Anomalous heavy-fermion and ordered states in the filled skutterudite $PrFe_4P_{12}$

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Specific heat and magnetization measurements have been performed on high-quality single crystals of filled skutterudite $PrFe_4P_{12}$ in order to study the high-field heavy-fermion state (HFS) and low-field ordered state (ODS). From a broad hump observed in C/T vs T in HFS for magnetic fields applied along the $\langle 100 \rangle$ direction, the Kondo temperature of ~ 9 K and the existence of ferromagnetic Pr-Pr interactions are deduced. The ^{141}Pr nuclear Schottky contribution, which works as a *highly-sensitive on-site probe* for the Pr magnetic moment, sets an upper bound for the ordered moment as $\sim 0.03\ \mu_B$/Pr ion. This fact strongly indicates that the primary order parameter in the ODS is nonmagnetic, and most probably of quadrupolar origin, combined with other experimental facts. Significantly suppressed heavy-fermion behavior in the ODS suggests a possibility that the quadrupolar degrees of freedom is essential for the heavy quasiparticle band formation in the HFS. Possible crystalline-electric-field level schemes estimated from the anisotropy in the magnetization are consistent with this conjecture.

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I. INTRODUCTION

Studies of U-based intermetallic systems have revealed that the nature of strongly correlated electron states based on the f^2 configuration can be qualitatively different from those based on the f^1 configuration. Such an example is the possible quadrupolar Kondo coupling of a non-Kramers doublet ground state to conduction electrons in cubic symmetry.[1,2] This coupling, which may be viewed as a screening process of the fluctuating quadrupole moment on the ion by the conduction electrons, can lead to a non-Fermi-liquid (NFL) behavior if the coupling has two symmetric channels.[3] This unconventional scenario has been applied to explain NFL behaviors observed in some cubic U compounds.[4–6] However, doubts have been cast on the realization of the $5f^2$ configuration or a non-Kramers doublet ground state.[7,8] The required substitution with nonmagnetic elements for realization of NFL behavior allows other possible explanations to be proposed instead.[9,10]

In this respect, the exploration of Pr-based correlated-electron systems is highly indicated because $Pr^{3+}(4f^2)$ is the most direct analog of U^{4+}. Compared to $5f$ systems, the smaller spatial extent of the $4f$ orbitals usually causes more localized character with less valence fluctuation. There is little debate regarding the existence of crystalline-electric-field (CEF) levels, and therefore comparison with the aforementioned theoretical models becomes more reliable. Although resulting weaker hybridizations of the $4f$ electron might lead to a smaller energy scale (Kondo temperature T_K), which characterizes the renormalized properties developing at low temperatures, experimental observations are possible in limited systems. Such compounds reported to date are $PrInAg_2$ and $PrFe_4P_{12}$. The former is characterized by the enhanced Sommerfeld coefficient $\gamma \sim 6.5$ J/K^2 mol.[11] The unusual $+\ln T$ dependence[12] of electrical resistivity ρ might indicate the NFL nature of the ground state in this compound.

In the present study, we focus on $PrFe_4P_{12}$, which exhibits a heavy-fermion state (HFS) in applied fields where an ordered state (ODS) is suppressed (see Fig. 2 for a field-vs-temperature H-T phase diagram). The *Fermi-liquid* (FL) nature of the HFS is evidenced by the enormous γ value [$\simeq 1.4$ J/K^2 mol in $\mu_0 H = 6$ T for $H \| \langle 110 \rangle$ (Ref. 13)], which satisfies the Kadowaki-Woods relation[14] along with the T^2 coefficient of electrical resistivity $\rho(T)$ (2.5 $\mu\Omega$ cm/K^2 at 6 T), and the huge cyclotron mass ($m_c^* \simeq 70 m_0$) determined by de Haas–van Alphen (dHvA) studies.[15] To our knowledge, $PrFe_4P_{12}$ is the one and only system in which such definitive evidence for the $4f^2$-based FL heavy-fermion ground state has been obtained. In this paper, we report possible evidence indicating that the HF state is formed via nonmagnetic (most likely quadrupolar) interactions.

II. EXPERIMENT

Single crystals of $PrFe_4P_{12}$ were grown by tin-flux method described in Ref. 16. The observation of the dHvA oscillations[15] ensures high-quality of the sample. Specific heat $C(H,T)$ for $H \| \langle 100 \rangle$ was measured by a quasiadiabatic heat pulse method described in Ref. 17 using a dilution refrigerator equipped with an 8-T superconducting magnet. The temperature increment caused by each heat pulse is controlled to $\sim 2\%$ for the usual measurement and to $\sim 0.5\%$ in limited temperature ranges where the phase transition occurs. The bulk magnetization $M(\mu_0 H \leqslant 5.5\ \mathrm{T}, T \geqslant 2.0\ \mathrm{K})$ was measured with a commercial superconducting quantum-interference device (SQUID) magnetometer (Quantum Design).

