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Topological insulators in the quaternary chalcogenide compounds and ternary famatinite compounds

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\textbf{Abstract.} We present first-principles calculations to predict several three-dimensional (3D) topological insulators in quaternary chalcogenide compounds of compositions I\textsubscript{2}–II–IV–VI\textsubscript{4} and ternary famatinite compounds of compositions I\textsubscript{3}–V–VI\textsubscript{4}. Among the large number of members of these two families, we give examples of naturally occurring compounds that are mainly Cu-based chalcogenides. We show that these materials are candidates for 3D topological insulators or can be tuned to obtain topologically interesting phases by manipulating the atomic number of the various cations and anions. A band inversion can occur at a single point $\Gamma$ with large inversion strength, in addition to the opening of a bulk bandgap throughout the Brillouin zone. We discuss how the two investigated families of compounds are related to each other by cross-substitution of cations in the underlying tetragonal structure.

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1. Introduction

The recent discovery of topological insulators [1–11] has realized a long-sought opportunity for implementing exotic quantum phenomena in practical materials [12–18]. However, existing topological materials are restricted to binary and ternary compositions of heavy elements [5–7, 19–28], which limits the possibility of combining correlated electronic, magnetic, superconducting and other local order properties with topological phenomena. It is highly desirable, therefore, to expand the menu of available materials to the domain of compounds that are relevant for device fabrication with tuning capabilities and accessible crystalline cleavage.

Topological insulator order and local order resulting from spontaneous symmetry breaking such as magnetism and superconductivity have recently been classified into different spatial dimensions. The band topology in the two-dimensional (2D) quantum spin-Hall effect or in the 3D nontrivial topological insulators is required to possess a time-reversal invariant number $Z_2 = -1$. Materials with strong spin–orbit coupling (SOC) can host nontrivial topological phases in two as well as three spatial dimensions when the time-reversal symmetry remains invariant. For example, the 2D topological insulator Hg(Cd)Te [6] is a quantum spin-Hall insulator. The 3D topological insulating materials realized to date are based on the binary and ternary combinations of mostly heavy metals ranging from Bi/Sb-based binary systems [5, 7, 19–26] to Tl-based ternary compounds [28]. However, the promise of topological insulators for technological applications will be greatly enhanced if the topological ground state could be combined with the broken symmetry of local orders [12–18]. Of particular interest is doping with magnetic atoms for realizing effects of magnetic impurities and ferromagnetism on the topological surface states [29–31]. Furthermore, the possibility of elementary excitations that satisfy non-Abelian statistics—the so-called Majorana fermions, important for topological quantum computers—requires the proximity of superconducting and ferromagnetic insulating phases [15, 32, 33]. These considerations make it clear that it is important to continue searching for materials that can provide greater chemical and structural flexibility through cross-substitution of elements.

Here, we report the theoretical prediction of 3D topological insulators in the pristine state of existing materials in the quaternary chalcogenide compounds of composition $\text{I}_2\text{II}–\text{IV}–\text{VI}_4$ and in ternary famatinites of compositions $\text{I}_3\text{V}–\text{VI}_4$. These two families of compounds are related by cross-substitution of cations in the underlying tetragonal structure. Quaternary semiconductors particularly exhibit more flexible properties due to their enhanced chemical and structural freedom and provide surface quantum control through substitution with magnetic, nonmagnetic and other elements involving correlated electrons.
We begin the discussion with the ternary compounds I$_3$–V–VI$_4$, which are known to crystallize in famatinite, sphalerite-type structures. These materials belong to the space group $I\bar{4}2m$ in which the group VI atoms are surrounded by three group I and one group V atoms. As a result, they obey the octet rule and form an (I–VI)$_3$(V–VI) superlattice structure; see figure 1(a) for Cu$_3$SbSe$_4$ as an example. In contrast to the high-symmetry zinc-blende sublattice of ternary compounds [28, 34, 35], famatinite structure naturally achieves a tetragonal lattice distortion along the $c$-axis ($c < 2a$) due to the turning on of a strong interlayer coupling between the two cation planes. This also results in a mismatch between the cation–anion bond lengths in two zinc-blende formula units of the unit cell, which helps lower the total energy of the famatinite ground state phase.

