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Nd-based possibly heavy-fermion compound $\text{NdOs}_4\text{Sb}_{12}$ is investigated by soft x-ray spectroscopy. It is revealed by Nd 3d core-level photoabsorption measurement that the Nd ions are nearly trivalent in the bulk. Combined study by Nd 3d core-level photoelectron spectroscopy and valence band resonant photoelectron spectroscopy suggests that Nd is divalent at the surface and, moreover, that a Kondo-like state is realized in the bulk because of the hybridization between the Nd 4f and the conduction band states.

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I. INTRODUCTION

The filled skutterudite compounds with general formula RT_4X_{12} , where R is a rare-earth atom, T is a transition metal atom (Fe, Ru, Os), and X is a pnictogen atom (P, As, Sb), have attracted much attention because they show various interesting physical properties, such as Kondo effect, superconductivity, and heavy-fermion behaviors.¹ Especially, in ROs_4Sb_{12} which has the largest X -icosahedron cage around the R atom in RT_4X_{12} , unusual behaviors such as Kondo insulating behavior in $\text{CeOs}_4\text{Sb}_{12}$ (Ref. 2), Pr-based heavy-fermion superconductivity in $\text{PrOs}_4\text{Sb}_{12}$ (Ref. 3) and heavy-fermion behavior which is robust against the magnetic field in $\text{SmOs}_4\text{Sb}_{12}$ (Ref. 4) have been observed. The electronic states of these compounds have been studied directly by means of photoelectron spectroscopy,⁵⁻⁷ and the roles of the R 4f electronic states in the physical properties have been clarified.

$\text{NdOs}_4\text{Sb}_{12}$ (Refs. 1 and 8) has been reported to show ferromagnetism and possible Nd-based heavy-fermion behavior.⁸ However, the electronic states have not been investigated directly by spectroscopic methods despite its importance for the systematic understanding of the unusual properties of ROs_4Sb_{12} . In general, Nd is trivalent in most Nd compounds. In a series trivalent rare-earth compounds, the lattice constant is usually decreased from $R=\text{La}$ to Lu (so-called “lanthanide contraction”). For example, R -Sb distance is decreased by 0.083 Å (from 3.244 to 3.161 Å) from $R=\text{La}$ to Nd in the rare-earth antimonide series.⁹ In the ROs_4Sb_{12} skutterudites, the amount of contraction is much smaller. Detailed structural analyses have shown that the decrease in the distance between the rare-earth atom and the Sb atom from $\text{LaOs}_4\text{Sb}_{12}$ to $\text{NdOs}_4\text{Sb}_{12}$ is only 0.016 Å (from 3.496 to 3.480 Å).^{10,11} This might mean that the space around Nd is expanded in $\text{NdOs}_4\text{Sb}_{12}$ compared to usual situation. In other words, Nd is under a negative pressure in $\text{NdOs}_4\text{Sb}_{12}$. In several rare-earth systems, applying pressure leads to the increase of the valence number. For example, SmS experiences a transition from Sm^{2+} to $\text{Sm}^{2.6+}$ above a pressure of 6.5 kbar in room temperature.¹² Therefore, the

above-mentioned negative pressure on Nd atom may lead to a decrease of valence number of Nd, resulting in the $\text{Nd}^{(3-\delta)+}$ state.

The large electronic specific heat coefficient ($\gamma \sim 520 \text{ mJ/K}^2 \text{ mol}$) of $\text{NdOs}_4\text{Sb}_{12}$ may be related to the heavy-fermion state-based Nd 4f states. Namely, the heavy-fermion state may be based on the mixed state with a small amount of Nd^{2+} component in addition to the main Nd^{3+} component, which is realized by the hybridization between the Nd 4f state and the conduction band state. The aim of this study is to verify this scenario by investigating the Nd 4f state utilizing the soft x-ray spectroscopy methods.

