Thermodynamical Study on the Heavy-Fermion Superconductor PrOs$_4$Sb$_{12}$: Evidence for Field-Induced Phase Transition

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We report measurements of low-temperature specific heat on the $4f^2$-based heavy-fermion superconductor PrOs$_4$Sb$_{12}$. In magnetic fields above 4.5 T in the normal state, distinct anomalies are found which demonstrate the existence of a field-induced ordered phase (FIOP). The Pr nuclear specific heat indicates an enhancement of the $4f$ magnetic moment in the FIOP. Utilizing a Maxwell relation, we conclude that anomalous entropy, which is expected for a single-site quadrupole Kondo model, is not concealed below 0.16 K in zero field. We also discuss two possible interpretations of the Schottky-like anomaly at $\sim 3$ K, i.e., a crystalline-field excitation or a hybridization gap formation.

The $f$-electron-related heavy fermion (HF) systems exhibiting superconductivity had been found only in Ce and U intermetallic compounds. Therefore, the recent observation of the first Pr-based heavy fermion superconductor (HFSC) in a filled skutterudite PrOs$_4$Sb$_{12}$ [1] has profound scientific significance.

The $4f^2$ configuration of Pr ions in intermetallic compounds had been considered to be quite stable in view of no observation of strongly correlated electron behaviors until recent studies on PrIn$_3$Ag [2] and PrFe$_4$P$_{12}$ [3–5], in which this picture breaks down. In PrFe$_4$P$_{12}$, which is also a member of the filled skutterudites, we have shown by specific heat [3], electrical resistivity [4] and de Haas-van Alphen (dHvA) effect measurements [5] that HF behaviors appear in high fields where a nonmagnetic ordered state, probably of quadrupole origin, is suppressed. To our knowledge, PrFe$_4$P$_{12}$ is the only system in which such definitive evidence for the $4f^2$-based Fermi-liquid HF ground state has been obtained.

Compelling evidence for the HFSC in PrOs$_4$Sb$_{12}$ was given by a large specific heat jump $\Delta C/T = 0.5$ J/K$^2$ mol at $T_c = 1.85$ K on a pellet of compressed powdered single crystals [1]. The jump is superimposed on a Schottky-like anomaly appearing at $\sim 3$ K. Bauer et al. attributed this peak to a doublet-triplet ($\Gamma_3 - \Gamma_5$ in $O_h$-type notation) crystalline-electric-field (CEF) thermal excitation, combining with their magnetic susceptibility $\chi(T)$ and inelastic neutron scattering data. Since the $\Gamma_3$ non-Kramers doublet ground state has quadrupole degrees of freedom, they pointed out a possibility that the HF behavior is associated with a quadrupolar Kondo effect [6] on the Pr-ion lattice. In order to confirm this scenario, it is especially important to clarify how the entropy $R \ln 2$ associated with the $\Gamma_3$ ground state is released and whether any residual entropy is hidden far below $T_c$ or not.

In this letter, we report two important findings in PrOs$_4$Sb$_{12}$ based on specific heat and magnetization measurements on high-quality single crystalline samples: (1) clear evidence for the existence of a field-induced ordered phase (FIOP) and (2) a confirmation of no anomalous entropy concealed below 0.16 K in zero field.

Single crystals of the filled skutterudite PrOs$_4$Sb$_{12}$ and the reference compound LaOs$_4$Sb$_{12}$ were grown by Sb-flux method [7]. The raw materials were 4N(99.99% pure)-Pr, 4N-La, 3N-Os and 6N-Sb. No impurity phase was detected in a powder x-ray diffraction pattern. The lattice parameter was determined to be $a=9.301$ Å for PrOs$_4$Sb$_{12}$ and $a=9.306$ Å for LaOs$_4$Sb$_{12}$. The observation of the dHvA oscillations in both compounds [7] ensures high-quality of the samples. The electrical resistivity $\rho(T)$ for PrOs$_4$Sb$_{12}$ shows qualitatively the same behavior as reported in ref. [1]. No Kondo-like behavior is visible in $\rho(T)$ although we cannot conclude whether any such behavior exists or not in the small 4f-electron contribution $\rho_{4f}(T)$ estimated by subtracting $\rho(T)$ of LaOs$_4$Sb$_{12}$. Specific heat $C(H,T)$ for $H \parallel \langle 100 \rangle$ was measured by a quasidiabatic heat pulse method described in ref. [8] using a dilution refrigerator equipped with an 8-T superconducting magnet. The temperature increment caused by each heat pulse is controlled to be $\sim 2\%$. The bulk magnetization $M(\mu_0 H \leq 7$ T, $T \geq 1.9$ K) was measured with a Quantum-Design superconducting quantum-interference device (SQUID) magnetometer.

