Orbital-selective confinement effect of Ru 4d orbitals in SrRuO₃ ultrathin film

Soonmin Kang,¹,² Yi Tseng,³ Beom Hyun Kim,⁴ Seokhwan Yun,¹,² Byungmin Sohn,¹,² Bongju Kim,¹,² Daniel McNally,¹ Eugenio Paris,³ Choong H. Kim,¹,² Changyoung Kim,¹,² Tae Won Noh,¹,² Sumio Ishihara,⁵ Thorsten Schmitt,³,* and Je-Geun Park¹,²,†

¹Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Korea
²Department of Physics, Tohoku University, Sendai 980-8578, Japan
³Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea
⁴Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
⁵Korea Institute for Advanced Study, Seoul 02455, Korea

(Received 2 August 2018; published 7 January 2019)

DOI: 10.1103/PhysRevB.99.045113

I. INTRODUCTION

The orbital degree of freedom (DOF) is relatively less well understood among the four fundamental DOFs of solids: charge, spin, lattice, and orbital. The role of the orbital DOF was originally recognized by the now famous Kugel-Khomskii model [1]. It took another decade before its full consequence was experimentally observed from numerous studies on so-called colossal magnetoresistance (CMR) manganites [2]. The most direct effect of the orbital DOF can be found in the so-called orbital ordering and the associated metal-insulator transition (MIT) with unique magnetic or structural transitions [3,4]. A more recent breakthrough in the understanding of the orbital DOF is in the discovery of the orbital-selective mechanism. It is now believed that several Ru and V oxides exhibit the phenomena that arise from the orbital-selective physics [4–7]. One notable example is the orbital-selective Mott transition [8].

SrRuO₃ is a well-known member of the ruthenate family with a ferromagnetic phase below a Curie temperature of 165 K. Unlike other ferromagnetic materials, the conductivity of bulk SrRuO₃ is high enough to make it a popular choice of electrode for various thin-film samples with a stable perovskite structure [11]. At the same time, it is one of the rare itinerant ferromagnetic oxides and has attracted significant interest in its own right [12,13]. For example, it has long been suspected that some kind of coupling between the lattice and spin degrees of freedom works for the ferromagnetic ground state. It was also found both theoretically and experimentally that RuO₆ octahedra of SrRuO₃ undergo quite irregular plastic distortion below the ferromagnetic transition temperature [14,15]. More recently, the unusual temperature dependence of the spin gap found by inelastic neutron scattering was attributed to a possible magnetic monopole in the k space [16]. Interestingly, it is known too that the metallic phase of bulk SrRuO₃ is close to a transition between Fermi-liquid and non-Fermi-liquid states [12,17]. Another interesting point, more relevant to our work, is that SrRuO₃ thin films undergo MIT with decreasing thickness, whose origin is, to date, not well understood [18–20]. Thus, SrRuO₃ thin films can be a fertile ground for exploring some of the fundamental physics related to MIT and correlation physics with the orbital DOF.

In addition, first-principles local-density approximation + U calculations found that the Ru orbitals of SrRuO₃ thin films exhibit rather unusual quantum confinement effects (QCEs) when reducing thickness [20]. As the thickness of the film gets reduced, the proportion of RuO₆ octahedra exposed to the surface increases, which makes Ru t₂g orbitals like dₓz or dᵧz prefer to form one-dimensional (1D) strips. As a result of the geometrical restriction, the enhanced QCE was theoretically predicted to induce a distinctive change in the electronic structures for Ru 4d orbitals. To be more specific, the density...
of states (DOS) for a two-dimensional (2D) square lattice with a tight-binding model has a Van Hove singularity at the band center, whereas the DOS for a 1D line case has two separate singularities one at each edge of the band [21]. For example, the 2D-type Van Hove singularity of $d_{xy}$ DOS persists down to monolayer SrRuO$_3$. However, $d_{xz}$ and $d_{yz}$ orbitals in the monolayer limit do not have electron hopping along the $z$ axis due to spatial confinement, which induces the 1D-type singularities of their DOS. This orbital-selective QCE was theoretically suggested to be the main driving force of the intriguing paramagnetic phase found for very thin SrRuO$_3$ samples [20]. We also note that the QCE was used to explain the Mott insulating phase of LaNiO$_3$/LaAlO$_3$ thin films [22].