II. EXPERIMENTAL

Single crystals of $\text{NdOs}_4\text{Sb}_{12}$ were grown by the Sb self-flux method by using high purity raw materials.¹ Characterization of the sample has been reported elsewhere.¹³ Successful observation of de Haas van Alphen oscillation¹⁴ also indicates that the samples are of high quality. Soft x-ray (SX) spectroscopy measurements were performed at the twin-helical undulator SX beamline BL25SU in SPring-8 (Ref. 15). Clean surfaces of the samples were obtained by fracturing the samples *in situ* in ultrahigh vacuum ($\sim 3 \times 10^{-8} \text{ Pa}$) at $\sim 20 \text{ K}$. For the Nd 3d \rightarrow 4f absorption spectroscopy (XAS) measurement, the total electron yield method was adopted. The SX photoelectron spectroscopy (SXPES) measurements were carried out using a GAMMADATA-SCIENTIA SES-200 spectrometer. Samples were so set as the photoelectrons emitted nearly normally from the surface are detected by the analyzer. The total energy resolution (ΔE) of the SXPES measurement was set to $\Delta E \sim 100 \text{ meV}$ in the highest resolution measurements.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the Nd 3d \rightarrow 4f XAS spectrum of $\text{NdOs}_4\text{Sb}_{12}$. The calculated spectrum of the $3d^{10}4f^3 \rightarrow 3d^9 4f^4$ process reflecting the Nd trivalent initial state ($4f^3$) (Ref. 16) is also shown in the lower part of Fig. 1(a). This

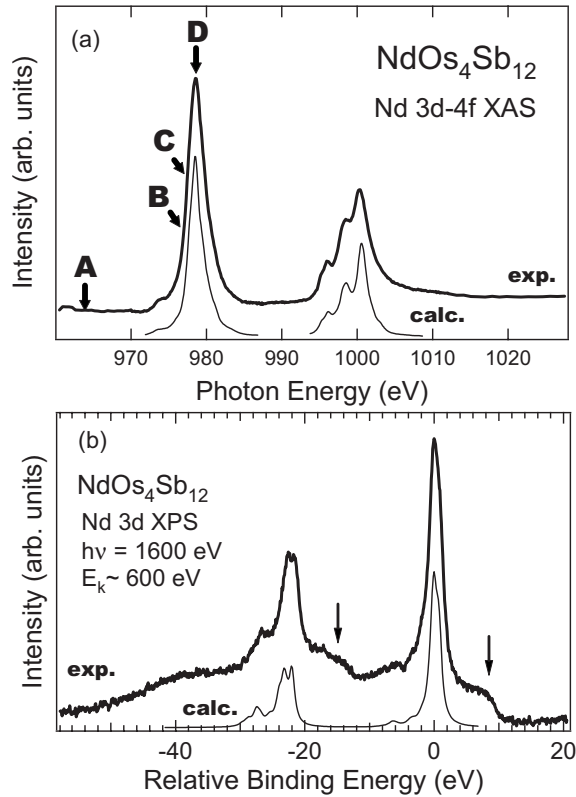


FIG. 1. (a) The observed Nd $3d \rightarrow 4f$ XAS spectrum of $\text{NdOs}_4\text{Sb}_{12}$ (exp.) and calculated Nd XAS (calc.) assuming the $3d^{10}4f^3 \rightarrow 3d^9 4f^4$ process (Ref. 16). The arrows with labels A–D represent the photon energies with which RPES was taken. (b) The observed Nd $3d$ XPS spectrum of $\text{NdOs}_4\text{Sb}_{12}$ (exp.) and calculated Nd XAS (calc.) assuming the $3d^{10}4f^3 \rightarrow 3d^9 4f^3$ process. The arrows indicate the structures in the observed spectrum that do not correspond with the calculation.

calculation is a so-called “atomic multiplet calculation” which takes into account both the spin-orbit interaction and the electron-electron interaction in a fairly accurate manner. A good correspondence is recognized between the experimental and calculated spectra. If there is a Nd^{2+} component of the order of 5%, it would be distinguishable in XAS. XAS measurement is known to be one of the most bulk-sensitive measurements. Therefore, we can interpret that Nd ions are mainly trivalent in the bulk of $\text{NdOs}_4\text{Sb}_{12}$. If there is any Nd^{2+} component in the bulk, it would be at most a few percent.

Figure 1(b) shows the Nd $3d$ core-level photoemission spectrum ($3d$ XPS) of $\text{NdOs}_4\text{Sb}_{12}$. The Nd trivalent spectrum, i.e., $3d^{10}4f^3 \rightarrow 3d^9 4f^3$ process obtained by the atomic multiplet calculation, is also shown in the lower part of Fig. 1(b). In Fig. 1(b), there are remarkable differences as indicated by the arrows. These additional structures are thought to be the contribution of the $3d^9 4f^4$ component in the final state. In this experiment, the Nd $3d$ core photoelectrons’ kinetic energy (E_k) is not so high ($E_k \sim 600$ eV). Thus, the bulk spectral weight is lower than that of the XAS spectrum. Therefore, the observed $3d^9 4f^4$ component can be resulting from the Nd^{2+} state near the surface. This is probable because, in general, rare-earth atoms tend to take divalent state

