Three-dimensional topological insulators: A review on host materials

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In recent years, three-dimensional topological insulators (3DTI) as a novel state of quantum matter have become a hot topic in the fields of condensed matter physics and materials sciences. To fulfill many spectacularly novel quantum phenomena predicted in 3DTI, real host materials are of crucial importance. In this review paper, we first introduce general methods of searching for new 3DTI based on the density-functional theory. Then, we review the recent progress on materials realization of 3DTI including simple elements, binary compounds, ternary compounds, and quaternary compounds. In these potential host materials, some of them have already been confirmed by experiments while the others are not yet. The 3DTI discussed here does not contain the materials with strong electron-electron correlation. Lastly, we give a brief summary and some outlooks in further studies.

three dimension, topological insulator, host material

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1 Introduction

In the past few decades, topological quantum states characterized by specially topological orders [1,2] have become one of the most critical physical phenomena in condensed matter physics. In general concept, topological insulator contains two classes of topological quantum states depending on whether the system has time-reversal symmetry (TRS) or not. In the case of two-dimension, the first is the quantum Hall (QH) state [3], in which the TRS is explicit broken due to external magnetic field or internal magnetization. This topologically nontrivial state can be classified by the first Chern number proposed by Thouless et al. [2], directly connected to the quantized Hall conductivity. The second is the quantum spin Hall (QSH) state [4–6], which is protected by TRS and essentially resulted from spin-orbit coupling (SOC). Similar to the role of the Chern number, Z₂ topological invariant in TRS protected systems was introduced by Kane and Mele [7], that is, \( Z_2 = 1 \) (0) represents topologically nontrivial (trivial) state. The topological insulator with the common feature, having gaped insulating states in the bulk but gapless surface states on the edge, fundamentally distinguishes itself from the ordinary insulating state originally defined by Kohn [8].

The QSH state, i.e., two-dimensional topological insulator, has attracted research focus because of its promising applications in spintronic devices. The existence of QSH state in graphene was first proposed by Kane and Mele [5,6], however, subsequent works [9–11] showed that the band-gap induced by the SOC is too small (\( \sim 10^{-6} \) eV) and QSH state in graphene can not be observed in current experimental conditions. A more realistic material is the HgTe/CdTe quantum well, theoretically predicted by Bernevig et al. [12] and then experimentally confirmed by König et al. [13]. Soon after the QSH state was discovered, topological quantum states under TRS were also extended in three-dimension [14–16], i.e., the three-dimensional topological insulators (3DTI). In 3D, there are four \( Z_2 \) topological invariants, \( \nu_0; (\nu_1, \nu_2, \nu_3) \), used to classify the topology of an insulator [17]. A nonzero \( \nu_0 \) indicates that the system is a strong topological insulator (STI). When \( \nu_0 = 0 \), the systems are further classified according to \( \nu_1, \nu_2 \), and \( \nu_3 \). The systems with \( \nu_1, \nu_2, \nu_3 = 0 \) (not all of them) are called weak topological insulators (WTI), while \( 0;0;0 \) is a normal insulator (NI). A STI can not be directly connected to a WTI or a NI by any adiabatically continuous transformation of band structure. In the WTI or NI, the surface states

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2 How to search for 3D-topological insulators

As a first step towards various applications of 3DTI, material realization is of crucial importance. During the search of 3DTI in real materials, first-principles calculations guided by the topological band theory \cite{18,19} have played a pivotal role. We briefly introduce four widely used methods to search 3DTI. In practice, two or more among these methods are usually combined together to determine the band topology of a crystal.

2.1 Surface state electronic structure

As a fundamental feature in 3DTI, there is gapless surface state inside the bulk band-gap \cite{18–21}. The gapless surface state has the form of linear Dirac cone, which holds massless relativistic particles described by the Dirac equation \cite{24,25}. Furthermore, the spin and momentum of surface Dirac electrons are locked together in the sense that the electrons with opposite spin must propagate in opposite direction along the boundary due to TRS. Hence, one can determine whether an insulator is a 3DTI or not by calculating the surface state electronic structure. An odd number of surface states crossing the Fermi level indicates a 3DTI, otherwise it is a normal insulator. At the experimental aspect, the surface state electronic structure can be directly measured by the angle-resolved photoemission spectroscopy (ARPES). The comparison between theoretical calculations and experimental ARPES measurements becomes possible.

Although the bulk-boundary correspondence as a basic routine can be used to find the topologically nontrivial materials, it is not effective in first-principles calculations. Physically speaking, the surface band dispersion is sensitive to the details of the surface, such as the terminations and orientations \cite{26–28}. Furthermore, some topologically trivial states, for example the dangling bonds on the surface of group-IV materials, it is not easy to identify the quantum spin Hall phase in HgTe/CdTe quantum well \cite{12} and silicene \cite{29}, but can also be introduced into the 3DTI. The basic idea is that the Hamiltonian of a system can be adiabatically connected to that of another system. For the former and latter systems, the topological invariants can only change when the bulk band-gap closed. Therefore, if the band structure of a material can be smoothly transformed to that of another one without closing the band-gap, then they must share the same topological classification. For example, the band-gap closes during the band transformation, the topological phase transition may occur. In practice, the adiabatic continuity transformation of band structure can be artificially controlled, for example, by altering the composition $x$ in solid alloy Bi$_{1-x}$Sb$_x$, \cite{17,30,31} or Pb$_{1-x}$Sn$_x$Te \cite{17}. By starting $x$ from zero, these systems undergo the topological phase transition from trivial state to nontrivial state. If we continue increasing $x$ for Pb$_{1-x}$Sn$_x$Te, a further transition from nontrivial state to trivial state will happen. Tuning other parameters, such as atomic number and strength of SOC, are also widely used in literatures. The obvious advantage of this method is its apparent ease. One can predict new 3DTI candidates based on some well-known topologically nontrivial or trivial materials. While many intermediate phases are required along the transformational path connecting the initial state and the final one, which makes this method computationally demanding.

