Theoretical study of the crystal and electronic properties of α-RuI₃

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The material α-RuCl₃, with a two-dimensional Ru honeycomb sublattice, has attracted considerable attention because it may be a realization of the Kitaev quantum spin liquid. Recently, a new honeycomb material, α-RuI₃, was prepared under moderately high pressure, and it is stable under ambient conditions. However, different from α-RuCl₃, α-RuI₃ was reported to be a paramagnetic metal without long-range magnetic order down to 0.35 K. Here, the structural and electronic properties of the quasi-two-dimensional α-RuI₃ are theoretically studied. First, based on first-principles density functional theory calculations, the ABC stacking honeycomb-layer R3 (No. 148) structure is found to be the most likely stacking order for α-RuI₃ along the c axis. Furthermore, both R̅3 and P31c are dynamically stable because no imaginary frequency modes were obtained in the phononic dispersion spectrum without Hubbard U. Moreover, the different physical behavior of α-RuI₃ compared to α-RuCl₃ can be understood naturally. The strong hybridization between Ru 4d and 5p orbitals decreases the “effective” atomic Hubbard repulsion, leading the electrons of RuI₂ to be less localized than in RuCl₂. As a consequence, the effective electronic correlation is reduced from Cl to I, leading to the metallic nature of α-RuI₃. Based on the DFT+U (U_eff = 2 eV) plus spin-orbital coupling, we obtained a spin-orbit Mott insulating behavior for α-RuCl₃ and, with the same procedure, a metallic behavior for α-RuI₃, in good agreement with experimental results. Furthermore, when introducing large (unrealistic) U_eff = 6 eV, the spin-orbit Mott gap opens in α-RuI₃ as well, supporting the physical picture we are proposing. Our results provide guidance to experimentalists and theorists working on two-dimensional transition metal tri-iodide layered materials.

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I. INTRODUCTION

Due to their rich physical properties, low-dimensional materials continue to attract considerable attention in the condensed-matter community [1–19]. In systems with 3d transition-metal (TM) atoms, the electronic correlation couplings (i.e., Hubbard repulsion U and Hund’s coupling J_H) play a key role in understanding their physical properties. Their spin-orbital coupling (SOC) λ is considered to be negligible. In those compounds, a wide variety of remarkable physical phenomena have been found to be driven by the bandwidth W (corresponding to the kinetic hopping parameter t) and the electronic correlation couplings. The unusual states induced include high-T_c superconductivity [1,20–23], ferroelectricity triggered by spin or charge ordering [24–27], orbital ordering [28–30], and charge or spin density waves [9,31,32].

However, the 4d and 5d orbitals are more spatially extended than the 3d orbitals, leading to increased hopping t in the 4d/5d case. Furthermore, U and J_H are also reduced in the 4d/5d systems compared to those for 3d electrons [33,34]. Moreover, the SOC parameter λ is enhanced in 4d/5d systems [35], inducing comparable values of λ with U and J_H. In this case, several intriguing electronic phases have been reported in 4d and 5d low-dimensional materials. In some dimer systems with 4d or 5d TM atoms, an interesting orbital-selective Peierls phase could be stable [36,37] when the intrahopping t is larger than the typical Hund’s couplings. This phase resembles the previously discussed orbital-selective Mott phase [38–41], but with the localized band induced by a Peierls distortion instead of Hubbard interactions [36,37]. The Hubbard repulsion U can lead to the localization of the spin-orbit coupled pseudospin degrees of freedom, resulting in a “spin-orbit Mott” insulating phase [42–44].

More interestingly, due to the strong bond-dependent anisotropic coupling among spins, a quantum spin liquid (QSL) ground state due to spin quantum fluctuations and frustration is theoretically obtained in the spin-1/2 honeycomb lattice via the Kitaev model [45]. Honeycomb lattice materials with spin-1/2 were proposed to realize the Kitaev physics, such as the 5d⁵ iridates A₂IrO₃ (A = Na, Li) [46–51]. In those systems, the concept of spin-1/2 arises from the effective J_eff = 1/2 pseudospins induced by the strong SOC and crystal-field splitting [42]. However, due to substantial lattice distortions, such as dimerization under hydrostatic pressure, the J_eff = 1/2 physical picture is destroyed [52,53], and the Kitaev QSL is not realized.

