

Angle-Resolved Photoemission Study on Insulator-to-Metal Transition of $\text{Sm}_{1-x}\text{Y}_x\text{S}$

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Samarium monosulfide (SmS) is a prototypical compound that exhibits an insulator-to-metal transition, namely black-golden phase transition, by applying external pressure or by a chemical pressure owing to the substitution of Sm ions by yttrium (Y) ions. To directly observe the change of the electronic structure of the black-golden phase transition, we have performed angle-resolved photoemission spectroscopy on $\text{Sm}_{1-x}\text{Y}_x\text{S}$. From $x = 0$ (insulator) to 0.33 (metal), the $\text{Sm}^{2+} 4f$ multiplet structure continuously shifts to the Fermi level (E_F). On the other hand, the S $3p$ bands show the discontinuous shift with respect to $x = 0.17$. Furthermore, on metallic compound of $x = 0.17$, we find that an electron pocket appears at the X point, where the bottom of Sm $5d$ states is expected to be located just above E_F in insulating SmS by a band calculation. Thus, the observed electron pocket is considered to originate from Sm $4f-5d$ hybridization due to the chemical pressure and it is a possible origin of the insulator – metal transition of SmS.

KEYWORDS: SmS, ARPES, band structure, insulator – metal transition, heavy fermion, valence fluctuation

1. Introduction

Samarium monosulfide (SmS) is a prototypical valence fluctuating compound that exhibits pressure-induced electronic transition, namely insulator (black) – metal (golden yellow) phase transition by applying external pressure (~ 6.5 kbar at room temperature) [1, 2]. Across the insulator – metal transition, the valence of Sm changes from $2+$ to $2+\delta$, so-called valence fluctuating state. In spite of many efforts from experiment and theory [3], the origin of this anomalous phase transition especially the essential role of $4f$ electrons has not been elucidated yet within 30 years. So far, there are two contrary

models for understanding this state: “local” Sm^{2+} and Sm^{3+} coexist and configure a mixed-valence state, and Sm $4f$ electrons and Sm $5d$ conduction electrons hybridize “itinerantly” and form a heavy fermion state [4, 5].

Angle-resolved photoemission spectroscopy (ARPES) is a powerful technique to directly study the electronic structure of solids as a function of momentum. However, the technique is hard to apply under pressure. Thus, to study the pressure-dependent change of the electronic structure by ARPES, we need help of the chemical pressure effect, i.e., substitution dependence. From this viewpoint, recently, it has been realized on $\text{Sm}_{1-x}\text{Y}_x\text{S}$. Actually, the lattice constant of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ decreases like SmS as Y substitution, and shows the slight jump around $x = 0.17$ [6] where the color of sample surface changes from black to golden, and the resistivity changes from insulating to metallic one. To clarify the change of the electronic structure across the black-golden phase transition, we have compared the normal emission spectra between $x = 0$ (black) and 0.33 (golden) in the previous study [6]. Then we found that the Sm^{2+} $4f$ multiplet structures shift to lower binding energy side from $x = 0$ to 0.33 in consistent with increasing metallic nature. However, both the origin of the change of the electronic structure and its relation with the character of Sm $4f$ electrons have not been elucidated.

In the present work, we investigated the change of the electronic structure of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ across the insulator – metal transition using ARPES [6, 7]. The results indicate that the Sm^{2+} $4f$ multiplet structure is gradually moved to the Fermi level (E_F) from $x = 0$ (black insulator) to 0.17 (black metal) and 0.33 (golden metal), while the S $3p$ bands show the discontinuous energy shift. In addition, we have observed on $x = 0.17$ the electron pocket appearing at the X point, where the Sm $5d$ states are expected just above E_F on SmS. Furthermore, the observed electron pocket shows typical hybridization with the Sm^{2+} $4f$ multiplet state. These results suggest that the increase of the Sm $4f$ - $5d$ hybridization intensity is a possible origin of the anomalous insulator – metal transition under the pressure of SmS.