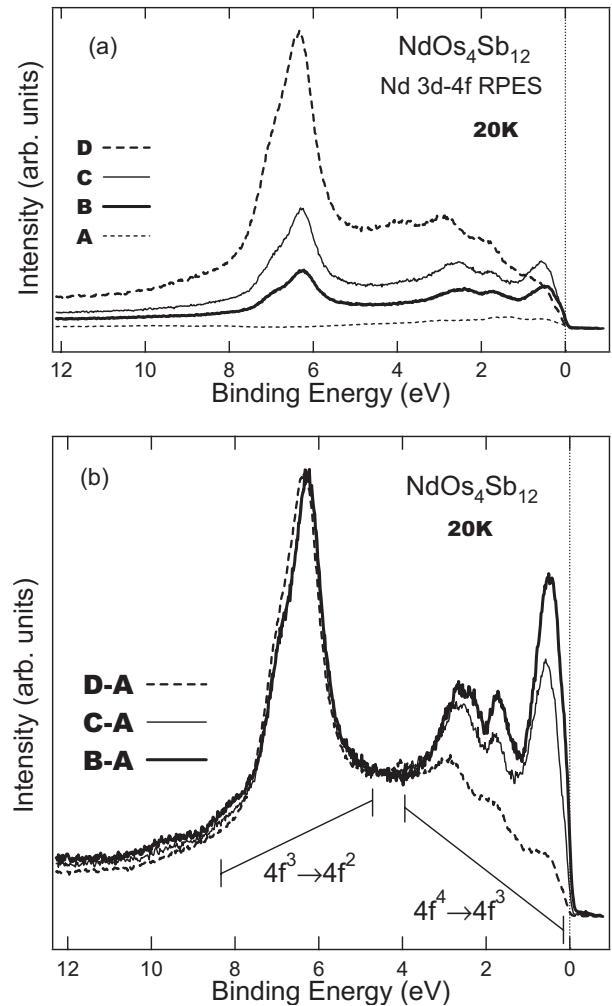


FIG. 2. (a) The observed valence band RPES spectra of $\text{NdOs}_4\text{Sb}_{12}$ observed at the photon energies in the Nd $3d \rightarrow 4f$ photoabsorption region indicated by the arrows in Fig. 1(a). (b) Spectra obtained by subtracting the spectrum A from the spectra B, C, and D of Fig. 2(a). Structures corresponding to the $4f^3 \rightarrow 4f^2$ and $4f^4 \rightarrow 4f^3$ transitions are observed. See also the calculated multiplet structures shown in Fig. 3(a).

at the surface. On the other hand, $3d^9 4f^4$ final-state component can also be caused by the hybridization between the Nd $4f$ state and the conduction band state in the initial and the final states.

Next we carried out the valence band resonant photoelectron spectroscopy (RPES) measurements in the Nd $3d \rightarrow 4f$ photoabsorption region. The on-RPES spectra of $\text{NdOs}_4\text{Sb}_{12}$, measured at the photon energies B–D in Fig. 1(a), are shown in Fig. 2(a), together with the off-RPES spectrum taken at the photon energy A. In order to reveal the contribution of the Nd $4f$ electrons, we subtract the off-RPES spectrum from the on-RPES spectra as shown in Fig. 2(b). Figures 2(a) and 2(b) are normalized, respectively, by the photon flux and the peak intensity at around binding energy (E_B) of ~ 6.3 eV. Structures between the Fermi level (E_F , $E_B=0$) and $E_B \sim 4$ eV and those in 5–8 eV are attributed respectively to the “ $4f^4 \rightarrow 4f^3$ ” and “ $4f^3 \rightarrow 4f^2$ ” processes as shown below. In Fig. 2(b), we find that the Nd divalent component in-

