Confinement-driven electronic and topological phases in corundum-derived 3d-oxide honeycomb lattices

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I. INTRODUCTION

Progress in growth techniques like molecular beam epitaxy and pulsed laser deposition has enabled the growth of transition metal oxide (TMO) superlattices with atomic precision. This has opened possibilities to explore emergent phenomena and electronic as well as magnetic phases in reduced dimensions that are not available in the parent compounds. Beyond the [001] growth direction, where confinement can lead to a metal-to-insulator transition e.g. in LaNiO$_3$/LaAlO$_3$ (001) superlattices (SLs), in (111)-oriented perovskite superlattices a buckled honeycomb lattice is formed by each two $\text{X}$-cation triangular lattices of the $\text{AXO}_3$ perovskite structure, as suggested by Xiao et al. Already in 1988 Haldane predicted a quantized Hall conductance arising from spinless fermions on a honeycomb lattice in the absence of an external magnetic field. This model serves as a prototype of the quantum Hall anomalous insulators (QAHI) that are of interest for future applications in low-power electronics devices or in the search of Majorana fermions. Materials realizations of QAHI are being sought in Mn doped HgTe or Cr$_x$-Fe-doped Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$ or 5d transition metals on graphene, or in TMO with rocksalt- (EuO/CdO) and EuO/GdO$_2$ or rutile-derived heterostructure or double perovskites. While the relevant orbitals in common topological insulators are $s$ and $p$, the correlated nature of the $d$ electrons in transition metal oxides suggests a richer functional behavior.

In this context, the initial proposal of Xiao et al. offered a fertile playground to explore the realization of topologically nontrivial phases in perovskite superlattices with a honeycomb pattern. A recent systematic DFT+$U$ study of the 3d series in (LaOsO$_3$)$_2$/LaAlO$_3$(111) superlattices revealed a broad set of competing charge, magnetic and orbitally ordered phases. Among the 3d series, the LaMnO$_3$ buckled honeycomb bilayer represents a promising candidate with a topological transition from a high-symmetry Chern insulator with a substantial gap (150 meV) to a Jahn-Teller distorted trivial Mott insulating ground state. The insight obtained in this study especially on the effect of band filling and strain has served to identify robust Chern insulators in the 4d and 5d series (e.g. LaOsO$_3$ and LaRuO$_3$ bilayers).

FIG. 1: (a) Side view of the (X$_2$O$_3$)$_1$/Al$_2$O$_3$(0001) superlattice where one metal ion bilayer in the corundum structure is exchanged by a $X = 3d$ ion. (b) Top view of the buckled honeycomb lattice in $a$$-b$ plane solid and dashed lines connect the next nearest TM-ion neighbors residing on the two sublattices.

Besides the (111) oriented perovskite SLs, a honeycomb lattice can be found also in other structure types.
as e.g. the corundum structure, as mentioned in, where each metal ion bilayer forms a honeycomb pattern with a much lower degree of buckling than in the perovskite case. Another qualitative difference is the type of connectivity in the structure. While in the perovskite only corner connectivity is present, in the corundum the XO₆ octahedra are edge-sharing in-plane and alternating corner- and face-sharing out-of-plane (cf. Fig. 1). This difference in connectivity implies different interaction mechanisms between neighboring sites with potential impact on the electronic and magnetic behavior compared to the perovskite superlattices. Therefore, we perform here a systematic study of the ground state properties of 3d honeycomb layers sandwiched in the band insulator α-Al₂O₃, as shown in Fig. 1 and compare those to the perovskite analog. Recently, Afonso and Pardo addressed the possibility of topological phases in 5d honeycomb layers incorporated in the band insulator α-Al₂O₃, as shown in Fig. 1 and compare those to the perovskite analog. The internal parameters α and the out-of-plane lattice parameter c were optimized for each system within GGA+U and the results are given in Table II in Suppl. Material. Additionally, we calculated the structural and electronic properties of bulk X₂O₃, displayed in Tab. 1 in Suppl. Material. The lateral strain is defined as \( \sigma(\%) = \frac{\Delta a}{a_{\text{Al}_2O_3}} \) where \( \Delta a = a_{\text{Al}_2O_3} - a_{X_2O_3} \) is the difference between the lateral lattice parameters of \( \text{Al}_2O_3 \) and bulk \( X_2O_3 \). We have considered both ferro- (FM) and antiferromagnetic (AFM) coupling and performed the relaxations for each spin arrangement for both the bulk compounds and the SLs. As mentioned above, the degree of buckling is much lower for the corundum-derived honeycomb layers (0.39-0.63 A, see Table II in Suppl. Material) compared to the perovskite analogs (2.27-2.44 A).