2. Experiment

Single crystals of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ ($x = 0, 0.17$ and 0.33) were grown by the Bridgman technique using a high-frequency induction furnace installed at NIMS. ARPES measurement was performed at BL5U of UVSOR-III, Institute for Molecular Science [8]. The total energy and angular resolutions were set at $60 - 180$ meV and 0.16° , respectively. A clean surface of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ (001) plane was obtained by *in-situ* cleaving at $10 - 20$ K just before the measurement. The crystal orientation was determined by the Laue diffraction method.

3. Results and Discussion

Figure 1 show the photon-energy-dependent ARPES spectra at $T = 10$ K in the normal emission geometry of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ [$x = 0$ (a), 0.17 (b), and 0.33 (c)], respectively. From the comparison with the ARPES on black SmS [6, 7], the highly-dispersive feature at 4 eV is ascribed to the S $3p$ band, while nondispersive ones near the Fermi level (E_F) to the Sm^{2+} $4f$ multiplet structures. With increasing x , it is clear that the Sm^{2+}

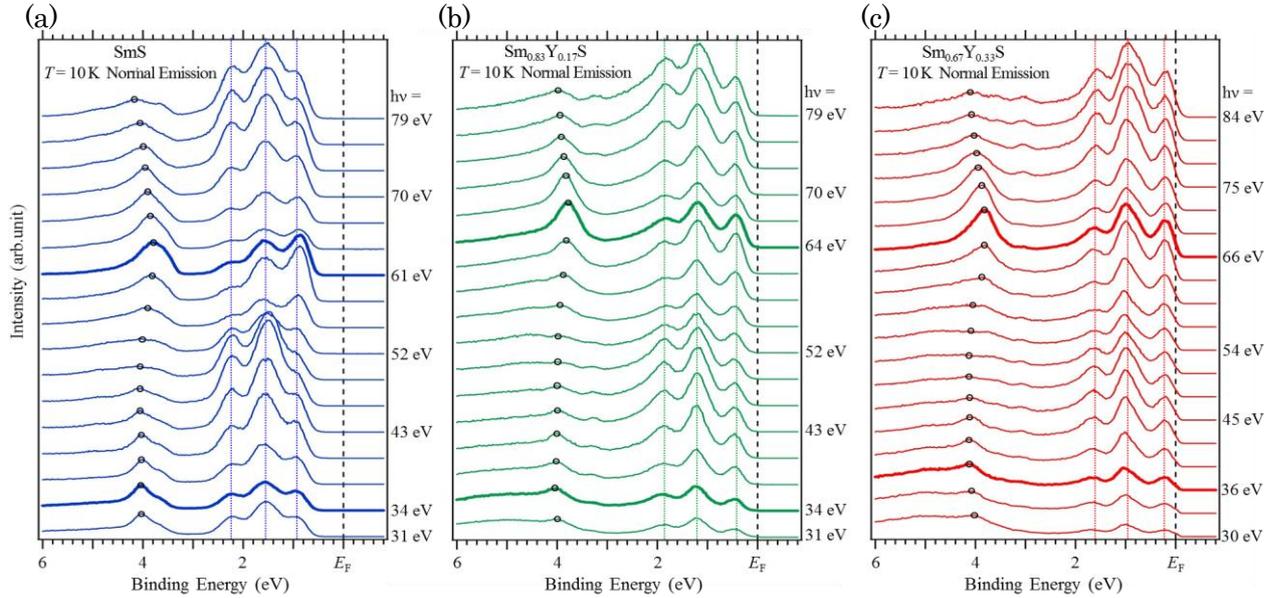


Fig. 1. Photon-energy-dependent ARPES spectra at normal emission of (a) $x = 0$, (b) 0.17, and (c) 0.33 of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ measured at $T = 10$ K.

