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Investigation of electronic states of infinite-layer $SrFeO_2$ epitaxial thin films by X-ray photoemission spectroscopy

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Introduction

Recently, an antiferromagnetic (AFM) insulator, $SrFeO_2$ (Fe^{2+}: d^6, S = 2), in which FeO_4 square-planes composed of corner-sharing FeO_6 octahedra are alternately stacked with Sr layers, was synthesized via solid-phase reduction of $SrFeO_{2.875}$ using CaH_2 [1]. The Fe spins in $SrFeO_2$ are three-dimensionally (3D) ordered in an antiparallel way, with a Néel temperature of T_N = 473 K, despite the two-dimensional crystal structure. First-principles density functional theory (DFT) calculations for $SrFeO_2$ suggested that down-spin Fe 3*d* electrons occupy the nondegenerate d_{z2} level rather than the degenerate d_{xz} or d_{yz} levels [2]. This electronic picture reasonably explains the 3D AFM ordering, the absence of Jahn–Teller instability, and the magnetic anisotropy with an in-plane easy axis. To prove the proposed band model, a direct spectroscopic approach to the electronic structure of $SrFeO_2$ is highly desirable. Here, we report soft X-ray photoemission spectroscopic (PES) studies of single-crystal epitaxial thin films of $SrFeO_2$ prepared via solid-phase reduction of $SrFeO_{2.5}$ precursor films grown by pulsed-laser deposition (PLD).

Experiment

Epitaxial thin films of $SrFeO_{2.5}$ were grown on $SrTiO_3$ (001) substrates by PLD method. These precursor films were embedded with CaH_2 in an evacuated Pyrex tube in an Ar-filled glove box. The tubes were sealed in vacuum and then kept at 280°C for 24 hours. X-ray diffraction was used for structural characterization. PES measurements were carried out at beamline 2C of the Photon Factory, KEK. The PES spectra were taken with an energy resolution of ~0.10–0.25 eV at a photon-energy range of 600–1000 eV. The Fermi levels of the samples were referred to that of Au foil in electrical contact with the samples.

Results and Discussion

Figure 1 shows the valence-band PES spectrum of the reduced $SrFeO_2$ film. First-principles DFT calculations predict that the valence band of $SrFeO_2$, which is in the mixed states of Fe 3*d* and O 2*p*, spreads from the binding energies (E_b) of ~7 eV to ~0 eV [2]. The experimentally observed valence band in Fig.1 is broader and extends to the higher E_b side than in the case of the theoretical valence band. However, as can be seen from the close-up spectrum near the Fermi level (E_F) (the inset in Fig.1), the density of states (DOS) begins to rise just below E_F, consistent with the DFT results [2].

According to DFT calculations [2], the Fe 3*d* partial DOS in the valence-band region consists of three major components: a mixture of up-spin $3d_{x2-y2}$ and down-spin $3d_{z}$ located at E_b = 0–2 eV, up-spin $3d_{z}$ at around 4 eV, and a superimposition of up-spin $3d_{xz}$ + $3d_{yz}$, $3d_{xy}$, and $3d_{x2-y2}$ located at 5–7 eV. In order to investigate the contribution of Fe 3*d* states to the valence band of $SrFeO_2$, we carried out Fe 2*p*–3*d* resonant PES. The PES intensities at 3–5 eV and 6.5–8.5 eV were resonantly enhanced, indicating that the corresponding energy states are contributed by the Fe 3*d* orbital. In contrast, the PES intensity from the E_F to ~1 eV was essentially independent of the photon energy, implying that the Fe 3*d* partial DOS has a negligible weight near E_F. Thus, it is reasonable to assume that the states below E_F are mostly contributed by oxygen. From a comparison of the PES results with the Fe 3*d* partial DOS calculated by the DFT method [2], we tentatively identify the peak at 3–5 eV as Fe $3d_{z2}$ and that at 6.5–8.5 eV as Fe $3d_{xz}$ + $3d_{yz}$ + $3d_{xy}$ + $3d_{x2-y2}$.

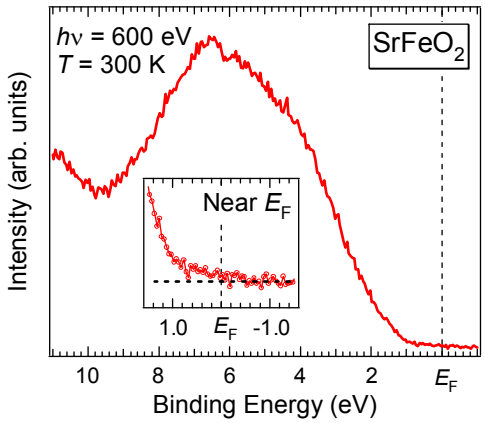

Fig.1. Valence-band PES spectrum of reduced $SrFeO_2$ film. The inset shows the valence-band spectrum close to E_F.

References

[1] Y. Tsujimoto, et al., Nature **450**, 1062 (2007).
[2] H. J. Xiang, et al., Phys. Rev. Lett. **100**, 167207 (2008).

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