The purpose of this study was twofold. First, we investigated the proposed QCE by measuring the orbital-dependent charge transfer with the high-resolution resonant inelastic x-ray scattering (RIXS) studies as a function of thickness. Second, we studied how the charge dynamics changes across the MIT by examining low-energy excitations across the critical thickness. Furthermore, we tried to find a correlation between those two distinct characteristics of the SrRuO$_3$ thin film.

II. EXPERIMENTAL METHODS

Epitaxial SrRuO$_3$ thin films were deposited on TiO$_2$-terminated SrTiO$_3$ (001) substrates by pulsed-laser deposition at $670 \, ^\circ\text{C}$ with an oxygen pressure of 100 mTorr. Ultraviolet light coming from the excimer laser with a power of 2.1 J/cm$^2$ is applied to the target with a spot size of 2 mm$^2$. We optimized the growth conditions by measuring the resistivity of our samples and thereby monitoring the quality in addition to the usual inspection of the reflection high-energy electron diffraction (RHEED) patterns. The RHEED pattern in time variation implies good surface quality, which shows a clear change in the growth mode from a layer-by-layer growth to a step flow growth as a function of time. On the other hand, the high residual resistivity ratio of 8.2 obtained for the samples attests to the high-quality of our samples. In addition to the resistivity measurement, we verified the roughness of the samples in atomic force microscopy (AFM) images, another sign of the high quality of the surface in thin films (Fig. 1).

We carried out O $K$-edge RIXS at the ADRESS beamline of the Swiss Light Source [23,24]. RIXS is a powerful tool to study the charge dynamics related to orbital physics as one can tune the energy to a specific absorption resonance of the elements. The energy of the ruthenium $L$ edge ($\sim 3 \, \text{keV}$), however, just happens to be situated in between soft and hard x-ray regimes. For this technical reason, it is not easy to get enough photon flux and energy resolution at the Ru $L$ edge, which makes it experimentally challenging to do RIXS at the Ru $L$ edge. Instead, we carried out our experiment at the oxygen $K$ edge to study the charge dynamics of the Ru $4d$ orbitals while varying the thickness of thin-film samples.

The proper energy of the incident beam was chosen through x-ray absorption spectroscopy (XAS) with different thicknesses from 1 to 33 unit cells (u.c.), as shown in Fig. 2. The first peak at around $529.8 \, \text{eV}$ gets weaker as the thickness of the samples becomes reduced. From the fact that the relative intensity changes for different samples and also based on previous XAS studies in SrTiO$_3$ [25,26], we conclude that peaks above $530 \, \text{eV}$ are due to absorptions from the substrates. Therefore, we chose $529.8 \, \text{eV}$ as the incident energy for our RIXS experiment with high statistics, which is slightly lower than the pure O $K$ edge. The energy difference between the pure O $K$ edge and absorption from our sample comes from the hybridization energy. We verified the energy resolution is less than 70 meV by checking the full width at half maximum of the elastic line from diffuse scattering at a carbon tape reference.

All our samples were aligned with a grazing angle ($\theta = 15^\circ$) to increase the scattering cross section especially for ultrathin samples. The scattering angle from the incident beam to the detector was fixed to $130^\circ$, with a corresponding momentum transfer of $q_0 = 0.28[2\pi/a]$. We employed two different polarizations for our experiments: $\sigma$ polarization is parallel to the sample plane, and $\pi$ polarization is nearly perpendicular to the plane. Thus, the former is more sensitive to the $p_x$ ($p_y$) orbital, while the latter is more sensitive to the $p_z$ orbital due to the incident angle. All experiments were performed at 20 K.