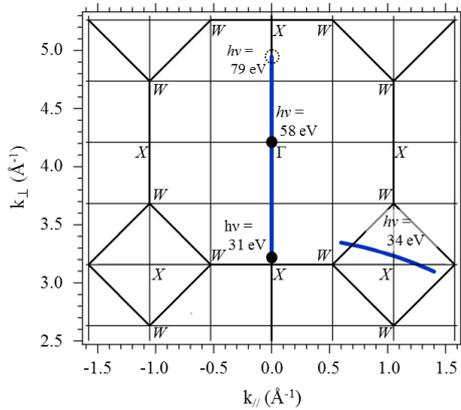


Fig. 2. Schematic Brillouin zone in the k_{\parallel} - k_{\perp} plane of black SmS (the lattice constant $a = 5.97$ Å). The Γ and X points correspond to the photon energies of $h\nu = 58$ and 31 eV at E_F , respectively. The blue vertical line and the blue curved line indicate the ARPES trace lines in Fig. 1 (Fig. 3) and Fig. 5, respectively.

$4f$ multiplet peaks shift to E_F . On the other hand, the dispersive features show no distinct change around 4 eV, though the photon energy of the S $3p$ folding point shifts to the higher photon energy side.

In order to see the change of the electronic structure more clearly, we have mapped out the experimental band structures of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ ($x = 0, 0.17$ and 0.33) in Fig. 3. The experimental band structures correspond to the trace of the electronic structure along the ΓX high-symmetry line of k_{\perp} axis (see Fig. 2) following

$$k_{i\perp} = \sqrt{\frac{2m}{\hbar^2} [(h\nu - E_B - \Phi)\cos^2\theta + V_0]} \quad (1)$$

where $h\nu$ is photon energy, E_B is binding energy, Φ is work function evaluated from the E_F edge of reference gold, $\theta = 0^\circ$, and V_0 is inner potential estimated from the symmetry

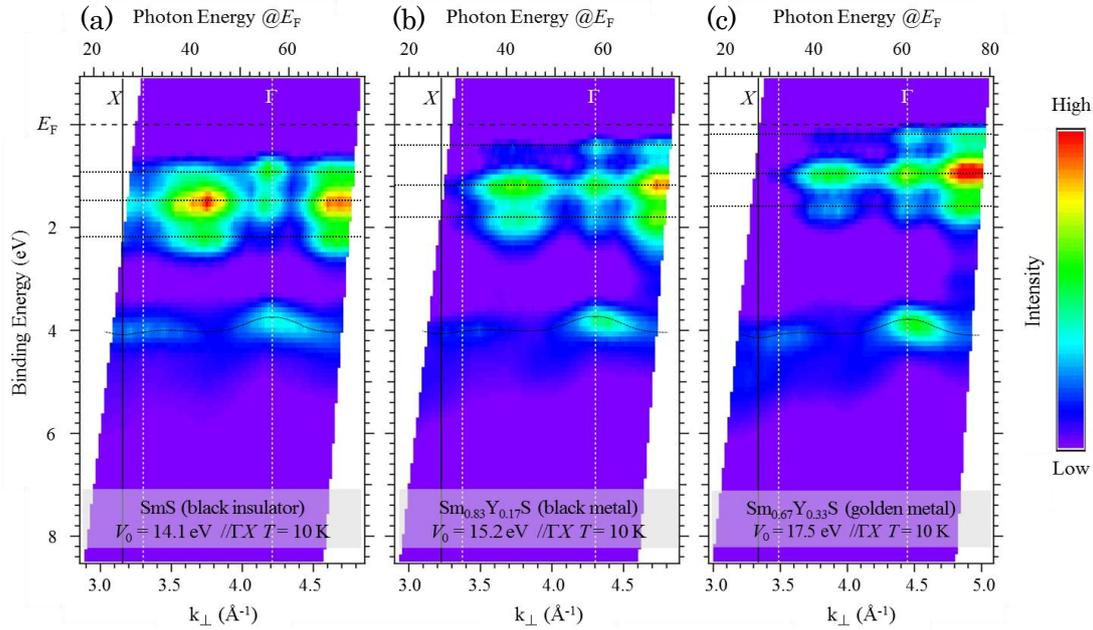


Fig. 3. Band structure along ΓX line (k_{\perp}) of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ [(a) $x = 0$, (b) 0.17 and (c) 0.33].

