X-ray magnetic circular dichroism at Os L-edge under multiple extreme conditions in SmOs$_4$Sb$_{12}$

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Abstract. X-ray absorption spectrum (XAS) and X-ray magnetic circular dichroism (XMCD) in a filled skutterudite SmOs$_4$Sb$_{12}$ were measured at Os L-edge under multiple extreme conditions, $T = 2.2$ K, $H = 10$ T, and $P$ up to 3.5 GPa in order to obtain information of Os 5$d$ electronic states. At ambient pressure, small dichroic signal of 0.1% was clearly observed and the orbital and spin magnetic moments of Os 5$d$ are estimated to be -0.001 $\mu_B$ and 0.012 $\mu_B$, respectively. At high pressure, the XMCD intensity reaches a maximum around 0.6 GPa, and decreases with increasing pressure as to finally disappear at 3.5 GPa. This trend is similar to the reported magnetization under high pressure. The behavior of Os 5$d$ electronic states strongly connects with a novel feature observed in SmOs$_4$Sb$_{12}$.

1. Introduction

The filled skutterudites RT$_4$X$_{12}$ (R = rare earth, T = Fe, Ru, and Os, X = P, As, and Sb) show a variety of interesting phenomena such as magnetic ordering, superconductivity, heavy fermion (HF) behavior, metal-insulator transition, valence fluctuation and so on [1]. These phenomena originate from strongly correlated electrons behaviors based on hybridization between intrinsically localized $f$-electrons and conduction electrons ($c$-$f$ hybridization). It is believed that the cage structure of pnictogen and transition metal atoms surrounding rare-earth atoms plays a key role in the strong $c$-$f$ hybridization correlated with novel features in rare-earth filled skutterudites. The difference in the nature of the superconductivity between PrRu$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$ is one of the examples [2]. In this manner, the role of itinerancy of $d$ electrons is hardly negligible on the physical properties in RT$_4$X$_{12}$, indicated by recent band calculation [1, 3].
A filled skutterudite SmOs$_4$Sb$_{12}$ has attracted much attention because this material exhibits unconventional HF behavior with a large electronic specific heat coefficient $\gamma \approx 840$ mJ/K$^2$mol insensitive to applied magnetic field [4-6]. SmOs$_4$Sb$_{12}$ also shows a weak ferromagnetic ordering with a small magnetic moment of 0.02 $\mu_B$/Sm below $T_C \approx 3$ K at ambient pressure (A. P.) [4]. Moreover, this compound forms a mixed-valence state of Sm$^{3+}$ ($J = 5/2$) and Sm$^{2+}$ ($J = 0$) [7, 8]. Although the insensitiveness to the magnetic field suggests that the origin of the unconventional behavior is non-magnetic, the mechanism of the HF behavior has not been revealed yet. The experimental results at high pressures suggest that SmOs$_4$Sb$_{12}$ is located at the vicinity of a quantum critical point [9]: the $T_C$ increases with increase of pressure; temperature dependence of electric resistivity deviates from $T^2$ dependence, a characteristic phenomenon due to Fermi liquid (FL) behavior, at $\sim 0.7$ GPa. However, most of the physical properties have been investigated by macroscopic measurements. Therefore, microscopic measurements are necessary to understand the unconventional HF behavior in SmOs$_4$Sb$_{12}$ at high pressure.

X-ray absorption spectrum (XAS) and X-ray magnetic circular dichroism (XMCD) are powerful tools to investigate element-specific features from the viewpoint of electronic and magnetic states. In particular, high-pressure measurement is extremely effective in a hard X-ray region because of unusable window materials in a soft X-ray region and little background from the pressure cell as observed in magnetization measurement. Recently, XAS spectrum at Sm $L$-edge dependent on pressure was observed, which indicates that the Sm valence state is connected with a behavior unlike FL like behavior around 0.7 GPa [10]. In addition, the Sm 5$d$ polarization was observed even in non-magnetic Sm$^{2+}$ by Sm $L$-edge XMCD under $T \approx 2$ K, $H = 10$ T, and $P = A. P.$, suggesting a magnetic Sm$^{3+}$ state is realized [11]. Since the ground state of Sm$^{2+}$ is intrinsically non-magnetic $J = 0$ state, the result indicates the presence of strong $c$-$f$ hybridization. On the other hand, the possibility of magnetic contribution from Os 5$d$ electrons with a large itinerant feature is also undeniable through the $c$-$f$ hybridization. Furthermore, the recent band calculation points out the delocalization of 5$d$ electrons in ROs$_4$Sb$_{12}$ system [1]. Therefore, the role of Os 5$d$ electronic and magnetic states is important to understand the anomalous behavior of this system. However, no information on Os 5$d$ electronic states has been reported.

