-fold at 16 T for the two field directions. The low-field MR anomaly overlaps with a field-induced transition previously detected by NMR and magnetization around $B = 2$ T $\parallel [001]$, whereas such transition is absent for $B \parallel [111]$.22,24 We note that the MR exhibits weak RRR dependence for high-quality single crystals (Fig. S4), and thus the observed anisotropy is intrinsic rather than caused by the difference in sample quality. The low-temperature MR anisotropy observed in PrTi$_2$Al$_2$0 (Fig. 2(a) and (d)) is more pronounced than the anisotropy observed in LaTi$_2$Al$_2$0 (Fig. 2(b) and Fig. S1(b)), suggesting that the $4f$ multipolar moments, along with their remaining interaction with the conduction electron sea in the ordered state could offer an additional mechanism for the magnetotransport anisotropy in PrTi$_2$Al$_2$0 other than the open-orbit FS topology.

To further investigate the anisotropic low-$T$ transport in PrTi$_2$Al$_2$0, we outline the highly anisotropic temperature-field ($T$-$B$) phase diagrams under $B \parallel [111]$ and $B \parallel [001]$ based on isofield resistivity measurements (Figs. 3(a), (b) and Figs. S3). The phase diagrams based on transport data shown in Figs. 3(c) and (d) agree with those obtained by previous NMR and thermodynamic measurement.22,23,24,25 For $B \parallel [111]$, the FQ transition remains well-defined up to $\sim 10$ T, with $T_Q$ decreasing as $B$ rises beyond 5 T (Fig. 3(a), Fig. 3(c) and Fig. S3(a), (c)). In contrast, the long-range FQ order is “soft” for $B \parallel [001]$. A small field of $B \sim 2$ T $\parallel [001]$ turns the second-order FQ transition into a smooth crossover, evidenced by the drastic broadening of the resistivity anomaly at $T_Q$ (Fig. 3(b) and Fig. S3(b), (d)); the FQ-paramagnet (PM) phase boundary bends toward higher $T$ with increasing $B$ (Fig. 3(d)). The observed anisotropic field evolution of the FQ-PM transition boundary results from the strongly anisotropic response of the FQ order to [111] and [001] magnetic fields, which can be explained by the competition between the Zeeman effect and the field-induced quadrupolar-quadrupolar interaction.22 The possibility for a metastable domain structure is also discussed theoretically.26

The quadrupolar short-range fluctuations associated with the crossover under $B \parallel [001]$ can alter the carrier scattering and thereby the magnetotransport near $T_Q \sim 2$ K, leading to the sharply different behavior of MR compared to that in $B \parallel [111]$.

Below $T_Q \sim 2$ K, the MR anomaly near 2 T for $B \parallel [001]$ (Fig. 2(a)) is likely associated with a change in the quadrupolar ordering structure.22,23,25,26 Earlier comparison of the NMR and specific heat results with theoretical analysis suggests that the low-field transition might be driven by FQ order parameter switching accompanied by a change in the $c$-$f$ hybridization, which may cause FS reconstruction.22,23,25 Then the difference in quadrupolar ordering structure between [111] and [001] direction can induce the transport anisotropy via modifying the anisotropy pattern of the scattering rate on the FS.

The Hall resistivity may offer more insight into the interplay of multipolar order with FS and transport properties. PrTi$_2$Al$_2$0 is ideal for investigating the Hall effect in a multipolar heavy fermion system, which has yet to be explored. Figure 4(a) shows the magnetic field $B$ dependence of the Hall resistivity $\rho_{HT}$ for PrTi$_2$Al$_2$0 at various temperatures and the $B$
dependence of the Hall coefficient $R_{H} \equiv \rho_{H}/B$ of PrTi$_2$Al$_{20}$ obtained at selected temperatures shown in Fig. 4(c). $R_{H}$ shows clear $B$ dependence, reflecting nonlinear $\rho_{H}$ as a function of $B$. Such nonlinearity indicates the multiple-band signature, as discussed below. The high-field anomaly at $\sim 11$ T (Figs. 4(a) and (c)) is likely related to a field-induced re-arrangement of multipolar moments within the FQ ordered phase, similar to the transition reported for the sister compound PrV$_2$Al$_{20}$ under $B \sim 11$ T $[001]$. Further experiments on detecting the FQ order parameter are necessary to confirm this scenario.

