Electronic structures and stability investigation of the new class of large band gap topological insulators $MTl_4Te_3$ ($M = Cd, Hg$)

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By means of ternary chemical potential phase diagram and phonon spectrum calculations, we propose that $MTl_4Te_3$ ($M = Cd, Hg$), the derivatives of $Tl_2Te_3$, are thermodynamically and dynamically stable in the body centered tetragonal crystal structure with $I4/mcm$ symmetry. Our electronic structures calculations confirm that a robust s-p band inversion occurs near the Fermi level in $MTl_4Te_3$, and a topological band gap about 0.13 eV in $CdTl_4Te_3$ is induced by the spin-orbit coupling. These results suggest that $MTl_4Te_3$ are a new class of large band gap 3D strong topological insulators that are stable and synthesizable in experiment, which could be used to design efficient spin torque equipment and spin device.

I. INTRODUCTION

In the past two decades, topological electronic materials, including topological insulators (TIs) [1–5], topological semimetals [6–14], and topological superconductors (SC) [5, 15–20], have attracted great interest and reshaped perception of the materials. In particular, large band gap three-dimensional (3D) TIs have many intriguing properties in both fundamental physics [21–23] and device applications [24–28]. TIs with the spin momentum locked surface states are robust against perturbations, and thus have high performance on the spin torque [29, 30], topotronic [31, 32] and spintronic devices [33, 34]. Furthermore, many exotic topological states are realized by modulating the TIs. For example, the quantum anomalous Hall (QAH) effect has been achieved by the magnetic doping in $Bi_2Te_3$ films [35–42]. Besides, topological superconductivity is reported in the Cu-intercalated $Bi_2Se_3$ ($Cu_{1-x}Bi_2Se_3$) [17, 18, 43, 44], $Bi_2Te_3$ under high pressure [45] and TI/SC heterostructures [46]. However, easily synthesized TIs with relatively large band gap and clear two-dimensional (2D) Dirac cone surface states as the $Bi_2Se_3$ family [33, 34, 40, 47–49] remain rare until now. Therefore, it is desirable to search for large band gap 3D TIs for potential utilizations.

First-principles calculations have played remarkable roles in the development of topological physics and topological materials. Many topological materials are predicted by first-principles calculations firstly, and then confirmed by experiments, including $HgTe$ quantum well [2, 50], bismuth antimony alloy $Bi_{1−x}Sb_x$ [22, 51, 52], $Bi_2Se_3$-family of TIs [33, 34, 40, 47–49], topological crystalline insulator (TCI) $SnTe$ [13, 14], topological semimetals [6, 7, 11, 12, 53–59] and so on. Recently, $Tl_2Te_3$ [60] has been found to be a topological material that host Dirac surface states at 0.5 eV above the Fermi level ($E_F$). After then, by using 4c site substitution, many derivatives $MTl_4Te_3$ ($M = Cu, Sn, Mo, Pb, Bi, Sb, La, Nd, Sm, Gd, Tb, Dy, Er, Tm$) [61–65] have been experimentally synthesized and reported. Among them, $SnTl_4Te_3$ with 8-electron configuration is expected to be a TI. Unfortunately, the band inversion in $SnTl_4Te_3$ disappears so that it becomes a trivial insulator [66, 67].

Inspired by the above understanding, we propose that $CdTl_4Te_3$ and $HgTl_4Te_3$ are a new class of large band gap 3D strong topological insulators that are stable and synthesizable experimentally, through the 4c site substitution of Cd or Hg. For this purpose, ternary chemical potential phase diagram with precursors and convex hull diagram are constructed. Both of them demonstrate that $CdTl_4Te_3$ is thermodynamically stable and easily synthesized in Cd-rich, $Tl_2Te_3$-rich and Ti-poor condition. The phonon spectrum reveal that $CdTl_4Te_3$ adopts the body centered tetragonal structure with $I4/mcm$ symmetry. Further electronic structures calculations identify that a robust band inversion between $Cd-5s$ and $Te-5p$ orbitals exists at $Γ$ point even without spin-orbit coupling (SOC). When SOC is considered, a topological band gap about 0.13 eV is induced in $CdTl_4Te_3$, which is larger than the energy scale of room temperature in theory. As a result, one single Dirac cone formed by the topological surface states is discovered at $Γ$ point of the surface. The corresponding left-hand momentum locking texture is also studied, which can be applied on the efficient spin torque equipment and spin device design. Finally, the topological electronic structures and stability of the other derivative $HgTl_4Te_3$ are discussed, which is expect to possess the same crystal structure and strong TI nature as $CdTl_4Te_3$.

