Anomalous Correlation between Cage Size and Valence State in SmOs$_4$Sb$_{12}$

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Abstract. We have carried out the synchrotron powder diffraction and x-ray absorption experiments of a valence-fluctuated heavy fermion compound SmOs$_4$Sb$_{12}$. The size of the Sb cage which includes a Sm atom shows significant temperature dependence. This correlates with the temperature dependence of the Sm valence. However, the cage size shrinks with decrease of temperature although the averaged ionic radius becomes large. This anomalous temperature dependence suggests the correlation between the cage size and the hybridization of the 4f electron with the conduction electrons in SmOs$_4$Sb$_{12}$.

1. Introduction

Change of unit cell volume at certain temperature was reported in valence fluctuated or intermediate valence compounds such as SmB$_6$ [1] and Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$ [2]. This correlates with the radii of rare-earth ions. In the case of Sm compounds, for example, increase of the number of Sm$^{3+}$ ions expands the unit cell volume, because Sm$^{3+}$ ionic radius is larger than Sm$^{2+}$ one. The measurement of the lattice constant is useful to know the change of the valence in intermediate-valence compounds. Synchrotron powder diffraction (PD) experiment is one of the useful tools to investigate the valence state in these compounds. Also, x-ray absorption spectroscopy (XAS) is a more quantitative probe to investigate the valence state. Its chemical shift demonstrates the change of the valence and its
intensity ratio reflects that of the different valence state. We have investigated the correlation between the unit cell volume and averaged valence state by PD and XAS experiments.

2. Experimental Procedure
We have carried out the PD of SmOs$_4$Sb$_{12}$ at BL02B2 and XAS at BL01B1 at SPring-8 in Japan. The energy used in the PD experiment is 14.978 keV, calibrated by the lattice constant of CeO$_2$ at room temperature. The PD experiments were carried out between 10 and 300 K with He closed-cycle cryostat. The parameters were determined by Rietveld analysis with RIETAN-2000 program [3]. The XAS spectra were measured at Sm L$_3$ edge. The energy used was calibrated by the XAS spectrum of Sm$_2$O$_3$ at room temperature. The way of the determination of the averaged valence was reported in the Ref. 4.

3. Experimental Results and Discussion
All the PD patterns obtained at various temperatures in SmOs$_4$Sb$_{12}$ were successfully analyzed with Im$ar{3}$ symmetry as was reported in Ref. 5. The obtained lattice constant monotonically decreases with the decrease of temperature. This suggests that the unit cell volume is insensitive to the change of the Sm valence state. The temperature dependence of the averaged Sm valence suggests that the change of the unit cell volume is expected [4], because Sm$^{2+}$ ionic radius is larger than Sm$^{3+}$ one. Especially, the gradual expansion due to the change of the averaged valence is expected between $T_A$ and $T_B$ defined by Ref. 4. This demonstrates that SmOs$_4$Sb$_{12}$ differs from the previous valence fluctuation compounds as mentioned above.

Since the Sm ions are surrounded by twelve Sb atoms, we have also investigated the ratio of the Sb cage volume to the unit cell volume. Figure 1 shows the temperature dependence of the $\left(y^2 + z^2\right)^{3/2}$ value and averaged Sm valence, where $y$ and $z$ are atomic position parameters at the 24g site in Im$\bar{3}$ symmetry, corresponding to the Sb site in SmOs$_4$Sb$_{12}$. The $\left(y^2 + z^2\right)^{3/2}$ value corresponds to the ratio

