

Disentangling bulk and surface electronic structure using targeted cleave planes in RuO₂

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Rutile RuO₂ has attracted significant interest due to its putative unconventional electronic and magnetic properties and its proximity to superconductivity. However, the measurement and interpretation of its electronic structure have been complicated by a strongly three-dimensional crystal structure. Here, we demonstrate how the preparation of targeted (110) and (100) surfaces via focused-ion-beam-engineered cleaving allows the acquisition of high-quality measurements of the electronic structure using angle-resolved photoemission spectroscopy. Our results demonstrate that angle-resolved photoemission spectroscopy spectra of RuO₂ are, in fact, largely dominated by signatures of distinct surface electronic states. From comparison with density functional theory, we resolve a surface termination-dependent variation of these, and disentangle them from highly-three-dimensional bulk states and surface resonances. Moreover, we find a marked role of the substantial spin-orbit coupling of the Ru 4*d* orbitals in the surface region, where a breaking of spatial inversion symmetry leads to significant Rashba-type spin splittings of the surface bands.

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I. INTRODUCTION

Ruthenium dioxide is a rutile-structured oxide metal, well-known for its excellent catalytic activity [1]. Recently, it has also come to prominence for its electronic and potential magnetic properties: it hosts superconductivity under strain [2,3] while Dirac nodal lines are found in its electronic structure as a result of its nonsymmorphic crystal structure [4]. The presence of such symmetries has also led to suggestions that RuO₂ could host an altermagnetic phase [5]. Early neutron and x-ray diffraction studies found the required antiparallel magnetic ordering [6,7]. These, however, were contradicted by more recent studies, in which magnetic signatures are absent in bulk crystals [8,9]. Other probes sensitive to magnetic order, such as muon spin rotation (μSR), have also failed to find robust signatures of magnetism [8,10], although some μSR studies on thin films have found indications of possible surface magnetism [11]. Transport experiments in thin films have found signatures of spin-charge conversion and an anomalous Hall effect, again raising suggestions of altermagnetism [12–14]. Similar studies on bulk crystals, however, have found no such signatures and their results are consistent with a paramagnetic ground state [15,16]. Direct probes of the electronic

structure, including quantum oscillations and angle-resolved photoemission spectroscopy (ARPES), generally have also found good agreement with the nonmagnetic band structure for bulk crystals, although some ARPES studies have noted discrepancies between the measured and theoretically calculated band structure, something we return to below [17–21].

Overall, therefore, the bulk material seems to be unambiguously nonmagnetic. However, strain and disorder effects have been proposed to stabilize the altermagnetic phase in thin films [22,23], and the material has been theoretically predicted to host surface magnetism [24,25]. Indeed, given the three-dimensional crystal structure, a distinct surface magnetic and electronic environment can naturally be expected. Quasi-one-dimensional “flat-band” surface states have already been observed [19], which have been proposed to support RuO₂’s catalytic activity [26]. Such a distinct surface environment may also provide a natural route to understand reported spin-polarized signatures in ARPES measurements [20].

Together, this motivates a re-examination of the bulk vs surface electronic structure in RuO₂. ARPES should be an ideal probe for this [19–21,27]. Such studies are, however, significantly complicated by the strongly three-dimensional crystal structure. As a result, the material lacks a natural cleaving plane, which hinders the preparation of the required flat and clean surfaces by conventional methods. Second, significant *k_z*-broadening can be expected, which can add substantial challenges for identifying the relevant bulk states, especially when paired with limited effective angular resolution stemming from rough cleave surfaces. Indeed, although quantum oscillation measurements show good agreement with calculations of the bulk electronic structure from density functional theory [17,18,28], ARPES studies have proposed bulk bands

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which, in some cases, require significant energetic shifts to match those in the calculations [19,20,27].

To investigate the origin of these apparent discrepancies and to overcome the challenges associated with the three-dimensional crystal structure, here we utilize a fabrication method [29] based on focused ion beam (FIB) structuring to stimulate cleaving along desired crystallographic planes. This allows us to obtain high-quality surfaces oriented along the (110) and (100) directions, making high-resolution ARPES experiments possible. From these experiments and supporting bulk and surface electronic structure calculations, we identify a rich spectrum of bulk and surface bands, the latter of which exhibit a strong dependence on surface stoichiometry and structural relaxations. We further identify a marked influence of spin-orbit coupling on the surface electronic states, giving rise to significant spin splittings in the broken-inversion-symmetry environment that the surface hosts.

II. METHODS

A. Sample preparation

Single crystals of RuO_2 were grown by chemical vapor transport, using TeCl_4 as the transport agent [30]. The amount of TeCl_4 was calculated to yield a final pressure in the ampoule of approximately 1 bar at the target temperature. A powder of RuO_2 (Alfa Aesar, 99.9%, anhydrous) was mixed thoroughly with TeCl_4 (Fisher Scientific, 99.9%) under inert atmosphere. The final mixture was loaded into a quartz ampoule, evacuated, and sealed. The ampoule was introduced into a horizontal two-zone furnace and heated for 10 days to 950 °C at the source and 820 °C at the sink. Finally, millimeter-sized, prism-shaped crystals were collected on the sink side of the ampoule.

