

Heavy fermion behaviors in the Pr-based filled skutterudites

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Abstract

In filled skutterudites, which have attracted much attention as candidate materials for thermoelectric applications, rare Pr-based heavy-fermion (HF) behaviors have been revealed recently. We review recent studies focusing on $\text{PrFe}_4\text{P}_{12}$ and $\text{PrOs}_4\text{Sb}_{12}$; the former shows HF behaviors in high-fields where a quadruple ordering is suppressed, and the latter shows the first known Pr-based HF superconductivity as well as an anomalous field-induced quadruple ordering. We suggest that quadrupole degrees of freedom on the Pr-ions commonly play key roles in these exotic states.

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1. Introduction

The filled skutterudites, named after a mine town Skuterud in Norway, have attracted much attention as candidate materials for thermoelectric applications [1–3]. The family of compounds has the general formula RT_4X_{12} , where R is the rare-earth or uranium ions; T is Fe, Ru, or Os; and X is P, As, or Sb. A remarkable feature in the crystal structure shown in Fig. 1 is that the R ions are located at the center of the X_{12} icosahedron cages. This allows local vibrations of the R ions called “rattling” [4], which is considered to reduce the thermal conductivity, improving the efficiency for thermoelectric materials.

The heavy-fermion (HF) behaviors based on 4f-electrons have been observed mainly in Ce- or Yb-based compounds. In contrast, Pr^{3+} ions had been considered to be quite stable in intermetallic compounds since in many cases the magnetic properties are well understood in terms of the well localized $4f^2$ configuration. Therefore, it is surprising that HF behaviors have been revealed recently in several Pr-based filled skutterudites, as summarized in Table 1. In this paper, we discuss present understanding on the Pr-based exotic electronic states focusing on $\text{PrFe}_4\text{P}_{12}$ and $\text{PrOs}_4\text{Sb}_{12}$.

2. $\text{PrFe}_4\text{P}_{12}$: quadrupole ordering and HF behaviors

In $\text{PrFe}_4\text{P}_{12}$, an ordered state sets in below $T_A = 6.5$ K [10]. Large specific heat anomaly evidences the phase transition originates in 4f electrons. At the early stage, it was interpreted as an antiferromagnetic (AFM) ordering of the Pr magnetic moments [10] since the magnetic susceptibility (χ) shows a sharp drop below T_A . However, recent studies revealed that the ordered state is not of magnetic origin; most probably it is an ordered phase of antiferro-electric-quadrupole (AFQ) moments, as shown below. Schematic representation of the magnetic field (H) versus temperature (T) phase diagram is shown in Fig. 2, which has been constructed based on our measurements using high-quality single crystals. It is remarkable that $-\ln T$ dependence of electrical resistivity ρ , suggesting Kondo scattering, was observed above ~ 30 K in the single-crystalline samples [11]; this anomaly was not seen in the early study [10]. The existence of highly correlated electrons at the high- T region is also reflected in a largely enhanced thermoelectric power $S \sim 70$ $\mu\text{V}/\text{K}$ at ~ 10 K [11].

In conventional Ce-based Kondo lattice compounds, χ is suppressed and the Weiss temperature θ_p is usually negative, providing a rough estimate of the Kondo temperature as $T_K \sim |\theta_p|/4$. In $\text{PrFe}_4\text{P}_{12}$, however, χ does not show any such features and follows a Curie–Weiss law above T_A with

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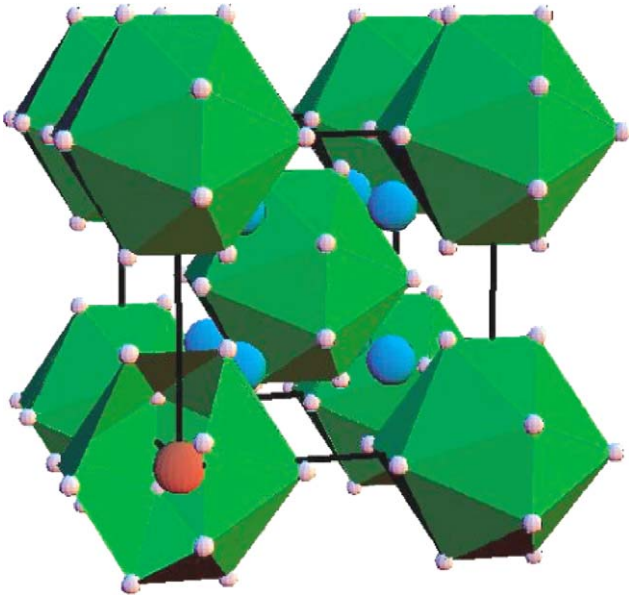


Fig. 1. Crystal structure of the filled skutterudite RT_4X_{12} (the space group: $Im\bar{3}, T_h^5, \#204$). R (rare-earth ions) are surrounded by X_{12} (pnictogen) icosahedron cages. T (transition metal ions) are located between the cages, forming a simple cubic sublattice.

