Realization of predicted exotic materials: The burden of proof

Alex Zunger1*, Oleksandr I. Malyi1,2, Gustavo M. Dalpian1,3, Xingang Zhao1 and Zhi Wang1

1Renewable and Sustainable Energy Institute, University of Colorado, Boulder, Colorado 80309
2Centre for Materials Science and Nanotechnology, Department of Physics, University of Oslo, P.O. Box 1048 Blindern, NO-0316 Oslo, Norway
3Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 09210-580, Santo André, SP, Brazil

*Corresponding author
e-mail: Alex.Zunger@Colorado.edu

Abstract

Trove of exotic topoloid structures has recently been predicted by searching for compounds whose calculated band structure crossing points fulfill specific symmetry requirements. Discovery of exciting physical phenomena by experimental studies of such predicted compounds is just around the corner. Yet, examination of some of these assumed high-symmetry structures suggests that not always will assembly of atoms in a configuration that yields exotic topological properties be protected against energy-lowering symmetry breaking modes. Although bulk topological characteristics lead to protected surface/edge states, nothing protects bulk states from structural instability. It is illustrated how the use of the calculated total (electron + ion) energy of such candidate structures can be used as the next ‘material selection filter’, identifying and removing false-positive predicted topoloids from the list of likely realizable compounds, to the benefit of the much-cherished iterative process of theory-experiment materials discovery.

Keywords: topological materials, stability, electronic structures, symmetry breaking, materials discovery.
Introduction

One of the most exciting recent developments in condensed matter physics and solid-state chemistry is the discovery of topological behavior of matter[1–8] that has predicted unique transport properties at lower dimensions. Laboratory examination of the fascinating predicted properties of such topological phases naturally requires identifying synthesizable and stable, topology-bearing compounds (‘topoloids’). The approach used stipulated ‘given the target property, find the compound that hosts it’, (the inverse problem[9,10]) and involves two steps. First, define the requisite theoretical target conditions that would, in principle, enable topology, (such as specific crystal symmetries and band degeneracies), and second, search for physical realizations (i.e., compounds) that will have such symmetry-mandated band structures. This approach has already provided thousands of specific predictions of real topoloid compounds[11–25] (recently reviewed in Nature News25) that should be topological insulators (TI’s), or topological crystalline insulators (TCI), Dirac and Weyl semimetals or unconventional quasiparticles. Experimental discovery of exciting new physical properties in these predicted compounds is a much-anticipated exciting prospect[25].

Yet, despite the recent predictions of thousands of topological compounds in the world, very few such compounds have been actually synthesized and proven to be topological. We note that the predicted topoloids were generally based on the assumption that the crystal will take up the highest symmetry possible, not considering the possibility of energy-lowering symmetry breaking that obviates topological properties. Both experimental and theoretical databases of structures and properties of compounds sometimes omit information on magnetism, spontaneous defect formation, or how would the structure change should significant doping be required. Furthermore, in the case of polymorphous networks—structures requiring for their description large unit cells because they have a distribution of different local motifs—experimental X Ray structure determination often approximate the structure by an artificial, high symmetry primitive unit cell describing the macroscopic average configuration. All of these factors can affect the assumed symmetry of the structure and the ensuing wavefunctions, thereby misrepresenting the real correct topological class. While undoubtedly more of the projected topoloids from the published lists of candidates[11–24] will be confirmed with time, we hold that the required next steps before offering theoretically predicted topoloid compounds for experimental synthesis and evaluation should involve the theoretical projection of their stability towards symmetry breaking perturbations, as well as their synthesizability. Indeed, assembling atoms in a configuration that yields the topology-promoting band structure energies, does not necessarily protect against symmetry breaking modes that lower the total energy, signaling structural instability. Although bulk topological characteristics lead to protected surface/edge states, nothing protects bulk states from thermodynamic instability. Fortunately, this type of assessment can be readily accomplished by using the sister quantity that goes hand-in-hand with the band structure calculation of such compounds – the total electron+ ion energy of the said compounds. This needed next step of inspecting the total energies, following the already remarkable search for single-particle (band) energies that promise topological properties[11–24] would complete the burden of proof (as far as theory is concerned) for recommending for experimentation not only exotic, but also potentially realizable materials that host with structural impunity exotic properties.

We illustrate a number of prototypical failure modes that can arise from restricting the predictions of topoloids to the examination of their band structures single particle energies alone. We show how the use of the total energy[26,27] as an additional material selection filter might help avoid such false-positive predictions. The prototype modalities discussed are:

(i) The hypothetical structure that host topology is unstable: The selected crystal structure that manifests topology may not be the lowest energy structure. This is illustrated for the first predicted Dirac semimetal in three dimensions BiO$_2$ in assumed cristobalite SiO$_2$ structure[19] which is shown here to be dynamically (phonon) unstable and disappears if its structure is allowed to relax to the energy-lowering stabler structure.
(ii) **Symmetry lowering by spontaneous defect formation defeats topology:** The newly predicted unconventional quasiparticle in BaBiO$_3$[17] is destabilized by the spontaneous (energy lowering) formation of Bi vacancies that condense into Ordered Vacancy Compounds (OVC’s)—whose symmetry defeats topology.