From these, crystals with large (110) or (100) faces were selected for measurements. The compound, however, lacks a good cleaving plane. We therefore performed microstructuring to improve the quality and uniformity of the cleaved surface, following the method pioneered by Hunter *et al.* [29]. The selected crystals were cut into pillars of $\approx 300 \times 300 \times 600 \mu\text{m}^3$ with their long axis aligned along a desired cleaving direction, here the [110] or [100] direction. FIB milling was then used to create a narrow constriction at the base of the sample. First, two triangular patterns were milled at high ion currents (0.2–0.5 μA) and an acceleration voltage of 30 kV, reducing the width to $\approx 100 \mu\text{m}$. The constriction was then narrowed to 50 μm with two rectangular patterns at a lower ion current (60 nA). Afterwards, the pillar was rotated by 90° to also reduce the cross section from the orthogonal side. Again, first rough triangular patterns were cut at high ion currents (0.2–0.5 μA) to reduce the width to $\approx 100 \mu\text{m}$. Afterwards, triangular patterns were milled, first at 15 nA to decrease the width to $\approx 80 \mu\text{m}$ and then at 4 nA to decrease the width to $\approx 60 \mu\text{m}$. This made it possible to use smaller ion currents to get sharper cuts, while having a reasonable process time. Lastly, a thin line was milled across the neck of the constriction at a current of 0.79 nA to define the final cleaving plane. The linecut was extended slightly beyond the neck, to ensure that its edges were also patterned and the constriction was fully defined from two perpendicular directions. For the (110)

orientation, a Xe-plasma FIB was used for all cuts. For the less favorable (100) direction, a Ga FIB was used for the final steps at low currents, as this was found to give smoother cuts.

The FIB-bed constriction acts as a “strain lens” that focuses the stress induced during cleaving into one weak point. The upper half of the sample then acts as the “top post” of a conventional cleaving setup, so that when we apply force to it, the sample cleaves along the defined plane with a smooth and flat surface. To controllably cleave the small and fragile samples, we used a custom sample plate with a built-in cleaving mechanism (Supplemental Fig. 1 [31]). The sample plate consists of a flag-style plate, to which a cylinder with a small arm is attached. The arm sits at a fixed height of 0.5 mm above the sample holder and can be rotated with a hex key wobble stick that slots in the cylinder, to cleave the sample in ultrahigh vacuum.

B. Angle-resolved photoemission spectroscopy

Micro-ARPES measurements were performed at the Bloch A-branch end station of the MAX IV synchrotron with a beam spot size of $\approx 10 \mu\text{m}$. The measurements were performed using photon energies between 20 and 180 eV, with linear horizontal and vertical light polarizations as indicated in the figure captions. All measurements were performed at base temperature (18 K). ARPES data analysis was performed using the PEAKS package [32].

C. Electronic structure calculations

Density functional theory (DFT) calculations were performed with the QUANTUM ESPRESSO package [33,34]. Bulk band structure calculations of the nonmagnetic ground state were performed using fully relativistic optimized norm-conserving Vanderbilt pseudopotentials with a Perdew-Burke-Ernzerhof (PBE)-type exchange potential [35], and a plane-wave cutoff energy of 84 Ry. Spin-orbit coupling was included. The unit cell parameters and atomic positions were taken from Ref. [36] and the cell was allowed to fully relax to a total force of 2 meV/Å before the band structure calculations. A $10 \times 10 \times 14$ k -mesh was used in the self-consistent field calculations. We used the same parameters to model the proposed altermagnetic phase, but included an additional Hubbard U factor with $U = 2.0$ eV, as has been found to stabilize the altermagnetic phase in previous studies [22,37].

We obtained bulk-projected band structures by performing bulk band structure calculations at 81 k planes along the out-of-plane momentum direction ($k_{[110]}$). The final spectra were obtained by summing the band structures along these cuts with a small energy broadening (40 meV) and weighed with a Lorentzian factor to simulate the $k_{\perp}$ plane probed and corresponding $k_{\perp}$ broadening given a photon energy (50, 68, or 87 eV) and a mean free path (here taken to be 2.5 Å).