Famatinite compounds I$_3$–V–VI$_4$ evolve into the quaternary chalcogenides I$_2$–II–IV–VI$_4$ when one of the group-I elements of the former compounds is replaced by a group-II element.
and the group-V element is changed to the group-IV element as can be seen in figure 1(b) for the example of Cu$_3$CdSbSe$_4$. High-resolution transmission electron microscopy and x-ray diffraction analyses show that these materials have tetragonal crystallographic structure, which belongs to $I42m$ space group. The structure can be described by an (I–II)$_2$(II–VI)(IV–VI) sublattice of the two zinc-blende formula units [36]. The substitution of larger atoms in the tetragonal basis of these systems helps expand the lattice and thus both the tetragonal distortion and the crystal-field splitting increase considerably. Although these changes are relatively small, quaternary chalcogenides have greater structural freedom and possess more complicated electronic and chemical properties than their binary or ternary counterparts.

The typical topological phases can be classified into a trivial band insulator, a nontrivial topological semimetal (zero-bandgap) and a nontrivial topological insulator (finite-bandgap). The corresponding band symmetries near the $\Gamma$-point are represented schematically in figures 1(c)–(e), respectively. For a trivial topological phase with the $Z_2$ topological order equal to +1 in a zinc-blende crystal such as CdTe, a bandgap exists at the Fermi level as well as the twofold degenerate $s$-like states marked by dark blue dot lines in the conduction band. In the case of a nontrivial topological phase such as HgTe, band inversion occurs in that the $s$-like states drop below the fourfold degenerate $p$-like states of the $J = 3/2$ multiplet, yielding $Z_2 = -1$. The fourfold degeneracy is due to the cubic symmetry of the zinc-blende structure. In order to achieve a topological insulating state, the degeneracy is required to be lifted to open a bandgap (figure 1(e)). Since the noncubic famatinites and quaternary chalcogenides are derived from zinc-blende structures, the nontrivial topological insulating phase could be realized in these materials. Indeed, our first-principles calculations predict that the 3D nontrivial topological insulating phase exists in the compounds of famatinite and quaternary chalcogenide families.

2. Methods

The crystal structures of ternary famatinite compounds and quaternary chalcogenide compounds are taken from the literature [37–51]. First-principles band calculations were performed with the linear augmented-plane-wave (LAPW) method using the WIEN2K package [52] within the framework of density functional theory (DFT). The generalized gradient approximation (GGA) of Perdew et al [53] was used to describe the exchange-correlation potential. SOC was included as a second variational step using the basis of scalar-relativistic eigenfunctions.

3. Results

The bulk band structures along the high-symmetry path $M(\pi, \pi)\rightarrow\Gamma(0, 0)\rightarrow X(\pi, 0)$ are shown in figure 2 for two representative compounds Cu$_3$SbS$_4$ and Cu$_3$SbSe$_4$ that belong to the famatinite family. The effect of zone-folding is clearly evident at the high-symmetry point $\Gamma$. In the ground state of these compounds, the structural compression along the $c$-axis (i.e. $c < 2a$) compared with the cubic zinc-blende lattice lifts the fourfold degeneracy of the cation $p$-states at the $\Gamma$-point owing to the crystal-field splitting. In Cu$_3$SbS$_4$, an insulating energy gap between the $p$-states is present at the Fermi level throughout the Brillouin zone as shown in figure 2(a). However, as the nuclear charge of the anion increases from S to Se, the conduction band drops below the Fermi level at the $X$-point, yielding an electron pocket as seen in figure 2(b). Simultaneously, the valence band maximum gradually moves above the Fermi level, making Cu$_3$SbSe$_4$ a metal. Nevertheless, a finite direct gap persists throughout the Brillouin zone and
Figure 2. Bulk band dispersion of famatinite compounds with nontrivial topological phases. (a, b) Electronic structure of Cu$_3$SbS$_4$ and Cu$_3$SbSe$_4$. In both figures, the black dots are the p-states of the cation sites, while the size of the blue dots is proportional to the probability of s-orbital occupation on the anion site. Gray shadings highlight the low-energy region near the Γ-point where the band inversion has occurred.

thus the $Z_2$ topological invariant can still be defined for the valence bands in these two materials and the inverted band order is retained only at the Γ-point. Therefore, Cu$_3$SbS$_4$ and Cu$_3$SbSe$_4$ are topologically nontrivial insulator and metal, respectively.