A related Kitaev QSL candidate material is α-RuCl₃ with a 4d⁵ electronic configuration analog to the 5d⁵ iridates [54]. This material also forms layered two-dimensional honeycomb structures, and the 4d⁵ electronic configuration of Ru is in a low-spin state with S = 1/2, producing J_eff = 1/2 pseudospins [55,56]. At ambient conditions, α-RuCl₃ exhibits spin-orbital Mott insulating behavior with a zigzag antiferromagnetic (AFM) ordering at 7–13 K [56,57]. Several stacking
orders have been reported that belong to different space groups, such as $C2/m$ (No. 12) [55,56,58], $P3_11c$ (No. 163) [72], and $R3$ (No. 148) [60]. Its unconventional interesting behavior, such as highly unusual magnetic excitations, the emergence of Majorana fermions, and a possible Kitaev QSL, has attracted considerable attention in both experiments and theories related to this compound [58,60–70].

Very recently, a new honeycomb-structured material, $\alpha$-Ru$I_3$, was synthesized at moderately high pressures [71,72]. In general, considering the atomic number of I, the SOC effect should be larger than in Cl, which may lead to more interesting physical properties in Ru$I_3$. Before the experimental preparation of $\alpha$-Ru$I_3$, there were only a few theoretical studies focusing on the monolayer form [73,74]. Preliminary characterization reveals metallic and paramagnetic behavior, with the absence of long-range magnetic order down to 0.35 K [71,72]. For $\alpha$-Ru$I_3$ two different stacking orders were reported along the $c$ axis: the $R3$ (No. 148) structure with three-layer ABC stacking honeycomb-layer centrosymmetric rhombohedral symmetry [71] and a two-layered honeycomb structure model with space group $P3_11c$ (No. 163) [72]. In each $RuI_6$ plane, the honeycomb layers are built of edge-sharing $RuI_6$ octahedra. Different from the Ru-Cl bonds in $\alpha$-RuCl$_3$ [55], the Ru-Ru bonds are identical, with a Ru-Ru bond of length 3.92 Å [71]. The van der Waals (vdW) layer distance is about 6.3 Å, larger than the value for $\alpha$-RuCl$_3$ (~5.7 Å) [71], suggesting a weaker interlayer coupling in $\alpha$-Ru$I_3$ than in $\alpha$-RuCl$_3$. Then, all current experimental information suggests that $\alpha$-Ru$I_3$ is different from $\alpha$-RuCl$_3$.

To better understand the different physical behaviors of $\alpha$-Ru$I_3$ and $\alpha$-RuCl$_3$, here, using the density functional theory (DFT), we provide a comprehensive first-principles study of these bulk systems. First, we found the ABC stacking honeycomb-layer $R3$ (No. 148) structure is the most likely stacking order of $\alpha$-Ru$I_3$ along the $c$ axis. Furthermore, both $R3$ and $P3_11c$ are dynamically stable because no imaginary frequency modes were obtained in the phonon dispersion spectrum. In addition, the $p$-$d$ hybridization increases from Cl to I, leading to the “effective” decrease of the atomic Coulomb repulsion $U$, resulting in the electrons of Ru$I_3$ being less localized than in RuCl$_3$. The effective electronic correlation is reduced in I to a value not large enough to open the spin-orbit Mott gap in $\alpha$-Ru$I_3$, leading to its metallic nature. Furthermore, we observed that introducing large (unrealistic) $U_{\text{eff}} = 6 \, \text{eV}$, the spin-orbit Mott gap does open in $\alpha$-Ru$I_3$, supporting the consistency of the physical picture we proposed.