Figure 1 shows the $C$-vs-$T$ data for $H \parallel \langle 100 \rangle$. In zero field, the data exhibit a Schottky-like anomaly with a maximum of 6.82 J/Kmol at 3.1 K, clearly showing the existence of a low-lying excitation in the $f$-electron system. In a $C/T$ vs $T$ plot (not shown), the peak appears at 2.1 K with a height of 2.8 J/Kmol, which is 39 % larger than the value reported in ref. [1] for the compressed powdered single crystals, although the overall temperature dependence is similar. In our data, a jump of $\Delta C/T = 0.52$ J/K$^2$ mol associated with the SC transition is observed at $T_c = 1.81$ K. Details on the SC properties will be reported elsewhere [9].

As Fig. 1 reveals, the anomaly at $\sim 3$ K is found to be drastically suppressed with increasing magnetic field. This field-sensitive behavior confirms that the low-lying excitation has a magnetic character. In 5 T, a kink appears at $\sim 0.7$ K and changes the shape into a clear $\lambda$-type peak at $T_s = 0.98$ K in 6 T. With further increasing field, the peak in the $C(T)$ curve grows and $T_s$ shifts to higher temperatures. This is the clear thermodynam-
Negligibly small and smoothly-increasing C (netic field is due to the nuclear Schottky contribution both the Schottky-like anomaly at \( \sim 3 \) K and the FIOP below \( T_x \) in PrOs\(_4\)Sb\(_{12}\).

An upturn in \( C(T) \) below 0.5 K developing with magnetic field is due to the nuclear Schottky contribution \( (C_n) \). The observed \( C_n \) is mostly caused by Pr nuclei (nuclear spin \( I = 5/2 \) for \(^{141}\)Pr with the natural abundance of 100\%) because of the strong intrasite hyperfine coupling between the nucleus and 4f-electrons on the same

To estimate the phonon contribution to the specific heat, \( C_{ph} \), we measured \( C(T) \) of a single crystal LaOs\(_4\)Sb\(_{12}\). The obtained \( C_{ph}(T) \) is shown in Fig. 1. Negligibly small and smoothly-increasing \( C_{ph} \) below 4 K strongly indicates that 4f electrons play essential roles in both the Schottky-like anomaly at \( \sim 3 \) K and the FIOP below \( T_x \) in PrOs\(_4\)Sb\(_{12}\).

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![FIG. 1. Specific heat \( C(T) \) of PrOs\(_4\)Sb\(_{12}\) in different magnetic fields. The broken curve represents the phonon part \( C_{ph}(T) \) determined from the \( C(T) \) data of LaOs\(_4\)Sb\(_{12}\).](image)

![FIG. 2. Magnetic field vs temperature phase diagram. The superconducting boundary is the data from ref. [1]](image)

![FIG. 3. Magnetic field dependence of estimated \( A_n^{1/2} \) in the nuclear specific heat \( C_n = A_n/T^2 \). (\( CT^2 \))\(^{1/2} \) at \( T = 0.2 \) K is also shown to provide an upper bound for \( A_n^{1/2} \). The lines are guides to the eye.](image)

