Logarithmic temperature dependence of samarium ion valence in the heavy-fermion $Sm_xLa_{1-x}Os_4Sb_{12}$

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We have measured x-ray absorption spectra at the Sm L_3 edge to investigate the Sm-ion valence of $(Sm_xLa_{1-x})Os_4Sb_{12}$, in which field-insensitive heavy-fermion behavior appears at low temperatures for $x = 1$. It has been found that the Sm-ion valance shifts to 2+ with La ion substitution; from $v = +2.78$ ($x = 1$) to $v = +2.73$ ($x = 0.2$) at 10 K. For all x investigated, its temperature dependence shows a $\log T$ behavior, indicating that the valence change is caused by "an unconventional Kondo effect" associated with Sm $4f$-electron charge degrees of freedom. Almost x independence of "the associated Kondo temperature" ($\tilde{T}_K = 56 \pm 10$ K) indicates that the Kondo effect has a local nature, attributable to the cage structure of the filled skutterudite.

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Filled skutterudite $SmOs_4Sb_{12}$ shows a quite rare Sm-based heavy-fermion (HF) state at low temperatures [1,2]. One of the most striking features is the robustness of mass enhancement against magnetic field. The largely enhanced electronic specific-heat coefficient $\gamma = 820\,\mathrm{mJ/K^2\,mol}$ and the T^2 coefficient of electrical resistivity do not show any noticeable decrease in applied fields up to 14 T [1], in contrast with ordinary Ce- or U-based HF compounds. These findings point to an unconventional mechanism of the heavy-quasiparticle formation in $SmOs_4Sb_{12}$.

The mass enhancement may be associated with anharmonic large-amplitude vibrations (called "rattling") of Sm ions in the Sb_{12} cage structure. In ROs_4Sb_{12}-type filled skutterudites, the rattling behaviors have been confirmed experimentally by elastic- and inelastic-neutron scattering [3,4], inelastic x-ray scattering [5], Raman scattering [6], x-ray diffraction [7,8], and nuclear magnetic resonance [9]. The rattling phonon mode in $SmOs_4Sb_{12}$ has the characteristic Einstein temperature of 43 K [6,7,10]. Theoretically, several models has been discussed for quasiparticle mass enhancement (or Kondo effect) originating from rattling [11–15]. At the moment, however, no convincing experimental evidence has been obtained yet for the realization of such phenomena.

Importance of charge degrees of freedom has been pointed out by the observation of the temperature dependent Sm-ion valence in $SmOs_4Sb_{12}$ [16,17]. The x-ray absorption spectroscopy (XAS) measurement has revealed that the valence shifts from +2.83 at room temperature to +2.76 at 10 K. This fact indicates that Sm ions are in a mixed valence state and $4f$ electrons are strongly hybridized with the conduction electrons. The temperature range of the valence shift ($20 < T < 150$ K) almost coincides with the temperature range of the development of the Sommerfeld coefficient γ [18]. This fact indicates that the mixed valence phenomenon is a key factor to understand the field-insensitive HF state in $SmOs_4Sb_{12}$. In this paper, we report measurements of the Sm-ion valence of $(Sm_xLa_{1-x})Os_4Sb_{12}$ to investigate the La ion substitution effect on the mixed valence behavior.

Single crystals of $Sm_xLa_{1-x}Os_4Sb_{12}$ with $x = 1$, 0.6, 0.5, 0.2 and 0 were grown by the Sb-self-flux method using starting elements of 3N(99.9% pure)-Sm grain, 3N-La grain, 4N-Os powder, and 6N-Sb chips. In order to obtain homogeneous distribution of Sm ions, the Sm and La metals were alloyed using a tetra electric arc furnace before the Sb-flux single crystal growing. The raw materials mixed in the ratio of 1:4:30 were sealed into a quartz tube and heated in a box furnace up to 1050 °C for 10 h, and then cooled down to 650 °C with a rate of 1 °C/h. The lattice constant determined by x-ray powder diffraction at room temperature is 9.30325(5), 9.30575(8), 9.3068(2), 9.3074(4), and 9.3079(2) Å for $x = 1$, 0.6, 0.5, 0.2 and 0, respectively. The clear x dependent shift of the lattice constant confirms that Sm and La ions are uniformly distributed across the entire composition range.

