

Correlated Insulator at the Surface of the Polar Metal $\text{Ca}_3\text{Ru}_2\text{O}_7$

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We investigate the electronic structure at the surface of the correlated oxide $\text{Ca}_3\text{Ru}_2\text{O}_7$, a low-symmetry ruthenate oxide which hosts an unconventional polar-metal phase. From a combination of angle-resolved photoemission spectroscopy and scanning tunneling spectroscopy measurements, we demonstrate that the surface hosts an insulating phase, a distinct departure from metallicity within the bulk. Utilizing quantitative low-energy electron diffraction in conjunction with electronic structure calculations, we show how this results from a combined surface structure relaxation and the impact of marked electronic correlations in this system. Our findings highlight the proximity of $\text{Ca}_3\text{Ru}_2\text{O}_7$ to an insulating metallic state, and illustrate how subtle structural distortions can control its emergent electronic phases.

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In materials where the electron-electron interactions are strong, numerous nearly degenerate ground states can arise from the complex interplay of various degrees of freedom, including lattice, orbital, charge, and spin [1]. In these so-called strongly correlated electron materials, a subtle perturbation to any of these can result in a significant change in the material's physical properties. Consequently, strongly correlated materials exhibit diverse phase diagrams that encompass exotic many-body quantum phases, including strange metallicity, unconventional superconductivity, and Mott insulators [2,3]. The Ruddlesden-Popper (RP) ruthenates are an ideal materials class in which to explore this physics. They host a wide range of ground states which can be accessed via only rather minor modification of the crystal structure and composition, including unconventional superconductivity, magnetism and correlated insulating states [4–7].

In particular, $\text{Ca}_3\text{Ru}_2\text{O}_7$, the bilayer member of the RP series of calcium ruthenates, displays competing electronic and magnetic orders, and appears to lie on the verge of

multiple electronic and magnetic instabilities [8–10]. Upon cooling from a bad-metal-like metallic state at room temperature, it undergoes a sequence of magnetic and structural phase transitions. A Néel ordering occurs to an antiferromagnetic (AFM) phase at $T_N \approx 56$ K, where the spins orient along the crystallographic a axis, aligning ferromagnetically within a bilayer but antiferromagnetically between neighboring bilayers (AFM_a). At $T_s \approx 48$ K, the spins reorient to point along the b axis (AFM_b), coupled with an isostructural phase transition which leads to a large jump in the measured resistivity [11–14]. While there has been debate regarding the nature of the ground state, the observation of quantum oscillations unambiguously points to a low carrier-density semi metallic state [15]. A trilinear coupling between structural rotation and tilt modes and a polar distortion in the Ca-O layer furthermore makes the crystal structure noncentrosymmetric. $\text{Ca}_3\text{Ru}_2\text{O}_7$ is therefore an interesting example of a so-called polar metal [16–21], where ferroelectriclike distortions remain stable, despite the itinerant electrons which would be expected to screen the associated internal electric fields [22,23]. However, a marginal doping of the Ru sites with non-magnetic Ti is sufficient to drive a transition to an insulating state at low ($\approx 4\%$) Ti doping [24,25], as shown in Fig. 1(b).

This change in the electronic ground state of $\text{Ca}_3\text{Ru}_2\text{O}_7$ is accompanied by a change in the low-temperature magnetic structure. Increasing the Ti concentration, the material transitions from the AFM_b phase to an AFM_G phase, with G -type AFM order and spins canted along the c

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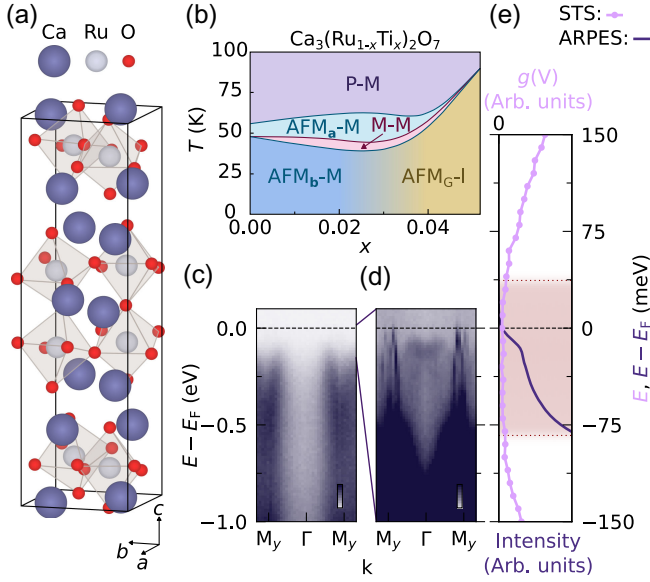