2.2 Adiabatic continuity band transformation

The argument of adiabatic continuity was once used to identify the quantum spin Hall phase in HgTe/CdTe quantum well \cite{12} and silicene \cite{29}, but can also be introduced into the 3DTI. The basic idea is that the Hamiltonian of a system can be adiabatically connected to that of another system. For the former and latter systems, the topological invariants can only change when the bulk band-gap closed. Therefore, if the band structure of a material can be smoothly transformed to that of another one without closing the band-gap, then they must share the same topological classification. In contrast, if the band-gap closes during the band transformation, the topological phase transition may occur. In practice, the adiabatic continuity transformation of band structure can be artificially controlled, for example, by altering the composition $x$ in solid alloy Bi$_{1-x}$Sb$_x$, \cite{17,30,31} or Pb$_{1-x}$Sn$_x$Te \cite{17}. By starting $x$ from zero, these systems undergo the topological phase transition from trivial state to nontrivial state. If we continue increasing $x$ for Pb$_{1-x}$Sn$_x$Te, a further transition from nontrivial state to trivial state will happen. Tuning other parameters, such as atomic number and strength of SOC, are also widely used in literatures. The obvious advantage of this method is its apparent ease. One can predict new 3DTI candidates based on some well-known topologically nontrivial or trivial materials. While many intermediate phases are required along the transformational path connecting the initial state and the final one, which makes this method computationally demanding.

2.3 Band inversion picture

Sometimes, topologically nontrivial materials can be well
recognized at the first glance by the so-called band inversion picture [12]. In most of the common semiconductors, the valence band-edges are formed by the \( p \)-orbits of electrons, whereas the conduction band-edges are formed by the \( s \)-orbits of electrons. This situation belongs to normal band order, i.e., topologically trivial phase. In other cases, the relativistic effect from heavy elements can be so large that the \( s \)-orbits is pushed below the \( p \)-orbits, that is, the inverted band order appears. A typical example is HgTe in which the effective positive charge of Hg core is increased due to the partly delocalization of its \( d \)-orbits. This causes the \( s \)-orbits to be more attracted by the Hg core, and consequently, the \( s \)-orbits are pushed below the \( p \)-orbits, i.e., the inverted band structure forms [32].

The band inversion is a strong indication that a material falls into topologically nontrivial phase. The first application is the prediction of quantum spin Hall effect in HgTe/CdTe quantum well proposed by Bernevig et al. [12]. The quantum well structure is that the HgTe with inverted band order is sandwiched by the CdTe with normal band order. The topological property of entire quantum well is determined by the thickness \( d \) of HgTe layer. The critical thickness \( d_c \) is predicted to be about 6.5 nm [12]. For a thin well when \( d < d_c \), the CdTe has the dominant effect and the entire quantum well is topologically trivial with normal band order, while for a thick well when \( d > d_c \), the HgTe has a critical role role and the entire quantum well is topologically nontrivial with inverted band order.

Similar to HgTe and CdTe, the band topology of other cubic semiconductors with zinc-blende-like structure can also be determined by the band inversion picture. To do this, one need to define a useful physical quantity, namely, the band inversion strength (BIS). Specially at \( \Gamma \) point, the BIS is defined as the energy differences between \( \Gamma_8 \) state (formed by \( s \)-orbits) and \( \Gamma_8 \) state (formed by \( p \)-orbits) [33,34] i.e.,

\[
\Delta E = E_{\Gamma_8} - E_{\Gamma_8}.
\]

In general, negative \( \Delta E \) typically indicates that the materials are in topologically nontrivial phase, while those with positive \( \Delta E \) are in topologically trivial phase.

Moreover, the conventional \( sp \)-orbits semiconductors, the band inversion has also been found in \( pp \)-orbits and \( df \)-orbits semiconductors. In Bi\(_2\)Se\(_3\) family, both the valence and conduction band-edges are formed by \( p \)-orbits but with opposite parities. It was predicted that Bi\(_2\)Se\(_3\) family is 3DTI due to the inverted band order between \( \{P1^+\} \) and \( \{P2^+\} \) orbits [35]. Here, the + (−) means the parity of the corresponding Bloch wavefunctions. The band inversion can be interpreted that at \( \Gamma \) point these two \( p \)-orbits with opposite parities are exchanged when SOC turns on. Other examples are actinide compounds AmX (X=N, P, As, Sb, and Bi) and PuY (Y=Se and Te), which were recently discovered by Zhang et al. [36] as a new class of 3DTI driven by strong electron-electron interactions. In these compounds, the \( \Gamma_8 \) state of \( 6f \)-orbit locates below the \( \Gamma_8 \) state of \( 5f \)-orbit at \( X \) point, and as a result, the inverted band order occurs.

Although the band inversion at some high-symmetry points is a convenient way to find topologically nontrivial materials, for example HgTe/CdTe quantum well, Bi\(_2\)Se\(_3\) family, and actinide compounds, it should be used with more care because the band topology is a global property within the entire Brillouin zone and is not only limited to some high-symmetry points.

