Exotic Heavy-Fermion State in Filled Skutterudite SmOs₄Sb₁₂

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Specific heat and transport measurements have revealed an unconventional heavy-fermion (HF) state in SmOs₄Sb₁₂ single crystals. The electronic specific-heat coefficient (γ = 0.82 J/K²mol) and the coefficient (A) of the quadratic temperature dependence of electrical resistivity are largely enhanced, although the ratio Aγ⁻² is reduced from the Kadowaki-Woods ratio of HF materials. Both γ and A do not show any significant decrease in applied field in contrast with Ce-based HF compounds, suggesting an unconventional origin of the heavy quasiparticles. A weak ferromagnetic ordering sets in below ~ 3 K, probably originating in the itinerant quasiparticles.

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Friede skutterudite compounds, with a general formula RT₄X₁₂ (R=rare earth or U; T=Fe, Ru or Os; X=P, As or Sb) crystallizing in the unique bcc structure of the space group Im3 (no 204) [1], show a variety of interesting physical phenomena [2, 3]. Among these, the Pr-based compounds PrFe₄P₁₂ and PrOs₄Sb₁₂ have attracted special attention because of their unusual heavy-fermion (HF) behavior. PrFe₄P₁₂ exhibits HF behavior in magnetic fields [4] in close proximity to an antiferroelectric-quadrupole (AFQ) ordering phase. PrOs₄Sb₁₂ is the first-known Pr-based HF superconductor [7], which shows unconventional superconducting behavior [8, 9] and an anomalous field-induced AFQ ordered phase above 4.5 T [10, 11, 12, 13]. These findings of HF behavior in the Pr-based filled skutterudites are surprising since 4f electrons of Pr³⁺ ions are generally considered to be quite stable (well localized) in intermetallic compounds. The HF state in PrFe₄P₁₂ is quite unusual because no magnetic-moment screening is observed, in contrast with Ce- or Yb-based HF compounds where the magnetic Kondo effect plays a key role. This fact, along with the AFQ phases appearing in these compounds, indicates that quadrupole interactions play an important role in the Pr-based filled skutterudites.

In this paper, we demonstrate that Sm ions also show strongly correlated behaviors in the filled skutterudites. SmOs₄Sb₁₂ is a new HF material with the Sommerfeld coefficient γ = 0.82 J/K²mol, which is the largest among the known Sm-based compounds. Note that Sm-based HF behaviors have been found only in a few materials, e.g., SmPd₃ (γ = 0.28 J/K²mol) [14] and SmFe₄P₁₂ (γ = 0.37 J/K²mol) [15].

Single crystals of SmOs₄Sb₁₂ were grown by the Sb-self-flux method using high-purity raw materials of 4N(99.99% pure)-Sm, 4N-Os and 6N-Sb [16]. No impurity phase has been detected in a powder X-ray diffraction pattern, except small amounts of Os and Sb metals of the order of ~ 1% in volume. The residual resistance ratio (RRR) is ~13. The lattice parameter was determined to be a=9.301 Å, consistent with the reported value [17]. Specific heat C(H, T) for H || [100] was measured by a quasi-adiabatic heat pulse method described in ref. [10] using a dilution refrigerator equipped with an 8 T superconducting magnet. The bulk magnetization M(μ₀H ≤ 7 T, T ≥ 2.0 K) was measured with a Quantum-Design superconducting quantum-interference device (SQUID) magnetometer. The electrical resistivity was measured by the ordinary dc four-probe method, using a top-loading ³He cryostat with a 16 T superconducting magnet above 0.4 K.