The mutation of the crystal structure from the ternary to a quaternary compound is also reflected in the electronic structure of these two families of materials. Due to tetragonal symmetry, all the Cu-based quaternary materials shown in figure 3 host a gap in the p-states close to the Fermi level, where the magnitude of the gap depends on the extra cation cross-substitutions. The Fermi level goes through the energy gap of the p-states in most materials, harboring a topological insulating state in these compounds. However, only in two compounds, Cu$_2$ZnGeTe$_4$ and Cu$_2$CdGeTe$_4$, do the low-energy electronic properties reveal that the conduction band minimum is shifted to the M-point and drops below the Fermi level to form bulk electron pockets. Simultaneously, the concave-upward-shaped valence band maximum pops up above the Fermi level at the Γ-point, making these systems intrinsically bulk metallic. We find a very similar nature of the band inversion across these materials in which the split p-states lie in energy above the twofold-degenerate s-states at a single time-reversal momentum Γ-point, representing a band-inversion relative to the natural order of s- and p-type orbital-derived band structure. Therefore, all these materials are intrinsically bulk nontrivial topological insulators or semimetals, except for Cu$_2$ZnGeS$_4$, Cu$_2$ZnSnS$_4$ and Cu$_2$HgGeS$_4$ that are trivial topological insulators. Note that, as one of the predicted topological nontrivial cases in figure 3, Cu$_2$HgSnS$_4$ has I-4 space group symmetry, which is slightly different from other I-42m symmetry quaternary chalcogenide compounds. In table 1, we list the computed bandgap values at the Γ-point of the ternary famatinite and quaternary chalcogenide compounds. The band inversion strength (BIS), which is defined as the energy difference between the lowest conduction state and the highest s-like valence state at the Γ-point, is also given.
Figure 3. Electronic structure of quaternary chalcogenide compounds. Bulk electronic structure of several Cu-based quaternary chalcogenides. Black dots, blue dots and gray shading have the same meaning as in figure 2. Compounds without a gray-shaded area are trivial topological insulators without any inverted band symmetries, whereas others are nontrivial topological insulators or semimetals with $Z_2 = -1$ topological order.

Finally, we demonstrate our tuning procedure for generating a nontrivial topological phase from a trivial band insulator. Specifically, we take advantage of the structural freedom in the ternary famatinite and quaternary chalcogenides. In figure 4, we illustrate this route using the example of going from the quaternary chalcogenide Cu$_2$ZnSnS$_4$ as the starting point to the ternary famatinite Cu$_3$SbS$_4$. Note that the topological phase transition is a generic feature and there exist numerous such routes. In their pristine conditions, Cu$_2$ZnSnS$_4$ is a trivial band insulator, whereas Cu$_3$SbS$_4$ is a topological insulator as discussed above in connection with figures 3(i) and 2(b). We systematically manipulate the overall crystal structure of our starting compound by making the atomic number $Z$ of the constituent atoms, the lattice constant and the internal displacement of the anion variable parameters.