For calculations of the (110)- and (100)-surface electronic structures, we performed DFT calculations on symmetric 12- and 10-layer slabs with a stoichiometric termination on both sides. Scalar relativistic pseudopotentials were used with a PBE exchange potential [38] and a plane-wave cutoff energy of 75 Ry on a k -grid of $7 \times 7 \times 1$. Spin-orbit coupling was not included. All atomic positions in the slab were allowed

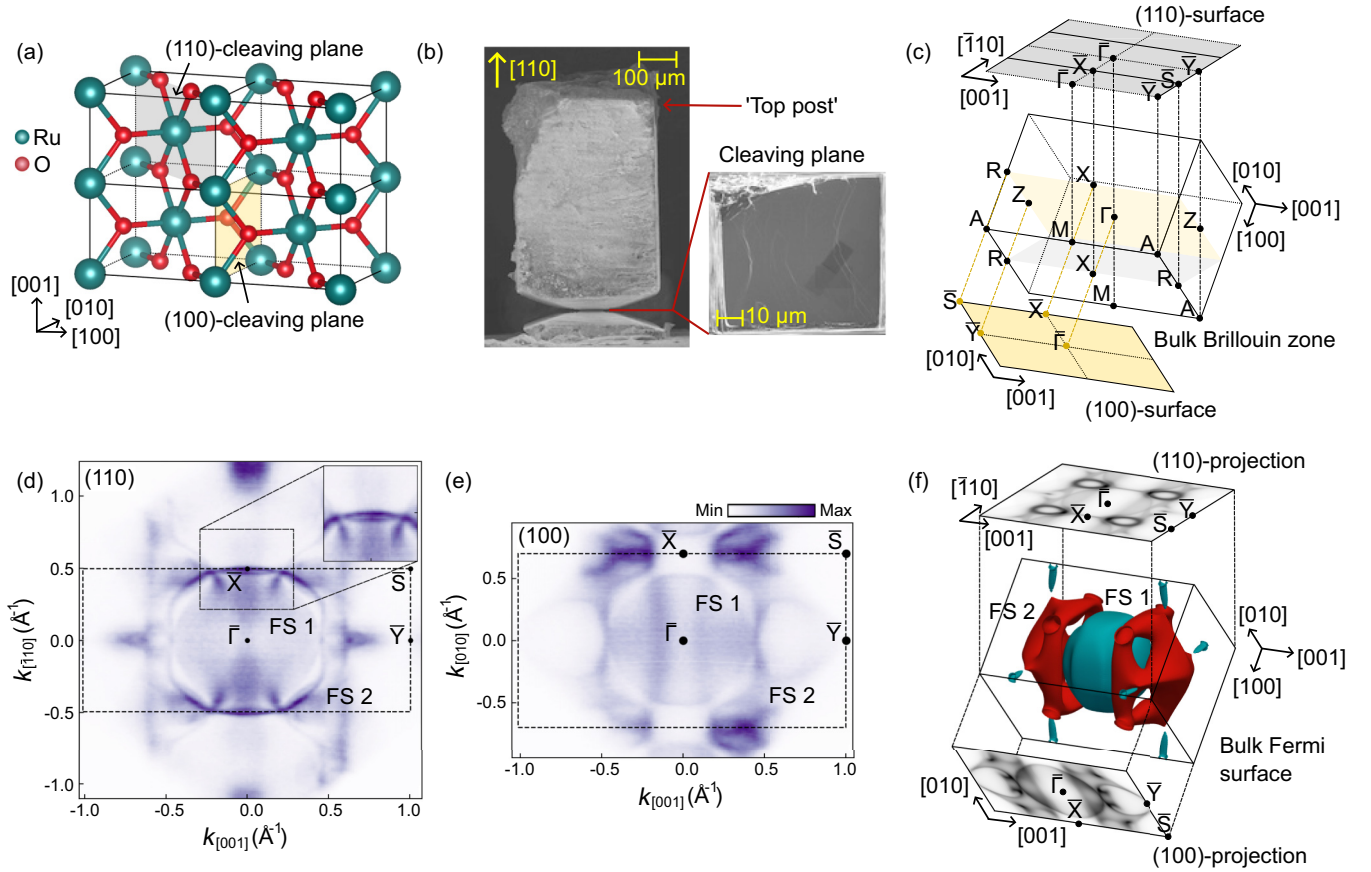


FIG. 1. Fermi surfaces from FIB-designed cleaving planes in ruthenium dioxide. (a) Crystal structure of RuO₂. The (110) and (100) cleaving planes are indicated in gray and yellow. (b) Scanning electron micrograph of a FIB-structured sample, which allows for designed cleaving planes along the (110) (as shown) and (100) surfaces. The cleaved surface is shown inset. (c) Schematic of the bulk Brillouin zone and its projections onto the (110) and (100) surfaces. (d), (e) ARPES Fermi surfaces of the (110) and (100) surfaces, measured at $h\nu = 68$ eV using linear vertical light polarization for the (110) surface and linear horizontal light polarization for the (100) surface. (f) The calculated bulk Fermi surface and its projections onto the (110) and (100) surface Brillouin zones to simulate the expected intensity in the ARPES measurements shown in panels (d) and (e). The gray and yellow highlighted planes in the bulk zone indicate the XR and Γ XRZ planes, respectively.

to relax to 10 meV/Å before band structure calculations. We considered the top/bottom two layers of the slab as the surface layers for the surface projections.