II. CRYSTALS STRUCTURES AND METHODOLOGY

In our work, the same crystal structure of $SnTl_4Te_3$, i.e., the body centered tetragonal phase with $I4/mcm$ space group (No. 140, $D_{4h}^{18}$) as shown in Fig. 1(a), is used for the calculation of $MTl_4Te_3$ ($M = Cd, Hg$). The corresponding first Brillouin zone (BZ) [68] and its pro-
projection on the (100) surface of the primitive cell are displayed in Fig. 1(c). In Fig. 1(a), M atom locates at Wyckoff position 4c (0.5, 0.5, 0.0) which is the center of the corner-sharing CdTe octahedron; Tl is located at 16f (x₁, 0.5 + x₁, z₁); two types of Te locate at 4a (0.5, 0.5, 0.25) and 8h (−x₂, −x₂ + 0.5, 0.0). The lattice parameters, atomic coordinates x₁, x₂ and z₁ are fully relaxed. The detailed structure information of MTl₃Te₃ is summarized in Table. I. Besides, all the compounds used in our ternary phase diagram calculation are based on their ground phase in experiment, and their crystal parameters are fully relaxed as tabulated in Table I to make the energies comparable.

Our first-principles calculations are performed by the Vienna ab initio simulation package [69, 70] with the projected augmented wave method [71]. The energy cutoff is set as 400 eV, and 9 × 9 × 7 k-meshes are adopted. Local-density approximation (LDA) type of the exchange-correlation potential [72] is used in all calculations. All the different compositions Cd₃Tl₃Te₉ are fully relaxed until the Hellmann-Feynman forces on each atom are less than 0.01 eV/Å and the total energy converge up to 10⁻⁶ eV. The ternary phase diagram is constructed by calculating the total energy of Cd₃Tl₃Te₉ without SOC. The phonon spectrum calculations are carried out by the PHONOPY code [73] with a 2 × 2 × 2 supercell through the density-functional perturbation theory approach [74]. The band inversion is further confirmed by the modified Becke-Johnson (MBJ) potential [75] with the MBJ parameter C_{MBJ} setting as 1.35. We note that C_{MBJ} = 1.1 ~ 1.7 is usually used for semiconductors including IIb-VIA compounds as proposed by Tran and Blaha [75, 76]. Its reliability and accuracy have been identified to be at the same level as the hybrid functional [77] and GW methods [78] for a wide variety of semiconductors [76, 79–85]. The maximally localized Wannier functions are constructed by the Wannier90 package [86] based on the MBJ+SOC calculations. The surface states are calculated by iterative Green’s function method as implemented in the WannierTools package [87].

FIG. 1. (a) The unit cell of CdTl₄Te₃. (b) Top view of the unit cell. (c) Bulk BZ and its projection to the (100) surface of its primitive cell. High symmetry k path is indicated.

III. THE STABILITY OF CdTl₄Te₃

In this section, we would like to take CdTl₄Te₃ as example to study its thermodynamical and dynamical stability. By choosing three stable compounds Cd, Tl and Tl₃Te₃ as the precursor materials, the target compound CdTl₄Te₃ can be synthesized by the following reaction:

\[ Tl₂Te₃ + Cd + 2Tl \rightarrow CdTl₄Te₃. \]  