Figure 1 shows C/T as a function of log T measured in applied field H || [100]. In this temperature range, C consists of three components: the electronic (Cₑ), nuclear Schottky (Cₙ), and phonon (Cₚh) contributions. An upturn below 0.5 K developing with increasing magnetic...
field is due to $C_n$, which can be approximated as $A_n/T^2$. This term is dominated by Sb nuclear contribution; the zero-field value of $A_n = 1 \times 10^{-3}$ JK/mol is close to the expected value of $8.2 \times 10^{-4}$ JK/mol calculated based on the Sb-NQR measurement of PrOs$_4$Sb$_{12}$ [18]. At 8 T, the experimental value of $A_n = 3.5 \times 10^{-3}$ JK/mol is close to the calculated Sb magnetic contribution of $3.6 \times 10^{-3}$ JK/mol. Unfortunately, because of the small natural abundances and the weak onsite hyperfine coupling of $^{147}$Sm and $^{149}$Sm magnetic nuclei [19], one cannot obtain information on the 4f magnetic moment of Sm ions. Note that in PrFe$_4$Sb$_{12}$ [5] and PrOs$_4$Sb$_{12}$ [10], $C_n$ data have been utilized to clarify the nonmagnetic nature of the ordered state in the former compound and the magnetic behavior in the field-induced AFQ ordering phase in the latter compound. In Fig. 4 the increase in $C/T$ above $\sim 3$ K can be explained by the phonon contribution ($C_{ph}$) obtained from the LaOs$_4$Sb$_{12}$ data [10]. We have obtained the electronic contribution $C_e$ by subtracting $C_n$ and $C_{ph}$ from the experimental C data.

The most significant finding shown in Fig. 3 is the almost temperature-independent $C_e/T$. This term dominates in $C/T$ in the temperature range between 0.3 and 3 K, where both $C_n$ and $C_{ph}$ are reduced. The weak hump appearing at $T = 2 \sim 3$ K in zero field will be discussed below. The Sommerfeld coefficient $\gamma$, obtained by fitting the data to $C(T) = A_n/T^2 + \gamma T$ below 1 K, is plotted in Fig. 4 as a function of applied field. The quite large $\gamma$ value of 0.82 J/K$^2$mol, 15 times larger than that for the no-4f reference LaOs$_4$Sb$_{12}$ ($\gamma = 0.055$ J/K$^2$mol), suggests that the electron mass is highly enhanced by the many-body correlation effect. Note that $\gamma$ is insensitive to the applied field, in contrast to the strong field dependence in the typical Ce-based HF compounds [21] [22].

The electrical resistivity $\rho$ measured in the longitudinal magnetic field geometry is shown in Fig. 3, where $\rho$ can be described well by $\rho = \rho_0 + AT^2$, indicating that electron-electron scatterings dominate at low temperatures. The obtained coefficient $A$ is plotted in Fig. 3. The slight enhancement of $A$ in zero field is probably due to the addition of ferromagnetic magnon scattering contribution since a weak ferromagnetic ordering sets in at $2 \sim 3$ K as discussed below. This interpretation is also consistent with the negative magnetoresistance $\rho(8T) < \rho(0T)$. The positive magnetoresistance $\rho(14T) - \rho(8T) > 0$ is ascribed to the ordinary contribution caused by the electron’s cyclotron motion. If this contribution was subtracted from the data using Kohler’s rule, the field depen-
fore, one can conclude that evidence of the ferromagnetic nature of the ground state.

Hysteretic behavior provides clear evidence of the ferromagnetic nature of the ground state. The temperature dependence of $M_s$, provided by the $H/M \rightarrow 0$ intercept, is shown in Fig. 7. Compared with Fig. 4, we conclude that the weak hump in $C(T)$ in the zero field appearing at $2 \sim 3$ K ($= T_C$) is due to the ferromagnetic transition. With increasing field, the hump structure becomes broader and shifts to higher temperatures, which is the typical behavior expected for a ferromagnet.

In the well-localized 4f-electron picture, the $J = 5/2$ multiplet of $\text{Sm}^{3+}$ ions splits into a doublet $\Gamma_6$ ($\Gamma_7$) and a quartet $\Gamma_{67}$ ($\Gamma_{8}$) in the $T_h$ site symmetry (More familiar cubic $O$ labels are shown in the parentheses. See ref. [29] for details). The CEF level scheme in SmOs$_4$Sb$_{12}$ can be estimated using the experimentally determined CEF parameters for PrOs$_4$Sb$_{12}$ ($B_{1}^{0} = +0.0237$ K and etc) [11, 27] using the following extrapolation procedure. The CEF parameters have the empirical form $B_{\gamma}^{0} = \Theta_{\gamma}(r^{\gamma})A_{\gamma}^{0}$, where Stevens’ multiplicative factors $\Theta_{\gamma}$ and the radial integrals over the unfilled 4f electrons ($r^{\gamma}$) depend on the rare-earth ions (the values are given in refs. [28] and [29]). For a good approximation (in the point charge model), $A_{\gamma}^{0}$ are independent of the particular rare-earth ions $\gamma$ in the filled-skutterudite isostructure of $\text{ROs}_4\text{Sb}_{12}$ [30]. The scaled CEF parameter for SmOs$_4$Sb$_{12}$ is $B_{4}^{0} = -0.0546$ K, predicting a quartet $\Gamma_{67}$ ground state and a doublet $\Gamma_{5}$ excited state with a small energy separation $\Delta_{CEF}/k_B = 19$ K. The strong $c$-$f$ hybridization effect in SmOs$_4$Sb$_{12}$ neglected above could modify the CEF level scheme to some extent from the present estimation.

