Crystal structure and magnetism in \( \alpha \)-RuCl\(_3\): an \textit{ab-initio} study

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\( \alpha \)-RuCl\(_3\) has been proposed recently as an excellent playground for exploring Kitaev physics on a two-dimensional (2D) honeycomb lattice. However, structural clarification of the compound has not been completed, which is crucial in understanding the physics of this system. Here, using \textit{ab-initio} electronic structure calculations, we study a full three-dimensional (3D) structure of \( \alpha \)-RuCl\(_3\) including the effects of spin-orbit coupling (SOC) and electronic correlations. Three major results are as follows: i) SOC suppresses dimerization of Ru atoms, which exists in other Ru compounds such as isostructural Li\(_2\)RuO\(_3\), and making the honeycomb closer to an ideal one. ii) The nearest-neighbor Kitaev exchange interaction between the \( j_{\text{tot}}=1/2 \) pseudospin depends strongly on the Ru-Ru distance and the Cl position, originating from the nature of the edge-sharing geometry. iii) The optimized 3D structure without electronic correlations has \( P31m \) space group symmetry independent of SOC, but including electronic correlation changes the optimized 3D structure to either \( C2/m \) or \( Cmcm \) within 0.1 meV per formula unit (f.u.) energy difference. The reported \( P31m \) structure is also close in energy. The interlayer spin exchange coupling is a few percent of in-plane spin exchange terms, confirming \( \alpha \)-RuCl\(_3\) is close to a 2D system. We further suggest how to increase the Kitaev term via tensile strain, which sheds new light in realizing Kitaev spin liquid phase in this system.

I. INTRODUCTION

There have been a number of studies on quasi-two-dimensional systems having both spin-orbit coupling (SOC) and on-site Coulomb interactions, which are believed to host unconventional magnetic orders and spin liquid phases\(^{1,2} \). One promising candidate is \( \alpha \)-RuCl\(_3\), where edge-sharing RuCl\(_6\) octahedra form two-dimensional RuCl\(_3\) layers in which Ru honeycomb layers reside\(^{3-11}\). Compared to its 5\(d\) transition metal oxide counterparts \( \alpha \)-\( A_2\)IrO\(_3\) (\( A=\text{Li,Na} \))\(^{12-16} \), \( \alpha \)-RuCl\(_3\) has closer-to-ideal RuCl\(_6\) octahedra\(^8\), so it was proposed as an excellent platform to explore the Kitaev physics and related magnetism despite weaker SOC\(^{4,9,11,17,18} \). A few recent reports suggest the presence of strong Kitaev-type bond-dependent exchange interactions in \( \alpha \)-RuCl\(_3\)\(^5\), which originate from the cooperation between the intermediate SOC in Ru atom and the Coulomb interaction\(^8\). A zigzag-type magnetic order within the RuCl\(_3\) layer is also predicted and observed, which is proximate to the Kitaev spin-liquid phase\(^{5,8} \).

In previous studies \( \alpha \)-RuCl\(_3\) was considered as a two-dimensional system with an ideal Ru honeycomb lattice, but such assumption needs further clarification. A potential Ru layer distortion, which is observed in an isostructural compound Li\(_2\)RuO\(_3\)\(^9,20\), might happen in this compound. Furthermore, \( \alpha \)-RuCl\(_3\) has a three-dimensional crystal structure consisting of RuCl\(_3\) layer stacking, and interlayer coupling and interaction terms can introduce another complication. Experimentally, both \( P31m \) and \( C2/m \) space groups have been suggested as the crystalline symmetry in this compound\(^{11,21,22} \). As an illustrative example, Fig. 1(a) shows the crystal structure of \( \alpha \)-RuCl\(_3\) with a \( C2/m \) space group symmetry, where adjacent RuCl\(_3\) layers within the unit cell is related to each other by a translation along the \( \alpha \)-axis in the figure. Stacking faults can easily be introduced in this layered structure as in the case of \( \alpha \)-\( A_2\)IrO\(_3\)\(^{23} \), which obscures further clarification of the crystal structure. Effect of interlayer exchange interactions from the layer stacking on the ground state magnetic properties of this system is not well understood either. More interestingly, a sample-dependent two-transition behavior is reported, where two different magnetic order peaks at \( T_{N1} \approx 14 \) K and \( T_{N2} \approx 8 \) K with two- and three-layer \( c \)-axis periodicity, respectively, are observed in neutron diffraction measurement\(^{11} \). These issues pose a question on the relation between crystal structure and magnetism in this system.