III. RESULTS AND DISCUSSIONS

Figure 1 shows the C/T-vs-T data for $H \| \langle 100 \rangle$. In zero field, a clear anomaly indicating the second-order nature of the phase transition appears at $T_A = 6.51$ K. In the early stage, this was regarded as a signature of an antiferromagnetic transition since the magnetic susceptibility (χ) drops below T_A.[16] With decreasing T below T_A, C/T decreases, showing two weak shoulders at around 4 and 1 K. A slight

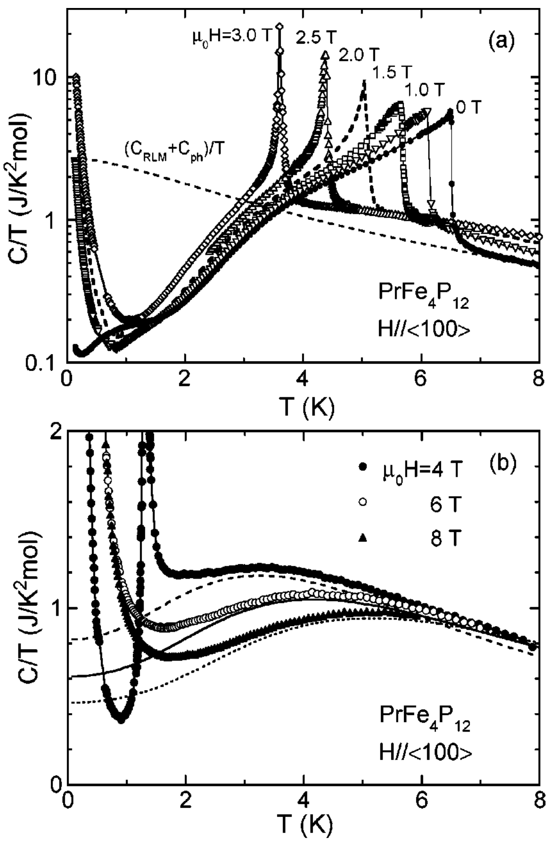

FIG. 1. Total specific heat of $PrFe_4P_{12}$ in magnetic fields of (a) $\mu_0 H \leqslant 3$ T and (b) $\mu_0 H \geqslant 4$ T for $H \| \langle 100 \rangle$. The thin curves represent the best model fittings of the HFS data using RLM (see text).

upturn below 0.2 K, which grows strongly in applied fields, is due to the nuclear Schottky contribution (C_n). With increasing field, the anomaly at T_A shifts to lower temperatures and changes its shape from second-order-like to first-order-like at $\sim$2 T. Actually, at temperatures very close to the phase transition in $\mu_0 H = 2$–4 T, Barkhausen-like heating is intermittently observed during heat pulse measurements. The determined phase boundary between the HFS and ODS is plotted in a H-T phase diagram in Fig. 2. In the HFS above $\mu_0 H = 4$ T, a broad hump appears at a temperature $T_{\max}$, which shifts to higher temperatures with increasing field. For $H \| \langle 110 \rangle$,[13] no such hump is observed up to 8 T although the overall T dependence of C/T is similar to that of the present data. The hump structure and the enormously enhanced C/T in the temperature range of $T \lesssim T_{\max}$ cannot be explained by a simple Schottky model with a few separated levels. Actually, C/T does not show any exponential decrease with lowering temperature below $T_{\max}$. This fact indicates that, at least in the measured temperature range, ''well-localized Pr ions with a dominant CEF effect'' does not provide an appropriate picture in $PrFe_4P_{12}$ and many-body effects should be taken into account.

The measured specific heat C can be expressed as $C_{\mathrm{el}} + C_n + C_{\mathrm{ph}}$. For an estimation of the phonon contribution C_{ph}, we use βT^3 with $\beta = 2.59 \times 10^{-4}$ J/K^4 mol reported for $LaFe_4P_{12}$.[18] Even at 8 K, C_{ph} amounts to only 3% of the total value of C due to the huge contribution of C_{el}.