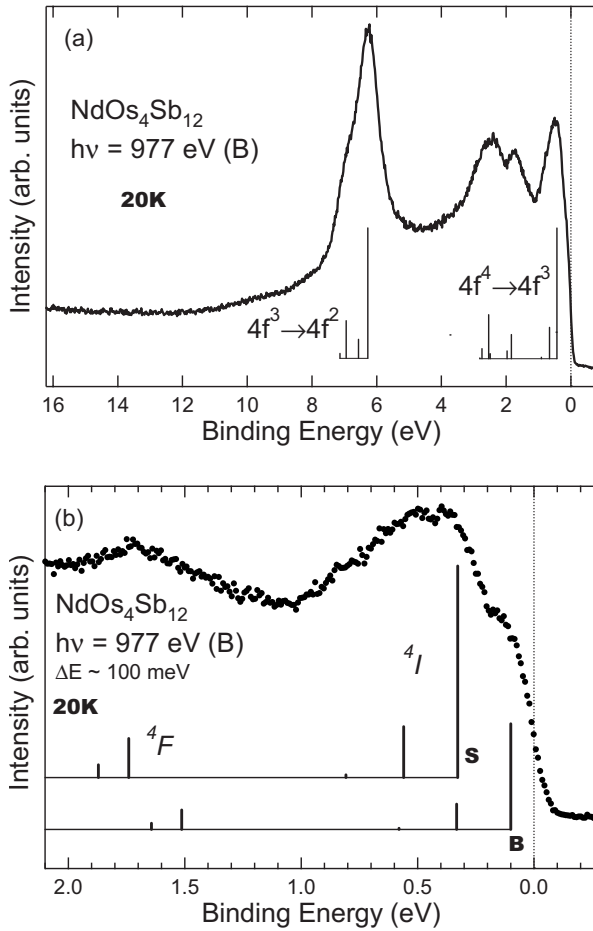


FIG. 3. (a) Comparison between the RPES spectrum B of Fig. 2(a) with the calculated PES multiplet structures for $4f^3 \rightarrow 4f^2$ and $4f^4 \rightarrow 4f^3$ processes (Ref. 19). (b) The result of high-resolution RPES with energy resolution of about 100 meV. In the lower binding energy region of the peak around 0.4 eV, a structure is observed around the binding energy of 0.1 eV. This suggests that there are two different sets of $4f^4 \rightarrow 4f^3$ multiplets energetically shifted from each other such as the structures labeled S and B .

creases monotonously from energy D to B . The “ $4f^4 \rightarrow 4f^3$ ” structure is stronger than in Nd metal.¹⁷

If we assume that the Nd^{2+} state ($4f^4$) is present, $4f^4 \rightarrow 3d^9 4f^5$ photoabsorption is expected to occur. This process for the Nd^{2+} state is expected in the photon energy region of a few eV lower than the photoabsorption peak D of Nd^{3+} , based on the results for mixed valence state between Sm^{2+} and Sm^{3+} (Ref. 18). At the photon energy B , for example, $4f^4 \rightarrow 3d^9 4f^5$ photoabsorption process starting from the Nd^{2+} state is followed by the direct recombination process $3d^9 4f^5 \rightarrow 4f^3 + \text{photoelectron}$. This process results in the enhancement of the $4f^4 \rightarrow 4f^3$ structures in Fig. 2(b).

In Fig. 3(a), the spectrum B in Fig. 2(a) is compared with the multiplet structures of $4f^3 \rightarrow 4f^2$ and $4f^4 \rightarrow 4f^3$ photoemission processes obtained by the atomic multiplet calculation (Ref. 19). The $4f^4 \rightarrow 4f^3$ multiplet structure is obtained by scaling the energy axis of the calculated result of Pm^{3+} (Ref. 19), which has the same $4f^4$ initial state as Nd^{2+} . The good correspondence between the observed structures with the calculated multiplet structures confirms that the experi-

mentally observed structures between E_F and $E_B \sim 4$ eV are coming from the $4f^4 \rightarrow 4f^3$ process.

High-resolution photoemission result obtained at the same excitation photon energy as Fig. 3(a) is shown in Fig. 3(b). A clear shoulder structure is found around $E_B \sim 0.1$ eV in the lower binding energy region of the main peak at around 0.4 eV. This structure most probably comes from the $4f$ electrons because the intensity around E_F of $3d$ resonant photoelectron spectrum of La, which has no $4f$ electrons, is far smaller.²⁰ If there was only one set of $4f^4 \rightarrow 4f^3$ multiplet structures, this shoulder cannot be explained. Therefore, there are probably two sets of $4f^4 \rightarrow 4f^3$ structures shifted by roughly 0.2–0.3 eV as indicated by the two sets of multiplet lines labeled “ S ” and “ B .”

