Topological Insulators

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Topological Insulators from a Chemist's Perspective**

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Topology and chemistry are deeply entangled subjects, which manifests in the way chemists like to think and approach problems. Although not at first glance, topology allows the categorization of fundamental inherent properties of the huge number of different chemical compounds, carving out the unique features of a class of materials of different complexity, a topic which Turro worked out in his treatise on geometrical and topological thinking in chemistry.[1] Chemists most frequently encounter the concept of topology with regards to chirality, as molecules with different chiralities can have different physical and chemical properties (Figure 1 a). The isolobal concept is a topological principle on a more abstract level, grouping together compounds with similar properties independent of their composition. Topologically interesting compounds are $4n$ aromatics with Möbius geometry,[2] whereas normal $4n$ compounds are anti-aromatic (Figure 1 b). Furthermore, topology (knot theory) has inspired the synthesis of new kinds of catenanes, which are a truly synthetic challenge.[3]

These approaches all deal with the real-space topology of molecules. In physics, however, it is the topology of the underlying mathematical space that has been explored, beginning with the work of Chern,[4–6] and it has been studied in the context of high-energy extensions of the standard model using quantum field theory.[7] A recent idea has been to study these concepts by condensed matter physics in real systems.[8] Topological insulators (TIs), a newly identified class of compounds, might thus bring together condensed matter physics and solid-state chemistry. Not only are TIs the subject of intensive research in fundamental and applied branches of condensed matter physics,[8–15] but they could also be a new exciting subject for solid-state chemists and materials scientists.[16] Herein, a simple treatise of new topological insulators based on bonds, bands, symmetry, and nuclear charge will be given to motivate a systematic search for new topologically nontrivial materials by chemists and materials scientists.

The mathematical space of interest here is the reciprocal space (k space); that is, the topology of the band structure of compounds. Inorganic chemists are experts in understanding materials and their electronic structure. The topological classification of k space can be mapped onto simple pictures in inorganic chemistry, such as crystal structures, valence electrons, nuclear charges, and the phase of orbitals. Moreover, TIs can be predicted by electronic-structure calculations and even designed by band engineering.[17,18]

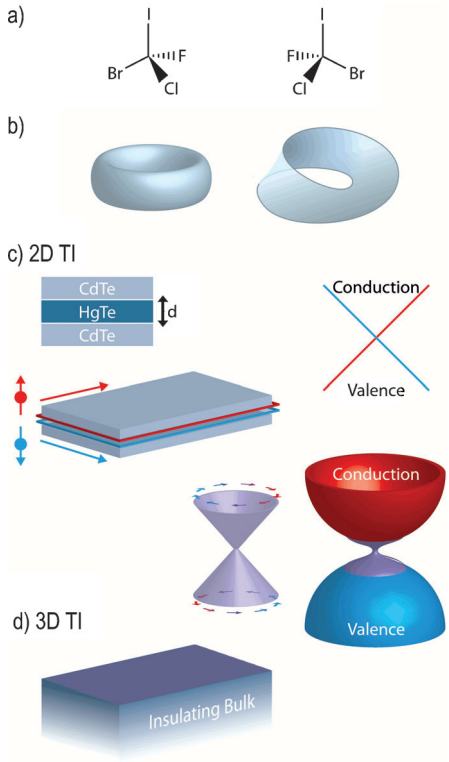

Figure 1. a) A pair of nonsuperimposable isomers (enantiomers) b) Two topologically different structures that cannot be converted into each other by stretching and bending alone. c) A two-dimensional topological insulator (2D TI). Only one of the one-dimensional counter-propagating edge states is shown for each surface. d) 3D TI and schematic band structure with a Dirac cone.

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Topological insulators are materials with a bulk band gap generated by strong spin–orbit coupling (SOC) and topologically protected metallic surface states. The material is insulating in the bulk, but metallic at the surface. A TI can be identified by a few rules: SOC, an odd number of band inversions (BIs) between the conduction and the valence band by increasing the average nuclear charge, and a sign change of the symmetry of the molecular orbitals. These signatures in the electronic structure usually cause TIs to be excellent thermoelectric materials,[19] because similar features in the band structures are favorable for both properties. Although the understanding of the direct theory behind this relationship is incomplete, the correlation between TIs and thermoelectric materials has guided the discovery of new TIs.[16,20] However, excellent thermoelectric materials can be also topologically trivial (a compound is called topologically trivial if there is an even number of BI and thus no special surface state).