To illustrate this process, we denote the atomic numbers $Z$ of various elements by $Z_{M1}$, $Z_{M2}$, $Z_{M3}$ and $Z_{M4}$. For our starting element Cu$_2$ZnSnS$_4$, we have $Z_{M1} = 29$, $Z_{M2} = 30 - x$, $Z_{M3} = 50 + x$ and $Z_{M4} = 16$, where $x$ varies between 0 and 1 in the phase transformation process. At each step of changing the parameter $x$, we also pay attention to the lattice constant and the internal displacements of the anion by keeping the same ratio of changes corresponding to the change in $x$ of atomic numbers ($Z$) from Cu$_2$ZnSnS$_4$ to Cu$_3$SbS$_4$. Note that the variation of $Z$ can also be considered as a doping effect in the spirit of the virtual crystal
Table 1. Band gap and BIS (see text) based on GGA for the 2 ternary famatinite and 13 quaternary chalcogenide compounds investigated. In the column ‘Gap’, ‘Metal’ indicates that the lowest conduction band drops below the Fermi level and has no bandgap at the Γ-point. In the column ‘BIS’, positive values imply the topologically nontrivial case, whereas a negative value gives the bandgap energy for topologically trivial cases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gap (eV)</th>
<th>BIS (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃SbS₄</td>
<td>0.042</td>
<td>0.198</td>
</tr>
<tr>
<td>Cu₃SbSe₄</td>
<td>Metal</td>
<td>0.615</td>
</tr>
<tr>
<td>Cu₂ZnGeSe₄</td>
<td>0.069</td>
<td>0.165</td>
</tr>
<tr>
<td>Cu₂ZnSnSe₄</td>
<td>0.056</td>
<td>0.315</td>
</tr>
<tr>
<td>Cu₂CdGeSe₄</td>
<td>0.003</td>
<td>0.131</td>
</tr>
<tr>
<td>Cu₂CdSnSe₄</td>
<td>0.003</td>
<td>0.254</td>
</tr>
<tr>
<td>Cu₂HgGeSe₄</td>
<td>0.006</td>
<td>0.385</td>
</tr>
<tr>
<td>Cu₂HgSnSe₄</td>
<td>0.007</td>
<td>0.543</td>
</tr>
<tr>
<td>Cu₂ZnGeTe₄</td>
<td>Metal</td>
<td>0.348</td>
</tr>
<tr>
<td>Cu₂ZnGeS₄</td>
<td>0.481</td>
<td>−0.481</td>
</tr>
<tr>
<td>Cu₂ZnSnS₄</td>
<td>0.115</td>
<td>−0.115</td>
</tr>
<tr>
<td>Cu₂CdSn₄</td>
<td>0.033</td>
<td>0.078</td>
</tr>
<tr>
<td>Cu₂HgGeS₄</td>
<td>0.016</td>
<td>−0.016</td>
</tr>
<tr>
<td>Cu₂HgSnS₄</td>
<td>0.060</td>
<td>0.217</td>
</tr>
<tr>
<td>Cu₂CdGeTe₄</td>
<td>Metal</td>
<td>0.288</td>
</tr>
</tbody>
</table>

Figure 4. Topological phase transition between quaternary chalcogenide and famatinite compounds. Bulk electronic structure of the compounds at various stages of the topological phase transition process is shown as a function of x (see text). Trivial band insulators are obtained for small values of x in (a) and (b). A semimetal state is obtained at the topological critical point in (c). Nontrivial topological insulators are obtained at large values of x in (d) and (e).
approximation [54, 55], while the total nuclear charge is fixed throughout this process. It will be interesting to examine doping effects using first-principles approaches [56, 57] for tuning topologically interesting electronic structures.

We monitor the band structure along the high-symmetry path \( M(\pi, \pi) \rightarrow \Gamma(0, 0) \rightarrow X(\pi, 0) \) at every step of the transition process from figures 4(a)–(e). While the overall band structure remains very much the same, the band characters and the bandgap vary dramatically. In figure 4(b), upon increasing \( x \) by 0.25, the size of the bandgap at \( \Gamma \) starts to shrink compared to the parent compound in figure 4(a), although the s-character continues to dominate in the conduction band (blue dots). The critical point is reached when the value of \( x \) is increased to 0.5 in figure 4(c), at which point the bottom of the conduction band and the top of the valence band touch at the single momentum point \( \Gamma \), leading to a critical topological point. A full band inversion is achieved in figure 4(d), that recreates an insulating bandgap which is topologically nontrivial in nature and the s-like orbital character shifts well below the valence band. Finally, in figure 4(e), when \( x = 1 \), Cu$_3$SbS$_4$ emerges as a nontrivial topological insulator.

4. Conclusion

We have shown via first-principles calculations that the ternary famatinite and quaternary chalogenide compounds are nontrivial topological insulators in their pristine phase. The involvement of partially filled d- and f-electrons in these compounds naturally opens up the possibility of incorporating magnetism and superconductivity within the topological order. The large tuning possibilities available in the quaternary compounds add versatility in using topological insulators in multifunctional spin-polarized quantum and optical information-processing applications. Notably, the copper-based quaternary chalcogenides are known to have nonlinear optoelectronics and thermodynamics applications [36].

After we completed this study, we became aware of the work of Chen et al [58], who have also proposed that some of the multinary chalcogenides are potential candidates to be nontrivial topological insulators.

Acknowledgments

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