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Fermi surface of the heavy-fermion superconductor $PrOs_4Sb_{12}$

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We have investigated the de Haas–van Alphen effect in the Pr-based heavy-fermion superconductor $PrOs_4Sb_{12}$. The topology of Fermi surface is close to the reference compound $LaOs_4Sb_{12}$ and well explained by the band-structure calculation based on the FLAPW (full potential linearized augmented-plane-wave)-LDA (local-density approximation) $+U$ method, where the $4f$ electrons are localized. We have confirmed a highly enhanced cyclotron effective mass $(2.4–7.6)m_0$, which is apparently large compared to the usual Pr-based compounds.

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The Pr-based compounds in the filled skutterudites have attracted much attention because of their exotic properties, such as metal-insulator transition at $T_{MI}=60$ K in $PrRu_4P_{12}$[1] and unusual heavy-fermion (HF) behavior in $PrFe_4P_{12}$.[2–4] The quadrupolar interaction is thought to be a key mechanism to explain such anomalous behaviors. Especially for $PrFe_4P_{12}$, both the extraordinarily enhanced effective mass ($m_c^*=81m_0$) and the nonmagnetic low-field ordered state below 6.5 K are inferred to originate from the quadrupolar interaction.[3–5]

Recently, $PrOs_4Sb_{12}$ was reported to exhibit superconductivity below $T_C=1.85$ K.[6,7] From the large specific-heat jump at T_C, $\Delta C/T_C \sim 500$ mJ/K^2 mol, Bauer *et al.* claimed that $PrOs_4Sb_{12}$ is the first example of the Pr-based HF superconductor.[6,7] They also inferred that the quadrupolar interaction plays an important role in the HF superconductivity, since the magnetic susceptibility, specific heat $C(T)$, and inelastic-neutron-scattering measurements suggest the crystal electric-field (CEF) ground state to be a non-Kramers doublet carrying quadrupole moments. The recent Sb-NQR (nuclear quadrupole resonance) measurement on $PrOs_4Sb_{12}$ have revealed that the temperature T dependence of nuclear-spin-lattice-relaxation rate $1/T_1$ shows neither a coherence peak nor T^3 like power-law dependence below T_C.[8] The muon-spin-relaxation measurements suggest an isotropic superconducting (SC) energy gap,[9] while the anisotropy of thermal conductivity against the magnetic-field directions indicates that the SC energy gap has point nodes.[10] Such unusual properties cannot be consistently explained neither by a conventional isotropic nor by any anisotropic gap superconductivity reported until now, suggesting some type of HF superconductivity of this compound.[6–11] In the normal state above ~ 4.5 T, Aoki *et al.* reported an anomalous field-induced ordered phase (FIOP) based on the specific-heat measurements; possibly a quadrupolar ordering.[12]

In order to understand these unusual properties, it is essential to determine the electronic structure of this compound and to directly confirm the highly enhanced effective mass. In this paper, we report the de Haas–van Alphen (dHvA) experiment on $PrOs_4Sb_{12}$,[13] which is the most powerful tool to clarify the Fermi-surface (FS) topology and to determine the cyclotron effective mass. The experimental result is compared with the band-structure calculation based on the FLAPW (full potential linearized augmented-plane-wave)-LDA (local-density approximation) $+U$ method.

Single crystals of $PrOs_4Sb_{12}$ and the reference $LaOs_4Sb_{12}$ were grown by Sb-self-flux method basically same as in Refs. 14 and 15, using high-purity elements, 4N (99.99% pure)-Pr, 4N-La, 3N-Os, and 6N-Sb. The typical forms of the single crystals were cubic or rectangular shape with a largest dimension of about 3 mm. The crystal structure of filled skutterudite, belonging to the space group $Im\bar{3}$ (T_h^5, #204), was verified by the powder-neutron-diffraction experiments performed by VEGA at KEK Tsukuba, Japan. The lattice constant of $PrOs_4Sb_{12}$ obtained from the Rietveld refinement is $a=9.303\,11$ Å, which is close to the reported value.[16] Fractional coordinates of Sb at the 24g site are determined as $x=0$, $y=0.3405$, $z=0.1561$, which is used in the band-structure calculation. The residual resistivity ρ_0 and the residual resistivity ratio (RRR) of the present samples are $\rho_0=8\ \mu\Omega$ cm and RRR=55 for $PrOs_4Sb_{12}$, and $\rho_0=2.8\ \mu\Omega$ cm and RRR=100 for $LaOs_4Sb_{12}$. The dHvA experiments were performed in a top loading dilution refrigerator cooled down to 30 mK with a 17 T superconducting magnet. The dHvA signals were detected by means of the conventional field modulation method with a low frequency ($f\sim 10$ Hz).