The XAS spectra at the Sm L_3 edge were measured for $(Sm_xLa_{1-x})Os_4Sb_{12}$ at BL01B1 of SPring-8 in Japan. A double-crystal monochromator equipped with a Si 111 crystal and a Rh coated mirror eliminates the higher harmonics [19]. The XAS spectra were recorded under a fluorescence mode using a 19-element Ge solid-state detector. The XAS spectra of $(Sm_xLa_{1-x})Os_4Sb_{12}$ with $x = 1$, 0.6, 0.5, and 0.2 were obtained at various temperatures from 5 to 300 K. The energy resolution was about 1 eV around the Sm L_3 edge. The incident photon energy was calibrated using the Sm L_3-edge XAS spectrum of Sm_2O_3 at 300 K.

The Sm-ion valence was determined by the relative intensities of Sm^{2+} and Sm^{3+} components in the same manner as described in Ref. [16]. Each component is modeled by the sum of a Lorentz and an arctangent function, representing the sharp excitation due to the strong density of $5d$ empty states present at the threshold and the following continuum excitations, respectively. This model of the XAS spectra can therefore be expressed as

$$f(E) = \sum_{i=2}^{3}\left[\frac{A_i\left(\frac{\Gamma_i}{2}\right)}{(E-E_i)^2+\left(\frac{\Gamma_i}{2}\right)^2} + \frac{A_i\Gamma_i}{A_2\Gamma_2+A_3\Gamma_3} I \times\left\{\frac{1}{2}+\frac{1}{\pi}\arctan\frac{E-(E_i+\delta)}{\frac{\Gamma_i'}{2}}\right\}\right], \quad (1)$$

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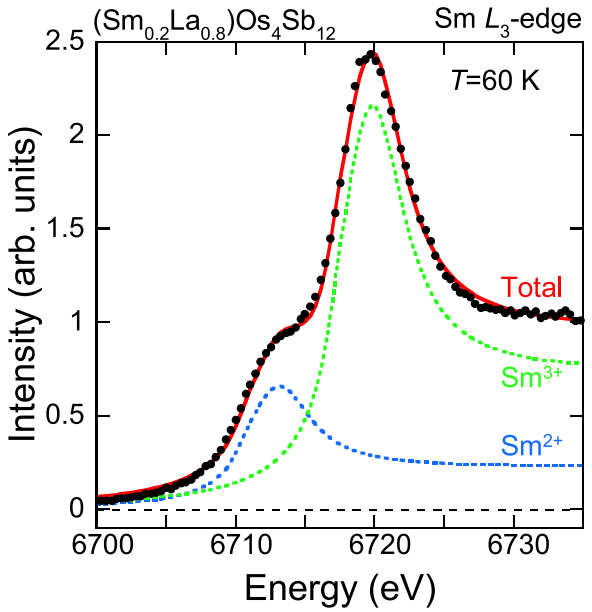

FIG. 1. (Color online) XAS spectra at the Sm L_3 edge of $(Sm_{0.2}La_{0.8})Os_4Sb_{12}$ measured at $T = 60$ K. The green, blue, and red lines indicate the Sm^{3+}, Sm^{2+}, and total components fitted to the experimental data (closed circles), respectively.

where E denotes the photon energy. The suffix $i = 2$ and 3 denotes the divalent and trivalent states, respectively. A_i, Γ_i, Γ_i', I, and δ are fitting parameters. The observed spectra for $x = 0.2$ are shown in Fig. 1 along with a model fitting result. The spectra consist of double peaks; the lower energy peak at $E = 6712$ eV corresponds to the divalent component and the higher energy one at $E = 6719$ eV to the trivalent. This fact indicates that the Sm ions do not have an integral number of 4f electrons and are in an ionic state which is a dynamic admixture of Sm^{2+} and Sm^{3+}; hence they are described as being in a mixed valence (intermediate valence) state. As demonstrated in Fig. 1, the model curve reproduces well the experimental data, confirming the validity of the present model expressed by Eq. (1). The average valence v is given by

$$v = 2 + \frac{A_3\Gamma_3}{A_2\Gamma_2 + A_3\Gamma_3}. \quad (2)$$

Figure 2(a) shows the temperature dependence of XAS spectra at the Sm L_3 edge for $x = 0.2$. The Sm^{2+} component developing with decreasing temperature indicates a stabilization of the divalent state at low temperatures, as observed in $x = 1$ [16]. The x dependence of the XAS spectra measured at 10 K is shown in Fig. 2(b), where the Sm^{2+} component evidently develops with decreasing x.

