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Band Structure Engineering of Multinary Chalcogenide Topological Insulators

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Abstract

Topological insulators (TIs) have been found in strained binary HgTe and ternary I-III-VI₂ chalcopyrite compounds such as CuTlSe₂ which have inverted band structures. However, the non-trivial band gaps of these existing binary and ternary TIs are limited to small values, usually around 10 meV or less. In this work, we reveal that a large non-trivial band gap requires the material having a large negative crystal field splitting Δ_{CF} at top of the valence band and a moderately large negative $s-p$ band gap E_g^{s-p} . These parameters can be better tuned through chemical ordering in multinary compounds. Based on this understanding, we show that a series of quaternary I₂-II-IV-VI₄ compounds, including Cu₂HgPbSe₄, Cu₂CdPbSe₄, Ag₂HgPbSe₄ and Ag₂CdPbTe₄ are TIs, in which Ag₂HgPbSe₄ has the largest TI band gap of 47 meV because it combines the optimal values of Δ_{CF} and E_g^{s-p} .

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I. INTRODUCTION

The search for new topological insulators (TIs) has intensified recently due to their scientific importance as a novel quantum state and the associated technological applications in spintronics and quantum computing[1, 2]. So far, experimental realizations have been limited to a few classes of simple materials, including zinc-blende based HgTe quantum wells[3–5], $\text{Bi}_{1-x}\text{Sb}_x$ alloys[6, 7] and binary tetradymite semiconductors such as Bi_2Se_3 and Bi_2Te_3 [8–10]. Most recently, the search for TIs has extended to ternary compounds[11–14], e.g., strained Half-Heusler compounds, in the hope that the presence of more chemical elements would bring greater material flexibility. Despite the success of identifying these TIs, the design of new TI materials with the following advantages is still desired: (i) realizing a topological insulating state with a significant non-trivial band gap (i.e., larger than kT at room temperature) at its natural equilibrium state (i.e., not under external strain), (ii) easy integration with electronic and spintronic devices based on tetrahedral semiconductors, and (iii) easy to be synthesized or already have been synthesized.

Based on the direct evaluation of the Z_2 topological invariant, Feng et al.[15] proposed that a series of I-III-VI₂ chalcopyrite compounds (such as CuTlSe_2) could have topologically non-trivial band structure, and some of them can realize a topological insulating phase in their natural equilibrium structure. This is an important observation because the chalcopyrite structure is derived from the zinc-blende structure, and the band structure properties are well understood, mostly for solar cell applications[16, 17]. Some of the proposed Cu and Ag based TIs, such as CuTlSe_2 and AgTlTe_2 , have already been synthesized experimentally[16, 18]. However, the predicted band gaps of these TIs are very small, usually around 10 meV or less, similar to that observed in strained HgTe[4].

In this Letter, we show that the non-trivial band gaps of zinc-blende derived compounds with inverted band structure are mainly determined by the crystal field splitting Δ_{CF} at the top of the valence band and the size of the inverted s-p band gap E_g^{s-p} , which can be better tuned by changing the component elements in a multinary ordered compounds. A large non-trivial band gap requires the material having a large negative Δ_{CF} and a large negative E_g^{s-p} as long as it has no band crossing at the Fermi energy. For I-III-VI₂ topological insulators, because the band inversion requires the group-III elements to be large and heavy, whereas a large negative Δ_{CF} requires group-III elements to be small and light, the possibilities for

obtaining a large TI band gap are limited. Through further cation mutation, large negative Δ_{CF} and E_g^{s-p} is achievable in quaternary II₂-II-IV-VI₄ compounds. We have identified four topological insulators (Cu₂HgPbSe₄, Cu₂CdPbSe₄, Ag₂HgPbSe₄ and Ag₂CdPbTe₄), in which Ag₂HgPbSe₄ has the largest TI band gap of 47 meV. In the following, we will discuss the evolution of the band structure of zinc-blende derived structures at first, explain what kind of band structure can lead to the largest TI band gap, and then show how to design quaternary TIs through cation mutation.

