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Structurally unstable $A^{\mathrm{III}}\mathrm{BiO}_3$ perovskites are predicted to be topological insulators but their stable structural forms are trivial band insulators

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The quest for broadening the materials base of topological insulators (TIs) beyond the handful of presently known examples has recently led to exploratory calculations of the topological Z_2 metric from the band structure of various candidate compounds in *assumed crystal structures*. However, structural transformations such as volume compression, lattice straining, or atom swaps that are used to instigate in a trivial insulator the band inversion underlying TI-ness, might also destabilize the system to the point that it either distorts into a more stable structure or does not form at all. Whether the more stable form of the candidate material is a TI, it is to be determined. Yet, often TI discovery calculations do not assess whether the postulated structural forms predicted to be TIs are also the stable forms of these compounds. Here, we show that in the broad family of III-Bi-O_3 oxides (III = Al, Ga, In, Sc, Y, and La), the cubic $A^{\mathrm{III}}\mathrm{BiO}_3$ perovskite structure, which has been recently predicted to be TI for YBiO_3, is unstable, whereas the stable $A^{\mathrm{III}}\mathrm{BiO}_3$ structural forms are trivial band insulators.

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Topological insulators as a material search problem with potentially mutually-contradicting design requirements. Topological insulators (TIs) offer the interesting case where intrinsic bulk electronic properties can be used as a predictor of certain surface properties of the same material, a rather unusual occurrence in standard surface science of semiconductors and insulators [1], where surface effects are explained by the structure of the surface itself. In a bulk TI, an energy band that is normally an unoccupied conduction state switches order with a band that is normally an occupied valence state. The relevant states must occur at a time-reversal invariant momentum (TRIM), such as the wave vector Γ, X, or L in the Brillouin zone of a face-centered cubic lattice. The bulk-calculated topological metric [2] Z_2 determines if the material is a TI (when $Z_2 = 1$) or a normal band insulator (with $Z_2 = 0$, sometimes called "trivial"). Thus, $Z_2 = 1$ in the *bulk crystal* is a predictor of the *surface* electronic structure of the same material: the material will have within the surface band gap two states that cross each other ("gapless") and are linearly-dispersed ("massless Dirac cones") with an interesting spin-orbit induced spin texture [3,4] that is resilient to nonmagnetic surface passivation. The quest for broadening the materials base of TIs beyond the handful of presently known examples has recently led to exploratory calculations of the topological Z_2 metric from the band structure of various candidate compounds [5–12].

Often the practice in the field of TI discovery is to propose hypothetical compounds constructed starting from previously established TIs postulating the same crystal structure and substituting the chemical elements, or by subjecting the structure to significant strain. These composition and structural perturbations aim at inducing the transformation from normal to topological insulator, but they might contribute to loss of structural stability, e.g., when the strain is too big to maintain mechanical stability or when antibonding states get populated and bonding states get depopulated. The system could then respond by transforming into a different, more stable structure that cannot be guessed. *Whether that structure is still a TI or not needs to be examined.* The stability of hypothetical materials in a family of compounds cannot be guessed either, and it is hard to predict by extrapolating the results of stability calculations on a subset of compounds [13].