FIG. 1. (a) Unit cell of bulk $\text{Ca}_3\text{Ru}_2\text{O}_7$ with lattice vectors labeled. (b) Magnetic and electronic phase diagram of $\text{Ca}_3(\text{Ru}_{1-x}\text{Ti}_x)_2\text{O}_7$. P: paramagnetic; -M: metallic phase; -I: insulating phase; AFM_a : antiferromagnetic order with spins orientated along the a axis; AFM_b : antiferromagnetic order with spins orientated along the b axis; M: mixed magnetic phase and AFM_G : antiferromagnetic type G order, with spins canted along the c axis. Data taken from Refs. [26,27]. (c,d) ARPES measurements ($h\nu = 33$ eV, linear horizontal polarization, $T = 18$ K) taken along the $M_y - \Gamma - M_y$ direction. (e) Tunneling spectrum for the surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$ ($I_{\text{set}} = 100$ pA, $V_{\text{set}} = -1$ V, $T = 4.2$ K) (pink line) and angle-integrated photoemission intensity extracted from panel d (purple line). The red dotted lines mark the edges of the gap (indicated by red shading) inferred from scanning tunneling spectroscopy (STS) measurements see Fig. 1 in [28] for details of their extraction.

axis [27]. Interestingly, the Ti doping into the crystal lattice drives a change in the rotation and tilt of the RuO_6 octahedra [26], highlighting the sensitivity of the physical properties of $\text{Ca}_3\text{Ru}_2\text{O}_7$ to subtle distortions of its constituent RuO_6 octahedra.

This sensitivity offers rich opportunities to explore different correlated phases. Within prior studies, pressure and strain have been utilized to alter the structure of the RuO_6 octahedra, and hence, the magnetic and electronic properties of $\text{Ca}_3\text{Ru}_2\text{O}_7$ [31,32]. The local structure can also, however, be different at the surface of the crystal to the bulk [33,34], providing a clean route to track the impact of subtle structural distortions on the electronic states and phases that form. In this Letter we report on the impact of such surface structural distortions in $\text{Ca}_3\text{Ru}_2\text{O}_7$, demonstrating how they not only tune the electronic structure but, in fact, also allow for a distinct, correlated insulating ground state to be stabilized.

Single crystal samples of $\text{Ca}_3\text{Ru}_2\text{O}_7$ were grown by the floating zone method [35]. Both antiphase and polar domains are typically present in growths of $\text{Ca}_3\text{Ru}_2\text{O}_7$. The spatial

extent of antiphase domains is such that we could select monodomain samples for angle-resolved photoemission spectroscopy (ARPES) using polarized light microscopy [36] or measure diffracted intensity from a single antiphase domain in (LEED) (see Fig. 2 in [28]). In comparison, polar domains are significantly smaller [23]. Consequently, our LEED measurements average over an approximately equal population of polar domains (see Fig. 3 in [28]).

All samples were cleaved *in situ* before the measurements. For $\text{Ca}_3\text{Ru}_2\text{O}_7$, the intralayer coupling is much stronger than the interlayer coupling [37]. This means the crystal cleaves between bilayers, exposing a CaO_2 terminated surface [38]. ARPES measurements were performed on a freshly cleaved surface using the BLOCH beamline of the Max-IV synchrotron. The samples were measured at a temperature of $T \approx 18$ K using 33 eV synchrotron light. Scanning tunneling spectroscopy (STS) measurements were performed using a home-built low temperature scanning tunneling microscope (STM) operating in a vector magnet [39]. The measurements were performed at 4.2 K unless stated otherwise. The bias voltage was applied to the sample with the tip on virtual ground. The differential conductance was recorded using a standard lock-in technique, adding an AC modulation to the sample bias. Samples for STM are cleaved using a cleaving stage mounted to the 4 K plate of the insert, with a cleaving temperature of ~ 20 K. LEED measurements were performed using an OCI LEED BDL800IR optics mounted onto an ultrahigh vacuum system. Measurements were performed at a temperature of $T \approx 10$ K. Images of the LEED pattern were acquired using a CCD camera, and taken in steps of 1 eV between 150 and 500 eV. Experimental $I(V, \mathbf{Q})$ spectra were extracted from the LEED images using Python code before being analyzed using the CLEED package [40,41]. To estimate the uncertainties associated with our LEED analysis, we measured and fit the structures for two different samples of $\text{Ca}_3\text{Ru}_2\text{O}_7$. The displacements presented below are the mean best-fit displacement, and uncertainties are one standard deviation from the mean.

