Strongly anisotropic electronic and magnetic structures in oxide dichlorides RuOCl$_2$ and OsOCl$_2$

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The van der Waals oxide dichlorides MOX$_2$ ($M = V$, Ta, Nb, Ru, and Os; $X =$ halogen element), with different electronic densities, are attracting considerable attention. Ferroelectricity, spin-singlet formation, and orbital-selective Peierls phases were reported in this family with $d^1$ or $d^2$ electronic configurations, all believed to be caused by the strongly anisotropic electronic orbital degree of freedom. Here, using density functional theory and density matrix renormalization group methods, we investigate the electronic and magnetic properties of RuOCl$_2$ and OsOCl$_2$ with $d^4$ electronic configurations. Different from a previous study using VOI$_2$ with $d^1$ configuration, these systems with $4d^2$ or $5d^4$ do not exhibit a ferroelectric instability along the $a$ axis. Due to the fully occupied $d_{yz}$ orbital in RuOCl$_2$ and OsOCl$_2$, the Peierls instability distortion disappears along the $b$ axis, leading to an undistorted Immm phase (No. 71). Furthermore, we observe strongly anisotropic electronic and magnetic structures along the $a$ axis. For this reason, the materials of our focus can be regarded as “effective one-dimensional” systems even when they apparently have a dominant two-dimensional lattice geometry. The large crystal-field splitting energy (between $d_{x^2-r^2}$ and $d_{xy}$ orbitals) and large hopping between nearest-neighbor Ru and Os atoms suppresses the $J = 0$ singlet state in MOCl$_2$ ($M =$ Ru or Os) with electronic density $n = 4$, resulting in a spin-1 system. Moreover, we find staggered antiferromagnetic order with $\pi$ wave vector along the $M$-$O$ chain direction ($a$ axis) while the magnetic coupling along the $b$ axis is weak. Based on Wannier functions from first-principles calculations, we calculated the relevant hopping amplitudes and crystal-field splitting energies of the $t_{2g}$ orbitals for the Os atoms to construct a multiorbital Hubbard model for the $M$-$O$ chains. Staggered AFM with $\uparrow - \downarrow - \uparrow - \downarrow$ spin structure dominates in our density matrix renormalization group calculations, in agreement with density functional theory calculations. Our results for RuOCl$_2$ and OsOCl$_2$ provide guidance to experimentalists and theorists working on this interesting family of oxide dichlorides.

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I. INTRODUCTION

One-dimensional (1D) material systems continue to attract considerable attention due to their rich physical properties induced by their 1D geometry and reduced dimensional phase space [1–9]. In these systems, many interesting phenomena have been found that are driven by intertwined charge, spin, orbital, and lattice degrees of freedom. For example, driven by electronic correlation effects (i.e., Hubbard repulsion $U$ and Hund coupling $J_H$), high critical temperature superconductivity was reported in 1D copper or iron chains and ladders [10–17]. By considering the phonon instability caused by the coupling between empty $d$ and fully occupied $O$ $2p$ states, ferroelectricity was found in the chain compound WOX$_2$ ($X =$ halogen element) [18]. Furthermore, by mixing spin-phonon and charge-phonon instabilities, multiferroelectric states were predicted in some 1D systems [19–22]. Due to the partial or complete condensation of excitations, a charge density wave or a spin density wave were also reported in some 1D systems [2,23–25].

A wide variety of real materials also have dominant 1D-like physical properties, even without restrictive 1D geometries in their crystal structure, due to the strongly anisotropic electronic orbital degree of freedom. Recently, several different interesting 1D physical properties were reported in oxide dichlorides MOX$_2$ ($M =$ V, Ta, Nb, Ru and Os; $X =$ halogen element) with various electronic densities $n$ for the $M$ atoms [26–32]. The parent phase of MOX$_2$ ($M =$ V, Ta, Nb, Os; $X =$ halogen element) is a typical member of the layered van der Waals (vdW) family [26–28], where the MO$_2$X$_4$ octahedra are corner sharing along the $a$ axis, while edge sharing along the $b$ axis (see Fig. 1). The remarkable effective 1D-like behavior of this family can be understood from the strong anisotropic behavior of different orbitals.

In MOX$_2$, the MO$_2$Cl$_4$ octahedra are edge-sharing connected, opening the possibility of strong overlap of $d_{xy}$ orbitals along the $xy$ plane. Due to the 1D $M$-$X$ chain geometric structures along the $b$ axis [see Figs. 1(b) and 1(c)], the band structure resulting from the $xy$ orbital displays strong anisotropy. Furthermore, the $d_{z^2}$ and $d_{xy}$ orbitals also display anisotropy along the $a$ axis due to the $M$-$O$ geometric chain, while it forms the vdW layer along the $c$ axis. For the $n =$ 1 case with $d^1$ electronic configuration ($V$ or Nb), a ferroelectric (FE) distortion [29–31,33] was theoretically predicted along the $M$-$O$ direction ($a$ axis), where the “pseudo-Jahn-Teller” effect caused by the coupling between empty $d$ ($d_{z^2}$ and $d_{xy}$) and $O$ $2p$ orbitals plays an important role to stabilize the FE distortion [34]. In addition, Peierls distortions were
found along the $b$ axis \[31,34\], resulting in a spin-singlet configuration for the $d_{xy}$ orbitals \[34\], due to the formation of molecular states in the $d_{xy}$ bands. Very recently, the FE and Peierls distortions were confirmed experimentally for NbOCl$_2$ with $4d^1$ electronic configuration \[35\]. With additional spin-orbit coupling (SOC), a spin texture was also found at the $Y$ point along the $M$-$X$ chain direction \[36\].

