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Study of electronic states of a pyrochlore-type molybdate (Sm$_2$Mo$_2$O$_7$) at low temperature by means of hard x-ray photoemission spectroscopy

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Abstract. We have carried out the measurement for a pyrochlore-type Mo oxide (Sm$_2$Mo$_2$O$_7$) by means of hard-x-ray and soft-x-ray photoemission spectroscopy (PES) with high energy resolution. The PES spectrum obtained with the hard x-ray clearly shows a coherent part and an incoherent part. And its boundary is relatively distinguishable. The ratio of the coherent part to the incoherent part is more enhanced in the hard-x-ray PES compared to the soft-x-ray PES. The results indicate that hard-x-ray photoemission spectroscopy (HAXPES) is powerful method for investigating the bulk electronic state.

1. Introduction

Pyrochlore A$_2$B$_2$O$_7$ is one of oxides included 3$d$, 4$d$ and 5$d$ electron systems. It has a cubic structure with the space group Fd3m, in which A, B, O(1) and O(2) occupy the sites 16d, 16c, 48f and 8b, respectively [1]. The A \( (B) \) site forms a three-dimensional network of corner-sharing tetrahedra and formally takes \( A^{3+} \) \( (B^{4+}) \) state. Various phenomena closely related to its characteristic crystal structure have been reported.

The pyrochlore-type Mo oxide R$_2$Mo$_2$O$_7$ \( (R = \) rare-earth element) shows the metal-insulator (M-I) transition with changing the rare-earth element and has been reported to exhibit a systematic variation in transport and magnetic properties with changing \( R \) [2, 3]. The M-I transition seems to take place around Gd, namely the systems with \( R = \) Nd and Sm are ferromagnetic metal. Those with \( R = \) Tb-Yb and \( R = \) Y are spin-glass insulator, whereas the
system with $R = \text{Gd}$ becomes either metallic or insulating depending on sample preparation conditions [4]. M-T transition is thought to originate that both the Mo-O bond length and the Mo-O-Mo bond angle decrease with changing $R$ in the order through $R = \text{Nd}$, ..., Tb, and Y [3].

Since $R$ is likely to become trivalent, Mo becomes tetravalent. Therefore, each Mo atom has two 4$d$ electrons. The Mo atom is surrounded by six O atoms octahedrally, which makes the Mo 4$d$ state split into doubly degenerate $e_g$ and triply degenerate $t_{2g}$ states. The $t_{2g}$ states are split into the nondegenerate $a_{1g}$ state and the doubly degenerate $e'_g$ states because the octahedron is distorted leading to a trigonal symmetry [5]. In the high-spin Mo$^{4+}$ state, the $a_{1g}$ and $e'_g$ states are occupied by one electron each and the $a_{1g}$ electron acts as a local spin and the $e'_g$ electron is potentially itinerant.

Photoemission spectroscopy (PES) is a powerful tool to probe electronic structures of various solids. Generally, the photoelectron in the conventional PES below photon energy ($h\nu$) of 100 eV has the short inelastic mean free path (IMFP) and then this method provides rather surface sensitive information. Soft x-ray photoemission spectroscopy (SXPES) is inevitable for studying strongly correlated electron systems [6]. Namely, the electronic structures in the surface region is much different from those in the bulk in the systems. In the soft x-ray PES around $h\nu=500$ - 800 eV, the relative spectral weight of the bulk is still in the range of 50~70 % in many strongly correlated electron systems. Therefore higher bulk sensitivity by means of hard x-ray PES (HAXPES) is thought to be inevitable[7]. In the HAXPES around $h\nu=8$ - 10 keV, the IMFP is about 100 Å and the relative spectral weight of the bulk is more than 90 %.

In order to investigate the bulk electronic states for Sm$_2$Mo$_2$O$_7$, we have carried out the HAXPES measurement at $T=20$ K. By comparing the result with spectra, which are measured with soft-x-ray, we report the difference of electronic state of between in the bulk and on the surface.

2. Experiment

For measurements, single crystals were employed. HAXPES was performed at BL19LXU in SPring-8 with MB Scientific A1-HE spectrometer. Since the photoionization cross sections decreases exponentially with increasing photon energy, high photon flux is required for the HAXPES experiment. This beamline is equipped with the in-vaccum 27 m long planar undulator[8] and therefore the required high photon flux is available. Figure 1 shows the PES spectrum around Fermi level ($E_F$) of Au measured with $h\nu=7940$ eV at about 20 K. In the figure, the black circle and the red line indicate the obtained spectrum and the fitting curve for estimating the total energy resolution ($\Delta E$). This result shows the best energy resolution of about 60 meV at this photon energy. The energy resolution for measurements is set to about 120 meV. The other PES experiments were carried out with SCIENTA SES 200 analyzer for $h\nu=40.8$ eV (soft-x-ray) at BL25SU [9] of SPring-8 and SES 2002 analyzer using ultraviolet light of $h\nu=40.8$ eV (VUV) produced by the He RF discharge lamp. The $\Delta E$ for valence band PES spectra at $h\nu=40.8$, 270 eV and 900 eV was set to 40 meV, 75 meV and 140 meV, respectively. The clean surfaces were obtained by fracturing the samples in situ in

![Figure 1. The PES spectrum around $E_F$ of Au at $h\nu=7940$ eV. The red line is fitting curve for estimating the total energy resolution.](image-url)
ultrahigh vacuum just before the measurements at 20 K and the samples were kept at the same temperature during the measurements. The base pressure in the PES measurement chamber was better than $3 \times 10^{-8}$ Pa.