II. CALCULATION METHODS

The band structures are calculated within the DFT formalism as implemented in the VASP code[19]. For the exchange-correlation functional, we used the HSE (Heyd-Scuseria-Ernzerhof) hybrid functional in which one quarter of Hartree-Fock non-local exchange interaction is added to the GGA functional, and a screening of $\mu=0.2 \text{ \AA}^{-1}$ is applied to partition the exchange potential into short-range and long-range terms[22–24]. The d states of group-III and IV elements are treated explicitly as valence. The interaction between the core electrons and the valence electrons is included by the frozen-core projector augmented-wave method, and an energy cut-off of 300 eV was applied for the plane-wave basis set. A $4\times 4\times 4$ Monkhorst-Pack k -point mesh is used for the Brillouin-zone integration of the 8-atom chalcopyrite and kesterite cells. All lattice vectors and atomic positions were fully relaxed.

III. FACTORS DETERMINING THE NON-TRIVIAL BAND GAP

For a normal zinc-blende semiconductors such as CdTe, the band gap is between the s-like conduction band minimum (CBM) Γ_{6c} state and the p-like valence band maximum (VBM) Γ_{8v} state, as shown in Fig. 1. The non-trivial band structure of a TI is characterized by the band inversion in the Brillouin zone[6, 15], i.e., the position of the conduction and valence bands is switched. In zinc-blende compounds, the band inversion means that the Γ_{6c} level falls below the Γ_{8v} level. In the inverted band structure, the Γ_{6c} level is occupied, while the quadruply-degenerate Γ_{8v} level is half occupied, making the Fermi level stay at the Γ_{8v} level and the system become a zero-gap semi-metal. This is the case for bulk HgTe.

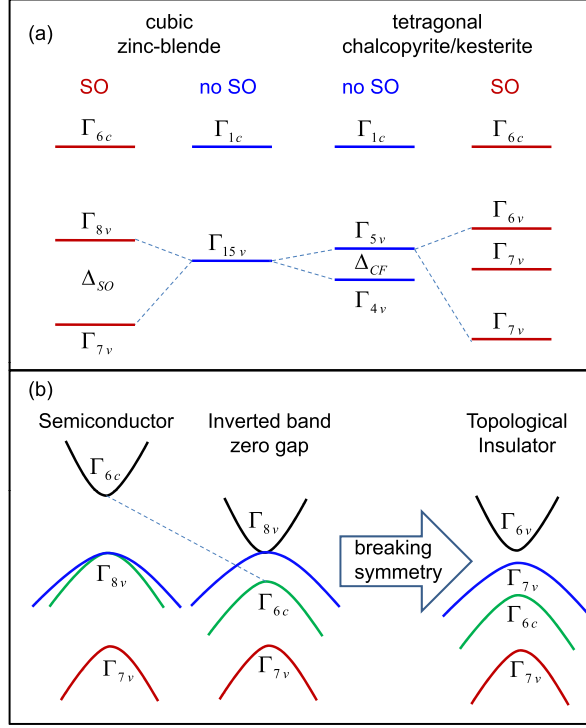


FIG. 1: (Color online) (a) The conduction and valence band splitting of cubic and tetragonal semiconductors. (b) A plot showing how the band structure of normal semiconductors transfers into the inverted and topological insulator band structures. Note that the subscript v (c) represents the state belongs to the valence (conduction) band in the normal band structure.

To open a band gap and change the zinc-blende semi-metal HgTe into a topological insulator, one has to induce a crystal field splitting Δ_{CF} by reducing the T_d symmetry of the zinc-blende structure to, e.g., D_{2d} , by applying an epitaxial strain or forming a quantum well[4]. For D_{2d} symmetry, the half-filled Γ_{8v} state splits into Γ_{6v} and Γ_{7v} state, and a gap can be opened around the occupied Γ_{7v} (Γ_{6v}) and unoccupied Γ_{6v} (Γ_{7v}) levels (Fig. 1(b)) if Δ_{CF} is positive (negative). On the other hand, the crystal field splitting can also be induced by chemical ordering, e.g., by mutating two Hg (group II) atoms into one Cu (group I) and one Tl (group III), forming ordered I-III-VI₂ chalcopyrite-structured compounds such as CuTlTe₂[15]. In Fig. 2(a) we plot the chalcopyrite structure, which can be taken as derived from the binary zinc-blende structure[20, 30].