Additionally, we used WANNIER90 to obtain a tight binding model based on the maximally localized Wannier functions [39]. We included the Ru 4d and O 2p orbitals. This tight binding model was used for calculations of the bulk Fermi surface and for surface Green's function calculations. The latter were performed within the WANNIERTOOLS package [40]. Bulk projected Fermi surfaces were obtained by taking 100 slices through this calculated bulk Fermi surface along the out-of-plane direction ($k_{[110]}$ or $k_{[100]}$) and summing these cuts with a small broadening (40 meV) and Lorentzian factor to simulate the plane that is probed at 68 eV, assuming a mean free path of 2.5 Å.

III. RESULTS AND DISCUSSION

A. FIB-designed cleaving planes in ruthenium dioxide

Ruthenium dioxide crystallizes in the tetragonal rutile crystal structure [Fig. 1(a)], comprised of edge-sharing RuO₆ octahedra. This renders the structure highly

three-dimensional, lacking a good natural cleaving plane. As a result, when conventional top-post cleaving methods are used to prepare clean surfaces for ARPES, they typically result in small exposed facets oriented along the (110) direction, while high-quality surfaces of other orientations are extremely difficult to obtain. As described in Sec. II A, we therefore use FIB structuring to stimulate cleaving along a desired crystalline direction. An example of this is shown in Fig. 1(b). Using this approach, we were able to obtain facets of at least $20 \times 20 \mu\text{m}^2$ for the (110) orientation [see inset in Fig. 1(b)] and $10 \times 10 \mu\text{m}^2$ for the less favorable (100) orientation. Such surfaces are well-suited for ARPES experiments using small ($\lesssim 10 \mu\text{m}$) photon beams (see Sec. II).

B. Fermi surfaces and bulk nodal lines of RuO₂(110) and RuO₂(100)

We show the measured Fermi surfaces from samples prepared in this way in Figs. 1(d) and 1(e). These were taken under measurement conditions (i.e., at a photon energy of 68 eV) which should probe the region centered around the XR and Γ XRZ planes for the (110) and (100) orientations,

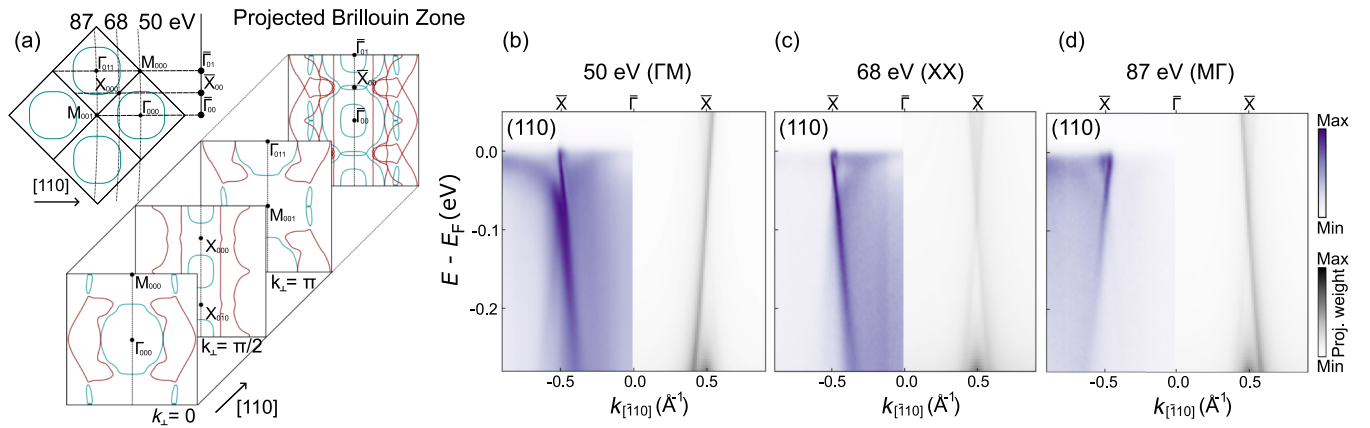


FIG. 2. Reconciling apparent bulk band crossing from surface projections. (a) Schematic of how the bulk Brillouin zones stack together and project onto the surface Brillouin zone. The colored lines show the bulk Fermi surface contours extracted from DFT. (b)–(d) Dispersions along $\bar{\Gamma}\bar{X}$ at photon energies of 50, 68, and 87 eV. These probe planes centered on $\bar{\Gamma}\text{MAZ}$, XR , and $\text{M}\bar{\Gamma}\text{Z}$, respectively. Left sides show the ARPES data, compared with a bulk projected DFT calculation (including $k_{\perp}$ integration) on the right. The color bars indicate the photoemission intensity and the simulated projected weight, respectively.