The temperature dependence of the average Sm-ion valence in $(Sm_xLa_{1-x})Os_4Sb_{12}$ determined by the fitting of each spectra is shown in Fig. 3. For all x, the valence decreases gradually with decreasing temperature. In the middle temperature range, the valence shows a logarithmic temperature dependence. In $T > 200$ K and $T < 20$ K, the valence shows a tendency to saturate deviating from the log T dependence, as reported already for $x = 1$ [16]. With decreasing x, the valence at 10 K decreases from $v = +2.78$ ($x = 1$) to $v = +2.73$ ($x = 0.2$).

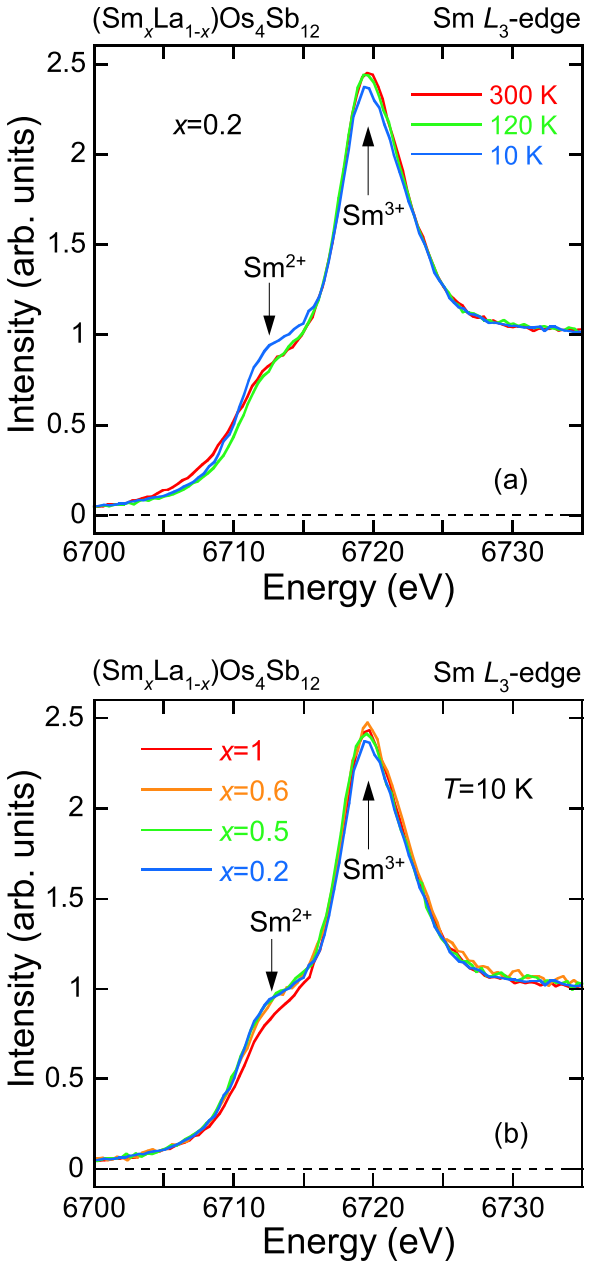

FIG. 2. (Color online) (a) Temperature dependence of XAS spectra around the Sm L_3 edge for $x = 0.2$. (b) Sm concentration dependence of XAS spectra measured at 10 K.

The observed log T-like dependence of the Sm-ion valence indicates the existence of "an unconventional Kondo effect associated with charge degrees of freedom" of Sm ions. From the slightly S-shaped behaviors appearing in Fig. 3, the associated characteristic temperature of the Kondo effect (referred to below as "the Kondo temperature $\tilde{T}_K$") is inferred to be a few tens of Kelvin.