In pursuit of such motivations, in this work we perform \textit{ab-initio} calculations for the structural properties of \( \alpha \)-RuCl\(_3\) and their impact on magnetism. We present three main results; i) Role of SOC and zigzag magnetic order on the single-layer RuCl\(_3\) structure is discussed. We found that SOC prefers ideal honeycomb lattice by preventing Ru-Ru dimer forma-
tions, and the presence of in-plane zigzag order tends to give small monoclinic distortion commensurate to the magnetic order. ii) Effect of Ru-Cl and Ru-Ru distance to the exchange interactions and magnetism is discussed, where the hopping channels within the nearest-neighbor (NN) Ru $t_{2g}$ orbitals and the resulting exchange interactions between the SOC-induced $j_{\text{eff}}=1/2$ pseudospins strongly depend on the Ru-Cl and Ru-Ru distance. Such behavior originates from the existence of multiple hopping channels in the $t_{2g}$ orbitals, which enables 'leveraging' magnetism with rather small amount of structural changes. iii) Stability of crystal structures with different stacking orders is discussed by comparing relative total energies. We have found that, structures with $C2/m$ and $Cmce_1$ space group symmetries are most favorable with almost degenerate energies. Previously suggested $P3_112$ structure yields total energy comparable to those of $C2/m$ and $Cmce_1$ structures with the energy difference smaller than 0.4 meV per formula unit (f.u.). Energy differences between different interlayer magnetic orders are smaller than 0.1 meV / f.u., and magnitude of interlayer exchange interactions estimated from interlayer hopping integrals are smaller than 0.05 meV. These observations justify the employment of two-dimensional spin models in exploring magnetism in $\alpha$-RuCl$_3$. We further propose how to increase the Kitaev term using tensile strain or uniaxial pressure to realize the Kitaev spin liquid phase.

This manuscript is organized as follows. After showing computational details in Sec. II, structural properties of single-layer RuCl$_3$ and its relation to magnetism is presented in Sec. III. The effect of SOC and zigzag magnetic order to the single-layer RuCl$_3$ structure, and the relation between the structure and magnetism are discussed in Sec. III A and Sec. III B, respectively. In Sec. IV and V, results on the stacking without and with the Coulomb interaction and magnetism are shown, respectively. Summary and conclusion follow in Sec. VI.

II. COMPUTATIONAL DETAILS

For the electronic structure calculations, we employed the Vienna ab-initio Simulation Package (VASP), which uses the projector-augmented wave (PAW) basis set. 370 eV of plane wave energy cutoff was used, and for $k$-point sampling $15 \times 15$ and $8 \times 6 \times 4(6)$ Monkhorst-Pack grid were adopted for single-layer primitive cell and monoclinic cells with three (two) layer $c$-axis periodicity. Tetrahedron method with Blöchl correction was used for the calculation of density of states. On-site Coulomb interactions are incorporated using the Dudarev’s rotationally invariant DFT+U formalism with effective $U_{\text{eff}}=U-J=2$ eV. For each configuration with different unit cell, $U_{\text{eff}}$ value, and magnetic order, structural optimization is performed with a force criterion of 1 meV / Å. Unless specified, a revised Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol) was used for structural optimization and total energy calculations. Note that, PBEsol functional yielded reasonable results for the stacking order of bilayer transition metal dichalcogenides in comparison to the van der Waals functionals. Results with employing vdW functionals are shown in Appendix. Interlayer hopping integrals were obtained by employing maximally-localized Wannier orbital (MLWF) formalism implemented in Wannier90 package. Also, for comparison of the magnetism in the single-layer structures in Sec. III, a linear-combination-of-pseudo-atomic-orbital basis code OPENMX was used, where double zeta plus polarization (DZP) bases, 500 Ry of energy cutoff for real space integrations, and the Perdew-Zunger parameterization for the local density approximation were employed.

III. RELATION BETWEEN STRUCTURE AND MAGNETISM IN RUCl$_3$ SINGLE LAYER

In this section, structural changes due to the lattice optimization and their effect to the magnetism is discussed in the RuCl$_3$ single layer. The initial trial structure we chose is the one reported in Ref. 37, which was used in the Ref. 8. The lattice optimization gives rise to in-plane structural changes, and here we present the optimized structures focusing on the difference from the old one. Since we found that such behavior and the resulting changes in magnetism also occur in the full 3D structures, which are presented in Sec. IV and V, below we first discuss the single layer results.

A. Effect of SOC on in-plane Ru dimerization

First, the effect of SOC and magnetism with $U_{\text{eff}}$ on a Ru honeycomb lattice is discussed in this subsection. Fig. 2 summarizes the results, where the sizes of Ru displacements $\delta$ from the ideal honeycomb lattice after structural optimizations under different conditions are shown. Positive and negative values of $\delta$ in Fig. 2(b) correspond to Ru dimerization and Ru zigzag chain formation, respectively, as shown in Fig. 2(a). Note that, the lattice constants are fixed to the experimentally observed $a = a_0 = 5.96$Å and $b=\sqrt{3}a_0$. Without including SOC and Coulomb interactions, the two Ru atoms in the unit cell tend to dimerize to lower the energy as shown in Fig. 2(a). The presence of dimer formation is robust against different choice of exchange-correlation functionals — Perdew-Zunger parametrization of local density approximation (LDA) , PBE, and PBEsol — with slightly different size of $\delta$ as shown in Fig. 2(b). Similar dimer formation was reported in other layered honeycomb compound Li$_2$RuO$_3$, of which origin is suggested to be the $\sigma$-like direct bonding between the neighboring Ru $t_{2g}$ orbitals.