Figure 3 shows RIXS results for all seven samples with different thicknesses. To explain the RIXS spectra, we divided the spectra into two groups depending on the characteristic

![FIG. 1. In situ RHEED pattern and topography image with AFM. The sample growth starts from 10 s. The growth mode change that occurs at 40 and 60 s shows the good surface quality of thin films. The insets show RHEED patterns before and after the sample growth. The AFM image indicates the clean surface and the apparent steps with a height of 4 Å, which is the size of 1 u.c. for SrRuO$_3$.](image)

![FIG. 2. XAS results as a function of the thickness of the sample. An energy of 529.8 eV was used for our RIXS experiments because other peaks mainly originate from the SrTiO$_3$ substrate.](image)
FIG. 3. (a) and (b) RIXS spectra at the O K edge with σ and π polarizations for SrRuO3 thin films. (a) and (b) show the overall features of RIXS spectra depending on the thickness of the samples and the polarization of the incident beam. As the thickness decreases, the peak on the low-energy side (dot line) becomes weaker, while the peak at 5 eV (dashed line) gets stronger for both polarizations. In addition to the 5 eV peak, the peak around 4.5 eV (dash-dotted line) also appears for the σ polarization. Note that this 4.5 eV peak becomes stronger below the 5 u.c. sample and shifts towards higher energy with decreasing thickness. (c) The whole spectrum for the 1 u.c. sample with σ polarization. Altogether, seven Gaussian fitting functions are needed to fit the spectra based on the CI and DFT calculations. Different types of peaks are marked by different letters in (c).

energy of the peaks and their apparent relevance to our two main questions: QCE and MIT. For example, on the high-energy side ranging from 2 to 10 eV there are several strong peaks, marked as C and D. These peaks are due to the charge transfer from O 2p to Ru 4d orbitals and so reflect the expected change in the Ru 4d orbitals. On the other hand, there are two relatively weaker peaks below 2 eV with a strong thickness dependence. These low-energy excitations can be interpreted as arising from d-d excitations or coherrent peaks connected to quasiparticle states that are closely related to the metallic phase of SrRuO3. In the remainder of this paper, we focus on the charge transfers to explain the QCE first and then move on to the low-energy part for the MIT.

III. RESULTS AND DISCUSSION

A. Configuration interaction calculation of cluster models

In order to explain the charge transfer peaks and d-d excitations in detail, we performed the configuration interaction (CI) calculations using two cluster models of RuO6 and Ru-O-Ru [see Fig. 4(a)] and found that each of the calculations with different clusters shows distinct features of SrRuO3. We note that our model calculation suits t2g orbitals of a more localized character. For instance, this calculation with the RuO6 cluster model has the advantage of explaining the charge transfer between O 2p and Ru d orbitals because the cluster consists of six oxygen atoms. On the other hand, the calculation with the Ru-O-Ru cluster gives a better description of intersite d-d excitations. These calculations can also reflect the QCE by the extra control of adjusting the amount of Ru d splitting. For example, we can set Ru d orbitals to split into εxy = 2/3Δt2g, εxz = εyz = −1/3Δt2g, εx2−y2 = 10Dq + 1/2Δεz, and εr−r′ = 10Dq + 1/2Δεz. It should be noted that we used an unusually large energy splitting between dxy and dzz (dyz) orbitals (Δt2g = 0.8 eV) from the results of the first-principles calculation in Ref. [20], which is the energy difference between the 2D-type singularity of dxy and the 1D-type singularity of dz2. We also take into account both the spin-orbit coupling λ and the Kanamori-type Coulomb interaction (U and JH) among d orbitals [27]. The energy levels of oxygen p orbitals in the valence band can depend on whether they are hybridized with Ru d orbitals or not [28–30]. For example, O p orbitals are assumed in our calculations to be noninteracting, and their energy levels are given as ep for nonbonding p orbitals and ep − Δp for bonding p orbitals. Here, ep is determined as ep = 4U − 7JH − Δ, where Δ is the charge transfer energy in the cubic symmetry defined as the energy difference between the lowest d5L5 and d3 states. The hopping integrals between p and d orbitals are parameterized by Vpdt for t2g orbitals and Vpds for eg orbitals according to the Slater-Koster theory [31]. We used the parameters shown in Table I in order to fit the experimental RIXS spectrum.

For more details on our calculations, let |Ψg⟩ and Eg be the ground state and its energy, respectively. In the dipole and fast collision approximation, the oxygen K-edge RIXS intensity
TABLE I. Physical parameters used for the cluster calculations (in eV).

