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

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Core-level spectra of the Mn-doped Sr3Ru2O7 and Sr3Ru3+xO3n+1 (n = 1, 2 and 3) crystals are investigated with X-ray photoelectron spectroscopy. Doping of Mn to Sr3Ru2O7 considerably affects the distribution of core-level spectral weight. The satellite of Ru 3d core levels exhibits a substantial change with doping, indicating an enhanced electron localization across the doping-induced metal-insulator transition. However, the Ru 3p core levels remain identical with Mn-doping, thus showing no sign of doping-induced multiple Ru valences. In the Sr3Ru3+xO3n+1 (n = 1, 2 and 3), the Ru 3d core-level spectra are similar, indicating that the chemical bonding environment around Ru ions remains the same for different layered compounds. While the Sr 3d 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 Srn+1RuO3n+1 (see Fig. 1), where n (n = 1, 2, 3, ... ∞) is the number of layers of corner sharing RuO6 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 Srn+1RuO3n+1 exhibit strong dependence on the number (n) of RuO6 octahedral layers in crystal structure, reflecting the effect of dimensionality in the system. Single-layered Sr2RuO4 (n = 1), as the most two-dimensional-like compound in the perovskite series, is an unconventional superconductor with possible spin-triplet pairing. The bilayered Sr3Ru2O7 (n = 2) shows behavior consistent with proximity to a metamagnetic quantum critical point. The magnetic ground state of the triple-layer Sr4Ru3O10 (n = 3) is poised between an itinerant metamagnetic and itinerant ferromagnetic state SrRuO3 (n = ∞), regarded as a three-dimensional compound, is an itinerant ferromagnet with unusual transport characteristic. On the other hand, the replacement of Sr with Ca or Ru with other transition metal ions such as Mn 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.

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 (TMOs). One example is the XPS study of various ruthenates, where Ru 3d 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 Sr3Ru2O7, 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 Sr3Ru2O7 suggest that Mn impurities do not exhibit the same 4+ valence as Ru, but act as 3+ acceptors and the observed MIT is purely electronic. Therefore, it is expected that Ru core-level XPS spectra may give further indication about doping-induced multiple Ru valences (Ru3+ and Ru5+) and, more importantly, the nature of the doping-induced MIT. In addition, one expects that the change of the number n of RuO6 octahedral layers should affect the electronic structures and the electron correlation in the layered Sr3Ru3+xO3n+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 Sr3Ru3+xO3n+1 series (n = 1, 2 and 3) and Mn-doped Sr3(Ru1−xMnx)2O7 (x = 0.0, 0.1 and 0.2).

II EXPERIMENTS

The single crystals of Srn+1RuO3n+1 (n = 1, 2 and 3) and Mn-doped Sr3(Ru1−xMnx)2O7 (x = 0.0, 0.1 and
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$_2$RuO$_4$ is tetragonal with I4/mmm (Fig. 1) symmetry while the structures of Sr$_3$Ru$_2$O$_7$ and Sr$_4$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. These rotations result in a decrease of the Ru – O – Ru angle in the ab plane to 165$^\circ$ in Sr$_3$Ru$_2$O$_7$ and 158$^\circ$ in the middle layers of Sr$_4$Ru$_3$O$_{10}$ from the 180$^\circ$ in tetragonal Sr$_2$RuO$_4$. 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$_2$RuO$_4$, while two kinds of distinct bonding environments (Sr – O(1)/Sr – O(3) and Sr – O(2)/Sr – O(3)) are present in both the double- and triple-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$_4$Ru$_3$O$_{10}$ have primary p(1 × 1) structure without reconstruction. However, a $(\sqrt{2} \times \sqrt{2})R45^\circ$ superstructure with respect to the tetragonal structure in the bulk was observed in Sr$_2$RuO$_4$, due to the rotation of the surface RuO$_6$ octahedra about the axis normal to the surface. This surface reconstruction corresponds to a bulk soft-phonon mode freezing into a static lattice distortion.

