Band Structure Engineering of Multinary Chalcogenide Topological Insulators

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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 $\Delta_{CF}$ 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 I-2-II-IV-VI4 compounds, including Cu$_2$HgPbSe$_4$, Cu$_2$CdPbSe$_4$, Ag$_2$HgPbSe$_4$ and Ag$_2$CdPbTe$_4$ are TIs, in which Ag$_2$HgPbSe$_4$ has the largest TI band gap of 47 meV because it combines the optimal values of $\Delta_{CF}$ and $E_{g}^{s-p}$.

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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], Bi$_2$-xSb$_x$ alloys[6, 7] and binary tetradymite semiconductors such as Bi$_2$Se$_3$ and Bi$_2$Te$_3$. 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 CuTlSe2) 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 CuTlSe2 and AgTlTe2, 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 $\Delta_{CF}$ at 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 $\Delta_{CF}$ 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 $\Delta_{CF}$ requires group-III elements to be small and light, the possibilities for obtaining a large TI band gap are limited. Through further cation mutation[19], large negative $\Delta_{CF}$ and $E_{g}^{s-p}$ is achievable in quaternary I-2-II-IV-VI4 compounds. We have identified four topological insulators (Cu$_2$HgPbSe$_4$, Cu$_2$CdPbSe$_4$, Ag$_2$HgPbSe$_4$ and Ag$_2$CdPbTe$_4$), in which Ag$_2$HgPbSe$_4$ 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 and explain what kind of band structure can lead to the largest TI band gap.

For a normal zinc-blende semiconductors such as CdTe, the band gap is between the s-like conduction band minimum (CBM) $\Gamma_{6c}$ state and the p-like valence band maximum (VBM) $\Gamma_{8v}$ 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, 12], i.e., the position of the conduction and valence bands is switched. In zinc-blende compounds, the band inversion means that the $\Gamma_{6c}$ level falls below the $\Gamma_{8v}$ level. In the inverted band structure, the $\Gamma_{6c}$ level is occupied, while the quadruply-degenerate $\Gamma_{8v}$ level is half occupied, making the Fermi
level stay at the Γ8v level and the system become a zero-gap semi-metal. This is the case for bulk HgTe.

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 $\Delta_{CF}$ by reducing the $D_{2d}$ symmetry to, e.g., $D_{3d}$, by applying an epitaxial strain or forming a quantum well [4]. For $D_{2d}$ symmetry, the half-filled $\Gamma_{8v}$ state splits into $\Gamma_{6v}$ and $\Gamma_{7v}$ state, and a gap can be opened around the occupied $\Gamma_{7v}$ ($\Gamma_{6v}$) and unoccupied $\Gamma_{6v}$ ($\Gamma_{7v}$) levels (Fig. 1(b)) if $\Delta_{CF}$ is positive. 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-VI$_2$ chalcopyrite compounds such as CuTlTe$_2$ [17, 20].

In Fig. 2(a) we plot the calculated band structure of HgTe under an $\epsilon = 0.02$ (001) tensile strain with $\Delta_{CF} = 76$ meV and CuTlTe$_2$ in the chalcopyrite structure with $\Delta_{CF} = 76$ meV. As we can see, a small gap is opened near the $\Gamma$ point for both systems. 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, which can correctly predict the band gaps of many zinc-blende and chalcopyrite semiconductors [22–24].