For the case of a $d^2$ electronic configurations, MoOCl$_2$ was experimentally reported to be a strongly correlated dimerized metal based on temperature-dependent transport measurements along the $M$-$X$ chain direction \[32\]. The metallic conductivity arises from the strongly anisotropic Mo-$d_{xz/yz}$ bands \[37,38\]. Furthermore, an interesting orbital-selective Peierls phase was also found to be stable in MoOCl$_2$ \[38\] because the intrahopping amplitude $t$ is larger than the typical Hund couplings. This phase resembles the previously discussed orbital-selective Mott phase \[39-43\] but with the localized band induced by Peierls distortions instead of Hubbard interactions \[38,44\]. Moreover, highly anisotropic plasmons were also discussed in the monolayer MoOCl$_2$ \[45\].

Yet almost no research has been done for other electronic densities $n$ of $M$ atoms in this family. RuOCl$_2$ and OsOCl$_2$ with $d^1$ electronic configuration were synthesized \[26\], and it was reported that orthorhombic structures are formed with the space group $Immm$ (No. 71) (see Fig. 1). Due to a reduced $J_H$, often $4d/5d$ atoms favor the total $S = 1$ configuration in compounds with more than half-filled $t_{2g}$ states, leading to four electrons occupying three $t_{2g}$ orbitals in both RuOCl$_2$ and OsOCl$_2$. Considering the development of different 1D behaviors caused by different $t_{2g}$ orbitals, a simple question naturally arises: Can RuOCl$_2$ and OsOCl$_2$ also display similar physical properties? In addition, with additional SOC, $d^1$ materials are expected to be nonmagnetic insulators formed by local two-hole $J = 0$ singlets \[46,47\]. Is it possible to obtain $J = 0$ singlets in RuOCl$_2$ and OsOCl$_2$ as well?

To answer these questions, we employ both density functional theory (DFT) and density matrix renormalization group (DMRG) methods to numerically investigate RuOCl$_2$ and OsOCl$_2$ in detail. Based on DFT calculations, we have found that there are no FE distortions and Peierls instabilities occurring along the $a$ or $b$ axis in the undistorted phase of this system. Furthermore, we also observed a strongly anisotropic electronic structure along the $a$ axis. Because of the large crystal-field splitting energy (between $d_{xz/yz}$ and $d_{xy}$ orbitals) and the large nearest-neighbor (NN) hopping, the $J = 0$ singlet ground state is suppressed in this system with the $d^1$ electronic configuration, leading to a spin-1 system. In addition, based on DFT calculations, we also found a strongly anisotropic electronic structure, with strong couplings along the $a$ axis and much weaker coupling along the $b$ axis for both RuOCl$_2$ and OsOCl$_2$. For this reason, surprisingly, these systems can be regarded as “effective 1D” materials, although naively they should be planar two-dimensional (2D) systems.

Using Wannier functions from first-principles calculations, we obtained the relevant hopping amplitudes and crystal-field splitting energies for the $t_{2g}$ orbitals of the Ru/Os atoms. We found that staggered spin order is the most likely magnetic ground state, with a $\pi$ wave vector order along the chain direction. Finally, we constructed a multiorbital Hubbard model for the $M$-$O$ chains and analyzed this model using DMRG. Our results show that staggered AFM order with $\uparrow - \downarrow - \uparrow - \downarrow$ spin structure is dominant, consistent with the DFT calculations.

II. METHOD AND DFT CALCULATIONS

In this study, first-principles DFT calculations were performed using the Vienna $ab$ initio simulation package (VASP) code \[48-50\] with the projector augmented wave (PAW) method. Electronic correlations were considered by using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) potential \[51\]. The $k$-point mesh adopted was $16 \times 16 \times 5$ for the conventional cell of the bulk system, while the plane-wave cutoff energy was 600 eV. We have tested explicitly that this $k$-point mesh already leads to converged energies. Furthermore, 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 van der Waals (vdW) interactions Becke-Jonson damping vDW-D3 \[52\] were considered to deal with interactions between different layers. The phonon spectra were calculated using the density functional perturbation theory approach \[53,54\] and analyzed by the PHONOPY software \[55,56\]. In addition to the standard DFT calculation discussed thus far, the maximally localized Wannier functions (MLWFs) method was employed to fit the Ru $4d$’s or Os $5d$’s three $t_{2g}$ bands near the Fermi level using the WANNIER90packages \[57\]. All the crystal structures were visualized with the VESTA code \[58\].

To better understand the magnetic properties, we also relaxed the crystal structures for selected different spin configurations based on the $2 \times 2 \times 1$ supercell. Furthermore, the onsite Coulomb interactions were considered by using the local spin density approximation (LSDA) plus $U$ with the Liechtenstein formulation for the double-counting term \[59\]. Based on previous experimental and theoretical studies for $4d$ and $5d$ compounds \[60-62\], the onsite Coulomb interaction $U$ and onsite exchange interaction $J$ were chosen as $U = 3$ eV.
FIG. 2. Phonon spectrum of the bulk system for (a) RuOCl$_2$ and (b) OsOCl$_2$. A $4 \times 4 \times 1$ supercell was used in our calculations and the nonmagnetic state. The coordinates of the high-symmetry points in the bulk Brillouin zone (BZ) are $\Gamma = (0, 0, 0), X = (0.5, 0, 0), S = (0.5, 0.5, 0), Y = (0.5, 0.5, 0), Z = (0, 0, 0.5), U = (0.5, 0, 0.5), R = (0.5, 0.5, 0.5),$ and $T = (0.5, 0.5, 0.5)$ in units of $2\pi$.

and $J = 0.6$ eV for RuOCl$_2$, and $U = 2$ eV and $J = 0.4$ eV for OsOCl$_2$, respectively.