Next, we explore the temperature dependence of the initial Hall coefficient $R_{H}^{0}$ for PrTi$_2$Al$_{20}$ (Fig. 4(e)), where $R_{H}^{0}$ is defined as the slope of the Hall resistivity versus field isothermals at the zero-field limit. $R_{H}^{0}$ is positive in the entire measured $T$ range, indicating hole-type majority charge carriers. With decreasing $T$, $R_{H}^{0}$ exhibits a mild increase below $\Delta_{CEF} \sim 60$ K, then forming a plateau in the FL state ($7$ K $\leq T \leq 17$ K); a more pronounced upturn of $R_{H}^{0}$ occurs near $T_{coh} \sim 2$ K, followed by saturation in the ordered state.

Such temperature dependence of $R_{H}^{0}$ is qualitatively different from the behavior typically seen in magnetic heavy fermion metal $[30]$. The Hall coefficient consists of the normal Hall component $R_{H}^{N}$ and the anomalous Hall component $R_{H}^{A}$. As shown by the dashed lines in Fig. 4(e), the initial Hall coefficient $R_{H}^{0}$ of various classes of magnetic heavy fermion compounds displays a common feature $[30]$, a broad maximum near the coherence temperature $T_{coh}$, marking a crossover from the high-$T$ regime dominated by the skew-scattering-induced anomalous Hall effect $R_{H}^{A}$ to the low-$T$ coherence regime where $4f$ moments enters the Fermi volume, forming a heavy FL. In the high-$T$ regime, the $R_{H}^{A}$ is well-scaled by the magnetic susceptibility, such that $R_{H}^{A} \propto \chi$ or $R_{H}^{A} \propto \rho_{H}$, where $\rho$ is the longitudinal resistivity. In contrast, the coherence peak is absent in $R_{H}^{0}$ of PrTi$_2$Al$_{20}$, and $R_{H}^{0}$ cannot be scaled by either $\chi$ or $\rho$ (Figs. 5(a), (b) and Fig. S5 $[30]$). Thus, the anomalous Hall component associated with the magnetization is negligibly small at least below $100$ K in PrTi$_2$Al$_{20}$, as expected from the lack of dipolar degrees of freedom in its CEF ground-state doublet and the sizeable gap $\Delta_{CEF} \sim 60$ K between the ground-state doublet and the first-excited magnetic triplet. Moreover, the overall field dependence and magnitude of $\rho_{H}$ and the Hall coefficient $R_{H} \equiv \rho_{H}/B$ in the FQ ordered state of PrTi$_2$Al$_{20}$ are similar to that of LaTi$_2$Al$_{20}$ (Fig. 5(a)), indicating that the anomalous Hall contribution from the high-rank multipolar moments has minor influence on the low-$T$ Hall effect. Altogether, our findings indicate that $R_{H}$ of PrTi$_2$Al$_{20}$ is governed by the normal Hall contribution $R_{H}^{N}$, same as in LaTi$_2$Al$_{20}$, which allows comparison of the Hall coefficient behavior in the two systems.