Note that such "nonmagnetic Kondo effect" has been the subject of considerable scientific interest and extensive research work has been performed experimentally towards the realization of such phenomena because exotic nature is theoretically expected to appear (e.g., non-Fermi-liquid behaviors in the two-channel Kondo case) [20]. Candidate materials reported so far are ThAsSe [21], $(U_xY_{1-x})Pd_3$

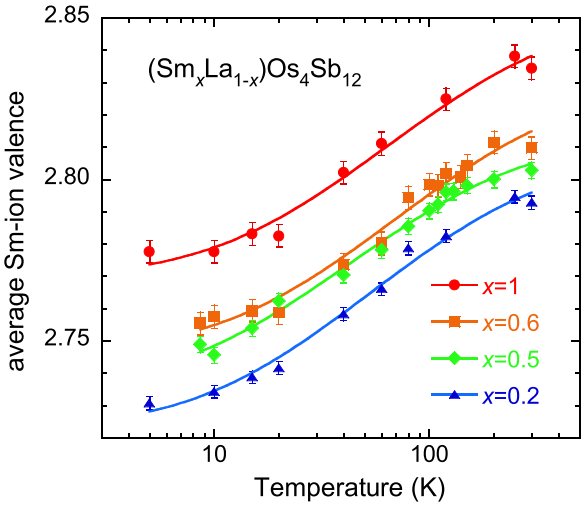

FIG. 3. (Color online) Temperature dependence of the average Sm-ion valence, $v(T)$, in $(Sm_xLa_{1-x})Os_4Sb_{12}$. $v(T)$ shows a $\log T$-like behavior in the middle temperature range. The solid lines are best fits of Eq. (3) to the data.

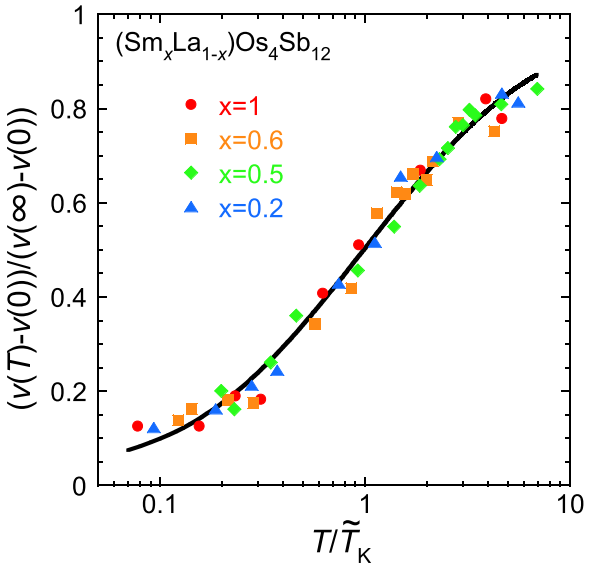

FIG. 4. (Color online) $T/\tilde{T}_K$ dependence of the normalized Sm-ion valence $[v(T) - v(0)]/[v(\infty) - v(0)]$ of $(Sm_xLa_{1-x})Os_4Sb_{12}$. The solid line, which can be approximated as $0.50 + 0.55\log_{10}(T/\tilde{T}_K) - 0.18[\log_{10}(T/\tilde{T}_K)]^3 + \cdots$, corresponds to the fitting curve of Eq. (3).

[22,23], $PrInAg_2$ [24], $Pr_xLa_{1-x}Pb_3$ [25], and $PrTi_2Al_{20}$ [26]. In those materials, it is expected that nonmagnetic internal variables coupled with conduction electrons are tunneling centers (atoms quantum mechanically tunneling among minima of a multiwell potential) and quadrupolar (orbital) moments possessed by the crystalline-electric-field ground state of non-Kramers Pr and U ions. In any of those compounds, however, such $\log T$ dependence in the ion valence has not been observed yet.