Here, using the III-Bi-O_3 oxides (III = Al, Ga, In, Sc, Y, and La) with members recently suggested to be new TIs [5], we show that to predict new topological insulating compounds it is necessary to establish their topological nature *and* predict their stable phase. Jin *et al.* [5] predicted through band structure calculations that YBiO_3 in the assumed CaTiO_3-type perovskite structure (with the cubic $Pm\bar{3}m$ space-group symmetry) with the Bi atoms located at the O_h ($1a$ Wyckoff position) is a TI with an insulating indirect gap of 0.183 eV (and a gap of 0.33 eV at the R point, a TRIM, where a band inversion is found). Their result is reproduced in the upper right corner of Fig. 1. However, if one instead allows Bi to be located at the cavity site ($1b$ Wyckoff position) of the same $Pm\bar{3}m$ perovskite structure, the total energy drops (see Fig. 1); relaxing the lattice constant of YBiO_3 from the previously used 5.428 Å to the density-functional equilibrium value for the same $Pm\bar{3}m$ perovskite ($a_{\mathrm{lat}} = 4.405$ Å) further lowers the total energy by $\sim$1 eV, whereas relaxing the condition that the structure is of the $Pm\bar{3}m$ perovskite type lowers the total energy by another $\sim$1 eV and the system is not a TI (Fig. 1). We find indeed that the $Pm\bar{3}m$ perovskite with Bi at the O_h site is never the ground-state structure, but it shows a metallic band structure with a band inversion between the Bi-s and Bi-p orbitals (see Fig. 2) induced by spin-orbit coupling (SOC). In contrast, the alternative competing structure types include the stable structures that nevertheless are trivial band insulators ($Z_2 = 0$).

We show that performing Z_2 calculations on a guessed structure can deliver the prediction of a TI, but the guessed structure could be unstable while the system could be topologically trivial in its stable structure, as in the case of the $A^{\mathrm{III}}\mathrm{BiO}_3$ compounds. Other theoretical works seeking new TIs [7,10–12] have not always examined the stability of the predicted compounds in the structures that make them TIs. We recommend the stability analysis to avoid predictions of new TIs that are unrealizable synthetically.

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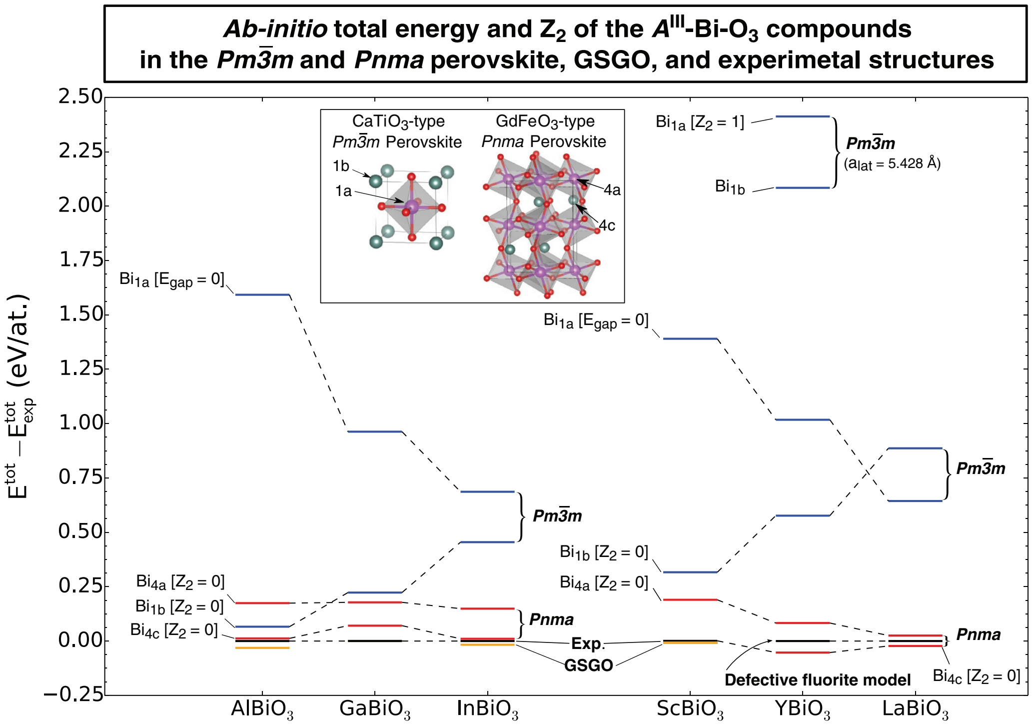