There are two large families of TIs currently known, the HgTe family and the Bi_2Se_3 family. Many of new exciting properties were predicted by theory, but only a few have been realized experimentally. The reason is the lack of high-quality samples with well-defined charge carriers and control over disorder and defects. There is a marked need for new materials such as highly correlated, magnetic, superconducting, and wide band-gap TIs for many applications, including those at high temperature.

These compounds constitute a new quantum state of matter, giving rise to the quantum spin Hall (QSH) effect.[10] The new states consist of two counter-propagating, dissipationless spin currents for spin-up and spin-down electrons (Figure 1c), and thus the total charge current vanishes in the ground state while a pure spin current is realized, which is a long envisioned dream of spintronics.[21] Using transport measurements, these spin currents can be observed, and the special dispersion of the surface state, called a Dirac cone, can be measured directly by angle-resolved photoemission spectroscopy (ARPES).[22] The Dirac cone is a well-known feature consisting of two bands with linear dispersion, shaped like an X (see Figure 1d), known from the electronic structure of graphene. The surface-state character can be proven, because it is two-dimensional (2D) without dispersion perpendicular to the surface. However, a TI hosts robust surface states forming an odd number of Dirac cones, while graphene, with four Dirac cones in the bulk, is topologically trivial.[23]

All compounds that are topologically nontrivial can be divided into two groups: 2D and 3D TI materials (Figure 1c,d). These dimensionalities are related to the crystal structures of the materials. 2D TIs are typically cubic semimetals with a zero bulk band gap originating from a degeneracy of the valence and conduction bands. For 2D TIs, the QSH effect was predicted and observed in the binary semiconductor HgTe.[22,24] To open a bulk gap and recover the QSH state, additional symmetry breaking is required. This was realized in a quantum-well structure composed of HgTe and CdTe.[25] For an HgTe layer of well-defined thickness, topological edge states are observed at the edge of the quantum well (Figure 1c). In 3D TIs, the topological states exist on the surface of a single crystal (Figure 1d) and are therefore easier to measure. These materials have lower symmetry and should be semiconductors in the bulk. However, this assumes that the single crystal is highly ordered and free of defects.[14,15] In Bi_2Se_3 and related structures, 3D TI behavior was observed in ARPES.[26,27] The surface states form robust Dirac cones in the electronic structure. However, the corresponding single crystals as well as the thin films often exhibit large metallic conductivity that strongly dominates the contribution of the topological surface states in transport measurements.

To develop a method for designing and searching for new TIs, we wish to focus on the relatives of HgTe that have a zinc blende structure, with the goal of elucidating all the ingredients of the electronic structure that contribute to its TI property. The quantum-well structure in CdTe/HgTe/CdTe is the only system for which transport properties have unambiguously proven the topological character, but recently experiments on InAs/GaSb quantum wells have shown similar results.[28,29]

Figure 2 shows the large family of newly identified TI systems related to HgTe.[17,18,22,24,30–32] A similar diagram could be drawn for compounds related to Bi_2Se_3. HgTe belongs to the large family of binary semiconductors that crystallize in a zinc blende structure, which can be described as a cubic-closest-packed (ccp) main-group metal lattice with tellurium in half the tetrahedral sides, as shown in Figure 2a. The filled structures are the Heusler compounds with additional atoms at the octahedral side (Figure 2c) and inverse Heusler compounds, such as Li_2AgSb (Figure 2e) with all tetrahedral and octahedral sides filled in the ccp structure of the main-group metal (Sb, Bi, or Te). Another variant is Ag_2Te in the high-temperature cubic phase, corresponding to an inverse CaF_2 structure (Figure 2b) with fully occupied tetrahedral