(iii) **Symmetry lowering by magnetism (spin-polarization) removes the topology-promoting band degeneracy:** This is illustrated for the predicted 8-fold band degeneracy of metallic CuBi$_2$O$_4$[17] in assumed nonmagnetic configuration, a degeneracy that is found here to disappear and be replaced by a wide energy gap, once energy-lowering, magnetic spin-polarization is allowed.

(iv) **The predicted topological property requires doping that inherently destabilizes the topological structure:** illustrated for BaBiO$_3$[18] that requires an upshift of the Fermi energy by ~2 eV to meet the inverting energy bands. This occupation of massively antibonding states leads to a destabilizing increase in $E_{\text{tot}}$, relieved by structural transformations that defeat topology.

We have studied only a few compounds from the published literature of conceived topoloids, but despite being a ‘low-throughput’ approach, these already illustrate possible failure modalities. Fortunately, these failure modes can be examined by using simple, additional ‘search filters’ from the same density functional theory used to establish the requisite target band structure, i.e., the total energy.

The approach

Identifying actual realizations of topological compounds requires theories with full atomic resolution that recognize site and space symmetries in crystals. Here, the definition of ‘compounds’ may be thought as a trio of descriptors—atomic identities (A), compositions (C) and structure (S) (or ACS, in short). The recent rebirth of density functional band theory (DFT) of solids (and higher-order theories that use DFT to initialize the problem, such as DFT-DMFT[28], DFT-GW[29,30]; DFT-QMC[31]) as a tool for uncovering topological behavior hidden in the spaghetti-like energy band structure, lies in DFT’s ability to directly decode the consequences of an assumed ACS on the band structures. This affords a direct mapping of the theory onto the Periodic Table, via explicit incorporation of the electron-ion potential $V_{\text{ext}} = \sum -Z_{\alpha} |r - R_{\alpha}|$ in the single-particle problem, where $\{Z_{\alpha}\}$ are the atomic identities defined by atomic numbers or pseudopotentials, $\{R_{\alpha}\}$ are the atomic positions with the appropriate periodic boundary conditions defined by the lattice vectors, and the sum extends over all atoms in the compound, thereby defining composition and stoichiometry. This remarkable recent development of searching for ACS that host the conditions for topology[11–22,25] departs from the more traditional approaches to the search for compounds hosting other types of quantum behavior—unusual superconductivity; quantum spin liquids, or Kitaev unconventional magnetism. Such approaches[32,33] provide general guidance by specifying via ‘scenario Hamiltonians’ the required, generic renormalized interactions that are not mappable onto the Periodic Table, and thus do not commit to the chemical identity of the compound hosting such interactions, making the material identification process one of the successive guesses.

To examine realizability of the predicted ACS that host topology it may be wise to use not only the band single-particle energies as design filters but also the DFT total energy ($E_{\text{tot}}$) and its derivatives with respect to displacements (forces, force constants) of the given crystal.[27] This total energy is given by

$$E_{\text{total}} = \sum_{i} \psi_{i}^*(r)(-\nabla^2)\psi_{i}(r)dr^3 + \sum_{i,\mu,\lambda} \psi_{i}^*(r)U_{\mu\lambda}^{(i)}(r - R_{\mu})\hat{P}_{\lambda}(r)dr^3 + \frac{1}{2}E_{\text{ex}} + \frac{1}{2}E_{\text{ion-ion}} + E_{\text{sc}}$$

Where the kinetic energy is

$$\sum_{i} \psi_{i}^*(r)(-\nabla^2)\psi_{i}(r)dr^3$$

The electron-ion energy is
The electron-electron Coulomb energy is

$$\sum_{i,\mu,l} \psi_i^*(r) V_{\mu i}^{(l)} (r - R_\mu) \hat{P}_l \psi_i(r) dr^3$$

(3)

The electron-electron Coulomb energy is

$$E_{ee} = \frac{2}{3} \int \frac{\rho(r) \rho(r')}{|r - r'|} dr^3 dr'^3$$

(4)

The ion-ion lattice energy is

$$E_{\text{ion-ion}} = \sum_{\mu,\nu} \frac{2Z^2}{|R_\mu - R_\nu|}$$

(5)

Here, $E_{xc}$, $Z$, $R_\mu$ are the exchange-correlation energies, valance of the ion and the lattice vector, respectively. And $\hat{P}_l$ is the projection operator on angular momentum $l$.