FIG. 1. (Color online) GGA total energies of the $A^{\mathrm{III}}\mathrm{BiO}_3$ systems, where A^{III} = Al, Ga, In, Sc, Y, and La. The blue and red lines, respectively, correspond to the assumed CaTiO_3-type ($Pm\bar{3}m$) and GdFeO_3-type ($Pnma$) perovskite structures, shown in the inset. The subscript of the Bi symbol indicates the Wyckoff site taken by this element in the two perovskite structures. The orange lines correspond to the GSGO structures, while the black lines correspond to the experimental structures (or the model random anion-defective fluorite configurations in the case of YBiO_3 and LaBiO_3) taken as the zero of the energy for each $A^{\mathrm{III}}\mathrm{BiO}_3$ system.

Methods to screen the stability of hypothetical structures via first-principles approaches. To explore the stable structures of the $A^{\mathrm{III}}\mathrm{BiO}_3$ compounds, we use two approaches. The simplest, conventional method is to remove the symmetry restrictions present in the CaTiO_3-type structure to allow tilting of the octahedra and perform a standard relaxation of the cell vectors and atom positions to the nearest minimum-energy structure. The local minimization might produce a daughter structure that is globally stable or metastable. We then determine whether the topological character of the wave functions in the assumed $Pm\bar{3}m$ perovskite structure is preserved or destroyed in the distorted perovskite phases. This approach provides a bridge with solid-state chemistry constructs that predict the degree of octahedral tilting from intuitive, heuristic concepts [14,15].

A second, more general, but computationally more demanding, approach to predict the low-energy structures of the $A^{\mathrm{III}}\mathrm{BiO}_3$ compounds is assumption-free global energy minimization, starting from randomly chosen lattice vectors and atom positions. To this end, we apply the global space-group optimization (GSGO) [16–20] method, which uses an evolutionary algorithm with variable cell shape and atom coordinates to predict the global minimum-energy structure of a material modeled by density functional theory (see, e.g., Refs. [17,19–24] for some applications). This algorithm predicts also a range of structures close in energy to the ground-state one that might be targeted by synthesis. The evolutionary GSGO algorithm searches for the global energy-minimum structure by replacing at each generation a subset of the population including the highest energy structure (e.g., 25% of the whole population) with new ones that are generated by the cut-and-splice crossover [16,19,20] or mutation operations and then it is fully relaxed and included in the next generation of the population. We note that ternary Bi oxides of A^{III} species have been synthesized with the $A^{\mathrm{III}}\mathrm{BiO}_3$ composition [25–27], thus here we focus on comparing the relative stability of each $A^{\mathrm{III}}\mathrm{BiO}_3$ compound in various ABX_3 structure types.

Method of total energy calculations. We applied density functional theory as implemented in the VASP [29,30] package to calculate total energies and band structures. The lattice vectors and atom positions of each structure were fully optimized using the PBE generalized gradient-corrected approximation. On the relaxed geometry, we included spin-orbit coupling to calculate the energy bands and the Z_2 invariant.

Method of calculation of the Z_2 topological invariant. To determine the topological character of the compounds with centrosymmetric structures, we calculated the Z_2 topological invariant using the formula derived by Fu and Kane [2]:

$$(-1)^{Z_2} = \prod_{n=1}^{N_e/2} \prod_{\mathbf{k_i}} P(n,\mathbf{k_i}), \qquad (1)$$

in which N_e is the number of electrons and $P(n,\mathbf{k_i})$ is the parity of the Bloch states $\psi_{n,\mathbf{k_i}}(\mathbf{r})$ at the time-reversal invariant momenta $\mathbf{k_i}$ in the Brillouin zone calculated for each occupied band n by comparing $\psi_{n,\mathbf{k_i}}(\mathbf{r})$ to $\psi_{n,\mathbf{k_i}}(-\mathbf{r})$. Materials with $Z_2 = 0$ are topologically trivial band insulators, while those with $Z_2 = 1$ have a nontrivial topological phase characterized