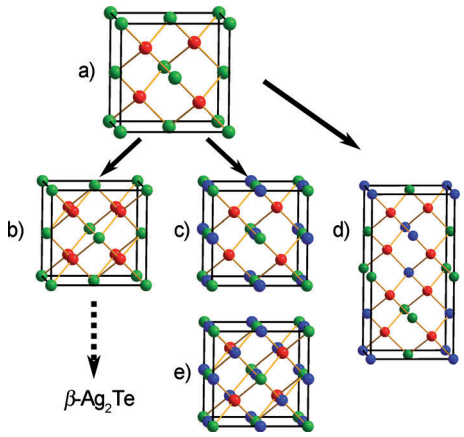

Figure 2. Crystal structures of topological insulating compounds based on the tetrahedral structure. HgTe (a) is the parent compound. Occupation of the tetrahedral vacancies (b) leads to a family with an inverse CaF_2 structure (high-temperature α-phase of Ag_2Te), whereas filling up the octahedral vacancies leads to the family of Heuslers (LaPtBi) (c). By adding more "stuffing" atoms to a Heusler, the so-called "inverse" Heusler structure is obtained (Li_2AgSb) (e). Doubling the cubic Heusler unit cell leads to a chalcopyrite structure ($AuTlS_2$) (d).

positions. A second low-symmetry structure family is the chalcopyrites, which are famous for their low-cost solar-cell applications ($CuIn_{1-x}Ga_xSe_2$). Their structure can be viewed as a doubled zinc blende cell with a trivalent In or Ga and a divalent Zn substituted by monovalent Cu (Figure 2d). The tetragonal symmetry breaks the $p_{x,y,z}$ degeneracy and thus opens a finite band gap.

To understand the nature of TI materials, we do not need to delve into the theoretical background or call upon quantum field theory. The great advantage of TIs is that they can be designed by following simple recipes in contrast to other phenomena, such as superconductivity. Binary semiconductors, such as GaAs and CdTe, are semiconducting because of a hybridization gap between the bonding and antibonding sp^3 bands, similar to those in diamond and silicon. The band gap of these tetrahedral structures is determined by the energy separation of the bonding (eight electrons filling up four bands, one s and three p bands or four sp^3-bands) and the antibonding states. The band gap is large if the bonding interaction is strong and small or even nonexistent if the bonding strength is small. CdTe is a trivial semiconductor with a 1.5 eV gap between the p-type valence band (blue) and an s-type conduction band (red; Figure 3a). Binary semiconductors containing light elements, such as ZnS and GaN, exhibit strong hybridization of the s and p bands; the hybridization, however, is weaker for binary semiconductors containing heavy elements. The band structure of HgTe (without SOC) is shown in Figure 3b.The bonding and antibonding s states nearly fall together with the blue (parabolic-like) degenerated p bands at the Γ point. The SOC (Figure 3c) splits the degenerated p states into $p_{1/2}$ and $p_{3/2}$ components. In contrast to a lighter CdTe, the s band of HgTe appears below E_F. The resulting band structure of HgTe is semimetallic, as the cubic symmetry keeps the parabolic-like $p_{3/2}$ states degenerate, preventing the opening of a real band gap. If the cubic symmetry is broken, the SOC opens a finite band gap at E_F.

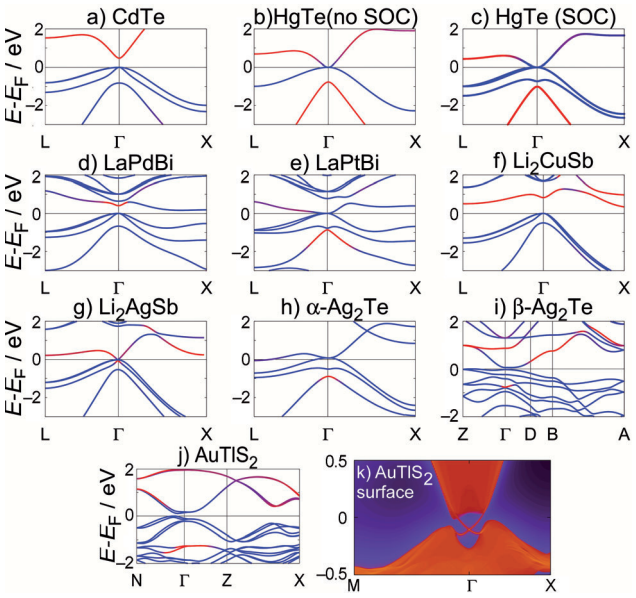

Figure 3. Comparison of the electronic structure of semiconductors and semimetals within different structures types. The s bands are drawn in red and p bands in blue.