To model the surface electronic structure of $\text{Ca}_3\text{Ru}_2\text{O}_7$, density functional theory (DFT) calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) code [42–44] and local density approximation exchange-correlation functional. Both spin-orbit coupling (SOC) and magnetic order along the b axis were included within the calculations and correlations were included by adjusting the U value of the Ru atoms within the Dudarev approximation [45]. To model the effect of structural distortions at the surface while maintaining acceptable computational cost, calculations were performed for a free-standing bilayer of $\text{Ca}_3\text{Ru}_2\text{O}_7$, with a 15 Å gap to the next bilayer. A $\mathbf{k}$ grid of $8 \times 8 \times 1$ was used for self-consistent calculations, and a finer $\mathbf{k}$ grid of $15 \times 15 \times 1$ for density of states (DOS) calculations, both with a plane wave energy cutoff of 600 eV.

In Fig. 1(c), we show our ARPES measurements over a broad energy range below the Fermi level. Consistent with prior studies, we observe significant spectral weight in the deep-lying valence band, originating from Ru t_{2g} states [36,46,47], but with broad linewidths that point to rather incoherent states. Close to the Fermi level, this spectral weight becomes strongly suppressed. Over a narrow energy range below the Fermi level, we observe a vanishing spectral weight. Nonetheless, with an enhanced contrast, we can observe sharp but extremely weak states close to and crossing the Fermi level [Fig. 1(d)], before their spectral intensity becomes dominated by the incoherent states beyond ~ 100 meV. The finite albeit small DOS at the Fermi level [Fig. 1(e)] is consistent with the ground state of $\text{Ca}_3\text{Ru}_2\text{O}_7$ being a low carrier-density metal, as known from bulk studies [15]. However, within this picture, the almost vanishingly small coherent spectral weight at E_F as compared to the incoherent weight at higher binding energies would suggest an extremely small quasiparticle residue.

To better understand the electronic structure, we have therefore performed STS measurements, displayed also in Fig. 1(e). These data, taken on the same batch of crystals as the ARPES measurements, display a full gap of ~ 150 meV asymmetrically distributed around the Fermi level, seemingly at odds with our photoemission measurements which show bands crossing the Fermi energy. We will show below that this is due to a distinct surface and bulk electronic structure, and different depths of the two techniques.

First, we consider the geometry of the $\text{Ca}_3\text{Ru}_2\text{O}_7$ (001) surface, as shown in Fig. 2(a). In Fig. 2(b), we present a topographic image of this CaO-terminated surface. Prominent within the topography are stripes. These stripes represent channels with a decreased (darker) or increased (lighter) density of oxygen atoms [48], resulting from the tilting of the RuO_6 octahedra, as illustrated in Fig. 2(a). As the tilting of the RuO_6 octahedra is unidirectional in

$\text{Ca}_3\text{Ru}_2\text{O}_7$, we observe stripes only along the [010] crystallographic direction, and thus within the Fourier transform of the topography [inset in Fig. 2(b)] the (1,0) and $(-1,0)$ Bragg peaks are present while the (0,1) and $(0,-1)$ Bragg peaks are extinct. The unidirectional tilt of the RuO_6 octahedra is also observed in our LEED analysis of a pristine (001) surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$ [Fig. 2(c)]. A tilting of the RuO_6 octahedra in RP crystals destroys one glide line in the two-dimensional unit cell. If the octahedral tilt is along a single axis, only a single glide line symmetry is broken while the orthogonal glide line is preserved. This is illustrated by the dot-dashed lines in the top-down view of the two-dimensional unit cell in Fig. 2(a). Therefore, in our LEED measurements, we observe spots along a single direction, the [100] direction, while those along the orthogonal [010] direction are extinct.