$\theta_p = +3.5$ K [12], suggesting ferromagnetic interactions among the Pr ions. Therefore, the anomalies in $\chi(T)$ and $\rho(T)$ cannot be understood consistently in terms of the conventional magnetic Kondo effect.

The most striking finding is the HF behaviors appearing in high fields where the ordered state is suppressed. This is evidenced by the largely enhanced electronic specific-heat coefficient ($\gamma \equiv C_e/T|_{T \rightarrow 0} = 1\text{--}2$ J/K² mol depending on the field direction) [12,13]. The γ value and the T^2 coefficient of $\rho(T)$ [14] satisfy the Kadowaki–Woods relation [15]. The largest value of the cyclotron mass m_c^* obtained from de Haas–van Alphen (dHvA) studies is $80 m_0$ [14].

A characteristic feature in the enhanced electronic specific-heat contribution is a broad peak in C_e/T versus T [12]. From this structure, using a resonance level model, the width of the Kondo resonance peak Δ/k_B ($\sim T_K$) has been obtained to be ~ 9 K [12]. This energy scale is consistent with the width of quasielastic spectra observed in inelastic neutron scattering (INS) studies [16], which shows a typical $T^{1/2}$ -like temperature dependence. Note that in $T > T_A$

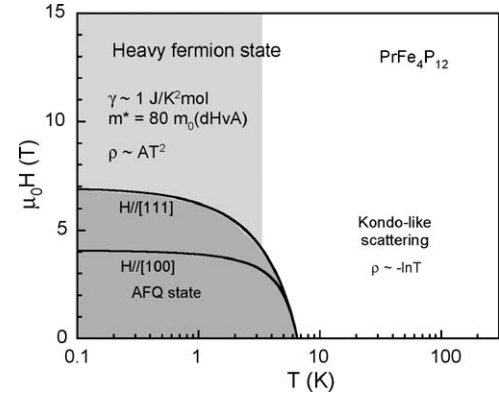


Fig. 2. Magnetic field vs. temperature phase diagram of $PrFe_4P_{12}$.

no clear crystalline-electric-field (CEF) excitation peaks are visible in the INS spectra, suggesting strong hybridizations of f-electrons with conduction electrons. This is also reflected in the T dependence of the spin-lattice-relaxation rate $1/T_1$ in P-NMR experiments [17].

Nuclear contribution to specific heat (C_N), which often dominates at low temperatures, is usually considered to be an obstacle in the study of electronic low-energy excitations. In the case of $PrFe_4P_{12}$, C_N comes mostly from the ^{141}Pr nuclei and, therefore, one can utilize this in order to obtain information on the 4f electron magnetism of Pr ions [12]. The temperature dependence of the Pr nuclear contribution reflects the strong intrasite hyperfine coupling between the nucleus and the 4f-electron magnetic moment on a same Pr ion. The Hamiltonian for the Pr nucleus can be written simply as [18,19]

$$\mathcal{H}_n = A_{hf} \langle J_z \rangle I_z, \quad (1)$$

where A_{hf} represents the magnetic dipole hyperfine interaction parameter and the z -axis lies in the direction of $\langle \mathbf{J} \rangle$ for each Pr ion.

By fitting the observed $C_N(T)$ data [20] to the model given by Eq. (1), we have obtained the site-averaged size of the Pr magnetic moment $m_{Pr} \equiv g_J |\langle J_z \rangle|^2 / 2$. Note that, in the ordered phase, Pr ions form two inequivalent sublattices and $C_N(T)$ is given by the sum of the two contributions.