II. THEORETICAL METHOD AND DETAILS

Density functional calculations were carried out for \((X_2O_3)_{1/3}/(Al_2O_3)_{3/5}(0001)\), \(X = 3d \) ion, with the VASP code using pseudopotentials and projector augmented waves (PAW). For the exchange-correlation functional we applied the generalized gradient approximation (GGA) of Perdew, Burke and Enzerhof and in some cases for comparison the local density approximation (LDA). An on-site Coulomb repulsion parameter was considered within the GGA+U approach with \( U = 5 \) eV and Hund’s exchange parameter of \( J = 0.7 \) eV on all TM ions \( X \). We used the approach of Dudarev et al. which considers \( U_{\text{eff}} = U - J \). We have verified that the results are robust w.r.t. a reasonable variation of \( U \), and that LDA+U and GGA+U give qualitatively similar behavior, further information is provided in Suppl. Material. Previous studies have shown that taking into account electronic correlations may result in a trivial AFM insulator for 5d systems, initially proposed as candidates for a Z₂ TIs within tight binding and DFT (GGA/LDA) studies. While for a SrIrO₃ honeycomb bilayer both DFT+DMFT and DFT+U show such a tendency, the effect of static vs. dynamic correlations needs to be addressed in more detail in future studies.

The \( k \)-point mesh contains at least \( 6 \times 6 \times 2 \) \( k \)-points including the Γ point, in some cases \( 9 \times 9 \times 3 \) \( k \)-points were used. A cutoff energy of 600 eV was chosen for the plane waves. Atomic positions were relaxed until the Hellman-Feynman forces were lower than 1 meV/Å. In selected cases, especially in order to explore high-symmetry metastable states or symmetry-broken states, calculations were performed using the all-electron full-potential linearized augmented plane wave (LAPW) method as implemented in the Wien2k code. The anomalous Hall conductivity (AHC) for potentially interesting cases is computed on a very dense \( k \)-point mesh of \( 300 \times 300 \times 50 \) using the wanne90 code.

To model the \((X_2O_3)_{1/3}/(Al_2O_3)_{3/5}(0001)\) superlattices, an Al-bilayer in the corundum structure is substituted by a \( X = 3d \) bilayer (cf. Fig. 1). Systems grown on \( \alpha-Al_2O_3(0001) \) are simulated by fixing the lateral lattice constant to the GGA value of \( Al_2O_3 \). The lattice parameters of \( \alpha-Al_2O_3 \) within GGA are \( a = 4.81 \) Å, \( c = 13.12 \) Å, approx. 1% larger than the experimental values \( a = 4.76 \) Å and \( c = 12.99 \) Å. The internal parameters and the out-of-plane lattice parameter \( c \) were optimized for each system within GGA+U and the results are given in Table II in Suppl. Material. Additionally, we calculated the structural and electronic properties of bulk \( X_2O_3 \), displayed in Tab. 1 in Suppl. Material. The lateral strain is defined as \( \sigma(\%) = \frac{\Delta a}{a_{\text{Al}_2O_3}} \) where \( \Delta a = a_{\text{Al}_2O_3} - a_{X_2O_3} \) is the difference between the lateral lattice parameters of \( Al_2O_3 \) and bulk \( X_2O_3 \). We have considered both ferro- (FM) and antiferromagnetic (AFM) coupling and performed the relaxations for each spin arrangement for both the bulk compounds and the SLs. As mentioned above, the degree of buckling is much lower for the corundium-derived honeycomb layers (0.39-0.63 Å, see Table II in Suppl. Material) compared to the perovskite analogs (2.27-2.44 Å).