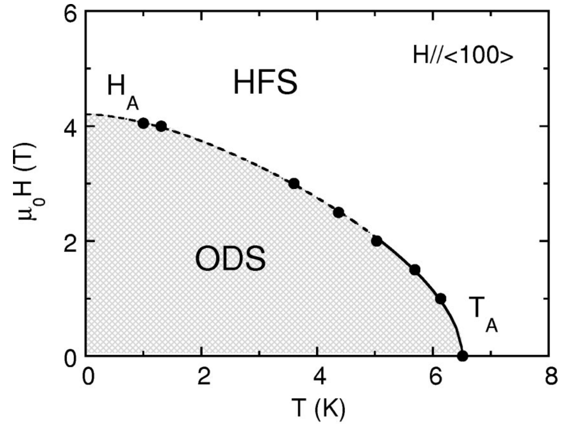

FIG. 2. Magnetic field vs temperature phase diagram. The broken and solid curves represent first-order and second-order phase boundaries, respectively.

The hump structure in C/T vs T is attributed to the low-energy thermal excitations in heavily renormalized quasiparticle bands formed around the Fermi level (E_F). As a phenomenological model to describe the excitations, we employ the resonance level model[19] (RLM), which assumes a Lorentzian density of states centered at E_F with a T-independent width ($\Delta \sim T_K$). Although this model is unrealistic, it has been applied successfully to describe the $C(T)$ data and to extract the characteristic energy scale on Ce-based HF compounds, e.g., $CeRu_2Si_2$ (Ref. 20) and $CeCu_6$ (Ref. 21). We use the following slightly modified definition for the electronic specific heat, entropy, and magnetization:

$$C_{\mathrm{RLM}} = \delta C_{SS}(T, \Delta, g\mu_B H_{\mathrm{eff}}), \tag{1a}$$

$$S_{\mathrm{RLM}} = \delta S_{SS}(T, \Delta, g\mu_B H_{\mathrm{eff}}), \tag{1b}$$

$$M_{\mathrm{RLM}} = \delta M_{SS}(T, \Delta, g\mu_B, H_{\mathrm{eff}}), \tag{1c}$$

where the functions of C_{SS}, S_{SS}, and M_{SS} are defined in Ref. 19 and H_{eff} denotes an effective field acting on the electrons. The prefactor δ is phenomenologically introduced considering that the entropy release associated with the hump structure is larger than $R \ln 2$ (see Fig. 5). The connotation of δ will be discussed below.

In zero field ($H_{\mathrm{eff}} = 0$), experimental values of $C_{\mathrm{el}}/T = 0.465$ J/K^2 mol and electronic entropy $S_{el} = 10.2$ J/K mol at $T = 8$ K (see Fig. 5) uniquely lead to $\Delta = 8.7$ K and $\delta = 2.7$. A model calculation of C_{el}/T using these values is shown in Fig. 1(a) by a broken thin curve. The model curve, which satisfies the entropy balance with the zero-field data, approaches 2.7 J/K^2 mol as $T \rightarrow 0$. For the high-field data shown in Fig. 1(b), the only fitting parameter is $g\mu_B H_{\mathrm{eff}}$, which is determined so that $T_{\max}$ can be reproduced. Thus determined model curves shown in Fig. 1(b) demonstrate that the hump structure is described fairly well by Eq. (1a). The resulting effective Zeeman energy $(1/2) g \mu_B H_{\mathrm{eff}}$ as a function of H falls on a straight line as shown in Fig. 3. Assuming the effective g factor to be H independent between 4 and 8 T, $g = 2.2$ is obtained from the slope in Fig. 3. The absence of the hump structure in C/T for $H \| \langle 110 \rangle$ up to 8 T

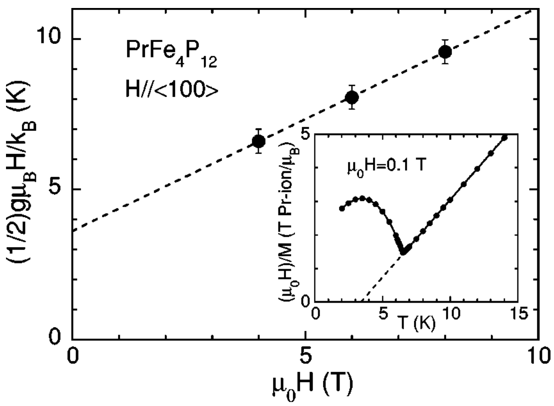

FIG. 3. Magnetic field dependence of the effective Zeeman energy determined by the fitting shown in Fig. 1(b). The inset shows the T dependence of inverse magnetic susceptibility.

(Ref. 13) is due to the smaller g for this geometry, in accordance with the anisotropy in M, as will be discussed below. The positive intercept in Fig. 3 indicates ferromagnetic interactions among the Pr ions with an energy scale of $\sim$3.6 K, which is consistent with the positive Weiss temperature $\theta_p = +3.5$ K determined from the magnetic susceptibility $\chi \equiv M/(\mu_0 H)(\mu_0 H = 0.1$ T) data below 20 K (inset of Fig. 3). This feature contrasts strikingly with the negative θ_p's observed in Ce-based Kondo lattice compounds, where $|\theta_p|$ provides a rough estimate of T_K. We also compare $M(T)$ measured in $\mu_0 H = 5.5$ T with $M_{\mathrm{RLM}}(T)$ given by Eq. (1c). At 2.0 K, M and M_{RLM} are 1.83 and 1.58 μ_B/Pr ion, respectively. Except for the slightly smaller value of M_{RLM}, the general feature of gradually decreasing M with increasing T is well reproduced (not shown).

