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Electronic states of layered perovskite oxyfluoride $Sr_2RuO_3F_2$ thin films by X-ray absorption spectroscopy and theoretical calculations

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1 Introduction

The electronic properties of strontium ruthenates can be readily altered by anion doping. For example, $Sr_3Ru^{5+}{}_2O_7F_2$, which was obtained by inserting F^- ions into the $(SrO)_2$ rocksalt blocks in double-layered $Sr_3Ru^{4+}{}_2O_7$ [1], exhibits antiferromagnetism with *G*-type ordering of the Ru^{5+} spins. More recently, $Sr_2RuO_3F_2$ was synthesized in the form of epitaxial thin films by the topotactic fluorination of single-layered Sr_2RuO_4 precursor films using polyvinylidene fluoride (PVDF) [2]. In this reaction, both fluorine insertion into the $(SrO)_2$ blocks and the formation of oxygen vacancies in the O^{2-} sites of the RuO_6 octahedra take place simultaneously, while the oxidation state of Ru remains at 4+ after fluorination. The $Sr_2RuO_3F_2$ thin film exhibits insulating behavior, with a resistivity of $\sim 4.1 \times 10\ \Omega$ cm at 300 K, which is five orders of magnitude higher than that of the metallic Sr_2RuO_4 film ($\sim 6.7 \times 10^{-4}\ \Omega$ cm). To unveil the origin of the physical properties of $Sr_2RuO_3F_2$, spectroscopic approaches to investigate the electronic states of $Sr_2RuO_3F_2$ are highly desirable. In this study, we investigated the electronic structure of a $Sr_2RuO_3F_2$ thin film by X-ray absorption spectroscopy (XAS) and density functional theory (DFT)-based calculations.

2 Experiment

Precursor Sr_2RuO_4 and fluorinated $Sr_2RuO_3F_2$ thin films were prepared on $LaAlO_3$ (001) substrates by pulsed laser deposition and successive topotactic fluorination using PVDF. The thicknesses of the Sr_2RuO_4 and $Sr_2RuO_3F_2$ thin films were ~100 nm and ~135 nm, respectively. X-ray diffraction measurements confirmed that both the thin films exhibited a K_2NiF_4-type structure with no impurity phases. XAS measurements were conducted using linear polarized light at the BL-2A beamline of Photon Factory, KEK. The XAS spectra were measured at 300 K and vacuum pressure of $\sim 3 \times 10^{-8}$ Pa using the total electron-yield method.

DFT calculations were performed using the VASP package [3]. We employed the GGA+*U* method to treat Coulomb repulsion between the Ru 4*d* electrons [4,5]. The valence electronic states were calculated with a plane wave basis set and the projector augmented wave approach [6,7]. We assumed an antiferromagnetic spin arrangement on Ru atoms, taking into consideration the experimental observation that $Sr_2RuO_3F_2$ exhibited no spontaneous magnetization [2].

3 Results and Discussion

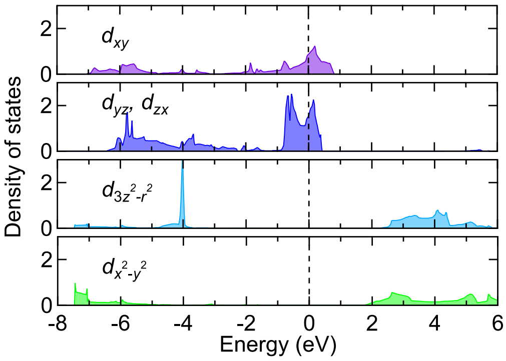
Figure 1 shows the partial density of states (PDOS) of Ru d_{xy}, $d_{yz} + d_{zx}$, $d_{3z^2-r^2}$, and $d_{x^2-y^2}$ bands in Sr_2RuO_4 and $Sr_2RuO_3F_2$. Ru^{4+} oxides with octahedral geometry are usually a low-spin configuration $(xy, yz, zx)^{\uparrow\uparrow\uparrow\downarrow}$, such as $SrRuO_3$ and Ca_2RuO_4 [8,9], or non-spin-polarized $(xy, yz, zx)^4$, such as Sr_2RuO_4 and RuO_2 [10,11]. In these compounds, the fourth *d* electron occupies not a e_g band but a t_{2g} band due to the large crystal field splitting between the t_{2g} and e_g orbitals. Figure 1(a) shows PDOS for Sr_2RuO_4. It depicts the $(t_{2g})^4$ configuration as reported in Ref. [12]. However, PDOS for $Sr_2RuO_3F_2$ (Fig. 1(b)) suggests the Ru^{4+} exhibited a high-spin configuration $(xy)^{\uparrow}(yz, zx)^{\uparrow\uparrow}(3z^2\text{-}r^2)^{\uparrow}$. This anomalous occupation of the $(3z^2\text{-}r^2)^{\uparrow}$ orbital would be due to the change in crystal field around Ru atoms.