B. Doping dependence of core level spectra

Previous XAS on Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ (x = 0.0 and 0.1) suggests that the driving mechanism for the observed doping-induced MIT is purely of electronic origin. To verify this, we have performed the XPS study on Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$. Figure 3 presents the valence band and some characteristic core-level spectra of the Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ (x = 0.0, 0.1, and 0.2). With Mn doping, a clear spectral weight transfer can be seen in the valence spectra (see Fig. 3(a)). The spectral weight of the quasi particle band considerably decreases and transfers to higher binding energy region of 3.0 to 10 eV. This should be associated with the enhanced electron localization with increasing Mn doping and consequently the doping-induced MIT observed in the system. There is yet no clear microscopic understanding for the doping-induced MIT. Structural studies indicate that when the
system is doped with Mn the RuO$_6$ octahedra are compressed along c-axis in a Jahn-Teller-like fashion, resulting in the bulking 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 Fig. 3(b), (c) and (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 of screening to core holes with Mn doping. With the increase of Mn doping, the valence electrons are becoming more localized and reduce their screening to core hole, thus resulting in an increase of 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 of chemical environment known as initial state effects.

One important issue for the understanding the nature of Mn-doped Sr$_3$Ru$_2$O$_7$ is the valence of Mn impurity in the doped compounds. In Sr$_3$Ru$_2$O$_7$, the valences of ions are Sr$^{2+}$, Ru$^{4+}$ and O$^{2-}$, respectively, which would suggest the substitution of Ru$^{4+}$ with Mn$^{4+}$ upon doping. However, the XAS measurements on the Sr$_3$(Ru$_{0.9}$Mn$_{0.1}$)$_2$O$_7$ suggested that Mn impurities did not exhibit the same 4+ valence as Ru, but acted as 3+ acceptors. This conclusion was obtained by comparing the isotropic Mn L$_{2,3}$-edge XAS data from Sr$_3$(Ru$_{0.9}$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$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ acts as a Mn$^{3+}$ electron acceptor, a substantial charge transition disproportionation of Mn$^{4+} + $ Ru$^{4+} \rightarrow $ Mn$^{3+} + $ Ru$^{5+}$ should exist in the system, and the Ru ions in doped samples should be mixed-valent with Ru$^{4+}/$Ru$^{5+}$. This would result in two components in the Ru core level spectra associated with Ru$^{4+}$ and Ru$^{5+}$ ion, respectively. As long as these two components have difference in binding energy based on the scenario of initial state effect, one would expect that the lineshape of Ru core spectra varies with doping. As shown in Fig. 3(f) where we shifted the 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 Ru 3p$_{3/2}$ peaks of these three samples completely overlap, showing no change in lineshape 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$_{1/2}$ at $\sim 653$ eV and 2p$_{3/2}$ 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 of Mn core levels with doping.

As we have mentioned above, Mn-doping induces a
MIT in Sr$_3$Ru$_2$O$_7$ 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. The broad u peak is the satellite (referred to as shake-up peak) 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 3d$_{3/2}$ and 3d$_{5/2}$ 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 3d$_{3/2}$ and d$_{5/2}$ 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 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 3d$_{5/2}$ 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 quasi-particle spectra in valence band with doping, suggesting the gradual enhancement of electron localization towards MIT. This behavior is also consistent with the results of the measured transport properties, including Mn doping-induced MIT.

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. According to the basic sum rules for all excitations which generate both the main core level peak and the associated shakeup satellites in core level spectra, the first moment of the intensity-weighted energy distribution equals the single-particle Hartree-Fock eigenenergy, i.e.,

$$E_k^{HF} = \int_{-\infty}^{\infty} \epsilon A(k, \epsilon) d\epsilon \approx \sum_i \epsilon_i I_i / \sum_i I_i + \text{Continuum}$$

(1)

where $A(k, \epsilon)$ 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 of bonding configurations caused (in this case) by doping. For Sr$_3$(Ru$_{1-x}$M$n_x$)$_2$O$_7$, we can determine $E_k^{HF}$ of the Ru 3d$_{5/2}$ 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.,

$$\gamma(x) = [E_k^{HF}(x) - E_k^{HF}(x=0)] / \Delta E$$

(2)

where $\Delta E = 1.33$ eV is the same for both $x = 0.1$ and 0.2 samples from our analysis. For the undoped compound, we have $\Delta E = 1.47$ 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 of 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 ($x_c$) for the metal-to-insulator transition observed in the system.