The need to use the total energy as additional filters for material selection arises both because some candidate topoloid has been assumed to take up a hypothetical structure or composition not known to exist. Also, even if the selected structure does exist nominally, it is possible that simple microscopic mechanisms can create structural changes that defeat topology. Such situations are easily diagnosed by co-evaluation band structure conditions for topology, along with the potential instability with respect to total energy lowering deformations that defeat topology. The details of the methods used are described in Supplementary S1.

We note that long-lived metastable structures protected by practically insurmountable activation barriers certainly exist in special structures. Famous examples include the high activation barrier in the diamond-to-graphite transformation associated with the need to break three strong hexagonal bonds before remaking four tetrahedral bonds; or the low likelihood of two nitrogen atoms to meet and form the ultra-stable N₂ molecule in unstable nitrides. However, seeking stable topoloid compounds from ordinary three-dimensional inorganic compounds is nevertheless a good idea, because metastable compounds in given structures may be difficult to make, in the first place, and if made, may create vulnerability towards decomposition during the inevitable perturbations (current; temperature) common in the conceived device applications. We also note that even though energy lowering symmetry breaking can remove the intended topological class originally assigned, other topological symmetries may exist in the symmetry broken state. For example, whereas cubic bulk HgTe might have been a TI because of its band inversion, it is a TI only after some gentle perturbation is applied to infinitesimally remove the degeneracy of the hole band (e.g creating a quantum well CdTe/HgTe/CdTe), thereby converting it from metal to insulator[34]. However, the symmetry breakings illustrated below are not particularly gentle, and seem unlikely to leave remnant topology.

**Results and Discussion**

**A. False-Positive type 1: The hypothetical structure that host topology is thermodynamically unstable**

BiO₂ in the assumed cubic (Fd-3m) SiO₂ Cristobalite crystal structure was predicted to be the first 3D Dirac semimetal (the special degeneracy point circled in Fig 1a in red)[19]. However, Bi with its five $s^2p^3$ valence electrons may not have the type of bonding akin to fourfold valent Si ($s^2p^2$); even if Bi would disproportionate to $\text{Bi}^{3+}(s^2p^0) + \text{Bi}^{5+}(s^0p^0)$, its electronic structure cannot reflect an *average* configuration $\text{Bi}^{4+}(s^2p^2)$.

To examine this basic intuition, we calculated the Bi-O ground state (T=0) convex hull — the total energy of all conceivable known and hypothetical leading structures, examining the lowest energy structure at each composition and then identifying stable compositions that do not decompose into pairs of lower + higher compositions. The resulting ground state line (Fig. 1b) shows that hypothetical BiO₂ structure is a high energy
phase; the Cristobalite structure is significantly higher in energy (263 meV/atom above the convex hull) than numerous non-cristobalite structures at lower energies (squares in Fig.1b), so there is no apparent reason that it will form in that structure rather than any of the many lower energy phases. In order to check the finite temperature effects on the ground state diagram, we calculated the free energy at high temperature by using the machine learning model reported by Bartel et al.[35] as described in the supplementary section S2. Our conclusion is that raising the temperature does not turn the cristobalite structure into a stable or near-stable structure. Examination of the harmonic phonon dispersion curves (Fig 1c) shows that this SiO$_2$ structure of BiO$_2$ is dynamically unstable, and therefore cannot exist as such. In the band structure of the phase that replaces the SiO$_2$ polymorph (Fig 1d) we observe that this material is, in fact, an insulator (see the gapped region in green) and so does not have the topological band property akin to the predicted hypothetical cristobalite structure. We conclude that the cristobalite crystal structure of BiO$_2$ is not a likely stable compound and the structures that are stable are not 3D Dirac semimetals.

**Figure 1.** Electronic and phonon structure of the predicted first 3D Dirac semimetal BiO$_2$: Band structure of the metallic cristobalite SiO$_2$-type, Fd-3m assumed structure showing the Dirac point (red circle) (a). Total energy convex hull of all phases showing that SiO$_2$-type BiO$_2$ is significantly (263 meV/atom) above the ground state line (b). Phonon dispersion of the cristobalite structure (c), showing dynamically unstable modes (yellow highlights) and band structure of the lowest energy monoclinic (C2/c) BiO$_2$ phase that is no longer a metal (gap in green highlight), (d).

There are scores of other structures that were predicted to be topological in what was found to be chemically or thermodynamically unstable forms[20–22]. Among other channels, a structure can be unstable with respect to another structure type, or with respect to decomposition into its constituents. Both channels of instability, as well as the effect of finite temperature (supplementary S1 and S2) can be examined[36].

