

Manifestation of correlation effects in the photoemission spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$

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We have measured soft x-ray photoemission and O 1s x-ray absorption spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$ thin films prepared *in situ*. The coherent and incoherent parts have been identified in the bulk component of the photoemission spectra, and spectral weight transfer from the coherent to the incoherent part has been observed with decreasing x , namely, with increasing orthorhombic distortion. We propose that, while the Ru 4d one-electron bandwidth does not change with x , the distortion, and hence the splitting of the t_{2g} band, effectively increases electron correlation strength. Although strong mass enhancement is found in the electronic specific heat data, the coherent part remains wide, suggesting enhanced band narrowing only in the vicinity of E_F .

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Metal-insulator transition has been extensively studied because of its fundamental importance in condensed matter physics as well as of its close relationship with remarkable phenomena such as the high-temperature superconductivity in cuprates and the colossal magnetoresistance in manganites.¹ Broadly speaking, metal-insulator transition occurs in two ways. One is bandwidth control and the other is filling control. In bandwidth control, bandwidth, and hence electron correlation strength, is changed through the modification of, e.g., the lattice parameters. Recent developments of dynamical mean-field theory (DMFT), have led to a lot of progress in understanding many problems inherent in strongly correlated electron systems, including Mott metal-insulator transition.² According to DMFT, as U/W increases, where U is the on-site Coulomb energy and W is the one-electron bandwidth, spectral weight is transferred from the coherent part (the quasiparticle band near E_F) to the incoherent part (the remnant of the Hubbard bands 1–2 eV above and below E_F).³ Metal-to-insulator transition thus occurs as the spectral weight of the coherent part vanishes.

In perovskitetype ABO_3 compounds, bandwidth control is realized through the modification of the radius of the A site ion r_A . As r_A decreases, the B–O–B bond angle decreases from 180° and the cubic lattice transforms to the orthorhombic (GdFeO₃-type) structure. This reduces W , because the effective transfer integrals between the neighboring B sites is governed by the supertransfer process via the O 2p state. $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ is a typical bandwidth control system but remains metallic for the entire x range. Inoue *et al.*⁴ have reported that in the photoemission (PES) spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$, as one decreases x , that is, as one decreases W , spectral weight is transferred from the coherent part to the incoherent part centered at ~ 1.5 eV below E_F . Recently, however, Sekiyama *et al.*⁵ have reported that spectral weight transfer is not observed in the PES spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ measured using high photon energies, i.e., in so-called “bulk

sensitive” photoemission spectra. In the present paper we have observed clear spectral weight transfer in the bandwidth-control system $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$ (CSRO) after decomposition of the spectra into surface and bulk components.

Despite their more extended nature of the 4d orbitals than the transition-metal 3d orbitals, ruthenates are found to show various phenomena associated with electron correlation such as unconventional superconductivity in Sr_2RuO_4 (Ref. 6) and metal-insulator transition in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$.⁷ CSRO studied in the present paper is metallic in the entire x range. SrRuO_3 is metallic and shows ferromagnetism below $T_C \simeq 160$ K.⁸ In going from SrRuO_3 to CaRuO_3 , the Ru—O—Ru bond angle is reduced from $\sim 165^\circ$ to $\sim 150^\circ$ (Ref. 9) and T_C decreases to zero at $x \sim 0.4$.¹⁰ Optical studies of CSRO have shown characteristic behavior of a Mott-Hubbard system predicted by DMFT.¹¹ The anomalous Hall effect of SrRuO_3 has been explained as due to the presence of magnetic monopoles in the momentum space.¹²

Previous photoemission studies of polycrystalline SrRuO_3 samples have revealed that the effect of electron correlation is substantial within the Ru 4d t_{2g} band.^{13,14} Recent Ru 3d core-level x-ray photoemission studies of various ruthenates¹⁵ have also revealed the importance of electron correlation effects in the ruthenates. Recently, the growth of high-quality perovskite oxide single-crystal thin films has become possible by pulsed laser deposition (PLD),^{16,17} and a setup has been developed for their *in situ* photoemission measurements.^{18,19} In this paper, we have measured soft x-ray PES and absorption spectra of a CSRO thin film. An ultraviolet PES experiment of *ex situ* prepared CSRO thin films²⁰ has also been reported recently.