In Fig. 3 we plot the calculated band structure of HgTe under a $\epsilon = 0.02$ (001) tensile strain with $\Delta_{CF}=70$ meV and CuTlTe₂ in the chalcopyrite structure with $\Delta_{CF}=76$ meV. As we can see, a small gap is opened near the Γ point for both systems, which is the so-called

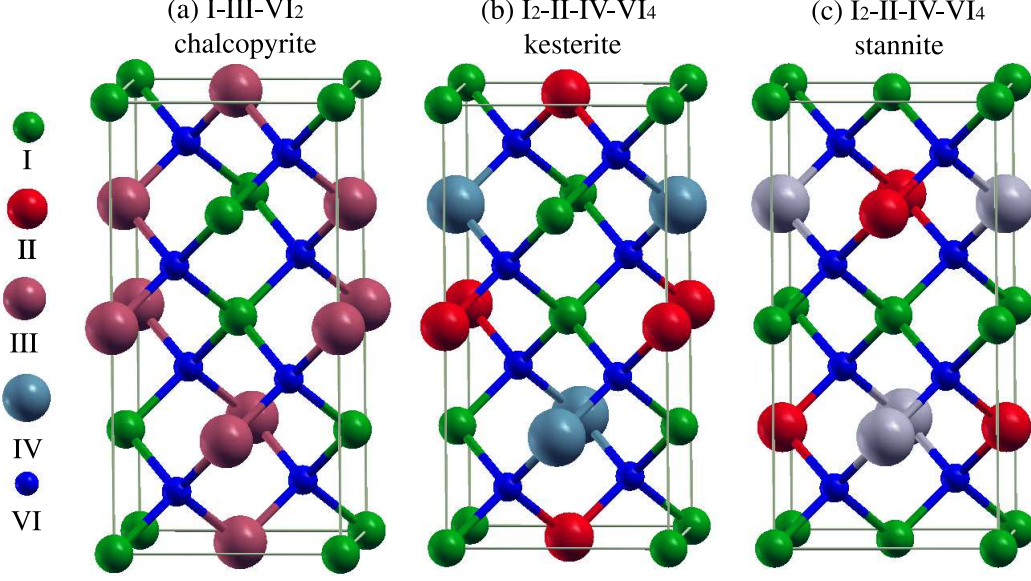


FIG. 2: (Color online) Crystal structure plot of (a) ternary I-III-VI₂ chalcopyrite structure, (b) quaternary I₂-II-IV-VI₄ kesterite structure and (c) quaternary I₂-II-IV-VI₄ stannite structure.