The normal Hall effect yields information about carrier density and mobility. In the high-field limit $\omega_{c}\tau \geq 2\tau$, the Hall coefficient $R_{H}$ reaches a field-independent value, $R_{H}(\infty) = 1/(e\tau_{\parallel} - \tau_{\perp})$, that provides a measure of the net carrier density enclosed by the FS. For both $B \parallel [001]$ and $[111]$, the $\rho_{H}$ of PrTi$_2$Al$_{20}$ becomes nonlinear in $B$ for $T_{Q} < T < 50$ K, and its magnitude is strongly $T$-dependent (Fig. 4(a), inset and Fig. S6(a), inset). Such nonlinearity is more pronounced than that observed in LaTi$_2$Al$_{20}$ (Fig. 4(b) and Fig. S6(c)), suggesting carrier mobility misbalances on the electron and hole FS sheets due to the interplay between $4f$ quadrupolar moments and conduction electrons. Moreover, $R_{H}$ of PrTi$_2$Al$_{20}$ does not fully saturate up to $9$ T (Fig. 4(c), inset and Fig. S6(b), inset), in contrast with $R_{H}$ in LaTi$_2$Al$_{20}$ that levels off at $\sim 3$ T (Fig. 4(d) and Fig. S6(d)); namely, a higher-$B$ is necessary for PrTi$_2$Al$_{20}$ to reach the high-field limit. These facts suggest that the transport properties above $T_{Q}$ are strongly affected by substantial quadrupolar fluctuations as an addi-
tional scattering mechanism. This point is corroborated by the above-mentioned MR crossover in PtTi$_2$Al$_{20}$ from low-field $B^2$-dependence to quasi-$B$-linear dependence without saturation in the same $T$ range (Fig. 2(a), inset and Fig. S1(a)).

With suppressed quadrupolar fluctuations below $T_Q$, the isothermal field-sweeps of $\rho_{\|}(B)$ become nearly $T$-independent but still exhibits nonlinearity (Fig. 4(a), main panel). For $B \parallel [001]$, the Hall coefficient $R_{H}$ (Fig. 4(c), main panel and Fig. 5(a)) displays a smooth crossover from the low-field increase to a field-independent regime above $\sim 8 \, T$; the high-field $R_{H}$ value is larger than that of LaTi$_2$Al$_{20}$, indicating a lower net carrier density in the FQ ordered state. This feature indicates that the 4$f$ moments only weakly contribute to the Fermi volume below $T_Q$. Unlike the magnetic susceptibility shown in Fig. 5(b), $R_{H}$ does not exhibit any sharp anomaly at $B \sim 2 \, T \parallel [001]$; therefore, the field-induced change in quadrupolar ordering structure does not seem to trigger noticeable FS reconstruction, possibly owing to the strongly suppressed $c$-$f$ hybridization below $T_Q$.

The multiband effect is a typical mechanism for the nonlinear $B$ dependence of the normal Hall effect. We therefore estimate the carrier densities and mobilities by fitting $\rho_{\|}$ to the widely-used two-band model that simplifies multi-band scenario into one electron-type band and one hole-type band such that

$$\rho_{\|}(B) = \frac{B}{e} \left( n_e \mu_e^2 + n_h \mu_h^2 \right) + \left( n_h - n_e \right) \mu_e^2 \mu_h^2 B^2,$$

where $n_{e,h}$ are the electron-type and hole-type carrier densities, and $\mu_{e,h}$ are their respective mobilities (see details in the Supplementary Materials). Though the two-band fitting cannot fully capture the complex multiband FS of PrTi$_2$Al$_{20}$ and LaTi$_2$Al$_{20}$, it reasonably estimates the carrier properties (see Supplementary Table 1). We note that the field range of the fits is limited to $0 \, T \leq B \leq 9 \, T$ to avoid inclusion of the high-field anomaly located around $\sim 11 \, T$. The electron and hole densities and mobilities obtained from the two-band fit are shown in Figs. 5(c) and (d), compared with the results estimated from the initial Hall coefficient $R_{H0}$ (i.e., the one-band model). The increasing deviation between the two-band and one-band fitting results reflects the nonlinear field dependence of $\rho_{\|}$ at low $T$s, originating from the multiband effect.