In order to examine the conduction band structure of the Sr_2RuO_4 and $Sr_2RuO_3F_2$ thin films, we measured the O 1*s* XAS spectra using polarized light. In this measurement, the O 1*s* electrons are excited into unoccupied 2*p* orbitals hybridized with Ru 4*d* orbitals. Due to the dipole selection rule, the direction of the 2*p* orbitals to which the 1*s* electrons are transferred depends on the angle between the incident beam and the surface normal (θ_{inc}) [13]. When θ_{inc} is zero, 1*s* electrons are transferred to the $2p_x$ or $2p_y$ orbital. The final state gradually changes to $2p_z$ as θ_{inc} increases up to 90º. Therefore, the position of the XAS peak and its θ_{inc} dependence indicate the energy position of the Ru 4*d* states and the direction of the O 2*p* orbitals (p_x, p_y, and p_z), respectively. Figure 2 exhibits the XAS spectra measured at $\theta_{\mathrm{inc}} = 0°, 30°$, and 60º. The angular dependence of the O 1*s* XAS spectra could be clearly observed for both the Sr_2RuO_4 and $Sr_2RuO_3F_2$ films.

The results obtained for the Sr_2RuO_4 film are in good agreement with those reported previously on a Sr_2RuO_4 (001) single crystal prepared by *in situ* cleaving at 160 K [13]. The peak at 528.2 eV (structure *A*) decreased with increasing θ_{inc}, while the peak at 529.2 eV (structure *B*) considerably increased with θ_{inc}. According to Ref. [13], structure *A* is assigned to the $2p_x$ and $2p_y$ states of the apical oxygen hybridized with Ru $4d_{yz}$ and $4d_{zx}$ and structure *B* is a combination of the $2p_x$, $2p_y$, and $2p_z$ states of the in-plane oxygen hybridized with the Ru 4*d* t_{2g} orbitals. The weight of *A* from the apical oxygen was much smaller than that of *B* from the in-plane oxygen, reflecting twice smaller amount of the apical oxygen than in-plane one. The structures *C* and *D* at ~531 eV and

533.1 eV are derived from Ru 4d with e_g symmetry ($d_{3z^2-r^2}$ and $d_{x^2-y^2}$) hybridized with both apical and in-plane O 2$p\sigma$ states.

(a) Sr_2RuO_4



(b) $Sr_2RuO_3F_2$

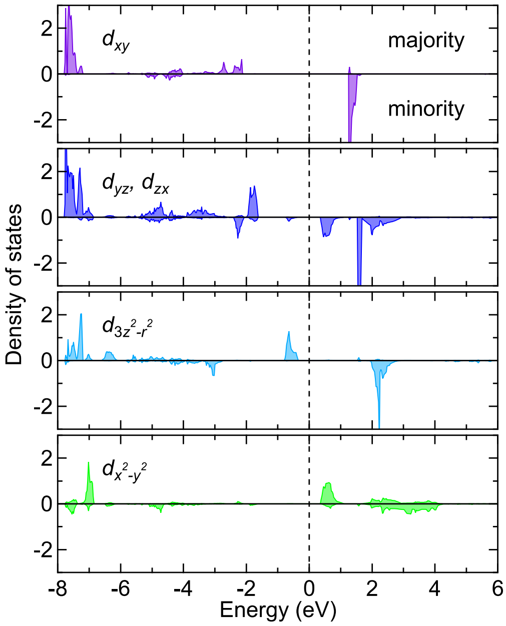


Fig. 1: PDOS for the Ru-4d electrons in (a) Sr_2RuO_4 and (b) $Sr_2RuO_3F_2$. The lines in positive and negative regions denote the PDOS of majority and minority of spin electrons, respectively.