III. ELECTRONIC AND MAGNETIC PROPERTIES

In this Section we discuss the electronic and magnetic properties of stable and metastable \((X_2O_3)_{1/3}/(Al_2O_3)_{3/5}(0001)\) superlattices with AFM and FM order. Among the 3d series we have identified four cases \( X = Ti, Mn, Co, Ni \) with common features whose band structures and spin-densities are shown in...
FIG. 2: Band structures and spin density distributions of \( (X_2O_3)_1/(Al_2O_3)_5(0001) \) with \( X = Ti, Mn, Co, Ni \) for FM and AFM coupling. The spin density is integrated in the energy range between \(-8 \text{ eV to } E_F\) except for d-f and j) where the integration interval is \(-0.6 \text{ eV to } E_F\). In the band structure blue/orange denote majority/minority bands and the Fermi level is set to zero. In the isosurfaces of the spin density blue (red) show the majority (minority) contributions. The energies of metastable states are given in red, also the magnitude of the spin moments of the \( X \) ions are displayed in the spin-densities.

Fig. 2. The remaining systems are discussed towards the end of this Section (cf. Fig. 3). The four above mentioned cases exhibit an AFM insulating ground state. In the ferromagnetic cases with constrained symmetry of the two sublattices, we identify a common band structure with a characteristic set of four bands.
around $E_F$. Two of these bands are flat and nearly dispersionless, while the other two show a Dirac-like crossing at K close to $E_F$. This bears similarities to the perovskite analogs (LaXO$_3$)$_2$/(LaAlO$_3$)$_2$(111) with $X = \text{Mn, Co, Ni}$ and originates from the single occupation of the $e_g'$ and $e_g$ manifold, respectively, as will be discussed below. Distinct to the perovskite case, however, the Dirac crossing is not exactly at $E_F$, but $\sim 200$ meV below (Ti) or slightly above (Mn, Co and Ni) the Fermi level. The resulting electron (hole) pockets are compensated by hole (electron) pockets around $\Gamma$ (Ti) or along K-$\Gamma$ and $\Gamma$-M for the remaining cases. In Section 1 we will explore whether these coupled electron-hole pockets can be quenched and the Dirac point shifted to the Fermi level using epitaxial strain. A further notable feature is the variation of bandwidth of those bands: while for Ti the bandwidth is substantial ($\sim 2$ eV, cf. Fig. 2a), for $X = \text{Mn, Co, Ni}$ it is much narrower ($0.5 - 0.8$ eV, cf. Fig. 2i, l). In all four FM cases symmetry breaking stabilizes insulating states with significant band gaps (Fig. 2b, e, h, k). Moreover, narrower (0.5 - 0.8 eV) bands. It would be interesting to explore further these insulating states e.g. with DFT+DMFT.

In the corundum structure the symmetry of the XO$_6$ octahedron is reduced from octahedral to trigonal which splits the $t_{2g}$-orbitals into $a_{1g}$ and $e_g'$. Similar to the perovskite analog LaTiO$_3$33 the TiO$_3$ honeycomb layer reveals a competition between the cubic $t_{2g}$-orbitals ($d_{xy}$, $d_{xz}$, $d_{yz}$) and the above mentioned trigonal ones. In particular, a $d_{xy}$-shaped orbital is stabilized in the AFM ground state (Fig. 2f), while the symmetry-broken FM state exhibits a linear combination of two orbitals (e.g. $d_{yz} + d_{xz}$, cf. Fig. 2g). On the other hand, the FM case with constrained symmetry of the sublattices has an $e_g'$ orbital polarization (Fig. 2c). For comparison, in the perovskite LaTiO$_3$-bilinear the FM ground state comprises a staggered order of cubic orbitals ($d_{xz}$, $d_{yz}$) whereas in the corundum case the same orbital polarization occurs on both sublattices, likely related to the different (edge vs. corner) connectivity in the corundum-derived honeycomb layer. It is noteworthy that these orbital polarizations are at variance with the $a_{1g}$ occupation in bulk Ti$_2$O$_3$. As a result of the symmetry breaking and orbital order a gap opens for the AFM ground state ($2.33$ eV) and the FM state ($0.81$ eV) which lies $528$ meV higher in energy. In contrast, the FM state with symmetric sublattices is $84$ meV less stable owing to the different orbital polarization (single electron in the doubly degenerate $e_g'$ orbitals) and the resulting metallic phase with the above described set of four majority-spin bands. It would be interesting to explore further these states e.g. with DFT+DMFT.

