Coexistence of Strongly Mixed-Valence and Heavy-Fermion Character in $SmOs_4Sb_{12}$ Studied by Soft- and Hard-X-Ray Spectroscopy

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Sm-based heavy-fermion compound $SmOs_4Sb_{12}$ has been investigated by soft x-ray ($h\nu =$ 1070–1600 eV) and hard x-ray (HX; $h\nu = 7932$ eV) spectroscopy. The HX photoemission spectroscopy clearly demonstrates that the strongly mixed-valence state and the heavy-fermion state coexist in the bulk. It is found that the Sm valence decreases below 100 K, indicating that the Kondo coherence develops with approaching the proposed Kondo temperature. Our theoretical analyses suggest that the origin of the coexistence in $SmOs_4Sb_{12}$ is the coincidence of two conditions, namely, (i) the energy difference between Sm divalent and trivalent states is very small and (ii) the hybridization between Sm $4f$ and conduction electrons is weak.

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Recently, many heavy-fermion (HF) compounds with multiple f electrons (or holes) have been discovered in the lanthanide system [1–4]. Sm-based filled skutterudites have attracted much attention due to exotic behaviors, such as Kondo anomaly, weak ferromagnetism, and heavy electron mass [3–7]. Among them, $SmOs_4Sb_{12}$ has been discovered to show the HF character [3,4]. It is found that A/γ^2 (A is the coefficient of T^2 in $\rho - T$, where ρ is the resistivity; γ is the electronic specific heat coefficient) in $SmOs_4Sb_{12}$ follows the ''grand Kadowaki Woods relation'' [8], suggesting that this compound falls into the same category as other so-far-reported HF compounds and the orbital degeneracy in Sm $4f$ electron plays a key role in realizing the HF state. However, the crystalline-electric-field ground state of Sm^{3+} ($J = 5/2$) in $SmOs_4Sb_{12}$, which determines the degeneracy, is still in controversy [3,4]. Even the valence of Sm ions has not been clarified yet.

In general, RFe_4P_{12} (R denotes a rare-earth-metal atom) has a larger energy scale than ROs_4Sb_{12} as represented by higher superconducting transition temperature for La system [9,10], larger hybridization gap for Ce system [11,12], and higher Curie temperature (T_C) for Nd and Eu systems [13–15]. These results suggest that the hybridization between conduction and $4f$ electrons (c-f) and/or the direct exchange interaction between R atoms in ROs_4Sb_{12} are weaker than in RFe_4P_{12} due to the larger lattice constant. However, T_C and γ in $SmOs_4Sb_{12}$ (2–3 K and 820–880 mJ/(mol K^2)) are larger than those of $SmFe_4P_{12}$ (1.6 K and 370 mJ/(mol K^2)) [3–6]. These unusual tendencies must be originating from the specific nature of the Sm atom.

In order to reveal the bulk nature of Sm compounds, bulk-sensitive photoemission spectroscopy (PES) with soft and hard x rays (SXPES and HAXPES) is a very powerful tool since the Sm valence and electronic structures on the surface are often different from those in the bulk [16–18]. It has been demonstrated that the high-resolution bulk-sensitive SXPES can reveal bulk electronic states [19–21]. The bulk sensitivity arises from the long inelastic mean free path (IMFP) of the high-energy photoelectrons excited by soft x ray (SX). HAXPES is attracting much more attention for investigating the bulk electronic structures of rare-earth compounds [22–24] because it provides a longer probing depth than the SXPES due to the increase of the IMFP. The longer probing depth makes the measurement insensitive to surface contamination.

In this Letter, we report on detailed spectroscopic measurements with SX and hard x ray (HX) for Sm-based filled skutterudite $SmOs_4Sb_{12}$. It is demonstrated that the above mentioned HF character is accompanied by the strongly mixed-valence state. With the aid of the theoretical calculation based on the impurity Anderson model with configuration interaction, we have estimated the mean valence of bulk Sm ions. The mean valence is revealed to depend on temperature below 100 K, which is consistent with the development of Kondo coherence in $SmOs_4Sb_{12}$. Significant intensity at Fermi level (E_F) was observed in Sm $3d$-$4f$ resonant photoemission spectroscopy (RPES), indicating that Sm $4f$ electrons contribute directly to form the HF state.

SXPES and Sm $3d$-$4f$ x-ray absorption spectroscopy (XAS) were carried out at the twin-helical undulator SX beam line BL25SU in SPring-8 using GAMMADATA-SCIENTA SES-200 spectrometer [25]. The total energy resolution (ΔE) of the SXRPES was set to $h\nu/\Delta E =$ 4000–6700. The XAS spectra were measured by the total

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electron yield method. HAXPES was performed at the state-of-the-art beam line BL19LXU in SPring-8 with MB Scientific A1-HE spectrometer. The linearly polarized light was delivered from an in-vacuum 27 m long undulator [26]. The highest ΔE of the HAXPES (for the energy calibration using Au thin films) was set to 70 meV at $h\nu =$ 7932 eV.