The obtained m_{Pr} and bulk magnetization M measured at 2 K are compared in Fig. 3. Both quantity behaves in a similar

Table 1
Physical properties of Pr-based filled skutterudites PrT_4X_{12}

PrT_4X_{12}	X = P	As	Sb
T = Fe	Antiferro-quadrupole ordering, $T_A = 6.5$ K Heavy-fermion (HF) state in high fields $\gamma \sim 1$ [12]	–	Ferromagnet? $T_m = 5$ K $\gamma \sim 1$ in 3 T [7]
Ru	Metal–insulator transition, $T_{MI} = 62$ K $\Delta C/T_{MI} = 0.2$ [5,6]	Superconductor, $T_c = 2.4$ K $\gamma = 0.1$ [8]	Superconductor [9] $T_c = 1.08$ K, $\gamma = 0.06$
Os	No ordering above 2 K [5]	–	HF superconductor [37] $T_c = 1.85$ K, $\Delta C/T_c \sim 0.5$

Roughly estimated values of γ (or $\Delta C/T$ at phase transition) are given in the unit of J/K² mol.

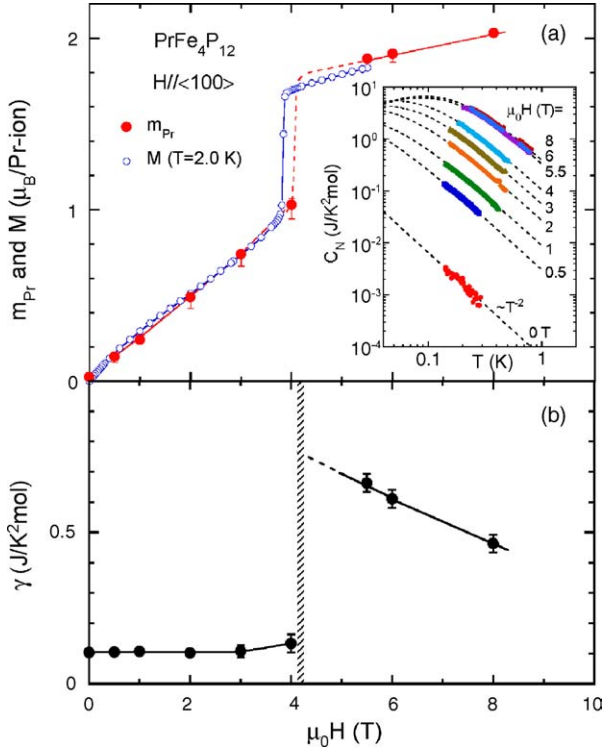


Fig. 3. (a) Magnetization curve $M(H)$ for $H \parallel \langle 100 \rangle$ compared with the site-averaged Pr magnetic moment $m_{\text{Pr}}(H)$ obtained from the nuclear specific heat $C_N(T)$ data shown in the inset. (b) Sommerfeld coefficient $\gamma \equiv C_e/T|_{T \rightarrow 0}$ [12,20].

manner showing a suppression in the ordered phase. This fact clearly shows that the Pr magnetic moment itself shrinks in the ordered phase; in any AFM phase where two sublattice magnetic moments cancel each other, significant difference should appear between M and m_{Pr} (see Ref. [21] for a case in HoGa_2). The zero-field data of m_{Pr} indicates that the size of the ordered 4f-magnetic-moment is $\lesssim 0.03 \mu_B/\text{Pr-ion}$. This upper bound is smaller than $\lesssim 0.1 \mu_B/\text{Pr-ion}$ provided by a neutron scattering experiment [22], in which no magnetic Bragg peaks are observed. This fact suggests that the ^{141}Pr nuclear Schottky contribution works as a *high-sensitive on-site probe for the Pr magnetic moment*. The non-magnetic nature of the ordered phase is consistent with a recent ZF- μSR study, which shows no visible internal fields below T_A [23].

Considering a quite large entropy change below T_A along with no development of the Pr magnetic moment, quadrupole (or higher order) moments are considered to be the most probable order parameter. Superlattice reflections in X-ray scattering [24] and a field-induced AFM component in neutron scattering [25] both characterized by a wave vector $\mathbf{q}_A = (1, 0, 0)$ strongly suggest an AFQ with \mathbf{q}_A as the order parameter, which is accompanied by the corresponding crystal-structure modulation. Note that the modulation changes the crystal structure from *bcc* to *sc*. A group theoretical analysis has been made to relate the crystal-structure modulation to possible AFQ order parameters [26]. To determine the order parameter, a study of resonant X-ray scattering, which has

been established to be a powerful tool [27], is in progress for $\text{PrFe}_4\text{P}_{12}$ (see Ref. [28]). The wave vector \mathbf{q}_A is exactly the same with the possible 3d-perfect-nesting vector, as pointed by Harima [29,30]. The AFQ ordering with \mathbf{q}_A in $\text{PrFe}_4\text{P}_{12}$ should remove a main part of the Fermi surface. This expectation agrees well with large increments observed in electrical resistivity and Hall coefficient just below T_A [11], and the suppressed electronic specific heat coefficient $\gamma = 0.1 \text{ J/K}^2 \text{ mol}$ in the ordered phase [12].

