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Abstract
Ternary tetradymites Bi2Te2S, Bi2Te2Se, and Bi2Se2Te are found to be stable, bulk topological insulators via theory, showing band inversion between group V and VI pz orbitals. We identify Bi2Se2Te as a good candidate to study massive Dirac fermions, with a (111) cleavage-surface-derived Dirac point (DP) isolated in the bulk-band gap at the Fermi energy (EF)-like Bi2Se3 but with a spin texture alterable by layer chemistry. In contrast, Bi2Te2S and Bi2Te2Se (111) behave like Bi2Te3, with a DP below EF buried in bulk bands. Bi2Te2S offers large bulk resistivity needed for devices.

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Ternary tetradymite compounds as topological insulators

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Materials that exhibit topological insulator (TI) behavior reveal a novel quantum state for electrons,1,2 where surface states of a three-dimensional (3D) system are topologically protected against disorder by time-reversal symmetry (TRS) and, as a result, electrons experience no backward scattering by nonmagnetic impurities. The unique feature of a 3D TI lies in its band dispersion—surface bands connect valence and conduction bands and cross the Fermi level \( E_F \) an odd number of times along two TRS-equivalent \( \mathbf{k} \) points, typically found in narrow-gap semiconductors with strong spin-orbit coupling (SOC). Since \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \) were concurrently observed1−5 and predicted6 to be 3D TIs, an intensive search7−10 continues for other systems. Notably, \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \) belong to a class of line compounds called \textit{tetradymites}. Ternary tetradymites, such as \( \text{Bi}_2\text{Te}_2\text{S}, \text{Bi}_2\text{Te}_2\text{Se}, \) and \( \text{Bi}_2\text{Se}_2\text{Te} \) are also stable11,12 and potentially offer a “chemistry knob” to control TI behavior. Here, we provide insight for device development—cleavage surface-band dispersion and location of Dirac point (DP) both relative to bulk bands, as well as the warping (out-of-plane spin component, referred hereafter as spin texture) of the Dirac cone (DC).

Upon band inversion and crossing of \( E_F \) due to SOC, a DP is formed leading to variety of unique physics. Using angle-resolved photoelectron spectroscopy, Chen et al.13 have shown that massive Dirac fermion is produced on \( \text{Bi}_2\text{Se}_3 \) (111) surface by breaking TRS via magnetic impurities. To do this, the position of DP must be in the gaps of both bulk and surface bands. \( \text{Bi}_2\text{Se}_3 \) has a DP isolated in the bulk-band gap region making it a good candidate for such studies, whereas the DP for \( \text{Bi}_2\text{Te}_3 \) is below \( E_F \), buried in bulk bands. \( \text{Bi}_2\text{Te}_3 \) offers large bulk resistivity needed for devices.

One costly method to tell a TI from an ordinary band insulator is to calculate the \( Z_2 \) topological order parameter.19 Yet, for structures with inversion symmetry, Fu et al.20 proposed inspecting the parity product of occupied bands on TRS equivalent \( \mathbf{k} \) points in the bulk bands. Here, we search for a band inversion and zero gap in bulk bands by tuning the SOC (\( \lambda \) from 0 to 100%), and then, once verified, we calculate surface bands and assess DP formation, an approach used for semi-infinite surfaces of the binaries by Zhang et al.6

Tetradymite compounds formed between group V and VI elements have a quintuple-layered structure, in which group VI element occupies the outmost and central (third) layer, and group V element occupies the second layer, e.g., for \( \text{Bi}_2\text{Se}_2\text{S} \), the layers stack as \( \text{Se}^\text{II}-\text{Bi}^\text{III}-\text{Se}^\text{I} \) along (111) in the primitive rhombohedral cell with the space group of \( \overline{R}3m \) (No. 166). The two group VI positions are not equivalent. The stacking is similar to fcc, but the interlayer distances are different; in particular, the distance between neighboring quintuple-layer units is the largest, making it easier to cleave with group VI element exposed as the surface layer. We use DFT with PW91 exchange-correlation functional21 and plane-wave basis set with projected augmented waves,22 as implemented in VASP.23,24 Bulk tetradymite can also be represented as a hexagonal lattice with 15 atomic layers, which also gives the basis in the slab model for the (111) surface. Both the atomic structure and Brillouin zone for tetradymite bulk and (111) surface have been shown before,6,23 so we do not repeat them. For bulk we use the primitive rhombohedral cell of five atoms with \( 7 \times 7 \times 7 \) \( k \)-point mesh. We use a three quintuple-layered slab along (111) with no vacuum for bulk band projection and a 14 Å vacuum for surface-band calculations. The kinetic...
bands, a semi-infinite surface is required and achieved with To show a TI surface band connects conduction and valence lattice constants (Table I) and fix atoms in their bulk positions. and 10 Fig. 1(d), shows an indirect gap along high-symmetry directions (Δ₁hs) and DP at Γ point (Δ₁). The data in Table I may be useful for device development. Below (above) 44% SOC, it is mostly composed of Bi (Te) p₉ orbital versus λ. Compared to the band structure without SOC in Fig. 1(a), the largest change is the lowering of the lowest-conduction band and the rising of the highest-valence band to form jointly a DP at Γ point at E_f. Upon further increase of λ, Fig. 1(c) shows that the gap at Γ point is reopened and two nearby maximum are formed. Figure 1(e) shows the projections of the lowest-conduction band on Bi and Te p₉ orbital versus λ. Below (above) 44% SOC, it is mostly composed of Bi (Te) p₉ components. Indeed, SOC causes the band inversion in Bi₂Te₂S, similar to the binaries, so Bi₂Te₂S is also a 3D TI. The data in Table I may be useful for device development.