In this paper, we present the XAS and XMCD spectra at Os $L$-edge in SmOs$_4$Sb$_{12}$ under multiple extreme conditions, $T = 2.2$ K, $H = 10$ T, and $P = A. P.$ up to 3.5 GPa. The Os 5$d$ spin and orbital moments at A. P. are estimated, and the pressure variation of XMCD intensity is demonstrated. The result provides us information on Os 5$d$ electrons in the physical properties of SmOs$_4$Sb$_{12}$.

2. Experimental

XAS and XMCD measurements at the Os $L$-edges under multiple extreme conditions, $T = 2.2$ K, $H = 10$ T, and $P = A. P.$ up to 3.5 GPa, were performed at BL39XU of SPring-8 using helicity-modulation method [12]. SmOs$_4$Sb$_{12}$ and EuOs$_4$Sb$_{12}$ powdered samples were used for the measurements. For high-pressure measurements, the sample put into a small diamond-anvil-cell (tiny-DAC), and Daphne oil 7373 was used as a pressure medium. Pressure at low temperature was monitored by using X-ray diffraction of NaCl [13]. Sample temperature was carefully controlled by monitoring a cernox sensor mounted near the DAC because a difference of temperature incurs a misestimate of magnetic moment.

3. Results and Discussion

3.1. Estimation of Os 5$d$ magnetic moment at ambient pressure

Figure 1 shows XAS and XMCD spectra at Os $L$-edges at 2.2 K, 10 T, and A. P. The main peak of XMCD is located at the initial rise of XAS profile at both $L_3$- and $L_2$-edges. The dichroic signal of 0.1% was clearly observed despite the small magnetic moment of this material. The observation of the dichroic signal indicates the presence of mixing between Sm 4$f$ and Os 5$d$ electronic states. The sign at $L_3$- and $L_2$-edges are positive and negative, respectively. These facts demonstrate that Os 5$d$ magnetic moments are antiferromagnetically coupled with Sm 4$f$ magnetic moments [14]. Compared with the
result of the other ferromagnetic compound including Os, Sr₂CrOsO₆, the intensity is less than 1/20 [15]. The sign is same so that Os 5d moments tend to couple antiferromagnetically with the major moment. The XMCD spectral shape between L₃- and L₂-edge has a slight difference in its width. The reason of the difference is still not clarified, although similar situation is often observed in ferromagnetic compounds including 5d transition metals such as W, Re, or Os [15-17]. Since the profile is affected by neighboring magnetic atoms in the XMCD at the K-edge of 3d transition metals or at the L-edges of 4f rare-earth elements [18-20], a similar phenomenon is one of possibilities in these observations.

To estimate the Os magnetic moment experimentally, the magneto-optical sum-rules [21, 22] are applied to the result. Here, contribution of magnetic dipole operator including in the spin sum-rule is negligible, and hole number of Os 5d, n₅d = 4.68, is employed [3]. Os 5d orbital and spin moments are estimated to be ~ 0 μB and 0.016 μB within the error of 10%, respectively. The obtained spin component is one digit smaller than the total magnetic moment of ~ 0.15 μB, which is an expected value induced by the magnetic field of H = 10 T [4, 23]. On the other hand, the orbital contribution seems to be extremely small. Since it has been reported that an orbital/spin ratio depends on temperature and/or magnetic field [24, 25], it is necessary to investigate temperature dependence of the relation.

For comparison, the XAS and XMCD spectra were measured under the same condition in EuOs₄Sb₁₂, which is also a ferromagnetic filled skutterudite with Os 5d state. Figure 2 shows the result of EuOs₄Sb₁₂ under T = 2.2 K and H = 10 T. The XAS spectra of both SmOs₄Sb₁₂ and EuOs₄Sb₁₂ are almost same at both Os L₃- and L₂-edges, reflecting the same crystal structure. The integrated intensities of white-line (WL) contribution are same within 3% at both Os L₃- and L₂-edges. On the other hand, the XMCD spectra of EuOs₄Sb₁₂ are quite different from that of SmOs₄Sb₁₂ except for their shapes and signs: an absolute intensity and an intensity ratio of L₃-edge to L₂-edge. The peak intensity of XMCD at L₃-edge (L₂-edge) in EuOs₄Sb₁₂ is about 9.6 (2.5) times larger than that in SmOs₄Sb₁₂. The enhancement of XMCD signal is due to a large magnetic moment of Eu²⁺ with ~ 7 μB/Eu [26]. The difference in multiplying factor obviously yields a finite orbital moment of Os 5d electrons. By applying the sum-rules, orbital and spin moments are estimated to be -0.027 μB and 0.055 μB within the error of 9%, respectively. Here, the same value of n₅d = 4.68 was used for the analysis. The large orbital contribution is quite different from the result in SmOs₄Sb₁₂. Although the origin of the intrinsically orbital contribution has not been clarified yet, these results on Os L-edge XMCD indicate that Os 5d polarization is induced by the strong hybridization with R 4f orbitals.
3.2. Pressure variation of Os L₃-edge XAS and XMCD

The resistivity measurements under pressure suggest a stabilization of the ferromagnetism in high pressure phase of SmOs₄Sb₁₂ [9]. Meanwhile, the spontaneous magnetic moments seem to be reduced by applied pressure over about 1 GPa [27]. However, the magnetization has been investigated in the pressure region up to 2 GPa. In order to investigate the magnetic properties in higher pressure region, the Os L₃-edge XAS and XMCD measurements were performed under multiple extreme conditions, $T = 2.2$ K, $H = 10$ T, and $P \leq 3.5$ GPa.