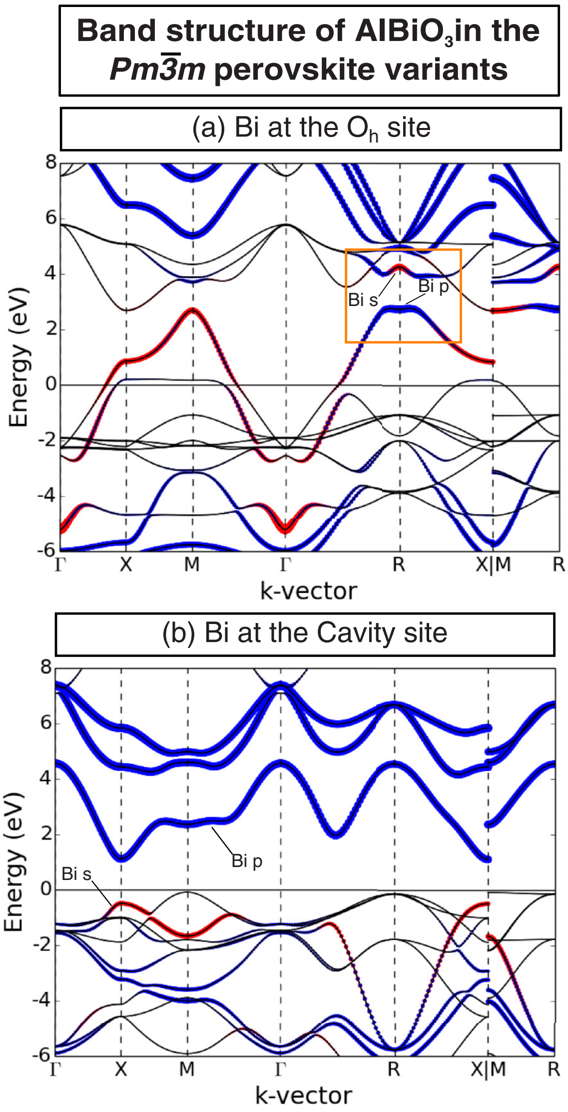

FIG. 2. (Color online) Electron bands of AlBiO_3 in the $Pm\bar{3}m$ perovskite structure with Bi at the O_h (a) and cavity site (b). The radius of the markers is proportional to the projection of the wave functions on the Bi-s (red) and p (blue) atomic orbitals.

by properties such as topologically protected dispersionless surface states.

Key results. Figure 1 compares the total energies of the $A^{\mathrm{III}}\mathrm{BiO}_3$ compounds with A^{III} =Al, Ga, In, Sc, Y, and La in the following structures: (i) the undistorted cubic $Pm\bar{3}m$ CaTiO_3-type perovskite (see Fig. 1, inset, left-hand side), which has two possible sites for Bi, the octahedral O_h site (1a Wyckoff position) and the cavity site (1b), at the corner of the cubic unit cell; (ii) the distorted orthorombic $Pnma$ GdFeO_3-type perovskite (see Fig. 1, inset, right-hand side); (iii) the GSGO lowest-energy structures (see Ref. [28]); and (iv) the experimentally observed structures (see Ref. [28]). The $A^{\mathrm{III}}\mathrm{BiO}_3$ compounds based on Al, Ga, In, and Sc have been synthesized [25–27] at high pressure (6 GPa), and the obtained phases are observed to be metastable at ambient pressure and temperature. Here, we performed total energy calculations and GSGO searches at zero pressure ($P = 0$). In Fig. 1, we also show the Z_2 value for the insulating structures that are centrosymmetric, which include the CaTiO_3-type and GdFeO_3-type perovskites, while not all of the GSGO and experimental $A^{\mathrm{III}}\mathrm{BiO}_3$ structures are centrosymmetric. The total energies of the $A^{\mathrm{III}}\mathrm{BiO}_3$ structures are referred to the total energy of the experimentally observed $A^{\mathrm{III}}\mathrm{BiO}_3$ structures (or the model anion-defective fluorite structure for YBiO_3 and LaBiO_3). We find that the cubic $Pm\bar{3}m$ perovskite with Bi at the O_h site is never the ground-state structure, but it shows a metallic band dispersion with a SOC-induced band inversion between the Bi-s and Bi-p orbitals (see Fig. 2). In contrast, phases (ii)–(iv) include the stable structures that nevertheless are trivial band insulators ($Z_2 = 0$). In what follows, we discuss the results in more detail.

