Doping and dimensionality effects on the core-level spectra of layered ruthenates

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Core-level spectra of the Mn-doped Sr$_3$Ru$_2$O$_7$ and Sr$_{n+1}$Ru$_{n}$O$_{3n+1}$ ($n=1, 2, 3$) crystals are investigated with x-ray photoelectron spectroscopy. Doping of Mn to Sr$_3$Ru$_2$O$_7$ considerably affects the distribution of core-level spectral weight. The satellite of Ru 3$d$ core levels exhibits a substantial change with doping, indicating an enhanced electron localization across the doping-induced metal-insulator transition. However, the Ru 3$p$ core levels remain identical with Mn doping, thus showing no sign of doping-induced multiple Ru valences. In the Sr$_{n+1}$Ru$_{n}$O$_{3n+1}$ ($n=1, 2, 3$), the Ru 3$d$ core-level spectra are similar, indicating that the chemical bonding environment around Ru ions remains the same for different layered compounds. While the Sr 3$d$ shallow core levels shift to higher binding energy with increasing $n$, suggesting their participation in Sr-O bonding with structural evolution.

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I. INTRODUCTION

The layered ruthenates of the Ruddlesden-Popper series Sr$_{n+1}$Ru$_n$O$_{3n+1}$ (see Fig. 1), where $n (n=1, 2, 3, \ldots, \infty)$ is the number of layers of corner-sharing Ru$_6$O$_8$ octahedra per formula unit, display a remarkable array of complex electronic and magnetic properties. The complexity, which is intimately related to the coexistence of competing nearly degenerate states which couple simultaneously active degrees of freedom: charge, lattice, orbital, and spin states, is directly responsible for their tunability. Specifically, the properties of Sr$_{n+1}$Ru$_n$O$_{3n+1}$ exhibit strong dependence on the number ($n$) of Ru$_6$O$_8$ octahedral layers in crystal structure, reflecting the effect of dimensionality in the system. Single-layered Sr$_2$RuO$_4$ ($n=1$), as the most two-dimensional-like compound in the perovskite series, is an unconventional superconductor with possible spin-triplet pairing. The bilayered Sr$_3$Ru$_2$O$_7$ ($n=2$) shows behavior consistent with proximity to a metamagnetic quantum critical point. The magnetic ground state of the triple-layer Sr$_4$Ru$_3$O$_{10}$ ($n=3$) is poised between an itinerant magnetic and itinerant ferromagnetic state. Sr$_2$RuO$_3$ ($n=\infty$), regarded as a three-dimensional compound, is an itinerant ferromagnet with unusual transport characteristic.

On the other hand, the replacement of Sr with Ca (Ref. 12) or Ru with other transition-metal ions such as Mn (Refs. 13 and 14) causes a metal-to-insulator transition (MIT), reflecting the manifestation on transport property by replacing ions with different sizes. Especially, the dilute Mn doping provides a remarkably effective pathway of tuning on electronic structure beyond disorder-induced electron localization. However, the nature of such a doping-induced MIT is still under investigation.

X-ray photoelectron spectroscopy (XPS) has been widely used to study the chemical environment and the electronic structure of materials. In particular, the satellite structures in the core-level photoemission spectra provide important information about the interactions of electrons in correlated systems such as transition-metal oxides. One example is the XPS study of various ruthenates, where Ru 3$d$ core-level XPS spectra have satellites which are suggested as a result of two different screening mechanisms in the Mott-Hubbard picture for the MIT.

Since the MIT was observed with partial substitution of Ru by Mn in Sr$_3$Ru$_2$O$_7$, one expects that the study of core-level structure may shed light on the nature of doping-induced MIT in this system. Recent results of the x-ray absorption spectroscopy (XAS) taken from Mn-doped Sr$_3$Ru$_2$O$_7$ suggest that Mn impurities do not exhibit the same 4+ valence as Ru but act as 3+ and the observed MIT is purely electronic. Therefore, it is expected that Ru