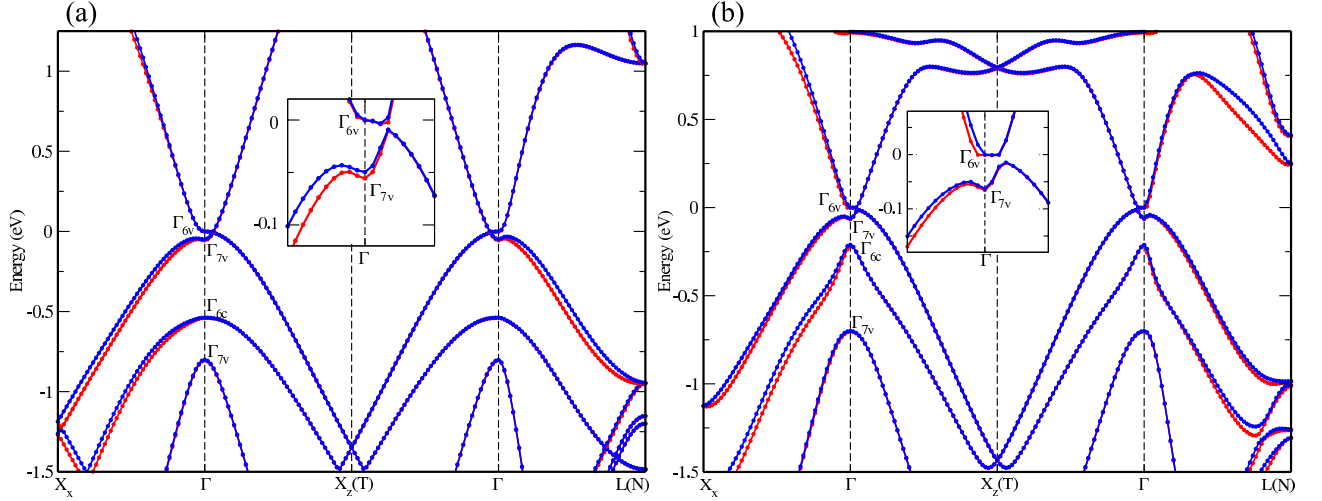


FIG. 3: (Color online) The calculated band structure along the high symmetry lines, $X_X : \frac{2\pi}{a}(1 \ 0 \ 0) \rightarrow \Gamma : (0 \ 0 \ 0) \rightarrow X_Z : \frac{2\pi}{a}(0 \ 0 \ 1) \rightarrow \Gamma : (0 \ 0 \ 0) \rightarrow L : \frac{2\pi}{a}(0.5 \ 0.5 \ 0.5)$ of (a) HgTe with a (001) tensile strain and $\Delta_{CF} = 70$ meV, and (b) CuTlTe₂ with $\Delta_{CF} = 76$ meV at its equilibrium state. X_X , X_Z and L are the notations of zinc-blende structure, and X_Z and L correspond to T and N respectively in the chalcopyrite structure. Red and blue color are used to show the two spin-dependent bands clearly.

non-trivial band gap of TIs. Although the size is small, this anticrossing gap is protected by the lattice symmetry[21]. For the band structure calculation we employed density functional theory with a hybrid exchange-correlation functional HSE[22], which can more correctly predict the band gaps of many zinc-blende and chalcopyrite semiconductors[23–25]. However, it should be mentioned that, due to the similar wavefunction characters of the band edge states and symmetry-protected nature of the TI band gap, the TI band gap does not disappear even in the calculated band structure using the local density approximation (LDA) to the exchange correlation functional, despite that LDA usually underestimates the $s - p$ band gap significantly.

Comparing the band structure of HgTe under a $\epsilon = 0.02$ (001) tensile strain and CuTlTe₂, we find that the overall shape is very similar, especially near the band gap. In both systems, the s-like Γ_{6c} state falls below the p-like Γ_{6v} and Γ_{7v} states, and the minimum gap occurs along the $\Gamma - X_Z$ line. This similarity between strained HgTe and CuTlTe₂ indicates that the strain and chemical ordering have the same effect in producing the crystal field splitting Δ_{CF} at the top of valence band[27], therefore, it could be an efficient way to tune the TI band gap.