The PES and x-ray absorption spectroscopy (XAS) measurements were performed at BL-2C of Photon Factory (PF), High Energy Accelerators Research Organization (KEK), using a combined laser molecular beam epitaxy (MBE) photoemission spectrometer system. Details of the experimental

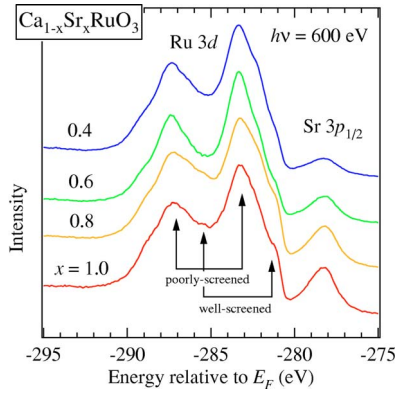


FIG. 1. (Color online) Ru 3d and Sr 3p core-level photoemission spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$.

setup are described in Ref. 18. Epitaxial films of CSRO were grown on single-crystal substrates of Nb-doped SrTiO_3 by the PLD method. The substrates were annealed at 1050°C under an oxygen pressure of $\sim 1 \times 10^{-6}$ Torr to obtain an atomically flat TiO_2 -terminated surface.²¹ CSRO thin films were deposited on the substrates at 900°C at an oxygen pressure of ~ 0.1 Torr. The surface morphology of the measured films was checked by *ex situ* atomic force microscopy (AFM), showing atomically flat step-and-terrace structures. Coherent growth on the substrate was confirmed by x-ray diffraction. Due to the coherent growth, the out-of-plane lattice constant decreased with Ca doping while the in-plane lattice constant did not vary. Thus the Ru–O–Ru bond angle is thought to be reduced in going from SrRuO_3 to CaRuO_3 in the CSRO thin films, too. The fabricated CSRO thin films showed metallic resistivity and the values of their T_C were almost the same as those of the bulk samples.¹⁰ All the photoemission measurements were performed under an ultrahigh vacuum of $\sim 10^{-10}$ Torr at room temperature using a Scienta SES-100 electron-energy analyzer. The total energy resolution was about 150 meV at the photon energy of 400 eV, about 200 meV at that of 600 eV, and about 500 meV at that of 900 eV. The Fermi level (E_F) position was determined by measuring gold spectra. The XAS spectra were measured in the total-electron-yield mode.

The Ru 3d core level shown in Fig. 1 reveals two sets of spin-orbit doublet peaks, well-screened peaks, and poorly screened peaks. One can see that the intensity of the well-screened peaks is decreased with Ca doping. According to Cox *et al.*,²² the ratio of the poorly screened to well-screened peaks should increase with electron correlation. Thus the Ru 3d core signals provide evidence for a progressive increase of electron correlation in going from SrRuO_3 to CaRuO_3 . Figure 2 shows a combined plot of the valence-band spectra and the O 1s XAS spectra, representing the electronic state below and above E_F . The band between ~ -2 to ~ 5 eV measured relative to E_F is mainly composed of Ru 4d states and that between ~ -10 to ~ -2 eV of O 2p states.^{13,14} For PES, we assign the emission within ~ 1 eV of E_F with a sharp Fermi edge and the broad band centered at ~ -1.2 eV peak, respectively, to the coherent and incoherent parts of the spectral function. Similarly for O 1s XAS, two peaks are seen within ~ 2 eV above the threshold, which we

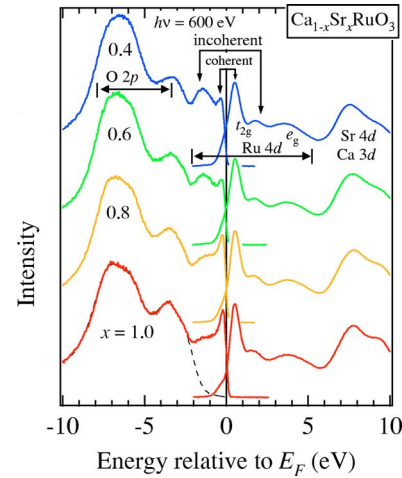


FIG. 2. (Color online) A combined plot of the valence-band spectra and the O 1s XAS spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$. The dashed curve shows how the O 2p band has been subtracted to obtain the Ru 4d band. For detail, see the text.

attribute to the coherent and incoherent parts of the unoccupied t_{2g} band. Above the t_{2g} band, one can see the empty e_g band centered at ~ 4 eV. Both in PES and XAS, one can see that spectral weight transfer occurs from the coherent part to the incoherent part with Ca doping. In XAS, spectral weight transfer is relatively small, partly because the core-hole potential distorts the single-particle excitation spectrum, and also because surface effects are much weaker in XAS than in PES, as described below.