Figure 1 shows (a) the typical dHvA oscillations and (b) the fast Fourier-transformation (FFT) spectra in $PrOs_4Sb_{12}$ for the field H along $\langle 100\rangle$ direction. The oscillations become detectable just above $H_{C2}=2.2$ T and a faint peak anomaly appears at $H_A\sim 4.4$ T, indicating a slight slope change in the field dependence of magnetization $M(H)$.[17] This field H_A almost agrees with the phase boundary of FIOP determined by the $C(T)$ measurement in the magnetic fields.[12] Above H_A a small spin splitting is observed in the dHvA frequencies reflected as beats in the oscillations, which is frequently observed in the magnetic materials.[18] The three fundamental dHvA branches α, β, and γ are identified.

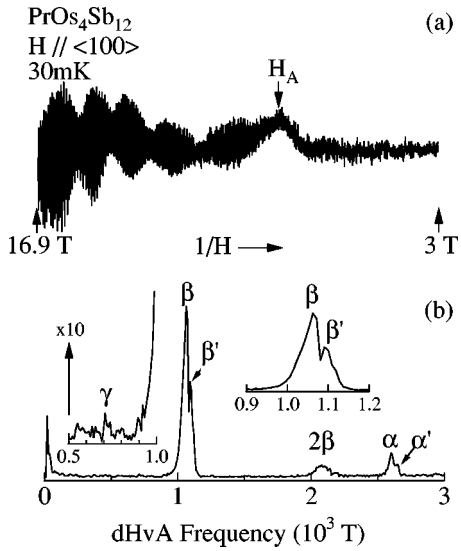

FIG. 1. (a) Typical dHvA oscillations and (b) the FFT spectra in $PrOs_4Sb_{12}$.

Figure 2 shows the angular dependence of dHvA frequency in $PrOs_4Sb_{12}$ along with that in $LaOs_4Sb_{12}$. α- and β-branches have been observed over the whole field directions in the cubic symmetry, indicating closed FSs. The branch γ observed only in the limited angular ranges centered at $\langle 100 \rangle$ suggests a part of the multiply connected one. The striking resemblance of the angular dependence of dHvA frequencies between $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$ indicates the closeness of FS topology between the two compounds, and evidences the well localized nature of $4f$ electrons in $PrOs_4Sb_{12}$.

In order to assign the origin of dHvA branches, the band-structure calculation is carried out using an FLAPW and LDA+U method, in which the $4f$ electrons in $PrOs_4Sb_{12}$ is treated as localized. Here, we assume the Γ_1 singlet to treat the localized $4f^2$ electrons with the cubic symmetry. The details of the calculation are described in Refs. 19 and 20. Figures 3 and 4 show the calculated energy-band structure and the FS in $PrOs_4Sb_{12}$, respectively. The FS is composed of the 48th and 49th band hole sheets. The 48th band forms

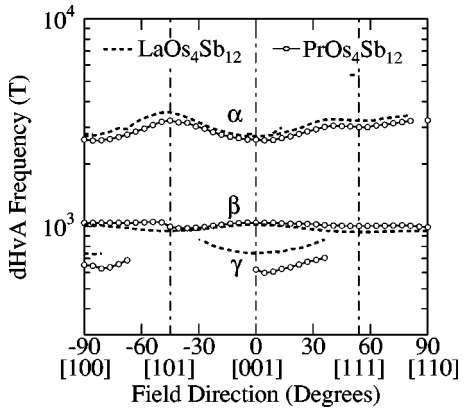

FIG. 2. Comparison of the angular dependence of the dHvA frequencies between $PrOs_4Sb_{12}$ (circles) and $LaOs_4Sb_{12}$ (dashed lines).

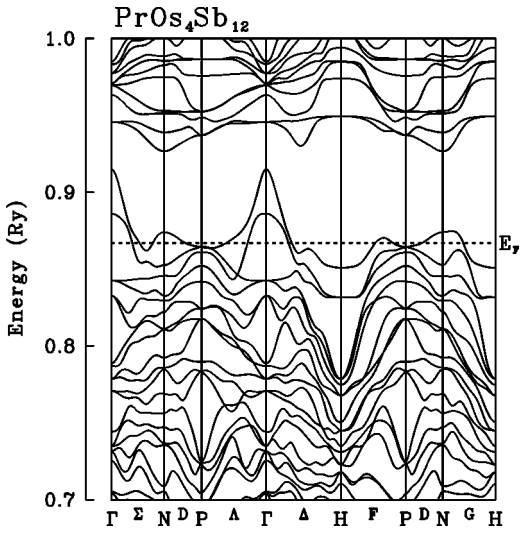

FIG. 3. Energy-band structure in $PrOs_4Sb_{12}$.