To achieve this goal, it is important to understand first how the splitting at the top of valence band is influenced by chemical ordering and what is the resulting dependence of the TI band gap. Based on the quasi-cubic model[26, 27], and assuming the Γ_{6c} state is far away from the band edge, we know that the splitting of the Γ_{8v} level into Γ_{6v} and Γ_{7v} under the tetragonal symmetry depends on two quantities: the spin-orbit splitting Δ_{SO} and the crystal field splitting Δ_{CF} . Δ_{CF} is defined to be positive if the doubly-degenerate Γ_{5v} is above the singly-degenerate Γ_{4v} state when the spin-orbit interaction is not considered, as shown in Fig. 1(a). For systems where Δ_{SO} is much larger than Δ_{CF} , the splitting between Γ_{6v} and Γ_{7v} is close to $2/3$ of Δ_{CF} . Previous studies[21] on strained zinc-blende compound showed that the non-trivial gap depends on the sign and size of Δ_{CF} : (i) when $\Delta_{CF} < 0$ the gap occurs along of the $\Gamma - X_X$ line near the Γ point and the gap increases quickly as a function of the magnitude of Δ_{CF} ; (ii) when $\Delta_{CF} > 0$, the gap occurs along the $\Gamma - X_Z$ line near the Γ point and the gap increases slowly as a function of Δ_{CF} . This can be seen clearly in Fig. 4(a), where the dependence of the non-trivial band gap on the size of Δ_{CF} for HgTe is plotted. For example, when $\Delta_{CF} = -100$ meV, the gap is almost 40 meV, but when $\Delta_{CF} = 100$ meV, the gap is only 5 meV. The reason for the more significant gap increase with negative

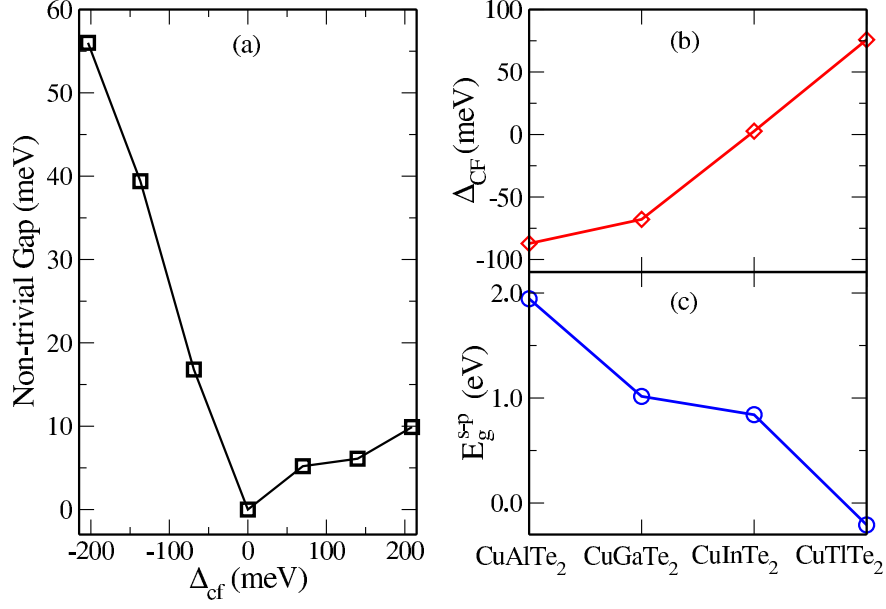


FIG. 4: (Color online) (a) The calculated non-trivial band gap as a function of Δ_{CF} for HgTe. Here Δ_{CF} is changed by tuning the (001) strain ϵ . (b) The calculated Δ_{CF} and (c) E_g^{s-p} of Cu-III-Te₂ with III=Al, Ga, In, Tl.

Δ_{CF} is that, $\Gamma - X_X$ line has lower symmetry than $\Gamma - X_Z$ line, so the band anticrossing is more significant when the gap shifts to the $\Gamma - X_X$ line. CuTlTe₂ has a calculated $\Delta_{CF} = 76$ meV. This positive value explains why the gap shifts to the $\Gamma - X_Z$ line with only a small value of about 14 meV [Fig. 3(b)]. Based on this observation, we know that large gap TI can only exist in zinc-blende derived compounds with large negative Δ_{CF} .

