Direct observation of the Mottness and p-d orbital hybridization in epitaxial monolayer α-RuCl₃

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Article

Keywords: α-RuCl₃, chemical physics, nanoscience

DOI: https://doi.org/10.21203/rs.3.rs-646319/v1

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Abstract

α-RuCl₃, with abundant studies in its bulk phase, has shown the promising potential to approach the two-dimensional Kitaev honeycomb model and to realize the consequential quantum spin liquids. In this material, some ingredients spark off the hunting of quantum spin liquid states: the localized magnetic moments on each Ru³⁺ ion guaranteed by the Mottness, the Kitaev-type interaction originating from the superexchange path over the p-d bonds, and the nearly two-dimensional nature of the van der Waals coupled honeycomb layers. Here, we worked out the growth art of α-RuCl₃ monolayer on highly oriented pyrolytic graphite substrate for the first time, and then studied its electronic structure, particularly the delicate orbital occupations. Through scanning tunneling microscopy and spectroscopy study, the bonding configurations are justified by the features of pronounced t₂g-pπ and e₉-pσ hybridization, and the Mott nature is unveiled by an ~ 0.6 eV full gap at the Fermi level located in the t₂g-pπ level. Our experimental results agree well with the density functional theory calculations of the monolayer system. In accordance with previous theoretical research, the epitaxial monolayer α-RuCl₃ system holds high tunability comparing to its bulk phase and provides a novel platform to explore the Kitaev physics.

Introduction

α-RuCl₃ is gifted of yielding quantum spin liquid (QSL) state, the prominent elusive phase of matter that exhibits high entanglement and topological order, through the intrinsic frustration embedded in the Kitaev-type bond-dependent interactions of magnetic moments in a honeycomb lattice¹⁻⁶. Conforming to the Jackeli-Khaliullin mechanism, a strong Coulomb repulsion localizes the spin-orbit entangled J_{eff}=1/2 moments in Mott-insulating α-RuCl₃, and the Kiteav interaction emerges from the superexchange process through the Ru-Cl-Ru path over its t₂g-pπ bonds (namely the t₂g-pz bonds in their proposal¹). Therefore, it has attracted enormous studies on α-RuCl₃ which show evidences of Kitaev-type magnetic interactions and itinerant Majorana fermions in the bulk phase⁷⁻¹⁴.

Comparing to the bulk, monolayer α-RuCl₃ is closer to the two-dimensional Kitaev model since the stacking faults in bulk may cause additional magnetic transitions at 8-14K¹⁵,¹⁶. In addition, the electronic and magnetic properties of monolayer are more tunable by the application of strain, doping, and interfacial effect which were recently predicted to be promising routes in searching for novel states of matter¹⁷⁻²⁰. However, it has been difficult to synthesize high-quality, high-coverage, and chemically pure monolayer α-RuCl₃ which enables access to its intrinsic properties, and the study of monolayer α-RuCl₃ remains scarce and challenging.

In this work, we successfully synthesized high-quality monolayer α-RuCl₃ on highly oriented pyrolytic graphite (HOPG) substrate by molecular beam epitaxy (MBE). Through low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) studies, we found an in-plane lattice expansion in the α-RuCl₃ monolayer compared to bulk and the persistence of the Mott nature as evidenced by an ~ 0.6
eV full Mott gap. Noting that the previous STM work on the $\alpha$-RuCl$_3$ thin film ($\approx$ 15–30 layers) shows an $\sim$ 0.25eV gap$^{21}$, the gap size of the monolayer is significantly magnified, which could result from the enhancement of the Coulomb correlation due to the reduced electronic screening in a two-dimensional system$^{22–24}$. The observed electronic states agree with the distinct features of $t_{2g}$-$p_\pi$ and $e_g$-$p_\sigma$ bonds. Both the energy spectroscopy and the real-space images are in good agreement with density functional theory (DFT) calculations. The Mott gap in the $t_{2g}$ manifold is justified by a comprehensive study of experiment and theory. Our attempts of the structural modification via interfacial effect on the monolayer scale are a rehearsal of tuning the relevant electronic/magnetic properties and exploring the Kitaev physics in $\alpha$-RuCl$_3$.$^{17,25–27}$