A phase diagram as function of the precursors’ chemical potentials could determine the ranges of the experimental synthesis condition within which the target compound can be stabilized and within which the undesired competing phases are formed by varying the composition of precursors [88–93]. In general, the synthesis process can be understood as the exchange of elemental components between precursors and the forming phases. Therefore, the formation energies of all forming compounds Cd₃Tl₃Te₉ could be expressed as:

\[
E^F(Cd₃Tl₃Te₉) = l\Delta\mu(Cd) + \frac{n}{3}\Delta\mu(Tl₂Te₃) \\
+ (m - \frac{2n}{3})\Delta\mu(Tl).
\]  

where \( \Delta\mu(i) = \mu(i) - \mu^F(i) \) with \( i = \text{Cd}, \text{Tl and Tl₂Te₃} \) are the chemical potentials of the precursors referenced to the total energy of their ground states. Therefore, Eq. 2 makes a connection between \( \Delta\mu(i) \) and experimental condition, which means a rich condition of the corresponding precursor if \( \Delta\mu(i) \) is close to zero, and a poor condition if \( \Delta\mu(i) \) has a large negative value. Based on our calculation, the formation energy of CdTl₄Te₃ is -1.032 eV/formula with respect to the precursors, which leads to two requirements for the chemical potentials. One is that each \( \Delta\mu(i) \) could only vary between 0 and -1.032 eV. The other is that there are only two independent variable chemical potentials. Therefore, the phase diagram can be visualized by a 2D graph with variables \( \Delta\mu(Tl₂Te₃) \) and \( \Delta\mu(Cd) \) as shown in Fig. 2(a).

The competing phases such as CdTl₂Te₂, Tl₂Te, Tl₅Te₃, CdTe and Te are considered. Their formation energies \( E^F(Cd₃Tl₃Te₉) \) with respect to the precursors are calculated and listed in Table II. Then the phase diagram of CdTl₄Te₃ as function of the chemical potentials \( \Delta\mu(Cd), \Delta\mu(Tl₂Te₃) \) and \( \Delta\mu(Tl) \) is constructed in Fig. 2(a) by using a general scheme [89, 90, 93]. More details are described in supplementary material (SM) [94]. Yielding to the constraint \( \Delta\mu(i) = 0 \sim -1.032 \) eV, the whole allowed chemical potential region is restricted in the triangle surrounded by \( \Delta\mu(Cd)=0 \) (blue solid line), \( \Delta\mu(Tl)=0 \) (green solid line) and \( \Delta\mu(Tl₂Te₃)=0 \) (black solid line). Our results reveal that CdTl₄Te₃ is most stable against to other competing compounds in the orange region manifested by the phase separation lines \( \Delta\mu(Tl₅Te₃) = 0, \Delta\mu(CdTeTl₂) = 0, \Delta\mu(TlTe)=0 \) and \( \Delta\mu(Te)=0 \). Here, \( \Delta\mu(Cd₃Tl₃Te₉) = \mu(Cd₃Tl₃Te₉) - E^F(Cd₃Tl₃Te₉) \) is the chemical potential of competing phase that is the function of precursor’s chemical
potentials. The competing phase Cd₄Tl₃Te₃ will precipitate out at \( \Delta \mu (Cd/Tl₄Te₃) = 0 \), and become unstable with a negative value. These results clearly demonstrate that CdTl₄Te₃ is easy to synthesize at Cd-rich, Tl₂Te₃-rich and Tl-poor condition. We would like to recall that the abundance of precursors is relative yielding to \( E^F(Cd/Tl₄Te₃) = -1.032 \) eV and Eq. 2. By increasing \( \Delta \mu (Tl) \) along the black arrow in Fig. 2(a), it means that Tl grows more and more rich while Cd and Tl₂Te₃ become poor. When the arrow cross \( \Delta \mu (Tl₂Te₃) = 0 \) and \( \Delta \mu (CdTlTe₂) = 0 \) lines, CdTl₄Te₃ becomes unstable accompanied with the precipitation of Tl₂Te₃ and CdTlTe₂, and the following decomposition will take place,

\[
\begin{align*}
\text{CdTl₄Te₃} & \rightarrow Tl₂Te₃ + 3TlTe + 2Cd \\
\text{CdTl₄Te₃} & \rightarrow CdTlTe₂ + TlTe + 2Tl
\end{align*}
\]

According to our calculations, the energy of the right products is 0.234 eV and 0.564 eV higher than that of left, respectively.