In Fig. 4(b) we plot the calculated Δ_{CF} of CuAlTe₂, CuGaTe₂, CuInTe₂ and CuTlTe₂. As we can see, Δ_{CF} increases from negative to positive as the group-III cations change from Al to Tl, i.e., from small light to large heavy elements. Considering that large negative Δ_{CF} enlarges the non-trivial gap, one may intend to search compounds with small group-III cation as candidates for TIs. However, the requirement of band inversion at the Γ point excludes Al, Ga and In compounds because CuAlTe₂, CuGaTe₂ and CuInTe₂ all have the normal band order, i.e., the s -like Γ_{6c} state is above the p -like Γ_{7v} and Γ_{6v} states. Their s - p band gaps $E_g^{s-p} = E(\Gamma_{6c}) - E(\Gamma_{6,7v})$ are all positive and decrease from Al to Ga to In compounds. This can be understood according to the band component of I-III-VI₂ chalcopyrites: the Γ_{6c} state has s -like anti-bonding character localized on group-III cation and group-VI anion, whereas Γ_{7v} and Γ_{6v} states mainly have the p component of the group-VI anion hybridized

with the d component of the group-I cation[28, 29]. Two factors shift the Γ_{6c} level down from Al to Ga to In compounds [17, 20, 29]: (i) the s orbital energy of Ga is deeper than Al and (ii) In is much larger than Ga. For Tl, its s orbital energy, like Hg, is very deep due to the large relativistic effect, so its band gap is much lower than that of the corresponding In compounds. This is confirmed in Fig. 4(c), where we plot the calculated E_g^{s-p} of CuAlTe₂, CuGaTe₂, CuInTe₂ and CuTlTe₂; only CuTlTe₂ has negative E_g^{s-p} , i.e., its s -like Γ_{6c} state falls below the p -like states at Γ point (band inversion). Unfortunately, CuTlTe₂ has a positive $\Delta_{CF} = 76$ meV, thus only a small TI band gap of about 14 meV.

In the above discussion, we have assumed that the Γ_{6c} state is deep inside the valance band, thus has no effect on the band splitting and the non-trivial gap of the TIs. However, if the Γ_{6c} is close to the band edge, then we have to consider its interaction with the band edge states. This is because when $\Delta_{CF} < 0$, the band gap of the TI at Γ point is between the unoccupied Γ_{7v} and the occupied Γ_{6v} (or Γ_{6c} , if it has a higher energy than Γ_{6v}) derived state. The coupling between the Γ_{6v} and Γ_{6c} states pushes the Γ_{6v} level up in energy, thus reduces the effective crystal field splitting between the Γ_{7v} and Γ_{6v} state and the non-trivial band gap. This is what we find for AgTlSe₂ and AgTlTe₂. According to our calculation, the non-trivial gap of AgTlSe₂ is limited at Γ point with a very small size, 1 meV, although it has a large negative $\Delta_{CF} = -50$ meV. Therefore, to reduce the interaction between the Γ_{6v} and Γ_{6c} states, one should move the Γ_{6c} level down, i.e., increase the magnitude of negative E_g^{s-p} as much as possible.

The above analysis indicates that to design large gap chalcopyrite I-III-VI₂ TIs, we face two contradictory requirements (large negative Δ_{CF} and large negative E_g^{s-p}). This severely limits the largest non-trivial gap obtainable for I-III-VI₂ compounds. Through the direct calculation, we find that most of the already-synthesized I-III-VI₂ have positive E_g^{s-p} and are normal semiconductors[16], except CuTlSe₂, CuTlTe₂, AgTlSe₂ and AgTlTe₂. But the non-trivial gaps of these four TIs are all small due to the positive Δ_{CF} for CuTlSe₂ and CuTlTe₂, and small E_g^{s-p} for AgTlSe₂ and AgTlTe₂.

IV. QUATERNARY TOPOLOGICAL INSULATORS

To further increase the non-trivial band gap, we need to make both the Δ_{CF} and E_g^{s-p} more negative. We find that this can be done by mutating two group-III cations in I-III-VI₂

TABLE I: The calculated E_g^{s-p} of $I_2-II-Pb-VI_4$ ($I=Cu, Ag, II=Cd, Hg, VI=S, Se, Te$) in their ground-state structure. TM, TI and NI in the parentheses represent topological metal, topological insulator and normal insulator, respectively.