On the other hand, as seen in Fig. 2(b), the behavior of the O 1s spectra of the $Sr_2RuO_3F_2$ film was different from that of the Sr_2RuO_4 film. The peaks at 528.6 eV and 532.0 eV (structures E and H) were observed at $\theta_{inc} = 0°$. With increasing θ_{inc}, the intensities of E and H slightly decreased and prominent peaks at 530.2 eV and 531.2 eV (structures F and G) evolved. Such θ_{inc} dependence suggests that the peaks E and H arise from the Ru 4d orbitals hybridized with the 2p_x, 2p_y, and 2p_z orbitals of the in-plane oxygen atoms and F and G arise from the 4d orbitals hybridized with the 2p_z orbitals of the in-plane oxygen. The weak peaks from the apical oxygen are possibly hidden by the intense peaks from the in-plane oxygen. The 4d orbitals responsible for F and G are hybridized with the 2p_z orbital in-plane oxygen only and thus they can be assigned to the Ru 4d_{yz} and Ru 4d_{zx} orbitals. The Ru 4d orbitals related to the structures E and H are hybridized with all the 2p_x, 2p_y, and 2p_z orbitals of the in-plane oxygen. The calculated PDOS for the Ru 4d states shown in Fig. 2(b) suggests that the conduction band minima, corresponding to peak E, are derived from 4d_{yz}, 4d_{zx}, and 4$d_{x^2-y^2}$ and that the highest 4d band (peak H) is attributable to 4$d_{x^2-y^2}$. It should be noted that 4$d_{x^2-y^2}$ can be hybridized with not only 2p_x and 2p_y but also the 2p_z orbital of the in-plane oxygen because the Ru atom is displaced toward the apical oxygen and the $O_{in\text{-}plane}$-Ru-$O_{in\text{-}plane}$ bond angle is not 180°.

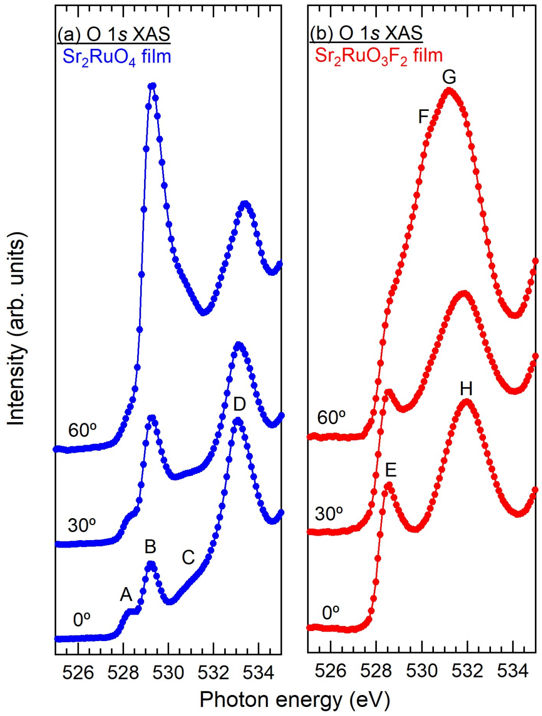


Fig. 2: O 1s XAS spectra of (a) Sr_2RuO_4 and (b) $Sr_2RuO_3F_2$ films. The spectra are shown at $\theta_{inc} = 0°$, 30°, and 60°; θ_{inc} is the angle between the incident beam and the surface normal.

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