To analyze the temperature dependent Sm-ion valence shown in Fig. 3, we tentatively apply a simplified theoretical model discussed by Tanikawa *et al.* [14]. In this model, a Sm ion is moving in an anharmonic potential interacting with conduction electrons [27–30]. Since, in each cage, the effective attractive interaction between conduction electrons (consisting mainly of Sb $5p$ electrons) and the Sm ion grows with decreasing temperature, the number of the conduction electrons with f symmetry with respect to the Sm ion increases with decreasing temperature, leading to a decrease of the Sm-ion valence as well as a decrease of the Sm-Sb bond length. This scenario provides a qualitative account for the observed anomalous temperature dependence of the Sm-Sb bond length (or the size of the Sb_{12} cage) [7,10], which decreases, while the average Sm-ion radius increases with decreasing temperature below ~200 K [31]. Recent theoretical analysis of the high-energy spectroscopic data [16,17] suggests that the Sm ground state has the nonmagnetic f^6 configuration ($J = 0$) [32], where conventional magnetic Kondo effect is not expected but the above-mentioned mechanism is allowed to work.

The theoretically calculated T dependence of the number of conduction electrons with f symmetry accumulating on the Sm ion, $n_c^{(f)}$, is presented in Fig. 6 of Ref. [14] (note that D/D_0 in Fig. 6 corresponds to $\alpha(T/\tilde{T}_K)$ with $\alpha = 2.7 \times 10^{-5}$). With the use of its functional form of $n_c^{(f)}[\alpha(T/\tilde{T}_K)]$, we fit the experimental data shown in Fig. 3 as

$$v(T) = an_c^{(f)}[\alpha(T/\tilde{T}_K)] + b, \tag{3}$$

where constants a, b, and $\tilde{T}_K$ are chosen so that Eq. (3) is the best fit of the data. As the best-fit curves depicted in Fig. 3 demonstrate, the overall temperature dependence of the Sm-ion valence is nicely reproduced by the Eq. (3). Note that $\tilde{T}_K$ corresponds to the temperature where the Sm-ion valence shows the steepest slope in Fig. 3 [33]. Figure 4 shows the $T/\tilde{T}_K$ dependence of the normalized Sm-ion valence $[v(T) - v(0)]/[v(\infty) - v(0)]$, where $v(0)$ and $v(\infty)$ are given by Eq. (3) with $T \to 0$ and $T \to \infty$, respectively [they can be calculated as $v(0) = 1.460a + b$ and $v(\infty) = 1.388a + b$ using the fitting constants of a and b].

The Kondo temperature $\tilde{T}_K$ determined by the fitting is shown in Fig. 5. The value of $\tilde{T}_K$ is 56 ± 10 K, which is close to the Einstein temperature of $LaOs_4Sb_{12}$ and $SmOs_4Sb_{12}$ [7,34]. It appears that $\tilde{T}_K$ does not depend on the Sm-ion concentration. This fact indicates that the unconventional Kondo effect associated with the valence fluctuation has mainly a local nature; i.e., Sm-Sm intersite interactions (or coherence effects) are not effective. Generally, a Kondo temperature may be expressed as $k_B\tilde{T}_K = W\exp[-1/(J\rho_c)]$, where W, J, and ρ_c represent the conduction band width, the relevant coupling constant, and the electronic density of states, respectively [20]. The observed x independence of $\tilde{T}_K$ indicates that $J\rho_c$ does not change much by the La doping in $(Sm_xLa_{1-x})Os_4Sb_{12}$. This is attributable to the characteristic feature of the filled-skutterudite crystal structure, i.e., each Sm (or La) ion is contained in respective Sb_{12} cages and is separated from one another. Consequently, the unconventional Kondo effect of each Sm ion does not tend to be affected by nearby rare-earth ions.