Pr ion. This feature allows one to use \( C_n \) as an on-site probe for the Pr 4f magnetic moment; utilizing this, we have demonstrated that the ordered state in PrFe\(_4\)P\(_{12}\) appearing below 6.5 K is non-magnetic in origin [3]. We analyze the \( C_n \) data to obtain information on the 4f magnetic moment of Pr ions in PrOs\(_4\)Sb\(_{12}\), although the situation is complicated compared to PrFe\(_4\)P\(_{12}\) because of a non-negligible Sb nuclear contribution. In order to separate \( C_n \) from \( C_{ph} \), we tentatively assume

\[
C(T) = A_n/T^2 + \gamma T + \alpha T^n
\] (1)
at low temperatures. In eq. (1), the first term represents \( C_n \) (the sum of all the nuclear contributions in PrOs\(_4\)Sb\(_{12}\)) and the other two terms represent the low-temperature excitation in \( C_{ph}(T) \). The field dependence of \( A_n^{1/2} \) obtained by fitting below 0.6 K is shown in Fig. 3. To show an upper bound for \( A_n^{1/2} \) based on eq. (1), (\( CT^2 \))\(^{1/2} \) at \( T = 0.2 \) K is also plotted. The observed zero-field-value of \( A_n^{1/2} = 2.9 \times 10^{-2} \) [JK/mol]\(^{1/2} \) is attributable to the Sb nuclei quadrupole contribution 2.87 \( \times 10^{-2} \) [JK/mol]\(^{1/2} \), which is calculated from recent \(^{121,123}\)Sb NQR measurements [10]. With increasing magnetic field, \( A_n^{1/2} \) increases gradually and shows a slight upward curvature around the boundary of the FIOP. At the upper critical field \( \mu_0 H_{c2} = 2.2 \) T, no anomaly can be seen. The field-dependent part in the \( A_n^{1/2} \) vs \( H \) curve is mostly due to the magnetic Pr nuclear contribution; the magnetic contribution from Os and Sb nuclei gives only \( \sim 1 \% \) of the observed field dependence. This contribution to \( A_n \) can be expressed by

\[
A_n^{Pr} = R(A_{hf}m_{Pr}/g_I)^2 I(I + 1)/3,
\] (2)

where \( R, A_{hf}, m_{Pr} \), and \( g_I \) are the gas constant, the magnetic dipole hyperfine coupling constant, the
site-averaged magnitude of the Pr magnetic moment
\( gJ\sqrt{(\langle J_z \rangle^2)} \) \(^{1/2} \) and the Landé \( g \)-factor, respectively.
Therefore, the field-dependent part of \( A_n^{1/2} \) in Fig. 3 reflects the \( m_{Pr} \) vs \( H \) curve. Using \( A_{hf} = 0.052 \) K, which was determined for PrFe\(_4\)P\(_{12}\) [3] and is consistent with theoretical calculations [11,12], the experimental value \( A_{hf}^T = 0.105 \) JK/mol for \( \mu_0H = 8 \) T leads to an estimation \( m_{Pr} = 1.01 \mu_B/\text{Pr} \) in this field. The upturn at \( \sim 4.5 \) T in \( A_n^{1/2}(H) \) compared to a smooth extrapolation from the lower fields indicates that \( m_{Pr} \) (and probably also \( M \)) is enhanced in FIOP.

An enhancement of \( M \) in the FIOP is expected independently from the Ehrenfest’s theorem:

\[ \Delta(\partial M/\partial T)_H = -\langle \Delta C/T_c \rangle (dT_x/d(\mu_0H)), \quad (3) \]

which should be satisfied at the second-order phase boundary of the FIOP. Since \( dT_x/dH \) is positive in the measured field range as shown in Fig. 2, \( \Delta(\partial M/\partial T)_H \) should be negative; this feature was actually observed in a recent low-temperature magnetization study [13]. For \( \mu_0H = 6 \) T, \( \Delta(\partial M/\partial T)_H \approx -0.04 \mu_B/\text{Pr} \) K is calculated.