III. DFT RESULTS

A. Structural properties

Based on our structural optimization calculation of the bulk nonmagnetic (NM) state, the optimized crystal lattices are $a = 3.666$, $b = 3.554$, and $c = 11.266$ Å for RuOCl$_2$, close to experimental values ($a = 3.673$, $b = 3.520$, and $c = 11.258$ Å) [26]. We also obtained the lattice constants of OsOCl$_2$ ($a = 3.718$, $b = 3.615$, and $c = 11.079$ Å), also in agreement with experiments ($a = 3.701$, $b = 3.575$, and $c = 11.083$ Å) [26].

Before turning to the physical properties of MOCl$_2$ ($M =$ Ru or Os), we discuss their structural properties. We carried out phononic dispersion calculations using a $4 \times 4 \times 1$ supercell to understand the structural stability of the undistorted Immm phase (No. 71). Figure 2 indicates that there is no imaginary frequency mode obtained in the phononic dispersion spectrum for the Immm phase of RuOCl$_2$ and OsOCl$_2$. Therefore, the undistorted Immm phase of bulk MOCl$_2$ ($M = $ Ru or Os) is dynamically stable, in agreement with experiments [26].

In previous studies for this vdW family of layered oxide dichlorides MOX$_2$ ($M = V, Ta, Nb, Os; X =$ halogen element), the FE distortion along the $a$ axis and the $M-M$ dimerization along the $b$ axis induced structural instabilities, leading to lower symmetry structures [34], such as in the case of the FE distortion in VOI$_2$ ($3d^1$) [29,33] or NbOI$_2$ ($4d^1$) [31,35] and the Peierls distortion in MoOCl$_2$ ($4d^2$) [32] or TaOI$_2$ ($5d^1$) [28].

How do we understand why the FE and Peierls distortions disappeared in RuOCl$_2$ and OsOCl$_2$? This can be easily understood in the following way: In the octahedral crystal field, the five $d$ orbitals split into two higher-energy $e_g$ ($d_{x^2−y^2}$ and $d_{3z^2−r^2}$) and three lower-energy $t_{2g}$ ($d_{xy}$, $d_{xz}$, and $d_{yz}$) orbitals, as in Fig. 3(a). Due to their reduced coupling $J_H$, the $4d^2$ and $5d^4$ atoms always favor the total $S = 1$ electronic configuration when the $t_{2g}$ orbitals are more than half-filled. Then, replacing the Cl atoms of the octahedral apex by O atoms, it would induce two shortened $M-O$ bonds ($M = $ Ru or Os) along the $a$ axis ($z$ axis) and four elongated $M$-$Cl$ bonds ($M = $ Ru or Os) along the $bc$ ($xy$) plane in the MO$_2$Cl$_4$ ($M = $ Ru or Os) octahedral configuration, leading to the splitting between the $t_{2g}$ orbitals [see Fig. 3(a)]. In this case, the four electrons form a total $S = 1$ electronic configuration with one fully occupied lower $d_{xy}$ orbital and two half-filled higher-energy $d_{3z^2−r^2}$ bands.

Because two electrons occupy two $d_{3z^2−r^2}$ orbitals in MOCl$_2$ ($M = $ Ru or Os), the FE distortion along the $a$ axis is energetically unfavorable, as discussed in VOI$_2$ with the $d^1$ configuration [34]. Furthermore, the spin-singlet formation using $d_{xy}$ orbitals would also be suppressed along the $b$ axis since $d_{xy}$ is a double-occupied state in MOCl$_2$ ($M = $ Ru or Os). Hence, both FE and dimerized instabilities are
suppressed for RuOCl$_2$ and OsOCl$_2$, resulting in a stable undistorted $Immm$ phase (No. 71).

**B. Electronic properties of the NM state**

Next, we focus on the electronic structures of bulk MOCl$_2$ ($M =$ Ru or Os) for the NM state without SOC. Figures 3(b) and 3(c) show that the $e_g$ ($d_{x^2−y^2}$ and $d_{z^2−r^2}$) bands of Ru’s $4d$ and Os’s $5d$ orbitals are located at high energy, and therefore are unoccupied. The local $z$ axis is the $a$ axis, while the local $x$ or $y$ axis is along the $M$-Cl directions [see Fig. 1(c)], leading to a $d_{yz}$ orbital lying on the $bc$ plane. In addition, we estimated that the energy splitting $\Delta_2$ between $d_{x^2−y^2}$ and $d_{z^2−r^2}$ orbitals is about 1.7 and 1.6 eV for RuOCl$_2$ and OsOCl$_2$, respectively, by the weight-center positions of the energy bands. Furthermore, we estimated that the energy splitting $\Delta_1$ between $d_{z^2}$ and $d_{r^2}$ orbitals, contributing to the Fermi surface. We also estimated that the energy splitting $\Delta_0$ (between $d_{xy}$ and $d_{z^2}$) is $\Delta_1 = 1.2/1.3$ eV and $\Delta_0 = 1.2/1.4$ eV for RuOCl$_2$ and OsOCl$_2$, respectively. Considering the large crystal-field splitting $\Delta_0$, the $J = 0$ singlet ground state induced by SOC may be suppressed in MOCl$_2$ ($M =$ Ru or Os), as discussed for the OsCl$_4$ case with the $d^4$ electronic configurations [63].

