

Off-stoichiometric surface reconstruction in the altermagnetic candidate $\text{RuO}_2(100)/\text{Ru}(10\bar{1}0)$ Sungsoo Hahn^{1,*}, Minkyu Park^{1,*}, Yeonghoon Lee,¹ Changsoo Kim,¹ Jahyun Koo,¹ Minhyuk Choi¹, Seungwoo Song,¹ S. H. Rhim², Changyoung Kim,³ and Chanyong Hwang^{1,‡}¹Quantum Technology Institute, Korea Research Institute of Standards and Science (KRISS), Daejeon 34113, Republic of Korea²Department of Semiconductor Physics and Engineering, University of Ulsan, Ulsan 44610, Korea³Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea

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Recently, RuO_2 has gained significant attention as a promising altermagnetic candidate. However, the presence of magnetism in RuO_2 has been a topic of ongoing debate, with stoichiometry identified as a key factor by Smolyanyuk *et al.* [Phys. Rev. B **109**, 134424 (2024)]. To explore the stoichiometric effects in RuO_2 , we oxidized pure single-element Ru at several temperatures. The band structure modulation near Fermi level by stoichiometric variation was clearly observed by *in situ* angle-resolved photoemission spectroscopy. First-principles calculations revealed that this evolution was relevant to surface reconstruction induced by excessive O rather than altermagnetism. Additionally, our results indicate that the experimentally measured band structure of $\text{RuO}_2(100)/\text{Ru}(10\bar{1}0)$ aligns well with the nonmagnetic band calculations. Our findings not only provide a clue to resolve the current experimental discrepancy but also support the nonmagnetic ground state of RuO_2 films grown on Ru metal.

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I. INTRODUCTION

Ruthenium dioxide (RuO_2), a transition metal dioxide with a rutile structure, has attracted considerable attention due to its practical properties such as high chemical stability, catalytic activity, and conductivity [1–7]. However, the observation of superconductivity [8,9] and topological band structures [7,10,11] has brought the fundamental aspect of RuO_2 into the spotlight. Among these properties, the magnetism of RuO_2 is currently the most intriguing subject since being reported in Ref. [12]. In this regard, RuO_2 has recently been proposed as a material exhibiting altermagnetism, a ground state of *collinear* magnetism distinct from ferromagnetism and antiferromagnetism [13]. In altermagnets, zero net magnetization is achieved by a rotational symmetry so that the order of spin-polarized bands alternates in momentum space. These features allow the development of new spintronic devices that cannot be achieved with ferromagnets or antiferromagnets [13–16]. Furthermore, altermagnetic systems are expected to serve as a new field that accommodates novel physical phenomena [17–24].

Among many altermagnetic candidates such as MnTe [25–27], CrSb [28–31], and Mn_5Si_3 [32–34], the largest spin-splitting energy is expected in RuO_2 [13]. Accordingly,

there have been extensive attempts to find evidence of altermagnetism in RuO_2 . On the one hand, various experimental studies support altermagnetism [12,35–42]. On the other hand, recent studies of muon spin rotation and neutron scattering [43,44] have raised questions about the intrinsic magnetism of RuO_2 . Thus, the genuine magnetic ground state of RuO_2 remains controversial [45,46].

In oxide systems, phase transitions, especially magnetic transitions [47,48], can be induced by oxygen vacancies, namely, by stoichiometry variation. Furthermore, a recent density functional theory (DFT) calculation suggested that the altermagnetism is achieved via tuning the composition ratio of Ru to O [49]. In this context, the stoichiometry of RuO_2 is expected to be a key parameter for determining its magnetic state. However, there has been no experimental evidence for this claim to date, leaving us with a limited understanding of how the stoichiometry of RuO_2 affects its properties.

Here, we report the results of *in situ* angle-resolved photoemission spectroscopy (ARPES) study of RuO_2 with varying stoichiometry. We oxidized the surface of pure single-element Ru at several temperatures. Thereby the stoichiometry of RuO_2 during the synthesis process is more effectively controlled than conventional postannealing. This approach allows us to study the wide range of stoichiometric effect systematically. From our ARPES measurements, we observed band structures that appear only in RuO_2 oxidized at high temperature and not in RuO_2 oxidized at low temperature. We further performed DFT calculations to elucidate the origin of this difference and found that it emerges from surface reconstruction due to excessive O rather than altermagnetism. We also report the results of the ARPES and DFT study on the bulk band structure to find evidence of altermagnetism. Our investigation suggests that the physics of RuO_2 is highly affected by stoichiometry associated with growth conditions.