To see the surface bands of Bi₃Te₂S(111), we plot in Fig. 1(f) the dispersion of a three-quintuple slab on top of the projected bulk bands. Similar to Bi₂Te₃ [see Fig. S1(d)], we find the DP for Bi₃Te₂S(111) is below E_f and buried by other states around the Γ point, showing that the two outmost surface layers in tetradymite determine the position of DP.

Ternary Bi₂Te₂Se is similar to Bi₂Te₂S, with the central Te layer in Bi₂Te₁ replaced by Se. In Figs. 2(a) and 2(b) we show its bulk and surface band dispersion. By tuning λ, we find that the bulk band inversion occurs when λc = 21% (Table I). Thus, Bi₂Te₂Se is also a 3D TI, with a Δ₁ of 0.28 eV—larger than that of Bi₂Te₃, mostly due to a smaller lattice constant. Looking at slab surface bands, we find similar features to that of Bi₂Te₁ for the position of DP; i.e., the DP of Bi₂Te₂Se is buried deeper below E_f (−0.08 eV) than that of Bi₂Te₃ (−0.02 eV) and Bi₂Te₂S (−0.05 eV); see Fig. 2.

Figures 2(c) and 2(d) show bulk and surface dispersions for the hypothetical Bi₂Se₂Te-I, where Te replaces Se in the central layer of Bi₂Se₂. At λc = 71%, a band inversion at the Γ point for bulk indicates that it is a 3D TI. The surface bands in Fig. 2(d) show that it behaves much like Bi₂Se₂ with the DP located in the gap region and not buried by other valence bands. In contrast, if Te substitutes instead in the outer layers, consistent with Hume-Rothery’s rules, we find the Bi₂Se₂Te-II surface band structure in Fig. 2(e), where the highest-valence band around Γ point becomes more flat (beyond the effect of energy cutoff is 280 eV. The k-point meshes used are 10×10×2 and 10×10×1, respectively. The convergence with respect to k-point mesh was carefully checked, with total energy converged, e.g., well below 1 meV/atom. We use experimental lattice constants (Table I) and fix atoms in their bulk positions. To see the surface bands of Bi₂Te₂S(111), we plot in Fig. 1(f) the dispersion of a three-quintuple slab on top of the projected bulk bands. Similar to Bi₂Te₃ [see Fig. S1(d)], we find the DP for Bi₂Te₂S(111) is below E_f and buried by other states around the Γ point, showing that the two outmost surface layers in tetradymite determine the position of DP.
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FIG. 2. Band structure with full SOC for Bi$_2$Te$_2$Se and Bi$_2$Se$_2$Te. For Bi$_2$Te$_2$Se, we show (a) bulk dispersion and (b) slab dispersion along ⟨111⟩. For Bi$_2$Se$_2$Te-I, (c) and (d) are similar to (a) and (b). For Bi$_2$Se$_2$Te-II, we show slab dispersion (e) along ⟨111⟩ (no bulk for clarity).

zone folding), and the isolation of the DP in the gap region remains but is less prominent than for Bi$_2$Se$_2$Te-I. This direct comparison again shows that the outer two surface layers mostly determined the locations of the valence band and DP.

A significant difference between the surface band structures of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ is the shape of DC and the associated spin texture. Figure 3 shows the shape of the conduction band of each compound around the Γ point. Comparing Figs. 3(a) and 3(d), the DC for Bi$_2$Te$_3$ remains ideal up to 0.2 eV above $E_F$, while for Bi$_2$Se$_3$, it is 0.4 eV, agreeing with previous experiments and theory. Above these energies, there is significant warping of the DC for Bi$_2$Te$_3$, as evidenced by the change in the shape—first to a hexagon, then to a snowflake. Such nonconvex shapes produce more pairs of stationary points on the constant-energy contours, allowing scattering processes among different pairs of stationary points. This result is in contrast to no scattering for a convex DC as observed in STM experiment, where a line defect on Bi$_2$Te$_3$(111) suppresses scattering only in the energy range of circular constant-energy contours, not snowflake types.