One example is the prediction of new topological insulators with the highly desirable light elements ($Z < 50$) LiAgSe and NaAgSe in the assumed honeycomb-lattice[20]. On examination, it turns out that the ZrBeSi-type structure of LiAgSe and NaAgSe is not the ground-state structure.[37] According to total energy calculations performed on more than 50 potential crystal structures, LiAgSe crystallizes in a LiCaN structure while NaAgSe...
crystallizes in the PbCl₂-type structure. Furthermore, LiAgSe in the ZrBeSi-type structure is unstable with respect to dissociation into Li₂Se and Ag₂Se[37].

Lin et al.[22] predicted topological insulators among the ~ 2000 tested 18-electron half Heusler ABX compounds, assuming universally the cubic F-43m structure (α-type), finding exceptionally promising large inversion energies in 11 compounds, 8 based on I-Au-XVI (I = Li, Na, K, Rb and XVI = O, S) and 3 involving Pd and Pt: LiPdCl, SrPtS, and BaPtS. However, the same DFT calculations extended to standard stability check[36] find that these latter compounds are unstable with respect to decomposition into their constituent binary compounds, and that[38] the assumed α-type structure for the former group (Li, Na, K, Rb)Au(O,S) are not the ground state; the latter involve rather different structure types instead.

Another example is the predicted wide gap oxide TI YBiO₃[21]. Finding an oxide topological insulator that has a wide inversion gap has been sought for a long time, as it would overcome the inadvertent doping problem common in narrow gap TIs such as Bi₂Se₃ and could be integrated with the many oxide material functionalities such as ferroelectricity. Jin et al.[21] predicted through band structure calculations that YBiO₃ in the assumed CaTiO₃-type cubic perovskite structure (Pm-3m) with the Bi atoms located at the Oh (1a Wyckoff position) would be a TI with an insulating indirect gap of 0.18 eV and a direct gap of 0.33 eV. However, relaxing the lattice constant of YBiO₃[39] from the previously used 5.43 Å to the density-functional minimum energy equilibrium value for the same Pm-3m perovskite (a = 4.405 Å)[39] lowers the total energy by ~1 eV, whereas relaxing the condition that the structure is of the Pm-3m perovskite type lowers the total energy by another ~1 eV. The resulting stable structure is not a TI.

### B. False-Positive type 2: Symmetry lowering by spontaneous defect formation defeats topology

Ba₃Bi₃ in space group 220 is an example of a recently predicted unconventional quasiparticle[17] that remarkably has no analogy in particle physics. Its characteristic feature is the 8-fold degeneracy at the H point and 3-fold degeneracy at the P point of Brillouin zone (Fig 2a, red circled ellipse). This degeneracy is a consequence of specific non-symmorphic symmetry existing in the space group 220. Fig 2a constitutes the electronic structure description of the predicted unconventional quasiparticle.

The band structure of Fig 2a has a particularly unusual feature: a band gap (light-green shaded) above the Fermi level Er, the latter being deep inside the valence band, indicating plenty of hole states (blue shaded region) in the valence band. This particulate electronic configuration might be unstable with respect to the spontaneous formation of intrinsic structural defects that compensate holes, i.e., defects that form electrons (donors). Such donors, formed above the Fermi energy would then transfer their electrons to the lower energy unoccupied hole states, thereby lowering the total energy of this defected structure relative to the ideal, perfect lattice. The formation of low-temperature stable defects is known in other systems with a band gap above the Fermi level e.g., in Sc₂S₃[40–43] or in electrides such as Ag₃Al₂₂O₃₄[44]. Note that spontaneously formed defects are different from conventional defects that require energy for their formation and therefore exist in small quantities and only at elevated temperatures.

To examine this basic physical intuition, we calculated the total energy of the simplest donor defect namely Bi vacancy (see supplementary section S1 for details of defect calculations) in 16 formula units of Ba₃Bi₃ supercell (112 atoms). Fig 2b shows the DFT calculated formation enthalpy of dilute Bi vacancy in Ba₃Bi₃, as a function of the Bi chemical potential, indicating that such defects would indeed form exothermically. The existence of dilute, stable defects further suggests the possibility of condensation of vacancies into ordered arrays (as in Sc₂S₃). To examine this possibility, we have calculated the T=0 K stable phases of such structures by considering a replica of 16 Ba₃Bi₃ units with p Bi vacancies, searching via total energy minimization for stable and metastable configurations. The result detailed in supplementary section S3 shows that ideal Ba₃Bi₃ with holes in the valence
band is a metastable structure with energy above the ground state convex hull, whereas Ba$_4$Bi$_{3-x}$ with vacancies is the ground state, as donor electrons relax into the low energy hole states.