For both PrTi$_2$Al$_{20}$ and LaTi$_2$Al$_{20}$, the hole band dominates the electrical transport process at all measured $T$s. The electron-like contribution $n_e$ becomes appreciable near $T_Q$ in PrTi$_2$Al$_{20}$ (Fig. 5(c)); the electron and hole mobilities, $\mu_e$ and $\mu_h$, are both dramatically enhanced on cooling below $T_Q$, then leveling off in the FQ ordered state (Fig. 5(d)). These results support the scenario that the suppression of quadrupolar-fluctuation-induced scatterings below $T_Q$ leads to sufficiently high carrier mobilities, which are necessary for observing the linear XMR induced by open-orbit trajectories on the large electron-like FS sheet. The qualitative behavior and low-$T$ values of carrier densities and mobilities in LaTi$_2$Al$_{20}$ resemble the behavior in PrTi$_2$Al$_{20}$. A key difference is that the enhancement of electron-contribution appears at much higher temperatures ($T \lesssim 70 \, K$) in LaTi$_2$Al$_{20}$ (Fig. 5(c) and (d)), likely due to the lack of quadrupolar fluctuations. This difference naturally explains why the onset of XMR occurs at a lower temperature in PrTi$_2$Al$_{20}$ than in LaTi$_2$Al$_{20}$. Moreover, the electron and hole mobilities overlap in LaTi$_2$Al$_{20}$ but differ ($\mu_e \ll \mu_h$) at low-$T$ regime in PrTi$_2$Al$_{20}$, which explains the stronger nonlinearity of $\rho_{\|}(B)$ in PrTi$_2$Al$_{20}$. The imbalanced $\mu_e$ and $\mu_h$ in PrTi$_2$Al$_{20}$ might result from the mildly enhanced $m^*$ on the electron FS, the anisotropic scattering time $\tau$ induced by the quadrupolar order parameter or both.

Similar to the MR, the Hall resistivity $\rho_{\|}(B)$ in the FQ ordered phase of PrTi$_2$Al$_{20}$ is strongly anisotropic in [001] and [111] magnetic fields. For $B \parallel [111]$, the $\rho_{\|}(B)$ shows concave curvature above $\sim 4 \, T$, and its magnitude at $0.1 \, K$ is only about one-third of that for $B \parallel [001]$ (Figs. S6(a) and (b)). The simple two-band scenario cannot describe the field dependence of $\rho_{\|}(B)$ under $B \parallel [111]$. Again, such a pronounced anisotropy is absent in LaTi$_2$Al$_{20}$ (Figs. 4(b), (d), Figs. S6(c) and (d)), implying that the anisotropic transport in PrTi$_2$Al$_{20}$ originates from the field-induced change of FQ order structure under $B \parallel [001]$.

To summarize, our comprehensive study of magnetotransport of PrTi$_2$Al$_{20}$ reveals extremely large magnetoresistance (XMR) reaching $\sim 10^3\%$ in its FQ ordered state. Based on comparison with the non-4$f$ analog, LaTi$_2$Al$_{20}$, we attribute this XMR to the open-orbit topology of the Fermi surface.

FIG. 5. (a) Low-$T$ Hall coefficient $R_{H}$ vs $B$ of PrTi$_2$Al$_{20}$ and LaTi$_2$Al$_{20}$ compared with (b) the $B$ scaling of the magnetic susceptibility $\chi$ and the quantities $\chi_P$ and $\chi_Q^2$ of PrTi$_2$Al$_{20}$ measured at 0.3 K. (c) The evolution of the charge carrier density $|n|$ and (d) mobility $\mu$ as a function of temperature $T$ estimated based on the two-band fits with fitting range $0 \, T \leq B \leq 9 \, T$ (solid symbols) in LaTi$_2$Al$_{20}$ ($n_e$ and $\mu_e$: orange, $n_h$ and $\mu_h$: yellow) and PrTi$_2$Al$_{20}$ ($n_e$ and $\mu_e$: dark blue, $n_h$ and $\mu_h$: light blue) and from the initial Hall coefficient $R_{H0}$ (i.e., one-band fitting) in LaTi$_2$Al$_{20}$ (open yellow circles) and PrTi$_2$Al$_{20}$ (open light blue circles). The one-band fitting yields dominated hole-type charge carriers, consistent with the two-band fitting results.
The $B$-dependence of the Hall resistivity $\rho_H$ displays stronger nonlinearity than that of LaTi$_2$Al$_{20}$ on approaching the FQ state. Analysis using the two-band model indicates that the contribution from the electron-type FS sheet featuring open orbits becomes effective upon suppression of the quadrupolar-fluctuation scattering, further supporting the FS topology’s key role in generating the XMR. Both the MR and $\rho_H$ become highly anisotropic under $B \parallel [111]$ and $B \parallel [001]$ in the FQ state, following the distinct response of the FQ order parameter under the two field orientations. Our study indicates that multipolar ordered state without involving spin degrees of freedom can realize large magnetoresistance. These findings provide essential insights that may help identifying universal mechanisms behind large magnetotransport phenomena and thereby widen their applications.

