Orbital-Dependent Band Narrowing Revealed in an Extremely Correlated Hund's Metal Emerging on the Topmost Layer of Sr₂RuO₄

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We use a surface-selective angle-resolved photoemission spectroscopy and unveil the electronic nature on the topmost layer of Sr_2RuO_4 crystal, consisting of slightly rotated RuO_6 octahedrons. The γ band derived from the $4d_{xy}$ orbital is found to be about three times narrower than that for the bulk. This strongly contrasts with a subtle variation seen in the α and β bands derived from the one-dimensional $4d_{xz/yz}$. This anomaly is reproduced by the dynamical mean-field theory calculations, introducing not only the onsite Hubbard interaction but also the significant Hund's coupling. We detect a coherence-to-incoherence crossover theoretically predicted for Hund's metals, which has been recognized only recently. The crossover temperature in the surface is about half that of the bulk, indicating that the naturally generated monolayer of reconstructed Sr₂RuO₄ is extremely correlated and well isolated from the underlying crystal.

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The transition metal oxides isostructural to La₂CuO₄ with 3d orbitals have attracted much interest owing to their intriguing electronic properties. The ruthenate $Ca_{2-r}Sr_{r}RuO_{4}$ is a 4*d* analogue of cuprates, offering diverse states ranging from a superconductor to a Mott insulator [1–4]. It is tuned by a rotation, tilt, and/or shrinkage of the RuO₆ octahedrons induced by Ca substitution [5,6], while the electronic origin has not been fully understood [7,8]. The metallic ruthenates are categorized as "Hund's metal," in which the correlated state is induced by Hund's coupling under a moderate interaction U [9–15]. Notably, the crucial role of Hund's coupling on electronic correlations has been recognized only recently [16]. Much attention has been also given to the correlated insulator Sr_2IrO_4 , a 5d analogue of cuprates [17–20], on the prospect that a carrier doping to it might give rise to superconductivity [21,22]. Significantly, a Fermi arc similar to that for underdoped cuprates was found in the electron-doped surface [23,24]. The analogy to cuprates is, however, still debated; a small electron pocket rather than the arc might be formed, associated with the IrO_6 rotation [25]. Since the octahedral rotation is commonly observed in various perovskite oxides, its effect on the electronic properties should be identified.

The ruthenate Sr₂RuO₄ has a unique surface layer of RuO₆ octahedrons slightly rotated by $\sim 8^{\circ}$ [6,26,27], whereas it has no distortion in the bulk crystal. The Ca doping to generate a RuO₆ rotation in bulk causes weak and broad spectra in angle-resolved photoemission spectroscopy (ARPES), possibly due to introduced disorders [28–30]. In contrast, the reconstructed Sr₂RuO₄ surface is free from such a difficulty and thus provides an excellent platform to investigate the effect of octahedral rotation on the electronic properties [8]. This compound has more of an advantage than Sr_2RhO_4 with an inherent RhO₆ rotation in the bulk [31,32], in that the effect of octahedral rotation can be distinguished through a direct comparison between the surface and bulk states in the same compound. The ruthenate is also fascinating, being a candidate for the topological superconductor [4]; the theoretically predicted edge state [33-39] has been detected [40]. This novel state should stay on the boundary between the crystal surface and the underlying bulk, thus clarifying the interrelation between the two is desired.

The electronic structure of the Sr₂RuO₄ surface has been observed separately from that of the bulk by ARPES [41]. A hallmark of the surface, except for folded-back bands, is the holelike Fermi surface (FS) of the γ band, which contrasts with the electronlike FS in the bulk. The mass enhancement for the surface is estimated to be even larger than that of the bulk, which is attributed to the reduced d-d hopping caused by the RuO₆ rotation [27,41,42]. Nevertheless, the investigation of the surface has been limited so far, suffering from a contamination by the bulk signature in ARPES. A gradual progression of crystal distortion onto the crystal surface over the multiple RuO₆ layers is reported to cause an even more complex situation, generating several splitting bands [27]. These prevent one from uncovering the full scope of the electronic properties in the topmost layer of this compound.