**Figure 2.** Spontaneous vacancy formation destroying band degeneracy in Ba$_4$Bi$_3$. The band structure(a) of ideal Ba$_4$Bi$_3$ in space group 220, showing the special degeneracy points (red circles) creating the topological properties of this predicted unusual quasiparticle. (b) Defect formation energy of Bi vacancy in Ba$_4$Bi$_3$ as a function of the Bi chemical potential. The chemical potential stability zone is shown in light yellow color, demonstrating the negative (i.e., exothermic) formation of Bi vacancies over a broad chemical potential range. The unfolded band structures for Ba$_4$Bi$_{3-x}$ containing about 2% of Bi vacancies is shown in (c) with a zoom-in shown in (d), indicating the disappearance of the special, topology-creating degeneracy. Supplementary section S3 shows the splitting of the Dirac cone as a function of the concentration of Bi vacancies.

The energy bands of the Ba$_4$Bi$_3$ structure with 2% of Bi vacancies are shown in Fig 2c, d. To follow what happens to the special degeneracy point in the band structure of the ideal solid (ellipse in Fig 2a) once vacancies are formed, we unfolded the 16 formula unit supercell band structure containing vacancies to the band structure in the primitive Brillouin zone, using the Effective Band Structure method[45–47]. We see that upon formation of even dilute Bi vacancies, the special degeneracies at the H and P points, responsible for the topological properties, are removed, as the defects lower the symmetry of the lattice, hence also breaks the symmetry operators that protect the degenerate points. Supplementary section S3 shows the energy splitting of the two degenerate points as a function of vacancy concentration, demonstrating a sizeable splitting of over 100 meV is possible. We conclude that Ba$_4$Bi$_3$ in space group 220 structure is unlikely to retain this local symmetry needed to sustain the special, 8-fold degenerate topological point because intrinsic, symmetry breaking vacancies would form exothermically. The experimental literature on Ba$_4$Bi$_3$ is very limited. Synthesis of Ba$_4$Bi$_3$ was achieved by direct reaction of the corresponding elemental by Li, Mudring and Corbett[48], who noted 1/9 random vacancies on the (Bi) anion lattice in this family, and resistivity characteristic of a moderately poor metal, consistent with an anticipated one electron deficiency per formula unit for Ba$_4$Bi$_3$. These observations are entirely consistent with our picture of the electronic structure that may defeat topology.
C. False-Positive type 3: Symmetry lowering by magnetism (spin-polarization) removes the topology-promoting band degeneracy: CuBi$_2$O$_4$

CuBi$_2$O$_4$ in the tetragonal P4/ncc crystal structure (space group 130), was predicted\cite{49} to be a realization of an exotic eightfold metallic Fermion (Fig 3a) owing to its specific Bravais lattice, that requires this degeneracy at the time-reversal invariant A point. The band structure (Fig 3a) and the density of states (Fig 3b) – calculated\cite{49} assuming a non-spin polarized configuration for the Cu atoms—show a metallic behavior and an ‘intermediate band’ where the degenerate Fermi energy resides. This constitutes the electronic description of the exotic eightfold metallic Fermion. However, the Cu$^{2+}$ (d$^9$) ion might be stabilized by developing a gap-opening spin-polarized magnetic structure.

To examine this basic physical intuition, we allow for magnetism in the form of different spin arrangements among neighboring Cu atoms, still in the space group 130. We find that an antiferromagnetic arrangement of the Cu spins can lower the total energy by as much as 498 meV/formula units. Different spin configuration (antiferromagnetic or ferromagnetic) lead to very similar total energies within a few meV/atom (see supplementary section S4). Breaking time-reversal symmetry through the inclusion of magnetic moments on the Cu atoms is found here to open a large energy gap in the Fermi energy (green shaded area in Fig 3c), splitting the metallic intermediate band into a valence band and conduction band with a DFT gap of 1.63 eV. Indeed, literature calculations and experiment\cite{50} show that this material is an insulator with a large enough gap to be suggested as a photocatalyst. The Paramagnetic (PM) phase is modeled as in the recent polymorphous approach to binary oxides\cite{51} as a supercell that allows moments to develop on individual Cu sites but keeps the total moment zero, as appropriate for paramagnets. Using a supercell with 756 atoms, with the same lattice parameters as the AFM phase (for simplicity) we find a band gap of 1.62 eV and a distribution of local magnetic moments around 0.63 Bohr Magneton. This polymorphous representation of the PM phase is significantly

**Figure 3.** Spontaneous magnetism destroying topology-enabling band degeneracy in CuBi$_2$O$_4$. (a) Band structure and (b) atom-resolved density of states of CuBi$_2$O$_4$ in the tetragonal P4/ncc crystal structure (space group 130), constraining it to be non-spin-polarized, leading to a metallic solution. (c) and (d) are the band structure and density of states for the antiferromagnetic configuration, that leads to the opening of the band gap and significant energy lowering. In (c), the spin-up and spin-down bands are degenerated.
lower in energy (by ∼0.5 eV/formula unit) than the naïve approximation to a PM as a nonmagnetic structure. We conclude that development of insulation-promoting magnetism in this system has such a significant energy lowering potential that it might very likely defeat the intended metallic state of the predicted new Fermion.