The AFM ground state of $X = \text{Mn}$ ($d^4$) is insulating with a gap of $1.35$ eV that separates very flat bands (see Fig. 2l). Its origin is a Jahn-Teller (JT) distortion which lifts the degeneracy of the singly occupied $e_g$ band and reduces the symmetry to P1. Due to the superposition of trigonal and JT distortion the relaxation pattern is more complex, the Mn-O distances change from 1.98, 2.10 Å (symmetric FM case) to apical distances of 2.21 and 2.09 Å and basal ones varying between 1.92 and 2.03 Å for the JT distorted case. The spin-density integrated between $-0.6$ eV to $E_F$ indicates a $d_{xz}$-shaped orbital polarization and a strong hybridization with O2p states. We note that the orbitals on both sublattices have the same orientation, in contrast to the perovskite JT-distorted (LaMnO$_3$)$_2$/(LaAlO$_3$)$_2$(111) case, which shows alternating orientation of the $d_{xz}$-shaped orbitals on the two sublattices. Starting from the FM solution with symmetric sublattices (Fig. 2f), which is $0.66$ eV/u.c. higher in energy, a similar orbital polarization as in the AFM case arises that opens a gap of $1.20$ eV in the initially metallic set of four bands (Fig. 2j). This case lies $110$ meV higher in energy than the AFM ground state.

$X = \text{Co and Ni}$ show also a number of intriguing stable and metastable states. While bulk Co$_3$O$_4$ is an insulator with Co $^{3+}$ ($d^6$) in a low spin state ($S = 0$), the ground state of the confined honeycomb corundum-derived lattice is an antiferromagnetic insulator with a band gap of $1.61$ eV and Co in the high spin state (calculated magnetic moment of $3.15 \, \mu_B$, Fig. 2k) with a full $d$ band in one spin direction and a single electron in the other. For ferromagnetic coupling two metastable states arise: With imposed symmetry of the two sublattices in the honeycomb layer the previously observed set of four bands emerges (Fig. 2l). This state is $332$ meV less stable than the ground state. When the symmetry constraint is lifted, a band gap opens separating the two occupied from the two empty bands, $143$ meV above the ground state (cf. Fig. 2g). Remarkably, the symmetry breaking mechanism here is a dimerization of the Co sites, manifested in alternating Co-Co distances of $2.80$ Å and $2.85$ Å, in contrast to the $2.82$ Å in the symmetric case (note also the alternating $X - X$ distances for $X = \text{Ti and Mn}$, Fig. 2e and c, respectively).