The observed nuclear Schottky contribution C_n is mostly caused by Pr nuclei (nuclear spin $I = 5/2$ for ^{141}Pr with the natural abundance of 100%). The contribution from Fe and P nuclei is negligibly small. The nuclear magnetic moment averaged over the existing isotopes $\overline{I(I+1)g_N^2}$ is 5.3×10^{-4} and 3.84 for Fe and P, respectively. Using these values, the contribution from Fe and P nuclei can be estimated as $C_n = 1.7\times 10^{-5}(\mu_0 H_{\mathrm{hf}}/T)^2$ J/K mol, which amounts to only 0.4% of the observed C_n in 8 T assuming $\mu_0 H_{\mathrm{hf}} \simeq 8$ T.

The observed Pr nuclear Schottky contribution is largely enhanced. This is due to the strong intrasite hyperfine coupling between the nucleus and $4f$ electrons on the same Pr ion. The Hamiltonian for the Pr nucleus can be written as[22]

$$\mathcal{H}_n = a' I_z + P[I_z^2 - I(I+1)/3], \tag{2}$$

where the z axis lies in the direction of $\langle \mathbf{J} \rangle$ for each Pr ion. Here $a'(=A\langle J_z\rangle)$ and $P[=B\langle J_z^2 - J(J+1)/3\rangle]$ are the magnetic dipole hyperfine interaction parameter and the electric quadrupole coupling constant, respectively. For each magnetic field, the values of a' and P can be determined by fitting the observed $C_n(T)$ data to the model given by Eq. (2). Consequently, if the coupling constant A is known, $\langle J_z\rangle$ will be obtained. In the following data analysis, we replace $\langle J_z\rangle$ by the site-averaged quantity $(\overline{|\langle J_z\rangle|^2})^{1/2}$ since the Pr ions are most probably separated into inequivalent sites in the ODS and the measured specific heat provides the site-averaged quantity. Using this, we define the site-averaged magnitude of the Pr magnetic moment $m_{\mathrm{Pr}} \equiv g_J(\overline{|\langle J_z\rangle|^2})^{1/2}$.

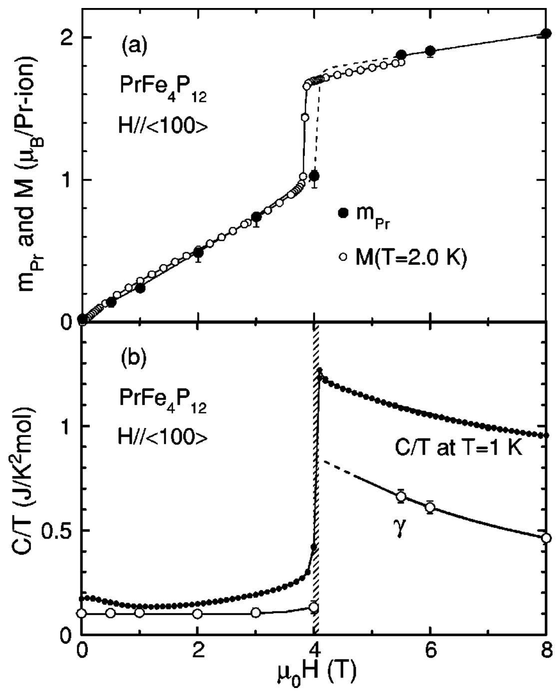

FIG. 4. (a) Magnetic field dependences of the site-averaged magnitude of the Pr magnetic moment m_{Pr} and bulk magnetization $M(T=2.0$ K). (b) $\gamma \equiv C_{\mathrm{el}}/T|_{T\to 0}$ estimated by the fitting below 2 K (see text). C/T vs $\mu_0 H$ measured at 1 K is shown for comparison.

We experimentally determine the coupling constant A in the HFS, where $\langle \mathbf{J}\rangle$ is polarized along the applied field for all Pr ions. In $\mu_0 H = 5.5$ T, $M(T\to 0) = g_J\langle J_z\rangle = 1.89$ μ_B/Pr ion and a' is obtained to be 0.122 K. The determined $A = 0.052$ K agrees well with reported theoretical values.[23,24]

In order to separate C_n and C_{el}, we use Eq. (1a) in the HFS and $\gamma T + \alpha T^n$ in the ODS for C_{el}. The H dependences of m_{Pr} and γ, obtained by fitting $C(T)$ data below 2 K, are shown in Fig. 4. The resulting exponent n ranges from 4.1 to 4.3. In the HFS, P is determined to be $(7\pm 2)\times 10^{-3}$ K; for the precise determination of P in low fields, the measurement should be extended further below 0.1 K.