FIG. 1. (Color online) Units cells of Sr$_2$RuO$_4$ (I4/mmm), Sr$_3$Ru$_2$O$_7$ (Pbam), and Sr$_3$Ru$_2$O$_{10}$ (Ibam). The different cites of oxygen ions in Sr$_3$Ru$_2$O$_7$ are labeled. The surfaces were created by cleaving the crystals between two SrO layers without breaking RuO$_6$ octahedra.
core-level XPS spectra may give further indication about doping-induced multiple Ru valences (Ru$^{4+}$ and Ru$^{5+}$) and, more importantly, the nature of the doping-induced MIT. In addition, one expects that the change in the number $n$ of RuO$_6$ octahedral layers should affect the electronic structures and the electron correlation in the layered Sr$_{n+1}$Ru$_n$O$_{3n+1}$ series. However, the relationship between the changes in the electron correlation strength and the changes in the dimensionality ($n$) as well as the doping effect is far from clear. In this study, we used XPS to systematically investigate both the dimensionality and doping effects on the electronic structure and correlation in the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ series ($n=1, 2,$ and $3$) and Mn-doped Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ system ($x=0.0, 0.1,$ and $0.2$).

II. EXPERIMENTS

The single crystals of Sr$_{n+1}$Ru$_n$O$_{3n+1}$ ($n=1, 2,$ and $3$) and Mn-doped Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ ($x=0.0, 0.1,$ and $0.2$) were grown by the floating zone technique. The x-ray diffraction on these crystals did not reveal any impurity phase. The samples were cleaved at room temperature in ultrahigh vacuum conditions to form a (001) surface and were immediately transferred into the μ-metal-shielded analysis chamber equipped with a computer controlled low-energy electron-diffraction (LEED) diffractometer and XPS. The crystals were cleaved between two SrO layers without breaking RuO$_6$ octahedra (see the cleavage planes in Fig. 1). XPS measurements were carried out with a Phoibos-150 hemispherical energy analyzer (from SPECS) by using photons of energy of 1486.7 eV from a Micro-Focus 500 ellipsoidal crystal monochromator with Al $Kα$ x-ray source and focusing x-ray spot capabilities. A pass energy of 10 eV was used for the measurements. The overall energy resolution for the XPS spectra is 0.16 eV. The Fermi level ($E_F$) of a Au sample was measured and used to calibrate the binding energy of all core-level spectra. All the XPS data were measured as the samples were at room temperature ($T=300$ K). The base pressure of our system during the measurements was 2 × 10$^{-10}$ Torr.

The binding energy, linewidth, and intensity of all measured core levels were determined through the standard fitting procedure. All core-level peaks were fitted to Voigt function, which is a convolution of Lorentzian and Gaussian components. The Lorentzian component accounts for the intrinsic line profile of core-level excitations with finite lifetime while the Gaussian one represents the contributions from other extrinsic broadening such as inhomogeneities in the surroundings of the emitting atoms as well as thermal and instrumental broadening. We used Shirley background profile to fit the background of XPS spectra. The Shirley empirical function has been widely used to take account of the inelastic background of a core-level peak with a relatively small amount of inelastic scattering. This background profile is proportional to the integrated photoelectron intensity to higher kinetic energy.

III. RESULTS AND DISCUSSION

A. Structures and LEED results

The structure of Sr$_3$Ru$_2$O$_7$ is tetragonal with $I4/mmm$ (Fig. 1) symmetry while the structures of Sr$_3$Ru$_2$O$_7$ and Sr$_3$Ru$_3$O$_{10}$ are orthorhombic through rotations about the $c$ axis of the neighboring corner-sharing octahedra within each layer of the double or triple perovskite blocks. However, a recent single-crystal x-ray study suggests that the bulk Sr$_3$Ru$_2$O$_7$ can still be modeled by $I4=mmm$ symmetry, where the rotation is represented by the splitting of the equatorial O positions. These rotations result in a decrease in the Ru-O-Ru angle in the $ab$ plane to 165° in Sr$_3$Ru$_2$O$_7$ and 158° in the middle layers of Sr$_3$Ru$_3$O$_{10}$ from the 180° in tetragonal Sr$_3$Ru$_2$O$_7$. Although the RuO$_6$ octahedra in these crystals have very similar size, the bond environment of cation Sr changes with number $n$ of RuO$_6$ octahedral layers. Inside the crystals, Sr has only one kind of bonding environment [Sr-O(1)/Sr-O(3)] in the single-layered Sr$_3$Ru$_2$O$_7$ (Ref. 23) while two kinds of distinct bonding environments [Sr-O(1)/Sr-O(3) and Sr-O(2)/Sr-O(3)] present in both the double$^{24}$ and triple$^{25}$-layered compounds (see Fig. 1).