The ground state of (Ni$_2$O$_3$)$_1$/((Al$_2$O$_3$)$_5$(0001)) is also an AFM insulator with a band gap of $\sim 0.69$ eV which separates two nearly flat bands (see Fig. 2f). If for FM coupling the symmetry of the two sublattices is constrained, a metastable state occurs $84$ meV above the ground state with the familiar set of four bands and a Ni-magnetic moment of $1.32 \, \mu_B$ (cf. Fig. 2f), similar to the perovskite-derived LaNiO$_3$ bilayer27,31. Releasing the symmetry constraint results in a ferromagnetic insulating state with a gap of $\sim 1.0$ eV which arises due to disproportionation of the two Ni sublattices, reflected in a large magnetic moment $1.72 \, \mu_B$ on one site and a nearly quenched one on the second, $0.03 \, \mu_B$ (cf. Fig. 2k). This is accompanied by a bond disproportionation with Ni-O bond lengths of $2.05, 1.97$ Å at the first and $1.91, 1.92$ Å at the second site. The corresponding NiO$_6$ volumes are $10.6$ and $9.2$ Å$^3$, respectively. This behavior bears analogies to the site-disproportionation in rare earth nickelates and LaNiO$_3$/LaAlO$_3$(001) and (111)
The band structures and spin densities for the remaining $X = V, Cr, Fe$ with FM and AFM coupling are shown in Fig. 3. For $X = V$ ($d^2$), the $e'_g$ doublet is fully occupied and both the AFM and FM cases are insulating with broad band gaps (e.g. 2.70 eV for AFM). For FM alignment, the set of four bands that is half-occupied for Ti is fully occupied and lies 0.2 eV below $E_F$ (Fig. 3b).

Interestingly, $X = Fe$ ($d^5$) shows almost degenerate FM and AFM states with a slight preference for FM coupling by 3 meV/u.c., indicating weak exchange interaction. This is consistent with bulk $\alpha$-Fe$_2$O$_3$ that has small AFM in-plane magnetic interaction parameters (note that the strongest AFM coupling in bulk $\alpha$-Fe$_2$O$_3$ occurs to the next layer which is quenched in the SL due to the presence of Al ions). For the FM case of $X = Fe$ the set of four bands is fully occupied and lies 0.2 eV below $E_F$ (Fig. 3f).

### IV. EFFECT OF STRAIN

![Figure 4: Energy difference w.r.t. the ground state per u.c. vs. in-plane lattice constant for $X = Ti$. For each value of the lateral strain, the out-of-plane lattice constant was optimized within GGA+U. Additionally, the band structure is shown prior and after the switching of orbital polarization from $e'_g$ to $a_1g$ at $a = 5.11\text{Å}$.](image)

As discussed above, in the symmetric ferromagnetic phases of $X = Ti, Mn, Co$ and $Ni$ a set four bands with a linear crossing at $K$ is observed. However, this Dirac-like crossing is either slightly below ($Ti$) or slightly above ($Mn, Co, Ni$) the Fermi level when the system is strained at the lateral lattice constant of $\alpha$-Al$_2$O$_3$. In this Section we explore if it is possible to tune the position of the Dirac-point (DP) to the Fermi level using strain. The energy vs. lateral lattice constant and the band structure at the optimum lattice parameter are plotted in Figs. 4 and 5.

![Figure 5: Stability of the FM and AFM phases of $X = Mn$ as a function of strain is displayed in Fig 5a.](image)
AFM phase corresponds to the ground state for compressive strain, the energy difference to the FM state is reduced with increasing tensile strain. Moreover, a complete compensation of the electron and hole pockets can be achieved for the FM state under tensile strain for \( a = 5.31 \text{ Å} \) (Fig. 5a). For the metastable Co-bilayer this state is reached at a smaller lateral lattice parameter, \( a = 5.08 \text{ Å} \) (Fig. 5c). Finally, for \( X = Ni \) this state occurs for a lateral lattice constant of \( a = 4.94 \text{ Å} \) just slightly above \( \alpha_{\text{AlO}_3} \) (not shown here). Overall, in the latter three cases the DP can be readily tuned to the Fermi level by tensile strain, whereas the level of strain decreases with increasing band-filling. We note that due to the well-known overestimation of lattice constants within GGA+U the actual transitions may occur at smaller lattice constants.