The convex hull analysis is another useful method to investigate the thermodynamical stability [95, 96]. In this way, the formation energy of all possible atomic configurations with respect to constituent elements needs to be calculated, which is defined as \( E^F = E^T(Cd/Tl₄Te₃) - nE^T(Cd) - mE^T(Tl) - nE^T(Te) \). Using this definition, our calculations demonstrate that CdTl₄Te₃ is thermodynamically stable against to elements with formation energy of -0.213 eV/atom. With all possible \( E^F \) as listed in Table II, the convex hull diagram is constructed in Fig. S1 [94], which shows that only the binary compounds are on the convex hull, and all ternary compounds such as CdTl₄Te₃ and CdTlTe₂ are within a viable energy window for potentially metastable phases. Even so, we estimate that CdTl₄Te₃ is potentially synthesizable based on the following facts. One is that CdTl₄Te₃ is just a little above the convex hull with small energy and even 0.020 eV/atom lower than CdTlTe₂. Since CdTlTe₂ has already been synthesized in 1969 [97], it is expected that CdTl₄Te₃ is highly feasible in proper condition, especially at Cd-rich, Tl₂Te₃-rich and Tl-poor condition in the reaction Eq. 2.

To further check the dynamical stability of CdTl₄Te₃, the phonon spectrum based on the body centered tetragonal phase with \( I4/mcm \) symmetry is calculated. As shown in Fig. 2(b), there is no phonon mode with negative frequency in the entire BZ, which indicates that CdTl₄Te₃ is dynamically stable by adopting the body centered tetragonal structure. The above thermodynamical and dynamical investigations strongly demonstrate that CdTl₄Te₃ is readily synthesized in experiment.

### IV. ELECTRONIC PROPERTIES OF CdTl₄Te₃

The projected density of states (PDOS) of tetragonal CdTl₄Te₃ are calculated and plotted. As shown in Fig. 3(a), Tl-6s orbitals mainly contribute to the states

### TABLE I. Detailed crystallographic information of corresponding compounds used in Fig. 2.

| Compounds | Space group | a, b, c (Å) | Atomic coordinates (fractional) |
|-----------|-------------|-------------|-------------------------------|
| Cd        | P6₃/mmc     | 2.9179 Cd   | 2c (\( \frac{1}{2} \), \( \frac{1}{2} \), \( \frac{1}{2} \)) |
| Tl        | P6₃/mmc     | 3.4108 Tl   | 2c (\( \frac{1}{2} \), \( \frac{1}{2} \), \( \frac{1}{2} \)) |
| Te        | P3₁21       | 4.2786 Te   | 3a (0.2879, 0, 0) |
| CdTe      | F - 43m     | 6.4082 Cd   | 4a (0.0, 0.0, 0) |
| TlTe      | 14/mcm      | 8.6445 Tl   | 4c (0.0, 0.0, 0.25) |
| Tl₂Te₃    | C2/c        | 8.6449 Tl   | 4c (0.5, 0.5, 0.0) |
| CdTlTe₂   | P - 3m1     | 7.3925 Tl   | 4b (0.5, 0.5, 0.25) |
| Tl₅Te₃    | 14/mcm      | 8.6689 Tl   | 4a (0.0, 0.5, 0.0) |
| CdTl₄Te₃  | I4/mcm      | 8.6512 Cd   | 4c (0.0, 0.5, 0.0) |
| HgTl₄Te₃  | 14/mcm      | 8.6668 Hg   | 4c (0.5, 0.5, 0.0) |

### TABLE II. The calculated energy/formula used in Fig. 2.

| Compounds | \( E^F (eV) \) | \( E^T (eV) \) | \( E^F (eV) \) |
|-----------|---------------|---------------|---------------|
| Cd        | -1.0376       | -1.0376       | -1.0376       |
| Tl        | -2.9543       | -2.9543       | -2.9543       |
| Te        | -3.8046       | -3.8046       | -3.8046       |
| Tl₂Te₃    | -17.9934      | -17.9934      | -17.9934      |
| CdTe      | -6.0324       | -6.0324       | -6.0324       |
| TlTe      | -7.1281       | -7.1281       | -7.1281       |
| Tl₅Te₃    | -28.0154      | -28.0154      | -28.0154      |
| CdTl₄Te₃  | -6.4082       | -6.4082       | -6.4082       |