FIG. 1. (a1),(a2) Fermi surface of Sr₂RuO₄ obtained by DFT calculations without and with a RuO₆ rotation by 8°, respectively. The $4d_{xy}$ and $4d_{xz/yz}$ bands are indicated by red and blue curves, respectively. (b) Fermi surface mapping by ARPES. (c) Spectral intensity for the bulk estimated from the MDC peaks in (f). We have normalized the MDCs for different photon energies to the background intensities around $k_x/\pi = 0.8$. (d1),(d2) Magnified image around the zone edge [light blue rectangle in (b)]. Green ellipses mark the bulk FS. (e1),(e2) Dispersions across the zone edge [magenta arrows in (d1) and (d2)], measured at high and low photon energies, respectively. The color scale is maximized to the strongest intensity in each image. (f) MDCs at E_F of (e1) and (e2). Blue arrows indicate Fermi crossings of the bulk band.

In this Letter, we thereby use a surface-selective technique in ARPES to unveil the electronic nature in the topmost layer of the Sr₂RuO₄ crystal. We find that this material has a threshold photon energy ($h\nu \sim 13 \text{ eV}$), below which only the topmost layer is selectively detected [Fig. 1(c)]. Accordingly, we use a laser ARPES ($h\nu = 7 \text{ eV}$) with a high energy resolution and reveal an extremely correlated Hund's metal state on the surface, which causes an orbital-selective band narrowing.

Single crystals of Sr₂RuO₄ were grown by the floatingzone technique. ARPES measurements were performed for the (001) cleaving surface with a Scienta R4000 analyzer at beam line 9A of the Hiroshima Synchrotron Radiation Center and using the same analyzer equipped with an ultraviolet laser ($h\nu = 7$ eV) at The Institute for Solid State Physics (ISSP), The University of Tokyo. The energy resolution was set to \sim 9 and \sim 3 meV, and the lowest measured temperatures were 8 and 5 K, for the synchrotron and lab experiments, respectively.

In the previous ARPES studies of Sr₂RuO₄, focusing on the bulk state [41,43–47], the sample surface was intentionally aged to eliminate the signature from the topmost layer [48]. In contrast, the extraction only of the surface-derived spectra is not straightforward [27,42]. It becomes possible, however, by utilizing the effect of the photoemission cross section. Figure 1(b) maps the FS of Sr_2RuO_4 with 28 eV photons. The FS sheets of the α , β , and γ bands of both the bulk $(\alpha^b, \beta^b, \text{and } \gamma^b)$ and surface $(\alpha^s, \beta^s, \text{and } \gamma^s)$ are observed [41]; the surface FS is complicated by the folding back of bands, and the γ^s FS becomes holelike centered at (π, π) as confirmed in Fig. 1(d1) with a magnified image of Fig. 1(b)around $(\pi, 0)$ (a dashed light blue square). The FS topology variation is due to a change in the energy of van Hove singularity, which is reproduced by density functional theory (DFT) calculations [Figs. 1(a1) and 1(a2)].

We find that the ARPES data are drastically changed at lower photon energies. The image for $h\nu = 10$ eV plotted in Fig. 1(d2) shows only the holelike FS in the γ band for the surface. In Figs. 1(e1) and 1(e2), we examine the photon energy dependence of the observed band dispersions along a momentum cut close to $(\pi, 0)$ [a magenta arrow in Figs. 1(d1) and $1(d_2)$]. The Fermi crossings for the bulk state are visible only at high photon energies [Fig. 1(e1)]. This is more clearly demonstrated in Fig. 1(f), where the momentum distribution curves (MDCs) at E_F are extracted. We find that the two peaks (blue arrows) signifying the Fermi crossings of the bulk band abruptly disappear below 13 eV. This should be, therefore, the threshold photon energy, below which the photoexcitation of bulk electrons is not allowed due to a matrix element effect; it is nontrivial that the bulk signature is absent at such low photon energies since the photoelectrons, if excited, should have a long escape depth according to the "universal curve." Previously, the γ FS in the second laver of crystal was found to have an electronlike shape similar to that of the underlying bulk system [27]. Thus, our data at the low photon energies most likely detect the topmost surface layer.