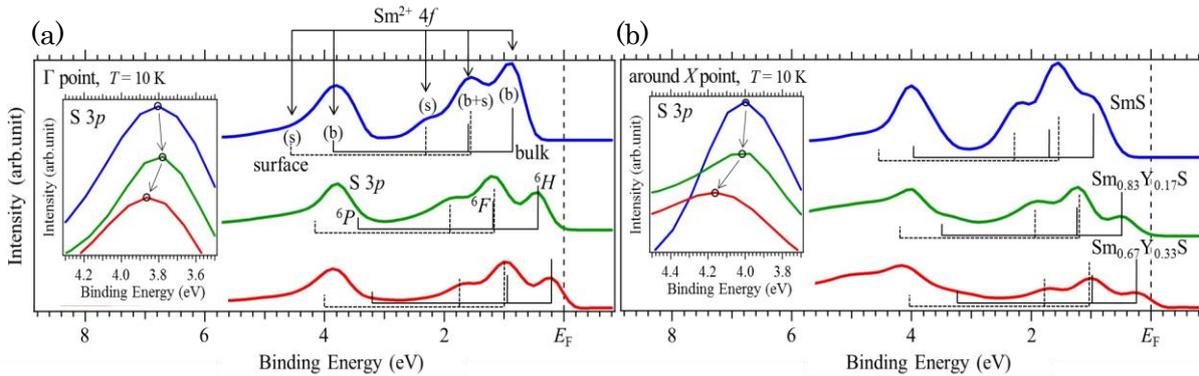


Fig. 4. Comparison of the EDCs of $x = 0, 0.17$ and 0.33 at the Γ point (a) and the X point. Solid and dotted lines indicate the $\text{Sm}^{2+} 4f$ multiplet peaks of bulk and surface states, respectively [7]. Inset shows the x -dependent $S 3p$ peaks in enlarged scale.

of dispersive features. From our systematic APRES experiment, we have obtained the inner potentials $V_0 = 14.1$ eV, 15.2 eV, and 17.5 eV for $x = 0, 0.17$, and 0.33 , respectively. With utilizing the clear dispersive features of $S 3p$ band in Fig 3, we have checked the consistency with the lattice constant and the size of the Brillouin zone along ΓX line for each sample carefully, and successfully obtain the reasonable inner potentials as shown above. In Fig. 4, the broad highly dispersive feature from 4 to 6 eV around the Γ point also appears on each band structure, which is consistent with the in plane $S 3p$ band dispersion of SmS [6]. Furthermore, even though the $\text{Sm}^{2+} 4f$ multiplet structure has no dispersion, the intensity is clearly modulated at the Γ point, which has been ascribed to be the implication of the existence of the lattice effect even in the black SmS [7].

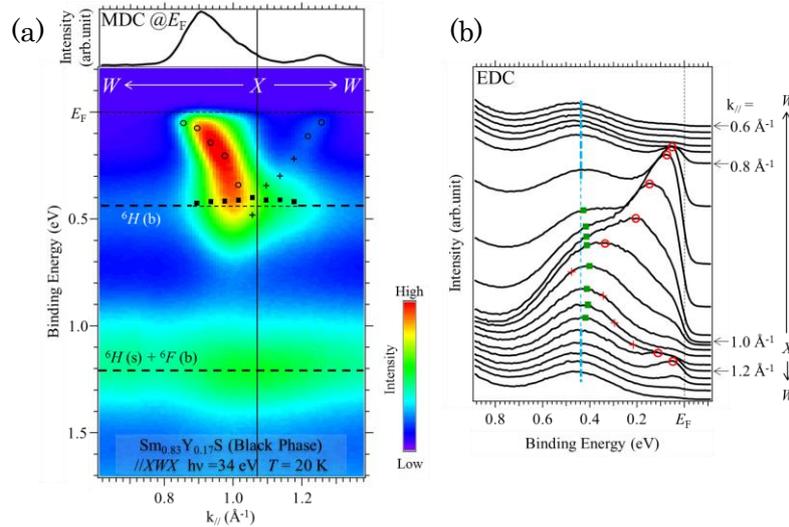


Fig. 5. (a) The thorough ARPES image of $x = 0.17$ along the XWX line using $h\nu = 34$ eV at $T = 20$ K. MDC at E_F is shown at the top of image. (b) ARPES spectra near E_F around the X point. Dashed lines indicate the $\text{Sm}^{2+} 4f$ multiplet structures. Solid circles (crosses) and solid squares are ARPES peak positions of strong (weak) dispersive features of $\text{Sm} 5d$ electron pocket and *itinerant* $\text{Sm} 4f$ features, respectively.