II. CALCULATION METHOD

In the present study, we performed first-principles DFT calculations using the projector augmented wave method, as implemented in the Vienna Ab initio Simulation Package (VASP) code [75–77]. For the electronic correlations, the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) potential was employed [78] in our DFT calculations. Our plane-wave cutoff energy was 400 eV. Furthermore, the $k$-point mesh was appropriately modified for different structures to make the in-plane $k$-point densities approximately the same in reciprocal space (e.g., $8 \times 8 \times 3$ for the $R3$ phase of $\alpha$-Ru$I_3$). Note that those $k$-point meshes were tested to confirm that converged energies were produced. Both the lattice constants and atomic positions were fully relaxed until the Hellman-Feynman force on each atom was smaller than 0.01 eV/Å. The phonon spectra were calculated using the finite-displacement approach and were analyzed using the PHONOPY software [79,80]. Moreover, on-site Coulomb interactions were considered by using Dudarev’s rotationally invariant DFT+$U$ formulation [81] with $U_{\text{eff}} = U - J = 2 \, \text{eV}$, where this effective $U_{\text{eff}}$ is believed to provide an excellent description of $\alpha$-RuCl$_3$ [82]. It should be noted that hybrid exchange-correlation functionals, such as B3LYP (Becke, 3-parameter, Lee-Yang-Parr), allow us to achieve excellent agreement with experiments for the band gaps of complex oxide materials [83,84], whereas the DFT technique usually underestimates the band gaps. The hybrid exchange-correlation functional provides only a correction for the band gap and does not change other physical properties. However, the scope of this publication is to focus on the physical properties of the metallic phase of Ru$I_3$. Hence, our DFT+$U$ calculations are good enough to qualitatively describe the system we focus on. All the crystal structures were visualized with the VESTA code [85].

Based on the $R3$ (No. 148) structure of $\alpha$-Ru$I_3$, we compared the results of optimized crystal structures using different exchange-correlation functionals with or without vdW interactions, including PBE [78], PBE functional revised for solids (PBEsol) [86], zero damping vdW DFT-D3 corrections of Grimme (vdW-D3) [87], and vdW-D3 with Becke-Jonson damping [88]. As shown in Table I, all the obtained in-plane lattice constants of different exchange-correlation functionals are close to the experimental values, with the largest discrepancy being 2.4% for the $a$ value in PBE. But the PBE+vdW-D3 with zero damping functional provides the most accurate description for the $c$ axis (a 1% difference from the experimental value). Furthermore, the obtained in-plane lattices of the PBE+vdW-D3 with zero damping functional are only 1.2% larger than experimental results. Hence, we use the PBE+D3 with zero damping method in the structural optimization of the bulk properties in the rest of the paper.

| $a$   | $b$   | $c$    |
|------|------|-------|
| PBE  | 6.957| 6.957| 20.369|
| PBE+D3| 6.875| 6.875| 18.841|
| PBE+D3(BJ)| 6.817| 6.817| 18.301|
| PBEsol| 6.821| 6.821| 18.487|
| PBEsol+D3| 6.761| 6.761| 17.918|
| PBEsol+D3(BJ)| 6.695| 6.695| 17.393|
| Expt. | 6.791| 6.791| 19.026|

TABLE I. The optimized lattice constants (Å) of the $R3$ (No. 148) structure of $\alpha$-Ru$I_3$, using the PBE, PBE+D3, PBE+D3, PBEsol, PBEsol+D3, and PBEsol+D3(BJ) methods. The experimental values (Expt. for short) are also listed for comparison and were reported to form the $R3$ (No. 148) structure [71]. Note that D3 denotes vdW-D3 with zero damping and D3(BJ) denotes vdW-D3 with Becke-Jonson damping.
To better understand the structural stability of \( \alpha \)-RuI\(_3\), we carried out the phononic dispersion calculations using a \( 2 \times 2 \times 1 \) supercell for the \( R\bar{3} \) (No. 148) and \( P\bar{3}1c \) (No. 163) phases. Figure 2 indicates that the \( R\bar{3} \) and \( P\bar{3}1c \) structures are dynamically stable because no imaginary frequency modes were obtained in the phononic dispersion spectrum.

In addition, we also considered the Coulombic repulsion \( U \) effect on the process of optimizing crystal lattices (see Table S1 in the Supplemental Material [89]). The lattice structures do not change much compared to the lattice structures without \( U_{\text{eff}} \), and the \( R\bar{3} \) structure of \( \alpha \)-RuI\(_3\) has the lowest energy among those five lattice configurations. Furthermore, we also compared the energies between the \( R\bar{3} \) and \( P\bar{3}1c \) structures with and without the effective Coulomb repulsion \( U \) effect, considering the experimentally reported lattice structures where \( R\bar{3} \) \( \alpha \)-RuI\(_3\) always has lower energy than \( P\bar{3}1c \) \( \alpha \)-RuI\(_3\). Moreover, we also calculated the phononic dispersion with \( U_{\text{eff}} = 2.0 \) eV for both the \( R\bar{3} \) and \( P\bar{3}1c \) phases. We found that the \( R\bar{3} \) phase is dynamically stable because no imaginary frequency modes were obtained in the phononic dispersion spectrum. However, the phononic dispersion spectrum of