	Structure	Te ₄	Se ₄	S ₄
Cu ₂ HgPb	stannite	-0.46 (TM)	-0.32 (TI)	0.07 (NI)
Cu ₂ CdPb	stannite	-0.21 (TM)	-0.07 (TI)	0.32 (NI)
Ag ₂ HgPb	kesterite	-0.37 (TM)	-0.14 (TI)	0.40 (NI)
Ag ₂ CdPb	kesterite	-0.12 (TI)	0.18 (NI)	0.72 (NI)

compounds to one group-II and one group-IV cation, thus forming the $I_2-II-IV-VI_4$ ($I=Cu, Ag, II=Zn, Cd, Hg, IV=Si, Ge, Sn, Pb, VI=S, Se, Te$) quaternary compounds. These compounds crystallize in either tetrahedral kesterite or stannite structures, as shown in Fig. 2(b) and 2(c). Due to the increased chemical and structural freedom in the quaternary compounds, their band structure can be better tuned. Also, because they are structurally derived from chalcopyrites, their band structures maintain similar characteristics as those of chalcopyrites[20, 30], therefore, the empirical rule that if the s-orbital originated Γ_{6c} state is completely occupied and below the valence band maximum the compound possesses a nontrivial topological band structure given by Feng *et al.* for the chalcopyrites are also valid for the quaternary compounds,[11] i.e., if these compounds have inverted band structure, they can also be TIs.

Similar to the chalcopyrites, we need to have compounds that contain heavy group-IV elements so that the Γ_{6c} level could fall below the Γ_{6v} and Γ_{7v} levels[20, 30]. Table I lists the calculated E_g^{s-p} of $I_2-II-Pb-VI_4$ compounds. The results show that most of the Pb-Te and Pb-Se compounds have negative E_g^{s-p} at Γ and are therefore candidates for TIs. The calculation also shows all sulphides and compounds containing other group-IV cations (Sn, Ge, Si) have positive E_g^{s-p} and are normal semiconductors.

We first look at the band structure of $Cu_2HgPbTe_4$ (Fig. 5(a)), which has the most negative E_g^{s-p} . The overall shape near the Γ point is similar to those of ternary $CuTiTe_2$ and binary $HgTe$ under (001) strain as shown in Fig. 3, indicating that the band structure character is kept in the cation mutation. However, $Cu_2HgPbTe_4$ is actually a topological metal (TM), because the conduction band near $L(N):\frac{2\pi}{a}(0.5\ 0.5\ 0.5)$ point drops below VBM