V. EFFECT OF SPIN-ORBIT COUPLING AND ANOMALOUS HALL CONDUCTIVITY

The band structures of the ferromagnetic cases of \( X = Ti, Mn, Co \) and Ni with symmetric sublattices indicate a possible topologically nontrivial character which we analyze in the following. In a first step we explore the effect of spin-orbit coupling for the optimum lateral lattice constants obtained in the previous Section and the resulting band structures are displayed in Fig. 6. SOC leads to a gap opening at the former DP of a few meV (\( \sim 2.0-5.9 \text{ meV} \) for the Mn and Co corundum bilayers, respectively), for Ti and Ni the avoided crossing is 50 meV below and 6 meV above \( E_F \), respectively. We note that here the effect of SOC appears to be much smaller than for the (111)-oriented \((\text{La}_2\text{O}_3)_2/(\text{LaAlO}_3)_4(111)\), where SOC opens a gap of \( \sim 150 \text{ meV} \) for \( \text{LaMnO}_3 \).

Likewise, the orbital moments are also small and range from 0.01\( \mu_B \) (Mn) to 0.03\( \mu_B \) (Ti) and 0.04\( \mu_B \) (Co and Ni).

For the analysis of the topological properties we project the bands around \( E_F \) to Wannier functions (WF) using the wannier90 code. To achieve a better localization of the WF, we have chosen a larger energy window for the Wannier interpolation, which includes besides \( X3d \) also \( O2p \) states. The Berry curvature \( \Omega(k) \) is calculated through summation over all occupied bands below the Fermi level:

\[
\Omega(k) = -\sum_{n<E_F} \sum_{m\neq n} 2Im \frac{\langle \Psi_{nk} | v_x | \Psi_{mk} \rangle \langle \Psi_{mk} | v_y | \Psi_{nk} \rangle}{(\epsilon_{mk} - \epsilon_{nk})^2}
\]

(1)

where \( \Psi_{nk} \) represents the spinor Bloch wave function of band \( n \) with an eigenenergy \( \epsilon_{nk} \) and \( v_x, v_y \) are the components of the anomalous velocity. The anomalous Hall conductivity (AHC) is computed by integrating the Berry curvature \( \Omega(k) \), weighted by an occupation factor \( f_n(k) \), over the BZ using a dense \( k \)-point grid of \( 300 \times 300 \times 50 \):

\[
\sigma_{xy} = -\frac{e^2}{2\pi h} \sum_n \int_{BZ} dk f_n(k) \Omega_{n,xy}(k)
\]

(2)

The anomalous Hall conductivity \( \sigma_{xy} \) of the corundum bilayers with the chemical potential varying \( \pm 0.2 \text{ eV} \) around \( E_F \) is displayed in Fig. 7. All four systems show significant values approaching +1 (Ti and Mn) or -1 (Co and Ni). In particular, \((\text{Mn}_2\text{O}_3)_1/(\text{Al}_2\text{O}_3)_5(0001)\)
and (CoO)\textsubscript{2}/(Al\textsubscript{2}O\textsubscript{3})\textsubscript{5}(0001) exhibit values of \sim 0.94 and \sim -0.78 e^2/h, respectively. In contrast to other systems, like e.g. TiO\textsubscript{2}/VO\textsubscript{2}\textsuperscript{3+}, the plateaus here are very narrow, of the order of the small band gap opened by SOC. Hence a small denominator and large velocities matrix elements in Eq. [1] give rise to large contributions to the Berry curvature \(\Omega(k)\) as shown in Fig. 8 where sharp peaks arise around \(K\) with values of 3000 and -8000 bohr\(^2\) for (MnO)\textsubscript{2}/(Al\textsubscript{2}O\textsubscript{3})\textsubscript{5}(0001) and (CoO\textsubscript{2})\textsubscript{3}/(Al\textsubscript{2}O\textsubscript{3})\textsubscript{5}(0001), respectively. The different signs in the Berry curvature correlate with the negative and positive signs of the Hall conductivity.

Besides the cases presented above, we have also investigated the effect of SOC for \(X = \text{Ti}\) at the lateral lattice constant of \(\alpha\text{-Al}_2\text{O}_3\). In particular, we performed two sets of calculations: one where SOC was included after the converged GGA+\(U\) calculations and one where SOC was switched on from the start. The band structure from the first set of calculations is similar to the one displayed in Fig. 6, with degenerate solutions for in- and out-of-plane magnetization. In contrast, with the second approach we obtained a particularly strong effect of SOC on the total energy and band structure, although the structural differences are very small (slight change in the degree of buckling of the honeycomb layer by 0.03\(\AA\)).