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**TABLE II.** Optimized lattice constants (\( \AA \)) and energy differences (meV/Ru) with respect to the \( R\bar{3} \) (No. 148) configuration taken as the reference of energy for the various structural configurations. The experimental values (Expt. for short) are also listed for comparison, which were reported to form the \( R\bar{3} \) (No. 148) [71] and \( P\bar{3}1c \) (No. 163) structures [72].

| Structure     | \( a \)  | \( b \)  | \( c \)  | Energy |
|---------------|---------|---------|---------|--------|
| \( R\bar{3} \) (No. 148) | 6.875   | 6.875   | 18.841  | 0.0    |
| \( P\bar{3}1c \) (No. 163) | 6.873   | 6.873   | 12.577  | 2.58   |
| \( P\bar{3}1c \) (No. 151) | 6.841   | 6.841   | 19.209  | 6.35   |
| \( P\bar{3}1m \) (No. 162) | 6.828   | 6.828   | 6.413   | 25.83  |
| \( C2/m \) (No. 12) | 6.865   | 11.827  | 6.764   | 7.68   |
| Expt. [71]   | 6.791   | 6.791   | 19.026  |        |
| Expt. [72]   | 6.778   | 6.778   | 12.579  |        |
Fig. S1(b). In this case, the electronic correlation effects may induce a structural phase transition for the $\alpha$-RuI$_3$. The coordinates of the high-symmetry points in the bulk Brillouin zone (BZ) are $\Gamma = (0, 0, 0)$, $M = (0.5, 0, 0)$, $K = (1/3, 1/3, 0)$, $A = (0, 0, 0.5)$, $L = (0.5, 0, 0)$, and $H = (1/3, 1/3, 0.5)$.

Fig. 2. The calculated phonon spectrum of $\alpha$-RuI$_3$ for the structures (a) $R\bar{3}$ and (b) $P\bar{3}1c$ in the nonmagnetic state without Hubbard $U$. The crystal field leads to three lower-degenerate-energy $t_{2g}$ orbitals, as sketched in Fig. 3(a). First, the crystal field splitting energy ($\sim 10$ Dq), resulting in a metallic phase because the $t_{2g}$ orbitals are not completely occupied. Then, by introducing the SOC effect, the $J_{\text{eff}} = 3/2$ states begin to separate from each other, leading to a half-occupied $J_{\text{eff}} = 1/2$ state and two fully occupied $J_{\text{eff}} = 3/2$ states, where the splitting energy depends on the SOC strength $\lambda$. In this case, the system is still metallic since the $J_{\text{eff}} = 1/2$ state is not completely occupied. Finally, increasing the onsite electron correlations $U$ leads to an energy gap for the $J_{\text{eff}} = 1/2$ band near its Fermi surface as well, resulting in a Mott transition. In this case, this insulating gap system is also referred to as the ‘spin-orbit Mott insulating’ gap.

For the benefit of our readers, we also present the corresponding electronic structures of $P\bar{3}1c$ $\alpha$-RuI$_3$ in the Supplemental Material [89]. We also remark that the main physical conclusion of our paper is not affected by the structural configurations because the difference between those structures is the stacking arrangement along the $c$ axis. In the rest of the text, we will focus on discussing the results for $R\bar{3}$ $\alpha$-RuI$_3$, starting in the next section.

B. Electronic structures.

Let us now discuss the energy splitting of the Ru $4d^5$ orbitals, as sketched in Fig. 3(a). First, the crystal field leads to three lower-degenerate-energy $t_{2g}$ orbitals ($d_{x^2}$, $d_{y^2}$, and $d_{z^2}$) and two higher-degenerate-energy $e_g$ orbitals ($d_{x^2−y^2}$ and $d_{z^2−r^2}$). In addition, by introducing the SOC effect, the three lower-degenerate-energy $t_{2g}$ orbitals split into two energy states, $J_{\text{eff}} = 3/2$ and $J_{\text{eff}} = 1/2$. The Ru $3^+$ state is considered a $d^5$ electronic configuration with a low-spin state. Thus, this system could be regarded as a $J = 1/2$ state (half-occupied $J_{\text{eff}} = 1/2$ state), while the two $J_{\text{eff}} = 3/2$ states are fully occupied, as shown in Fig. 3(a).