Since the dimer formation breaks the Ru $t_{2g}$ degeneracy, we expect that SOC would not favor the dimer formation. The spin-orbit entangled $j_{\text{eff}}$ orbitals, which emerges under the presence of cubic crystal fields and SOC, does not favor orbital polarization between the $t_{2g}$, $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals. Indeed, structural optimizations including SOC yield significant reduction of dimerization as shown in the middle of Fig. 2(b). Although there are small differences between LDA, PBE, and PBEsol results, the role of SOC in preventing the dimerization is evident. Additionally, inclusion of the on-
site Coulomb interaction without the presence of magnetism is expected to enhance the idealness of the Ru honeycomb lattice, since it was shown previously that the on-site Coulomb is expected to enhance the idealness of the Ru honeycomb lattice site Coulomb interaction without the presence of magnetism, respectively, where colors on Ru sites show the zigzag magnetic order in a monoclinic unit cell. (b) Size of Ru distortion \( \delta \) under different exchange-correlations functionals and with/without presence of SOC, \( U_{\text{eff}} \), and in-plane zigzag magnetic order. Note that, positive and negative \( \delta \) correspond to Ru dimer and zigzag chain formations, respectively.

Next we show the effect of in-plane zigzag magnetic order, which is predicted to occur when SOC and the Coulomb interaction are incorporated in \textit{ab-initio} calculations\(^8\) and observed in experiments\(^5,11\). Right columns of Fig. 2(b) show the results from calculations including SOC, \( U_{\text{eff}} = 2 \text{eV} \), and the zigzag order. The enlarged monoclinic unit cell and the magnetic configuration are shown in Fig. 2(a), where the red and blue colored circles represent Ru sites with antiparallel moments to each other. Regardless the choice of functional, \( \delta \) shows negative values with almost same magnitude. The resulting structure is commensurate to the zigzag magnetic order as shown in Fig. 2(a), suggesting a finite magneto-elastic coupling in this compound.

B. Effects of Cl displacement and lattice constant change to the exchange interactions between the \( j_{\text{eff}} = 1/2 \) pseudospins

Here we discuss the Cl displacement after the optimization and its impact to the exchange interactions between the neighboring Ru \( j_{\text{eff}} = 1/2 \) pseudospins. Fig. 3 shows the displacement of Cl atoms after structural optimization, where the two Cl atoms participating in each NN Ru bond move toward the bond center. When the in-plane lattice constants are fixed to be \( a = a_{0} \) and \( b = \sqrt{3} a_{0} \), structural optimization with SOC only (no \( U_{\text{eff}} \) and magnetism) yields reduced Cl height of 1.43\( \text{Å} \) to 1.34\( \text{Å} \) with respect to the Ru plane, and the Cl triangles above and below Ru plane rotates by 2.7\( ^{\circ} \) in opposite direction as shown in the figure. The Ru-Cl-Ru NN bond angle increases from 89.1\( ^{\circ} \) to 93.8\( ^{\circ} \). After allowing the lattice constants to relax, the lattice constants reduce to \( a = 0.981 a_{0} \) and \( b = 0.986 b_{0} \) when SOC was employed with the monoclinic distortion allowed. With \( U_{\text{eff}} = 2 \text{eV} \) and the zigzag magnetic order, they are increased to \( a = 1.011 a_{0} \) and \( b = 1.006 b_{0} \). The averaged Ru-Cl distance changes from 2.34\( \text{Å} \) to 2.36\( \text{Å} \) in the nonmagnetic calculation with \( U_{\text{eff}} = 0 \text{eV} \) to the magnetic results with \( U_{\text{eff}} = 2 \text{eV} \), but both of them are shorter than the distance of 2.45\( \text{Å} \) in the initial trial structure. Note that, when the monoclinic distortion is allowed, the NN Z-bond in Fig. 3 becomes inequivalent to the X and Y bonds, where the X and Y bonds form the zigzag chain in Fig. 2(a). Also, no Ru-Cl bond length disproportionation is observed in all of our results, implying no Jahn-Teller distortion in this system.