<table>
<thead>
<tr>
<th>10Dq</th>
<th>D_{Kg}</th>
<th>D_{Kg}</th>
<th>λ</th>
<th>U</th>
<th>J_H</th>
<th>Δ</th>
<th>Δ_p</th>
<th>V_{pdt}</th>
<th>V_{pdt}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>0.8</td>
<td>0.4</td>
<td>0.1</td>
<td>2.0</td>
<td>0.3</td>
<td>3.3</td>
<td>1.6</td>
<td>−1.0</td>
<td>0.46</td>
</tr>
</tbody>
</table>

at zero momentum is given as

$$I \sim -\frac{1}{\pi} \text{Im} \langle \Psi_k | \hat{R}(\epsilon, \epsilon') \rangle \frac{1}{\omega - H + E_g + i\delta} \langle \Psi_k | \hat{R}(\epsilon, \epsilon') | \Psi_k \rangle.$$  \hspace{1cm} (1)

And \( \hat{R}(\epsilon, \epsilon') \) is the RIXS scattering operator, given as

$$\hat{R}(\epsilon, \epsilon') = \frac{1}{2} \sum_{\mu,\nu} (U_{\mu,\nu})_{\epsilon \epsilon'}^* c_{\mu \sigma}^\dagger c_{\nu \sigma},$$  \hspace{1cm} (2)

where \( c_{\mu \sigma}^\dagger \) is the creation operator of the oxygen \( p \) electron with the \( m = (x, y, z) \) orbital and \( \sigma \) spin at the \( i \)th site and \( \epsilon \) and \( \epsilon' \) are the polarizations of incident and outgoing x rays, respectively [27]. Here, \( \delta \) is the Lorentz broadening, and we set \( \delta = 0.2 \text{ eV} \) for our calculations.

In our calculations, \( p \)-orbital states can be expressed with a linear combination of bonding and nonbonding states as

$$c_{im\sigma} = \sum_{\alpha} (U_{\alpha,im})_{\epsilon \epsilon'}^* c_{\alpha \sigma}^\dagger \sum_{\mu} (U_{\mu,im})_{\epsilon \epsilon'} c_{\mu \sigma},$$  \hspace{1cm} (3)

where \( U_{\alpha,im} \) and \( U_{\mu,im} \) are the coefficients of the \( m \) orbital at the \( i \)th site for bonding and nonbonding states \( \alpha \) and \( \mu \), respectively. Because nonbonding \( p \) orbitals are fully occupied in the ground state, only the annihilation operation is allowed. We can then get the scattering operator associated with nonbonding orbitals as follows:

$$\hat{R}^N(\epsilon, \epsilon') = \sum_{\mu,\nu} R_{\mu,\nu}^N(\epsilon, \epsilon') c_{\mu \sigma}^\dagger c_{\nu \sigma},$$  \hspace{1cm} (4)

where \( R_{\mu,\nu}^N = \frac{1}{2} \sum_{im\mu} (U_{\mu,im})_{\epsilon \epsilon'} c_{\mu \sigma}^\dagger c_{\nu \sigma} \). The RIXS intensity attributed to nonbonding \( p \) orbitals is given as

$$I^N = -\frac{1}{\pi} \text{Im} \sum_{\alpha,\beta,\sigma} R_{\alpha,\beta}^N(\epsilon, \epsilon')^* R_{\mu,\nu}^N(\epsilon, \epsilon') \times \langle \Psi_g | c_{\alpha \sigma}^\dagger c_{\beta \sigma} \rangle \frac{1}{\omega - H + E_g + E_p + i\delta} \langle \Psi_g | c_{\nu \sigma} \rangle.$$  \hspace{1cm} (5)

The RIXS intensity attributed to the bonding \( p \) orbitals can then be calculated using the following relation:

$$I^B = -\frac{1}{\pi} \text{Im} \langle \Psi_g | \hat{R}^B(\epsilon, \epsilon') \rangle \frac{1}{\omega - H + E_g + i\delta} \langle \Psi_g | \hat{R}^B(\epsilon, \epsilon') | \Psi_g \rangle,$$  \hspace{1cm} (6)

where

$$\hat{R}^B(\epsilon, \epsilon') = \frac{1}{2} \sum_{\alpha,\beta,\sigma,im\mu} U_{\alpha,im} (U_{\beta,im})^* c_{\alpha \sigma}^\dagger c_{\beta \sigma}^\dagger c_{\mu \sigma}^\dagger c_{\nu \sigma}.$$  \hspace{1cm} (7)