Figure 2(a) shows a typical LEED pattern taken from the cleaved surface of Sr$_3$Ru$_2$O$_7$ at room temperature, showing excellent diffraction beams. In addition to the bright spots, there are weak spots (marked by arrows) related to the orthorhombic structure through the alternating in-plane rotation of RuO$_6$ octahedra about the (001) axis in bulk [see Fig. 2(b)]. Our LEED images confirm that the surfaces of doped and undoped Sr$_3$Ru$_2$O$_7$ as well as Sr$_3$Ru$_3$O$_{10}$ have $p(1 \times 1)$ structure without surface reconstruction. The fractional spots observed in LEED (see Fig. 2) with a $(\sqrt{2} \times \sqrt{2})$R45° structure are with respect to the tetragonal structure notation.
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Sr$_3$ doping-induced MIT is purely of electronic origin. To verify when the system is doped with Mn, the RuO$_6$ octahedra are compressed along the $a$ axis in a Jahn-Teller-type fashion, resulting in the bulging of octahedral layer. Such structural modifications with doping cause a change in the relative energy of the $t_2g$ orbitals and consequently in the transport and magnetic properties.

As shown in Figs. 3(b)–3(d), both Sr and Ru core levels shift to higher binding energy with increasing Mn doping. In particular, Sr and Ru $3p$ core levels exhibit almost identical shifts with doping [see Fig. 3(e)]. Such similar shifts may be attributed to final-state effects due to the reduction in screening to core holes with Mn doping. With the increase in Mn doping, the valence electrons are becoming more localized and reduce their screening to core hole, thus resulting in an increase in apparent binding energy in the core-level spectra. However, as we will discuss below, we also need to take into account the effects of doping-induced change in chemical environment known as initial-state effects.

One important issue for understanding the nature of Mn-doped Sr$_3$Ru$_{2-x}$O$_7$ is the valence of Mn impurity in the doped compounds. In Sr$_3$Ru$_{2-x}$O$_7$, the valences of ions are $\text{Sr}^{2+}$, $\text{Ru}^{4+}$, and $\text{O}^{2-}$, which would suggest the substitution of $\text{Ru}^{4+}$ with $\text{Mn}^{4+}$ upon doping. However, the XAS measurements$^{17}$ on the Sr$_3$($\text{Ru}_{0.9}\text{Mn}_{0.1}$)$_2$O$_7$ suggested that Mn impurities did not exhibit the same $4^{+}$ valence as Ru but acted as $3^{+}$ ones. This conclusion was obtained by comparing the isotropic Mn $L_3$-edge XAS data from Sr$_3$($\text{Ru}_{0.9}\text{Mn}_{0.1}$)$_2$O$_7$ with these from stoichiometric Mn oxides of known valences such as LaMnO$_3$ and Sr$_3$Mn$_2$O$_7$. If the Mn substituent in Sr$_3$($\text{Ru}_{1-x}\text{Mn}_x$)$_2$O$_7$ acts as a $\text{Mn}^{3+}$ ion, a substantial charge transition disproportionation of $\text{Mn}^{4+} + \text{Ru}^{4+} \rightarrow \text{Mn}^{3+} + \text{Ru}^{5+}$ should exist in the system and the Ru ions in doped samples should be mixed valent with $\text{Ru}^{4+}/\text{Ru}^{5+}$. This would result in two components in the Ru core-level spectra associated with $\text{Ru}^{4+}$ and $\text{Ru}^{5+}$ ion, respectively. As long as these two components have different in binding energy based on the scenario of initial-state effect, one would expect that the line shape of Ru core spectra varies with doping. As shown in Fig. 3(f) where we shifted the $\text{Ru} 3p_{3/2}$ peaks measured from the $x=0.1$ and 0.2 samples to lower binding energy in order to line up with the peak of the undoped compound. The $\text{Ru} 3p_{3/2}$ peaks of these three samples completely overlap, showing no change in line shape with doping. Therefore, there is no indication of multiple Ru valences induced by Mn doping in the core spectra in contrast with the results of x-ray absorption spectroscopy. The doping dependence of the Mn $2p$ core-level spectra, with $2p_{3/2}$ at $\sim 653$ eV and $2p_{1/2}$ at $\sim 642$ eV, is shown in Fig. 4(a) (see the inset). Because of the relatively weak Mn XPS signal, we are unable to resolve any change in Mn core levels with doping.