Similar scenarios exist in analogous systems, such as the Heusler compounds. As the ternary *XYZ* Heusler class is extremely rich with more than 250 semiconductors and semimetals, it provides much greater flexibility in design by tuning the band gap and SOC. The electronic structure of the semiconducting 18-valence-electron Heusler compounds is strongly related to binary semiconductors, such as CdTe and HgTe, which also have 18 valence electrons (including the d electrons). The structure of the XYZ Heusler compounds can be viewed as "stuffed" YZ zinc blende.[17] Interestingly, the introduction of rare-earth metals into a semiconducting XYZ Heusler material does not change the electronic structure and semiconducting properties significantly, because the f states of the rare-earth materials are strongly localized. Formally, a RE element adds only three electrons to the total electron number, namely 2s and 1d electrons. An example of semiconducting compounds with rare-earth metals is the family of LnPdBi materials,[33] in which Pd, the rare-earth metal Ln, and Bi contribute 10, 3, and 5 valence electrons, respectively, which again sums to 18. Furthermore, the rare-earth atoms add new properties such as superconductivity or magnetism and defines this class of multifunctional materials.[34–40] Based on band-structure calculations, many Heusler materials have been suggested as potential TIs,[17,18] such as ScPtBi. Topological trivial and nontrivial semiconductors with inverted band structures can be designed by increasing the average nuclear charge of the ternary compound. LaPdBi (Figure 3d) exhibits a band structure similar to CdTe, whereas LaPtBi exhibits the same BI as HgTe (Figure 3e). A BI can be achieved even for the inverse Heusler compounds (Figure 3f,g). Li_2AgSb is a borderline compound, located at a so-called quantum critical point between a trivial and a topological insulator. The s and the p bands are degenerate at E_F even when SOC is taken into account. A similar situation was found for the XYZ Heusler compound YPtSb.[17,40,41] The heavier compound Li_2AuSb becomes metallic in the bulk however.

For all of the cubic TIs discussed herein, the problem still remains that the TI state is formed only by breaking the cubic symmetry, that is, by fabricating a quantum-well structure or by straining the structure on the surface. To expand the number of known TI materials, it is necessary to search for new low-symmetric chemical relatives exhibiting the intrinsic TI state, the 3D TIs. Fortunately, some relatives of HgTe exist in a distorted version of the cubic structure, such as Ag_2Te and the heavy chalcopyrite compounds. The structural distortion causes the degeneracy of the p states at the Fermi energy to be lifted and a band gap to be opened for Ag_2Te and $AuTlS_2$ (see Figure 3h–j). Owing to this symmetry breaking, the TI changes from 2D to 3D.[32,42] The Dirac cone can now be directly observed in surface state calculations, because of the bulk band gap (Figure 3k), which is the ultimate proof of the nontrivial nature of the compound. BI between the s and p states can be observed in many narrow-band-gap semiconductors with heavy elements, for example in PbTe, which is also known to be a good thermoelectric material. However,

PbTe is not a TI because the BI takes place on the L point in the reciprocal space and is therefore similar to graphene, as the L point appears four times and an even number of BIs does not lead to topological edge or surface states.

This even/odd condition enables the systematic search for new TI compounds. To find new 3D TIs, it is necessary to search for narrow-band-gap semiconductors consisting of period 4 elements having an odd number of BI. The BI at the Γ point is visualized in Figure 4 for the trivial semiconductor