In the case of the CI calculation of a Ru-O-Ru cluster, mainly explaining the low-energy excitations, we directly used Eqs. (1) and (2) instead of considering bonding and nonbonding states. In addition, we restricted the Hilbert space with the assumption that the oxygen atom between two Ru atoms has three possible states, \( p^3 \), \( p^2 \), and \( p^1 \) electron configurations. The result of this calculation is shown in Fig. 5.

The peaks in the O K-edge RIXS spectrum can also be categorized according to Ru 4d orbitals that participate in the RIXS process, as shown in Fig. 4. Electrons in the core oxygen levels are excited to vacant O 2p levels that are hybridized with Ru 4d orbitals as seen in the O K-edge RIXS, and the subsequent relaxation occurs from the occupied 2p states. We can, in principle, determine the origin of each peak by examining the energy of the emitted photons. For example, if the electrons are relaxed from the 2p level hybridized with 2g levels that are located right below the Fermi level, the process can be considered d-d excitations. In the case of charge transfers between the 2p and 4d orbitals, however, the relaxation starts from the 2p states not participating in the hybridization.

B. Quantum confinement effects

According to our CI calculations, the charge transfers correspond to peaks C and D as observed from 2 to 10 eV. Peak C, for instance, represents the charge transfer between nonbonding O 2p states and Ru \( t_{2g} \) orbitals, while peak D mainly originates from bonding O 2p states and Ru \( e_g \) orbitals. As shown in the top graphs of Fig. 3, both peaks C and D undergo a considerable change depending on the thickness of the sample and the polarization of the incident beam. The remarkable change in peak C is clearly seen around 4.4 eV. It is notable that this variation occurs only for the \( \sigma \) polarization. Meanwhile, an additional peak emerges around 5 eV that is most likely due to the charge transfer between O 2p and Ru \( e_g \) levels in both polarization channels, but the position of the peak is slightly different depending on the polarization (see Fig. 6).

The splitting of both peaks shown in Figs. 3 and 6 can be taken as evidence of the QCE, which is more pronounced for the thinner samples. The splitting of peaks around 4 and 5 eV reflects the energy splitting of Ru \( t_{2g} \) and \( e_g \), respectively. Of interest, the QCE in monolayer SrRuO$_3$ modifies the
electronic structure, which subsequently induces the separate orbital energy levels depending on the geometrical characteristics of each orbital. We comment that the energy difference between each singularity of the 2D-type band for $d_{xy}$ and the 1D-type band of $d_{xz}$ ($d_{yz}$) corresponds quite well to the amount of peak splitting in peak C [20]. It should also be noted that 0.8 eV of $t_{2g}$ energy splitting cannot be obtained in the cases of the usual Jahn-Teller distortion, which is typically about 0.1 eV for $t_{2g}$ of ruthenates [32].

A further interesting point is the polarization dependence of the peaks. In our explanation, the QCE pushes the energy levels of $d_{xz}$ ($d_{yz}$) or $d_{z^2}$ down, so that the energy of charge transfer related to those orbitals gets shifted towards lower energy. On the other hand, orbitals such as $d_{xy}$ and $d_{x^2-y^2}$ move in the opposite direction. In the case of the charge transfer between $d_{xz}$ ($d_{yz}$) and p orbitals, the same amount of energy shift compensates for the hopping integral $V_{pdr}$. Thus, the additional peak at 4.4 eV appears only with the orbitals parallel to the surface of the samples, and the one around 5 eV emerges at different energies depending on the polarization of the incident beam. Because each polarization excites different O p orbitals, we believe the "orbital-selective" characteristic of the QCE results in the observed polarization dependence.

