Three-Dimensional Topological Insulators in I-III-VI$_2$ and II-IV-V$_2$ Chalcopyrite Semiconductors

Wanxiang Feng,[1] Di Xiao,[2,*] Jun Ding,[1] and Yugui Yao[1,†]

[1]*Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

[2]*Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

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Using first-principles calculations within density functional theory, we investigate the band topology of ternary chalcopyrites of composition I-III-VI$_2$ and II-IV-V$_2$. By exploiting adiabatic continuity of their band structures to the binary 3D-HgTe, combined with direct evaluation of the Z_2 topological invariant, we show that a large number of chalcopyrites can realize the topological insulating phase in their native states. The ability to host room-temperature ferromagnetism in the same chalcopyrite family makes them appealing candidates for novel spintronics devices.

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The recent discovery of topological insulators [1–3] with exotic metallic surface states has garnered great interest in the fields of condensed matter physics and materials science [4]. A number of spectacular quantum phenomena have been predicted when the surface states are under the influence of magnetism and superconductivity [5–8], which could open up new opportunities for technological applications in spintronics and quantum computing. To achieve this goal, material realization of topological insulators with desired physical properties is of crucial importance. Early experiments on topological insulators are limited to alloys and binary compounds [9–15]. Motivated by their application potentials, the search for new topological insulators has extended to ternary compounds with greater material flexibility [16–22]. For example, it was proposed that in the Heusler family [16–18] the topological insulator can be made with coexisting magnetism, a much desired property for spintronic applications. However, a clear shortcoming of the Heusler family is that in their native states these materials are either zero-gap semiconductors or semimetals. Although alloying or proper strain can be used to achieve the insulating behavior, this creates extra complexity in material growth and could introduce detrimental effects upon doping.

In this Letter, based on first-principles calculations, we show that a large number of ternary chalcopyrite compounds of composition I-III-VI$_2$ and II-IV-V$_2$ can realize the topological insulating phase in their native states. Our argument is based on adiabatic continuity of their band structures to the topologically nontrivial binary compound HgTe [11], then confirmed by direct evaluation of the Z_2 topological invariant [16]. The crystal structure of chalcopyrites is derived from the frequently used zinc-blende structure, and many of them possess a close lattice match to important mainstream semiconductors, which is essential for a smooth integration into current semiconductor technology. The diverse optical, electrical, and structural properties of chalcopyrite semiconductors [23], and particularly their ability to host room-temperature ferromagnetism [24–26], make them appealing candidates for novel spintronics devices.

The ternary ABC_2 chalcopyrite compounds of composition I-III-VI$_2$ or II-IV-V$_2$ are isoelectronic analogs of the II–VI or III–V binary semiconductors, respectively [23]. The crystal lattice of chalcopyrites is described by the space group D_{2d}^{12} ($I\bar{4}2d$), which can be regarded as a superlattice of the zinc-blende structure with small structural distortions. As illustrated in Fig. 1, the chalcopyrite unit cell is essentially formed by two cubic zinc-blende unit cells, in which the A and B atoms are ordered on the two different cation sites. In view of the overall structural similarity between the ternary chalcopyrites and their binary analogs, the electronic states of the former are expected to closely resemble those of the latter. In particular, we anticipate that some of the chalcopyrites might fall into the same topological class as the topologically nontrivial

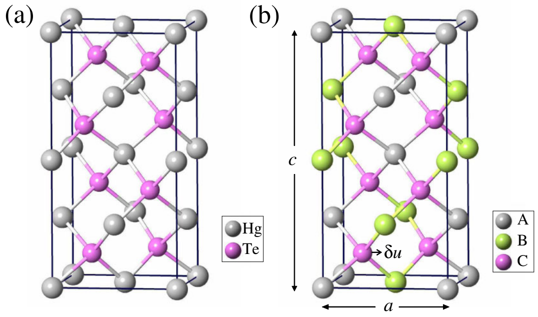

FIG. 1 (color online). Comparison of the zinc blende and the chalcopyrite structure. (a) The zinc-blende compound HgTe. (b) The chalcopyrite compound ABC_2. The internal displacement of the anion is defined as $\delta u = (R_{AC}^2 - R_{BC}^2)/a^2$, where R_{AC} and R_{BC} are the bond lengths between the anion C and its two nearest A and B cations.