Due to the presence of inversion symmetry at the bond center and additional trigonal distortion in RuCl\(_6\) octahedra, the hopping integrals between the NN Ru \( t_{2g} \) Wannier orbitals have the following form\(^{16,43}\),

\[
\hat{T} = \begin{pmatrix}
\tau_1 & \tau_2 & \tau_4 \\
\tau_2 & \tau_1 & \tau'_4 \\
\tau_4 & \tau'_4 & \tau_3
\end{pmatrix},
\]

where each hopping channel is displayed in Fig. 4 with the participating Ru \( t_{2g} \) Wannier orbitals therein. As shown in the figure, while \( \tau_1 \) originates mainly from the \( \delta \)- and \( \sigma \)-like \( d-d \) direct overlap integrals, \( \tau_2 \) is mostly from the \( \pi \)-type indirect overlap dominated by \( d-p-d \) hopping between the Ru and in-
tervening Cl $p$ orbitals. Note that, $t_3$ channel has both the $d$-$d$ direct overlap and $d$-$p$-$d$ indirect overlap which has opposite signs to each other. Also, due to the small trigonal distortion, the small $t_2$ and $t'_4$ terms are introduced, where the difference between them introduced by the monoclinic distortion is negligibly small.

Table I shows the hopping terms from the Wannier orbitals for four crystal structures optimized with different conditions. There are the old $P3_1\bar{1}2$ structure used in previous work, structure with internal coordinates and lattice constants optimized with SOC, structure with only internal coordinate optimized (fixed $a=a_0$ and $b=b_0$), and the one optimized with SOC, $U_{\text{eff}}$, and the zigzag order. Hereafter we denote the structures as Case 0 to III, respectively, as stated in Table I. With those optimized structures, calculations of the Wannier orbitals were performed without the inclusion of SOC, $U_{\text{eff}}$, and magnetism. Surprisingly, the hopping integrals are showing huge dependence to the structural change. Especially, the $t_3$ term varies from -0.229 to -0.062 eV depending on the structures, and $t_2$ also varies from 0.114 to 0.191 eV. Comparing the Case 0 and II results, the effect of Cl relaxation is to enhance $t_2$ and suppress $t_3$. The effect of increasing Ru-Ru distance, which can be seen by comparing Case I to III, is also similar to the role of Cl relaxation with less dramatic but still substantial trend. Such tendency can be understood from the character of participating Wannier orbitals shown in Fig. 4. The $t_3$ term, the most sensitive to the structural change, originates from the two distinct channels; one from the $\sigma$-like direct $d$-$d$ overlap and another from $d$-$p$-$d$ indirect channel. The two channels have opposite sign to each other, with minus sign for the $d$-$d$ channel and plus sign for the $d$-$p$-$d$ channel. As a result, enhancing $d$-$p$-$d$ channel by reducing the Ru-Cl distance or increasing the Ru-Cl-Ru angle will lead to better cancellation of the dominant $d$-$d$ channel and reduction of the overall $t_3$ term as shown in Table I. Enhancement of $t_2$ after Cl relaxation is also easy to understand since it mostly comes from the $\pi$-like $d$-$p$-$d$ channel, while the $t_3$ dominated by the $\delta$-like $d$-$d$ channel is reduced as the Ru-Ru distance is increased. The trend for the small $t_4$ term is less clear, but it tend to enhance when there are more trigonal and monoclinic distortion.

From the NN $t_{2g}$ hopping terms, one can estimate the values of exchange interaction terms in the $J_{\text{eff}} = 1/2$ spin Hamiltonian

$$\mathcal{H} = \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{M}_{ij} \cdot \mathbf{S}_j,$$

where the bond-dependent $3 \times 3$ matrix $\mathbf{M}_{ij}$ has the form of

$$\mathbf{M} = \begin{pmatrix} J & \Gamma & \Gamma' \\ \Gamma & J & \Gamma' \\ \Gamma' & \Gamma' & J + K \end{pmatrix}. $$

Note that, $\mathbf{M}_{ij}$ undergoes simultaneous cyclic permutations of rows and columns depending on NN bond directions. Explicit expressions for the Heisenberg $J$, the Kitaev $K$, and the symmetric anisotropy terms $\Gamma$ and $\Gamma'$ in terms of the hopping integrals, $U$, and the Hund’s coupling $J_H$ are reported in Ref. 16 and 43. Using the values of $t_4$ listed in Table I and setting $U = 3$eV and $J_H/U = 0.2$, we can calculate the values of exchange interactions which are listed in Table I. Note that, changing the values of $U$ and $J_H/U$ changes does not change the ratio between the exchange interactions when $J_H/U > 0.05$. As shown in the table, among the exchange interactions, the Kitaev term shows dramatic change of changing sign after the Cl relaxation. This is due to the enhancement and suppression of $t_2$ and $t_3$ terms. Increasing Ru-Ru distance gradually enhances $K$ and reduces $J$ and $\Gamma$, so driving the system closer to the Kitaev spin liquid limit with ferromagnetic $K$. Note that, comparing Case II and III, increasing the lattice constant by 1% enhances the $K$ term significantly. This implies the possibility of controlling the magnetism and realizing the Kitaev spin liquid phase with rather small amount of structural change such as epitaxial strain or uniaxial pressure. Another noticeable feature is the small but non-negligible $\Gamma'$ term from the trigonal distortion, which can stabilize the experimentally observed zigzag order near the Kitaev spin liquid phase with $K < 0.03$.