We use thereby a 7-eV laser ARPES with an excellent energy resolution to uncover the electronic nature of the Sr_2RuO_4 surface. In Fig. 2(c), the FS mapping is plotted, and indeed only the surface signature is detected as discussed above with synchrotron data. While the data only for the *s* polarization of light are presented here, we have confirmed that the bulk band is not detected with any polarization. Figures 2(a), 2(b), and 2(d) extract the band dispersions along high-symmetry lines [dashed arrows in Fig. 2(c) colored light blue, green, and red, respectively]. The mass enhancement compared to the DFT calculation (m^*/m_{DFT}) is seen in all the bands as expected for correlated states. The magnitude of m^*/m_{DFT} , simply



FIG. 2. Band structure of the topmost layer, selectively observed by a 7-eV laser ARPES. Dispersions along (a) the $(0, \pi)$ - (π, π) cut and (b),(d) the (0,0)- $(\pi, 0)$ cut [dashed, colored arrows in (c)]. Panel (b) plots a narrow region of (d) with a different color scale. (e) Energy contour images around $\overline{\Gamma}$ [orange arrows in (b) and yellow square in (c)]. (f) ARPES images and determined dispersions along typical momentum cuts [magenta and blue arrows in (c)]. (g),(h) The γ^s and β^s bands along (0,0)- $(\pi, 0)$, respectively, determined from spectral peaks in (d). The gray curves show the dispersions for the bulk γ^b and β^b [43]. The bulk bands narrowed by a factor of 2.7 and 1.3, respectively, are superimposed. (i) The off-diagonal ARPES images for γ^s very close to E_F [orange arrows in (c)]. The dispersions determined by ARPES (red circles) and the DFT results (solid curves) are compared.

obtained as the variation of Fermi velocity ($v_F^{\text{RPES}}/v_F^{\text{DFT}}$), is estimated to be 5.9, 4.2, and 8.6 for α^s , β^s , and γ^s , respectively, in Fig. 2(f), where dispersions along solid arrows in Fig. 2(c) are exhibited. The similar value of $v_F^{\text{ARPES}}/v_F^{\text{DFT}} \sim 9$ is consistently obtained for the γ^s band in the off-diagonal directions [orange arrows in Fig. 2(c)] as examined in Fig. 2(i). The mass enhancement is comparable to or even larger than that in strain-applied thin films epitaxially grown on the deliberately lattice mismatched substrates [49]. This points to a rather huge impact of structural reconstruction in the naturally generated perovskite monolayer on the crystal. Furthermore, we compare the whole band dispersion in our data with the results reported for the bulk bands of β^b and γ^b in Figs. 2(g)



FIG. 3. (a) The DFT + DMFT calculations in several conditions $(U, J, \text{ and } \text{RuO}_6 \text{ rotation by 8}^\circ)$. The $4d_{xy}$ and $4d_{xz/yz}$ bands along (0,0)- $(\pi, 0)$ at $k_z = 0$ are separately plotted in the top and bottom panels, respectively. The DFT dispersions are overlapped on each image. (b),(c) Energy distribution curves (EDCs) at (0,0) extracted for $4d_{xy}$ and $4d_{xz/yz}$, respectively. Magenta arrows in (a) and (b) indicate satellite peaks. (d1),(d2) Temperature dependence of the calculated mass enhancement (m^*/m_{DFT}) without and with the rotation.

and 2(h), respectively. While the β band shrinks only slightly (~1.3 times), the γ band on the surface is much narrower than that for the bulk by a factor of ~3, meaning that the band narrowing caused by the RuO₆ rotation is significantly orbital dependent.