an almost spherical sheet, which slightly projects along the $\langle 100 \rangle$ direction centered at the Γ point. The 49th band gives a round cubic sheet centered at Γ point and a multiply connected one whose main parts are centered at the N points. Figure 5 shows the angular dependence of the calculated dHvA frequencies, which reasonably well explains all the observed dHvA branches. A slight disagreement in the absolute values is probably ascribed to the assumption of the Γ_1 singlet ground state and/or the effect beyond the LDA+U treatment. Branch β originates from the 48th-band spherical FS, branch α is due to the 49th-band round cube FS, and branch γ originates from the extremal orbit surrounding the N point of the part of multiply connected one. Many other dHvA branches predicted in the band-structure calculation

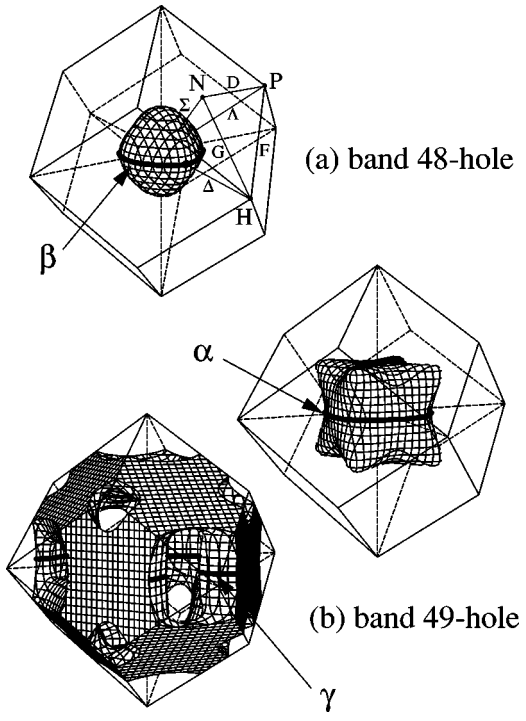

FIG. 4. Fermi surface of $PrOs_4Sb_{12}$.

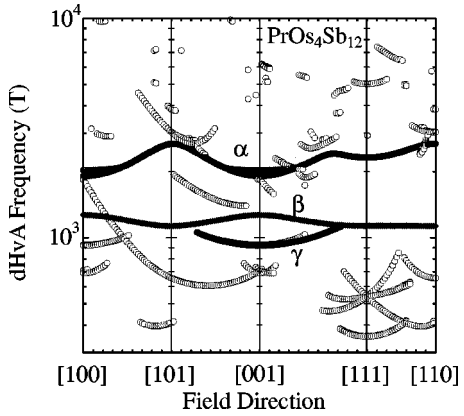

FIG. 5. Angular dependence of the theoretical dHvA branches in $PrOs_4Sb_{12}$. The dHvA branches indicated by the closed marks are identified by the experiments.

have not been observed in the present experiments. That can be understood as a large reduction of the dHvA amplitude due to the large curvature factors A'' of these branches; i.e., for $H\|\langle 100\rangle$, $|A''|=0.08$ for the γ branch, whereas $|A''|=2.72$ for the dHvA branch exhibiting the frequency of $F=0.71\times 10^3$ T.

As the most attractive information, we have estimated the cyclotron effective mass m_c^* from the temperature dependence of the dHvA amplitude. The comparison of dHvA frequencies and m_c^* between these compounds is given in Table I.[21] In contrast with the closeness of the FS topology, the cyclotron effective masses are up to ~ 6 times enhanced compared to those in $LaOs_4Sb_{12}$. The mass enhancement is apparently larger than those in the ordinary Pr-based compounds such as $PrIn_3$ and PrSb,[18] although it is not so large as that in $PrFe_4P_{12}$.[3] For the comparison with the mass enhancement estimated from the specific-heat measurement, we simply estimate the Sommerfeld coefficient from the FS volume and m_c^* in the present experiments assuming spherical FS's. The estimated value of ~ 150 mJ/K^2 mol is still a factor of 2 or more smaller than that in the specific-heat measurement; Bauer *et al.* estimated the Sommerfeld coefficient of $PrOs_4Sb_{12}$ to be 350–750 mJ/K^2 mol.[6]

We have no definitive explanation for this discrepancy only from the present information. Nevertheless, a possible origin may be hidden in the difference of the measuring conditions, such as magnetic field and temperature; the Sommerfeld coefficient in the specific heat was estimated at 0 T, and around T_C close to the Schottky-like peak at 3 K, while the dHvA measurements were made at high fields of 3–17 T and lower temperatures of 30–400 mK. If the peak is associated with the nearby magnetic CEF excited state situated about 8 K above the ground state,[6,12] an additional enhancement of effective mass could be expected from the magnetic instability. As another origin, the spin-splitting effect should not be discarded. In the present experiments, we have estimated m_c^* only for the larger amplitude spin direction, since the insufficient experimental resolution prevents to determine the masses for the higher frequencies [α' and β' as shown in Fig. 1(b)]. Only for β branch with the large amplitude, we could roughly estimate m_c^* of the higher-frequency branch β', which is about 20% enhanced compared with that of the lower one β. The larger mass enhancement for the higher-frequency branch might explain the discrepancy of the mass enhancement between the Sommerfeld coefficient and m_c^*.