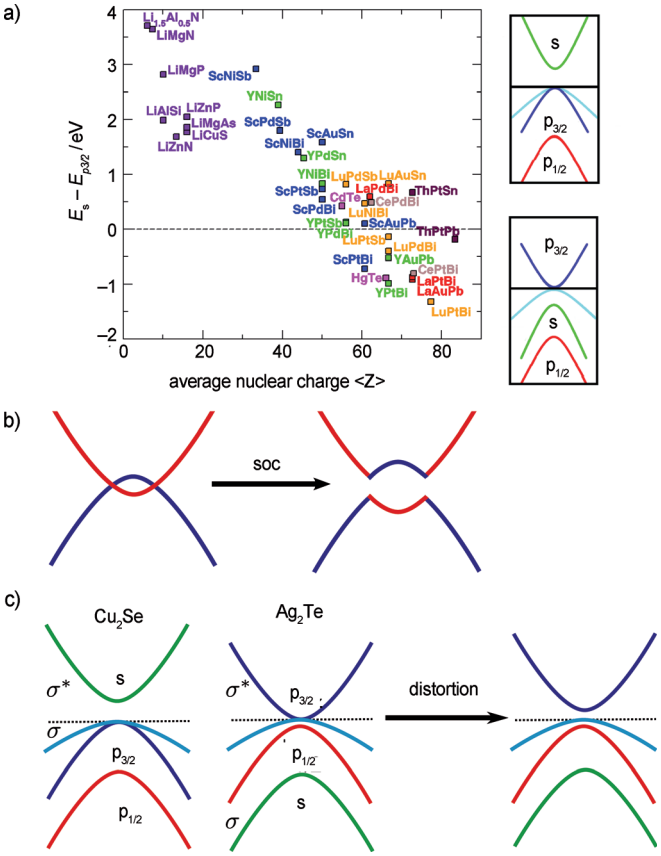

Figure 4. a) Band ordering as a function of the average nuclear charge in half-Heusler compounds. b) Mechanism of the opening of the bulk band gap owing to spin–orbit coupling. c) Change in bonding of the molecular orbitals at the Γ point for the trivial semiconductor Cu_2Se and the nontrivial semiconductor Ag_2Te. The BI of the s and p bands leads to a change of parity. Owing to symmetry breaking, a bulk band gap opens and the BI remains.

Cu_2Se and the nontrivial semiconductor Ag_2Te with an inverted band structure. In these compounds, the BI between the s and p states leads to a parity change. By inverting the antibonding s band and the p band, the s band becomes bonding below E_F. In the case of Bi_2Se_3, the BI occurs between the Bi p_z and Se p_z bands.[26,27] Another example are the skutterudites or PuTe, which both show a d–f inversion.[20,43] Suprisingly, PuTe is a 3D TI with a bulk band gap, although it crystallizes with the simple NaCl structure. The compound is strongly correlated, and as Pu is the element with the largest spin–orbit coupling, a large bulk band gap is opened.

Will the same mechanisms found in the diamond structure work in graphite-like systems as well? Some of the 18-valence-electron semiconductors crystallize in structures that are different to Heuslers, for example, in the ZrBeSi structure type, a "stuffed" heavy variant of graphite that is similar to MgB_2.[44] However, there is an important difference between KHgSb, a member of the ZrBeSi family, and LaPtSb, as the former has a double-layered honeycomb structure. KHgSb has two BIs between the Hg s and Sb p states at both the Γ and A point, causing the compound to be a trivial semiconductor.

Summarizing, we believe this is a sound methodology to guide the exploration for new TI materials. In general, good thermoelectric materials are candidates for TIs, as all TIs exhibit excellent thermoelectric properties, but many thermoelectrics are topologically trivial. Structure classes with a large number of semiconductors and a wide band-gap range are most promising. Semiconductors made of heavy elements have excellent potential, as they provide a strong SOC in addition to the small band gap. An odd number of BIs at high symmetry points of the Brillouin zone, which leads to an odd number of Dirac cones on the surface, is necessary. In the compounds discussed above, this will happen at the Γ point. Typically, this occurs in cubic zero-gap semiconductors where the symmetry reduction is necessary to recover the bulk insulating state. The critical characteristic for identifying TIs is the parity change, which can be easily proven for centrosymmetric compounds by drawing the orbitals based on the calculated eigenvectors.[45,46] Finally, to prove the existence of the topological surface states unambiguously, the presence of the Dirac cone in the surface band structure must be inspected.

In the end, there is still a need for new materials with large gaps to observe the predicted properties at room temperature. Also worth pursuing are materials possessing a combination of functionalities, such as the quantized anomalous Hall effect and topological superconductors.[14,15] It is furthermore time to search for new TIs in the rich class of oxides. A good point to start could be a period 4 compound that is semiconducting, while the period 5 compound is metallic. The period 6 compound should then be semiconducting again.

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