The two configurations of the unstable $Pm\bar{3}m$ CaTiO_3-type perovskite structure. When the $A^{\mathrm{III}}\mathrm{BiO}_3$ compounds are in the undistorted $Pm\bar{3}m$ perovskite structure, Bi could occupy the O_h (1a) site and A^{III} the cavity (1b) site, a configuration we denote as $A^{\mathrm{III}}_{1b}\mathrm{Bi}_{1a}$. Alternatively, one can also construct the antisite phase $\mathrm{Bi}_{1b}A^{\mathrm{III}}_{1a}$ with Bi at the cavity site. Figure 1 shows that the $Pm\bar{3}m$ perovskite structure of the $A^{\mathrm{III}}\mathrm{BiO}_3$ systems with Bi at the cavity site is more stable than the one with Bi at the O_h site, except when A^{III} is La. This reflects the fact that the optimal atom packing in the perovskite structure is achieved when Bi, which is larger than the A^{III} cations except La, is at the cavity site, thus maximizing the perovksite tolerance factor (see Ref. [28]). Moreover, the two cubic perovskite configurations become closer in energy as the difference between the Bi and A^{III} ionic radii decreases going from Al to In and from Sc to La. However, the $A^{\mathrm{III}}\mathrm{BiO}_3$ $Pm\bar{3}m$ perovskite form is never stable irrespective of the cation arrangement. YBiO_3, predicted to be a TI by Jin *et al.* [5], has an equilibrium lattice parameter in the $\mathrm{Y}_{1b}\mathrm{Bi}_{1a}\mathrm{O}_3$ and $\mathrm{Bi}_{1b}\mathrm{Y}_{1a}\mathrm{O}_3$ configuration respectively of 4.405 and 4.349 Å, much smaller than the 5.428 Å value reported by Li *et al.* [31] and assumed by Jin *et al.* in their calculations. YBiO_3 in the cubic perovskite structure with this expanded lattice parameter and Bi at the octahedral site is about 2.50 eV/atom above the lowest-energy structure and it is unlikely to be stable unless.

Electronic structure of the two variants of the unstable $Pm\bar{3}m$ perovskite structure. We find that all the $A^{\mathrm{III}}\mathrm{BiO}_3$ systems are metallic in the $Pm\bar{3}m$ perovskite structure irrespective of the Bi position in the lattice, and we illustrate this taking AlBiO_3 as an example. Figures 2(a) and 2(b) display the GGA+SOC band dispersion of AlBiO_3 calculated in the $Pm\bar{3}m$ perovskite structure in the configuration with Bi at the O_h (1a) and cavity (1b) sites, respectively. The size of the red and blue symbols is proportional to the projections of the Bloch wave functions on the Bi s and p atomic orbitals, respectively. When Bi is at the O_h site, AlBiO_3 as well as the Ga and In systems have metallic band structures with the Bi s states with antibonding character at a lower energy than the Bi p ones that have bonding character except at the time-reversal-invariant R point, where the ordering is inverted [see Fig. 2(a)]. Switching the positions of Bi and A^{III} and putting Bi at the cavity site [see Fig. 2(b)], AlBiO_3 and the other $A^{\mathrm{III}}\mathrm{BiO}_3$ systems become insulators with fully occupied Bi s states, but without s-p inversion, making the $Pm\bar{3}m$ $A^{\mathrm{III}}\mathrm{BiO}_3$ perovskites in this configuration trivial insulators (with $Z_2 = 0$).