Due to the fully occupied $d_{yz}$ state and large energy splitting $\Delta$, the magnetic properties of MOCl$_2$ ($M =$ Ru or Os) are dictated by the $d_{yz}$ and $d_{xy}$ orbitals to be discussed in the following sections. Moreover, near the Fermi level, MOCl$_2$ ($M =$ Ru or Os) displays strongly quasi-1D electronic behavior with contributions from the $d_{xz}$ and $d_{yz}$ orbitals, and the band structures are much more dispersive along the $a$ axis (i.e., $\Gamma$-$X$ path) than along other directions (i.e., $X$-$S$ and $\Gamma$-$Z$ paths). For this reason, these materials can be regarded as “effective 1D” systems, as mentioned before.

After considering SOC in the NM state of MOCl$_2$ ($M =$ Ru or Os), the bands begin to split as displayed in Fig. 4, opening an energy gap $\sim$0.12 eV for RuOCl$_2$ and $\sim$0.41 eV for OsOCl$_2$ along the $T$-$Z$ high-symmetry path at $\sim$1 eV below the Fermi level. However, introducing SOC, the band structures near the Fermi level do not change much. Furthermore, the large bandwidth of the $d_{z^2}$ states of MOCl$_2$ ($M =$ Ru or Os) suggests a large value for the NN hopping of Os or Ru atoms along the $a$ axis. Considering the typical SOC value of Ru and Os atoms [64,65], the $J_{\text{eff}}$ physics would be suppressed by the large crystal-field splitting and large hopping $t$. In this case, this system should be a spin-1 system, instead of a $J = 0$ singlet ground state, leading to the quenched orbital magnetic moment in those $d^4$ systems, as discussed in the following section. By considering the typically reduced Hubbard $U$ repulsion in $4d$ and $5d$ atoms, as compared to $3d$ atoms, and the large bandwidth of these systems (with the hopping $t$ providing the scale), this system is an “intermediate” electronic correlation system. Furthermore, we also considered the electronic correlations on Ru ($U = 3$ eV and $J = 0.6$ eV) or Os ($U = 2$ eV and $J = 0.4$ eV) sites, by using the LSDA+$U$ method with Liechtenstein format within the double-counting term [59]. Figure 4 also indicates that the lower-energy $d_{yz}$ states of MOCl$_2$ ($M =$ Ru or Os) begin to shift away from the Fermi level with fully occupied characteristics when electronic correlations on the Ru or Os sites are considered.

For the benefit of the readers, we construct a qualitative physical picture for the breakdown of the $J = 0$ singlet ground state in this system, as shown in Fig. 5. First, let us discuss the three nearly degenerate $t_{2g}$ orbitals in a low-spin $d^4$ system without electronic correlations. Because $\lambda$ (SOC strength) $\gg W$ (bandwidth, corresponding to the hopping $t$), the system is in a $J = 0$ insulator with fully occupied $J_{\text{eff}} = \frac{3}{2}$ states [see Fig. 5(a)]. In this case, the gap is opened by the splitting between $J_{\text{eff}} = \frac{3}{2}$ and $\frac{1}{2}$ states caused by SOC, as displayed in Fig. 5(a). If, however, $\lambda \ll W$, then, the system will keep a $S = 1$ state due to the Pauli rule, as shown in Fig. 5(b). In this state, four electrons occupy three degenerate $t_{2g}$ orbitals, leading to a metallic phase. In our case (RuOCl$_2$ and OsOCl$_2$), it is also a $S = 1$ state with one fully occupied ($d_{z^2}$) and two half-occupied ($d_{xz}$ and $d_{yz}$) orbitals, as presented in Fig. 5(c). Then, the $J = 0$ singlet ground state is suppressed in our case by the large crystal-field splitting ($\Delta_0$) and large bandwidth ($W$). Finally, as we will discuss in the following section, the system will be a Mott insulator when electron correlations are considered.

**C. DFT magnetic properties**

To better understand the in-plane magnetic properties of MOCl$_2$ ($M =$ Ru or Os), we also studied several magnetic
configurations in a $2 \times 2 \times 1$ monolayer structure by considering different NN couplings along the $a$ and $b$ axes, as shown in Fig. 6. In addition, we also relaxed the crystal structures for different spin configurations based on the LSDA+$U$ method with Liechtenstein format [59]. Here, we used $U=3$ eV and $J=0.6$ eV for RuOCl$_2$, and $U=2$ eV and $J=0.4$ eV for OsOCl$_2$, respectively, based on previous theoretical studies [61,66].

First, let us discuss the results without SOC, summarized in Table I. For RuOCl$_2$, the stripe-$b$ state has the lowest energy among all tested candidates, while for OsOCl$_2$ the G-type AFM order is the lowest energy. Furthermore, the energy differences between stripe-$b$ and G-AFM configurations are quite small ($\sim$1–2 meV per Ru or Os), suggesting a weak magnetic exchange coupling along the $MCl_2$ ($M =$ Ru or Os) chain direction, as in our intuitive analysis from the Wannier function results (see Appendix). In addition, the optimized crystal structures of different spin configurations are very similar to each other, indicating the spin-lattice coupling is not strong in this system. The calculated local spin magnetic moments are about 1.46 $\mu_B$/Ru and 1.02 $\mu_B$/Os for RuOCl$_2$ and OsOCl$_2$, respectively, corresponding to the $S = 1$ configuration in Ru$^{4+}$ or Os$^{4+}$.