### 2.4 \( Z_2 \) topological invariants

The most general and direct method of searching for 3DTI is to calculate the \( Z_2 \) topological invariants from the bulk band structure [14–16]. There exist two situations depending on whether the system has spatial inversion symmetry or not. If a system has inversion symmetry, the calculation of \( Z_2 \) topological invariants can be well simplified based on the parity criterion developed by Fu and Kane [17]. Conversely, if a system does not have inversion symmetry, Fukui and Hatsugai [37] have developed an effective algorithm, which requires Bloch functions (BFs) on a dense two-dimensional grid to compute the \( Z_2 \) topological invariants. The implementation of these two methods within full-potential linearized augmented plane-wave (FP-LAPW) formalism has been demonstrated [38]. In the following, we briefly introduce these two methods.

In the systems with inversion symmetry, the parity analysis only requires the knowledge of BFs on the time-reversal invariant momenta (TRIM) in the Brillouin zone (BZ) [17]. In 3D system, there are eight TRIMs, \( \Gamma_{i=(\nu_1,\nu_2,\nu_3)} = 1/2 (n_1G_1 + n_2G_2 + n_3G_3) \), where \( G_j \) are primitive reciprocal-lattice vectors with \( n_j = 0 \) or \( 1 \). The \( Z_2 \) invariants are determined by the quantities

\[
\delta_i = \prod_{m=1}^{N_{occ}} \xi_{2m}(\Gamma_i).
\]

Here, \( \xi_{2m}(\Gamma_i) = \langle \Psi_{2m,i} | P | \Psi_{2m,i} \rangle \) is the eigenvalue of parity operator \( P \) at the \( 2m \)-th occupied band and TRIMs \( \Gamma_i \). The \( \xi_{2m}(\Gamma_i) \) is equal to \( 1 \) (−1), corresponding to even (odd) parity of the BFs. The sum is over all of the occupied bands with only even band index due to the Kramers degeneracy at TRIMs. In 3D system, there are four independent invariants \( v_0; (v_1, v_2, v_3) \), given by [17]

\[
\langle -1 \rangle^{v_0} = \prod_{i=1}^{\nu} \delta_i ,
\]

\[
\langle -1 \rangle^{v_1} = \prod_{n=1, n_{32}=0,1} \delta_{i=(n_1, n_2, n_3)},
\]

where \( v_0 \) is independent of the choice of primitive reciprocal-lattice vectors \( G_j \) while \( v_1, v_2, \) and \( v_3 \) are not. The combina-
tion of these four independent invariants \( \nu_0; (\nu_1 \nu_2 \nu_3) \) clearly distinguish three classes of states: STI, WTI, and NI [17].

In the systems without inversion symmetry, an effective algorithm on a dense two-dimensional grid to compute the \( Z_2 \) invariants has been proposed by Fukui and Hatsugai within a tight-binding framework [37]. It was shown that under the time-reversal constraint the \( Z_2 \) invariants can be written in terms of the Berry gauge potential and Berry curvature associated with the BFs [39],

\[
Z_2 = \frac{1}{2\pi} \oint_{\partial B} dk \cdot \mathcal{A}(k) - \int_{B'} d^2k \mathcal{F}(k) \mod 2, \tag{5}
\]

where \( \mathcal{A}(k) \) and \( \mathcal{F}(k) \) are the Berry connection and Berry curvature, respectively,

\[
\mathcal{A}(k) = i \sum_n \langle \psi_n(k) | \nabla_k \psi_n(k) \rangle \tag{6}
\]

and

\[
\mathcal{F}(k) = \nabla_k \times \mathcal{A}(k) \mod . \tag{7}
\]

The \( B' \) and \( \partial B' \) indicate half of 2D-torus and its boundary, respectively (see Figure 1). By using the periodic gauge \[40, 41\]

\[
\left| \psi_n \left( k + G_i \right) \right| = e^{-iG_i \cdot k} \left| \psi_n (k) \right|, \tag{8}
\]

and two time-reversal constraints \[37, 39\]

\[
\left| \psi_n (-k) \right| = \Theta \left| \psi_n (k) \right|, \quad k \in B^+_x , \tag{9}
\]

and

\[
\left| \psi_{2n} (-k) \right| = \Theta \left| \psi_{2n-1} (k) \right|, \quad -k \text{ and } k \in B^0_x , \tag{10}
\]

one can obtain the periodic part of BFs \( \psi_n (k) \) at every \( k \)-point of the 2D-torus. Then, the Berry connection (eq. (6)) and Berry curvature (eq. (7)) can be calculated by the finite element expressions [37]. After that, the \( Z_2 \) invariants can be obtained by inserting eqs. (6) and (7) into eq. (5). In 3D system, there are six 2D-tori \( T(Z_0), T(Z_1), T(X_0), T(X_1), T(Y_0), \) and \( T(Y_1) \), supporting six \( Z_2 \) invariants \( z_0, z_1, x_0, x_1, y_0, \) and \( y_1 \). However, out of these six possible \( Z_2 \) invariant only four of them are independent due to the constraint \( x_0 + x_1 = y_0 + y_1 = z_0 + z_1 = 0 \mod 2 \). The \( Z_2 \) invariants are denoted in another way with \( \nu_0 = (z_0 + z_1) \mod 2, \nu_1 = x_1, \nu_2 = y_1 \) and \( \nu_3 = z_1 \), i.e., \( \nu_0; (\nu_1 \nu_2 \nu_3) \) \[14–16\]. By using topological invariants \( \nu_0; (\nu_1 \nu_2 \nu_3) \), one can determine the band topology for a given material.