respectively. However, due to the surface sensitivity of ARPES, we expect significant broadening of our measured features along the out-of-plane ($k_{\perp}$) direction ([110] or [100], respectively), contributing to the measured spectra. The measured Fermi surfaces are clearly strongly affected by this $k_{\perp}$ broadening. Despite exhibiting some sharp and clearly dispersive features (pointing to the good sample cleave quality), the majority of the surface Brillouin zone is filled with broad spectral weight for both surface orientations. From inspection of our calculated, non-magnetic, Fermi surface from DFT [Fig. 1(f)], it is clear that the central, almost circular, filled-in spectral weight for both the (110) and (100) surfaces originates from the near-spherical Fermi surface, centered at $\bar{\Gamma}$ (FS 1). Meanwhile, the FS 2 pockets contribute spectral weight shifted away from the $\bar{\Gamma}$ pocket along $k_{[001]}$. As for previous electronic structure studies [18,20,21], we find best agreement between our data and the nonmagnetic calculations, while qualitative differences with the magnetic calculation (see Supplemental Fig. 2 [31]) again favor that there is no (alter)magnetic ground state in bulk RuO_2 .

In the nonmagnetic state, both FS 1 and FS 2 disperse strongly along all three-momentum directions, and as a result, they are substantially broadened in our measurements. To simulate the effect of this, we project our calculations onto the (110) and (100) surfaces, accounting for the $k_{\perp}$ broadening expected to be present in the experimental measurements [Fig. 1(f); see Sec. III]. Our calculations well reproduce the filled-in weight from FS 1 and FS 2, although the intensity of some features on the (110) surface is overestimated. In particular, the simulations show sharp rings offset from the $\bar{X}$ points that are absent in the Fermi surface measurements shown in Fig. 1(d) measured at $h\nu = 68$ eV. This likely reflects matrix-element-induced variations in intensity that are not captured in the projection. To confirm this, we compare our projection calculations to Fermi surface measurements that were taken at a different photon energy probing a different but symmetry-equivalent plane in $k_{\perp}$ ($h\nu = 32.5$ eV, Supplemental Fig. 3 [31]), where we find the ringlike features

are more prominently experimentally. Thus, we conclude that the surface projections of the bulk electronic structure well capture the experimental spectral features.

Of particular interest are the features near the $\bar{X}$ point of the (110) surface, visible in the inset in Fig. 1(d). Here, Fermi pockets centered at $\bar{\Gamma}_{00}$ and the neighboring $\bar{\Gamma}_{01}$ appear to cross, leading to arcs forming at the $\bar{X}$ point. Similar band crossings can also be seen in our measured dispersions along the $\bar{\Gamma}\bar{X}$ direction [Figs. 2(b)–2(d)] and were previously attributed to one of the material’s Dirac nodal lines [19]. Such a nodal crossing is present in DFT calculations, but is not expected to intersect the Fermi level. Indeed, to reproduce the measured spectra required shifting the DFT bands downwards by ≈ 600 meV, seemingly at odds with the good agreement between the DFT Fermi surface and quantum oscillations [17,18].

We attribute this discrepancy to how the bulk features project onto the surface Brillouin zone due to the strong $k_{\perp}$ integration in ARPES. Figure 2(a) illustrates how the three-dimensional Brillouin zones stack along $k_{[110]}$. Because of this stacking, the periodicity of the surface Brillouin zone is halved along $k_{[110]}$ compared to the bulk zone. The extremal edge of FS 1 along the $\bar{\Gamma}_{000}\text{M}_{000}$ directions extends beyond the edge of the surface Brillouin zone and projects partly into the next zone. At the surface zone boundary, it then overlaps with the projection of FS 1 that originates in the second bulk Brillouin zone (along $\text{M}_{001}\bar{\Gamma}_{011}$) but extends slightly into the first zone. This gives rise to the appearance of a “crossing” of these two Fermi surfaces and the arcs around the $\bar{X}$ points, illustrated in Fig. 2(a) and visible in the Fermi surface of Fig. 1(d). Since the apparent crossing is the result only of a projection, the intensity of its two branches changes with photon energy, as the central $k_{\perp}$ value probed is tuned. This is visible in our measured dispersions and simulated ARPES projections [Figs. 2(b)–2(d)]. At a photon energy of 50 eV (probing dominantly the region centered on $\bar{\Gamma}\text{M}$), the positive dispersion contributes most strongly (additional sharper surface-derived features are also visible in the experiment which are discussed further below). This spectral weight shifts