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J Phys Conf Ser, vol. 592, 012099 (IOP Publishing, 2015).

33. H. Kusunose, Competing Kondo effects in non-Kramers doublet systems, J. Phys. Soc. Jpn. **85**, 064708 (2016).

34. T. Liang et al., Ultrahigh mobility and giant magnetoresistance in the Dirac semimetal Cd$_3$As$_2$, Nat. Mater. **14**, 280–284 (2015).

35. R. Mondal et al., Extremely large magnetoresistance, anisotropic Hall effect, and Fermi surface topology in single-crystalline WSi$_2$, Phys. Rev. B **102**, 115158 (2020).

36. Y.-Y. Lv et al., Mobility-controlled extremely large magnetoresistance in perfect electron-hole compensated α-WP$_2$ crystals, Phys. Rev. B **97**, 245151 (2018).

37. N. Kumar et al., Large out-of-plane and linear in-plane magnetoresistance in layered hafnium pentatelluride, Phys. Rev. B **95**, 155128 (2017).

38. M. Koseki et al., Ultrasonic investigation on a cage structure compound PrTi$_2$Al$_{20}$, J. Phys. Soc. Jpn. **80**, SA049 (2011).

39. B. Wu, V. Barrena, H. Suderow & I. Guillamón, Huge linear magnetoresistance due to open orbits in γ–PtBi$_2$, Phys. Rev. Research **2**, 022042 (2020).

40. A. Hasegawa & H. Yamagami, Effect of the spin-orbit interaction on the Fermi surface of LaSn$_3$, J. Phys. Soc. Jpn. **60**, 1654–1665 (1991).

41. I. Umehara, N. Nagai & Y. Onuki, High field magnetoresistance and de Haas-van Alphen effect in LaSn$_3$, J. Phys. Soc. Jpn. **60**, 1294–1299 (1991).  
42. A. B. Pippard, Magnetoresistance in metals, vol. 2 (Cambridge university press, 1989).

43. S. Zhang, Q. Wu, Y. Liu & O. V. Yazyev, Magnetoresistance from Fermi surface topology, Phys. Rev. B **99**, 035142 (2019).

44. D. M. Ginsberg, Physical properties of high temperature superconductors I (World scientific, 1998).

45. S. Kasahara et al., Evolution from non-Fermi-to Fermi-liquid transport via isovalent doping in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ superconductors, Phys. Rev. B **81**, 184519 (2010).

46. S. Lee, S. Trebst, Y. B. Kim & A. Paramekanti, Landau theory of multipolar orders in Pr(Y)$_2$X$_{20}$ Kondo materials (Y = Ti, V, Rh, Ir, X = Al, Zn), Phys. Rev. B **98**, 134447 (2018).

47. F. Freyer, S. Lee, Y. B. Kim, S. Trebst & A. Paramekanti, Thermal and field-induced transitions in ferroquadrupolar Kondo systems, Phys. Rev. Research **2**, 033176 (2020).

48. Y. Shimura, Y. Ohta, T. Sakakibara, A. Sakai & S. Nakatsuji, Evidence of a High-Field Phase in PrV$_2$Al$_{20}$ in a [100] Magnetic Field, J. Phys. Soc. Jpn. **82**, 043705 (2013).

49. A. Fert & P. M. Levy, Theory of the hall effect in heavy-fermion compounds, Phys. Rev. B **36**, 1907–1916 (1987).

50. R. G. Chambers, The two-band effect in conduction, Proc. Phys. Soc. A **65**, 903–910 (1952).