As we have mentioned above, Mn doping induces a MIT in Sr$_3$Ru$_2$O$_7$ (Refs. 13 and 14) which should be reflected in the Ru $3d$ spectral evolution. In fact, the Ru $3d$ spectra exhibit strong doping dependence. As shown in Fig. 4(a), both Ru $3d_{3/2}$ and $3d_{5/2}$ core levels show double peaks, one labeled as “screened (s)” peak with lower binding energy and the other labeled as “unscreened (u)” peak with higher binding energy. For Sr$_3$Ru$_2$O$_7$, the s peak of Ru $3d_{5/2}$ is located at 280.76 eV and the u one at 282.13 eV. The separation of these two peaks in both Ru $3d_{3/2}$ and $3d_{5/2}$ core levels is about 1.47 eV for the undoped sample and 1.33 eV for both doped samples. These peaks in the Ru $3d$ spectra shift to higher binding energy with doping. The spectral weight of the s peak decreases while the u peak increases with doping.
In order to further understand the nature of these Ru 3d core spectra, we have calculated the first moment of the intensity-weighted average binding energy vs Mn doping.

\[ E_{k}^{HF} = \int_{-\infty}^{\infty} \frac{eA(\vec{k}, e)dE}{\sum_{i} e_{i} \sum_{i} I_{i} + \text{continuum}}, \]

where \( A(\vec{k}, e) \) is the spectral function in the core-level photoelectron excitations. For a core-level spectrum with discrete main peak and satellites, the integration of the spectral function can be replaced by a simple summation of the intensity \( I_{i} \) weighted average energy, where index \( i \) refers to different discrete peaks, and the excitation continuum. Changes in \( E_{k}^{HF} \) truly reflect the chemical shifts related to the changes in bonding configurations caused (in this case) by doping. For \( \text{Sr}_{x} \text{Ru}_{1-x} \text{Mn}_{x} \text{O}_{3} \), we can determine \( E_{k}^{HF} \) of the Ru 3d core level for different doping concentrations by taking into account both the \( s \) and \( u \) peaks. For simplicity, we neglect the possible change in the excitation continuum with doping. Figure 4(b) presents the doping dependence of the relative shift \( \gamma \) of \( E_{k}^{HF} \) normalized to the energy difference \( \Delta E \) between the \( s \) and \( u \) peak, i.e.,

\[ \gamma(x) = \frac{[E_{k}^{HF}(x) - E_{k}^{HF}(x = 0)]}{\Delta E}, \]

where \( \Delta E(=1.33 \text{ eV}) \) is the same for both \( x=0.1 \) and 0.2 samples from our analysis. For the undoped compound, we have \( \Delta E=1.47 \text{ eV} \), slightly larger than that found in the doped ones. It is shown [see Fig. 4(b)] that \( \gamma \) of \( E_{k}^{HF} \) does increase with increasing doping, thus indicating a chemical shift in the core-level spectra. The increase in the binding energy indicates the enhanced localization of the wave functions of the initial states with doping. Therefore, the determination of \( \gamma(x) \), which can be used as an order parameter, reveals the critical doping concentration \( (x) \) for the metal-to-insulator transition observed in the system.

C. Dimensionality effect on core-level spectra

Figure 5 presents the valence band and core-level spectra of the \( \text{Sr}_{n+1} \text{Ru}_{x} \text{O}_{3n+1} \) (\( n=1, 2, \) and 3). The valence-band spectra display a well-defined Fermi edge for all three crystals. The Ru 3d and Sr 3p core levels are shown in Fig. 5(b). The positions, linewidth, and relative intensity of these features in both valence and Ru 3d exhibit similar change in spectral weight with different numbers of RuO6 octahedral layers, \( n \). The ratios of the coherent to incoherent part in the valence band and the ratio of the \( s \) to \( u \) component in the Ru 3d core level increase slightly with \( n \). The two ratios show a consistent behavior, indicating the electron correlation effects become smaller as the system gets closer to three dimensional. On the other hand, as shown in Fig. 5(c), the Ru 3p1/2 (at 485.94.1 eV) and 3p3/2 (at 463.44 eV) core-level spectra of \( \text{Sr}_{n+1} \text{Ru}_{x} \text{O}_{3n+1} \) (\( n=1, 2, \) and 3) are almost identical. It is worth to notice that the surface of the \( n=1 \) com-

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**FIG. 4.** (Color online) (a) Doping dependence of Ru 3d spectra with screened (s) and unscreened (u) components taken from Mn-doped \( \text{Sr}_{x} \text{Ru}_{1-x} \text{O}_{3} \) and (b) intensity ratio of the fitted s and u peaks of the Ru 3d5/2 and the relative change in the first moment of the intensity-weighted average energy vs Mn doping (see details in text). The inset shows the doping dependence of Mn 3p core-level spectra.