3D-HgTe [9,11], which is a II-VI zinc-blende semiconductor. Furthermore, the cubic symmetry in chalcopyrite compounds is explicitly broken due to the *AB* cation ordering, accompanied by two additional structural modifications [Fig. 1(b)]: the tetragonal distortion characterized by the ratio of the lattice constants $\eta = c/2a$, and the internal displacement δu of the anions away from their ideal zinc-blende sites. In an ideal structure, $\eta = 1$ and $\delta u = 0$. As we show below, this inherent symmetry reduction plays the same role as the uniaxial strain required in cubic topological materials such as 3D-HgTe [11] and the Heusler family [16–18], making it possible to realize the topologically insulating phase in the native state of chalcopyrite compounds.

To illustrate the band topology of the ternary chalcopyrites, we begin with their binary analog, HgTe, and follow its band structure under an adiabatic transformation during which the zinc-blende structure is gradually evolved into the chalcopyrite structure [Figs. 2(a)–2(c)]. The first-principles relativistic band structure is obtained by using the full-potential linearized augmented plane-wave method implemented in the WIEN2K package [27]. The exchange-correlation potential is treated using the modified Becke-Johnson potential [28], which is a semilocal potential designed to accurately predict the band gap [29]. The band structure of HgTe features a distinctive inverted band order at the Γ point, where the *s*-like Γ_6 states sit below the fourfold degenerate *p*-like Γ_8 states [Fig. 2(a)]. Away from the Γ point, the valence and conduction bands are well separated without crossing each other. Since the band inversion occurs only once throughout the Brillouin zone, HgTe is in a topologically nontrivial phase [11]. The fourfold degeneracy of the Γ_8 states is protected by the cubic symmetry of the zinc-blende structure; thus, in its native state HgTe is a zero-gap semiconductor. The band structure calculation is then repeated for HgTe in an ideal chalcopyrite supercell [Fig. 2(b)], which is 4 times larger than the zinc-blende one. During this procedure, every set of four different wave vectors of the original zinc-blende Brillouin zone fold into a single point of the chalcopyrite Brillouin zone. In particular, states at the original Γ point fold back to themselves; therefore, the low-energy electronic properties are still dominated by states around the Γ point. In the final step, to mimic the cubic-symmetry breaking in chalcopyrites, we let the system undergo a tetragonal distortion plus an internal displacement of the two Te atoms. This structural change lifts the degeneracy of the Γ_8 states and opens up an energy gap, while leaving the inverted band order intact [Fig. 2(c)]. The situation here thus is exactly like HgTe under a uniaxial strain [9,11], and the resulting compound, an artificial chalcopyrite Hg_2Te_2, is a topological insulator.

The above analysis of the tetragonally distorted HgTe suggests that the same Z_2 band topology can be realized in real ternary chalcopyrites. This is confirmed by our extensive first-principles band structure calculations over this family of materials. There are two possible scenarios, with the corresponding band structures of representative systems shown in Figs. 2(d) and 2(e). The most natural generalization of HgTe to chalcopyrites is the ternary compound $AuTlTe_2$, which can be obtained by replacing the two Hg atoms in Hg_2Te_2 with an isoelectronic pair of Au and Tl atoms. Conceptually, this process can be described by an adiabatic transformation in which the nuclear charges on the two Hg sites are continuously changed to that of Au and Tl, respectively. However, such a substitution causes the conduction bands to drop below the Fermi level at the *N* point, making the system effectively a semimetal. Note that a Z_2 topological invariant can still be defined for the valence bands in $AuTlTe_2$ because they are separated from the conduction bands by local energy gap throughout the Brillouin zone. Our further study shows that the semimetallic behavior can be removed by choosing a lighter element S in place of Te—we find that a global band gap of 0.14 eV can be realized in $AuTlS_2$ [Fig. 2(e)]. Remarkably, this band gap is much larger than typical