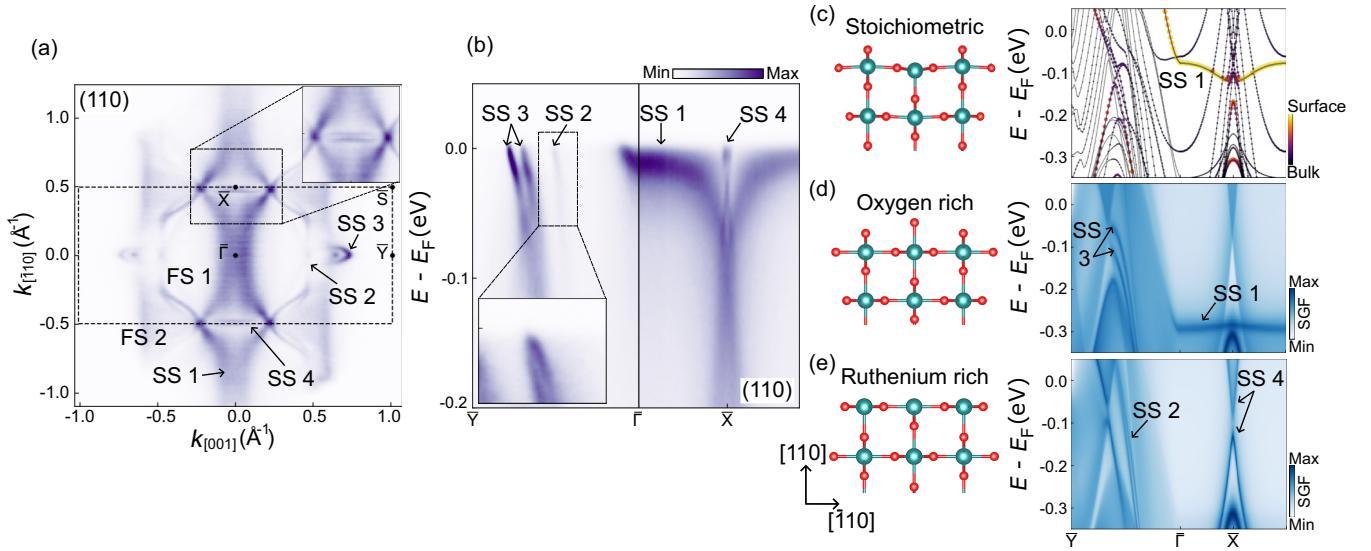


FIG. 3. Termination-dependent surface resonances on the (110) surface. (a) Measured (110) Fermi surface ($h\nu = 68$ eV, linear horizontal light polarization), highlighting the surface resonances SS 1–SS 4. (b) Corresponding dispersions measured along the $\bar{Y}\Gamma\bar{X}$ directions, showing the four surface resonances. The inset shows SS 2 measured in linear vertical light polarization, highlighting a small band splitting. (c) Surface structure of the stoichiometric termination of the (110) surface and the corresponding surface electronic structure from DFT slab calculations. The marker color and size indicate the projected surface weight. (d) Surface structure of the oxygen-rich termination and corresponding surface Green's function calculation, showing SS 1 and SS 3. (e) Surface structure of the ruthenium-rich termination and its surface Green's function calculation, showing SS 2 and SS 4.

to the negative dispersion at 87 eV (probing the region centered on $M\Gamma$). At 68 eV, probing the region centered on the XX line, both branches contribute similar spectral weight, leading to the apparent crossing and the arcs observed in Fig. 1(d). It is these crossing features that were previously assigned as a Dirac nodal line [19]. We conclude, however, that this is, in fact, a projection artifact of the measurement and that there is no additional, energy-shifted nodal line at the Fermi level. Importantly, the measured band features, including this crossing in the surface projection, are well accounted for in our simulations from bulk DFT calculations. This also resolves several discrepancies that were noted in Ref. [27], in which anisotropic correlation effects were suggested to explain the mismatch between the observed and calculated band structure. We thus conclude that no substantial energy shift or renormalization of the DFT bands is required to match the experimentally observed dispersions.

C. Surface states

Nonetheless, besides these projected bulk bands [which contribute rather broad spectral weight in Figs. 1(d) and 1(e) and Figs. 2(b) and 2(d)], additional sharper states are visible in our measurements which are not captured by our bulk DFT calculations. These additional states are most clearly visible in linear horizontal light polarization, and we show measurements of the corresponding Fermi surface and dispersions from the (110) surface in Figs. 3(a) and 3(b). A bright but somewhat broad quasi-one-dimensional Fermi surface is visible as a near-vertical stripe in our measured Fermi surface. This derives from the flat band visible along $\bar{\Gamma}\bar{X}$ in our dispersion [Fig. 3(b), marked SS 1]. We attribute this as the flat-band surface state observed previously [19], which was

found to originate from ruthenium-oxide chains on the (110) surface [26]. While this appears qualitatively similar to its observation in previous studies [19–21], we note that we can resolve here an additional, previously unobserved, splitting in the band in the vicinity of the $\bar{X}$ point [see also Fig. 2(c)]. This may suggest a significant hybridization between the bulk and surface bands here. This, as well as the generally broad nature of this state, is consistent with the fact that the surface state disperses through the momentum space region onto which the highly dispersive bulk bands project. It should, therefore, rather be considered as a surface resonance than an isolated surface state.