The mechanism that causes the rare $4f^2$ -based HF behaviors in $\text{PrFe}_4\text{P}_{12}$ has not been understood. In order to clarify this issue, it is important to identify the 4f-electron CEF level scheme, if exists. This will help to provide a starting model in the well-localized 4f-electron picture. Note that, however, it is not apparent from the INS data [16], where no sharp excitation peaks are visible, except in the ordered phase.

A non-Kramers doublet (Γ_{23} in the notation given in Ref. [31]) is one of the possible CEF ground states [32] as suggested from the anisotropy in M [12] and a softening in the elastic constant $C_{11}-C_{12}$ [33] in $T > T_A$. If this is the case, the quadrupole moments associated with the doublet (O_2^0 and O_2^2) can be ordered at low temperatures, giving rise to the AFQ phase. Outside of the AFQ phase, it might be possible that fluctuations of the quadrupole moments lead to a quadrupolar Kondo effect [34] through mixing with conduction electrons. As a possible evidence for that, non-Fermi-liquid-like behaviors have been observed for $H \parallel [111]$ in high-field HF state, e.g., a deviation from the typical T^2 dependence in $\rho(T)$ [35]. We hope that on-going La-substitution experiments will provide further information not only on this effect but also on the nature of the AFQ phase (see Ref. [36] for preliminary results).

3. $\text{PrOs}_4\text{Sb}_{12}$: HFSC and field-induced quadrupole ordering

Among the Pr-based filled skutterudites listed in Table 1, $\text{PrOs}_4\text{Sb}_{12}$ has the largest lattice constant, suggesting the weakest hybridization effect. Nevertheless, it has been found that this compound is a HF superconductor [37]. Large specific heat jump $\Delta C/T \sim 0.5 \text{ J/K}^2 \text{ mol}$ at the superconducting transition temperature $T_c = 1.85 \text{ K}$ [37] and the enhanced cyclotron-effective masses [38] reflect the existence of heavy quasiparticles, which form Cooper pairs. The magnetic field versus temperature phase diagram revealed by several experiments is summarized in Fig. 4. One remarkable feature is that a field-induced ordered phase (FIOP) appears in high fields where the superconductivity is suppressed [39]. Large entropy change associated with the phase transition indicates that it originates in the 4f electrons of Pr ions. The measurements of ρ [40,41] and M [42] indicate that the transition temperature has the maximum value of 1.3 K in 9 T and it approaches $T = 0$ in 14 T for $H \parallel [100]$. Neutron diffraction measurements [43] in FIOP revealed a small AFM mo-

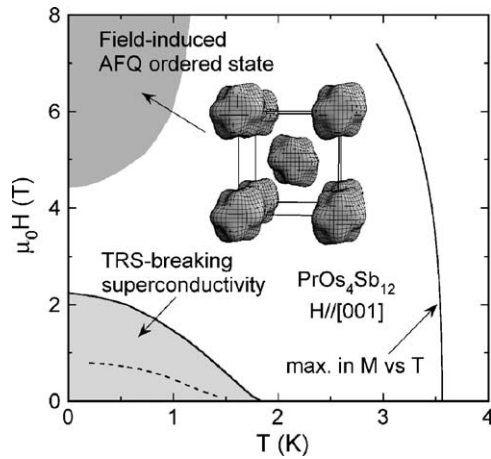


Fig. 4. Magnetic field vs. temperature phase diagram of $\text{PrOs}_4\text{Sb}_{12}$. Broken curve in the superconducting phase represents the possible boundary separating states with different superconducting symmetries suggested from thermal conductivity measurements [50].

ment parallel to the $[0\ 1\ 0]$ -direction in $H \parallel [0\ 0\ 1]$. This field-induced AFM structure cannot be explained as originating from AFM interactions but instead can be nicely explained to be due to a Γ_5 -type AFQ interaction in a molecular field approximation. That is, FIOP is primarily an AFQ ordered phase and the observed AFM structure is induced as a secondary effect. The inset of Fig. 4 shows a calculated spatial charge distribution of 4f electrons in FIOP. The ordering wave vector of FIOP is exactly the same with \mathbf{q}_A in $\text{PrFe}_4\text{P}_{12}$ and, therefore, a Fermi surface reconstruction should take place. However, no increment in ρ in FIOP [40,41] suggests that the nesting instability of the Fermi surface does not play a key role in the phase transition of $\text{PrOs}_4\text{Sb}_{12}$, contrary to $\text{PrFe}_4\text{P}_{12}$.