A remarkable feature in Fig. 4(b) is that γ is substantially reduced ($\simeq 0.1$ J/K^2 mol) and almost H independent in the ODS, and it rises sharply to ~ 1 J/K^2 mol at H_A. Field-scan data of C/T measured at 1 K [shown in Fig. 4(b) for comparison] also reflects this feature; the difference between the C/T and γ data comes mainly from the nuclear contribution in HFS and the magnetic excitation approximated as αT^n in the ODS. This observation evidently shows that the HF behavior is significantly suppressed in the ODS.

In Fig. 4(a), m_{Pr} is compared with $M(H)$ data measured at 2.0 K. A small difference in H_A is due to the temperature dependence of H_A (see Fig. 2). Agreement between the two sets of data is quite good even in the ODS taking into account the weak temperature dependence of M; e.g., $M(T\to 0)$ is only 1% smaller than $M(T=2$ K) in $\mu_0 H = 3$ T. This agreement clearly shows that the reduced M in the ODS

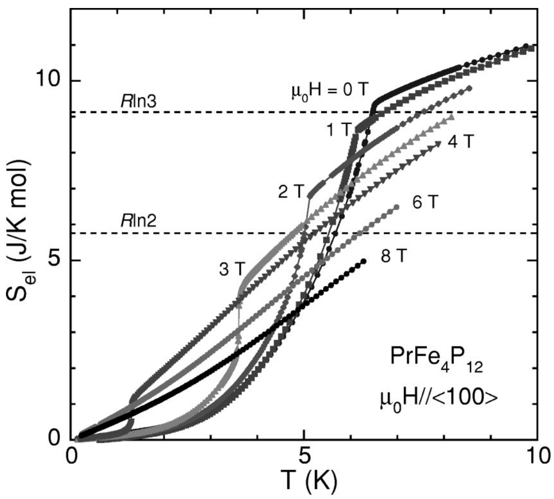

FIG. 5. Temperature dependence of the electronic part of entropy $S_{\rm el}$ calculated integrating the $C_{\rm el}/T$ data. Because of the Barkhausen-like heating occurring at the first-order phase transition in $\mu_0H=2$–4 T, thus calculated $S_{\rm el}$ above T_A becomes lower than the true values. By magnetization measurements using a Maxwell relation of $[\partial S/\partial(\mu_0H)]_T=[\partial M/\partial T]_{\mu_0H}$, we have corrected the $S_{\rm el}$ data in $T>T_A$. In zero field, $S_{\rm el}$ data for $T>T_A$ are nicely reproduced by the RLM model given by Eq. (1b), which provides an asymptotic entropy of $S_{\rm el}(T\to\infty)=R\ \ln(2^{\delta})\simeq R\ln(6.5)$.

is mainly due to the shrinkage of each Pr magnetic moment itself, not due to cancellation among the Pr magnetic moments as usually observed in classical antiferromagnets. For example, the $M(H)$ curve of $HoGa_2$ shows complex field-induced metamagnetic phase transitions, though the Ho nuclear specific heat (i.e., the magnitude of each Ho magnetic moment) is of H independence, reflecting that the metamagnetic behavior in $M(H)$ is due to the change in the Ho moment cancellation depending on the field-induced magnetic structures.[25]

As shown in Fig. 4(a), $m_{\rm Pr}$ decreases significantly as $H\to 0$. The extremely small $C_n\simeq 6.4\times 10^{-5}/T^2$ J/K mol observed in zero field sets an upper bound for the ordered $m_{\rm Pr}$, i.e., $\leqslant 0.03\ \mu_B$/Pr ion. The extremely small $m_{\rm Pr}$ along with the large entropy decrease below T_A as shown in Fig. 5 strongly suggests that the primary order parameter in the ODS is not the Pr magnetic moment but of nonmagnetic origin. This is consistent with the absence of magnetic Bragg peaks at 1.5 K in a powder neutron diffraction study[26] in which typical sensitivity is of the order of $0.1\mu_B$/Pr ion.