It might be informative to compare $PrOs_4Sb_{12}$ with another Pr-based filled skutterudite superconductor $PrRu_4Sb_{12}$ as shown in Table II.[22] The localized character of $4f$ electrons, namely, the closeness of the FSs with those in $LaRu_4Sb_{12}$, has been confirmed also in $PrRu_4Sb_{12}$ based on the dHvA experiment.[23] On the contrary, the mass enhancement is quite small in $PrRu_4Sb_{12}$, which is in sharp contrast to that in $PrOs_4Sb_{12}$. For $PrOs_4Sb_{12}$, the CEF ground state was inferred to be a non-Kramers doublet carrying quadrupole moments.[6,7] On the other hand, Takeda and Ishikawa inferred $PrRu_4Sb_{12}$ to have the Γ_1 singlet ground state.[24] On the T_C compared with the La references, the two compounds have different sense; T_C for $PrOs_4Sb_{12}$ is higher than that for La reference, that is unusual if we take into account that $PrOs_4Sb_{12}$ contains the magnetic element Pr. It should be also noted that the superconductivity observed in $PrRu_4Sb_{12}$ is the ordinary BCS type.[8,24] These facts naturally indicate the essential role of the mass enhancement associated with $4f$ electrons in the superconductivity of $PrOs_4Sb_{12}$.

In summary, we have directly confirmed the heavy mass in $PrOs_4Sb_{12}$ by the dHvA experiment, indicating $PrOs_4Sb_{12}$ to be the first member of HF superconductor as Pr compound. However, the well localized character of $4f$ electrons,

TABLE I. Comparison of the dHvA frequency F and the cyclotron effective mass m_c^* between $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$.

		$PrOs_4Sb_{12}$ (Exper.)		$PrOs_4Sb_{12}$ (Theor.)		$LaOs_4Sb_{12}$	
Field direction	Branch	$F(\times 10^3$ T)	m_c^* (m_0)	$F(\times 10^3$ T)	m_c^* (m_0)	$F(\times 10^3$ T)	m_c^* (m_0)
$H\|\langle 100\rangle$	α	2.61	4.1	1.91	0.88	2.79	2.5
	β	1.07	2.5	1.27	0.45	1.02	0.71
	γ	0.71	7.6	0.93	0.79	0.74	2.8
$H\|\langle 110\rangle$	α	3.24	4.9	2.68	1.82	3.55	4.1
	β	0.89	3.9	1.13	0.39	0.95	0.65
$H\|\langle 111\rangle$	α	3.00	5.8	2.32	1.27	3.23	2.8
	β	0.86	2.4	1.13	0.38	0.94	0.65

TABLE II. Comparison of the superconducting critical temperature T_C, superconducting specific-heat jump ΔC divided by T_C ($\Delta C/T_C$), Sommerfeld coefficient, and effective mass m_c^* in RT_4Sb_{12} (R=La, Pr, T=Ru, Os).

	$PrOs_4Sb_{12}$	$LaOs_4Sb_{12}$	$PrRu_4Sb_{12}$	$LaRu_4Sb_{12}$
T_C (K)	1.85[a]	0.74[b]	1.04[c]	3.58[c]
$\Delta C/T_C$ (mJ/K^2 mol)	500[a]	84[b]	110[c]	82[c]
Sommerfeld coefficient (mJ/K^2 mol)	350~750[a]	36, [d] 56[b]	59[c]	37[c]
m_c^*/m_0 for γ branch	7.6	2.8	1.6[e]	1.4[e]

[a]References 6 and 7.
[b]Reference 22.
[c]Reference 14.
[d]Reference 15.
[e]Reference 23.

evidenced in the closeness of the FS to those in $LaOs_4Sb_{12}$, indicates the uniqueness of this compounds compared to the typical HF superconductors such as UPt_3 and $CeCoIn_5$,[25,26] where the itinerant *f*-electron model is applicable. From the comparison with another Pr-based filled skutterudite superconductor $PrRu_4Sb_{12}$, the quadrupolar interaction associated with the non-Kramers doublet CEF ground state is thought to be responsible for the HF superconductivity in $PrOs_4Sb_{12}$.

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[22] We have also found $LaOs_4Sb_{12}$ to exhibit the superconductivity below $T_C=0.74$ K; H. Sugawara, S. Osaki, M. Kobayashi, S. R. Saha, T. Namiki, Y. Aoki, and H. Sato (unpublished).
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