We obtained the temperature dependence of the electronic part of entropy \( S_e(T) \) by numerically integrating the data of \( C_e/T \equiv (C - C_n - C_{ph})/T \) vs \( T \). Since our measurements are made above 0.16 K, only \( \Delta S_e(T) \equiv S_e(T) - S_e(0.16 \) K) can be obtained from the present study. Therefore, we tentatively plot \( S_e(T) \) in Fig. 4 putting \( S_e(0.16 \) K) = 0 for each magnetic field; if \( C_e/T \sim 0.047 \) J/K\(^2\)mol at 0.16 K in zero field continues down to \( T = 0 \), an error caused by this assumption would be \( S_e(0.16 \) K) = \( S_e(T = 0) \sim 7 \times 10^{-3} \) J/Kmol, which is negligibly small. As a next step, the \( S_e(T) \) curves for \( \mu_0H \neq 0 \) T are vertically shifted so that the Maxwell relation:

\[ (\partial S_e/\partial(\mu_0H))_T = (\partial M/\partial T)_{\mu_0H} \quad (4) \]

is consistently satisfied at 5 K by both the \( S_e \) and \( M \) data shown in Fig. 5. The maximum shift of \( S_e \) required for the adjustment is 0.02 J/K mol, which is invisible in Fig. 4. Two \( S_e(T) \) curves for adjacent magnetic fields in Fig. 4 cross at a temperature (\( 3 \sim 3.5 \) K), which coincides with the maximum temperature of the corresponding \( M/H \) vs \( T \) curve shown in Fig. 5, demonstrating the consistency of the present data with eq. (4). We also confirmed that results of magnetocaloric effect measurements are consistent with the \( S_e \) data shown in Fig. 4.

There are two possible interpretations for the Schottky-like anomaly appearing at \( \sim 3 \) K: (1) a CEF excitation superimposed on a moderately mass-enhanced quasiparticle excitation, or (2) a strongly energy-dependent quasiparticle excitation itself. In the case (1), \( \gamma \) is of the order of \( 10^{-1} \) J/K\(^2\)mol and \( \Delta C/\gamma T_c \) is not far from the BCS value, while in the case (2), \( \gamma(T) \) has a strong temperature dependence and \( \Delta C/\gamma(T_0)T_c \approx 0.1 \) is quite smaller than the BCS value.

In the case (1), the maxima at \( 3 \sim 3.5 \) K in the \( M/H \) vs \( T \) curves as well as the field-sensitive behavior of the Schottky peak indicate that the CEF first excited state lying at \( E_1/k_B \sim 8 \) K is magnetic. In the CEF model proposed by Bauer et al. [1], where the \( \Gamma_3 - \Gamma_5 \) excitation leads to the Schottky peak in \( C(T) \) at 3 K, an entropy of \( R\ln 2 \) associated with the \( \Gamma_3 \) ground state should be hidden below 0.16 K in zero field, if it is assumed that 4\( f \) electrons are well localized. Since applying magnetic field should cause a small but detectable splitting of the \( \Gamma_3 \) doublet (e.g. an energy splitting \( \Delta E = 1.5 \) K in 4 T is calculated using the CEF parameters of \( x = -0.72 \) and \( W = -5.44 \) K from ref. [1]), a new low-\( T \) peak would appear in \( C(T) \) and thereby the hidden entropy would be released, i.e., \( S_e(0 \) T) = \( S_e(4 \) T) \( \sim R\ln 2 \) at 0.16 K. Our

FIG. 4. Electronic part of entropy \( S_e(T) \) calculated integrating \( C_e(T)/T \) data. Slight adjustment has been made for the data of \( H \neq 0 \) so that the Maxwell relation \( (\partial S/\partial(\mu_0H))_T = (\partial M/\partial T)_{\mu_0H} \) is satisfied; see text for the details.

FIG. 5. Magnetization divided by applied magnetic field as a function of temperature. The inset shows the temperature dependence of inverse magnetic susceptibility.

\[ (\partial S_e/\partial(\mu_0H))_T = (\partial M/\partial T)_{\mu_0H} \quad (4) \]
$S_e$ data shown in Fig. 4 are clearly against this scenario, and we conclude that no anomalous entropy is concealed below 0.16 K in zero field. [14]