Finally, we discuss the evolution of the magnetic moments direction in the zigzag order with respect to structural changes. Fig. 5(a) shows the schematic figure of the zigzag order with an angle of the moments $\theta$ with respect to the $a$-axis. Note that, in all of our calculations the moments were residing on the $ac$-plane. In the Case 0 structure, both in the OpenMX and VASP results, the moments were parallel/antiparallel to the $a$-axis (i.e. $\theta = 0$), consistent to our previous result. After the structural optimization the moments gain nonzero $\theta$, which tends to increase when the lattice constant increases as shown in Fig. 5(b). There is difference in $\theta$ between the results from the two different codes, but the tendency of increasing angle remains the same. We speculate
TABLE I. Values of the averaged Ru-Cl distances, NN Ru-Ru distances, hopping integrals, and examples of exchange interactions for $U$ that, within a RuCl$_3$ can be understood as a sequence of sublattice indices. Note that, within a RuCl$_3$ layer, any two Ru or Cl layers cannot be in a same sublattice. As we take into account Ru hollow sites, additional degree of freedom is introduced to each Ru layer, and we denote this with primes in the triangular sublattice index (for example, A, A’, and A” as shown in the figure).

For structures with three-layer $c$-axis periodicity, we choose unit cells with $P3_112$ and $C2/m$ space groups. Note that, the $C2/m$ structure was reported also as the space group of this compound$^{6,22}$, and is similar to the $P3_112$ structure. The major difference in two structures is the $c$-axis ordering of the Ru honeycomb layers, where in the $C2/m$ unit cell three Ru layers are related by translation by ($a + a' + c$)/3 while in the $P3_112$ cell they are related by threefold screw axis. Besides, since the neutron diffraction result identified a magnetic peak with two-layer $c$-axis periodicity at $T_{N1} = 14$ K in a polycrystalline sample$^{11}$, we consider two-layered unit cells as well. Avoiding two Cl$^-$ triangular layers belonging to adjacent RuCl$_3$ layers to locate on top of each other (i.e. sitting on the same triangular sublattice), we have only three unit cells with space group $P31m$, $P31c$, and $Cmce_2$ as shown in Fig. 6. Note that, the $P31m$ cell is just a doubling of single-layer unit cell, and the $P31c$ structure differ from the $P31m$ structure by the position of Ru hollow sites, so that half of Ru sites avoid sitting on top of Ru sites in the neighboring layer as shown in bottom panels of Fig. 6. Finally, the $Cmce_2$ structure differs from other unit cells by anti-cyclic stacking of every other RuCl$_3$ layer as shown in the stacking sequence in the figure, which can be obtained by applying mirror operation to every other RuCl$_3$ layers.

Structure optimizations were performed including SOC, and Table II shows the optimized lattice constants with respect

| Case 0 structure: old $P3_112$ structure (from Ref. 3, $a$=a$_0$, $b$=b$_0$) | $d_{\text{avg}}^{\text{Ru-Cl}}$ (in Å) | $d_{\text{Ru-Ru}}$ (in Å) | $t_1$ (in eV) | $t_2$ (in eV) | $t_3$ (in eV) | $t_4$ (in eV) | $J$ (in meV) | $K$ (in meV) | $\Gamma$ (in meV) | $\Gamma'$ (in meV) |
|---|---|---|---|---|---|---|---|---|---|---|
| NN | 2.45 | 3.44 | +0.066 | +0.114 | -0.229 | -0.010 | -3.50 | +4.60 | +6.42 | -0.04 |
| Case I structure: $a$=0.981$a_0$, $b$=0.986$b_0$ (structure optimized with SOC) | NN-Z | 2.34 | 3.40 | +0.058 | +0.177 | -0.154 | -0.022 | -2.67 | -4.52 | +7.27 | -0.67 |
| | NN-X/Y | 3.38 | 3.44 | +0.042 | +0.176 | -0.107 | -0.030 | -1.55 | -6.47 | +5.24 | -1.08 |
| Case II structure: $a$=a$_0$, $b$=b$_0$ (structure optimized with SOC and lattice constants fixed) | NN-Z | 2.36 | 3.44 | +0.044 | +0.178 | -0.109 | -0.019 | -1.49 | -6.71 | +5.28 | -0.69 |
| | NN-X/Y | 3.38 | 3.44 | +0.042 | +0.176 | -0.107 | -0.030 | -1.55 | -6.47 | +5.24 | -1.08 |
| Case III structure: $a$=1.011$a_0$, $b$=1.006$b_0$ (structure optimized with SOC, $U_{\text{eff}}$, and zigzag order) | NN-Z | 2.36 | 3.47 | +0.036 | +0.191 | -0.062 | -0.024 | -0.74 | -9.34 | +3.71 | -1.04 |
| | NN-X/Y | 3.38 | 3.47 | +0.037 | +0.182 | -0.075 | -0.026 | -1.09 | -7.64 | +4.38 | -0.87 |
V. STACKING WITH ZIGZAG MAGNETIC ORDER