![FIG. 2. (a) The ternary phase diagram of CdTl₁₁Te₃ with respect to the chemical potentials of Cd, Tl₂Te₃ and Tl, \( \Delta \mu (Tl) = \frac{1}{2}[E^F(CTT) - \Delta \mu (Tl₂Te₃) - \Delta \mu (Cd)] \). (b) The Phonon dispersion curves of CdTl₄Te₃ without SOC.](image-url)
between -8 \sim -3.5 \text{ eV}, while Tl-6p orbitals mainly contribute to the states above 0.3 \text{ eV}. Considering the electronic configuration 6s^26p^1 of Tl, we conclude that Tl favors +1 valence in CdTl_4Te_3, similar to valence of Tl atoms at 16f site in Tl_5Te_3 [63, 67]. The states in energy range of -3.5 \sim 0 \text{ eV} are approximately from Te-5p orbitals with admixing of Tl-6p and Cd-5s states, which implies that the bonding between Cd, Tl and Te is not the pure ionic bond but has sizable metal-metal bond characters. Fig. 3(a) shows that the Cd-5s orbitals are almost empty and mainly contribute the states between 0 \sim 3 \text{ eV}. Therefore, we can understand the electron transfer roughly as follows. Each Tl atom donates one 6p electron, and Cd atom donates two 5s electrons to the Te-5p orbitals. As a result, CdTl_4Te_3 is close to the electronic configuration of the atomic insulator with the full filled sub-shell of Te^{2-}, Tl^{1+}, Cd^{2+} ions approximately.

However, we notice that the Cd-5s orbitals are very extended, which also exhibit considerable amplitude under the E_F, implying a band inversion between Cd-5s and Te-5p states. The character is further verified by the projected band structures in Fig. 3(b), which clearly demonstrates that the Cd-5s states with even parity are lower 1.82 \text{ eV} than Te-5p states with odd parity at \Gamma point. The band inversion in CdTl_4Te_3 is already occurred even without SOC and can be alternatively viewed as a consequence of the inert pair effect in chemistry, which is the propensity for the two electrons in the outermost 5s orbital to remain unpaired in heavier elements [98], just like that in HgTe [1, 2]. In Fig. 3(b), when SOC is excluded, the band crossing points between Cd-5s and Te-5p can be protected by time reversal symmetry (\mathcal{TRS}) and inversion symmetry (\mathcal{I}) symmetry and form nodal rings as plotted in Fig. S2(a) [94]. Since LDA type exchange-correlation potential usually overestimates band inversion between valence and conduction bands, then MBJ [75] is employed. The amplitude of band inversion in LDA is reduced to 1.10 \text{ eV} with MBJ calculations as shown in Fig. S2(b) [94]. Therefore, the band inversion in CdTl_4Te_3 is robust against the functional potentials, and the more accurate calculation of LDA with MBJ semilocal exchange functional potential is adopted to investigate the electronic and topological properties in the following.

When SOC is considered, the nodal rings are all gapped, inducing a 0.13 \text{ eV} band gap as shown in Fig. 3(c), which is larger than the range of room temperature theoretically. For insulators with \mathcal{I}, the topological invariant \nu_0 based on the Fu-Kane formula [99] can be characterized by the parity products (\xi_i) of the half numbers of the occupied states at eight time-reversal invariant momentum (TRIM) points (Kramers pairs have the same parities). As shown in Fig. 1(b), there are one \Gamma (0.0, 0.0, 0.0), one Z (0.5, 0.5, -0.5), two X (0.0, 0.0, 0.5) and four N (0.5, 0.0, 0.0) TRIM points in the first BZ. Therefore, only \xi_\mathcal{I} and \xi_\mathcal{Z} could determine the topological property of the tetragonal CdTl_4Te_3, while the other TRIM points always give the trivial products. Our calculations indicate \xi_\mathcal{I} = -1 and \xi_\mathcal{Z} = 1, and give rise to \nu_0 = 1. These results are consistent with the band inversion analysis at \Gamma point, and confirm that CdTl_4Te_3 is a strong TI.