Comparing the band structure of HgTe under an $\epsilon = 0.02$ (001) tensile strain and CuTlTe$_2$, we find that the overall shape is very similar, especially near the band gap. In both systems, the $s$-like $\Gamma_{6c}$ state falls below the $p$-like $\Gamma_{6v}$ and $\Gamma_{7v}$ states, and the minimum gap occurs along the $\Gamma - X_Z$ line. This similarity between strained HgTe and CuTlTe$_2$ indicates that the strain and chemical ordering have the same effect in producing the crystal field splitting $\Delta_{CF}$ at the top of valence band [20], 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 [25, 26], and assuming the $\Gamma_{6c}$ state is far away from the band edge, we know that the splitting of the $\Gamma_{8v}$ level into $\Gamma_{6v}$ and $\Gamma_{7v}$ under the tetragonal symmetry depends on two quantities: the spin-orbit splitting $\Delta_{SO}$ and the crystal field splitting $\Delta_{CF}$. $\Delta_{CF}$ is defined to be positive if the doubly-degenerate $\Gamma_{5v}$ is above the singly-degenerate $\Gamma_{4v}$ state when the spin-orbit interaction is not considered, as shown in Fig. 1(a). For systems where $\Delta_{SO}$ is much larger than $\Delta_{CF}$, the splitting between $\Gamma_{6c}$ and $\Gamma_{7v}$ is close to $2/3$ of $\Delta_{CF}$. Previous studies on strained zinc-blende compound showed that the non-trivial gap depends on the sign and size of $\Delta_{CF}$: (i) when $\Delta_{CF} < 0$ the gap occurs along of the $\Gamma - X_X$ line near the $\Gamma$ point and the gap increases quickly as a function of the magnitude of $\Delta_{CF}$; (ii) when $\Delta_{CF} > 0$, the gap occurs along the $\Gamma - X_Z$ line near the $\Gamma$ point and the gap increases slowly as a function of $\Delta_{CF}$. This can be seen clearly in Fig. 3(a), where the dependence of the non-trivial band gap on the size of $\Delta_{CF}$ 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 $\Delta_{CF}$ is that, $\Gamma - X_X$ line has lower symmetry than $\Gamma - X_Z$ line, so the band anticrossings is more significant when the gap shifts to the $\Gamma - X_X$ line. CuTlTe$_2$ 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. 2(b)]. Based on this observation, we know that large gap TI can only exist in zinc-blende derived compounds with large negative $\Delta_{CF}$.

In Fig. 3(b) we plot the calculated $\Delta_{CF}$ of CuAlTe$_2$, CuGaTe$_2$, CuInTe$_2$ and CuTlTe$_2$. As we can see, $\Delta_{CF}$ 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 $\Delta_{CF}$ 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 $\Gamma$ point excludes Al, Ga and In compounds because $\Gamma_{6c}$ state has s-like anti-bonding character localized on group-III cation and group-VI anion, whereas $\Gamma_{6v}$ and $\Gamma_{6c}$ states mainly have the p component of the group-VI anion hybridized with the d component of the group-I cation [27, 28]. Two factors shift the $\Gamma_{6c}$ level down from Al to Ga to In compounds [17, 20, 28]: (i) the s orbital energy of Ga is

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.
Fortunately, CuTlTe below the p-like states at Γ point (band inversion). Un-
only a small TI band gap of about 14 meV.

However, if the Γ point is between the unoccupied Γ6c and the occupied Γ6v (or Γ6c, if it has a higher energy than Γ6v) derived state. The coupling between the Γ6c and Γ6v states pushes the Γ6v level up in energy, thus reduces the effective crystal field splitting between the Γ7v and Γ6v state and the non-
trivial band gap. This is what we find for AgTISe2 and AgTITe2. According to our calculation, the non-trivial gap of AgTISe2 is limited at Γ point with a very small size, 1 meV, although it has a large negative ∆g = 50 meV. Therefore, to reduce the interaction between the Γ6c and Γ6v states, one should move the Γ6c level down, i.e., increase the magnitude of negative Eg−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 ∆g and large negative Eg−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 Eg−p and are normal semiconductors14, except CuTISe2, CuTITe2, AgTISe2 and AgTITe2. But the non-trivial gaps of these four TIs are all small due to the positive ∆g for CuTISe2 and CuTITe2, and small Eg−p for AgTISe2 and AgTITe2.

To further increase the non-trivial band gap, we need to make both the ∆g and Eg−p more negative. We find that this can be done by mutating two group-III cations in I-III-VI2 compounds to one group-II and one group-IV cation, thus forming the I2-II-IV-VI4 (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. 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 characteristics20, 21. Therefore, if these compounds have inverted band structure, they can also be TIs.