Now we present the stacking results that include the on-site Coulomb interaction and magnetism. Fig. 8 shows 10 trial structural and magnetic configurations, where the direction of magnetic moments in each layer is the same with the single-layer result in Sec. III. Fixing the in-plane zigzag order, we chose two interlayer magnetic configurations that we denote as cFM and cAF hereafter. As shown in Fig. 8, in the cFM configuration the zigzag-ordered layers are stacked along the c-direction so that the FM zigzag chains in adjacent layers become closer in distance, while in the cAF configuration the moments on one Ru layer are flipped. Note that, there can be additional magnetic stacking orders due to the three-fold rotational degree of freedom for each single-layer zigzag order — three different direction for FM zigzag chains — and in this work we chose the simplest configuration commensurate to the monoclinic unit cell (shown in Fig. 2(a)) for each structure. Structural optimizations were done first by varying c-axis with fixing a-lattice constants determined in the results without SOC (not shown) due to the presence of flat bands along the c-direction at the Fermi level. Inclusion of SOC smoothes the peaks, but the gross feature remains the same as shown in Fig. 7, so resulting in higher DOS at the Fermi level except the $P31m$ structure as shown in Table II. Note that, Stoner-type ferromagnetic (FM) instability is also observed, but in this study we concentrate on the experimentally observed zigzag magnetic order as discussed in the next section.

TABLE III. Optimized lattice constants for five stacking unit cells with using PBEsol functional and including SOC, $U_{eff}$ and magnetism. $a$, $b$, and $c$ are the optimized monoclinic lattice constants (shown in Fig. 1) with $a_0$, $b_0$, and $c_0$ being their experimentally observed values, respectively.

| Lattice constants | $P3_{12}$ | $C2/m$ | $P31m$ | $P31c$ | $Cmc2_1$ |
|-------------------|-----------|--------|--------|--------|----------|
| $a/a_0$           | 1.011     | 1.011  | 1.010  | 1.011  | 1.010    |
| $b/b_0$           | 1.006     | 1.006  | 1.006  | 1.006  | 1.006    |
| $c/c_0$           | 1.041     | 1.043  | 1.067  | 1.039  | 1.056    |
| $\Delta E$ / f.u. (meV) | 0.4 | 0.1 | 3.7 | 0.8 | 0.0 |
| $c$ /m | 0.4 | 0.2 | 4.1 | 0.9 | 0.4 |

TABLE II. Optimized lattice constants, relative total energies ($\Delta E$) per formula unit (f.u.), and densities of states (DOS) at the Fermi level for five stacking unit cells. Values are obtained using PBEsol functional and including SOC, but without electron interactions.

| Lattice constants | $P3_{12}$ | $C2/m$ | $P31m$ | $P31c$ | $Cmc2_1$ |
|-------------------|-----------|--------|--------|--------|----------|
| $a/a_0$           | 0.984     | 0.981  | 0.986  | 0.985  | 0.984    |
| $b/b_0$           | 0.984     | 0.986  | 0.986  | 0.986  | 0.983    |
| $c/c_0$           | 1.014     | 1.013  | 1.005  | 1.007  | 1.014    |
| $\Delta E$ / f.u. (meV) | 1.4 | 1.4 | 0.0 | 2.8 | 2.5 |
| DOS at $E_F$ (in states / eV / f.u.) | 9.2 | 7.9 | 6.0 | 10.8 | 8.5 |