In general, the density of states (DOS) of this $4d^5$ low-spin configuration can be intuitively understood as displayed in Fig. 3(b). Under a cubic crystal field, the five $4d$ electrons of Ru populate the lower $t_{2g}$ bands separated by the crystal-field splitting energy ($\sim 10$ Dq), resulting in a metallic phase because the $t_{2g}$ orbitals are not completely occupied. Then, by introducing the SOC effect, the $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$ states begin to separate from each other, leading to a half-occupied $J_{\text{eff}} = 1/2$ state and two fully occupied $J_{\text{eff}} = 3/2$ states, where the splitting energy depends on the SOC strength $\lambda$. In this case, the system is still metallic since the $J_{\text{eff}} = 1/2$ state is not completely occupied. Finally, increasing the onsite electronic correlations $U$ leads to an energy gap for the $J_{\text{eff}} = 1/2$ band near its Fermi surface as well, resulting in a Mott transition. In this case, this insulating gap system is also often referred to as the ‘spin-orbit Mott insulating’ gap.

To better understand the similarities and differences between $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$, we calculated the DOSs of $\alpha$-RuI$_3$ with the $R\bar{3}$ structure and $\alpha$-RuCl$_3$ with the $C2/m$ structure for the nonmagnetic phase. According to the calculated DOSs [see Figs. 4(a) and 4(b)], the bands near the Fermi level are mainly contributed by the Ru $4d$ $t_{2g}$ orbitals, hybridized with the I 5$p$ and Cl 3$p$ orbitals, respectively. Furthermore, the I 5$p$ orbitals are closer to the Fermi level than the Cl 3$p$ orbitals, as shown in Figs. 4(a) and 4(b). With increasing atomic radius from Cl to I, the $p$ components near the Fermi level become larger, leading to an increase in the $p$-$d$ hybridization tendency from I to Cl. In addition, the low-energy $t_{2g}$ bands are more extended in $\alpha$-RuI$_3$ than in $\alpha$-RuCl$_3$, indicating stronger electronic correlations ($U/W$, where $W$ is the bandwidth) in the $\alpha$-RuCl$_3$ case. To open the Mott gap in the $J_{\text{eff}} = 1/2$ state, $\alpha$-RuI$_3$ needs a larger
Coulomb repulsion $U$ than $\alpha$-RuCl$_3$. It should be noted that those results are obtained in the $P\overline{3}m1$ structure of $\alpha$-RuI$_3$ and the $P\overline{3}1$2 structure of $\alpha$-RuCl$_3$ (see the Supplemental Material [89]).

In addition, we also calculated the electron localization function (ELF) [90] for the $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$ cases, as displayed in Figs. 4(c) and 4(d), respectively. The ELF picture indicates that the charges are less localized inside the Ru-I bonds, resulting in large hybridized $p$-$d$ bonds in $\alpha$-RuI$_3$, in contrast to the localized charges along with the Ru-Cl bonds in $\alpha$-RuCl$_3$. The movement of electrons is by tunneling from Ru to I (or Cl) and then to another Ru. In other words, iodine (or chlorine) is the bridge between rutheniums. Hence, it is easy to imagine that RuCl$_3$ is more Mott localized than RuI$_3$ by using the same value of the on-site repulsion $U$ at the Ru site. The reason is that compared to RuCl$_3$, the bandwidth of RuI$_3$ is increased, indicating that the electronic correlation $U/W$ has decreased. In this case, due to the increase in the $p$-$d$ hybridization of $\alpha$-RuI$_3$, the “effective” Coulomb repulsion $U/W$ will decrease in $\alpha$-RuI$_3$, reducing or not even permitting the opening of an energy gap. Hence, RuI$_3$ displays metallic behavior, in contrast to the insulating behavior in $\alpha$-RuCl$_3$.