The formation of FIOP is intimately related to the 4f electron CEF level scheme. In the T_h site symmetry, the $J = 4$ multiplet of Pr^{3+} ions splits into four sublevels; a singlet Γ_1 , a non-Kramers non-magnetic doublet Γ_{23} and two triplets $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$ (see Ref. [31] for the notation). Although it is clear from specific heat, magnetic susceptibility, and inelastic neutron scattering (INS) studies [37,39,44,45] that the CEF ground state is non-magnetic and it is accompanied by a magnetic triplet excited state separated by $\Delta E/k_B \sim 8$ K, there has been a controversy about whether the ground state is a Γ_1 or a Γ_{23} .

In the Γ_1 ground-state model, FIOP can be understood in the following way. The low-lying singlet–triplet CEF states govern the low temperature physics since the other two are located above 100 K. Reflecting the non-magnetic ground state, $\chi(T)$ shows a maximum at 3.5 K (see Fig. 4). In applied fields, the excited triplet splits by Zeeman effect and its lowest level crosses with the singlet ground state at $H_x \sim 9$ T, forming a quasi-doublet ground state. This is clearly seen in the temperature dependence of the entropy S , which shows a plateau behavior with $S \simeq R \ln 2$ in $H \simeq H_x$ [39]. The quasi-doublet state has a quite large O_{yz} -type quadrupole moment in $H \parallel [0\ 0\ 1]$. By a Γ_5 -type AFQ interaction among Pr ions,

the quadrupole degrees of freedom are frozen out, causing the FIOP to occur [46–48].

On the other hand, in the Γ_{23} ground-state model [44,45], several experimental results cannot be explained, e.g., the aforementioned behavior in entropy, the weak-moment AFM structure observed in FIOP, and the fact that FIOP appears in all the field directions. Furthermore, possible existence of the residual entropy $R \ln 2$ associated with the Γ_{23} state has been ruled out in $\text{PrOs}_4\text{Sb}_{12}$ by magneto-caloric effect experiments [39].

Reported experimental results indicate that the superconducting state in $\text{PrOs}_4\text{Sb}_{12}$ is an anomalous one. Specific heat shows a structure around T_c [44,45,49] and it has been found that the structure depends on samples, as shown in Fig. 5. Clear double jump structure observed in some samples is similar with the one in the typical HF superconductor UPt_3 . This might suggest that $\text{PrOs}_4\text{Sb}_{12}$ also has multiple SC phases with different gap symmetries. Future experimental confirmation is needed to clarify whether the double jump structure is intrinsic or not.

Thermal conductivity measurements in magnetic fields rotated relative to the crystal axes indicate the presence of two distinct superconducting phases with different symmetries with point nodes [50]. This technique utilizes the fact that Doppler shift effect in the supercurrent rotating around fluxoids leads to quasiparticle excitations reflecting the SC gap structure. Thus obtained phase boundary is drawn in Fig. 4. Note that, however, the boundary differs largely from the one corresponding to the specific heat anomaly in Fig. 5. Sb-nuclear-quadrupole-resonance (NQR) $1/T_1$ exhibits no Hebel–Slichter peak just below T_c [51]. All these anomalies point to the SC gap function being anisotropic. In contrast, exponential T dependences of the quasiparticle part of $1/T_1$ in the lower T region [51] and of the magnetic penetration depth determined by a transverse-field muon–spin-rotation study [52] indicate, however, an isotropic SC gap. These inconsistencies, making it difficult to construct a simple picture of the SC state, may suggest that a novel type of HF superconductivity is realized in $\text{PrOs}_4\text{Sb}_{12}$.