![Fig. 1. Temperature dependence of the Sm valence (upper window) and $\left(y^2 + z^2\right)^{3/2}$ value (lower window) in SmOs$_4$Sb$_{12}$. $T_A$ ($T_B$) is an upper temperature (a lower temperature) where the averaged valence is constant at low (high) temperature region. The dotted curves are guides to the eye.](image-url)
of the Sb cage to the unit cell volume. Then, Fig. 1 suggests that the cage volume is more strongly connected with the valence state than the unit cell volume. As mentioned above, however, the Sm$^{2+}$ radius is larger than Sm$^{3+}$ one. Although the expansion of the cage size is expected by the change of the averaged valence [4], the results obtained at the present work demonstrate that the cage size is shrunk as temperature decreases. That suggests that shrinking the cage size does not correlate with the change of the Sm ionic radii, but with another factor. Since SmOs$_4$Sb$_{12}$ is a heavy fermion (HF) compound, the hybridization between 4f and conduction electrons is essential to realize HF behavior. In this sense, the temperature dependence of the cage correlates with the hybridization. In addition, the temperature dependence of the averaged valence is anomalous in magnetically ordered Sm compounds, because Sm$^{3+}$ is a magnetic ion but Sm$^{2+}$ is a non-magnetic ion. In fact, the presence of the strong hybridization between 4f and conduction electrons was pointed out by the photoemission spectroscopy [6]. The hybridization could affect the Sb cage size in SmOs$_4$Sb$_{12}$.

Figure 2 shows the temperature dependence of the atomic displacement factor at the 2a site in SmOs$_4$Sb$_{12}$. The dotted curve is a fitting one when the Einstein temperature at the 2a site is 40.1 K.

![Fig. 2. Temperature dependence of the atomic displacement factor at the 2a site in SmOs$_4$Sb$_{12}$. The dotted curve is a fitting one when the Einstein temperature at the 2a site is 40.1 K.](image)

The temperature dependence of the atomic displacement factor $U_{Sm}$ at the 2a site. In spite of the change of the Sb cage and Sm ionic radii, the atomic displacement factor monotonically decreases with decrease of temperature. Since the discovery of HF behavior in SmOs$_4$Sb$_{12}$, the origin of the HF behavior has been discussed. The robustness to applied magnetic field suggests that the origin is not conventional for the HF behavior. This means that a non-magnetic factor is needed as the origin. One of the possibilities is a low-lying phonon like an Einstein oscillator proposed by some theories [7-9]. Since the presence of an Einstein-like mode is expected on the crystallographic point of view, the temperature dependence of the atomic displacement factor was analyzed by the following equation:

$$U_{Sm} = \frac{\hbar^2}{2mk_B\theta_E} \coth\left(\frac{\theta_E}{2T}\right),$$

where $\hbar$ is Dirac constant, $m$ is the atomic mass, $k_B$ is Boltzmann factor and $T$ is temperature. We obtained the Einstein temperature $\theta_E = 40.1 \pm 1.7$ K from temperature dependence of the atomic displacement factor as shown in Fig. 2. This agrees with the phonon frequency obtained by second order Raman scattering, suggesting the Sm atomic motion [7]. In addition, the recent inelastic x-ray scattering in LaOs$_4$Sb$_{12}$ indicates that the nearly dispersionless La mode is seen around 5 meV [11]. Judging from the second-order Raman scattering and similar crystal structure to LaOs$_4$Sb$_{12}$, the Einstein temperature obtained in the present work suggests the presence of the dispersionless Sm mode around 3.5 meV, which agrees with a dispersionless mode observed by inelastic x-ray scattering [12]. The present results also suggest a possible origin of the HF behavior in SmOs$_4$Sb$_{12}$, insensitive to applied magnetic field.
4. Summary
We have investigated the temperature dependence of the averaged Sm valence and the crystal structure in a valence fluctuated compound SmOs$_4$Sb$_{12}$. Considering the only change of the ionic radii, the temperature dependence of the lattice constant and Sb cage seems to be anomalous. The present results infer some correlations between the cage size and the hybridization of the 4f electrons with the conduction electrons. The shrinkage of the Sb cage size suggests that the hybridization between the 4f-electrons and the Sb 5p-electrons become strong with decrease of temperature. The correlation between the crystal structure and valence state suggest that $T_A$ and $T_B$ determined by the XAS measurements also indicate some characteristic temperature associated with the HF behavior in SmOs$_4$Sb$_{12}$. In addition, since such temperature dependence of the atomic position parameters were not observed in a heavy fermion superconductor PrOs$_4$Sb$_{12}$ [13], the origin of HF behavior between SmOs$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$ may be different.

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