We find an electron pocket around $\overline{\Gamma}$ [Fig. 2(e)], which is not formed in the bulk. Its emergence is attributed to the $t_{2g} - e_g$ hybridization occurring with the octahedral rotation [8]. The signature for it seems to become more pronounced at higher binding energies. It should be due to the matrix element effect and compatible with the fact that the previous studies with higher photon energies could not detect the same pocket as presented here. The bottom of the pocket (~200 meV) is located in more than two times deeper binding energy than that (~90 meV) for the DFT calculations with a RuO₆ rotation by $\sim 8^{\circ}$ determined by diffraction measurements [6,27]. This discrepancy is rather surprising, considering that a bandwidth narrowing is instead expected for the correlated system. The $t_{2q} - e_q$ hybridization might be evolved more significantly than expected by the octahedral rotation. The correlation effect could also severely deform the Fermi surface as observed in cobalt oxides (Hund's metals with 3d orbitals) [50–52].

For a better understanding of the ARPES data, we have performed the DFT + DMFT calculations (where DMFT

stands for dynamical mean-field theory) for Sr₂RuO₄ in several conditions with on-site Hubbard interaction U and Hund's coupling J. The obtained results along (0,0)- $(\pi, 0)$ for $4d_{xy}$ - and $4d_{xz/yz}$ -derived dispersions (or γ and β bands) are separately plotted in the top and the bottom of Fig. 3(a), respectively. The band renormalization is enhanced by not only U but also J as previously reported for three-band Hund's metals [9,10]. Our calculations successfully reproduce the features reported for the bulk bands [44]: a narrowing of the $4d_{xz/yz}$ band (β band) to about half of DFT dispersions and a kink anomaly detected at a high energy around -1 eV in the $4d_{xy}$ band (γ band). A fascinating new finding here is the remarkable satellite peaks, emerging at ~ -1 eV around $\overline{\Gamma}$ [magenta arrows in the top-right panels of Fig. 3(a) with increasing U and/or J. These eventually become comparable to the main peaks at ~ -3.5 eV by introducing the RuO₆ rotation, as demonstrated in Fig. 3(b) by plotting the spectra at (0, 0) of panels in Fig. 3(a). The extremely shallow bottom of the γ band seen at ~ -1.2 eV in our ARPES data [magenta arrow in Fig. 2(d)] should correspond to the satellite peak. We observe the spectral peak around -3 eV [53] relevant to the bottom of the DFT band, which validates this conclusion. Note that the previously reported data for Sr₂RuO₄ measured at relatively high photon energies above 15 eV have never shown the similar structure around 1 eV observed here at low photon energies. The matrix element effect, therefore, should be a crucial factor to properly detect it.

Intriguingly, the similar band narrowing by a factor of ~ 3 from the DFT calculations (or development of satellite peaks) is also observed in cuprates, while the origin for it is still highly debated [69–77]. The similarity between the two distinct compounds with a single 3*d* band and multiple 4*d* bands would pave the way for solving the controversial issue.

The mass enhancement of conduction electrons in the bulk Sr_2RuO_4 is estimated to be 3–5 [78] by de Haas-van Alphen measurements and specific heat, and the comparable band renormalization near E_F is also obtained by ARPES [43]. As previously reported [11], such a significant renormalization is reproduced by calculation in a realistic combination of (U, J) = (2.3, 0.4) [eV]. In the same condition, we estimate the temperature dependence of the mass enhancement (m^*/m_{DFT}) in Fig. 3(d1) and 3(d2) without and with the octahedral rotation, respectively. A remarkable change can be seen with the rotation introduced as a model for the surface: while it is similar in both cases at high temperatures (above 300 K), the magnitude of $m^*/m_{\rm DFT}$ increases on cooling more sharply for the structure with rotation, and it reaches ~ 9 and ~ 5 for $4d_{xy}$ and $4d_{xz/yz}$, respectively, at the lowest temperature in our calculation [58 K(=5 meV)]. Importantly, this is in a good agreement with the ARPES results for the surface. For a further comparison, however, more detailed investigation would be necessary, since the electronic feature very close to E_F could be affected by couplings with bosonic modes [5,79–83] and the crystal-field effect [84].