Results

Synthesis and topography of RuCl$_3$

Two structural phases of RuCl$_3$ thin films were found in the growth process. First, $\beta$-RuCl$_3$ chains and disordered $\alpha$-RuCl$_3$ fragments are self-assembled on the surface. Highly ordered $\alpha$-RuCl$_3$ monolayer appears and proliferates gradually in the annealing process. Figure 1(a)[(b)] shows the crystal structure of monolayer $\alpha$-RuCl$_3$ ($\beta$-RuCl$_3$) where the edge (face)-sharing RuCl$_6$-octahedra constitute the honeycomb lattice (zigzag chains) of $\alpha$-form ($\beta$-form). In bulk, the $\beta$-phase is metastable and can be converted to $\alpha$-phase at 450–600 °C$^{30}$ and Fig. 1(c) shows the RHEED patterns of the sample after preliminary growth, further deposition, and annealing from the top down. The preliminary growth of submonolayer RuCl$_3$ gives the RHEED pattern [Top of Fig. 1(c)] of only $\beta$-phase and the corresponding STM image is given in Fig. 1(d). Further deposition leads to the coexistence of $\alpha$- and $\beta$-phase as shown in the RHEED pattern [middle of Fig. 1(c)]. Nanoscale STM topography [Fig. 1(e)] reveals compact domains of poorly ordered $\alpha$-area and highly crystalized $\beta$-area. The image Fig. 1(f) gives the detailed structure of $\beta$-RuCl$_3$ which shows neck-and-neck zigzag chains. The lattice constants of $a = 5.5$ Å, $b = 6.1$ Å are straightforward indications of $\beta$-RuCl$_3$. Post annealing of fully covered monolayer film does not cause a significant change of lattice constant [bottom of Fig. 1(c)]. However, a structural phase transition is inferred by the STM topographic image [Fig. 1(h)], where a reduction of coverage [Fig. 1(g)] and a proliferation of $\alpha$-RuCl$_3$ monolayer with $\beta$-RuCl$_3$ dressed in pieces can be seen. A blurred triangular lattice resolved at high tunneling resistance [Fig. 1(i)] stands for $\alpha$-RuCl$_3$ (See Fig. 3 for details) with a lattice constant of 6.19 Å, which can be well distinguished from the rectangular lattice of $\beta$-RuCl$_3$. Comparing to 5.99 Å in the bulk$^{31}$, the in-plane lattice constant of the $\alpha$-RuCl$_3$ layer is expanded by 3%, which fits the expectation for this heterostructure.$^{17}$

Electronic properties and orbital textures of d-p bonds

Figure 2(a) shows the typical dI/dV experimental spectrum of $\alpha$-RuCl$_3$ monolayer (black solid line) and the calculated total DOS where majority and minority spins are represented by green and orange dashed...
The total DOS was given by the LSDA + SOC + U calculations, where the lattice constant \( a = b = 6.19 \, \text{Å} \) and a vacuum spacing of 15 Å were employed. The DFT calculations come out with a Mott phase and an energy splitting of \( t_{2g} \) orbitals, which well explain the STS result. The Mott nature is supported by an \( \sim 0.6 \, \text{eV} \) full gap around Fermi level in the experimental curve. The \( \sim 1.0 \, \text{eV} \) peak-to-peak Mott gap is consistently given by both the experiment and calculation as marked in Fig. 2(a). In Fig. 2(b), the calculated partial density of states (PDOS) graph exhibits an \( \sim 2.0 \, \text{eV} \) splitting of \( t_{2g} \) and \( e_g \) orbitals due to the octahedral crystal field. The Cl-3p orbital occupies the valence band below \( \approx -2.0 \, \text{eV} \), while the Ru-4d orbital resides between \( \approx -2.0 \, \text{eV} \) and \( \approx 3.0 \, \text{eV} \). Meanwhile, the orbital hybridization induces the mixture of \( p \) and \( d \) components in the whole energy scale. We projected the \( p \) orbitals onto the degeneracy-lifting basis of \( p_{\pi} \) and \( p_{\sigma} \) orbitals and found that, specifically, the hybridization undergoes in the manner of \( t_{2g} \cdot p_{\pi} \) and \( e_g \cdot p_{\sigma} \) bonding in Fig. 2(b). In the energy range of \( t_{2g} \) orbitals, the PDOS of the \( p_{\pi} \) component is much larger than the \( p_{\sigma} \) one due to the dominant \( pd_{\pi} \) bonding. In the energy range of \( e_g \) orbitals, instead, the \( p_{\sigma} \) component is much larger due to the \( pd_{\sigma} \) bonding.