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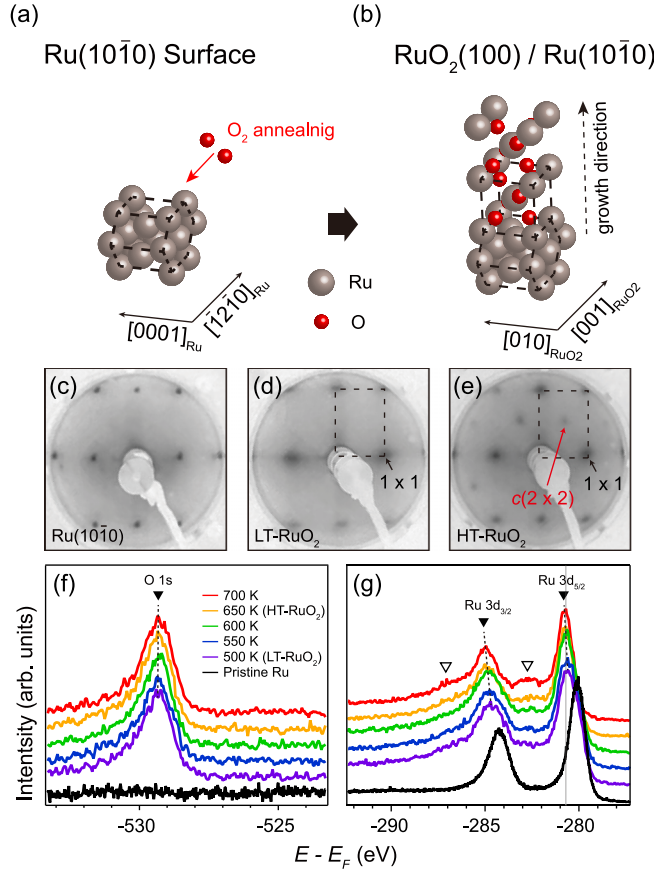


FIG. 1. Crystal structure of (a) Ru(10 $\bar{1}$ 0) before oxidation and (b) RuO₂/Ru(10 $\bar{1}$ 0) after oxidation. The black dashed line marks the unit cell of (a) Ru and (b) RuO₂. LEED patterns of (c) Ru(10 $\bar{1}$ 0), (d) RuO₂/Ru(10 $\bar{1}$ 0) oxidized at 500 K (LT-RuO₂), and (e) RuO₂/Ru(10 $\bar{1}$ 0) oxidized at 650 K (HT-RuO₂). The reciprocal 1×1 unit cell is highlighted by a black dashed line. The $c(2 \times 2)$ peak is indicated by a red arrow in panel (e). LEED measurements were performed with an electron kinetic energy of 58 eV at 300 K. Growth-temperature-dependent x-ray photoemission spectroscopy (XPS) spectrum of (f) O 1s and (g) Ru 3d peaks. Ru 3d peaks, shifting with growth temperature, are marked by black dashed lines and inverted triangles. Peaks from higher oxidation states are shown with empty inverted triangles. The Ru 3d_{5/2} peak in RuO₂ (Ru⁴⁺) single crystals at 280.7 eV [50] is shown for reference with a gray guideline.

II. RESULTS AND DISCUSSION

A. Off-stoichiometric surface reconstruction

See the Supplemental Material (SM) [51] for details of experimental methods and computational methods [52–65]. Schematics of the RuO₂ growth process is given in Figs. 1(a) and 1(b). When the Ru(10 $\bar{1}$ 0) surface is exposed to O₂ at the appropriate temperature, RuO₂ grows in the (100) direction [65–68]. The in-plane directions of single-crystalline RuO₂, [010] and [001], align with the [0001] and $[\bar{1}2\bar{1}0]$ directions of Ru, respectively. If the temperature is too low, the crystallinity of RuO₂ becomes poor, whereas excessively high temperatures lead to polycrystalline growth (see the SM [51], Fig. S1). The range of temperature conditions for synthesizing