Comparing with the surface electronic structure (sect. 2.1), adiabatic continuity band transformation (sect. 2.2), and band inversion picture (sect. 2.3), the calculation of the \( Z_2 \) topological invariants is a direct evidence for determining topologically nontrivial state. Furthermore, from the viewpoint of first-principles calculation, it is the most computationally efficient. Our implementation of the calculation of \( Z_2 \) topological invariants within FP-LAPW formalism has been recently applied to predict ternary half-Heuslers [33,34] and chalcopyrite [42] 3DTI and quantum spin Hall effect in siliconic thinfilm [29]. Since the critical factor is to calculate the eigenvalues of the parity operator and time-reversal operator in the systems with and without inversion symmetry respectively, it can be implemented in any other first-principles methods, such as the pseudopotential planewave and the linear muffin-tin orbital. There appears another approach to compute the \( Z_2 \) invariants by employing the charge center of Wannier functions [43,44].

### 3 3DTI host materials

We review the 3DTI host materials in the sequence of simple elements, binary compounds, pseudo-binary compounds, ternary compounds, and quaternary compounds. In each part, only one or several typical materials are discussed. Table 1 includes a list of all 3DTI host materials. In these potential host materials, some of them have been confirmed by experiments while the others are not yet. The readers can find the interesting materials in Table 1 and refer to the literatures therein. It also should be noted that the 3DTI discussed here does not contain the materials with strong electron-electron correlation.

#### 3.1 3DTI in simple elements

##### 3.1.1 \( \alpha \)-Sn

The group-IV element \( \alpha \)-Sn (grey tin) crystallizes in the diamond structure with space group \( \text{Fd} \overline{3}m \) (No. 227), as shown in Figure 2(a). The full-relativistic band structure in Figure 2(c) clearly shows that at the static lattice constant \( \alpha \)-Sn is a zero band-gap semiconductor with the feature of band inver-

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**Figure 1** Schematic drawing of lattice mesh in a 2D-torus. Under the time-reversal constraint, only half of 2D-torus \( B' \) is needed, which is denoted by shaded region. The thick lines indicate the boundary of \( B' \), i.e., \( \partial B' \), and the open arrows denote their directions. All \( k \)-points are divided into three classes: \( B^+_x, B^+_y \), and \( B^0_x \), which are represented by small solid, small open and large shaded circles, respectively. Adapted from ref. [38].
sion. The valence band maximum (VBM) and the conduction band minimum (CBM) are degenerated at $\Gamma$ point and the Fermi level crosses the fourfold-degenerated $\Gamma_8$ state (from $p$-orbitals). The $s$-orbit-like $\Gamma_7$ state is situated below the $\Gamma_8$ state, forming the inverted band structure [48,49]. Hence, the band structure of $\alpha$-Sn is qualitatively different from those of the other group IV elements C, Si, and Ge [49].

Fu et al. [17] proposed that a uniaxial strain can tune $\alpha$-Sn into a 3DTI. The basic idea is that after applying a uniaxial strain the fourfold-degenerated $\Gamma_8$ state is lifted and a band-gap opens around $\Gamma$ point. Consequently, the topologically nontrivial state forms because the band inversion does not change. Figure 2(d) shows the band structure of $\alpha$-Sn under a uniaxial strain $c/a = 1+3\%$ but with constant volume. One can see that the band-gap opens while the band inversion preserves. To further confirm the argument of band inversion, the $Z_2$ topological invariant is calculated. The result $1;(000)$ indicates that the strained $\alpha$-Sn is indeed a STI. Although the theoretical picture is very clear, there is not any experimental work on $\alpha$-Sn currently.

### 3.1.2 Sb

The Sb (antimony) crystallizes in rhombohedral space group R3m (No. 166), as shown in Figure 3(a). The full-relativistic band structure in Figure 3(c) shows Sb is a semimetals with small pockets of electron in the vicinity of the L point. There are also small pockets of hole around the low-symmetry H point (not shown). Although it is not an insulator, $Z_2$ topological invariant can still be defined because the local band-gaps (negative indirect band-gap) exist at every $k$-point throughout the entire BZ [17]. The result $1;(111)$ indicates that the Sb is a STI. As another group-V element, Bi (bismuth) has similar crystal and band structure comparing to Sb, as shown in Figures 3(a) and 3(d) respectively, but Bi is a NI with $Z_2$ topological invariant 0;(000). The different topological classes between Sb and Bi were well interpreted by their different parities at L points [17].

Hsieh et al. [51,52] have measured the bulk and surface electronic structure of Sb. Because bulk Sb is a semimetal, it is difficult to separate its surface state from the projection of bulk state around the Fermi level. While by using advanced spin-resolved ARPES technique, Hsieh et al. [51] successfully isolated the surface states of Sb(111) from its bulk states over the entire BZ. They also directly found the gapless and spin-splitting surface state, which characterizes the topologically nontrivial feature in Sb [51].

### 3.2 3DTI in binary compounds

#### 3.2.1 Bi$_{1-x}$Sbx alloy

Both Sb and Bi are group-V semimetals with the rhombohedral crystal structures and similar lattice constants, therefore, they can easily form solid alloy Bi$_{1-x}$Sbx [53]. By altering the concentration $x$ of Sb substitution, Bi$_{1-x}$Sbx undergoes a phase transition between semimetal and semiconductor. In the range of $0.07 < x < 0.22$, Bi$_{1-x}$Sbx becomes semiconductor with the largest global band-gap of 0.03 eV at $x = 0.18$. Based on a tight-binding model [54], Fu et al. [17,30] predicted that Bi$_{1-x}$Sbx is the first realistic 3DTI material. Subsequently, this prediction was confirmed by first-principles calculation [31] and experimental observations [55–57].