FIG. 4. Coherence-incoherence crossover with temperature. (a1) Temperature evolution of the spectral peak intensity at a k_F of the β^s band (blue circle in the inset). A dotted green circle indicates the crossover temperature, above which the quasiparticle peak becomes negligible. (a2),(a3) EDCs and those divided by the Fermi function at measured temperatures. In the top and bottom panels, the data are displayed with and without an offset, respectively. (b1)–(b3) The data for the γ^s band obtained in the same way as in (a1)–(a3).

The strongly correlated state should be sensitive to the thermal excitation at high temperatures. It is proposed that the electronic system of Sr_2RuO_4 is correlated so strongly that the long-lived quasiparticles disappear at relatively low temperatures [9–11]. The temperature at which the incoherent state emerges has been calculated to be ~350 K for the bulk [11], and an even lower temperature is obtained by ARPES (~200 K) [45].

In Figs. 4(a2) and 4(b2), we examine the temperature evolution of spectra at k_F points of the β^s and γ^s bands, respectively. To eliminate the Fermi cutoff, the original curves are divided by Fermi function at each measured temperature in Figs. 4(a3) and 4(b3). We find that the remarkably sharp quasiparticle peaks (~5 meV width) are drastically suppressed at elevated temperatures and almost completely disappear around ~100 K. This is examined in Figs. 4(a1) and 4(b1) by plotting the peak intensity for various temperatures. Note that the temperature cycle of measurements was conducted to make sure that it is an intrinsic behavior, not because of the surface aging. The most recent theoretical study found that the depletion of quasiparticle weight and its translation toward higher binding energies upon heating is one of anomalies for

Hund physics, not expected for Mott physics [9,12]. The crossover temperature in our data is about two times less than that reported for the bulk [45]; the quasiparticle peaks in the momentum regions studied here remain significant even at 180 K in the bulk band. This verifies that the extremely correlated nature beyond the bulk state is realized on the surface and moreover that the naturally generated monolayer of reconstructed Sr_2RuO_4 is well isolated from the underlying crystal. The result is compatible with the previous reports that the surface of $Ca_{2-x}Sr_xRuO_4$ has a phase diagram independent of that in the bulk [6,85].

The temperature evolution with a similar crossover temperature between the β and γ bands [Figs. 4(a1) and 4(b1)] seems incompatible with the observation of significantly orbital-dependent mass enhancement. Interestingly, it is in contrast to the case of the iron-based superconductors (Hund's metals with 3*d* orbitals) having an orbital variation in the crossover temperature [86,87]. This signifies that the interorbital interaction is significantly facilitated near E_F at elevated temperatures in Sr₂RuO₄. Recently, the focus has been shifted to properties at higher temperatures and energies in this material [14,15,88]. Further theoretical studies are required to clarify the scattering mechanism at finite temperatures observed in our ARPES data.

In conclusion, the electronic feature on the topmost layer of the Sr_2RuO_4 crystal, including the whole band structure, is unveiled for the first time by means of the surface-selective technique in ARPES using low energy photons. A highresolution ARPES with a 7-eV laser reveals an emergence of a Hund's metal state on the reconstructed surface and orbitaldependent band narrowing induced by the extremely correlated nature. The $4d_{xy}$ -derived band in Sr_2RuO_4 is found to be narrowed by a factor of ~3 from the DFT dispersion, similarly to the case for high- T_c cuprates, which is highly debated. We detect a coherent-incoherent crossover with temperature as expected for Hund metals. The temperature scale on the surface is clearly distinct from that of bulk system, indicating that the naturally generated monolayer of Sr_2RuO_4 is well isolated from the underlying crystal.

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