Together, these measurements suggest a surface symmetry consistent with the one expected from the bulk crystal structure. In fact, at all incident electron beam energies measured, we observe only LEED spots corresponding to the bulk-terminated unit cell, indicating that $\text{Ca}_3\text{Ru}_2\text{O}_7$ does not undergo a structural reconstruction at its surface. Surface relaxation can still occur, however, resulting in changes in RuO_6 octahedral rotation, tilt angle, or vertical displacements of atoms from their bulk positions. Indeed, the symmetry-preserving structural phase transition in the bulk indicates a strong coupling of electronic, magnetic and intra-unit-cell structural degrees of freedom in this system, necessitating searching for structural changes beyond simple reconstruction effects. This motivates quantitative LEED measurements, recording and modeling the intensity of the LEED spots as a function of energy in order to extract quantitative information about atomic displacements of the surface atoms.

We show such $I(V, \mathbf{Q})$ spectra for four selected LEED spots [highlighted in Fig. 3(a)], in Fig. 3(b) [with all the $I(V, \mathbf{Q})$ spectra shown in Fig. 4 in [28]]. Variations in the

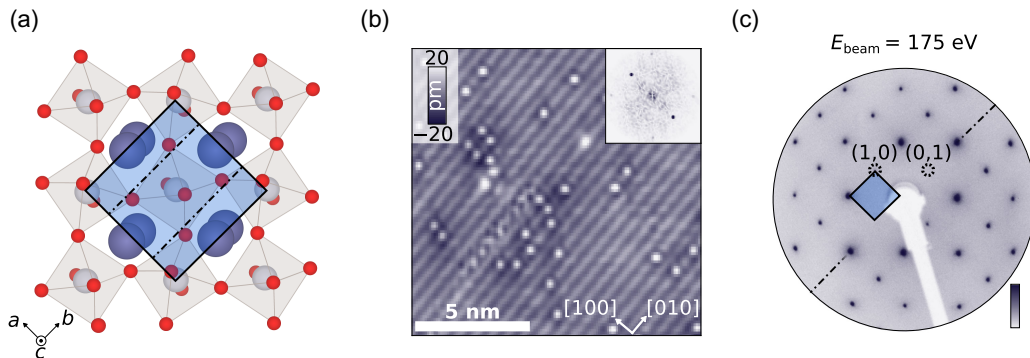


FIG. 2. (a) Top-down view of the two-dimensional bulk unit cell of $\text{Ca}_3\text{Ru}_2\text{O}_7$. (b) Low-temperature STM topography of the $\text{Ca}_3\text{Ru}_2\text{O}_7$ surface ($I = 100$ pA, $V = -2$ V, $T = 4.2$ K). Inset shows the Fourier transform of the topography. The image was low-pass filtered to remove high-frequency noise. (c) LEED pattern of $\text{Ca}_3\text{Ru}_2\text{O}_7$ measured at $T = 10$ K and an incident electron beam energy, $E_{\text{beam}} = 175$ eV. The locations of the present (1,0) and extinct (0,1) LEED spots have been highlighted by the black circles. The bulk unit cell is highlighted by the blue square, and the locations of the glide lines are marked by the dot-dashed lines in panels (a) and (b).