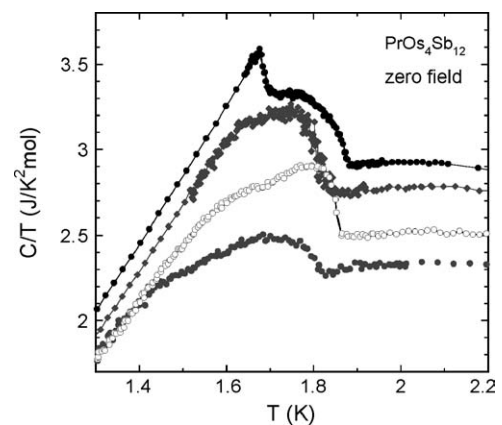


Fig. 5. Expanded view of the specific heat anomaly around the superconducting transition. The structure depends on samples.

One important aspect for characterizing a SC state is whether time-reversal symmetry (TRS) is broken or not [53]. In a state with broken TRS, the magnetic moments of Cooper pairs are non-zero and are ordered ferromagnetically or antiferromagnetically, and thereby spontaneous but extremely small internal magnetic fields can appear inside of the superconductor. To detect such fields, zero-field muon spin relaxation (ZF- μ SR) is the most powerful method, because of its high sensitivity ($\sim 10 \mu\text{T}$ in KEK-MSL). Our ZF- μ SR measurements on $\text{PrOs}_4\text{Sb}_{12}$ have revealed the appearance of spontaneous internal fields below T_c , providing unambiguous evidence for the breaking of TRS in the SC state [54]. Such TRS-broken SC state is quite rare; in addition to $\text{PrOs}_4\text{Sb}_{12}$, convincing observation has been reported only in Sr_2RuO_4 [55]. The broken TRS indicates that the SC state belongs to a degenerate representation, which has internal degrees of freedom. This is inline with the possible existence of multiple superconducting phases suggested by the thermal conductivity study. The breaking of TRS places strong experimental constraints on candidate SC gap functions in $\text{PrOs}_4\text{Sb}_{12}$.

In μ SR study on a no-4f-electron reference superconductor $\text{LaOs}_4\text{Sb}_{12}$ ($T_c = 0.74 \text{ K}$) [56], no sign of spontaneous internal fields is observed. This is consistent with the present understanding that conventional superconductivity is realized in $\text{LaOs}_4\text{Sb}_{12}$, as suggested by a clear Hebel–Slichter peak in Sb-NQR $1/T_1$ [51]. This fact provides convincing evidence for the Pr 4f-electrons playing an essential role for the realization of the TRS breaking superconductivity in $\text{PrOs}_4\text{Sb}_{12}$.

The phase diagram of Fig. 4 is analogous to those for the typical HF and cuprate superconductors, where a magnetically ordered phase exists close to the SC phase in the T -versus-pressure, -atomic-doping, or -oxygen-content phase diagrams [57,58]. In those superconductors, it is widely believed that the Cooper pairing is mediated by magnetic fluctuations. Therefore, in a similar manner, the phase diagram of $\text{PrOs}_4\text{Sb}_{12}$ may suggest that “quantum quadrupole fluctuations” of the Pr ions play an important role in the exotic superconductivity in $\text{PrOs}_4\text{Sb}_{12}$, as well as in the heavy quasiparticle formation. Although this speculation needs to be substantiated further by other means in future, $\text{PrOs}_4\text{Sb}_{12}$ provides with a new, and apparently unique, example of HF superconductivity.

4. Concluding remarks

It has been found that quadrupole ordering appears commonly in both of the typical Pr-based HF compounds $\text{PrFe}_4\text{P}_{12}$ and $\text{PrOs}_4\text{Sb}_{12}$. This fact suggests the scenario that quadrupole degrees of freedom on the Pr-ions play a key role for the HF state formation in this class of materials. In Ce- and Yb-based compounds, it is well understood that HF states often provides quite large thermoelectric power S [59]. We have found that S is also largely enhanced in the HF state of $\text{PrFe}_4\text{P}_{12}$, as mentioned above. Therefore, although these ex-

otic HF states discovered so far in filled skutterudites appear only at low temperatures, there is a hope that understanding of these unconventional electronic states may open a new route for designing thermoelectric materials.

Note added in proof

Recently, in $\text{PrFe}_4\text{P}_{12}$, the existence of a new ordered phase has been found for H//[111] above 7.5 T. Refer to T. Tayama, J. Custers, H. Sato, T. Sakakibara, H. Sugawara, H. Sato, J. Phys. Soc. Jpn. 73 (2004) 3258.

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