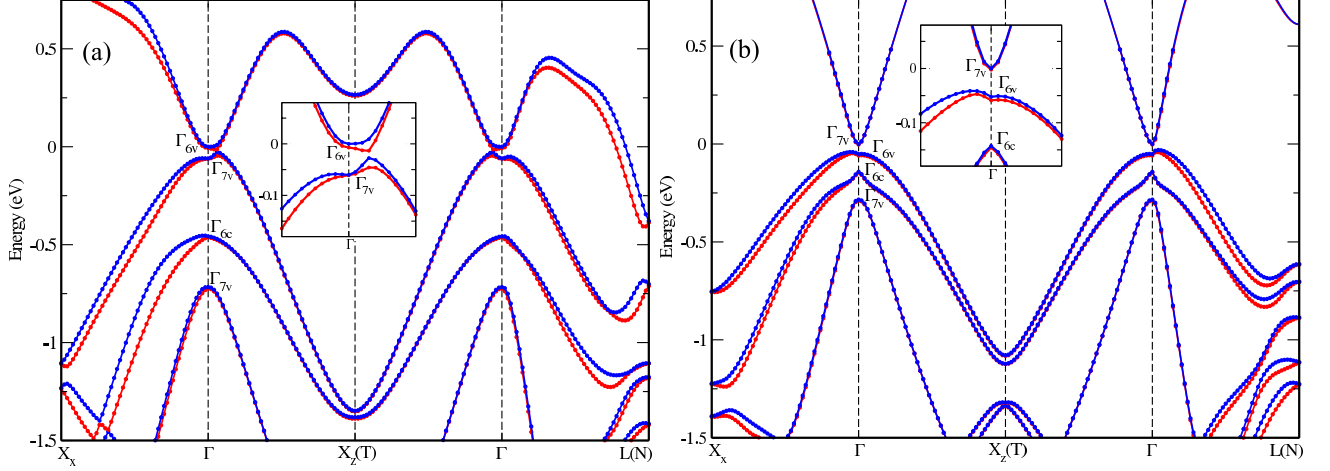


FIG. 5: (Color online) The calculated band structure along the high symmetry lines, $X_X \rightarrow \Gamma \rightarrow X_Z(T) \rightarrow \Gamma \rightarrow L(N)$ of (a) $\text{Cu}_2\text{HgPbTe}_4$, and (b) $\text{Ag}_2\text{HgPbSe}_4$ at their equilibrium states.

and crosses the Fermi level (see Fig. 5(a)). The reason is that the conduction band state at $L(N)$ point has similar character to the Γ_{6c} state, so when the Γ_{6c} energy is too low, the $L_{1c}(N_{1c})$ state energy is also below VBM, making the system metallic. To avoid this situation, therefore, we should search for TI material with mildly negative E_g^{s-p} .

Our previous study[20, 29] has shown that replacing Cu by Ag or replacing Te by Se can increase E_g^{s-p} , i.e., raising the Γ_{6c} and L_{1c} energy level relative to Γ_{6v} and Γ_{7v} , because (i) at the top valence band, the lower $4d$ level and larger size of Ag compared to Cu weakening the p-d hybridization, and the $4p$ level of Se is lower than $5p$ level of Te, which both shift the Γ_{6v} and Γ_{7v} levels down, (ii) the displacement of anion towards Pb in the Ag compounds and the smaller size of Se than Te also both reduce the Pb-anion bond lengths, increasing the energy of the Pb(s)-anion(s) antibonding states at the bottom conduction band. This expectation is supported by the calculated band structure of $\text{Ag}_2\text{HgPbSe}_4$, which has no band crossing at the Fermi level and thus is a topological insulator, as shown in Fig. 5(b). Similarly, we predict that $\text{Cu}_2\text{CdPbTe}_4$ and $\text{Ag}_2\text{HgPbTe}_4$ are topological metals, while $\text{Cu}_2\text{HgPbSe}_4$, $\text{Cu}_2\text{CdPbSe}_4$ and $\text{Ag}_2\text{CdPbTe}_4$ are topological insulators. The results are shown in Table I.

Among the four identified quaternary TIs, $\text{Ag}_2\text{HgPbSe}_4$ has the largest non-trivial gap of 47 meV. This is because $\text{Ag}_2\text{HgPbSe}_4$ is more stable in the low symmetry kesterite structure with large group-I element, therefore, it has a large negative Δ_{CF} (-51 meV). It also has a reasonably large negative E_g^{s-p} gap, so the coupling between the Γ_{6c} and the Γ_{6v} state is weak. Its band structure is shown in Fig. 5(b). As expected, we see the gap of $\text{Ag}_2\text{HgPbSe}_4$

occurs at a position along the low symmetry $\Gamma - X_X$ line, consistent with our discussion above.

V. CONCLUSIONS

In conclusion, we have shown that the non-trivial band gaps of zinc-blende derived topological insulators depend on the crystal field splitting at the top valence band as well as the size of the inverted s-p band gap. In general, a material with large TI band gap should have a large negative crystal field splitting and a moderate size of the inverted band gap. Compared to binary zinc-blende and ternary chalcopyrite compounds, these parameters can be more easily tuned through the chemical ordering in quaternary compounds. Based on this understanding, we have identified four ground state quaternary topological insulators, among which $\text{Ag}_2\text{HgPbSe}_4$ has the largest TI band gap of 47 meV because it has the optimal band structure parameters.

VI. ACKNOWLEDGEMENTS

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