FIG. 9: Strong effect of SOC for (TiO\textsubscript{2})\textsubscript{3}/(Al\textsubscript{2}O\textsubscript{3})\textsubscript{5}(0001) at \(\alpha\text{-Al}_2\text{O}_3\): a) band structure, b) AHC plotted vs. the chemical potential.

FIG. 7: AHC \(\sigma_{xy}\) in units of \(e^2/h\) as a function of the chemical potential for the corundum bilayers (\(X_2\text{O}_3\))\textsubscript{1}/(Al\textsubscript{2}O\textsubscript{3})\textsubscript{5}(0001) (\(X = \text{Ti, Mn, Co, Ni}\)).

FIG. 8: Side and top views of the Berry curvature distributions \(\Omega_k(k_x, k_y)\) for (CoO\textsubscript{2})\textsubscript{3}/(Al\textsubscript{2}O\textsubscript{3})\textsubscript{5}(0001) (left) and (MnO\textsubscript{2})\textsubscript{3}/(Al\textsubscript{2}O\textsubscript{3})\textsubscript{5}(0001) (right). Note the opposite sign of magnetization along [0001].

\(\sigma_{xy} (e^2/h)\)

\(E_{g} = 1.7\,eV\)

\(a = 4.81\,\text{Å}\)

\(c/a = 2.81\)

\(\theta = 88^\circ\)

\(\left|\frac{1}{\sqrt{3}}(d_{xy}) + e^{\pm i\theta} (d_{yz}) + e^{\mp i\theta} (d_{xz})\right|\), with \(\theta = \frac{2\pi}{3}\), whereas the \(a_{1g}\) orbital is higher in energy. As discussed recently by Kim and Kee for BFPO\textsubscript{2}\textsuperscript{2+}, SOC acts as an atomic orbital Zeeman term: The solution with \(L_z = 1\) and magnetization along the [0001] direction breaks the degeneracy of the \(e_{g}'\) orbitals, causing
a transfer of charge from the \( e'_g^+ \) to the \( e'_g^- \) orbital and thereby opening the significant gap as in BFPO\textsuperscript{34}. Due to the antiparallel alignment of the spin and orbital moment the total moment is almost quenched and \((\text{T}_2\text{O}_3)_1/(\text{Al}_2\text{O}_3)_5\) can be regarded as a possible realization of Haldane’s model of spinless fermions hopping on a honeycomb lattice\textsuperscript{34}. The advantage compared to BFPO is that there are no further \( d \) electrons, e.g. in the other spin-channel, to interfere with this state. Because the strong SOC effect occurs only for FM coupling, the energy difference between the AFM and FM decreases by an order of magnitude from 814 meV (GGA+) to 56 meV/u.c. (GGA+U+SOC), making this intriguing state more likely to be realized. Moreover, a calculation of \( \Gamma \)-phonon modes indicates an unusual case where strong SOC dynamically stabilizes the system (for more details see Suppl. Material\textsuperscript{34}).

A further analogy to BFPO\textsuperscript{34} appears analyzing the band structure and QAH conductivity in Fig. 9a and b: although \( \sigma_{xy} = 0 \) at \( E_F \) points to a trivial FM Mott insulator, positive/negative spikes at -0.8 eV and 2.2 eV indicate an occupied/empty set of nontrivial bands with opposite Chern numbers and chirality. For BFPO Kim and Kee\textsuperscript{35} proposed substitution of Ba\textsuperscript{2+} by mono or trivalent cations in order to shift \( E_F \) between the lower or upper pair of Chern bands and thereby design a QAHI. This scenario is more difficult to realize for the corundum case, since cations other than trivalent are less common in this structure, but needs to be explored in further studies.