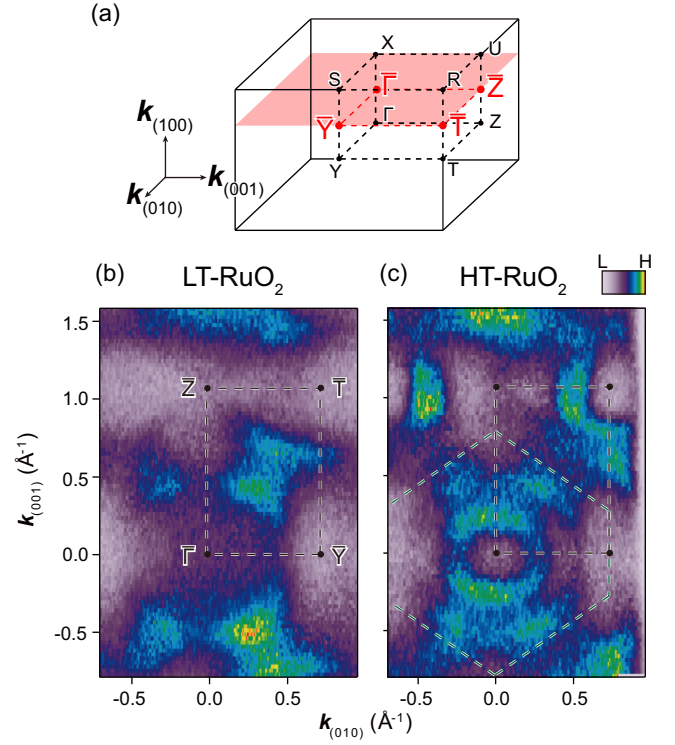


FIG. 2. (a) Brillouin zone (BZ) of RuO₂ in the convention of orthorhombic lattice. The red-shaded plane corresponds to the k plane where ARPES was carried out with a photon energy of $h\nu = 40.8$ eV. Constant energy maps at the Fermi level (E_F) of (b) LT-RuO₂ and (c) HT-RuO₂ measured by ARPES at 10 K. Each map was obtained by integrating over an energy window of ± 5 meV around the E_F . The black dashed line marks the quadrant of BZ; the green dashed line in panel (c) marks the first BZ of the reconstructed HT-RuO₂.

single-crystalline RuO₂ was from 500 to 700 K. In this study, we compare RuO₂ oxidized at 500 K (LT-RuO₂) and RuO₂ oxidized at 650 K (HT-RuO₂) to highlight the difference.

The low-energy electron diffraction (LEED) images of the clean Ru(10 $\bar{1}$ 0) surface before oxidation, LT-RuO₂, and HT-RuO₂ are shown in Figs. 1(c)–1(e), respectively. The LEED images indicate that both LT-RuO₂ and HT-RuO₂ grew as single crystals without any misaligned domains. Notably, HT-RuO₂ displays $c(2 \times 2)$ peaks, which are absent in the LT-RuO₂ image. Previous studies have reported that this surface reconstruction originates from the formation of tetrahedral RuO₄ at the surface [61,62]. Within the optimal growth range, increasing growth temperature gradually enhances the intensity of the $c(2 \times 2)$ peak (see SM [51], Fig. S1). This reflects an increased proportion of the reconstructed area across the entire sample surface.

To further investigate the growth-temperature dependence of RuO₂, we performed x-ray photoemission spectroscopy measurements. Figures 1(f) and 1(g) show the core-level spectra of RuO₂ as a function of growth temperature. The Ru 3d peak shows an evident shift depending on the growth temperature, while the O 1s peak remains constant. As the growth temperature increases, the Ru 3d peak shifts towards a higher binding energy, which implies a decreasing