The electronic entropy $S_e(T)$ calculated numerically integrating the $C_e(T)/T$ data is shown in Fig. 8. The insensitivity of $S_e$ to the applied field is significant, as already seen in the $\gamma$ vs $H$ plot. Without showing any tendency of saturation, $S_e$ increases monotonically exceeding $R \ln 2$ at 6 K. This behavior agrees with the quartet $\Gamma_{67}$ ground-state model [31].

![Figure 5: Magnetization $M$ vs magnetic field $H$ isotherms at $T = 2.0$ and 4.0 K. Hysteretic behavior provides clear evidence of the ferromagnetic nature of the ground state.](image)

![Figure 6: Arrott plot $M^2$ vs $H/M$.](image)

![Figure 7: Spontaneous magnetization determined by Arrott plot $M$ vs $H/M$ in Fig. 6.](image)
In Ce-based HF compounds, like CeCu6 and CeRu2Sb2, $C_e/T$ starts to decrease above around the Kondo temperature ($T_K$). In contrast, $C_e/T$ of SmOs$_4$Sb$_{12}$ does not show any decrease with increasing $T$ (see Fig. 4). Therefore, the characteristic temperature of the HF state in SmOs$_4$Sb$_{12}$ (tentatively referred to as $T_K$) is probably higher than 10 K, which is comparable with the estimated value of $\Delta_{CEF}$.

The ratio $A\gamma^{-2}$ (in the unit of $\mu\Omega\cdot\text{cm/(mol-K)}^2$) of $1.1(2) \times 10^{-6}$ for SmOs$_4$Sb$_{12}$ is intermediate between $1 \times 10^{-5}$ for HF materials and $0.4 \times 10^{-6}$ for transition metals. While this may be attributed to the effect of moderate many-body correlations as discussed in ref. [22], the degeneracy due to the CEF effect could be another possible explanation. A theoretical study in the orbitally degenerate periodic Anderson model suggests that $A\gamma^{-2}$ can be expressed roughly as $1 \times 10^{-5}/N(N-1)/2$, where $N$ is the orbital degeneracy, i.e., $A\gamma^{-2}$ becomes smaller for $f$-electrons with larger degeneracy [33]. The reduced ratio in SmOs$_4$Sb$_{12}$ is close to the theoretically expected values of $1.7 \times 10^{-6}(N=4)$ or $0.7 \times 10^{-6}(N=6)$, suggesting the $f$-electron orbital degeneracy playing a role in the HF state.

The anomaly in $C_e/T$ associated with the ferromagnetic transition is very weak. The entropy released by the anomaly is only 2% of $R\ln 2$. Furthermore, the observed $M_s$ is far below the expected values of 0.24 and 0.67 $\mu_B$/Sm-ion for $\Gamma_5$ and $\Gamma_6$ CEF levels, respectively. These features indicate that the ferromagnetic ordering originates in the itinerant heavy quasiparticles.

In summary, the specific heat and transport measurements have revealed the unconventional heavy-fermion state in SmOs$_4$Sb$_{12}$. The Sommerfeld coefficient $\gamma = 0.82 J/K^2\text{mol}$ and the coefficient $A$ of the $T^2$ dependence of electrical resistivity roughly satisfy the Kadowaki-Woods relation. $\gamma$ and $A$ do not show any significant decrease in applied field, suggesting that the heavy quasiparticles have an unconventional origin. The simple CEF analysis suggests a quartet ground state, which has both magnetic moments, probably responsible for the weak itinerant ferromagnetism, and electric quadrupole degrees of freedom [34]. Thus, it is possible that the quadrupole moments of Sm ions play a role in the anomalous HF behavior. The present finding provides additional strong evidence that the filled skutterudite structure has unusual electronic states, where multi-$f$-electron ions can also show unprecedented strongly correlated electron behavior.

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