The broad u peak is the satellite (referred to as shake-up) due to particle-hole excitations in the presence of the one-particle-hole state. Generally, the intensity of satellites is directly proportional to the degree of electron localization, thus providing a signature for the MIT in a system.

To gain insight into the doping dependence, the spectra were analyzed through standard core-level fitting by assuming that both Ru 3d5/2 and 3d3/2 core levels exhibit two-peak structure. Peak positions, widths, and intensities were determined by fitting with Voigt function after Shirley background subtraction. Peak fittings of the Ru 3d3/2 and d5/2 spectra into two-peak structure gave a reasonably good fit to the experimental data. The Lorentzian component, which represents the excitation spectra of core-level states with finite lifetime, was found to be the dominant one for the s peaks. The fitting for u peaks contains significant Gaussian broadening. The obtained relative intensity ratio of the u and s component of the Ru 3d5/2 core level as a function of Mn-doping concentration is plotted in Fig. 4(b). The relative intensity ratio systematically decreases as the Mn concentration increases. This behavior is correlated with that of the spectral weight of the quasiparticle spectra in valence band with doping, suggesting the gradual enhancement of electron localization toward MIT. This behavior is also consistent with the results of the measured transport properties, including Mn-doping-induced MIT.
DOpending but not the $n=2$ or 3 one has a surface reconstruction. This may give rise to an additional change in the spectral weight of the $n=1$ sample compared to the $n=2$ or 3 compound. Nevertheless, the similar behavior of the Ru core-level spectra is consistent with the similar rigid two-dimensional RuO$_6$ octahedral layer in all of these layered compounds. It would be interesting to study the similar core-level spectra of layered ruthenates of the Sr-Ru-O system. It would be interesting to study the similar core-level spectra of layered ruthenates of the Sr-Ru-O system.

In order to understand the different shifts of the binding energy of Sr core-level spectra, it is necessary to examine the structural and bonding evolution of the cations with $n$ in ruthenate. As $n$ increases, the system evolves from quasi-two-dimensional to three-dimensional structure (see Fig. 3). Unlike the Ru ions which are located inside RuO$_6$ octahedron, the Sr ions has two distinct bonding environments in both Sr$_3$Ru$_2$O$_7$ and Sr$_4$Ru$_3$O$_{10}$. One bonding environment is the one with Sr-O(1) bond along $c$ axis and Sr-O(3) bond in $ab$ plane, referring to the Sr ions in the cleavage plane (see Fig. 1). The other bonding environment is that of Sr-O(2) bond along $c$ axis and Sr-O(3) bond in $ab$ plane, referring to the Sr ions within the RuO$_6$ layers. One can expect different chemical shifts due to the different bonding environments as well as the different bond lengths. In particular, the larger shift of Sr 3$d$ shallow core levels compared with that of Sr 3$p$ indicates a possible participation of 3$d$ in bonding. Upon further increasing $n$, such shifts should gradually diminish as the system approaches a three-dimensional structure such as SrRuO$_3$ (i.e., $n=\infty$).

In summary, we have investigated the core-level XPS spectra of layered ruthenates of the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ (n=1, 2, and 3) and Mn-doped Sr$_3$Ru$_2$O$_7$. We observed that the dimensionality does not affect the Ru but Sr core levels. The Ru 3$d$ core-level spectra maintain similar structure for crystals with different octahedral layers ($n$), suggesting that the chemical bonding environment around Ru ions remains the same for different layered compounds. While the Sr 3$d$ shallow core levels shift to higher binding energy with increasing $n$, indicating a variation in Sr-O bonding with structural evolution. On the other hand, the core levels of Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ show strong dependence of doping concentration ($x$), revealing the enhanced electron localization with doping toward to MIT. However, the line shape and linewidth of the Ru 3$p$ core levels remain identical with doping, showing no sign of multiple Ru oxidation states in Mn-doped system.

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