C. Metal-insulator transition

While the peaks related to the charge transfer seem to support our scenario of the QCE process in SrRuO$_3$ films, the ones in the low-energy range produce the clearest evidence of MIT. For instance, with decreasing thickness peak A is suppressed rapidly, but peak B gets enhanced simultaneously below the thickness of 5 u.c. The opposite trends of peaks A and B can be easily understood in terms of MIT, as seen in the resistivity data shown in Fig. 7. We note that the critical thickness can depend on the growth conditions, according to our fabrication of several SrRuO$_3$ films used for this work.

According to our CI calculations, peak B can be ascribed to $d$-$d$ excitations between intersite $t_{2g}$ orbitals [Fig. 4(c)]. Electrons are excited to O 2$p$ levels that hybridize with Ru $t_{2g}$ levels in the valence band, and afterwards, relaxation occurs from the $t_{2g}$ levels in the conduction band. Although the process can, in principle, involve oxygen p levels, it is intrinsically the excitations between two separate $t_{2g}$ bands in the valence and conduction bands.

Meanwhile, the origin of peak A can be found by calculating the joint density of states (JDOS) from first-principles calculations with density functional theory. The JDOS represents the probability of allowed interband transitions including absorption or energy-loss functions [33,34]. We calculated the JDOS by considering the energy levels in the valence and conduction bands. In our calculation, the JDOS is given as

$$J(q) = \sum_k \delta[\epsilon_f(k) - \epsilon_i(k - q)].$$

According to our experimental geometry with a grazing angle, we choose an interband transition with fixed momentum transfer of $q_{||} = 0.28[2\pi/a]$ and compute the DOS of the energy difference between two levels, which represent the theoretical spectrum of electron-hole excitations. By comparing our calculation results with the experimental data, as shown in Fig. 7, the calculated JDOS for the electron-hole continuum is in good agreement with the lowest peak seen in bulk SrRuO$_3$. This means that peak A corresponds to itinerant quasiparticle excitations, while peak B corresponds to excitations between lower and upper Hubbard bands. In this sense, the spectral weight transfer from peak A to peak B is in good agreement with the MIT in SrRuO$_3$ thin films. We note that the transfer of spectral weight from peak A to peak B is also consistent with MIT, as seen in the resistivity data.

Another interesting point is the connection between the QCE and MIT, whose experimental evidence can be readily found in the very thin SrRuO$_3$ sample. In particular, a new peak is seen to be separated from the $d_{xy}$ level below 5 u.c. and moves towards higher energy, as shown in Fig. 6. This means...
that the QCE gets enhanced in thinner SrRuO$_3$ samples. With the QCE splitting the Ru 4$d$ bands, the MIT in SrRuO$_3$ resembles that of Ca$_2$RuO$_4$, which is a classic example of an orbital-selective Mott insulator [35]. For our thinnest sample of 1 u.c. SrRuO$_3$, the QCE seems to split the otherwise selective QCE in ultrathin SrRuO$_3$ films. We also found that transfer peak splitting in the RIXS spectra suggests the orbital-cal calculation and the experimental observation of charge-different from the bulk sample. Therefore, we can maintain that a new way of realizing a Mott-type insulating phase is found in the ultrathin SrRuO$_3$ sample with thickness being a control parameter, which is different from the bulk sample.

IV. CONCLUSION

To conclude, the good agreement between the theoretical calculation and the experimental observation of charge-transfer peak splitting in the RIXS spectra suggests the orbital-selective QCE in ultrathin SrRuO$_3$ films. We also found that the suppression of the low-energy excitations arises from the electron-hole continuum across the metal-insulator transition. Finally, our studies provide clear experimental evidence that the QCE leads to a Mott insulating phase in ultrathin SrRuO$_3$.

ACKNOWLEDGMENTS

We would like to acknowledge D. Khomskii and B. Kim for helpful discussions. The work at IBS CCES is supported by the Institute of Basic Science (IBS) in Korea (Grants No. IBS-R009-G1, No. IBS-R009-G2, and No. IBS-R009-D1). The work at the Paul Scherrer Institut is supported by the Swiss National Science Foundation through NCCR MARVEL and the Sinergia network Mott Physics Beyond the Heisenberg Model (MPBH). We also thank the Korea Institute for Advanced Study for providing computing resources (KIAS Center for Advanced Computation Linux Cluster System) for this work.