Although both theories and experiments got a consistent conclusion that the topologically nontrivial phase exists in Bi$_{1-x}$Sbx alloy, the discrepancies about surface electronic structure still remain. The main concern is the surface band configuration, including the numbers of surface bands and the crossing times between the surface bands and the Fermi level along the $\Gamma-M$ line in surface BZ. All the experimental works [55–57] reported three surface bands ($\Sigma_1$, $\Sigma_2$, and $\Sigma_3$) lying inside band-gap of bulk projection, but with different crossing times with the Fermi level, five times in refs.
[55,56] and three times in ref. [57]. Conversely, both tight-binding [30] and first-principles [31] calculations can not reproduce the presence of the third surface band $\Sigma'$. Teo et al. [30] and Zhang et al. [31] give three and five times of band crossing, respectively. Therefore, more experimental measurements and theoretical calculations are needed for revealing the microscopic physics in Bi$_{1-x}$Sb$_x$.

3.2.2 Bi$_2$Te$_3$ family

Since the surface electronic structure of Bi$_{1-x}$Sb$_x$ is rather complicated and its bulk band-gap is too small, searching for new 3DTI host materials with simple surface electronic structure and large band-gap becomes extremely important. Fortunately, Bi$_2$Se$_3$ family compounds with larger band-gap and simpler surface spectrum have been found as a second generation of 3DTI materials [35,58–60], which support further study on various topologically protected phenomena at room temperature.

Tetradymite semiconductors Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$, have a rhombohedral crystal structure with space group R3m (No. 166). Although Sb$_2$Se$_3$ essentially has an orthorhombic crystal structure, a virtual rhombohedral crystal structure is used at here for comparing its topological property with tetradymite semiconductors. Zhang et al. [35] theoretically proposed that Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ are 3DTI while Sb$_2$Se$_3$ is not. More importantly, the band-gap of Bi$_2$Se$_3$ is as large as 0.3 eV, which is larger than the energy scale of room temperature. Almost at the same time, these family compounds were experimentally confirmed with the observation of single Dirac cone on the surface for Bi$_2$Se$_3$ [58], Bi$_2$Te$_3$ [59,60], and Sb$_2$Te$_3$ [60]. Because of the large band-gap and simple surface electronic structure, Bi$_2$Se$_3$ family compounds have been extensively studied ranging from bulk to thinfilm [61–71].

3.2.3 HgTe and strained InSb

HgTe is a zinc-blende compound with space group F43m (No. 216). It is a zero band-gap semiconductor due to large relativistic effect. The twofold-degenerated $\Gamma_6$ state is located below the fourfold-degenerated $\Gamma_8$ state, forming the inverted band order (see Figure 4(b)). Fu et al. [17] theoretically predicted that HgTe is a 3DTI under a uniaxial strain. The basic routine is similar to that of $\alpha$-Sn, that is, the uniaxial strain is used to break the cubic symmetry and open a band-gap at $\Gamma$ point without changing the band inversion. Recently, Brüne et al. [72] successfully observed the Dirac-like topological surface state on strained HgTe by ARPES measurement.

InSb is also a zinc-blende semiconductor, but in contrast to HgTe, it has a small band-gap of 0.235 eV [74]. The $\Gamma_6$ state is located above the $\Gamma_8$ state, forming the normal band order (see Figure 4(a)). Feng et al. [75] proposed that InSb can be turned into a 3DTI by a 2%–3% biaxial lattice expansion. The generic guiding principle is that lattice expansion decreases the coupling potentials of $ss$-orbits or $pp$-orbits, which leads to the band inversion (see Figure 4(c)). Here, we use different modes of strain in HgTe and InSb. In the former one, the uniaxial strain is just used to break the cubic symmetry. While in the latter one, the nonhydrostatic (2%–3% biaxial) lattice expansion is twofold because it not only changes normal band order to inverted band order but also breaks the cubic symmetry.

3.3 3DTI in pseudo-binary compounds

Although Bi$_2$Se$_3$ family as the second generation of 3DTI has attracted research focus because of its simple surface electronic structure, it hard to be applied in various real devices. The prominent difficulty is high bulk carrier concentration, which remarkably masks the contribution of surface carriers in the surface transport measurement [55,62,80–82]. The high bulk carriers concentration mainly originates from the native crystal defects [58–60]. Some experimental techniques including compensate doping in bulk [59,63] and tuning Fermi level by gate voltage [83–85] have been tested, but this issue is not perfectly solved.

Recently, a promising platform for reducing the bulk carrier concentration, Bi$_2$Te$_2$Se, has been proposed by Ren et al. [86] and Xiong et al. [87]. Bi$_2$Te$_2$Se has a large bulk resistivity because its chemical characteristic makes the formation of crystal defects more difficult. Motivated by this observation, there appears other tetradymite-like $M_2X_2Y$ ($M = Bi$ or Sb; $X$ and $Y = S$, Se or Te) compounds [88–90] and Bi$_{2-x}$Sb$_x$Te$_3$–Se$_y$ alloy [91–96]. The alloy system with a series of special combinations of $x$ and $y$ can further improve the bulk resistivity, and thus provide a diverse platform for investigating the surface transport phenomena.