FIG. 2: (Color online) The calculated band structure along the high symmetry lines, X_X : \( \frac{2\pi}{a}(1 0 0) \rightarrow \Gamma : (0 0 0) \rightarrow X_Z : \frac{2\pi}{a}(0 0 1) \) of (a) HgTe with a (001) tensile strain and \( \Delta g = 70 \) meV, (b) CuTITe2 and (c) AgZnHgPbSe4 at their equilibrium states. X_X and X_Z are the notations of zinc-blende structure, and X_Z corresponds to T in the chalcopyrite structure. Red and blue color are used to show the two spin-dependent bands clearly.

FIG. 3: (Color online) (a) The calculated non-trivial band gap as a function of \( \Delta g \) for HgTe. Here \( \Delta g \) is changed by tuning the (001) strain \( \epsilon \). (b) The calculated \( \Delta g \) and (c) \( E_g^{−p} \) of Cu-III-Te2 with III=Al, Ga, In, Tl.

In the above discussion, we have assumed that the Γ6c 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 Γ6c is close to the band edge, then we have to consider its interaction with the band edge states. This is because when \( \Delta g < 0 \), the band gap of the TI at Γ point is between the unoccupied Γ7v and the occupied Γ6v 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. 3(c), where we plot the calculated \( E_g^{−p} \) of CuAlTe2, CuGaTe2, CuInTe2 and CuTITe2; only CuTITe2 has negative \( E_g^{−p} \), i.e., its s-like Γ6c state falls below the p-like states at Γ point (band inversion). Unfortunately, CuTITe2 has a positive \( \Delta g = 76 \) meV, thus only a small TI band gap of about 14 meV.
TABLE I: The calculated $E_g^{s-p}$ of I$_2$-II-Pb-VI$_4$ (I=Cu, Ag, II=Cd, Hg, VI=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   | -0.46  | -0.32  | 0.07  |
| Cu$_2$CdPb   | -0.21  | -0.07  | 0.32  |
| Ag$_2$HgPb   | -0.37  | -0.14  | 0.40  |
| Ag$_2$CdPb   | -0.12  | 0.18   | 0.72  |

Similar to the chalcopyrites, we need to have compounds that contain heavy group-IV elements so that the $\Gamma_{6c}$ level could fall below the $\Gamma_{6v}$ and $\Gamma_{7v}$ levels. 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 $\Gamma$ 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$_2$HgPbTe$_4$ which has the most negative $E_g^{s-p}$. The overall shape near the $\Gamma$ point is similar to those of ternary CuTiTe$_2$ and binary HgTe under (001) strain as shown in Fig. 2(a) and 2(b), indicating that the band structure character is kept in the cation mutation. However, Cu$_2$HgPbTe$_4$ 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 and crosses the Fermi level. The reason is that the conduction band state at L(N) point has similar character to the $\Gamma_{6c}$ state, so when the $\Gamma_{6c}$ 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 has shown that replacing Cu by Ag or replacing Te by Se can increase $E_g^{s-p}$, i.e., raising the $\Gamma_{6c}$ and $L_{1c}$ energy level relative to $\Gamma_{6v}$ and $\Gamma_{7v}$, because (i) at the top valence band, the lower 4$d$ level and larger size of Ag compared to Cu weakening the p-d hybridization, and the 4$p$ level of Se is lower than 5$p$ level of Te, which both shift the $\Gamma_{6v}$ and $\Gamma_{7v}$ 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 Ag$_2$HgPbSe$_4$, which has no band crossing at the Fermi level and thus is a topological insulator, as shown in Fig. 2(c). Similarly, we predict that Cu$_2$CdPbTe$_4$ and Ag$_2$HgPbTe$_4$ are topological metals, while Cu$_2$HgPbSe$_4$, Cu$_2$CdPbSe$_4$ and Ag$_2$CdPbTe$_4$ are topological insulators. The results are shown in Table I.