Although our PES spectra are relatively bulk sensitive due to the use of soft x rays, surface effects are not negligible. Therefore, to study the intrinsic bulk electronic structure, we need to subtract the surface components from the measured spectra following the procedure of Ref. 23. The measured photoemission spectra are assumed to be expressed as $I(E) = \exp(-s/\lambda)I_{\text{bulk}}(E) + [1 - \exp(-s/\lambda)]I_{\text{surface}}(E)$, where s is the thickness of the surface layer, λ is the photoelectron mean-free path, and I_{bulk} and I_{surface} denote the spectra of the bulk and surface regions, respectively. Because λ is a function of photon energy, one can obtain the bulk and surface components separately from PES spectra measured at two photon energies. We measured PES spectra at different 400 and 900 eV as shown in Fig. 3. As we are interested in the Ru 4d band, the tail of the O 2p band has been subtracted after having fitted the O 2p band to multiple Gaussians as shown in Fig. 2, and the resulting Ru 4d spectra have been normalized to the integrated intensity from $E = 0.5$ to -3.0 eV, as shown in Fig. 3. In order to obtain the bulk and surface components of the Ru 4d band, we have used the mean-free paths of $\lambda_{900} = 18 \text{ \AA}$ and $\lambda_{400} = 6 \text{ \AA}$ at $h\nu = 900$ and 400 eV, respectively, according to Ref. 24, and the surface layer thickness of 4 \AA , the dimension of the unit cell.⁹ As shown in Fig. 3, the incoherent part of the bulk component thus obtained is weaker than that of the raw spectra, and manifests itself as a shoulder rather than a separate feature from the main structure near E_F . Nevertheless, there is still spectral weight transfer from the coherent part to the incoherent part with Ca doping (Fig. 3). The incoherent part

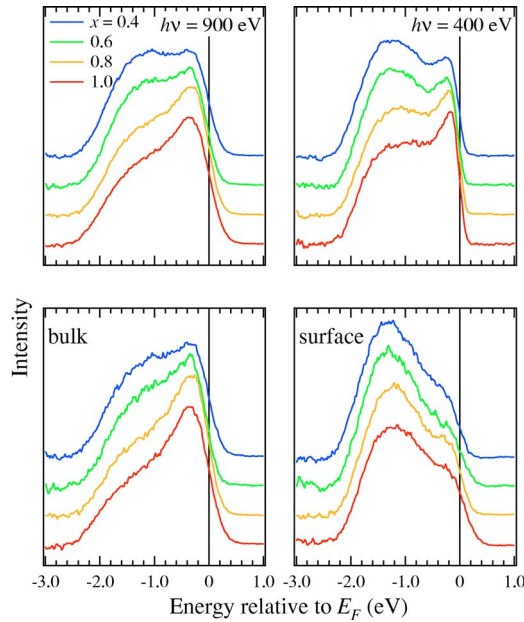


FIG. 3. (Color online) Ru 4d band of $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$. Top: Data taken at $h\nu=400$ and 900 eV. Bottom: The bulk and surface components deduced from different energies.

is strong in the surface components as expected,²⁵ similar to the spectra taken at low photon energies.²⁰

In order to see how the result is robust against the uncertainties in the parameters λ and s , we have made the decomposition by varying these parameters. The bulk components do not change their line shapes appreciably for the range of the parameters $4 \leq \lambda_{400} \leq 8$ Å and $4 \leq s \leq 8$ Å. The result is even less sensitive to variations in λ_{900} . Therefore, we consider that the obtained bulk component indeed represent the intrinsic bulk electronic structure. As for the surface component, on the other hand, the line shapes are somewhat more sensitive ($\sim \pm 10\%$ variation) to the parameters.

We have also examined the angle dependence of PES spectra to separate the bulk and surface components. From the PES spectra taken at emission angles 0° and 70° , we have obtained each component as shown in Fig. 4. While the surface component is a little different from that obtained from the photon energy dependence (dashed curve), the bulk com-