Figure 3 also shows the spin texture associated with the DC, i.e., the ratio of out-of-plane to total electron-spin moment color-mapped on the cone. For a perfect DC, the electron spin always lies in the surface plane and is perpendicular to the wave vector. In contrast, for a warped DC, Fu suggested that there should be a significant amount of out-of-plane spin moments (up to 60%) to maintain a Berry phase change of $\pi$ in one circuit, as required by topological invariance. Such behavior can lead to interesting features, such as spin-density waves on a 3D TI surface and opening of DP by an in-plane magnetic field. For Bi$_2$Te$_3$, our results in Fig. 3(a) agree with a previous calculation and show a large spin texture above 0.2 eV, except for $\overline{\Gamma} - \overline{M}$. In contrast, Bi$_2$Se$_3$ has a much smaller spin texture [Fig. 3(d)]. For Te-rich ternaries, compared to Bi$_2$Te$_3$, the upper warping limit of the cone convexity for Bi$_2$Te$_2$S and Bi$_2$Te$_2$Se are both increased to 0.3 eV [see Figs. 3(b) and 3(c)], and beyond that only small spin textures appear, with Bi$_2$Te$_2$Se being larger than Bi$_2$Te$_2$S. On the Se-rich side, compared to Bi$_2$Se$_3$, the upper warping limit of the cone convexity for Bi$_2$Se$_2$Te-II [see Fig. 3(e)] is slightly decreased, and beyond that a slightly larger spin texture appears; in contrast, for Bi$_2$Se$_2$Te-I [see Fig. 3(f)], the upper warping limit is reduced to 0.3 eV, and a much larger spin texture appears, similar to Bi$_2$Te$_3$. Thus, even though the position of DP and dispersion of valence bands are only slightly affected by the substitution of
Te in the central layer (Fig. 2), the warping and spin texture in conduction band are greatly affected by chemical substitutions. The change in the warping limit reflects the stronger trigonal crystal potential of Te than Se and S.

In Bi$_2$Te$_2$Se and Bi$_2$Se$_2$S, the binding of the site in the central layer to two Bi sites increases hybridization and decreases spin-orbit coupling. While in Bi$_2$Se$_2$Te-I, by replacing the central Se layer with Te, the spin-orbit coupling in the Bi-Te-Bi trilayer is enhanced and results in a large spin texture. Thus, introducing Te into the central layer of Bi$_2$Se$_2$ can make a superb TI candidate with a DP standing alone in bulk band gap (just like Bi$_2$Se$_3$) as well as a large spin texture (just like Bi$_2$Te$_3$ and larger than Bi$_2$Se$_3$). But finding feasible ways to introduce Te into the central layer poses a challenge. However, while spin texture in Bi$_2$Se$_2$Te-II is not as large as that in Bi$_2$Se$_2$Te-I, it is larger than Bi$_2$Se$_3$. All other electronic features are similar, including isolation of the DP in the gap, suggesting the lower-energy, partially disordered structure will also be a superb TI candidate.

Last, any potential use of these materials as a 3D-TI device requires control over the bulk resistivity. Binary tetradymites Bi$_2$Se$_3$ and Bi$_2$Te$_3$ are semiconductors, but defects (such as vacancy and Bi-Te-antisite) cause significant bulk conductivity, which overweighs the surface-state contribution. For example, Ren et al. measured that Bi$_2$Te$_2$Se has a much larger bulk resistivity than Bi$_2$Te$_3$ because the substitution of the central Te site with Se reduces the formation of a Se vacancy and Bi-Te antisite. The same mechanism should also be operative for Bi$_2$Te$_2$S because S is more electronegative and binds Bi stronger than Se, preserving the stoichiometric structure even better than Bi$_2$Te$_2$Se. For example, the energy cost to create a Bi-Te-antisite pair is increased by 0.06 eV when changing from Bi$_2$Te$_2$Se to Bi$_2$Te$_2$S. A similar situation holds for quaternary Bi$_2$(Te-Se)$_2$S.

In conclusion, we find that Bi$_2$Te$_2$S, Bi$_2$Te$_2$Se and Bi$_2$Se$_2$Te ternary tetradymites are bulk topological insulators, confirmed computationally by verifying band inversion between group V and VI $p_z$ orbitals. We validated and then used band structures of a large (three quintuple-layered) slab model to study surface-band features, including the warping of DC and its associated spin texture. The location of the DP for Bi$_2$Te$_2$Se and Bi$_2$Te$_2$S (111) surfaces is like that of Bi$_2$Te$_3$. We also present dispersion for the energetically preferred partially disordered Bi$_2$Se$_2$Te (via an ordered approximate) that showed it had a favorably located surface-derived DP near $E_f$ in the bulk-band gap like Bi$_2$Se$_3$ but with a larger spin texture. We studied a hypothetical Bi$_2$Se$_2$Te structure to show that substitution in the central layer affects the shape of DC and the associated spin texture, while substitution in outer layers affects the location of the DP and dispersion of valence band. Due to high defect-formation energy, Bi$_2$Te$_2$S should have a large bulk resistivity needed to realize a workable device.

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