In the nonordered state, it is found that the low-temperature properties cannot be described quantitatively in a well-localized Pr-ion picture. For example, the specific heat cannot be described by a simple CEF model producing a Schottky anomaly. It is expected, however, that some of the qualitative features may reflect the CEF effect playing a role in the background of the strong hybridization. The T_h site symmetry of the Pr^{3+} ions with no fourfold rotation axis leaves a nonvanishing $O_6^2-O_6^6$ term in the CEF Hamiltonian,[27] along with the usual cubic terms of $O_4^0+5O_4^4$ and $O_6^0-21O_6^4$. If the $O_6^2-O_6^6$ term is dominant, one of the two magnetic triplets will be stabilized as the CEF ground state and consequently the anisotropy in M will be $M(H\|\langle 111\rangle)>M(H\|\langle 110\rangle)>M(H\|\langle 100\rangle)$ at low temperatures. Magnetization curves measured in applied fields along the main symmetry directions are shown in Fig. 6. Since $M(H\|\langle 100\rangle)>M(H\|\langle 110\rangle)>M(H\|\langle 111\rangle)$ is observed in the nonordered state, the above possibility is ruled out. In the following analysis, therefore, we assume that the $O_6^2-O_6^6$ term is negligibly small and we use the O_h point-group notation for CEF levels described by Lea, Leask, and Wolf[28] (LLW) (see Ref. 27 for the $O_h\leftrightarrow T_h$ correlation table). In this notation, the two CEF parameters are represented by W and x. We calculated magnetization for a single-site Pr ion at 2.5 K in a magnetic field of 5.5 T in order to compare with the experimental data. The results are shown in Fig. 7 as a function of x. For each x, the absolute value of W is determined so that $S_{\rm el}(T=8\ {\rm K})=10.2$ J/K mol is satisfied. No molecular field for the dipole or multipole Pr-Pr interactions is taken into account in the calculation. The observed anisotropy in M is qualitatively reproduced when $0\lesssim x\leqslant 1$ for $W<0$ or $-1\leqslant x\lesssim 0$ for $W>0$. In these parameter regions, the CEF ground state is a Γ_1 singlet or a Γ_3 non-Kramers doublet; in

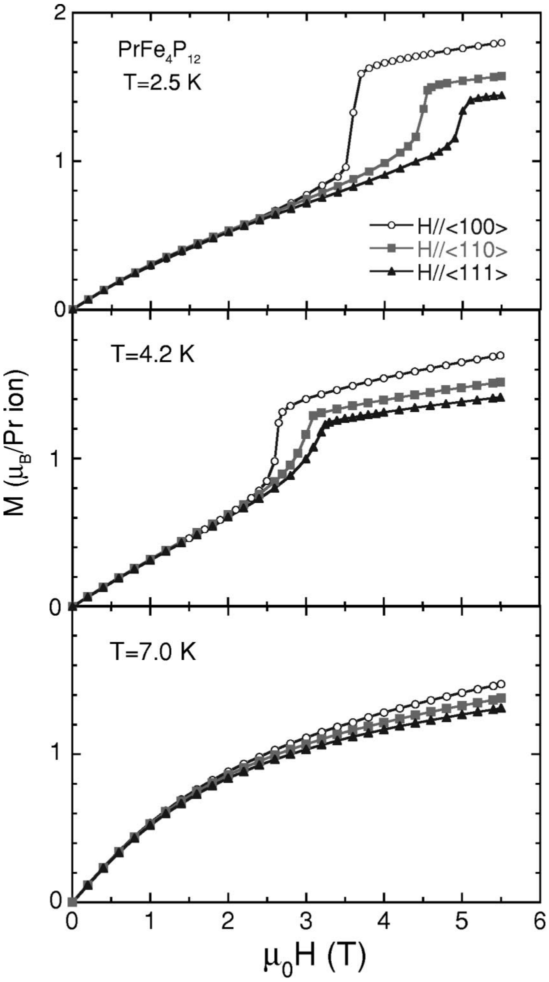

FIG. 6. Magnetization curves measured at 2.5, 4.2 and 7 K in external fields along the main symmetry directions. The observed magnetic anisotropy of $M(H\|\langle 100\rangle)>M(H\|\langle 110\rangle)>M(H\|\langle 111\rangle)$ is the feature of the nonordered state.