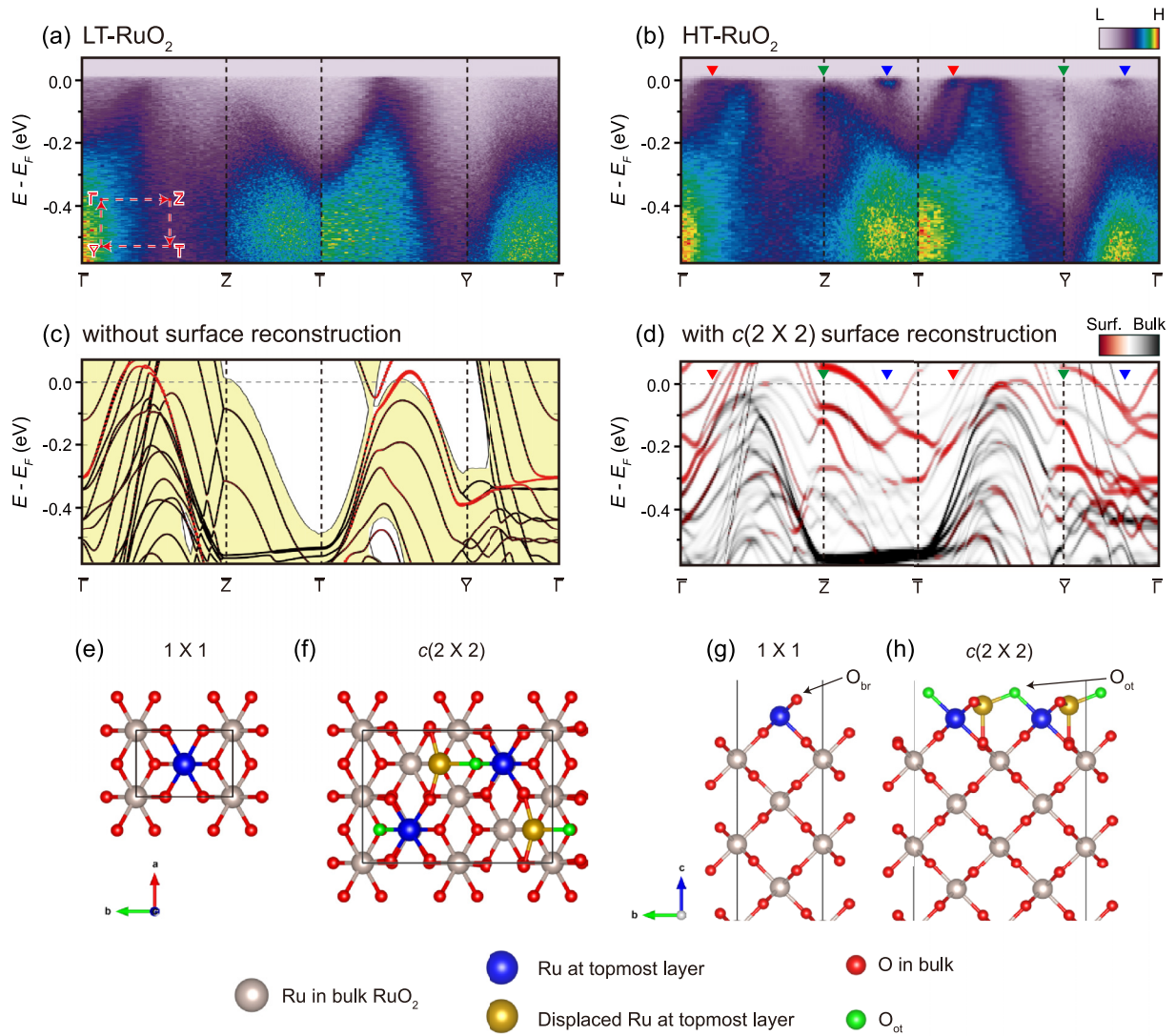


FIG. 3. E vs k dispersion of (a) LT-RuO₂ and (b) HT-RuO₂ from ARPES results along the high symmetric lines in the surface BZ. The differences in the band structure between LT- and HT-RuO₂ are marked with red, green, and blue inverted triangles in panel (b). DFT-calculated E vs k dispersions of nonmagnetic slab RuO₂ (c) without and (d) with surface reconstruction. Surface contributions are denoted in red. In panel (c), the bulk-band continuum is shown as a yellow background. In panel (d), the bulk band intensity represents the spectral weight obtained from band unfolding, whereas that of surface bands is slightly exaggerated for better visibility. (e)–(h) RuO₂(100) slab structure used in DFT calculations. Top views of RuO₂(100) slab structure (e) without and (f) with $c(2 \times 2)$ surface reconstruction. Side views of RuO₂(100) surface structure (g) without and (h) with $c(2 \times 2)$ surface reconstruction. The conventional unit cell after surface reconstruction is shown by a solid line in panels (f) and (h). As explained in the text, O_{ot} induces surface reconstruction. In panels (f) and (h), half of the surface Ru atoms denoted by yellow were displaced from their bulk positions toward O_{ot}.