Next, we compared the energies of different spin configurations with SOC. The stripe-$b$ and G-AFM states still have the lowest energies among all tested candidates for RuOsCl$_2$ and OsOsCl$_2$, respectively. Turning on the SOC, the spin quantization axis points to the [010] direction but with only a small difference in energy with respect to the [001] direction, indicating that the spin favors lying in the $bc$ crystal plane, corresponding to the $xy$ plane. Based on the energy difference between [010] and [001], we obtained that the magnetic anisotropy energies (MAE) are about 1.85 and 18.26 meV for RuOCl$_2$ and OsOCl$_2$, respectively. Furthermore, the calculated orbital magnetic moment is quenched closed to zero. In this case, the magnetism of this system is almost unaffected by the SOC.

In Fig. 7, we show the band structures of the stripe-$b$ AFM phase of RuOCl$_2$ calculated with or without SOC. Figure 7(a) indicates that the half-occupied $d_{xz/yz}$ orbitals display Mott-insulating behavior with a gap $\sim 1.4$ eV, while the $d_{xy}$ orbital is fully occupied. In this case, this system is in a total $S = 1$ state, where the magnetism is contributed by the $d_{xz/yz}$ states. Turning on the SOC, the bands begin to split at some high-symmetry points. In addition, we also calculated the band structure of the G-AFM state of OsOCl$_2$ without or with SOC, as displayed in Fig. 8. Similar to RuOCl$_2$, the $d_{xz/yz}$ orbitals show strong Mott-insulating behavior with a smaller gap $\sim 1$ eV, while the fully occupied $d_{xy}$ orbital does not contribute to the magnetism. However, the band splitting under SOC is stronger in OsOCl$_2$ than in RuOCl$_2$, as shown in Fig. 8(b), considering the Os atom column in the periodic table. Furthermore, the band structure of the magnetic systems is strongly anisotropic along the $a$ axis due to the strongly anisotropic $d_{xz/yz}$ orbitals, leading to an "effective 1D" magnetic system.

In addition, we also studied the effect of different values of $U$ (from 2 to 4 eV) without SOC, where $J$ is chosen as 0.6 or 0.4 eV for RuOCl$_2$ and OsOCl$_2$, respectively. The optimized crystal lattices are almost unchanged: for example, $a = 3.772$
FIG. 7. Projected band structures and density of states for the stripe-b state of RuOCl₂ (a) without SOC and (b) with SOC, respectively. The Fermi level is shown with dashed horizontal lines. The coordinates of the high-symmetry points in the BZ are Γ = (0, 0, 0), X = (0.5, 0, 0), S = (0.5, 0.5, 0), and Y = (0, 0.5, 0).

FIG. 8. Projected band structures and density of states for the G state of OsOCl₂ (a) without SOC and (b) with SOC, respectively. The Fermi level is shown with dashed horizontal lines. The coordinates of the high-symmetry points in the BZ are Γ = (0, 0, 0), X = (0.5, 0, 0), S = (0.5, 0.5, 0), and Y = (0, 0.5, 0).

TABLE II. The calculated total energy (in meV) per Ru or Os with different spin orientations (along [100], [010], and [001] crystal axes) and magnetic moments (in μB/Ru or μB/Os = units) for the ground state of RuOCl₂ and OsOCl₂. The total energy with [001] spin orientation (a crystal axis) is set to zero. MAE (in meV) per Ru or Os is obtained by comparing the energy difference between [010] and [001]. Here, we used different U (from 2 to 4 eV) at J = 0.6 and 0.4 eV for RuOCl₂ and OsOCl₂, respectively.

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and b = 3.556 Å for RuOCl₂ at U = 4 eV. By considering different effective U’s, the stripe-b and G-AFM states still have the lowest energies among all the tested candidates, with only a tiny difference in energy between RuOCl₂ and OsOCl₂. For RuOCl₂, the stripe-b AFM state has the lowest energy from U = 2 to 4 eV and the energy difference between stripe-b and G-AFM increases from 1.13 meV at U = 2 eV to 2.29 meV at U = 4 eV. For RuOCl₂, the G-type AFM has the lowest energy at U = 2 and 3 eV, while the stripe-b AFM order has the lowest energy at U = 4 eV.

Turning on the SOC for other values of U, the spin quantization axis still points along the [010] direction but with only a small difference in energy with respect to the [001] direction. The spin favors lying in the bc crystal plane, corresponding to the xy plane, independently of the choice of U in the range studied. As summarized in Table II, the MAE does not change much for RuOCl₂ and OsOCl₂ at different U’s slightly decreasing as U increases. Furthermore, all the calculated orbital magnetic moments are quenched closed to zero. In addition, we also studied the electronic structures of different U’s for RuOCl₂ and OsOCl₂ with SOC. As shown in Fig. 9, the Mott gap contributed by half-filling the dₓz/yzy orbitals begins to increases as U increases for both RuOCl₂ and OsOCl₂, as expected.

Finally, as a side remark, note that critical temperatures cannot be evaluated with DFT. Moreover, even with the DMRG to be used in the next section, due to the 1D nature of the chains studied, a finite critical temperature can only be obtained after including a weak coupling along the perpendicular directions, a formidable task for DMRG. Thus, estimations of those critical temperatures are postponed for future work.