To experimentally reported lattice constants $a_0 = 5.96\,\text{Å}$ and $c_0 = 17.2\,\text{Å}$ and their relative total energies. Note that, structures without threefold symmetry — monoclinic $C2/m$ and orthorhombic $Cmc2_1$ — shows slightly different $a/a_0$ and $b/b_0$. Among the five different structures, the $P31m$ structure yields the lowest energy. The $P3_{12}$ and $C2/m$ structures are closer in energy by 1.4 meV / f.u., and for the other phases energy differences are less than 3 meV / f.u. compared to the the $P31m$ structure. The lowest energy of the $P31m$ structure can be attributed to the larger kinetic energy gain originating from the larger band dispersion along the c-direction compared to other structures. This is reflected in the lower DOS of the $P31m$ cell at the Fermi level compared to other structures, as shown in Table II and Fig. 7. Fig. 7 presents total DOS for the five structures in the presence of SOC. Compared to the single-layer result depicted as grey shade in the figure, layer stacking yields pronounced peaks near the Fermi level except the $P31m$ structure in the results without SOC (not shown) due to the presence of flat bands along the c-direction at the Fermi level. Inclusion of SOC smoothes the peaks, but the gross feature remains the same as shown in Fig. 7, so resulting in higher DOS at the Fermi level except the $P31m$ structure as shown in Table II. Note that, Stoner-type ferromagnetic (FM) instability is also observed, but in this study we concentrate on the experimentally observed zigzag magnetic order as discussed in the next section.
FIG. 6. (Color online) Five different unit cells with two- and three-layer periodicity along c-direction. Upper and lower panels show the side view of the unit cell and schematic top view of Ru honeycomb stacking, respectively.

FIG. 7. Densities of states (DOS) for different α-RuCl$_3$ structures including SOC in the absence of $U_{eff}$ and magnetism. Grey shade shows DOS of single-layer RuCl$_3$ multiplied by 0.5 as a reference.

FIG. 8. (Color online) 10 trial magnetic configurations with in-plane zigzag order, where red and blue symbols depicting Ru sites with antiparallel magnetic moments to each other.

for each stacking with different magnetic configuration (either cFM or cAF configurations in Fig. 8) yielded negligible differences. All of the configurations become insulator with the gap of $\sim 1$ eV between the lower and upper Hubbard bands at $U_{eff} = 2$ eV. DOS for the resulting phases are almost identical to the one from single-layer calculation$^{10}$ and show no significant difference compared to each other, so we do not present the DOS plots here.

Table III shows the optimization results. Compared to the results without stacking and magnetism, a few differences can be noticed; i) Energy differences between structures are less
than 1 meV per f.u. except the $P\bar{3}1m$ structure, which is higher in energy by $\sim 4.0$ meV / f.u. compared to other structures. Note that, the $P\bar{3}1m$ structure showed the lowest energy in the calculation without $U_{\text{eff}}$ and magnetism. With $U_{\text{eff}}$ and magnetism introduced, gap is fully opened for all of the structures and the relative energy gain in the $P\bar{3}1m$ structure due to the c-axis dispersion (discussed in Sec. IV) becomes smaller. ii) Energy differences between cFM and cAF configurations are smaller than 0.1 meV / f.u. for the $P\bar{3}12$, $C2/m$, and $P31c$ structures, and for the $P31c$ and $Cmc2_1$ stackings the differences are about 0.4 meV / f.u. Such small energy differences can be attributed to weak interlayer exchange interactions, which will be discussed later in the last paragraph of this section. iii) Lattice constants are increased by 2 to 3 % compared to the results without $U_{\text{eff}}$. iv) Small monoclinic distortion, which manifests itself by the difference of $a/a_0$ and $b/b_0$ (and negative $\delta$ in Fig. 2), happens in every structures in the presence of the in-plane zigzag magnetic order.

Except the $P\bar{3}1m$ structure which is higher in energy by $\sim 4$ meV / f.u. compared to other structures, the structural energy differences are smaller than 1 meV. This result implies the coexistence of different structures in experimentally synthesizes samples. Especially, it is natural that the $P\bar{3}12$ and $C2/m$ structures have similar total energies; their only difference is the stacking of the Ru honeycomb order, which can be switched to each other by the ionic hopping of Ru atoms within the RuCl$_3$ layers. Indeed, both were reported as the crystal structure of $\alpha$-RuCl$_3$ by different groups$^{3,11,22}$. It is also interesting that, the $Cmc2_1$ structure (with cFM order) shows the lowest energy, which can be transformed into other structures by applying mirror operations to every other RuCl$_3$ layers. One can speculate that the $Cmc2_1$ structure forms in high temperature regime and freeze below $T \sim 150$ K, where an anomalous behavior in magnetic susceptibility observed$^{3,6}$, so contributing to the magnetic peak with two-layer periodicity in polycrystalline samples below $T_{N1} \sim 14$ K$^{5,7,11}$.

Finally, we comment on the interlayer exchange interactions. Major interlayer hopping channels are shown in Fig. 9, where the largest channel is depicted as green solid arrow while others are represented as dashed/dotted arrows. Note that, value of the largest interlayer $t_{2g}$ hopping term is about 35 meV, and magnitudes of other channels depicted in the figure are comparable to the largest one; about 20 to 30 meV.

The interlayer exchange Heisenberg term is roughly estimated to be $J = t_{2g}^2/9U \sim 0.05$ meV for the $j_{\text{eff}} = 1/2$ pseudospins. This value is two orders-of-magnitude smaller than the previously estimated in-plane exchange interactions in $\alpha$-RuCl$_3$$^{8,11}$, and is also consistent with the small energy differences between the cFM and cAF phases discussed above.