contribution of the peak corresponding to the lower oxidation state. In other words, lower growth temperatures induce oxygen vacancies, whereas increasing the growth temperature increases the oxygen contents of RuO₂. We can also observe a peak around 282.30 eV (marked with an empty inverted triangle), which is enhanced as the growth temperature increases. This peak was attributed to the signal of RuO_x, which has an oxidation state higher than that of RuO₂, formed on the surface due to excessive oxygen [50,69]. Our DFT calculation assuming the higher oxidation state matches the measured ARPES results well, which is discussed later, further supporting this interpretation. Overall, this result indicates that

the oxidation state of Ru varies with the growth temperature of RuO₂.

We characterized uniaxially strained RuO₂ by LEED measurements, and the results are presented in Fig. S7 of the SM [51]. The lattice of RuO₂ was strained by -4.5% along the [010] direction, whereas it was fully relaxed along the [001] direction due to a large lattice mismatch (-12.8%) [65]. Although the magnitude of applied strain was quite large, the RuO₂ band structure was expected to be similar (for the DFT result without and with strain, see Fig. S6 in the SM [51]). Note that high-symmetry points of the orthorhombic lattice were used in this work [see Fig. 2(a)]. Therefore, we leave the strain-induced effect [8,9,37,70] as a future study.

ARPES measurements are performed to study the effect of stoichiometric differences on the electronic structures. The light source used for the experiments was He-II ($h\nu = 40.8$ eV), which corresponds to $k_{(100)} = 0.5\pi/a$ in reciprocal space as shown in Fig. 2(a) (the inner potential was $V_0 \approx 15$ eV) [10,35]. Comparing constant energy maps taken at the E_F for LT- and HT-RuO₂ shown in Figs. 2(b) and 2(c), respectively, an additional circular pocket band surrounding the $\bar{\Gamma}$ in HT-RuO₂ was observed.

The differences between LT- and HT-RuO₂ are more evident in ARPES cuts along the high-symmetry lines shown in Figs. 3(a) and 3(b). Three distinct features that are absent in LT-RuO₂ appear in HT-RuO₂. First, we find the dispersive band near $\bar{T}$ that crosses the E_F (red inverted triangle). Second, there is another band, which has its band top at $E_F - 20$ meV, located at $\bar{Z}$ (green inverted triangle). Third, an intense spectral feature very close to the E_F , is observed near $\bar{\Gamma}$ (blue inverted triangle). Each feature is shown twice in ARPES cuts due to $c(2 \times 2)$ surface reconstruction.

To explain the ARPES results, the band structure of a slab is calculated without and with $c(2 \times 2)$ surface reconstruction. We constructed a slab with stoichiometric termination by bridging oxygen atoms (O_{br}) [65]. The $c(2 \times 2)$ surface-reconstructed structure is obtained by adding on-top oxygen atoms (O_{ot}) on one half of a 2×2 enlarged surface that induces displacement of half of the surface Ru atoms denoted by yellow in Figs. 3(f) and 3(h) [61]. In other words, this reconstructed surface contains two additional O atoms per 2×2 unit cell compared to the stoichiometric surface. The reconstructed surface structures are shown in Figs. 3(f) and 3(h), while Figs. 3(e) and 3(g) display the bulk-truncated stoichiometric surface of RuO₂(100). The computed band structure in each case is shown in Figs. 3(c) and 3(d) without and with surface reconstruction, respectively, where contributions from the surface layer are highlighted in red. The band at $\bar{Z}$ (green inverted triangle), the dispersive band along the $\bar{T}$ - $\bar{Y}$ line (red inverted triangle), and the band that slightly crosses the E_F on the $\bar{Y}$ - $\bar{\Gamma}$ line (blue inverted triangle) are clearly identified as surface bands of the reconstructed surface. On Fermi surface maps shown in Fig. 4(b), we can check that characteristic features of HT-RuO₂ and the calculated surface band of the slab with surface reconstruction show an excellent agreement again. Thus, evidently, the surface reconstruction of HT-RuO₂ is driven by excessive O.