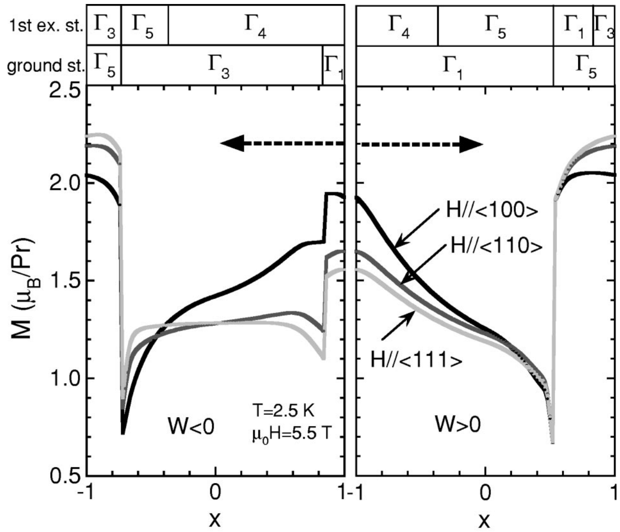

FIG. 7. x dependence of the calculated magnetization for a single-site Pr ion at 2.5 K in a magnetic field of 5.5 T. For each x, the absolute value of W is determined so that $S_{\mathrm{el}}(T=8\ \mathrm{K})=10.2$ J/K mol is satisfied. No molecular field for the dipole or multipole Pr-Pr interactions is taken into account. Broken arrows indicate the parameter region where the magnetization anisotropy is qualitatively consistent with the experimental data. The upper panel shows the ground and first excited CEF states.

either case the ground state is nonmagnetic, in accordance with the nonmagnetic nature of the ODS. A Γ_5 triplet ground state is highly unlikely.

The magnetic susceptibility χ in the ODS has quite large values, as readily recognized in both the inset of Fig. 3 and the magnetization curve shown in Fig. 4(a). If the observed χ in the ODS were attributed to itinerant electrons with $\gamma \simeq 0.1$ J/K^2 mol, an unreasonably large effective moment $\mu_{\mathrm{eff}}=15\ \mu_B$/carrier would be needed, indicating that the observed χ in the ODS is attributed to the well-localized $4f$ electrons, of which the c-f hybridization is substantially suppressed. Attributing $\chi \simeq 0.4\ \mu_B$/T Pr ion for $T \to 0$ in the ODS to a Van Vleck susceptibility, following possible CEF level schemes are deduced. (i) In the case of the Γ_1 ground state, a Γ_4 state is located at $E(\Gamma_4)\simeq 13$ K above the ground state, taking into account the Γ_1 ground state having only one nonzero matrix element of J_z with the Γ_4 state. Since the experimental $S_{\mathrm{el}}(T=8\ \mathrm{K})=10.2$ J/K mol shown in Fig. 5 denies the possibility that a Γ_5 state is located below $\sim$13 K as the first excited state, one can conclude that the Γ_4 state is the first excited state and the Γ_5 state should be located above it. The calculated entropy at 8 K in zero field (in the nonordered state) neglecting the Γ_5 state and the other higher levels is 8.9 J/K mol, which is not far from the experimental value. (ii) In the case of the Γ_3 ground state, $\Gamma_3^{(1)}$, referring to $\sqrt{7/24}(|4\rangle+|-4\rangle)-\sqrt{5/12}|0\rangle$ ($|M\rangle$ represents an eigenstate of J_z), has only one nonzero matrix element of J_z with a Γ_4 state and so does $\Gamma_3^{(2)}$, referring to $\sqrt{1/2}(|2\rangle+|-2\rangle)$, with a Γ_5 state. Therefore, with a similar consideration as in the case (i), one can conclude that the first excited state is a Γ_4 state, which is located at $E(\Gamma_4)\simeq 18$ K if it can be assumed that all the Pr ions have the $\Gamma_3^{(1)}$ ground state in the ODS. Using the value of $E(\Gamma_4)$, the calculated entropy at 8 K in zero field (in the nonordered state), neglecting the Γ_5 state and the other higher levels, is 9.6 J/K mol, which is also not far from the experimental value. From the rough discussion mentioned above based on the present specific-heat and magnetization results, we propose that the possible CEF level schemes are $\Gamma_1-\Gamma_4$ ($\sim$13 K) and $\Gamma_3-\Gamma_4$ ($\sim$18 K). Noted that the energy level of the first excited state should be considered as a rough estimation since we have made some assumptions in the discussion, e.g., the modification due to the ordering of the wave functions and the energy levels of the CEF levels to be small enough. In order to check our proposal, an inelastic neutron scattering measurement is planed.

An ultrasonic study reported by Nakanishi *et al.*[29] demonstrates that the elastic constants of c_{11} and $c_{11}-c_{12}$ shows softening below $\sim$20 K down to T_A while c_{44} does not. From this fact, they claim that the CEF level scheme is $\Gamma_3-\Gamma_4$, which is the same as one of our proposed models. Below T_A, both c_{11} and $c_{11}-c_{12}$ start to increase. From these observations, they proposed that the order parameter in the ODS would be an antiferroquadrupole ordering with Γ_3 symmetry, where the twofold degeneracy of the Γ_3 ground state is lifted. If this is the case, $S_{\mathrm{el}}(T=T_A)$, being larger than $R \ln 2$, indicates that the excited Γ_4 state, which also has the same types of quadrupole moments as the Γ_3 ground state, is also relevant to the ordering.