VI. DISCUSSION

The relative energies between different stacking order depends on the electronic structures of each system in our results, especially whether the system becomes fully insulating or not. Given that $\alpha$-RuCl$_3$ remains insulating in the paramagnetic phase above $T_{N1}$ with 1 eV of optical gap$^{4,10}$, we speculate that the four stacking orders — $P\bar{3}12$, $C2/m$, $P31c$, and $Cmc2_1$ — are almost degenerate as discussed in Sec. V.

The change of hopping integrals and exchange interaction terms after the structure optimization show that the physics of $\alpha$-RuCl$_3$ is sensitive the NN Ru-Ru distance and Cl position. For example, the strength of the Kitaev and $\Gamma$ terms are significantly modified by the Ru-Ru and Ru-Cl distances. This implies that, even a small amount of epitaxial tensile strain by 1% or uniaxial pressure perpendicular to the layer can significantly enhance the Kitaev term and push the system closer to the Kitaev limit. On the other hand, hydrostatic pressure or compressive strain can increase the $t_3$ term by decreasing the Ru-Ru distance. This reduces the FM Kitaev term and drive the effective model to the highly frustrated $\Gamma$-dominated regime. In addition, presence of the negative $\Gamma'$ term due to the trigonal distortion can stabilize the zigzag-ordered phase as discussed in previous study$^{43}$. Effects of the monoclinic bond disproportionation$^{44}$ is another factor that can change the magnetism. In this regard, full experimental structure determination including precise atomic positions and stacking order would be important for future studies.

In summary, structural properties of $\alpha$-RuCl$_3$ from $\textit{ab initio}$ calculations are presented in this study. SOC is found to prevent the Ru dimerization in the Ru honeycomb layers, and the presence of in-plane zigzag magnetic order further gives small monoclinic distortion. The relation between the hopping integrals and exchange interactions to the structure is also discussed. Total energy comparison between different RuCl$_3$ stacking orders yields the $Cmc2_1$ and $C2/m$ structures to be the almost degenerate ground state structures, and $P\bar{3}12$ structure to be comparable in energy; energy differences smaller than 0.4 meV per formula unit. In-plane exchange interactions are found to be sensitive to the structural distortions, and the $j_{\text{eff}} = 1/2$ pseudospin model is dominated by the FM Kitaev terms in the optimized structures with the presence of $U_{\text{eff}}$, similar to the two- and three-dimensional honeycomb iridates$^{45-47}$. As expected, interlayer exchange interactions are estimated to be weak compared to the in-plane exchange interactions, so this system can be a good platform in studying frustrated two-dimensional magnetism.

Note added — After the completion of the manuscript, we
became aware of the experimental work by Johnson and co-workers\textsuperscript{18}, which reports monoclinic $\text{C2} / \text{m}$ crystal structure and the in-plane zigzag magnetic configuration with antiferromagnetic interplanar order below $T_N \sim 13$ K.

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**Appendix A: van der Waals calculation**

In this Appendix we compare the results with using different exchange-correlation functionals including vdW interactions. Four functionals are considered; PBE, PBEsol, vdW-DF\textsuperscript{29} and vdW-optB86b\textsuperscript{50}, where vdW-DF2 and vdW-optB86b functionals showed accuracies comparable to RPA calculations in layered and bulk systems, respectively. Here SOC, $U_{\text{eff}}$, and magnetism are not included.

Fig. A1 shows relative energies versus $c$-lattice constant with fixed $a = a_0$ for the results with four functionals, where $\text{C2} / \text{m}$ stacking order is not considered. Except PBE, which yields unreasonably large value of $c$, other three functionals yields $P31m$ and $P31c$ as configurations with the lowest and second lowest energy. Compared to PBEsol, vdW functionals tend to yield steeper energy curve away from the optimum $c$ values and higher energy for $P3_112$ phase.

Table A1 shows the results from full lattice optimizations. Except the change of $a$-lattice constants, where vdW-DF2 results yields 3\% enhancement of $a$ value, the features are qualitatively similar to the results in Fig. A1. $P31m$ is still the most favored configuration, and optimized $c$-lattice constants do not change significantly from the values in Fig. A1. It is notable that the vdW results give high energies for $P3_112$ and $\text{Cmc2}_1$ phases, which were the favored phases in PBEsol+SOC+$U_{\text{eff}}$ calculations.

Compared to the vdW functionals, PBEsol yields reasonable estimates of total energy and lattice constants, although quantitative differences can be noticed. Since test calculations on combining vdW functionals and DFT+SOC+$U$, which is crucial in understanding physics of RuCl$_3$, have not been done yet, in this study PBEsol functional is employed for the rest of the calculations.
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