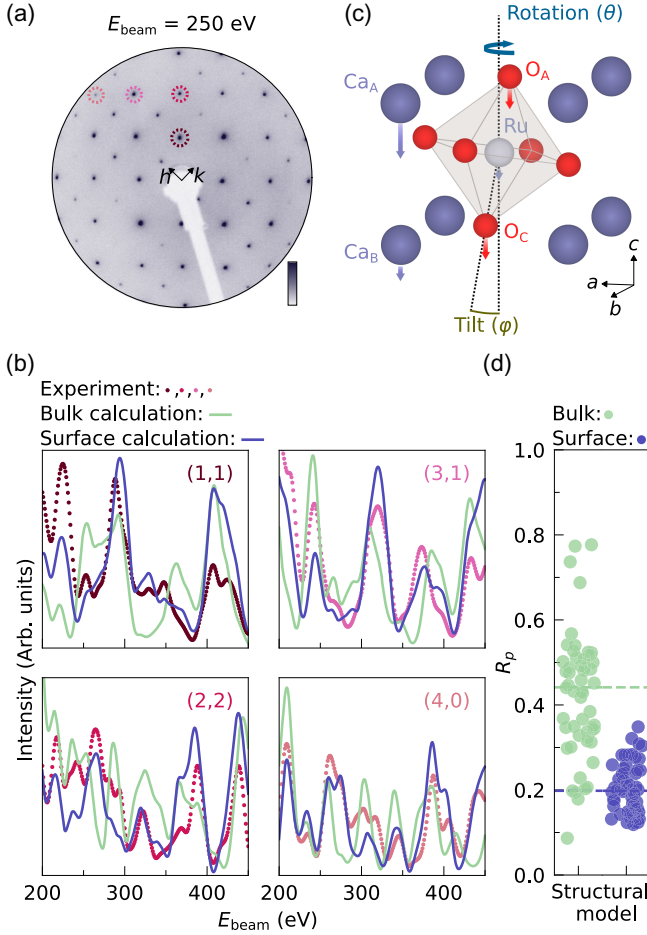


FIG. 3. (a) LEED image recorded at an incidence electron beam energy, E_{beam} , of 250 eV. Locations of the (1,1), (2,2), (3,1), and (4,0) LEED spots are highlighted by colored circles. (b) Four selected experimental (colored points) $I(V, \mathbf{Q})$ spectra of $\text{Ca}_3\text{Ru}_2\text{O}_7$. Calculated $I(V, \mathbf{Q})$ spectra correspond to the best-fit surface structure (purple lines) or the bulk structure taken from Ref. [22] (green lines). (c) The out-of-plane and in-plane displacements at the surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$. (d) R_p values for all the $I(V, \mathbf{Q})$ spectra for two different structural models: the best-fit surface structure (purple points) and the bulk structure from Ref. [22] (green points). The total R_p value for each model is indicated by the dashed line and points are offset horizontally for clarity.

intensity of these $I(V, \mathbf{Q})$ spectra encode structural information concerning atoms within the surface layer of $\text{Ca}_3\text{Ru}_2\text{O}_7$. To elucidate these atomic coordinates, we performed a fitting to the experimental $I(V, \mathbf{Q})$ spectra, considering only structures compatible with the symmetry of the diffraction pattern seen in the LEED pattern [Fig. 2(c)]. Figure 3(c) highlights the key structural parameters extracted from our analysis, which are presented in detail in Table I.

The results of this LEED $I(V, \mathbf{Q})$ analysis indicate a surface structure of $\text{Ca}_3\text{Ru}_2\text{O}_7$ which is markedly changed

TABLE I. Out-of-plane and in-plane displacements at the surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$. Displacements are the mean of two samples of $\text{Ca}_3\text{Ru}_2\text{O}_7$ measured and analyzed, while the uncertainties are reported as plus-minus one standard deviation from the mean. The direction of the vertical displacements and their relative magnitude are displayed in Fig. 3(c). We note that by careful fitting of structural parameters and vibrational amplitudes we were able to achieve very low R_p factors for both samples analyzed and a very high degree of precision.

LEED $I(V, \mathbf{Q})$	
θ_{surface}	$(13 \pm 0.1)^\circ$
ϕ_{surface}	$(13 \pm 0.5)^\circ$
$\Delta_c \text{Ca}_A$	(-12.5 ± 0.8) pm
$\Delta_c \text{O}_A$	(-5.7 ± 0.3) pm
$\Delta_c \text{Ru}$	(-2.5 ± 0.4) pm
$\Delta_c \text{Ca}_B$	(-3.3 ± 0.3) pm
$\Delta_c \text{O}_C$	(-6.4 ± 0.9) pm