It should be noted that in this review paper these tetradymite-like materials are classified into pseudo-binary 3DTI because their crystal and electronic structures are very similar to that of binary Bi$_2$Se$_3$ family.

3.4 3DTI in ternary compounds

3.4.1 Half-Heusler

The crystal structure of ternary half-Heusler compounds is...
Table 1 3DTI host materials in current literatures are classified by simple elements, binary compounds, pseudo-binary compounds, ternary compounds, and quaternary compounds. Here, the tetradymite-like materials are called pseudo-binary compounds because their crystal and electronic structures are very similar to that of binary Bi$_2$Se$_3$ family. In some materials with zero band-gaps, proper strains should be added to realize the topological insulating state. Note that ternary half-Heusler and chalcopyrite 3DTI are not list one by one due to their large numbers, but the readers can refer to Figures 5 and 6.

| Compounds | Bravais lattice | Space group (No.) | Band gap (eV) | Strain | Theory works | Experiment works |
|-----------|----------------|------------------|---------------|--------|--------------|------------------|
| α-Sn      | fcc            | Fd$ar{3}$m (227) | zero [17]     | yes    | [17]         | –                |
| Sb        | rho            | R$ar{3}$m (166) | semimetal [17] | no     | [17, 17, 57] | [51, 52]         |
| Bi$_{1-x}$Sb$_x$ | rho | R$ar{3}$m (166) | 0.03 (x=0.18) [17] | no | [17, 17, 27] |
| Bi$_2$Se$_3$ | rho | R$ar{3}$m (166) | 0.30 [66] | no | [35, 66] |
| Bi$_2$Te$_3$ | rho | R$ar{3}$m (166) | 0.12 [66] | no | [35, 66] |
| Sb$_2$Te$_3$ | rho | R$ar{3}$m (166) | 0.17 [66] | no | [35, 66] |
| HgTe     | fcc            | F$ar{4}$m (216) | zero [17]     | yes    | [17]         | –                |
| β-HgS    | fcc            | F$ar{4}$m (216) | 0.042 [73]    | no     | [73]         | –                |
| InSb     | fcc            | F$ar{4}$m (216) | zero [75]     | yes    | [75]         | –                |
| β-As$_2$Te | fcc | P$2_1$/c (14) | 0.08 [76] | no | [76] |
| Sr$_2$Pb | orthorhombic | Pnma (62) | 0.05 [77] | yes | [77] |
| β-GaS    | hex            | P$6_3$/mmc (194) | 0.025 [78]    | yes    | [78]         | –                |
| e-GaSe   | hex            | P6$_3$ (187)    | 0.135 [78]    | yes    | [78]         | –                |
| Na$_2$Bi | hex            | P$6_3$/mmc (194) | 0.006 [79]    | yes    | [79]         | –                |
| K$_2$Bi  | hex            | P$6_3$/mmc (194) | 0.013 [79]    | yes    | [79]         | –                |
| Rb$_2$Bi | hex            | P$_6$/mm (194)  | – yes         | [79]   | –            | –                |
| Bi$_2$TeS | rho | R$ar{3}$m (166) | 0.28 [89] | no | [88, 89] |
| Bi$_2$Te$_2$Se | rho | R$ar{3}$m (166) | 0.28 [89] | no | [88–90] |
| Bi$_2$Se$_2$Te | rho | R$ar{3}$m (166) | 0.29 [88] | no | [88] |
| Sb$_2$Te$_2$Se | rho | R$ar{3}$m (166) | 0.34 [88] | no | [88] |
| Bi$_2$Te$_1.5$S$_1.5$ | rho | – | 0.2 [90] | no | [90] |
| Bi$_2$Te$_3$S$_1.4$ | rho | – | 0.2 [91] | no | [91] |
| Bi$_2$Sb$_3$Te$_3$ | rho | – | – | no | [93] |
| Bi$_2$Ge$_3$Sb$_3$Te$_3$ | rho | – | – | no | [96] |
| half-Heusler (see Figure 5) | fcc | F$4$3m (216) | zero [33, 34] | yes | [33, 34, 97–99] | [100–104] |
| Li$_2$AgSb | fcc | F$4$3m (216) | zero [107] | yes | [107] |
| chalcopyrite (see Figure 6) | bct | I$4$2d (122) | 0.01–0.14 [42] | no | [42] |
| TIBiS$_2$ | rho | R$ar{3}$m (166) | 0.2 [118] | no | [112–114] |
| TIBiTe$_2$ | rho | R$ar{3}$m (166) | 0.14 [113] | no | [112–114] |
| TIBiSe$_2$ | rho | R$ar{3}$m (166) | 0.05 [113] | no | [112–114] |
| LaB$_2$Te$_3$ | rho | R$ar{3}$m (166) | 0.12 [119] | no | [119] |
| CeOs$_4$As$_12$ | bcc | Im$3$ (204) | zero [120] | yes | [120] |
| CeOs$_4$Sb$_12$ | bcc | Im$3$ (204) | zero [120] | yes | [120] |
| Cs$_2$NbI | cubic | Pm$3$m (221) | 0.03 [121] | yes | [121] |
| Sr$_2$NbI | cubic | Pm$3$m (221) | – yes | [121] |
| Ba$_2$NbI | cubic | Pm$3$m (221) | – yes | [121] |
| CsSnCl$_3$ | cubic | Pm$3$m (221) | 0.11 (122) | yes | [122] |
| CsPbCl$_3$ | cubic | Pm$3$m (221) | 0.354 (122) | yes | [122] |
| CsGeBr$_3$ | cubic | Pm$3$m (221) | 0.026 (122) | yes | [122] |
| CsSnBr$_3$ | cubic | Pm$3$m (221) | 0.099 (122) | yes | [122] |
| CsPbBr$_3$ | cubic | Pm$3$m (221) | 0.12 (122) | yes | [122] |
| CsSnI$_3$ | cubic | Pm$3$m (221) | 0.169 (122) | yes | [122] |
| Li$_2$AgSe | hex | P$6_3$/mmc (194) | 0.003 [123] | yes | [123] |
| Li$_2$AuSe | hex | P$6_3$/mmc (194) | 0.050 [123] | yes | [123] |
| Li$_2$AuTe | hex | P$6_3$/mmc (194) | – yes | [123] |
| Na$_2$AgSe | hex | P$6_3$/mmc (194) | 0.010 (123) | yes | [123] |
| Na$_2$AgTe | hex | P$6_3$/mmc (194) | 0.003 (123) | yes | [123] |
| Na$_2$AuSe | hex | P$6_3$/mmc (194) | 0.015 (123) | yes | [123] |
| Na$_2$AuTe | hex | P$6_3$/mmc (194) | 0.030 (123) | yes | [123] |
| K$_2$AuTe | hex | P$6_3$/mmc (194) | – yes | [123] |
| Li$_2$HgAs | hex | P$6_3$/mmc (194) | – yes | [123] |
| Li$_2$HgSb | hex | P$6_3$/mmc (194) | – yes | [123] |
| BiTe | hex | P$3$m (156) | – yes | [124] |
| Ge$_5$Sb$_7$Te$_3$(Petrov sequence) | hex | P$3$m (164) | 0.1 [125] | no | [125] |
| Ge$_5$Sb$_7$Te$_3$(KH sequence) | hex | P$3$m (164) | – no | [126, 127] |