For measurements, single crystals of $SmOs_4Sb_{12}$ were employed. They were grown by the Sb-self flux method using high-purity raw materials [27]. Clean surfaces were obtained by fracturing samples *in situ* in UHV ($\sim 2 \times 10^{-8}$ and $\sim 7 \times 10^{-8}$ Pa for SXPES and HAXPES) at measuring temperature ($T \simeq 20$ K) except for temperature-dependent measurements. Configurations of the apparatus were set so as to collect the normal emission of photoelectrons from samples.

Figure 1(a) shows the Sm $3d$-$4f$ XAS spectrum of $SmOs_4Sb_{12}$. The spectrum has a prominent shoulder structure at $h\nu \simeq 1076.5$ eV as indicated by the arrow labeled B. At this photon energy, one of the multiplet components of a pure-trivalent Sm ($4f^5$) ion is predicted from the atomic multiplet calculation [28]. The intensity of this shoulder is, however, suppressed in the spectrum of Sm_4As_3, which is known to have a well localized $4f^5$ ground state in the bulk [24]. In some Sm compounds, one can see the Sm divalent state on the lower photon energy side of the Sm trivalent state in the XAS spectrum [29]. The observation of the prominent intensity at this photon energy indicates the existence of the Sm divalent state together with the trivalent one. Therefore, we conclude that a mixed-valence state is realized in $SmOs_4Sb_{12}$.

By means of the Sm $3d$ core-level PES, one can investigate the Sm valence and $4f$ states through the interaction between the $4f$ electrons and the $3d$ core hole. In Fig. 2(a), Sm $3d$ core-level PES spectra of $SmOs_4Sb_{12}$ at two different photon energies are compared. At $h\nu = 7932$ eV, one can obtain the nearly true bulk spectrum for the Sm $3d$ core-level PES since the IMFP reaches into 87 Å in contrast to 12 Å at $h\nu = 1600$ eV [30]. The spectra have two components in this binding energy (E_B) range, that is, Sm^{3+} (the $|3d^9 4f^5\rangle$ final state) and Sm^{2+} (the $|3d^9 4f^6\rangle$ final state) components. The Sm^{2+} spectral weight increases with the photon energy, in contrast to the case of Sm_4As_3 where the surface Sm^{2+} component is reduced by increasing the photon energy [24]. This suggests that in $SmOs_4Sb_{12}$ there are much more divalent Sm ions in the bulk than on the surface. In other words, $SmOs_4Sb_{12}$ has the trivalent dominant state on the surface, although the valence of Sm ions often prefers to have the divalent state on the surface [17,24].

Presented experimental results clearly demonstrate that the mixed-valence state is realized in the bulk of $SmOs_4Sb_{12}$. In order to estimate the valence of Sm ions in $SmOs_4Sb_{12}$, we have calculated the Sm $3d$-$4f$ XAS and

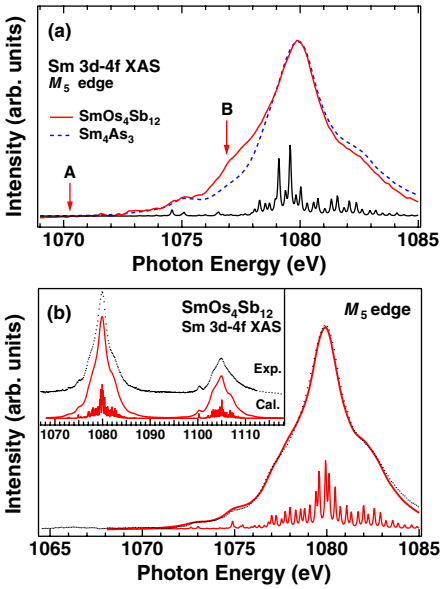

FIG. 1 (color online). Sm $3d$-$4f$ XAS spectrum of $SmOs_4Sb_{12}$ at the M_5 edge. The spectrum of Sm_4As_3 is also shown as a reference by a dashed line in (a). The solid line in the bottom of (a) is the calculated spectrum of a pure-trivalent Sm ion. Arrows indicate the photon energies employed in RPES measurements. (b) Calculated Sm $3d$-$4f$ XAS spectrum (solid line). The lower solid line is the calculated spectrum before Gaussian and Lorentzian broadening ($\Gamma_G = 100$ meV and $\Gamma_L = 1.0$ eV). Dots are the experimental spectrum of $SmOs_4Sb_{12}$. Inset shows the overall Sm $3d$-$4f$ XAS spectra.