Perovskite structures where the octahedra are allowed to tilt: relative stability of the two Pnma GdFeO$_3$-type perovskite variants. A whole range of distorted perovskite structure types can be obtained starting from the ideal cubic perovskite by octahedra rotations and cation shifts. These distorted structures can lower the energy by optimizing the atom packing. The $Pnma$ GdFeO$_3$ structure-type in particular is the perovskite in which the octahedra can tilt around a generic axis and distort from the ideal regular shape. As shown in Fig. 1, the energy of the A^{III}BiO$_3$ compounds decreases considerably going from the $Pm\bar{3}m$ to the $Pnma$ perovskite structure, regardless of the Bi position. The configuration with Bi at the cavity site is still energetically preferred, but with an energy distance from the configuration with Bi at the O_h site much reduced with respect to the $Pm\bar{3}m$ perovskite and as low as ∼0.1 eV/at. Moreover, the GdFeO$_3$-type structure with the A^{III} cation at the octahedral site, is close in energy to the experimentally observed structure of AlBiO$_3$ and InBiO$_3$ and degenerate with this in the case of ScBiO$_3$.

Electronic structure of the GdFeO$_3$-type perovskites. The A^{III}BiO$_3$ systems in the $Pnma$ perovksite structure are insulators but without the s-p band inversion observed in the $Pm\bar{3}m$ form. Figure 3 compares the GGA+SOC band structure of InBiO$_3$ in the $Pm\bar{3}m$ and $Pnma$ perovskite structures with Bi at the octahedral site. While InBiO$_3$ in the $Pm\bar{3}m$ structure is a metal with the Bi s-p band inversion at the R point at about 3 eV above the Fermi level, the octahedral tilting and internal distortions that produce the GdFeO$_3$-type structure open a band gap but remove the s-p inversion. We find that all A^{III}BiO$_3$ systems in this $Pnma$ perovskite are trivial insulators with $Z_2 = 0$ irrespective of the Bi position.

GSGO-predicted and experimental structures. The structural models of the experimental and GSGO structures of the A^{III}BiO$_3$ systems are shown in Ref. [28]. InBiO$_3$ [26] and ScBiO$_3$ [27] have been synthesized under pressure and form in distorted perovskite structures with Bi between the tilted octahedra. The observed phases are near-degenerate and structurally similar (or as in the case of InBiO$_3$ directly related) to the GdFeO$_3$-type structure, and are, thus, unlikely to exhibit a topological phase. GaBiO$_3$ [25] forms in a structure with Ga tetrahedrally coordinated to O that we found to have $Z_2 = 0$. The GSGO structure of GaBiO$_3$ is a variant of the experimental structure with a similar tetrahedral GaO$_4$ pattern and is also expected to be topologically trivial. AlBiO$_3$ [25] forms in the non-centrosymmetric LiNbO$_3$-type structure; the GSGO structure of AlBiO$_3$ is slightly lower in energy than the LiNbO$_3$-type at $P = 0$ and shows a tetrahedral bonding for Al similar to that in the GaBiO$_3$ phase, and is also expected to be a trivial band insulator.

YBiO$_3$ [32–34] and LaBiO$_3$ [35,36] form in oxygen-defective fluorite phases in which the Bi and Y (La) atoms randomly occupy the cation sublattice. We produced anion-defective fluorite structures with randomized cation positions (specifically, a special quasirandom structure [37] (SQS) in the case of YBiO$_3$) to model the random cation distribution in these phases. Interestingly, for these two compounds the $Pnma$ perovskite phase is found to be close in energy to (and even slightly lower than) the random anion-defective fluorite phase probably due to the octahedral coordination which approximates the near-to-octahedral sixfold packing which is locally possible in an anion-defective fluorite lattice.