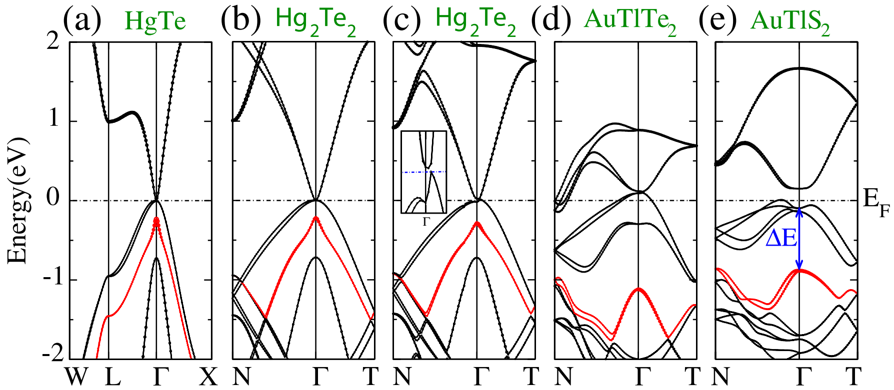

FIG. 2 (color online). Band structures of HgTe in comparison with $AuTlTe_2$ and $AuTlS_2$. (a)–(c) Band structures of HgTe (a), HgTe in an ideal chalcopyrite supercell (b), and HgTe in a chalcopyrite cell with $\eta = 1.016$ and $\delta u = -0.018$ (c). The size of red dots denotes the probability of *s*-orbital occupation on the cations. The inset in (c) shows the energy gap opened by chalcopyrite distortion. (d),(e) Band structures of $AuTlTe_2$ (d) and $AuTlS_2$ (e). Both display an inverted band order similar to HgTe, indicating a nontrivial band topology. ΔE in (e) indicates the band-inversion strength.

band gaps opened by uniaxial strain in Heusler compounds [16–18], and is also well above the energy scale of room temperature. In both $AuTlTe_2$ and $AuTlS_2$, the inverted band order at the Γ point is retained, with no band inversion at other places. We therefore conclude that, in their native states, $AuTlS_2$ is a topological insulator with a sizable band gap, and $AuTlTe_2$ a topological metal. On the other hand, compounds with normal band order are always semiconductors—our calculation did not find any semimetallic chalcopyrite with normal band order.

So far our argument has been based on the isoelectronic relation between the ternary chalcopyrites and their binary analogs; it is much desired to give a definite proof that the band topology of $AuTlTe_2$ and $AuTlS_2$ is Z_2 nontrivial. Because of the lack of inversion symmetry in these materials, the parity criterion developed by Fu and Kane [11] does not apply. Here we directly evaluate the Z_2 invariant in terms of the Berry gauge potential and Berry curvature associated with the Bloch functions [30]. In this approach, the Z_2 invariant is interpreted as an obstruction to smoothly defining the wave function throughout the Brillouin zone under a gauge that respects the time-reversal symmetry [1,31]. Unlike the parity criterion, this approach does not require any specific point-group symmetry. Following Ref. [32], we have carried out the lattice computation of the Z_2 invariant based on our first-principles method (see Ref. [16] and supplementary material [33] for details). We find that, for all the compounds presented in this work, the calculated Z_2 invariant agrees with the intuitive band-inversion picture. In practice, this translates into an empirical rule that if the s-orbital originated Γ_6 states are completely occupied and below the valence band maximum, the compound possesses a nontrivial topological band structure.

Armed with the above insight, next we explore the band topology of the chalcopyrite family of the I-III-VI_2 compounds ($I = Cu$, Ag, Au; $III = In$, Tl; $V = S$, Se, Te), as well as the II-IV-V_2 compounds ($II = Zn$, Cd, Hg; $IV = Ge$, Sn; $V = As$, Sb). Since the band inversion only occurs at the Γ point, the band order at that point can be used to characterize the band topology. In compounds with cubic symmetry, one can define the band-inversion strength as the energy difference between the Γ_6 and Γ_8 states [17,18]. However, in passing from the zinc-blende structure to the chalcopyrite structure, the original Γ_8 states split into states with Γ_7 and Γ_6 symmetry, which typically form the top set of the valence bands and the bottom set of the conduction bands. We therefore define the band-inversion strength ΔE as the energy difference between the s-orbital originated Γ_6 states and the valence band maximum at the Γ point. Figure 3 shows ΔE for a number of chalcopyrite compounds as a function of the lattice constant. Materials with $\Delta E > 0$ are topologically trivial and those with $\Delta E < 0$ are either topological insulators or topological metals. As shown in Fig. 3, there are quite a few chalcopyrite topological insulators with a close lattice matching to several mainstream semiconductors. Finally, we note that the impressive collection of chalcopyrite topological insulators