(To be continued on the next page)
described by space group \( \mathrm{F}\bar{4}3m \) (No. 216). The chemical formula of these materials is \( \text{XYZ} \), where \( X \) and \( Y \) are transition or rare earth metals and \( Z \) a heavy element. It can be regarded as a hybrid compound of \( \text{XZ} \) with rock-salt structure, and \( \text{XY} \) and \( \text{YZ} \) with the zinc-blende structure. The band structure of half-Heusler compounds at the \( \Gamma \) point near the Fermi level splits into twofold-degenerated \( \Gamma_6 \), twofold-degenerated \( \Gamma_7 \), and fourfold-degenerated \( \Gamma_8 \) states. Away from \( \Gamma \) point, the valence bands and conduction bands are well separated throughout the entire BZ.

Three research groups independently predicted that under a uniaxial strain ternary half-Heusler compounds are new family of 3DTI [33,97,98]. Since the low-energy electronic structure of half-Heusler compounds is dominated at \( \Gamma \) point and similar to other zinc-blende semiconductors. The identification of topologically nontrivial feature via the band inversion picture becomes possible [97,98], just as what occurs in HgTe. The authors in ref. [33] also directly calculated the \( \mathbb{Z}_2 \) topological invariants from the bulk band structure. The calculated \( \mathbb{Z}_2 \) topological invariant \( \mathbb{Z}_2^{(000)} \) definitively confirmed that some of ternary half-Heusler compounds are STI.

The band topology calculated by first-principles method is sensitive to the exchange-correlation potential [34,99]. Hence, different potentials should be used to explore the topological nature. The recently developed semilocal MB-DLDA potential is believed to be better suited for calculating the topological band structure [34,99]. As shown in Figure 5, the topologically nontrivial and trivial phases are located below and above the horizontal line, respectively. One can see that the topological phases of ScAuPb and YPdBi change by using different exchange-correlation potentials.

Recently, there have appeared a few experimental works about the electronic structures, transport properties, and topological phenomena of ternary half-Heusler compounds [100–104]. Since a large number of materials with half-Heusler structure possess additional properties such as magnetism [105] and superconductivity [106], the combination of the predicted topological order with ferromagnetic order and/or superconductive order may provide an exciting platform for novel quantum devices.

### 3.4.2 Chalcopyrite

The crystal structure of ternary chalcopyrite compounds is described by the space group \( \mathrm{I}\bar{4}2d \) (No. 122) with body-centered tetragonal structure. The chemical formula of these materials is \( \text{ABC}_2 \), which can be regarded as a superlattice of two cubic zinc-blende unit cells and the A and B cations are ordered on the two different sites. Since the overall structural similarity between the ternary chalcogenides and binary zinc-
blende analogs, the electronic structures of the former one are expected to closely resemble that of latter one. Therefore, some of the chalcopyrite compounds may have the same topological class with the 3DTI HgTe.

Feng et al. [42] predicted that a large number of chalcopyrite compounds can realize the topological insulating phase by exploiting adiabatic continuity of band structures and direct evaluation of the $Z_2$ topological invariants. Comparing with other 3DTI with cubic symmetry, a seeming advantage in chalcopyrite compounds is that topologically nontrivial state can be formed in their native states without any external strain. This is because the AB cation ordering and additional structural modifications explicitly break the cubic symmetry.