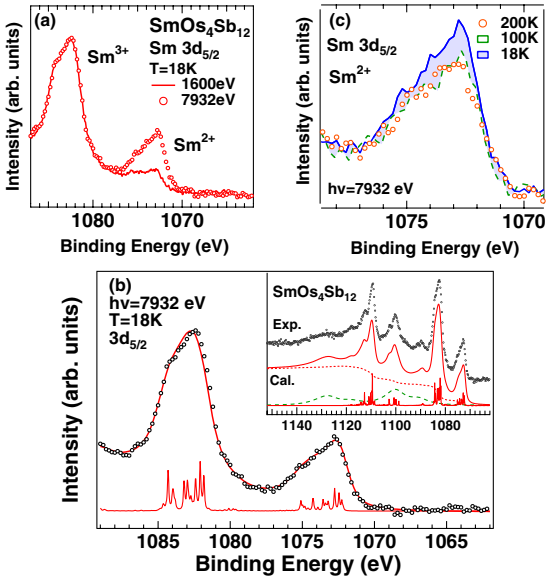

FIG. 2 (color online). Sm $3d$ core-level PES spectra of $SmOs_4Sb_{12}$. (a) Photon-energy dependence of the spectrum. (b) Calculated Sm $3d$ core-level PES spectrum ($\Gamma_G = 1.0$ eV, $\Gamma_L(E_B \geq 1072.6\ \text{eV}) = 1.4$ eV, and $\Gamma_L(E_B < 1072.6\ \text{eV}) = 0.6$ eV [49]). Open circles show the experimental spectrum. Inset shows the overall Sm $3d$ core-level PES spectra. Dashed lines and dotted lines are the plasmon contribution and the Shirley-type background [51], respectively. (c) Temperature dependence of the Sm^{2+} component in the Sm $3d$ core-level PES spectrum at $h\nu = 7932$ eV.

TABLE I. Best-fit values for the effective charge transfer energy ($\Delta_{\rm eff}$), effective hybridization strength ($V_{\rm eff}$), and core-hole potential (U_{fc}) in CI model calculations for $SmOs_4Sb_{12}$. Estimated Sm valences are also given.

	$\Delta_{\rm eff}$ (meV)	$V_{\rm eff}$ (meV)	U_{fc} (eV)	Valence
Sm $3d$-$4f$ XAS	65	178	11.0	2.807 ($T \simeq 20$ K)
Sm $3d$ core-level PES	65	310 ± 15	9.48	2.726 ± 0.006 ($T = 18$ K)
	65	237 ± 15	9.48	2.763 ± 0.006 ($T = 100$ K)

Sm $3d$ core-level PES spectra by the single-impurity Anderson model considering atomic multiplets with configuration interaction (CI) [34–36]. The periodic Anderson model (PAM) is known to be an appropriate model for the dense Kondo system [37,38]. At present, however, one cannot calculate the full multiplet structures of Sm atoms in the case of the PAM. Multiplet calculations of the spectra were performed using the XTLS 8.0 program [39]. The values of Slater integrals were reduced to 82% of their Cowan's Hartree-Fock values [40] in order to fit the experimental spectra [41]. We have considered the basis state consisting of two configurations, that is, the major $|4f^5\rangle$ state and the minor $|4f^6\underline{L}\rangle$ state arising from the c-f hybridization in the initial state, where $\underline{L}$ denotes an additional hole in the conduction band. The effective charge transfer energy $\Delta_{\rm eff}$ is defined as $\Delta_{\rm eff} \equiv E[4f^6\underline{L}]_{\rm gs} - E[4f^5]_{\rm gs}$, where $E[4f^6\underline{L}]_{\rm gs}$ and $E[4f^5]_{\rm gs}$ represent energies of $|4f^6\underline{L}\rangle$ and $|4f^5\rangle$ ground states, respectively.

The solid curves in Fig. 1(b) show the calculated Sm $3d$-$4f$ XAS spectra which are broadened by Gaussian and Lorentzian functions representing the experimental resolution and the lifetime broadening. The calculated Sm $3d$ core-level PES spectra are shown in Fig. 2(b). Both calculated spectra in Figs. 1(b) and 2(b) well reproduce the experimental spectra of $SmOs_4Sb_{12}$. In Table I, the best-fit parameters are summarized. The valences of the Sm ions estimated from fitting of the XAS and PES spectra are 2.807 and 2.726 at $T \simeq 20$ K, respectively. Both $\Delta_{\rm eff}$ and $V_{\rm eff}$ are much smaller than those previously obtained for $PrFe_4P_{12}$ [$\Delta_{\rm eff}(= E[4f^3\underline{L}]_{\rm gs} - E[4f^2]_{\rm gs}) = 2.3$ eV, $V_{\rm eff} = 1.2$ eV] [42]. The small $\Delta_{\rm eff}$ is an essential requirement for $SmOs_4Sb_{12}$ to realize the strongly mixed-valence state in spite of the very weak c-f hybridization. The difference in the best-fitted U_{fc} and $V_{\rm eff}$ between XAS and PES calculations, which may originate from incompleteness in the present model, is not a vital issue for the scenario of the weakly hybridized mixed-valence state.