from the bulk structure, despite the lack of a symmetry-breaking surface reconstruction. Specifically, we find RuO_6 octahedra at the surface which are slightly ($\approx 2^\circ$) more rotated than those within the bulk crystal ($\theta_{\text{bulk}} \sim 10.9^\circ$) [22], while their tilt angle (ϕ) is essentially unaffected by the creation of a surface. Importantly, we find notable vertical displacement of surface atoms from their bulk positions. In particular, a significant vertical displacement of both Ca atoms indicates an asymmetric uniaxial compression at the surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$. Similarly, we find that both apical O atoms displace from their bulk positions towards the underlying bulk, leading to a rigid shift of the surface RuO_6 octahedra away from the vacuum interface, while the Ru atoms undergo a vertical displacement which modifies the local symmetry of the surface octahedra, breaking the inversion symmetry of the surface bilayer. Due to destructive and constructive interference of the low-energy electron beam diffracted by the lattice, LEED $I(V, \mathbf{Q})$ is highly sensitive to such atomic displacements, and we show in Fig. 3(b) that the experimental and fitted $I(V, \mathbf{Q})$ spectra for such a surface are markedly different from one with a bulk-like truncation. Including such structural relaxation leads to a marked reduction of Pendry's R-factor (R_p) [49] for almost all of the extracted LEED spots [Fig. 3(d)]. The global R_p factor is reduced from the rather large value of $R_p^{\text{bulk}} \approx 0.44$ to a best-fit value of $R_p^{\text{surface}} \approx 0.20$.

To investigate the impact of these atomic displacements on the surface electronic structure, we have performed a series of DFT calculations. In Figs. 4(a) and 4(b), DFT band structure calculations are shown for a freestanding bilayer of $\text{Ca}_3\text{Ru}_2\text{O}_7$ within the low-temperature magnetic phase, AFM_b . The crystal structure of the bilayer was fixed to either the bulk structure (green) or surface structure (purple) from our LEED $I(V, \mathbf{Q})$ analysis.

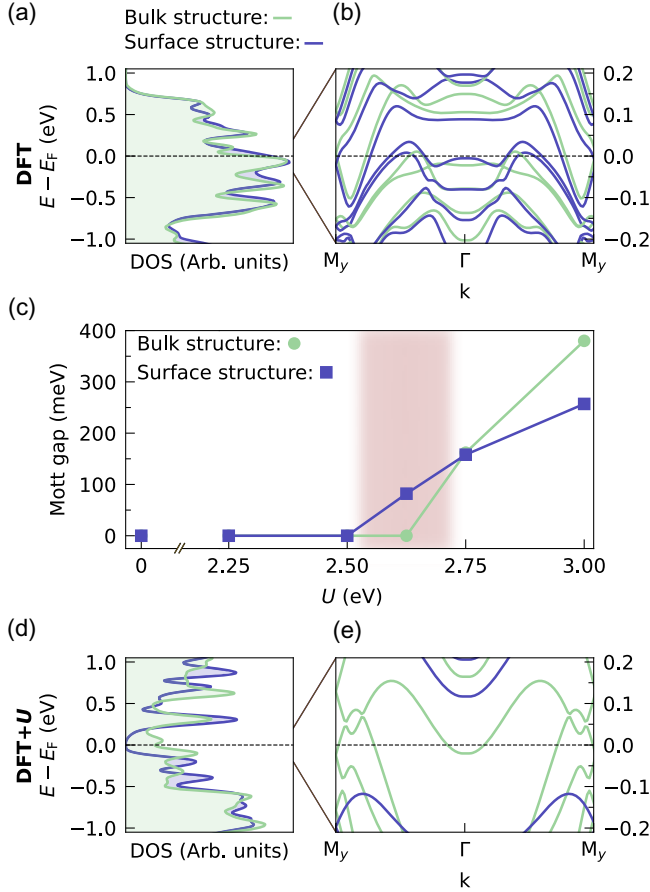


FIG. 4. (a,b) DOS and electronic band structure calculations for the bulk (green lines) and surface structure (purple lines) of $\text{Ca}_3\text{Ru}_2\text{O}_7$ for $U = 0$ eV. (c) Magnitude of the Mott-like gap around the Fermi level as a function of U value, calculated for the bulk crystal structure (green circles) and the surface structure (purple squares). The red region highlights the U range for which the surface is insulating but the bulk remains metallic. (d) and (e) DOS and electronic band structure calculations for the bulk (green lines) and surface structure (purple lines) of $\text{Ca}_3\text{Ru}_2\text{O}_7$ for $U = 2.625$ eV. All calculations also include SOC and magnetic order along the b axis.