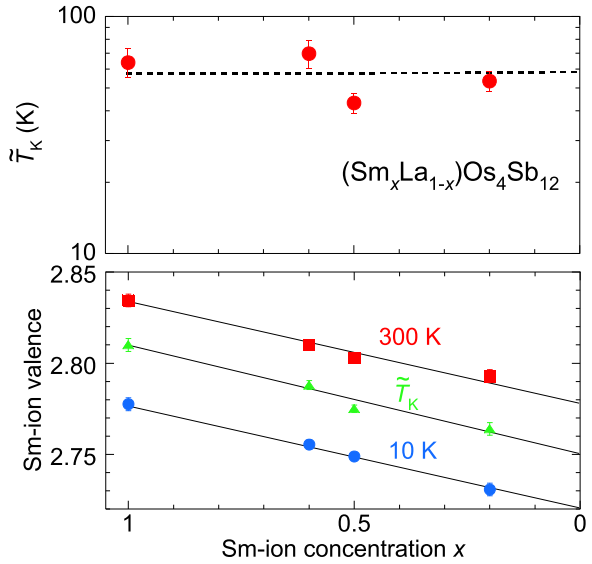

FIG. 5. (Color online) Sm concentration dependencies of "the associated Kondo temperature" $\tilde{T}_K$ and the Sm-ion valence.

With decreasing x, the Sm-ion valence shifts to 2+ as shown in Figs. 3 and 5. This behavior may be associated with the following factors. First, since a La^{3+} ion provides three conduction electrons, which is larger than those from a $Sm^{(2.7-2.8)+}$ ion, the conduction electron density (or the Fermi energy) will increase with decreasing x. Consequently, based on the model discussed by Tanikawa *et al.* [14], the shielding of a moving Sm ion by conduction electrons may become more effective, resulting in the further shift of the Sm-ion valence to 2+. Second, the La ion substitution causes a negative chemical pressure effect. Since a La^{3+} ion has an ionic radius larger than that of a $Sm^{(2.7-2.8)+}$ ion, the lattice expands with decreasing x in $(Sm_xLa_{1-x})Os_4Sb_{12}$, as actually observed by the x-ray powder diffraction measurement. Therefore, a Sm^{2+} ion, whose ion radius is larger than that of Sm^{3+}, becomes more acceptable in the expanded lattice of $(Sm_xLa_{1-x})Os_4Sb_{12}$. This interpretation is consistent with a recent study of the pressure effect on the Sm-ion valence in $SmOs_4Sb_{12}$; the Sm-ion valence shifts to 3+ by applying pressure [35].

The presence of extraordinary charge fluctuations in $SmOs_4Sb_{12}$ has been detected by other physical quantities. In the temperature dependence of the spin-spin relaxation rate $1/T_2$ in the ^{121,123}Sb nuclear quadrupole resonance (NQR) measurements, a pronounced peak appears at $T_x = 125-150$ K [36]. An increase in the linewidth of the Sb-NQR spectrum below T_x suggests that this peak is due to a slowing down of charge fluctuations (or the electric-field-gradient fluctuations at the Sb site), crossing the correlation time of 1 μs with decreasing temperature. Note that no corresponding anomalies appear in ZF-μSR [37], which is sensitive to "magnetic" fluctuations with almost the same time window. In ultrasound measurements, anomalous Debye-type dispersions are observed [38]. At the moment, however, it is not clear whether these anomalies are associated with the temperature dependent shift of the Sm-ion valence.

Nevertheless, all these anomalies appear in the temperature range of 10−100 K, where the Sm-ion valence shifts dramatically. In the same temperature range, the heavy-fermion state develops gradually with decreasing temperature, ending up with attaining the Fermi-liquid characteristics below $\sim$ 2 K [39]. Based on these facts, it is highly probable that the unconventional Kondo effect associated with the charge degrees of freedom observed in the present study is deeply involved in the field-insensitive heavy-quasiparticle formation in $SmOs_4Sb_{12}$.

In summary, we have revealed the systematic T and x dependent variation of the Sm-ion valence in $(Sm_xLa_{1-x})Os_4Sb_{12}$ by x-ray absorption spectroscopy measurements at the Sm L_3 edge. The temperature dependence shows a $\log T$ behavior, indicating that the valence change is caused by an unconventional Kondo effect associated with Sm $4f$-electron charge degrees of freedom. Almost x independence of the associated Kondo temperature ($\tilde{T}_K = 56 \pm 10$ K) indicates that the Kondo effect has a local nature, attributable to the cage structure of the filled skutterudite.

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