IV. MULTIORBITAL HUBBARD MODEL AND DMRG RESULTS

For low-dimensional systems, interesting phenomena caused by strongly anisotropic electronic structures have been
DMRG, which includes quantum fluctuations [71–73], to bet-
an effective multiorbital Hubbard model and then used
properties. Because DFT neglects fluctuations, we constructed
may be important to clarify the true magnetic ground-state
understand the quasi-1D magnetic behavior of
M

atomic configurations. The model studied here includes ki-
ors orbitals, including 1D spin order [67], orbital ordering [68,69],
and (b) the G-AFM state of OsOCl2, both with SOC and
The standard interaction part of the Hamiltonian is given
relation \( U' = U - 2J_H \) is assumed due to rotational invari-
The third term represents the Hund’s coupling between electrons occupying the \( d \) orbitals, and the fourth term is the
pair hopping between different orbitals at the same site \( i \), where \( P_{iy} = c_{iy\uparrow}c_{iy\downarrow} \).
As explained above, to solve this multiorbital Hubbard
model and obtain magnetic properties along the \( a \) axis we
used DMRG, as implemented in the DMRG++ software [74].
Specifically, we employed a 24-site chain with open-boundary conditions (OBC). Furthermore, at least 1400 states were kept
and up to 21 sweeps were performed during our DMRG
calculations. The electronic filling \( n = 4 \) in the three orbitals was considered. This electronic density (four electrons in three orbitals) corresponds to the total \( S = 1 \) configurations of the \( d^4 \) configuration of Ru\(^{4+}\) or Os\(^{4+}\).
In the tight-binding term, we only considered the NN
hoppings of OsOCl2 along the \( a \) axis. The crystal-field splitting \( \Delta \)'s of orbitals \( \gamma \) are also obtained from the Wannier results of OsOCl2. More details about the
Wannier functions and hoppings can be found in Appendix B.
The total kinetic energy bandwidth \( W \) is 3 eV. To reproduce
the data shown in this publication, we prepared notes and
input files in [75] and in the Supplemental Material [76].
This system can be regarded as an “effective” low-energy model with four electrons in three orbitals, corresponding to
an electronic density per orbital \( \frac{4}{3} \). In addition, the SOC is not
important for the magnetism, hence, we do not introduce SOC
in our model. The NN hopping matrix used here is
\[
t_{iy\gamma} = \begin{bmatrix}
-0.713 & 0.013 & 0.000 \\
0.013 & -0.717 & 0.000 \\
0.000 & 0.000 & -0.011
\end{bmatrix}
\]
This reduction in complexity allows us to perform unbiased
DMRG calculations for this system. As displayed in Fig. 10,
the three-orbital tight-binding band structure agrees qualita-
tively with the DFT band structure along the \( a \) axis. Note that
a perfect agreement between Wannier and the tight-binding
bands for DMRG would require more long-range hoppings.
In our band structure calculation we employ unit cells with two Os atoms. Specifically, in Fig. 6 in the range from −2.5 to 0 eV
there are six bands because of the two Os atoms used, each

\[
H_k = \sum_{i\sigma\gamma\gamma'} t_{iy\gamma}(c_{i\gamma\sigma}^\dagger c_{i+1\gamma'\sigma} + \text{H.c.}) + \sum_{i\gamma\sigma} \Delta_{\gamma} n_{i\gamma\sigma},
\]
where the first part represents the hopping of an electron from
orbital \( \gamma \) at site \( i \) to orbital \( \gamma' \) at the NN site \( i+1 \) on a chain of
length \( L \). \( \gamma \) and \( \gamma' \) represent the three different orbitals \( \{d_{xz}, d_{yz}, d_{xy}\} \) indexed as \( \gamma = \{0,1,2\} \).

The standard interaction part of the Hamiltonian is given by
\[
H_{\text{int}} = U \sum_{i\gamma} n_{i\gamma\uparrow} n_{i\gamma\downarrow} + \left(U' - \frac{J_H i}{2}\right) \sum_{i\gamma<\gamma'} n_{i\gamma} n_{i\gamma'},
\]
\[
-2J_H \sum_{i\gamma' \gamma'} S_{i\gamma'} \cdot S_{i\gamma'} + J_H \sum_{i\gamma<\gamma'} (P_{i\gamma'}^\dagger P_{i\gamma'} + \text{H.c.}).
\]
The first term describes the intrapixel Hubbard repulsion and
the second term the interpixel repulsion, where the standard

FIG. 9. Band structures for (a) the stripe-b AFM state of RuOCl\(_2\) and (b) the G-AFM state of OsOCl\(_2\), both with SOC and \( U \). The Fermi level is shown with dashed horizontal lines.

FIG. 10. Three-orbital tight-binding model with nearest-
neighbor hoppings of OsOCl\(_2\) along the \( a \) axis. In the text in this
section we explain that using three bands is a simplification from
the six bands found in Fig. 6 near the Fermi level because in the
tight-binding calculation only one Os atom is used, while in the
band structure calculation we employ unit cells with two Os atoms.
spin structure factor is defined as in real space) for.

The real-space spin–spin correlations are defined as

and the orbital Hubbard model and the DMRG algorithm. The real-space spin–spin correlations are defined as

where \( J_{H} \) is used. Nevertheless, qualitative features related to magnetic states are expected to be captured by this simplification.

Next, we measured several observables by using the three-orbital Hubbard model and the DMRG algorithm. The real-space spin–spin correlations are defined as

where \( \gamma \) is the matrix elements of the Pauli matrices. The spin structure factor is defined as

The site-average occupancy of orbitals is

The squared local spin, averaged over all the sites, is

Figure 11 illustrates our calculation of the dominant magnetic coupling along the a axis based on the DMRG measurements of spin–spin correlations and spin structure factors.