We find that the surface relaxation alone does not cause a significant change in the electronic structure within a normal DFT calculation. While disentangling the qualitative changes within the electronic structure due to the different components of the surface relaxation is challenging, reflecting a delicate interplay between all of the structural distortions (see Fig. 5 in [28]), our calculations without considering correlations still show a metallic surface. This rules out the possibility of a conventional band insulator at the surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$. However, when including electronic correlations through a local Coulomb repulsion U , we find a marked difference for the electronic structures. As shown in Fig. 4(c), a band gap opens at the Fermi level with increasing U , pointing to a correlation-driven metal-to-insulator transition (MIT). While susceptibility to such

a correlated-insulating state is not surprising in and of itself, intriguingly our calculations find that the surface relaxation causes this transition to occur at a different (slightly lower) U value than in the bulk. For a narrow range of U values (~ 2.5 to 2.75 eV), we calculate that the bulk crystal is metallic, while for the surface structure we find a correlated insulator, as shown for $U = 2.625$ eV in Figs. 4(d) and 4(e).

These DFT + U calculations provide a natural explanation for the seemingly contradictory results introduced in Figs. 1(d) and 1(e). While both ARPES and STS are surface-sensitive probes, they probe the electronic structure with different effective information depth. Within ARPES measurements, where the surface sensitivity is determined by the mean free path of the escaping photoelectrons, there is a finite contribution to the signal from the bulklike layers immediately below the surface. In contrast, STS probes the tails of the wave functions of the surface electrons, and is thus practically only sensitive to the outermost surface layer. Consequently, within our ARPES measurements in Figs. 1(c) and 1(d), we observe both the surface and (with lower intensity) bulklike electronic states. STM, however, probes only an insulating surface layer. We thus assign the metallic bands with weak spectral weight visible in ARPES to be those of the bulk crystal, consistent with prior transport studies which reveal metallicity in the bulk crystal [15,37]. Contrastingly, we attribute the incoherent states located at energies > 100 meV away from the Fermi level, which carry the dominant spectral weight in ARPES and which will dominate the gap edges in STS, as the lower and upper edges of a small Mott-gap. Our interpretation of these states as bulk and surface, respectively, are supported by additional ARPES experiments shown in Fig. 6 in [28]. Alternative origins for gap formation, such as charge or spin density waves or reorientation of the magnetic moments, would not be expected to open a full gap. Substantial surface doping is not expected to play a significant role due to the charge neutrality of the surface layer. We thus conclude that correlations, combined with the surface relaxation, drive the insulating gap we observe.

While our calculations highlight that the stability of the insulating surface state depends on the selected U value, we note that bulk $\text{Ca}_3\text{Ru}_2\text{O}_7$ is often considered close to an insulating instability [8,12], suggesting that the appropriate U value may lie close to the critical MIT in the bulk. Indeed, our calculations provide a qualitative rationalization of this instability of $\text{Ca}_3\text{Ru}_2\text{O}_7$, and demonstrate how the insulating state is hence stabilized by the surface relaxation [50].

In summary, via a combined approach of precise surface structural and spectroscopic measurements, accompanied by electronic structure calculations, we have found that a structural relaxation at the surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$ facilitates the formation of a correlation-driven insulating phase. This allows us to reconcile seemingly conflicting spectroscopic

measurements, and reveals the striking role that surface relaxations can have, even when they do not lead to a symmetry-lowering reconstruction. Our calculations highlight that this insulating phase is rather fragile, being on the verge of metallicity. This raises an opportunity to drive a phase transition into a metallic state with moderate external stimuli, for example, via the application of strain or electric field. Furthermore, the subtle structural relaxations at the surface of $\text{Ca}_3\text{Ru}_2\text{O}_7$ and the narrow U window within which we calculate the surface to be insulating while the bulk remains metallic indicate that the bulk material is also on the verge of a MIT, raising the possibility of driving the bulk through a phase transition.

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Data availability—The research data supporting this publication can be accessed at Ref. [52].

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