Among the four identified quaternary TIs, Ag$_2$HgPbSe$_4$ has the largest non-trivial gap of 47 meV. This is because Ag$_2$HgPbSe$_4$ is more stable in the low symmetry kesterite structure with large group-I element, therefore, it has a large negative $\Delta_{CF}$ (-51 meV). It also has a reasonably large negative $E_g^{s-p}$ gap, so the coupling between the $\Gamma_{6c}$ and the $\Gamma_{6v}$ state is weak. Its band structure is shown in Fig. 2(c). As expected, we see the gap of Ag$_2$HgPbSe$_4$ occurs at a position along the low symmetry $\Gamma$ – $X$ line, consistent with our discussion above.

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 Ag$_2$HgPbSe$_4$ has the largest TI band gap of 47 meV because it has the optimal band structure parameters.

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[1] X. L. Qi and S. C. Zhang, Physics Today 63, 33 (2010).
[2] J. E. Moore, Nature (London) 464, 194 (2010).
[3] M. König et al., Science, 318, 766 (2007).
[4] B. A. Bernevig, T. L. Hughes, and S. C. Zhang, Science 314, 1757 (2006).
[5] J. W. Luo and A. Zunger, Phys. Rev. Lett. 105, 176805 (2010).
[6] L. Fu and C. L. Kane, Phys. Rev. B 76, 045302 (2007).
[7] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature (London) 452, 970 (2008).
[8] Y. Xia et al., Nature Phys. 5, 398 (2009).
[9] Y. L. Chen et al., Science 325, 178 (2009).
[10] H. Zhang, C. X. Liu, X. L. Qi, X. Dai, Z. Fang, and S. C. Zhang, Nature Physics 5, 438 (2009).
[11] H. Lin et al., Nature Mater. 9, 546 (2010).
[12] D. Xiao et al., Phys. Rev. Lett. 105, 096404 (2010).
[13] S. Chadov, X. Qi, J. Kibler, G. H. Fecher, C. Felser, and S. C. Zhang, Nature Materials 9, 541 (2010).
[14] H. Lin et al., Phys. Rev. Lett. 105, 036404 (2010); B. Yan et al., Europhys. Lett. 90, 37002 (2010); Y. Chen et al., Phys. Rev. Lett. 105, 266401 (2010); T. Sato et al., Phys. Rev. Lett. 105, 136802 (2010).

[15] W. Feng, D. Xiao, J. Ding, and Y. Yao, Phys. Rev. Lett. 106, 016402 (2011).

[16] O. M. Madelung, Semiconductors: Data Handbook (Springer, Berlin, 2004), 3rd ed.

[17] S.-H. Wei and A. Zunger, J. Appl. Phys. 78, 3846 (1995).

[18] M. Bohm, G. Huber, A. MacKinnon, O. Madelung, A. Scharmann, and E.-G. Scharmer, Physics of Ternary Compounds (Springer, New York, 1985).

[19] The band structures are calculated within the DFT formalism as implemented in the VASP code. For the exchange-correlation potential, we used the HSE hybrid functional ($\alpha=0.25$, $\mu=0.2$ Å$^{-1}$). The $d$ states of group-III and IV elements are treated explicitly. An energy cut-off of 300 eV was employed for the plane-wave basis set. A 4×4×4 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.

[20] S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei, Phys. Rev. B 79, 165211 (2009).

[21] C.-Y. Moon and S.-H. Wei, Phys. Rev. B 74, 045205 (2006).

[22] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. Gerber, and J. Angyan, J. Chem. Phys. 124 (2006).

[23] K. Hummer, A. Gruneis, and G. Kresse, Phys. Rev. B 75 (2007).

[24] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).

[25] J. E. Rowe and J. L. Shay, Phys. Rev. B 451, 3 (1971).

[26] S.-H. Wei and A. Zunger, Phys. Rev. B 49, 14337 (1994).

[27] J. E. Jaffe and A. Zunger, Phys. Rev. B 28, 5822 (1983).

[28] S. Chen, X. G. Gong, and S.-H. Wei, Phys. Rev. B 75, 205209 (2007).

[29] S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei, Appl. Phys. Lett. 94, 041903 (2009).