Furthermore, we calculated band structures of $R\overline{3}$ $\alpha$-RuI$_3$ with and without the SOC effect and with the Coulomb repulsion $U$ ($U_{\text{eff}} = 2$ eV). As shown in Fig. 5, band structures both with and without SOC suggest metallic behavior in $\alpha$-RuI$_3$. Taking into account SOC and the Coulomb repulsion $U$ ($U_{\text{eff}} = 2$ eV), $\alpha$-RuI$_3$ still displays metallic behavior of the $J_{\text{eff}} = 1/2$ bands but opens gaps on some high-symmetry points in the Brillouin zone, as displayed in Fig. 5(b). Those results are consistent with our previous analysis that the effective Coulomb repulsion would reduce or not even allow the gap to open in $\alpha$-RuI$_3$. For comparison, we also calculated the band structure of $\alpha$-RuCl$_3$ using the $C2/m$ structure with and without the SOC effect and with the Coulomb repulsion $U$ ($U_{\text{eff}} = 2$ eV). As displayed in Fig. 6, the band structure clearly shows insulating behavior for the $J_{\text{eff}} = 1/2$ bands with a Mott transition caused by the Coulomb repulsion $U$. Based on our estimation, the spin-orbital couplings are about 0.12 and 0.2 eV for RuCl$_3$. 

FIG. 4. (a) and (b) Density of states near the Fermi level based on the nonmagnetic states for $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$, respectively. Gray: total; red: Ru; blue: I; cyan: Cl. The Fermi level is marked by the vertical dashed green line. (a) Results for the $R\overline{3}$ structure of $\alpha$-RuI$_3$. (b) Results for the $C2/m$ structure of $\alpha$-RuCl$_3$. (c) and (d) Electron localization function of one Ru honeycomb layer for $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$, respectively, corresponding to nonmagnetic phases, in the $a$-$b$ plane.

FIG. 5. Calculated electronic band structures of $\alpha$-RuI$_3$ in the $R\overline{3}$ structure using a nonmagnetic state: (a) without and with SOC (the color convention is indicated) and (b) with SOC plus $U_{\text{eff}} = 2$ eV. The coordinates of the high-symmetry points in the bulk BZ are $\Gamma = (0, 0, 0)$, $M = (0.5, 0, 0)$, $K = (1/3, 1/3, 0)$, $A = (0, 0, 0.5)$, $L = (0.5, 0, 0)$, and $H = (1/3, 1/3, 0.5)$.

FIG. 6. Calculated electronic band structures of $\alpha$-RuCl$_3$ with the $C2/m$ structure in the nonmagnetic state: (a) without and with SOC (the color convention is indicated) and (b) with SOC plus $U_{\text{eff}} = 2$ eV. The coordinates of the high-symmetry points in the bulk BZ are $\Gamma = (0, 0, 0)$, $Y = (0.5, 0.5, 0)$, $M = (0.5, 0.5, 0.5)$, $A = (0, 0, 0.5)$, $L_2 = (0, 0.5, 0.5)$, and $V_2 = (0, 0.5, 0)$. 

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and RuI$_3$, respectively, in agreement with other theoretical studies [61,72]. Hence, after using suitable parameters, we obtained metallic behavior in $\alpha$-RuI$_3$ and insulating behavior in $\alpha$-RuCl$_3$, in excellent agreement with the experimental results. This can be naturally explained in simple terms: increasing the $p$-$d$ hybridization of $\alpha$-RuI$_3$ decreases the effective electronic correlations $U/W$ because the bandwidth $W$ increases and thus allows for the conduction of charge along with the Ru-I bonds.

C. Comparing $\alpha$-RuI$_3$ with $\alpha$-RuCl$_3$ using zigzag AFM order

Preliminary experimental characterization of $\alpha$-RuI$_3$ reveals the absence of long-range magnetic order down to 0.35 K, suggesting a paramagnetic metallic state [71,72]. On the contrary, $\alpha$-RuCl$_3$ is in a spin-orbital Mott state with zigzag AFM ordering in the ground state at low temperatures [56,57]. To better understand the different conductive behaviors of $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$, we calculated the electronic structures for the two materials assuming zigzag AFM order. Because we are simply performing a qualitative analysis of the effect of the Coulomb repulsion $U$, we used the $C_2/m$ symmetry for the crystal structure for both $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$.