D. False-Positive type 4: The predicted topological property requires doping that destabilizes the topological structure BaBiO₃

Cubic (Fm-3m) BaBiO₃ was predicted[18] to be an exciting large gap oxide topological insulator, if it could be doped so as to shift up its natural Fermi level (zero of energy in Fig 2a) by about 2 eV, where band inversion is predicted to occur (ellipse in Fig 4a). Such doping is equivalent to one added electron per formula unit or doping density of ≈10²² electrons/cm³. If one simulates doping by raising the Fermi level while disallowing the atoms to respond to such a perturbation, then indeed theory[18,52] would predict band inversion in the doped cubic solid (see supplementary section S5). However, doping is rarely a rigid-band event that does not provoke an electronic response[53,54]. Indeed, shifting E_F to higher energy often leads at least to a self-regulating spontaneous formation of ‘killer defects’, or at the extreme, to decomposition of the host compound into stabler structures involving the dopant atoms[55]. In general, a significant up shift of E_F leads to occupying antibonding states, an effect likely to contribute to the destabilization of the lattice if carried out over a significant volume of the Brillouin zone. In oxides, this is particularly true because of the limited ability of the polar lattice to screen such instabilities[56].

\[\text{Figure 4. } n\text{-type doping destroying excited state band inversion in BaBiO}_3. \text{ Band structure of cubic BaBiO}_3 \text{ showing band inversion (Bi } p \text{ states in green below Bi } s \text{ in red) at about 2 eV above the Fermi level. However, this cubic structure is unstable with respect to disproportionation of two of its BiO}_6 \text{ octahedra into different (small vs large) octahedra, giving the known stable monoclinic structure (space group 14) that also has excited state band inversion at about 2 eV above the Fermi level. This high energy band inversion is unstable with respect to } n\text{-type doping as shown for (c) electron-doped and (d) Li-doped monoclinic phases where a normal band order (Bi, } s \text{ in red below Bi, } p \text{ in green) is seen. Supplementary section S4 shows that the high energy band inversion is also not stable with respect to } O\text{-vacancy doping.}\]

To examine this basic physical intuition, we calculated the equilibrium structure of the undoped as well as doped system by evaluating its total energy. We find first that the cubic (Fm-3m) phase of BaBiO₃ having a single
Bi$_6$ octahedron is unstable with respect to disproportionation into two octahedra with different volumes (often loosely described as Ba$_2$(Bi$_3^{3+}$ Bi$_5^{5+}$)O$_6$ (Ref [57]), best described as the monoclinic structure (space group 14; P$2_1$/c), with metallic band structure shown in Fig 4b. Once doped (by electron, by Li, or via O-vacancies), this structure responds to the occupation of its previously empty conduction bands, rearranging its bonds, and leading to a fundamentally new band structure (Fig 4c, d and supplementary section S5 showing also doping of the cubic phase) that is a normal insulator, not a topological insulator. A similar situation applies to cubic RbTlCl$_3$ and KBiO$_3$. [56]

A more extreme example of a destructive response to doping is the recent suggestion[52] of replacing 1/3 of the O atoms by the nominal n-type dopant fluorine to shift $E_f$ to the point where a TI state is expected. This was attempted in a recent paper where following doping the band structure was monitored, but the total energy was not probed either with respect to nudging the atoms in BaBiO$_2$F or with respect to decomposition reactions. We find hypothetical cubic BaBiO$_2$F is highly unstable with respect to competing phases, specifically decomposes to ground state Bi$_2$O$_3$, Ba$_2$Bi$_2$O$_5$, and BaF$_2$ compounds with exothermic decomposition energy of 285 meV/atom. Recent experimental attempts to synthesize BaBiO$_2$F were unsuccessful, a failure attributed to the formation of different decomposition products.[58] We thus conclude that highly doped BaBiO$_3$ is unstable in the hypothetical structure that would have made it a topological insulator. We note that the recently predicted exotic topoloids include a significant fraction that need to be artificially doped by a substantial carrier concentration so as to reach the special band crossing point.

Conclusions
Looking at instability modes of highly symmetric structures that harbor exotic properties reveals a number of basic symmetry breaking channels that cancel exotic behavior. We focused our study on four main design principles that should be valid to several families of topoloid compounds. These additional filters are related to the stability of hypothetical topological materials with respect to (i) decomposition to ground state crystalline compounds, (ii) spin polarization, (iii) formation of spontaneous intrinsic defects, (iv) and external doping. All these extra filters can be probed by considering the total electron-ion energy. The action needed is rather straightforward: assumed structures can be perturbed by 'nudging' its atoms or spins or electrons, then evaluating the total energy of competing configurations, examining if the low energy ones still possess the topology-enabling symmetry of the originally assumed structure. Such additional material selection filters will help to avoid false-positive predictions and would complete the burden of proof for recommending to experimentalists not only exotic, but also potentially realizable materials that host with structural impunity exotic properties. This would convert ‘theory of effects’ to the theory of real structures that could harbor such effects with impunity. This would enhance the friendship (and credibility) between theorists with experimentalists.