In addition to this flat band, we also observe several much more dispersive states. SS 2 has been identified as a surface state by Liu *et al.* [20], while the pair of states along $\bar{\Gamma}\bar{Y}$ (which we attribute as SS 3) were previously assigned as bulk states [19,20]. There is, however, a significant energy mismatch between this feature and the calculated bulk band. As discussed, once surface projection effects are accounted for, we find a good general agreement between calculation and observed bulk features. Moreover, we find that the states we denote as SS 3 have a dispersion which is independent of the probing photon energy (Supplemental Fig. 4 [31]). We thus also attribute this state as a surface state or resonance here. Finally, an additional, previously unidentified, sharp state (SS 4) is visible close to the $\bar{X}$ point of the surface Brillouin zone, contributing additional sharp and $h\nu$ -independent bands in Figs. 2(b)–2(d).

To better understand the origin and nature of this rich array of apparently surface-related bands, we have performed surface electronic structure calculations with DFT. We show in Fig. 3(c) calculations (see Sec. II) modeling the surface with a symmetric 12-layer slab with a stoichiometric termination

on both sides. Consistent with prior work [19,21,24,26], these calculations reproduce the flat-band surface resonance (SS 1), although they locate it at a binding energy slightly higher than that observed in our experimental measurements. We note that the binding energy of this state appears highly sensitive to surface relaxation in our DFT calculations (Supplemental Fig. 5 [31]), again likely reflecting a strong coupling of the surface band to the underlying bulk. Our DFT surface projections also reveal some increased wave function weight at the surface for states close to the $\bar{X}$ point and between the $\bar{\Gamma}$ and $\bar{Y}$ directions. However, clearly resolving these as distinct surface bands from the strongly dispersive bulk states is challenging for feasible sizes of a DFT supercell. To better capture these, we have therefore performed additional surface state calculations using a surface Green's function (SGF) method (see Sec. II). These model a surface on a semi-infinite system, where we consider bulklike truncations of the unit cell. While this does not capture the effects of surface relaxations, it does allow us to model the effect of having an oxygen-rich surface vs a ruthenium-rich one [Figs. 3(d) and 3(e)], both terminations that could be expected experimentally [41]. Due to a lower computational cost, they also allow us to include the effects of spin-orbit coupling (SOC) in our calculations (see Supplemental Fig. 6 for a comparison with and without SOC [31]).

The calculated spectra for the oxygen- and ruthenium-rich surfaces are shown in Figs. 3(d) and 3(e). Together, these show features that are in excellent qualitative agreement with our measured band structures. The oxygen-rich calculation reproduces the “flat-band” surface state between the $\bar{\Gamma}$ and $\bar{X}$ directions, albeit located at a significantly too high binding energy, which is consistent with previous work [20,21]. We attribute the binding-energy overestimation to the effects of structural relaxation at the surface, which we find in our DFT slabs to dramatically lower the energy of this flat-band surface state (Supplemental Fig. 5 [31]). Interestingly in the experiment, we find that the flat band is located only ≈ 10 meV below the Fermi level, suggesting a modest surface doping or strain could move its associated large density of states to E_F , potentially triggering a surface instability to a magnetic or other collective state.

Our calculations also reproduce a pair of additional surface resonances (marked SS 3), located at the momentum space location at which the bulk Dirac nodal line (DNL2 from Ref. [4]) intersects the (110) plane. Like the flat-band state, the calculations locate them at a too high binding energy, which we similarly attribute to missing relaxation effects. SS 3 is strongly split in the vicinity of the nodal line, consistent with experimental observations from our measured Fermi surfaces and dispersions [Figs. 3(a) and 3(b)]. Our calculations show how this splitting is a consequence of spin-orbit coupling, which we find lifts the spin degeneracy of these states (Supplemental Fig. 6 [31], see also Ref. [20]). We therefore attribute the band splitting to a Rashba-like spin-orbit coupling in the presence of surface inversion symmetry breaking. Although previous ARPES studies have observed signatures of Rashba-like spin splitting in the bulk bands along $\bar{\Gamma}\bar{X}$, these have not been observed any splitting along the $\bar{\Gamma}\bar{Y}$ direction [20].