If a $\Gamma_1$ singlet is the CEF ground state, the first excited state should be a magnetic triplet $\Gamma_5$ ($\Gamma_5$ in $T_h$ notation [15]). Observed anisotropy in $M$, i.e., $M(H//\langle 110 \rangle) \approx M(H//\langle 111 \rangle) = 1.110 \, \mu_B/\text{Pr} > M(H//\langle 100 \rangle) = 1.095 \, \mu_B/\text{Pr}$ at 1.9 K in 7 T, asserts the $\Gamma_1 - \Gamma_5$ level scheme (see Fig. 7 of ref. [3] for a calculation of $M$ for a single-site Pr ion), although the absence of clear downward curvature in $M(H)$ curves for all the three field directions (see Fig. 5 for $H//\langle 100 \rangle$) is not in agreement with the simple CEF predictions not only for the $\Gamma_1 - \Gamma_5$ but also for the $\Gamma_3 - \Gamma_5$ level schemes. The $\Gamma_1 - \Gamma_5$ level scheme is consistent with the fact that $S_e$ is lower than $R \ln 4$ at 8 K and increasing gradually. The maximum value of $C$ at $\sim 3$ K is smaller than 8.5 J/K mol expected for the singlet-triplet Schottky peak, [16] indicating that the triplet excited state has a energy dispersion due to Pr-Pr magnetic interactions.

The FIOP appears in the field region where one level out of the $\Gamma_5$ triplet goes down due to the Zeeman effect and effectively degenerates with the ground state. Actually, $S_e$ shown in Fig. 4 increases with increasing field below $\sim 3$ K and seems to show a tendency of saturation (plateau) at $R \ln 2$ when the FIOP is fully developed in fields above 8 T. Therefore the formation of the FIOP probably needs the degree of freedom possessed by the quasi-degenerate doublet formed in the high fields. We speculate that the order parameter is of an antiferroquadrupole accompanied by a field-induced antiferromagnetism (AFM), as observed in CeB$_6$ [17,18] and TmTe [19,20]. In these compounds, the quadrupole ordering temperature shifts to higher temperatures with increasing field. In PrOs$_4$Sb$_{12}$, the negative Curie-Weiss temperature $\Theta_{\text{CW}} = -6.6$ K determined below 20 K as shown in the inset of Fig. 5 indicates the existence of AFM correlations. Therefore, by field-induced CEF components, the FIOP could be energetically stabilized leading to $dT_e/dH > 0$. Note that preliminary data of $\partial p/\partial T$ indicate that $dT_e/dH$ changes to negative above 10 T [7], as similarly observed in both CeB$_6$ and TmTe.

In the case (2), the Schottky-like peak in $C_e(T)$, similar to the one observed at $\sim 7$ K in CeNiSn [21], implies the existence of a hybridization gap in the energy spectrum of the renormalized quasiparticle excitations in PrOs$_4$Sb$_{12}$ [22]. From the $C_e(T)$ data, the size of the gap is roughly estimated to be $\Delta_e/k_B \sim 8$ K, which is four times larger than $T_c$. This fact suggests that the superconductivity appears in the temperature region where the gap structure is well developed. Figure 1 clearly shows that the gap structure is sensitive to magnetic field and is destroyed above $\sim 5$ T. In these fields, the quasiparticle density of states at the Fermi energy increases and consequently developed RKKY-type AFM interactions would help to form the FIOP.

For a clear distinction between the cases (1) and (2), no decisive experimental facts are available at this stage. However, this point should be clarified to understand the first $4f^2$-based HFSC in PrOs$_4$Sb$_{12}$.

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Note added.- The effect of the deviation from the $T^{-2}$ dependence of the Pr nuclear contribution becomes non-negligible in high fields (e.g., see Fig. 1 in Ref. 23). If one follow the analysis described in Ref. 3, $m_{\text{Pr}} = 1.15 \mu_B/\text{Pr}$ is obtained in 8 T. Note that the long heat pulse ($\sim 1$ min), the longtime $T$-response measurement ($> 10$ min) and our data fitting procedure fully dealing with the tau-2 effect caused by long nuclear-spin-lattice-relaxation times allow us the precise measurements of the nuclear contribution. After completion of this paper, we became aware of the result of Maple et al. who observed anomaly in $\rho$ corresponding to the FIOP. [24]

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