C. Dimensionality effect on core level spectra
the similar behavior of the layered number $n$ Sr core level spectra of the samples with different the from quasi-two-dimensional to three dimensional structure such as $\text{SrRuO}_3$ octahedra 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 3$p_{3/2}$ (at 485.941 eV) and 3$p_{1/2}$ (at 463.44 eV) core level spectra of $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ ($n = 1, 2$ and 3) are almost identical. It is worth to notice that the surface of the $n = 1$ compound but not the $n = 2$ or 3 one has a $\sqrt{2} \times \sqrt{2} R 45^\circ$ 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 $\text{RuO}_6$ octahedra layer in all of these layered compounds. It would be interesting to study the similar core levels in $\text{SrRuO}_3$ (i.e., $n = \infty$) which is supposed to be three-dimensional rather than quasi two-dimensional. So far there is still no measurement of the core level spectra from $\text{SrRuO}_3$ single crystal available for comparison.

However, obvious changes have been observed in the Sr core level spectra of the samples with different the layered number $n$ (see Fig. 5(b) and 5(d)), although their lineshape is unaltered. In order to compare these three compounds, we plot the shifts of $\text{Sr}$ 3$p$ and 3$d$ as well as Ru 3$p$ core spectra, as a function of the number of $\text{RuO}_6$ octahedra layers $n$ relative to $n = 1$ in Fig. 6. While Ru core does not change, the Sr cores exhibit increases of binding energy with $n$. Specifically, the Sr 3$d$ shallow core levels show stronger $n$-dependence while the shift of the Sr 3$p$ core is probably within the range of error bar. Interestingly, the linewidth of $n = 1$ sample ($\sim 0.77$ eV) is slightly larger than those from $n = 2$ and 3 samples ($\sim 0.74$ eV). This may be attributed to larger surface broadening due to the surface reconstruction of $\text{Sr}_2\text{RuO}_4\Delta$

![Image](image69x559 to 284x740)

**FIG. 5:** (Color online) Valence and core-level photoemission spectra of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ ($n = 1, 2$ and 3) measured at $T = 300$ K with monochromated Al Kα X-ray source: (a) Valence spectra, (b) Ru 3d and Sr 3p, (c) Ru 3p, and (d) Sr 3d core level spectra. The peak positions are marked by the solid bars. The Fermi edge is calibrated with that of a Au sample.

![Image](image357x466 to 522x590)

**FIG. 6:** (Color online) Measured energy shifts relative to the $\text{Sr}_2\text{RuO}_4$ ($n = 1$) plotted against the number of $\text{RuO}_6$ octahedra layers, $n$ in $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$.

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 $\text{RuO}_6$ octahedron, the Sr ions has two distinct bonding environments in both $\text{Sr}_3\text{Ru}_2\text{O}_7$ and $\text{Sr}_4\text{Ru}_3\text{O}_{10}$. One bonding environment is the one with $\text{Sr-O}(1)$ bond along $c$-axis and $\text{Sr-O}(3)$ bond in $ab$ plane, referring to the Sr ions in the cleavage plane (see Fig. 1). The other bonding environment is that of $\text{Sr-O}(2)$ bond along $c$-axis and $\text{Sr-O}(3)$ bond in $ab$ plane, referring to the Sr ions within the $\text{RuO}_6$ 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 $\text{SrRuO}_3$ (i.e., $n = \infty$).

**IV SUMMARY**

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

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