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Data availability
All data needed to evaluate the conclusions in the paper are present in the paper and the Supplementary Materials. Additional data for this study are available from the corresponding author upon request.
Appendix A. Supplementary data are available

References:
[1] B.A. Bernevig, T.L. Hughes, S.-C. Zhang, Science 314 (2006) 1757–1761.
[2] C.L. Kane, E.J. Mele, Phys. Rev. Lett. 95 (2005) 226801.
[3] Z.K. Liu, B. Zhou, Y. Zhang, Z.J. Wang, H.M. Weng, D. Prabhakaran, S.-K. Mo, Z.X. Shen, Z. Fang, X. Dai, Z. Hussain, Y.L. Chen, Science 343 (2014) 864–867.
[4] S.-Y. Xu, I. Belopolski, N. Alidoust, M. Neupane, G. Bian, C. Zhang, R. Sankar, G. Chang, Z. Yuan, C.-C. Lee, S.-M. Huang, H. Zheng, J. Ma, D.S. Sanchez, B. Wang, A. Bansil, F. Chou, P.P. Shibayev, H. Lin, S. Jia, M.Z. Hasan, Science 349 (2015) 613–617.
[5] X.-L. Qi, S.-C. Zhang, Physics Today 63 (2009) 33–38.
[6] M.Z. Hasan, C.L. Kane, Rev. Mod. Phys. 82 (2010) 3045–3067.
[7] X.-L. Qi, S.-C. Zhang, Rev. Mod. Phys. 83 (2011) 1057–1110.
[8] N.P. Armitage, E.J. Mele, A. Vishwanath, Rev. Mod. Phys. 90 (2018) 015001.
[9] A. Franceschetti, A. Zunger, Nature 402 (1999) 60–63.
[10] A. Zunger, Nature Reviews Chemistry 2 (2018) 0121.
[11] B. Bradlyn, L. Elcoro, J. Cano, M.G. Vergniory, Z. Wang, C. Felser, M.I. Aroyo, B.A. Bernevig, Nature 547 (2017) 298–305.
[12] F. Schindler, A.M. Cook, M.G. Vergniory, Z. Wang, S.S.P. Parkin, B.A. Bernevig, T. Neupert, Science Advances 4 (2018) eaat0346.
[13] Materiae - Material Sciences Database | IOP and CNIC, CAS | Materiae. Available at: http://materiae.iphy.ac.cn/#/. (Accessed: 7th December 2018)
[14] T. Zhang, Y. Jiang, Z. Song, H. Huang, Y. He, Z. Fang, H. Weng, C. Fang, ArXiv:1807.08756, (2018).
[15] F. Tang, H.C. Po, A. Vishwanath, X. Wan, ArXiv:1807.09744, (2018).
[16] Z. Song, Z. Wang, W. Shi, G. Li, C. Fang, B.A. Bernevig, ArXiv:1807.10676, (2018).
[17] B. Bradlyn, J. Cano, Z. Wang, M.G. Vergniory, C. Felser, R.J. Cava, B.A. Bernevig, Science 353 (2016) aaf5037.
[18] B. Yan, M. Jansen, C. Felser, Nature Physics 9 (2013) 709–711.
[19] S.M. Young, S. Zaheer, J.C.Y. Teo, C.L. Kane, E.J. Mele, A.M. Rappe, Phys. Rev. Lett. 108 (2012) 140405.
[20] H.-J. Zhang, S. Chadow, L. Mückler, B. Yan, X.-L. Qi, J. Kübler, S.-C. Zhang, C. Felser, Phys. Rev. Lett. 106 (2011) 156402.
[21] H. Jin, S.H. Rhim, J. Im, A.J. Freeman, Scientific Reports 3 (2013) 1651.
[22] S.-Y. Lin, M. Chen, X.-B. Yang, Y.-J. Zhao, S.-C. Wu, C. Felser, B. Yan, Phys. Rev. B 91 (2015) 094107.
[23] X. Zhang, Q. Liu, Q. Xu, X. Dai, A. Zunger, J. Am. Chem. Soc. 140 (2018) 13687–13694.
[24] Q. Liu, A. Zunger, Phys. Rev. X 7 (2017) 021019.
[25] E. Gibney, Nature 560 (2018) 151.
[26] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864–B871.
[27] J. Ihm, A. Zunger, M.L. Cohen, J. Phys. C: Solid State Phys. 12 (1979) 4409.
[28] G. Kotliar, S.Y. Savrasov, K. Haule, V.S. Oudovenko, O. Parcollet, C.A. Marianetti, Rev. Mod. Phys. 78 (2006) 865–951.
[29] F. Giustino, M.L. Cohen, S.G. Louie, Phys. Rev. B 81 (2010) 115105.
[30] M. Govoni, G. Galli, J. Chem. Theory Comput. 11 (2015) 2680–2696.
[31] L. Delle Site, in: V. Bach, L. Delle Site (Eds.), Many-Electron Approaches in Physics, Chemistry and Mathematics: A Multidisciplinary View, Springer International Publishing, Cham, 2014, pp. 361–375.