B. Altermagnetism

Now, we carefully examine the band dispersion of the bulk bands (which is not related to surface reconstruction) observed in the spectra of LT- and HT-RuO₂ to find evidence of altermagnetism. One defining property of altermagnets is the lack of PT symmetry, i.e., broken Kramers degeneracy in momentum space. (P , inversion; T , time reversal.) Therefore, a spin-split band should be observed in any regions of reciprocal space except at high-symmetry points or planes in an altermagnetic system. Note that He-II light, which can measure the most distant reciprocal points from high-symmetry lines [represented as red shaded plane in Fig. 2(a)],

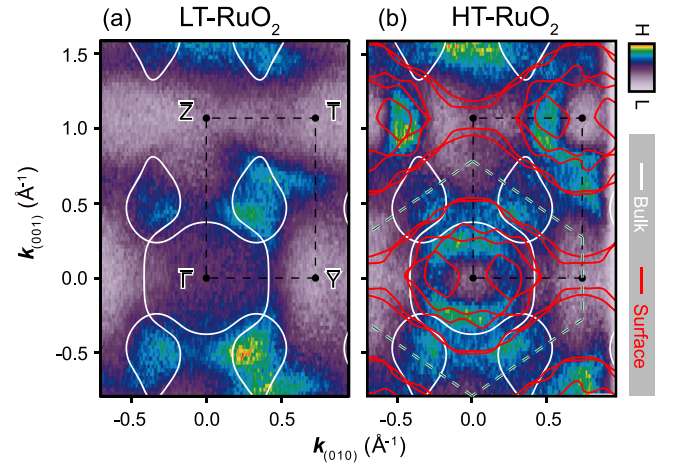


FIG. 4. Constant energy maps at the Fermi level (E_F) of (a) LT-RuO₂ and (b) HT-RuO₂, overlaid with the Fermi surface at the $k_{(100)} = 0.5\pi/a$ plane obtained by nonmagnetic bulk calculation (white solid lines). In panel (b), calculated surface-layer-dominant bands of nonmagnetic $c(2 \times 2)$ slab are also overlaid (red solid line).

is an ideal choice for observing the altermagnetic spin-split gap that closes at high-symmetric points.

Our bulk calculation results predict a distinct Fermi surface at $k_{(100)} = 0.5\pi/a$ for nonmagnetic and altermagnetic phases, as shown in Figs. 5(a) and 5(b). The lifting of spin degeneracy in the altermagnetic state leads to a modulation of the bulk band structure relative to the nonmagnetic state. We found that nonmagnetic calculation predicts features that closely match the measured Fermi surface of LT-RuO₂, whereas the altermagnetic calculation shows some discrepancies with the experimental data. For example, a band parallel to the $k_{(001)}$ direction near the $\bar{Y}$ point and a small spin-split pocket around the $\bar{\Gamma}$ point, predicted by the altermagnetic calculation, were not observed in the experimental spectra. For a more detailed analysis, we compared the experimental bulk band dispersion of LT-RuO₂ with nonmagnetic and altermagnetic calculations along high-symmetric lines as shown in Figs. 5(c) and 5(d). Calculation results show a spin-split band structure along the $\bar{Z}$ - $\bar{T}$ and $\bar{Y}$ - $\bar{\Gamma}$ lines, which are parallel to $k_{(010)}$. Band dispersion along the $\bar{\Gamma}$ - $\bar{Z}$ and $\bar{T}$ - $\bar{Y}$ lines also shows a slight change. Unfortunately, broad ARPES spectra made it impossible to clarify the presence of spin-split bands. However, considering the overall energy positions and number of bands, the nonmagnetic calculation appears to match the experimental results better than the altermagnetic calculation. We further examined whether the stoichiometric effect could change the magnetic ground state of RuO₂ (see the SM [51], Fig. S9). However, the measured bulk band of HT-RuO₂ (e.g., all bands except for characteristic features from surface reconstruction) showed no significant change when compared to that of LT-RuO₂. Therefore, based on the comparison between DFT calculations and ARPES results, RuO₂ appears to be nonmagnetic regardless of its stoichiometry. However, determining the magnetic ground state of the system through a comparison of ARPES and DFT is a very indirect and uncertain approach. Therefore, we cannot confirm the genuine magnetic ground state of