To investigate the change of electronic structure with the Y substitution clearly, we directly compare the energy distribution curves (EDCs) at the Γ and X points obtained from the vertical cut (white dashed line) in Fig. 3. With choosing the electronic structure at the exactly same Brillouin zone point, the direct comparison of electronic structure among different Y substitution samples with different lattice constants becomes possible. In Fig. 4, $\text{Sm}^{2+} 4f$ multiplet structures of bulk (b) and surface (s) components systematically shift to E_F with increasing x and touch to E_F at $x = 0.33$ as described above. With respect to $S 3p$ features, however, we find very slight energy shift at both Γ and X points as shown in the inset of Fig. 4. From black insulating ($x = 0$) to black metallic ($x = 0.17$) phase, the $S 3p$ band at the Γ (X) point shifts to about 20 meV (10 meV) to lower (higher) binding energy side. In addition, the $S 3p$ peak at the X point becomes broader than one at the Γ point. On the other hand, from black metallic ($x = 0.17$) to golden metallic ($x = 0.33$) phase, $S 3p$ bands at both the Γ and X points show high binding energy shift of 90 meV and 130 meV, respectively. The observed discontinuous change of the $S 3p$ band at $x = 0.17$ might be the discontinuous change of the interactions between $S 3p$ and other electrons, as the lattice constant jumps at $x = 0.17$ [6]. To understand the origin of the discontinuous change of the electronic structure, we have investigated the electronic structure near E_F in the wide Brillouin zone.

Figure 5 shows an ARPES image and energy distribution curves of $x = 0.17$ near E_F around the X point (see Fig. 2). We successfully find an electron pocket along WXW high-symmetry line. Though the dispersive feature becomes much broader at the second Brillouin zone than that at the first Brillouin zone possibly due to the matrix element effect, we find a symmetric dispersive feature against to the strong dispersion at the X point (see circles/crosses in Figs. 5(a) and 5(b)). According to the band calculation of insulating SmS , $\text{Sm} 5d$ states have been expected to be located just above E_F at the X point. Thus we conclude that the E_F crossing band can be ascribed as the electron pocket at the Brillouin zone boundary. In strong contrast to the nondispersive $\text{Sm}^{2+} 4f$ multiplet

structure (6H (s) and 6F (b)) around 1.2 eV, 6H (b) structure shows anomalous dispersive feature around the X point, where the bottom of the electron pocket merges (see squares in Figs. 5 (a) and 5(b)). From the analogue of the occupied c - f hybridized band reported on heavy fermion compounds [9], the observed anomaly seems to suggest the *itinerant* Sm $4f$ character hybridized with the Sm $5d$ band. From the observed electron pocket formation at $x = 0.17$, we expect that the increase of the hybridization intensity between Sm $5d$ and S $3p$ electrons in the metallic phase is one possible origin of the larger energy shift as well as the broadening of S $3p$ band around the X point. To further insight into the anomalous phase transition in SmS, more systematic ARPES studies on $\text{Sm}_{1-x}\text{Y}_x\text{S}$ are intended.

3. Conclusion

We performed high-resolution angle-resolved photoemission spectroscopy on $\text{Sm}_{1-x}\text{Y}_x\text{S}$ ($x = 0, 0.17$ and 0.33) to observe the change of the electronic structure across the insulator – metal transition. With increasing x , the $\text{Sm}^{2+} 4f$ multiplet structure shifts to E_F systematically, but the S $3p$ bands shift to the lower binding energy side from $x = 0$ to 0.17 and are pushed down to high binding energy side from $x = 0.17$ to 0.33 . In the metallic phase of $x = 0.17$, we successfully observed the Sm $5d$ electron pocket that possibly hybridizes with Sm $4f$ state around the X point. The results suggest that the increase of the Sm $4f$ – Sm $5d$ hybridization intensity is one possible origin of the insulator – metal transition of SmS.

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