[32] E. Pavarini, E. Koch, A. Lichtenstein, D. (Eds) Vollhardt, The LDA+DMFT Approach to Strongly Correlated Materials, 2011.

[33] C.-X. Liu, X.-L. Qi, H. Zhang, X. Dai, Z. Fang, S.-C. Zhang, Phys. Rev. B 82 (2010) 045122.

[34] J.-W. Luo, A. Zunger, Phys. Rev. Lett. 105 (2010) 176805.

[35] C.J. Bartel, S.L. Millican, A.M. Deml, J.R. Rumptz, W. Tumas, A.W. Weimer, S. Lany, V. Stevanović, C.B. Musgrave, A.M. Holder, Nature Communications 9 (2018) 4168.

[36] R. Gautier, X. Zhang, L. Hu, L. Yu, Y. Lin, T.O.L. Sunde, D. Chon, K.R. Poeppelmeier, A. Zunger, Nature Chemistry 7 (2015) 308–316.

[37] J. Vidal, X. Zhang, L. Yu, J.-W. Luo, A. Zunger, Phys. Rev. B 84 (2011) 041109.

[38] J. Vidal, X. Zhang, V. Stevanović, J.-W. Luo, A. Zunger, Phys. Rev. B 86 (2012) 075316.

[39] G. Trimarchi, X. Zhang, A.J. Freeman, A. Zunger, Phys. Rev. B 90 (2014) 161111.

[40] G.L.W. Hart, A. Zunger, Phys. Rev. Lett. 87 (2001) 275508.

[41] J.P. Dismukes, J.G. White, Inorg. Chem. 3 (1964) 1220–1228.

[42] H.F. Franzén, R.T. Tuenge, L. Eyring, Journal of Solid State Chemistry 49 (1983) 206–214.

[43] H.F. Franzén, J.C.W. Folmer, Journal of Solid State Chemistry 51 (1984) 396–402.

[44] X. Zhang, L. Zhang, J.D. Perkins, A. Zunger, Phys. Rev. Lett. 115 (2015) 176602.

[45] L.-W. Wang, L. Bellaiche, S.-H. Wei, A. Zunger, Phys. Rev. Lett. 80 (1998) 4725–4728.

[46] V. Popescu, A. Zunger, Phys. Rev. Lett. 104 (2010) 236403.

[47] P.V.C. Medeiros, S. Stafström, J. Björk, Phys. Rev. B 89 (2014) 041407.

[48] B. Li, A.-V. Mudring, J.D. Corbett, Inorg. Chem. 42 (2003) 6940–6945.

[49] D. Di Sante, A. Hausoel, P. Barone, J.M. Tomczak, G. Sangiovanni, R. Thomale, Phys. Rev. B 96 (2017) 121106.

[50] G. Sharma, Z. Zhao, P. Sarker, B.A. Nail, J. Wang, M.N. Huda, F.E. Osterloh, J. Mater. Chem. A 4 (2016) 2936–2942.

[51] G. Trimarchi, Z. Wang, A. Zunger, Phys. Rev. B 97 (2018) 035107.

[52] B. Khamari, B.R.K. Nanda, ArXiv:1901.08751 [Cond-Mat] (2019).

[53] A. Zunger, Applied Physics Letters 83 (2003) 57.

[54] A. Walsh, A. Zunger, Nature Materials 16 (2017) 964–967.

[55] Q. Liu, Q. Yao, Z.A. Kelly, C.M. Pasco, T.M. McQueen, S. Lany, A. Zunger, Phys. Rev. Lett. 121 (2018) 186402.

[56] X. Zhang, L.B. Abdalla, Q. Liu, A. Zunger, Advanced Functional Materials 27 (2017) 1701266.

[57] G.M. Dalpian, Q. Liu, J. Varignon, M. Bibes, A. Zunger, Phys. Rev. B 98 (2018) 075135.

[58] F. Hong, B. Saporov, W. Meng, Z. Xiao, D.B. Mitzi, Y. Yan, J. Phys. Chem. C 120 (2016) 6435–6441.