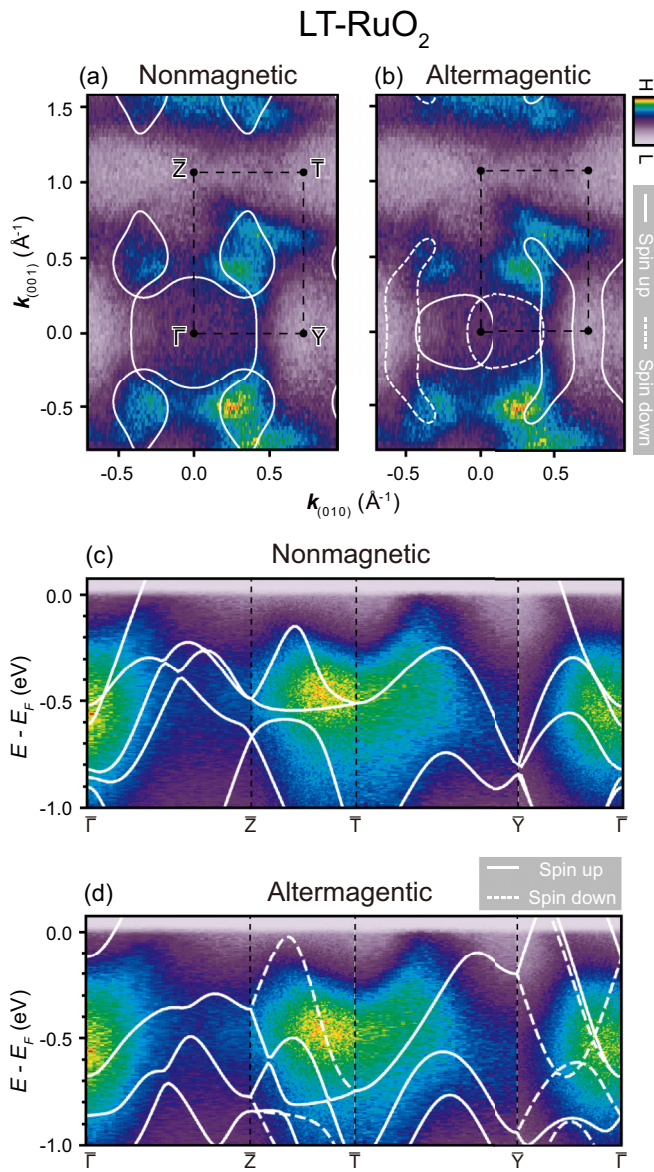


FIG. 5. Constant energy maps at the Fermi level (E_F) of LT-RuO₂ overlaid with the Fermi surface at the $k_{(100)} = 0.5\pi/a$ plane obtained by (a) nonmagnetic and (b) altermagnetic bulk calculations. E vs k dispersion of LT-RuO₂ from ARPES results overlaid with the band dispersions obtained by (c) nonmagnetic and (d) altermagnetic calculations.

RuO₂ in this study. To resolve this, clear ARPES (or spin-ARPES) measurements are needed to clarify the presence or absence of altermagnetic spin splitting in the RuO₂ bulk band.

In this study, we have focused on the (100) surface of RuO₂. Other stable surfaces such as (110) or (101) surfaces [71–74] may host similar surface bands we observed. We believe that these off-stoichiometric surface structures could be linked to outstanding catalytic properties of RuO₂. From the perspective of altermagnetism studies, however, these surface structures will complicate the determination of the genuine magnetic ground state of RuO₂, which could potentially explain the experimental discrepancies observed in previous reports.

III. CONCLUSIONS

In summary, we have grown RuO₂ by oxidizing Ru at various temperatures to tune stoichiometry systematically. We have demonstrated that the electronic structure of RuO₂ is modulated by the small difference in growth conditions. Even relatively small temperature variation induces surface reconstruction and modulation of electronic structures. With DFT calculations, we have verified that these changes are solely relevant to surface reconstruction caused by excessive O, not by altermagnetism. This off-stoichiometric surface reconstruction may have contributed to the experimental discrepancies in determining the true magnetic ground state of RuO₂. Furthermore, our ARPES results indirectly support the nonmagnetic state of RuO₂, regardless of its stoichiometry.

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DATA AVAILABILITY

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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