As expected, we observed distinct STM patterns in the energy ranges of different orbitals. Figure 3(a-f) are the typical constant-current STM images at indicated bias voltages. In the \( t_{2g} \) and \( p_{\pi} \) dominating energy range (-3.0 to 1.5 eV), three protrusions are resolved in each surface unit cell forming a “Kagome-like” lattice. However, in the energy range of \( e_g \) orbital, only one protrusion is observed appearing as a cluster of three, forming a triangular lattice of the trimers. Similar phenomena were observed in the STM images of CrI\(_3\) thin film\(^{33}\). Figure 3(g, h) show the simulated constant-current STM images, i.e. the isosurface of DOS integrated from Fermi level to the bias energy, based on Tersoff-Hamann model\(^{34}\). Figure 3(g) is the typical simulated image at 0.9V while all the images of the \( t_{2g} \) range show the same “Kagome-like” pattern. It is found that the images can be well explained by the two types of the Cl-3p states, specifically the \( p_{\pi} \) type for Fig. 3(g) and the \( p_{\sigma} \) type for Fig. 3(h). In detail, the lobes of \( p_{\pi} \) are perpendicular to the corresponding Ru\(_2\)Cl\(_2\) plane which is formed by two Ru ions and two bridging Cl ions [the case of experimental images Fig. 3(a-e) and the simulated image Fig. 3(g)], while the lobes of \( p_{\sigma} \) lie in the Ru\(_2\)Cl\(_2\) plane [the case of the experimental image Fig. 3(f) and the simulated image Fig. 3(h)]. The \( t_{2g} \) (\( e_g \)) orbital primarily hybridizes with the \( p_{\pi} \) (\( p_{\sigma} \)) orbital based on the large orbital overlap and thus forms the \( pd_{\pi} \) (\( pd_{\sigma} \)) bond. The STM images are dominated by the upper lobes of the topmost Cl- \( p_{\pi} \) and Cl- \( p_{\sigma} \) states which reside on the opposite sides of the Cl ion and evolve into the vacuum. The distinct orientations of the Cl-p states of two types produce the shift (orange and green arrows) of image intensity with respect to the Cl atom sites (blue balls) as marked in Fig. 3(g, h). Thus, Cl- \( p_{\pi} \) and Cl- \( p_{\sigma} \) orbitals directly link to the \( t_{2g} \) and \( e_g \) orbitals surrounding the Ru atoms, respectively. The same \( t_{2g} \cdot p_{\pi} \) textures across the fermi level clearly illustrates the monolayer system remains in Mott phase.

Conclusions

In conclusion, the strained \( \alpha \)-RuCl\(_3\) monolayer interfacing graphite was fabricated by the method of MBE.
monolayer was validated by the accordant STM measurements and DFT calculations. The monolayer system enables the local tunneling probes to join the search of topological quantum magnets as a powerful weapon targeting the atomic-scale structure, electronic properties, and correlations, microscopic magnetic order as well as the excitation of unusual quasiparticle\textsuperscript{35-37}. The strained $\alpha$-RuCl\textsubscript{3} would definitely make the spin-orbital structure, as well as inherent magnetic interactions, differ from the bulk system. Besides the stretched lattice (and the widened Ru-Cl-Ru bond angle) which may be advantageous for the advancement toward Kitaev limit\textsuperscript{17,26,27,38,39}, the magnetic anisotropy of the system could have a favorable out-of-plane easy axis. Thus, it’s intriguing and worth more studies that what the exact magnetic ground order is.