In the case of the $\Gamma_1-\Gamma_4$ level scheme, which cannot be ruled out by our present study, the Γ_1 ground state itself has no degrees of freedom. However, since the energy separation between the two levels is comparable to the estimated value of T_K, one can speculate that the Γ_4 excited state contributes much to the renormalized physical properties at low temperatures. Due to the quadrupole degrees of freedom relevant to the Γ_4 state, a quadrupole ordering could take place also in this case.

In the ODS, where the quadrupolar degeneracy is most probably lifted, the strong suppression of the HF behavior is observed as shown in Fig. 4(b). This observation points to a possibility that the fluctuation of the quadrupole moments in the nonordered state is playing an essential role for the heavy-fermion state formation. Figure 4(a) shows that m_{Pr} develops monotonically with increasing magnetic field and approaches as large as 60% of the HFS value at H_A. The insensitivity of the suppression of the HF behavior to the field-induced m_{Pr} in the ODS implies that the suppression of the HF behavior is not due to any magnetic sources, probably consistent with our conjecture.

Any sign of possible NFL behaviors, which could be caused by the quadrupolar Kondo effect, have not been observed in $PrFe_4P_{12}$, contrasting remarkably with $PrAgIn_2$. The instability of NFL state against FL state has been studied theoretically in some model cases,[30] although comparison with the real systems are still insufficient. In $PrFe_4P_{12}$, largely enhanced negative thermopower[31] below 50 K suggests the predominant hybridization process to be between f^2 and f^3 configurations.[32] The virtual f^3 configuration is expected to have a quartet ground state since the CEF ground state of $NdFe_4\ P_{12}$ is a quartet.[16] In this scheme, the c-f

hybridization should have complicated multichannels. Another factor needed to be considered is the closely located CEF excited state in the f^2 configuration in $PrFe_4P_{12}$. In the case of the $\Gamma_3-\Gamma_4$ level scheme, the Γ_4 excited state might cause the instability of the NFL state relevant to the Γ_3 ground state, as demonstrated in a non-Kramers doublet and a singlet case.[30] For deeper understanding of the NFL-against-FL stability issue, a theoretical study of the present case, which has not yet been done, is clearly indicated.

A band structure calculation on $LaFe_4P_{12}$, which consistently explains the observed angular dependence of the dHvA branches, indicates that the Fermi surface consists of a nearly spherical hole sheet (47th) and a multiply connected one (48th).[33] The latter is characterized by strong c-f hybridizations. Therefore, the heavily renormalized quasiparticle bands observed in $PrFe_4P_{12}$ are expected to be mostly attributed to the corresponding 48th sheet of $LaFe_4P_{12}$. As pointed out by Harima in Sugawara *et al.*[33] its nearly cubic shape may favor a commensurate three-dimensional nesting with $\mathbf{q}=\{1,0,0\}$. This conjecture is supported by some of the corresponding x-ray satellite peaks observed[34] in the ODS and the carrier reduction suggested by jumps in the electrical resistivity and the Hall coefficient at T_A.[31] The lattice distortion (or the charge ordering) and the associated gap opening on some part of the corresponding Fermi sheet should be also taken into account to understand the nature of the ODS.

IV. SUMMARY

We have studied the heavy-fermion and the anomalous ordered states in filled skutterudite $PrFe_4P_{12}$ by specific-heat and magnetization measurements. From a broad hump observed in C/T vs T for $H\|\langle 100\rangle$ in the HFS, the Kondo temperature of ~ 9 K and the existence of ferromagnetic Pr-Pr interactions are deduced. Utilizing the ^{141}Pr nuclear Schottky contribution, an upper bound for the site-averaged Pr ordered magnetic moment is obtained to be $\sim 0.03\ \mu_B$/Pr ion. This fact strongly indicates that the primary order parameter in the ordered state is nonmagnetic, most probably of quadrupolar origin, as suggested by the ultrasound measurements. Significantly suppressed heavy-fermion behavior in the ordered state suggests a possibility that the quadrupolar fluctuation of the Pr ions leads to the heavy quasiparticle band formation in the high-field heavy-fermion state. Possible crystalline-electric-field level schemes of the Pr^{3+} ions estimated from the anisotropy in the magnetization and the electronic part of entropy are $\Gamma_1-\Gamma_4$ and $\Gamma_3-\Gamma_4$ [(ground state)–(first excited state)], both of which are consistent with the aforementioned conjecture. The present study demonstrates that $PrFe_4P_{12}$ could be an unprecedented system, where the role of the quadrupole moments can be studied for the realization of the rare $4f^2$-based heavy-fermion state due to the existence of the ordered state, which is not available in $PrInAg_2$.

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