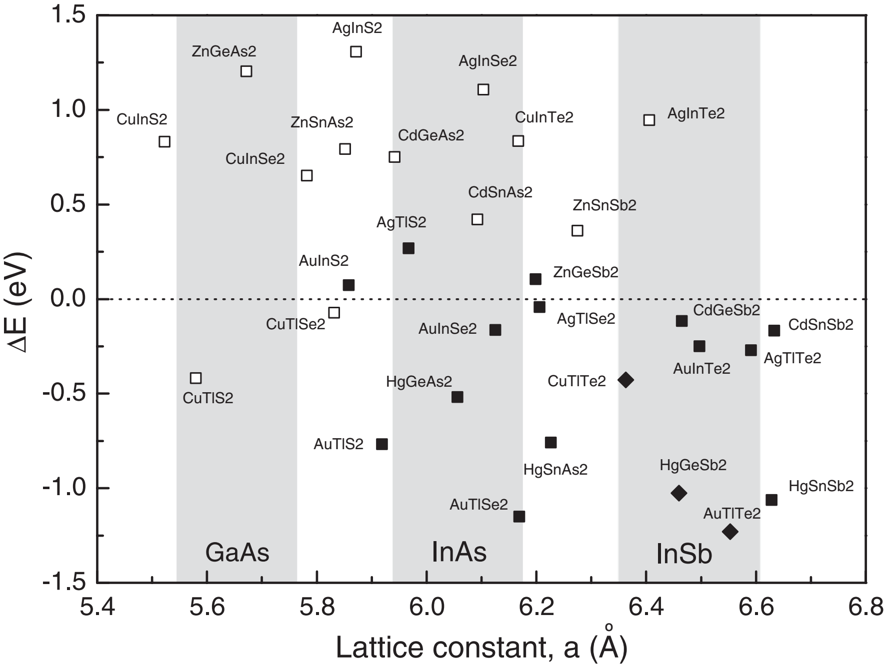

FIG. 3. Inverted band strength for various chalcopyrites as a function of the lattice constant. Open symbols mark the compounds whose lattice constant was reported in the literature. For the rest of the compounds their equilibrium lattice constants are obtained by first-principles total energy minimization. When $\Delta E < 0$, squares mark the compounds that are topological insulators and diamonds mark the systems that are topological metals. Shaded areas indicate materials that are expected to be closely (± 2%) lattice matched to either GaAs, InAs, or InSb.

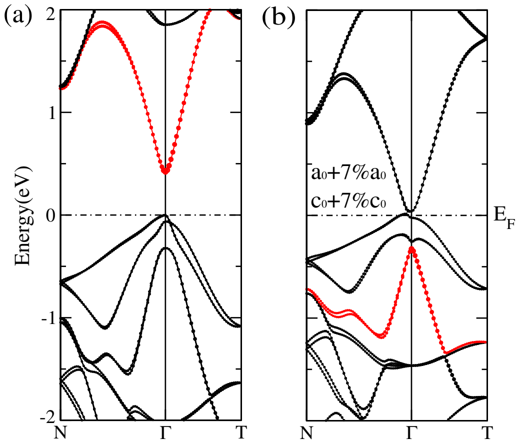

FIG. 4 (color online). Band structures of $CdSnAs_2$ without and with a hydrostatic strain. The application of a hydrostatic strain causes the s-like Γ_6 bands (marked by red dots) to jump below the valence band top, providing the necessary band inversion that leads to a nontrivial topological order.

can be further extended by proper strain engineering. Similar to the Heusler family [16–18], the topological phase is sensitive to the lattice constant, which offers a certain degree of tunability of these materials. For example, a 7% change in the lattice constant converts the trivial semiconductor $CdSnAs_2$ into a topological insulator (Fig. 4).

In summary, we have shown that a large number of ternary chalcopyrite compounds of composition I-III-VI_2 and II-IV-V_2 can realize the topological insulating phase in their native states. The interplay between topological surface states and ferromagnetism has been under extensive investigation because of the possibility of electric control of magnetization with low power consumption [5,8]. The room temperate ferromagnets have been reported in some chalcopyrite compounds by doping magnetic atoms [24,25], we expect that the chalcopyrite compounds with nontrivial topological phase also become room-temperature ferromagnetism by similar doping method. In addition, we also expect that the good interface can be formed between ferromagnetic semiconductor and chalcopyrite topological insulator due to similar zinc-blende structure, then topological order and ferromagnetism may appear at the same time due to proximity effect. Therefore, the wide availability of chalcopyrite semiconductors, the control of topological order via lattice tuning, and their excellent prospect for room-temperature ferromagnetism, make them the ideal platform to further investigate these novel topological phenomena and could enable the next-generation spintronic devices.

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*To whom correspondence should be addressed.
xiaod@ornl.gov

†To whom correspondence should be addressed.
ygyao@aphy.iphy.ac.cn

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