The temperature dependence of the Sm $3d$ core-level PES spectrum at $h\nu = 7932$ eV is shown in Fig. 2(c). The relative spectral weight of the Sm divalent component to the trivalent one (W_{2+}/W_{3+}) does not change above $T = 100$ K. However, it is found that W_{2+}/W_{3+} increases by about 15% at $T = 18$ K, which is close to the proposed Kondo temperature T_K (≃20 K), suggesting that the Kondo coherence develops with lowering temperature toward $T \sim T_K$. In fact, the fitted $V_{\rm eff}$ for the spectrum at $T = 18$ K is enhanced. Development of the Kondo coherence at few tens of Kelvin favors the HF formation. The temperature dependence of the Sm valence has also been seen in the Sm L-edge XAS measurement [43].

In filled skutterudites $CeRu_4Sb_{12}$ and $YbFe_4Sb_{12}$, mixed valence and electron mass enhancement ($\gamma \simeq 140$ mJ/(mol K^2)) were also reported [44,45]. At low temperatures, the hybridization gap opens in both compounds [46]. For $SmOs_4Sb_{12}$, however, there has been no experimental evidence which implies (pseudo) gap opening. This suggests that the c-f hybridization in $SmOs_4Sb_{12}$ is weaker than those in $CeRu_4Sb_{12}$ and $YbFe_4Sb_{12}$, consistent with our results and the observation of the larger γ in $SmOs_4Sb_{12}$.

SXRPES can reveal the contribution of Sm $4f$ states to the PES intensity at E_F. The on-RPES spectrum of $SmOs_4Sb_{12}$, measured at the photon energy B in Fig. 1(a), is shown in Fig. 3 together with the off-RPES spectrum taken at the photon energy A. On- and off-RPES spectra are normalized by the photon flux. The Sm divalent state is strongly enhanced due to the resonance effect. Figure 3(b) shows the on-RPES spectrum near E_F with higher energy resolution ($\Delta E \simeq 160$ meV). Two peaks, clearly seen in the spectrum, are attributed to ^6H and ^6F multiplet terms [18,47,48]. We note that these structures

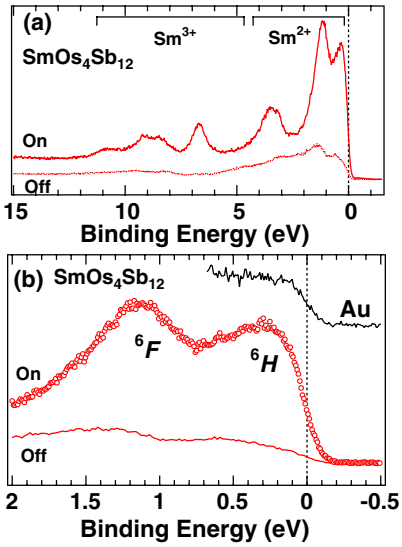

FIG. 3 (color online). Sm $3d$-$4f$ RPES spectra of $SmOs_4Sb_{12}$. On-RPES spectrum is taken at the photon energy B ($h\nu \simeq 1076.5$ eV) in Fig. 1(a). Off-RPES spectrum is taken at the photon energy A ($h\nu \simeq 1070$ eV) in Fig. 1(a). (b) High-resolution Sm $3d$-$4f$ RPES spectrum near E_F.

are not strongly influenced by the shape of the off-RPES spectrum, which originates dominantly from Os $5d$ states, because of the much smaller intensities of the off-RPES spectrum. It is found that the on-RPES spectrum has significant intensity at E_F. This indicates that the Sm $4f$ state contributes to the electronic states at E_F and is related to the formation of the HF state in $SmOs_4Sb_{12}$. Further discussion concerning the structures near E_F will be necessary within the framework of the PAM.

In conclusion, the soft and hard x-ray spectroscopy has revealed that the strongly mixed-valence state and the heavy-fermion state coexist in the bulk of $SmOs_4Sb_{12}$. Through theoretical analyses, the origin of the coexistence is found to be the coincidence of two conditions, namely, the small energy difference between the Sm divalent and trivalent states, and the weak c-f hybridization due to the Sm-centered large Sb cage in $SmOs_4Sb_{12}$. The estimated mean valence of bulk Sm ions is 2.7–2.8 and decreases with cooling down to $T \sim T_K$ due to the Kondo effect.

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