Figure 11(a) shows the spin–spin correlation \( S(r) = \langle S_i \cdot S_j \rangle \) vs distance \( r \), for different values of \( U/W \), at \( J_{H}/U = 0.15 \). Here, the distance is defined as \( r = |i - j| \), with site indices \( i \) and \( j \). For weak electronic correlations, the system displays paramagnetic (PM) behavior since the spin correlation \( S(r) \) decays rapidly with distance \( r \) [see the result at \( U/W = 0.2 \) in Fig. 11(a)]. At \( U/W = 0.6 \), the spin correlation \( S(r) \) indicates weak staggered AFM coupling along the M-O chain direction with a small peak of the spin structure factor \( S(q) \) at \( q = \pi \), as shown in Fig. 11(b). Then, by increasing \( U/W \), the spin correlation \( S(r) \) shows that the system transfers into the canonical staggered AFM phase with the up–down–up–down configuration in the whole region of our study (\( U/W \leq 8 \)) [see the results at \( U/W = 1.2 \) and 4 in Fig. 11(a)]. As shown in Fig. 11(b), the spin structure factor \( S(q) \) displays a sharp peak at \( q = \pi \) at \( U/W = 1.5 \) and \( U/W = 0.2 \), corresponding to the canonical staggered AFM phase. In addition, we also calculated the spin–spin correlation \( S(r) \) and spin structure factor \( S(q) \) at \( J_{H}/U = 0.2 \), which are similar to the results using \( J_{H}/U = 0.15 \), as shown in Figs. 11(c) and 11(d). Note that in one dimension, quantum fluctuations prevent full long-range order. But the staggered order tendency is clear at both \( J_{H}/U = 0.15 \) and 0.2.

In the range of \( U/W \) studied, a dominant AFM state was found (up–down–up–down) in our DMRG calculations. This is physically reasonable, considering known facts about the Hubbard model. Based on the hopping matrix from MLWFs calculations, the \( \gamma = 0 \) and 1 orbitals clearly have much larger hopping amplitudes than the \( \gamma = 2 \) orbital, leading to the formation of the AFM order. Furthermore, the diagonal hopping amplitudes are dominant and give rise to the direct exchange mechanism in this system. In this case, the standard superexchange Hubbard spin–spin interaction dominates, causing the spins to order antiferromagnetically along the chain, in agreement with our DFT calculations.

In addition, we also calculated the site-average occupancy of different orbitals \( n_{\gamma} \) vs \( U/W \), for \( J_{H}/U = 0.15 \) and 0.2, respectively. As shown in Fig. 12, the population of orbital \( \gamma = 2 \) is 2 for the whole region of \( U/W \), and this orbital decouples from the system. Furthermore, the other two orbitals \( \gamma = 0 \) and 1 remain half-filled for all values of \( U/W \). At the intermediate electronic correlation region, we observed a stable AFM Mott-insulating behavior, different from our previous studies on the same multiorbital model (four electrons in three orbitals) when using different hopping matrix elements corresponding to other materials, such as when we reported an orbital-selective Mott phase [42], PM insulating state [9], block AFM phase [41], and a noncollinear spiral phase [7]. In this case, the system is in a spin \( S = 1 \) per site Mott-insulator staggered AFM state. Thus, increasing \( U/W \) opens a gap. Furthermore, the average value of the squared local spin averaged over all the sites \( \langle S^{2} \rangle \) is also displayed in Fig. 12, as a function of \( U/W \). With increasing \( U/W \), as the system becomes Mott insulating and antiferromagnetically ordered, \( \langle S^{2} \rangle \) saturates to a value of 2, as expected. Note that while the limit of large \( U \) may be considered naïvely as always leading to an AFM state, our study shows that staggered order develops at intermediate coupling already, which requires a special calculation as shown here. Moreover, AFM order may...
In addition, we constructed a multi-orbital Hubbard model for the M-O chains. The staggered AFM with $\uparrow - \downarrow - \uparrow - \downarrow$ order was found to be dominant in our DMRG calculations, in agreement with DFT calculations. Different from the previously well-studied oxide dichlorides $\text{MOX}_2$ ($M = V, \text{Ta}, \text{Nb}, \text{Ru}$ and Os; $X =$ halogen element) with $d^1$ and $d^2$ configurations, note that thus far almost no research has been reported for other electronic densities $n$ of the M atoms in this family. Thus, we believe our results for $\text{MOCI}_2$ ($M = \text{Ru}$ or Os) will provide guidance to experimentalists and theorists working in the oxide dichlorides family at the interesting density $n$ studied here.

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APPENDIX

1. Wannier functions

According to the crystal-splitting analysis and electronic structures in the previous section, the $e_g$ orbitals of Ru or Os ($d_{xz}, d_{yz}$ and $d_{yz}$) are located at high energy on the conduction band, far away from the Fermi level with a large energy splitting between $e_g$ and $t_{2g}$ orbitals. In this case, those systems can be regarded as four electrons on a three $t_{2g}$ orbitals low-energy model. To better understand those low-energy orbitals, we constructed three disentangled Wannier functions based on the MLWFs method [57], involving the $t_{2g}$ orbital bases $d_{xy}$, $d_{xy}$, and $d_{xy}$ for each Ru or Os atom in the NM phase without SOC.

Figures 13(a) and 13(c) indicate that DFT bands are fitted very well with the Wannier bands obtained from MLWFs. In fact, the blue DFT bands near the Fermi level are totally hidden by the green Wannier bands, because of the quality of the fit. As displayed in Figs. 13(b) and 13(d), those orbitals obtained from MLWFs clearly display $d_{x^2}$, $d_{z^2}$, and $d_{y^2}$ characteristics. Based on the Wannier function basis [$d_{xz}, d_{yz}, d_{xy}$], here referred to as $\gamma = \{0, 1, 2\}$, we deduced the onsite energies of the three $t_{2g}$ orbitals, as well as the hopping parameters, for RuOCl$_2$ and OsOCl$_2$, respectively.