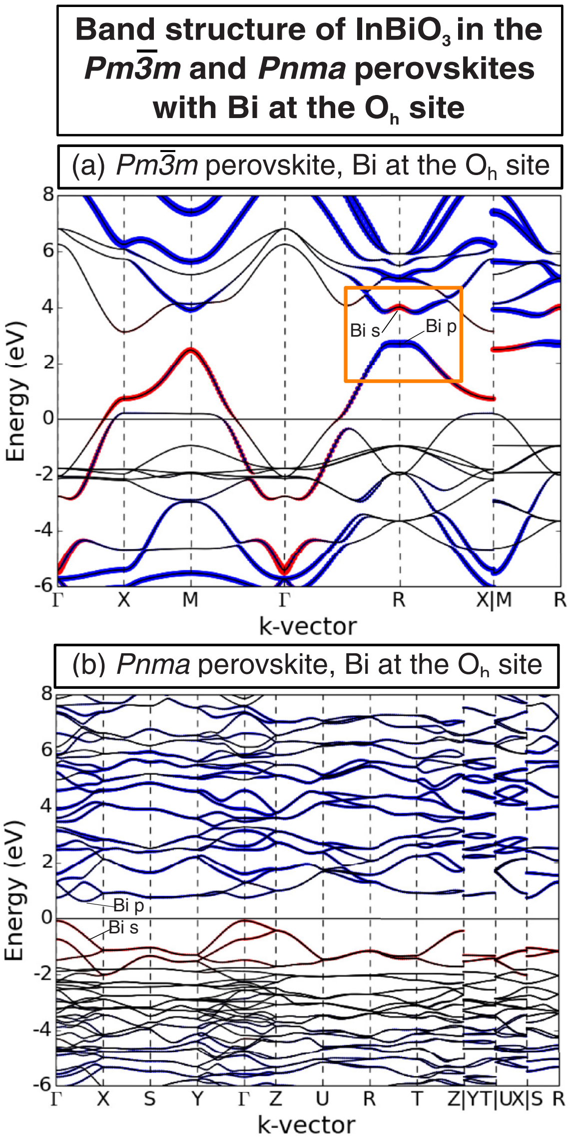

FIG. 3. (Color online) Electron bands of InBiO$_3$ in the $Pm\bar{3}m$ (a) and $Pnma$ (b) perovskite structure with Bi at the O_h site. As in Fig. 2, the radius of the markers is proportional to the projection of the wave functions on the Bi-s (red) and Bi-p (blue) atomic orbitals.

Discussion and Summary. The A^{III}BiO$_3$ perovskites were recently proposed [5] as systems with a valence configuration analogous to that of the Pb and Sn halide perovskites TIs [38], with the hope that also these oxides would show a topological band structure but with a larger gap than these halides. From this set of oxides, using band structure calculations, YBiO$_3$ was predicted to be a TI [5], while ScBiO$_3$ and LaBiO$_3$ were predicted to be topological metals [6]. Here, we calculated the Z_2 invariant of these three oxides and of the A^{III}BiO$_3$ oxides based on Al, Ga, and In in the previously assumed cubic perovskite structure and in the $Pnma$ GdFeO$_3$-type perovskite structure with tilted octahedra. We fully relaxed all phases to the equilibrium structure. We find that all A^{III}BiO$_3$ systems are, depending on the Bi position, metallic or trivial insulators in the cubic perovskite structure which is, however, unstable. When the octahedra are allowed to tilt, the cubic perovskite relaxes into distorted perovskite phases of much lower energy. However, we find that the distorted perovskites along with the experimental structures and the low-energy structures predicted by GSGO are trivial insulators. Here, we show that to predict new TIs one must establish both the topological character and the stable phase of the compound applying "first-principles thermodynamics."

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