Based on previous studies [54,56,61,91], $U_{\text{eff}}$ has been estimated to be about 1–2 eV for Ru atoms, which are often used in the band structure calculations of trihalogen ruthenium compounds. In addition, the effective $U_{\text{eff}} = 2.0$ eV is believed to provide an excellent description of the stacking order of RuCl$_3$ [82]. Hence, we used $U_{\text{eff}} = 2.0$ eV in our magnetic calculations. Note that we also tested other values of $U_{\text{eff}}$, but they do not change our main conclusion [89]. Furthermore, for RuCl$_3$, previous optical data found a small optical gap of about 0.3 eV [92], but this very small value was considered not to be associated with charge excitations [93]. Moreover, some other experiments suggested that the optical gap was around 1 eV [54,93]. Hence, our results are in good agreement with the optical data for $\alpha$-RuCl$_3$ qualitatively. Figure 7 indicates that $\alpha$-RuI$_3$ still displays metallic behavior, in contrast to the insulating behavior in $\alpha$-RuCl$_3$. The same SOC $+ U$ ($U_{\text{eff}} = 2$ eV) opens a gap ($\sim$0.7 eV) in $\alpha$-RuCl$_3$ but could not open the Mott gap in $\alpha$-RuI$_3$. This result supports the notion that the effective electronic correlation $U/W$ is reduced from Cl to I and is not enough to open a gap, leading to metallic behavior in $\alpha$-RuI$_3$. In this case, the results obtained, even including the effect of Coulomb repulsion, can naturally explain the metallic behavior in $\alpha$-RuI$_3$, in contrast to the spin-orbit Mott insulating behavior observed in $\alpha$-RuCl$_3$.

As discussed in the previous sections, the metallic nature of $\alpha$-RuI$_3$ is induced by the reduced effective Coulomb repulsion when moving from Cl to I. In essence, the spin-orbit Mott gap opens if $U$ is large enough. In this case, the Coulomb repulsion $U$ of the Ru atoms shifts Ru states to lower energies and reduces the $p$-$d$ hybridization and thus its bandwidth. To confirm this physical picture, we introduced artificially large (unrealistic) $U_{\text{eff}} = 6$ eV on the Ru sites. This $U_{\text{eff}}$ is too large for RuI$_3$. As expected, using the same lattice as in Fig. 7(a), a large spin-orbit Mott gap ($\sim$1.1 eV) emerges, this time in the DOS, as displayed in Fig. 8. These results support our physical picture for the explanation of the metallic behavior in RuI$_3$. Note that here, we did only a qualitative analysis for the metallic-insulating transition of RuI$_3$ because finding the specific critical value of the Hubbard repulsion $U$ is also affected by many other aspects besides $U$, such as the lattice structure, magnetic ordering, spin orientation, etc. However, our results are qualitatively sufficient to show that for a large enough $U_{\text{eff}}$ a spin-orbit Mott gap opens even in $\alpha$-RuI$_3$.

IV. CONCLUSIONS

In this paper, we have systematically studied the properties of $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$ by using first-principles DFT. We found that the most likely stacking order of $\alpha$-RuI$_3$ along the
$c$ axis is the ABC stacking honeycomb-layer $R \overline{3}$ (No. 148) structure. In addition, both $R \overline{3}$ and $P \overline{3}1c$ were found to be dynamically stable because no imaginary frequency modes were obtained in the phononic dispersion spectrum. By introducing GGA + SOC + $U$ calculations, the $U_{\text{eff}} = 1/2$ physics was obtained in both $\alpha$-RuI$_3$ and $\alpha$-RuCl$_3$. Different from the spin-orbit Mott insulating phase of $\alpha$-RuCl$_3$, on the other hand, $\alpha$-RuI$_3$ displays a strong metallic behavior, in agreement with the currently available experimental information. The strong hybridization between the Ru 4d and I 5p orbitals decreases the effective atomic Coulomb repulsion $U/W$, that is, increases the bandwidth $W$ in the ratio $U/W$. This effective electronic correlation $U/W$ is reduced from Cl to I, inducing metallic behavior in $\alpha$-RuI$_3$. In our study, by considering large (unrealistic) $U_{\text{eff}} = 6$ eV, the spin-orbit Mott gap finally opens in $\alpha$-RuI$_3$, supporting the physical picture we proposed. In summary, while the atomic $U$ of Ru must be very similar in both compounds, the bandwidth $W$ in the case of Cl is smaller than in I, and this is sufficient to place $\alpha$-RuCl$_3$ on the insulating side of the metal-insulator transition, while $\alpha$-RuI$_3$ is still on the metallic side.

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