![Figure 2. XAS and XMCD spectra of EuOs₄Sb₁₂ (a) at the L₁-edge and (b) at the L₂-edge. The solid curves represent fitting results for the XAS spectra. The XAS spectrum is decomposed by an arctangent and two Lorentz functions that are represented by the dotted lines and hatched areas. The threshold energy of arctangent curve is determined by the same manner in the case of SmOs₄Sb₁₂. The hatched area corresponds to the WL intensity.](image)

![Figure 3. (a) XAS and (b) XMCD spectrum of SmOs₄Sb₁₂ at the Os L₃-edge for various pressures. These results were obtained at $T = 2.2$ K and $H = 10$ T.](image)

The XAS spectrum between A. P. and high pressure (H. P.) notably changes in the WL part as shown in figure 3(a). The XAS profiles between 0.6 and 3.5 GPa are almost constant except for the energy shift according to Natoli’s rule $k \cdot r = \text{const.}$ [28]. The WL intensity is related to the 5d hole

![Figure 4. The integrated intensities of (a) the WL part of XAS and (b) XMCD spectrum of SmOs₄Sb₁₂ at the Os L₃-edge as a function of pressure. These results were obtained at $T = 2.2$ K and $H = 10$ T.](image)
number: a reduction of the WL intensity represents a decrease of 5d hole number [29]. To discuss the variation in the spectra at H. P. quantitatively, the integrated intensity of the WL is shown in figure 4(a) as a function of pressure. The WL intensity is independent of pressure up to 3.5 GPa, although the intensity rapidly decreases by applying pressure. The WL intensity at H. P. decreases in 0.77 as compared with that at A. P. The Os 5d band is expanded by compression, and the hybridization with neighboring Sb p states is strengthened. An increment of Sm valence at H. P. has been observed [10]. The charge transfer within conduction band might occur at H. P.

Figure 3(b) shows a variation of XMCD spectrum at Os L3-edge at H. P. The dichroic signal is enhanced up to ~ 2 GPa although the spectral profile is hardly changed. The XMCD at \( P = 0.6 \) GPa shows more than twice intensity of that at A. P. This result is consistent with the enhancement of magnetic moment predicted from the \( P-T \) phase diagram [27]. The enhancement indicates that a ferromagnetic state of SmOs4Sb12 is stabilized at H. P.

The dependence of the integrated intensity of the XMCD signal on pressure is shown in figure 4(b). The integrated intensity reaches a maximum near 0.6 GPa, and decreases with increasing pressure. The XMCD signal finally disappears at 3.5 GPa. It is widely accepted that the intensity is basically proportional to the sample magnetization [30, 31]. Therefore, this behavior well corresponds to the magnetization up to 1.96 GPa [27]. However, the XMCD signal finally disappears at 3.5 GPa. The disappearance is conflicting with the moderate increase in \( T_c \) below 4 GPa [9]. Kotegawa et al. proposed that the magnetic state at H. P. of SmOs4Sb12 is not usual ferromagnetic state, e.g., a canted antiferromagnetic state [27]. The disappearance of the XMCD might support their proposal.

4. Conclusion
We performed XAS and XMCD measurements in SmOs4Sb12 at Os L-edge under multiple extreme conditions in order to investigate Os 5d electronic and magnetic states from a microscopic viewpoint. A small dichroic signal of ~ 0.1% was clearly observed at ambient pressure. The Os 5d magnetic moment is antiferromagnetically coupled with the major Sm magnetic moment. The obtained orbital and spin magnetic moments of Os 5d electrons in SmOs4Sb12 are smaller than that in EuOs4Sb12, which agrees with the difference in magnitude of magnetic moment. The spin and orbital moments estimated by the sum-rules indicate that the Sm magnetic moments dominate the Os ones. Pressure variation of XMCD has a peak near 0.6 GPa and finally disappears at 3.5 GPa. The behavior is similar to the previous magnetization, and the result might suggest unconventional ferromagnetic states at high pressure in SmOs4Sb12. Judging from the observation of the XMCD signals and significant pressure dependence of the XAS and XMCD spectra, the behavior of Os 5d electronic states strongly connects with a novel feature observed in SmOs4Sb12. The success of the Os L-edge XAS and XMCD measurements under multiple extreme conditions indicates the usefulness of the investigation into the magnetic properties near the quantum critical point in SmOs4Sb12. This probably also indicates that the Os 5d electrons play an important role in the exotic electronic behavior in SmOs4Sb12.

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