First, we obtained the onsite matrices for the Ru or Os atoms, using the basis $\{d_{xz}, d_{yz}, d_{xy}\}$:

\[
\begin{bmatrix}
    d_{xz} & d_{yz} & d_{xy} \\
    3.901 & 0.000 & 0.000 \\
    0.000 & 3.903 & 0.000 \\
    0.000 & 0.000 & 2.680
\end{bmatrix},
\]

\[
\begin{bmatrix}
    d_{xz} & d_{yz} & d_{xy} \\
    3.721 & 0.000 & 0.000 \\
    0.000 & 3.727 & 0.000 \\
    0.000 & 0.000 & 2.255
\end{bmatrix},
\]

These matrices can be used to calculate the hopping parameters and onsite energies for the systems studied here.
FIG. 13. (a), (c) DFT and Wannier bands of the conventional cell of RuOCl$_2$ and OsOCl$_2$, respectively. The Fermi level is shown with dashed horizontal lines. Note that near the Fermi level the blue DFT bands are totally hidden by the green Wannier bands, indicating the high quality of the fit. (b), (d) Wannier functions of the three Ru or Os $t_{2g}$ orbitals, with lobes of opposite signs colored as blue and yellow. M (M = Ru or Os), O, and Cl atoms are in blue, red, and green, respectively. The local bases are marked in the inset of (b) and (d), with the $x$ or $y$ axis along the $M$-Cl directions, while the $z$ axis is along the $a$ axis.

Furthermore, we also obtained the NN hopping matrices along the $a$ axis.

For RuOCl$_2$,

$$ t_{\gamma \gamma'}^a = \begin{bmatrix} 0.003 & -0.081 & 0.000 \\ -0.081 & 0.020 & 0.000 \\ 0.000 & 0.000 & -0.070 \end{bmatrix}. $$  \tag{A3} 

For OsOCl$_2$,

$$ t_{\gamma \gamma'}^a = \begin{bmatrix} 0.004 & -0.103 & 0.000 \\ -0.103 & 0.033 & 0.000 \\ 0.000 & 0.000 & -0.103 \end{bmatrix}. $$  \tag{A4} 

In addition, we also obtained the nearest-neighbor hopping matrices along the $b$ axis.

For RuOCl$_2$,

$$ t_{\gamma \gamma'}^b = \begin{bmatrix} -0.632 & 0.009 & 0.000 \\ 0.009 & -0.633 & 0.000 \\ 0.000 & 0.000 & -0.012 \end{bmatrix}. $$  \tag{A5} 

For OsOCl$_2$,

$$ t_{\gamma \gamma'}^b = \begin{bmatrix} -0.713 & 0.013 & 0.000 \\ 0.013 & -0.717 & 0.000 \\ 0.000 & 0.000 & -0.011 \end{bmatrix}. $$  \tag{A6} 

All the onsite and hopping matrix elements are in eV units. Note that the angle formed by $M$-Cl-$M$ (M = Ru or Os) is not 90°, causing a slight deviation of the local $y$ axis from the direction of the $M$-Cl bond, as shown in Fig. 1. Hence, there are tiny differences in the values of the onsite energies and hopping amplitudes between the otherwise degenerate $d_{xz}$ and $d_{yz}$ orbitals. Furthermore, the NN hoppings between each Ru or Os layer along the $c$ axis are quite small and can be neglected compared with the others. In addition, the NN hoppings along the $d_{xz/yz}$ axis are much larger than the NN hoppings along the $b$ axis for both RuOCl$_2$ and OsOCl$_2$. Then, the magnetic properties of MOCl$_2$ (M = Ru or Os) are mainly determined by the hopping along the $a$ axis between NN Ru-Ru or Os-Os atoms, leading to strong anisotropic magnetism.

FIG. 14. Projected band structures of the undistorted $Immm$ NM state. (a) $U = 3$ eV and $J = 0.6$ eV for RuOCl$_2$. (b) $U = 2$ eV and $J = 0.4$ eV for OsOCl$_2$, respectively. Note that the local $\{x, y, z\}$ axes of projected orbitals are marked in Fig. 1, where the $z$ axis is the $a$ axis and $x$ or $y$ axes are along the $M$-Cl directions. The weight of each Ru or Os orbital is represented by the size of the (barely visible) circles.
Based on the NN hopping matrices along the $a$ axis of RuOCl$_2$ and OsOCl$_2$, the hoppings of the diagonal elements of $d_{xz/yz}$ orbitals are dominant, leading to a strong AFM coupling.

2. Band structures of NM states with $U$

Next, let us discuss the effect of different values of $U$ on the nonmagnetic state of RuOCl$_2$ and OsOCl$_2$. As shown in Fig. 14, the band structures of the NM states are almost unchanged. Hence, the crystal-field splitting, and nearest-neighbor hopping, do not change much.

3. Band structures of our LSDA calculations

Using pure LSDA calculations, we also obtained the stripe-b and G-type AFM insulating ground states for RuOCl$_2$ and OsOCl$_2$, respectively. For the benefit of the readers, the band structures arising from LSDA calculations of the ground state of RuOCl$_2$ and OsOCl$_2$ are displayed in Fig. 15.

![FIG. 15. Band structures of LSDA calculations for (a) the stripe-b AFM state of RuOCl$_2$ and (b) the G-AFM state of OsOCl$_2$ without SOC, respectively. The Fermi level is shown with dashed horizontal lines.](image)

[75] https://g1257.github.io/dmrgPlusPlus/.