3. Results and discussion

Figure 2 shows the valence band spectra of Sm$_2$Mo$_2$O$_7$ in the lower binding energy ($E_B$) region ($E_B \leq 3.0$ eV) measured at $h\nu=900$ eV, 270 eV and 40.8 eV. In these spectra, two structures are mainly recognized, namely the structures around $E_B=0.5$ eV and 1.5 eV as shown by broken and dotted lines. The structure around 0.5 eV increases with $h\nu$ and becomes prominent for $h\nu=900$ eV. On the other hand, the structure around 1.5 eV becomes prominent for $h\nu=40.8$ eV and is observed as broad hump for $h\nu=900$ eV. The intensity of those structures seems to be same at $h\nu=270$ eV. Also, only spectrum at $h\nu=900$ eV seems to have a shoulderlike structure around 0.2 eV (by a down arrow in Fig. 2). Furthermore, the spectral intensity at $E_F$ increases at $h\nu=900$ eV. In general, there are two main origins for the significant $h\nu$ dependence of PES spectra; one is the $h\nu$ dependence of the photoionization cross section, and the other is the $h\nu$ dependence of the photoelectron's escape depth in solids. The ratio of the photoionization cross-section between the O 2$^p$ electron and the Mo 4$d$ electron is about 1 : 8 at $h\nu=900$ eV, 1 : 3 at $h\nu=270$ eV and 1 : 1 at $h\nu=40.8$ eV.

According to the local-spin-density approximation (LSDA) band calculation, the Mo 4$d$ $t_{2g}$ bands locate in the region of $E_B \leq 1$ and well separate from O 2$p$ band that spreads from $E_B \sim 8.5$ eV to $E_B \sim 2.5$ eV. The Mo 4$d$ $e_g$ bands are located on the unoccupied side and the splitting energy between the $e_g$ and the $t_{2g}$ states is about 4 eV. Furthermore, the $t_{2g}$ states are split into the nondegenerate Mo 4$d$ $a_{1g}$ bands and the degenerated Mo 4$d$ $e'_{g}$ bands because the octahedron is further trigonally distorted. The center of gravity of the $a_{1g}$ band locates around 0.5 eV. The $e'_{g}$ band spreads in the region between $E_F$ and $E_B \sim 1$[5]. Judging from these ratios and the band calculation results that Mo 4$d$ states dominate near $E_F$, the spectra shown in Fig. 2 originate almost exclusively from the Mo 4$d$ states. Therefore, the prominent difference with changing $h\nu$ should be attributed to the difference of Mo 4$d$ electronic structures between in the bulk and on the surface.

In order to clarify the bulk electronic state for $R=$ Sm, we have carried out the measurement by means of HAXPES, which one can obtain more bulk sensitive information than in the SXPES. Figure 3 shows the valence band PES spectrum at $h\nu=7940$ eV and the comparison with the spectrum at $h\nu=900$ eV. These spectra are normalized by the integrated intensity between $E_B=3$ eV and $E_F$ after subtracting the background of the integral type. In the HAXPES spectrum, the ratio of the photoionization cross section between the O 2$p$ electron and the Mo 4$d$ electron is about 1:14. Therefore the spectral shape is thought to reflect the mainly Mo 4$d$ states. In the spectrum, the peak structure around 0.5 eV is more prominent than that at 900 eV. The spectral intensity of the hump structure around 1.5 eV at 7940 eV is as same as that at $h\nu=900$ eV. However, the region between $E_B \sim 0.7$ eV and $E_B \sim 1.2$ eV has the difference of both the spectral shape and its intensity. Furthermore, the intensity of the shoulderlike structure around $E_B=0.2$ eV becomes rather stronger than that at 900 eV.

By comparing the calculated LSDA band structure with the spectra, the structure between $E_F$ and $E_B \sim 0.5$ eV is corresponding to the coherent part. Because the LSDA results predict no band in the region between $E_B \sim 1$ eV and $E_B \sim 2.5$ eV, the hump structure around 1.5 eV corresponds to the incoherent part which reflects the strongly correlated character of Mo 4$d$ $t_{2g}$ electrons[10]. For more detail, the prominent peak around 0.5 eV and the shoulderlike structure near $E_F$ correspond to the Mo 4$d$ $a_{1g}$ state and the Mo 4$d$ $e'_{g}$ state, respectively. At 7940 eV, the coherent part and the incoherent part are more clearly discernible than that at 900 eV. The ratio of the coherent part to the incoherent part increases at HAXPES spectrum. In order to investigate the mechanism for M-I transition in these systems, we will study the other
compositions, which $R$ element is Gd and Tb, by means of HAXPES.

4. Summary

We have carried out the HAXPES measurement at $h\nu=7940$ eV for the pyrochlore-type Mo oxide with $R =$ Sm. The relative spectral weight and their shapes of the coherent part and the incoherent part change dramatically compared to the SX and VUV results. Especially, the increase of the coherent part intensity corresponding to $a_{1g}$ state relative to others was thought to reflect the bulk electronic state.

The results indicated that HAXPES is powerful method for investigating the bulk electronic structures of strongly correlated electron system.

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