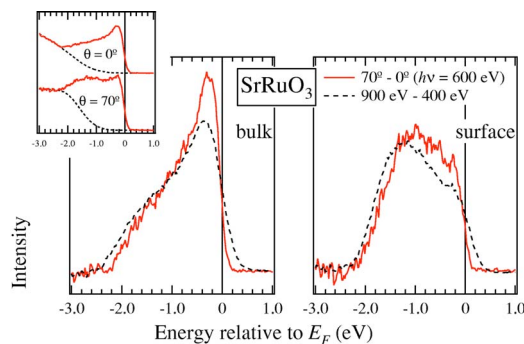


FIG. 4. (Color online) Bulk and surface components of SrRuO_3 deduced from the angle dependence of the PES spectra. The dashed curves show the surface and bulk components from Fig. 3. Inset: the raw spectra of SrRuO_3 taken at $h\nu=600$ eV

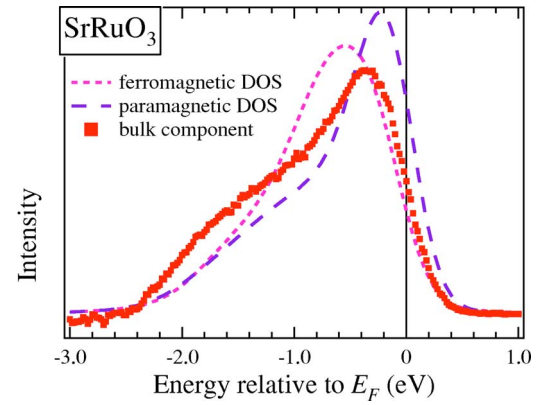


FIG. 5. (Color online) Comparison of the bulk component and the band-structure calculation for ferromagnetic and paramagnetic SrRuO_3 . The calculated DOS is broadened with a Gaussian and a Lorentzian function.

ponent is very similar to it. (The broader Fermi cutoff in the dashed curve is due to the lower resolution of the 900-eV spectra.) This gives additional evidence that the obtained bulk components represent the intrinsic bulk electronic structure.

Since all the measurements were made at room temperature, all the $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$ samples were in the paramagnetic state.²⁶ However, because the T_C decreases from 160 K for $x=1$ to ~ 0 K for $x=0.4$,¹⁰ the spectral change could be due to changes in the ferromagnetic fluctuations, which become stronger with Sr content, rather than changes in the correlation strength. In order to see whether this is the case or not, we compare in Fig. 5 the experiment with the calculated density of states (DOS) of SrRuO_3 in the ferromagnetic and paramagnetic states.²⁷ The calculated DOS for the paramagnetic state clearly shows more pronounced peak at E_F contrary to the x -dependent change in the spectra. This would exclude the magnetic fluctuations as the origin of the spectral weight transfer.

Since CaRuO_3 is more distorted than SrRuO_3 , one would naturally expect the narrowing of the Ru 4d band in going from SrRuO_3 to CaRuO_3 . However, the band-structure calculation has shown²⁸ that the bandwidth of Ru 4d does not change between SrRuO_3 and CaRuO_3 . Although the orthorhombic distortion does not reduce the t_{2g} bandwidth, it lifts the t_{2g} orbital degeneracy. Such a lift of the t_{2g} -orbital degeneracy has been shown to effectively increase the electron correlation strength in the case of Ti perovskites.²⁹ The spectral weight transfer from the coherent part to the incoherent part with Ca doping would therefore be due to the increased correlation strength due to the lifting of the orbital degeneracy.

Compared with the band-structure calculation, the bandwidth of experimental “bulk” data is similar to that of calculation. This may mean that m^*/m_b is ~ 1 , where m^* is the effective mass of the quasiparticle and m_b is the bare band mass, if the band narrowing occurs uniformly in the entire Ru 4d band. However, specific heat measurement indicated that the value of m^*/m_b is about 10 for SrRuO_3 and 17 for CaRuO_3 .²⁶ This implies that m^* is enhanced in the vicinity of E_F , which in turn means that the genuine coherent part exists

only in the vicinity of E_F . This is analogous to the case of U compounds ($\text{UAl}_2, \text{UPt}_3$) (Ref. 30) where the $5f$ band width is similar or larger than the band-structure calculation but the mass enhancement at E_F can be as large as $m^*/m_b \sim 100$. These features are consistent with the bad metallic behavior of SrRuO_3 .³¹

In conclusion, with bandwidth control, spectral weight transfer is observed between the coherent and incoherent parts. As the orthorhombic distortion lifts the t_{2g} orbital degeneracy, the effective correlation strength is increased. The similarity to U compounds in the spectrum of SrRuO_3 suggests that the spectral changes from $4f$ (Ce) to $5f$ (U) electron systems may correspond to that from $3d$ to $4d$ electron

systems, namely well separated coherent and incoherent features to unresolved ones.

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