**Methods**

The $\alpha$-RuCl\textsubscript{3} monolayer was grown on cleaved HOPG by MBE at a base pressure of $\sim 1\times 10^{-9}$ mbar. The commercial anhydrous RuCl\textsubscript{3} powder was evaporated at 324 °C and the substrate was kept at 180 °C during film growth. After the growth, the RuCl\textsubscript{3} sample was annealed up to 317 °C in half an hour. The process of growth was monitored by reflective high-energy electron diffraction (RHEED). The subsequent in situ STM and STS measurements were done at 5 K with tungsten tips. DFT calculations were performed by the full-potential augmented plane wave plus local orbital code (Wien2k)\textsuperscript{28}. The muffin-tin sphere radii of Ru and Cl atoms were chosen to be 2.2 and 2.1 Bohr, respectively. The plane-wave cut-off energy for interstitial wave functions was set to be 14 Ry. The integration over the Brillouin zone was carried out on a 14×14×1 k-mesh. To account for the electron correlation, the local spin density approximation plus Hubbard U (LSDA + U) method\textsuperscript{29} was employed and typical values of Hubbard U = 3.0 eV and Hund exchange $J_{\text{H}}$=0.5 eV were used for Ru 4d states. The spin-orbit coupling (SOC) was included for Ru 4d and Cl 3p orbitals via the second-variational method with scalar relativistic wave functions.

**Declarations**

**ACKNOWLEDGMENTS**

C. G. acknowledges funding from the National Key Research and Development Program of China (Grant No. 2019YFA0308404, 2016YFA0300904), National Natural Science Foundation of China (Grant No. 11427902 and 11674063), Science and Technology Commission of Shanghai Municipality (Grant No. 20JC1415900) and Shanghai Municipal Science and Technology Major Project (Grant No.2019SHZDZX01). H. W. acknowledges support from the NSF of China (Grant No. 11674064) and the National Key Research and Development Program of China (Grant No. 2016YFA0300700). F. Y. is sponsored by Shanghai Pujiang Program No. 19PJ1401000 and National Natural Science Foundation of China (Grant No. 12004076).

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**Figures**
Figure 1

Structure and STM topography of RuCl₃. (a,b) Atomic structures of α-RuCl₃ and β-RuCl₃. (c) RHEED patterns of β-RuCl₃ grown on HOPG substrate after preliminary deposition (top) and β-RuCl₃ as well as amorphous α-RuCl₃ grown during further deposition (middle) and sample after annealing at 317 °C (bottom). The diffraction stripes of HOPG, β-RuCl₃, and α-RuCl₃ are indicated. (d) Large scale STM image of β-RuCl₃ chains after preliminary growth (U=1.9 V, I=100 pA). (e) STM image shows the coexistence of β-RuCl₃ chains and amorphous α-RuCl₃ after further deposition (U=1.6 V, I=100 pA). (f) High-resolution image of β-RuCl₃ (U=1.4 V, I=100 pA). (g-i) STM images after post-annealing. (g,h) Large scale and small scale images show the coexistence of both forms of RuCl₃ (g: U=2.3 V, I=100 pA, h: U=1.5 V, I=300 pA). (i) STM image of α-RuCl₃ (U=2.8 V, I=100 pA) shows a triangular lattice with a 6.19 Å lattice constant.
Figure 2

Spectrum and DFT results. (a) STS of $\alpha$-RuCl$_3$ monolayer (solid black line, $U=2.2$ V, $I=5.8$ nA, bias modulation amplitude $\Delta U=20$ mV at frequency $f=983$ Hz) and calculated total DOS for the ground state of the $\alpha$-RuCl$_3$ monolayer by LSDA+SOC+U, the dashed green (orange) curve describes the majority (minority) spins. The size of the full gap and the peak-to-peak gap is indicated. (b) The orbital PDOS of the $\alpha$-RuCl$_3$ monolayer. The green (orange) curves describe the majority (minority) spins and the Fermi level is set to the middle of the gap.
Figure 3

energy-resolved orbital textures. (a-f) Bias-dependent STM images in the constant-current mode. (a: U=-3.0 V, I=-15 nA. b: U=-1.5 V, I=-10 nA. c: U=0.5 V, I=0.5 nA. d: U=0.9 V, I=0.6 nA. e: U=1.4 V, I=0.6 nA. f: U=2.8 V, I=100 pA). (g, h): The representative constant-current-image simulations at 0.9 V with the distorted “Kagome” lattice and 2.8 V with the triangularly arranged trimers, respectively. The Ru-hexagon (gray balls) and topmost Cl ions (blue balls) are put at the right positions in the lattice. The orange and green arrows represent the displacement from Cl sites to the bright protrusions.