The multiplet structures “ S ,” whose lowest- E_B multiplet is well below E_F , is considered to originate from the unhybridized Nd^{2+} state, which is expected near the surface of the sample as discussed above. On the other hand, the lowest- E_B component of the multiplet structure “ B ” is just below E_F . This is the characteristics of the quasiparticle peak (or Kondo peak²¹) as have been observed by bulk sensitive PES for Ce- and Yb-based heavy-fermion systems.^{20,22,23} If there is a small but finite hybridization between the Nd $4f$ and the conduction band states, the Kondo-like state can be realized with a small amount of Nd^{2+} ($4f^4$) component in addition to the main Nd^{3+} ($4f^3$) component. This Kondo-like ground state can be expressed as $|G\rangle = a|f^3\rangle + b|f^4\rangle$, where $|a| \gg |b|$. The photoemission final states will be composed of both $4f^2$ dominant state and $4f^3$ dominant state, namely, $|F_1\rangle = a_1|f^2\rangle + b_1|f^3\rangle$ ($|a_1| \gg |b_1|$) and $|F_2\rangle = a_2|f^2\rangle + b_2|f^3\rangle$ ($|a_2| \ll |b_2|$). $|G\rangle \rightarrow |F_1\rangle$ process results in the “ $f^3 \rightarrow f^2$ ” peak. In the $|G\rangle \rightarrow |F_2\rangle$ process, the f electron numbers of the initial and final states are nearly the same (~ 3). Therefore, this process corresponds to the “quasiparticle excitation,” in which the conduction electron is mainly excited, rather than being a genuine “ $f^4 \rightarrow f^3$ ” process. This process leads to a peak located at E_F , namely, the quasiparticle peak, and satellites corresponding to the excited atomic multiplet structures. Therefore, the presence of the multiplet structures “ B ” strongly suggests that the Kondo-like ground state is realized. If the Kondo-like ground state is realized in the bulk, the large specific heat will also be explained by the heavy-fermion state caused by the hybridization between the Nd $4f$ and the conduction band states.

$|F_2\rangle$ ($|F_1\rangle$) is the bonding (antibonding) state since the energy of $|F_2\rangle$ is lower than $|F_1\rangle$. $|G\rangle$ is of course the bonding state. Therefore, the intensity of the $|G\rangle \rightarrow |F_2\rangle$ process ($|a_2 a + b_2 b|^2$), corresponding to the quasiparticle peak, is larger than the weight of the $|f^4\rangle$ state in $|G\rangle$ ($|b|^2$) (Ref. 21). When the weight of the $|f^4\rangle$ state is of the order of 1% or larger in the ground state, the quasiparticle peak will be observable as in Fig. 3(b). Therefore, the bulk Kondo-like state with $|f^4\rangle$ state of ~ 1 –2% is consistent with all the spectra presented here.

In the Kondo-like ground state, a certain degree of freedom of the $4f^3$ state is considered to be screened by the conduction electrons. Ferromagnetism of $\text{NdOs}_4\text{Sb}_{12}$ in low temperatures ($T_C \sim 1$ K) with a Nd magnetic moment of nearly $2 \mu_B$ (Ref. 8) excludes the usual Kondo ground state,

which is spin-singlet as a result of the conduction electrons screening the $4f$ state's magnetic degree of freedom. Therefore, a degree of freedom other than the magnetic one, for example, the orbital degree of freedom, is considered to be screened in the Kondo-like ground state.

The Nd $4f$ state of $\text{NdOs}_4\text{Sb}_{12}$ suggested by the present study is on the line of the so far revealed R $4f$ states in $\text{ROs}_4\text{Sb}_{12}$. In $\text{CeOs}_4\text{Sb}_{12}$, $\text{PrOs}_4\text{Sb}_{12}$, and $\text{SmOs}_4\text{Sb}_{12}$, respectively, is realized the Kondo state composed of a small amount of Ce^{4+} component in addition to the main Ce^{3+} state, the Kondo state with a very small amount of Pr^{4+} and/or Pr^{2+} components and the main Pr^{3+} component, and the mixed valence state with a considerable amount of Sm^{2+} component and the main Sm^{3+} component. Together with the abovementioned Nd $4f$ state, systematic change of the R $4f$ state is found in the series of $R=\text{Ce, Pr, Nd, and Sm}$.

IV. SUMMARY

We have carried out XAS and SXPS measurements of the filled skutterudite compound $\text{NdOs}_4\text{Sb}_{12}$ using high-resolution soft x rays. The results suggest that Nd is mainly trivalent in the bulk. Nd divalent components are clearly ob-

served in Nd $3d$ XPS and RPES of the valence band. High-resolution study suggests that there exist two sets of Nd^{2+} -like RPES structures, namely, the real $4f^4 \rightarrow 4f^3$ structures and the quasiparticle peak. We tend to consider that the former process occurs near the surface and the latter occurs in the bulk. The quasiparticle peak originates from the Kondo-like state coming from the hybridization between the Nd $4f$ and the conduction band states. Then, the large electronic specific heat coefficient is well understood by considering the heavy-fermion state caused by the hybridization. It has further been confirmed that the R $4f$ state changes systematically in the series of $\text{ROs}_4\text{Sb}_{12}$.

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