In chalcopyrite compounds, the band inversion strength $\Delta E$ is defined as the energy difference between the $s$-orbital originated $\Gamma_6$ states and the VBM at the $\Gamma$ point. Figure 6 shows
the band topology of the chalcopyrite family of the I-III-VI₂ compounds (I = Cu, Ag, Au; III = In, Tl; V = S, Se, Te), as well as the II-IV-V₂ compounds (II = Zn, Cd, Hg; IV = Ge, Sn; V = As, Sb). One can see that there are a large number of topologically nontrivial materials. More importantly, many chalcopyrite topological insulators have a close lattice matching to several mainstream semiconductors, which is essential for a smooth integration into current semiconductor technology. The diverse physical properties of chalcopyrite semiconductors [108–111] make them appealing candidates for novel quantum devices.

3.4.3 Thallium-based chalcogenides

Thallium-based chalcogenides are narrow band-gap semiconductors with rhombohedral structure described by space group R3m (No. 166). The elemental composition of these materials is TIXY₂ (X = Bi, Sb and Y = S, Se, Te), which can be regarded as a sequence of hexagonally close-packed layers with the order of -Tl-Y-X-Y-. In contrast to Bi₂Se₃ family, the TIXY₂ are not layered compounds because each Tl or X atomic layer is sandwiched by two Y atomic layers and every two atomic layers are coupled by strong covalent bonds. As a consequence, the surface electronic structure is sensitive to surface relaxations and different terminations.

Although the identification of topologically nontrivial phase in these compounds is more complex than that of Bi₂Se₃ family, several first-principles studies have predicted that TlSbTe₂, TlSbSe₂, TlBiTe₂, and TlBiSe₂ are 3DTI [112–114]. The single Dirac cone surface state of TlBiTe₂, and TlBiSe₂ have been confirmed by ARPES measurements [115–118].

3.5 3DTI in quaternary compounds

The search for 3DTI has already been extended to quaternary I₂-II-IV-VI₄ compounds [133,134]. These materials are described by space group I42m (No. 121) with body-centered tetragonal structure. Structurally, quaternary I₂-II-IV-VI₄ compounds can be viewed as the subcompounds derived from chalcopyrite I-III-VI₂ compounds by mutating two group-III cations to one group-II and one group-IV cations. Because of the structural similarity, the band topology of these compounds is expected to be nontrivial in analogy to that of chalcopyrite 3DTI [42]. Based on first-principles calculations, Chen et al. [134] and Wang et al. [133] predicted that a number of I₂-II-IV-VI₄ compounds are indeed topologically nontrivial materials. More importantly, the electronic properties of these compounds can be better altered because of the enhanced chemical and structural degrees of freedom. For example, the nontrivial band-gaps can be further increased in Ag₂HgPbSe₂ (0.047 eV) and Cu₂ZnGeSe₂ (0.069 eV), which are larger than the band-gaps in strained HgTe and some of chalcopyrite compounds.

4 Conclusion and outlook

Since the potential applications in spintronic field and quantum computation, 3DTI has no doubt become topic of interest in the fields of condensed matter physics and material science. Thousands of scientific colleagues are attracted by its exotic quantum phenomena, pushing this field in a rapid pace. Similar to other stages of development in the history of condensed matter physics, for example the QH effect, the emergence of high quality samples is of crucial importance. For this purpose, this paper reviews the recent progress of materials realization in 3DTI.

Based on topological band theory [18,19], the first-principles calculation plays a pivotal role in the prediction of 3DTI host materials. We have introduced four methods of searching for new 3DTI, including surface state electronic structure, adiabatic continuity band transformation, band inversion picture, and Z₂ topological invariants. None of these methods is solely used in present literatures, but two or more of them are usually combined together to predict topologically nontrivial materials. To date, many materials have been predicted to be 3DTI (see Table 1). Some of them have been confirmed by experiments via the ARPES measurements of surface Dirac electronic structure. The most favorable materials are thus the Bi₂Se₃ family, which have been extensively studied from bulk to thin film [58–71]. But remarkably conducting bulk state even in high quality sample blocks further studies of the surface transport. For decreasing the bulk carrier concentration, the pseudo-binary compound derived from Bi₂Se₃ family, for example Bi₂Te₂Se, is found to be new class of 3DTI with much larger bulk resistivity [86–94]. The theoretical prediction of 3DTI was also extended to ternary and quaternary compounds, but there are rare experimental reports about these compounds mainly because of the difficulties in their synthesis and growth.

We propose several interesting and valuable directions in the further work. (i) Among the present known 3DTI host materials, there does not exist a unique one which can sufficiently meet various requirements in experimental observations. Therefore, searching for new 3DTI host materials, particularly for those with simpler surface electronic structure and easier synthetic and growing condition, is still needed. This should be a central task in this rapidly developing field. (ii) Although the present 3DTI host materials are often discussed in the context of the non-interacting band theory, the materials realization of topological Mott insulator [135,136] and topological Kondo insulator [137,138] with strong electron-electron interaction should also be taken into account. Furthermore, the topological order affected by disorder, i.e., topological Anderson insulator [139–141], is interesting and needs to be thoroughly studied. (iii) The realization of the quantum anomalous Hall effect and topological superconductor is also a frontier direction. For quantum anomalous Hall effect, some theoretical models were proposed by means of magnetic doping in the film or surface of 3DTI [142–147], but they have not been reproduced by
current experiments. For topological superconductor, one expects to realize it by constructing proper interface between 3DTI and conventional superconductors due to the proximity effect [18,148]. In addition, a mysterious particle obeyed non-Abelian statistics, the Majorana fermion, could be detected in the interface and it will be hopefully utilized in the topological quantum computations.

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