V. TOPOLOGICAL PROPERTIES OF CdTl_4Te_3

We construct the maximally localized Wannier functions of Cd-5s, Te-5p and Tl-6p bands to investigate the topological features more explicitly. The Wilson loop method [100] is used by calculating the evolution of Wannier charge centers for the occupied bands in k_1 = 0 (Fig. 4(a)) and k_1 = \pi planes (Fig. 4(b)). The evolution lines cross the reference line(red dashed line) once time in Fig. 4(a), indicating that the k_1 = 0 plane corresponds to a quantum spin Hall system with non-trivial 2D topological invariant. The evolution lines cross the reference line(red dashed line) zero time in Fig. 4(b), confirming that the k_1 = \pi plane is a trivial 2D system. These results combining with Wilson loops on other surface planes(Fig. S3) [94], give rise a complete topological index \mathbb{Z}_2 = (1;000), which further confirm that CdTl_4Te_3 fall into the strong TI phase. In Fig. 4(c), we plot the surface electronic structures on the (100) surface by the iterative surface Green’s function method [101, 102]. Two robust surface states connect the valence and conduction bands and form a Dirac cone in the bulk gap at \Gamma point due to the requirement of the \mathcal{TRS}. In Fig. 4(d), we plot the Fermi surfaces of the Dirac cone at 0.02 \text{ eV}
and their spin orientation, which exhibits a left-hand spin texture enclosed a π phase like that in Bi$_2$Se$_3$ [33], indicating a positive SOC in CdTl$_4$Te$_3$ [103]. Such kind of spin momentum locking surface states have been reported that have very highly efficient performance on spin torque equipment [29, 30] and spin device [33, 34].

VI. DISCUSSION AND CONCLUSION

Considering that Hg is isoelectronic with Cd in the IIB group of the periodic table, HgTl$_4$Te$_3$ is naturally expected to be stabilized into the same crystal structure of CdTl$_4$Te$_3$ with similar electronic structures and topological property. By using the optimized structure parameters in Table I, the calculated formation energy of HgTl$_4$Te$_3$ through the reaction Hg + 4Tl + 3Te → HgTl$_4$Te$_3$ is -1.459 eV with respect to elemental precursors. Limited by the stoichiometry, the products $\frac{1}{2}$Tl$_5$Te$_3$ + HgTe + $\frac{1}{2}$TlTe + Tl, Tl$_6$Te$_3$ + Hg + 2Tl, 3TlTe + Hg + Tl and 2TlTe + HgTe + 2Tl are taken into account by calculating the formation energy which are equal to -1.397, -0.671, -1.107, and -1.035 eV, respectively. Obviously, HgTl$_4$Te$_3$ will be formed in the reaction because it is thermodynamically favourable. The MBJ calculated band structures are presented in Fig. S4 [94]. As expected, the Hg-5s state with even parity is lower 2.26 eV than Te-5p state with odd parity at Γ point. Furthermore, 0.046 eV nontrivial band gap induced by SOC makes it a strong TI which is similar to CdTl$_4$Te$_3$.

In conclusion, we predict a new class of 3D topological insulators MTL$_4$Te$_3$ ($M = Cd, Hg$) by using first-principles calculations. Our ternary chemical potential phase diagrams and phonon spectrum calculations demonstrate that MTL$_4$Te$_3$ ($M = Cd, Hg$) are both thermodynamically and dynamically stable in the body centered tetragonal crystal structure with $I\bar{4}/mcm$ symmetry. Further electronic structures calculations confirm that the nontrivial band topology stems from the band inversion between M-5s and Te-5p orbitals at Γ point, and the SOC induced topological band gap is about 0.13 eV in CdTl$_4$Te$_3$ which is larger than the energy scale of room temperature in theory. The isolated Dirac cone type surface states with left-hand helicity of the spin momentum locking texture is obtained in the (100) surface spectra at Γ point. These results suggest that MTL$_4$Te$_3$ are synthesizable and suitable for the study of efficient spin torque equipment and spin device, which should stimulate many experimental efforts in the future.

VII. ACKNOWLEDGMENTS

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