While the oxygen-rich calculations naturally reproduce SS 1 and SS 3, they do not capture SS 2 and SS 4. These, however,

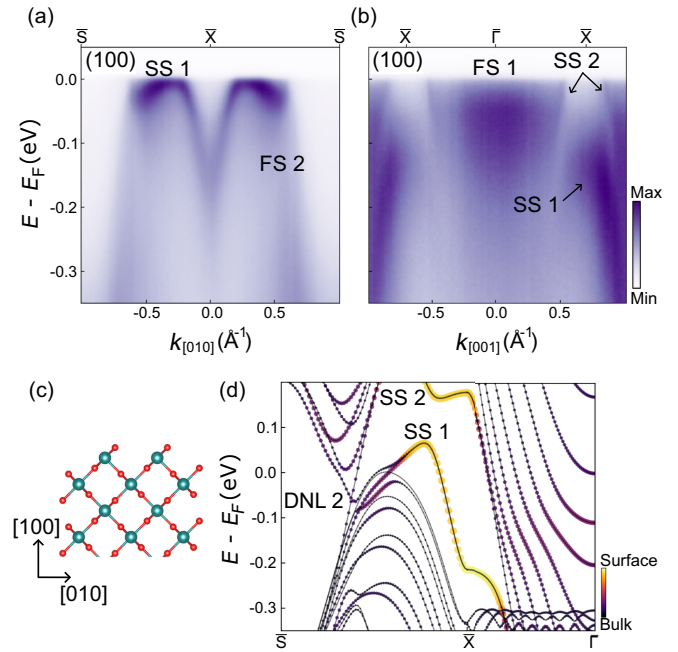


FIG. 4. Surface resonances of the (100) surface. (a, b) Measured dispersions along the $\bar{X}\bar{S}$ and $\bar{\Gamma}\bar{X}$ directions ($h\nu = 68$ eV, linear horizontal polarization), showing bulk projected states coming from the two Fermi sheets (FS 1 and FS 2) and two surface resonances (SS 1 and SS 2). (c) Stoichiometric termination of the (100) surface. (d) DFT slab calculation for this termination, showing the two surface states. The marker color and size indicate the projected surface weight.

can be realized in calculations of a Ru-rich surface. SS 2 is again split by spin-orbit coupling (Supplemental Fig. 6 [31]), albeit with a splitting much smaller than that for the O-rich surface. Although SS 2 was observed in earlier studies [20], its splitting has not been resolved to date. Here, however, we observe a small but clear band splitting in our experimental measurements see inset of Fig. 3(b)]. This points to the high surface quality resulting from our FIB-structured cleave planes. While a good macroscopic cleave surface is obtained, microscale spatial variation (smaller than the size of our probing light spot) can still be expected in the surface termination, given the lack of a natural cleaving plane. We average over these in our measurements, explaining the simultaneous presence of surface states from distinct terminations in our measured ARPES data.

As discussed above, FIB-structured cleaving also allows us to deterministically cleave along the distinct (100) surface orientation. We show the corresponding ARPES dispersions in Figs. 4(a) and 4(b) [see also Fermi surface measurements in Fig. 1(e)]. We observe broad spectral weight derived from the highly three-dimensional FS 1 and FS 2 bulk Fermi surfaces. In addition, we observe a significant enhancement of spectral weight close to the bulk projected band gap along $\bar{X}\bar{S}$ and on the edge of the projection of the bulk FS 1 states along $\bar{\Gamma}\bar{X}$. This is again suggestive of additional surface-derived bands. We assign the strong spectral weight along $\bar{X}\bar{S}$ as arising due to a surface state SS 1, which has previously been considered as having a drumheadlike character [21]. In this respect, we

note that the state is more dispersive than previously observed, forming a V-shaped band around the $\bar{X}$ point. In addition, we observe a sharp band along $\bar{\Gamma X}$, which we denote SS 2, that was not found in earlier work.

These assignments are in good agreement with our DFT slab calculations performed for the (100) surface. For the stoichiometric slab [Fig. 4(c)], we already find two additional surface states (SS 1 and SS 2) whose dispersions are in good general agreement with our measured electronic structures [Fig. 4(d)]. The binding energy of these surface states is again strongly impacted by surface relaxations (Supplemental Fig. 7 [31]), with SS 1 gaining additional dispersion and relaxing towards the bulk projected band gap. This again points to a significant hybridization between bulk and surface bands. We note that, for the (100) surface, the stoichiometric surface appears to describe the measured electronic structure better than calculations for oxygen- and ruthenium-rich terminations (Supplemental Fig. 8 [31]).

IV. CONCLUSIONS

Together, therefore, our measurements and calculations point to a very rich surface environment in RuO₂. A highly three-dimensional bulk couples to dangling-bond-derived states at the surface, providing multiple potential channels to enhanced catalytic activity. [26] Substantial bulk-surface hybridization is evident via the formation of surface resonances, while surface relaxation appears to favor surface bands pushed towards projected band gaps as much as possible. The inversion symmetry breaking inherent to the surface—together with a marked spin-orbit coupling of Ru 4d orbitals—further

allows significant Rashba-type spin splittings to develop. This provides a potential route to rationalize previous spin-resolved signatures in surface-sensitive spectroscopic measurements of RuO₂. More broadly, our measurements highlight that the measured spectra in this system (at least where dispersive bandlike features are resolved) are dominated by surface rather than bulk states. Significant care must therefore be taken in making alternative assignments—an inherently bulk property—in this and related highly three-dimensional compounds from ARPES alone.

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DATA AVAILABILITY

The research data supporting this publication can be accessed at [42].

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