VI. SUMMARY

In summary, our DFT+\( U \) results on \((\text{X}_2\text{O}_3)_1/(\text{Al}_2\text{O}_3)_5\) indicate a broad variety of electronic phases w.r.t. orbital polarization and spin state, induced by the confinement of the 3\( d \) honeycomb layer that are not available in the bulk \( \text{X}_2\text{O}_3 \) compounds. While the ground states in most cases are trivial Mott insulators, followed in stability by symmetry broken ferromagnetic insulating states, for \( \text{X}=\text{Ti}, \text{Mn}, \text{Co} \) and \( \text{Ni} \) with ferromagnetic coupling and imposed symmetry of the two sublattices, a characteristic set of four bands with two relatively flat and two crossing at \( K \) close to the Fermi level emerges. This feature is similar to the one obtained for \( \text{X}=\text{Mn}, \text{Cd}\textsuperscript{33} \) and \( \text{Ni}\textsuperscript{24,25,36} \) in the perovskite \((\text{La}_{\text{X}}\text{O}_3)_2/(\text{LaAlO}_3)_4\) superlattices and is a result of the single occupation of the degenerate \( e'_g \) or \( e_g \) bands. Further analogies arise to the nonmagnetic \( d^8 \) configuration in 5\( d \) corundum-derived honeycomb lattices (i.e. \( d^4 \), single occupation of \( e_g \) states in each spin channel). Still, the latter topologically nontrivial configuration is metastable (the ground state is found to be AFM for \( U > -3 \) eV) and transforms into a trivial one with increasing \( U \) or tensile strain\textsuperscript{35}. Further studies are necessary to address the effect of time-reversal symmetry breaking in 4\( d \) and 5\( d \) systems.

For \((\text{X}_2\text{O}_3)_1/(\text{Al}_2\text{O}_3)_5\) with \( \text{X}=\text{Mn}, \text{Co} \) and \( \text{Ni} \) and symmetric sublattices, the above mentioned Dirac-crossing can be tuned to the Fermi level using strain, while for Ti this is hampered by a switching of the orbital polarization from \( e'_g \) to \( a_{1g} \). SOC opens a small gap of several meV in these band structures and leads to a notable anomalous Hall conductivity at the Fermi level, arising from the sharp peak of the Berry curvature at the avoided band-crossing at \( K \). Overall the tendency towards topological phases is weaker and the gap sizes smaller than in the perovskite bilayers. For comparison, in the \( \text{LaMnO}_3 \) perovskite SL a significant gap of 150 meV is opened by SOC leading to a metastable Chern insulator\textsuperscript{33}.

Finally, for \((\text{T}_2\text{O}_3)_1/(\text{Al}_2\text{O}_3)_5\) we obtain a case of particularly strong SOC at \( a_{\text{Al}_2\text{O}_3} \) that opens a large trivial Mott insulating gap (1.7 eV) with an extremely high orbital moment (\( \sim 0.8 \mu_B \)) which almost compensates the spin moment 1.04\( \mu_B \), thus making the systems a promising candidate for the realization of Haldane’s model of spinless fermions on a honeycomb lattice. We note also the presence of nontrivial pairs of bands below and above \( E_F \), suggesting that a Chern insulator may be accessible through suitable electron/hole doping. This strong SOC effect stabilizes dynamically the system and reduces significantly the energy difference to the AFM ground state from 814 meV without SOC to 56 meV.

The epitaxial growth of corundum films and heterostructures has been less in the focus of investigation compared to perovskites, but offers the advantage that fewer elements are involved (e.g. only \( X \) and Al ions, instead of three or four different cations in a perovskite superlattice). Several studies have reported the successful growth of corundum thin films on \( \alpha_{\text{Al}_2\text{O}_3} \) using molecular beam epitaxy\textsuperscript{52,55}, pulsed laser deposition\textsuperscript{52}, helicon plasma\textsuperscript{56} or r.f. magnetron sputtering\textsuperscript{55}. These reports suggest that the growth of corundum-based superlattices is viable and we trust that the electronic phases predicted here will inspire new experimental studies for their realization.

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