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Theoretical prediction of topological insulator in ternary rare earth chalcogenides

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A different class of three-dimensional topological insulator, ternary rare-earth chalcogenides, is theoretically investigated with *ab initio* calculations. Based on both bulk band-structure analysis and the direct calculation of topological surface states, we demonstrate that $LaBiTe_3$ is a topological insulator. La can be substituted by other rare earth elements, which provide candidates for novel topological states such as quantum anomalous Hall insulator, axionic insulator, and topological Kondo insulator. Moreover, $YBiTe_3$ and $YSbTe_3$ are found to be normal insulators. They can be used as protecting barrier materials for both $LaBiTe_3$ and Bi_2Te_3 families of topological insulators for their well-matched lattice constants and chemical composition.

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I. INTRODUCTION

A topological insulator (TI) is a novel quantum state, which has attracted great attention in condensed-matter physics recently.[1–3] TIs in two or three dimensions have both insulating bulk energy gap and gapless edge or surface states on the sample's boundary. The surface states of three-dimensional (3D) TIs consist of odd number of massless Dirac cones, which are protected by the time-reversal symmetry. TIs can be most generally defined as a new state of quantum matter whose effective electromagnetic action is given by the topological term $S_\theta=(\theta/2\pi)(\alpha/2\pi)\int d^3xdt\mathbf{E}\cdot\mathbf{B}$ with α the fine-structure constant and the parameter $\theta=0$ or π for trivial insulator and TI, respectively.[4] Many novel properties have been proposed as a result of this topological response,[4–6] which are interesting in both fundamental physics and device applications. In proximity with an ordinary superconductor, TI also provides a new candidate for topological quantum computation.[7]

The first TI was theoretically predicted and experimentally observed in the HgTe quantum well.[8,9] This work discovered the basic mechanism of band inversion driven by spin-orbit coupling (SOC), which serves as a template for most TIs discovered later. Since then, several TIs in both two-dimensional (2D) and 3D have been theoretically proposed and experimentally realized, $Bi_{1-x}Sb_x$ alloy,[10,11] the family of Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3,[12–14] the family of $TlBiTe_2$ and $TlBiSe_2$.[15–17] Many other materials are theoretically predicted and still waiting for experimental verification.[18–24] Of particular interest are the magnetic atom-doped topological insulators for the effects of magnetic impurities and ferromagnetism on the topological surface states.[25–27] In this Rapid Communication, we report a different family of ternary chalcogenides compound $LnBT_3$ (Ln=rare earth elements, B=Bi, Sb, and T=Te, Se), which share the same crystal structure with Bi_2Se_3 family. $LnBT_3$ can be regarded as Bi_2Se_3 with half of the Bi atoms replaced by Ln. Unlike Bi_2Se_3 family, in these materials inversion symmetry is not always preserved. Since lanthanum (La) and Yttrium (Y) have no $4f$ electrons, $LaBiTe_3$, $YBiTe_3$, $LaSbTe_3$, and $YSbTe_3$ are four simplest ternary rare earth chalcogenides which have been synthesized in experiments.[28] In this work we focus on these four compounds based on *ab initio* calculations, among which we find that $LaBiTe_3$ is a strong topological insulator. Moreover, La and Y can be replaced by other rare-earth elements which have magnetic moments due to the localized f electrons. These systems could provide realizations of the topological Mott insulator state.[29] The versatility of rare earth elements will bring us new possibilities beyond Bi_2Te_3 family.

II. METHOD AND CRYSTAL STRUCTURE

The electronic structures of $LaBiTe_3$, $YBiTe_3$, $LaSbTe_3$, and $YSbTe_3$ are calculated in the framework of the density-functional theory with Perdew-Burke-Ernzerbof-type generalized-gradient approximation (GGA).[30] For our calculations, both the *Vienna ab initio simulation package* (VASP) (Refs. 31 and 32) with the projected augmented wave method[33] and the BSTATE package[34] with plane-wave pseudopotential method are employed. We adopt the $12\times12\times12$ k-point grid for self-consistent calculations. The kinetic energy cutoff for the plane-wave basis in BSTATE package is fixed to 340 eV. SOC is included in all of our calculation, except in the calculations for the ionic optimization which is confirmed to be insensitive to SOC.

$LaBiTe_3$, $YBiTe_3$, $LaSbTe_3$, and $YSbTe_3$ share the same rhombohedral crystal structure with the space group $D_{3d}^5(R\bar{3}m)$ (see Ref. 28 and references therein). Here we take $LaBiTe_3$ as an example. Similar to Bi_2Te_3, the crystal consists of triangular layers stacking along [111] direction with A-B-C$\cdots$ order. Five atomic layers form a quintuple layer with the order of Te-X-Te-X′-Te, where X and X′ denote La or Bi organized in certain pattern, as discussed below. Though the lattice parameters have been measured by experiments, up to our knowledge, the relative position between M and M′ has not been fully resolved experimentally. Thus we compare the total energy obtained in *ab initio* calculation for different configurations to search for the most stable structure. Our result indicates that the structures with La and Bi

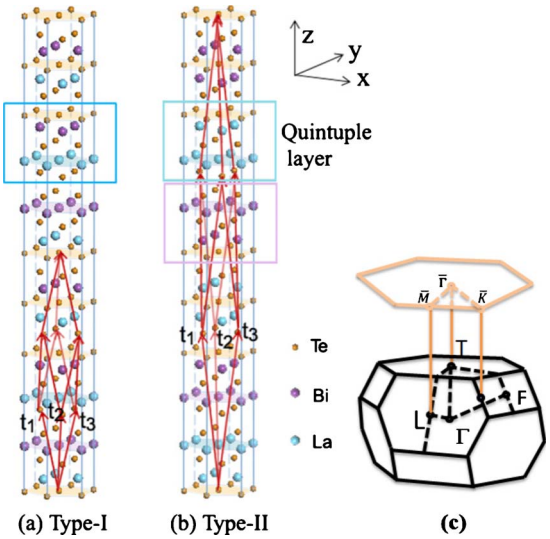

FIG. 1. (Color online) Crystal structures of $LaBiTe_3$ with three primitive lattice vectors denoted as $t1;2;3$ for (a) type-I and (b) type-II lattices. The quintuple layers, Te-La-Te′-Bi-Te for type-I lattice, and Te-La-Te′-La-Te, and Te-Bi-Te″-Bi-Te for type-II lattice are indicated by rectangles. The c axis of equivalent hexagonal lattice is along the z direction. (c) The first Brillouin zone is shown for the rhombohedral lattice as well as the 2D projected surface.

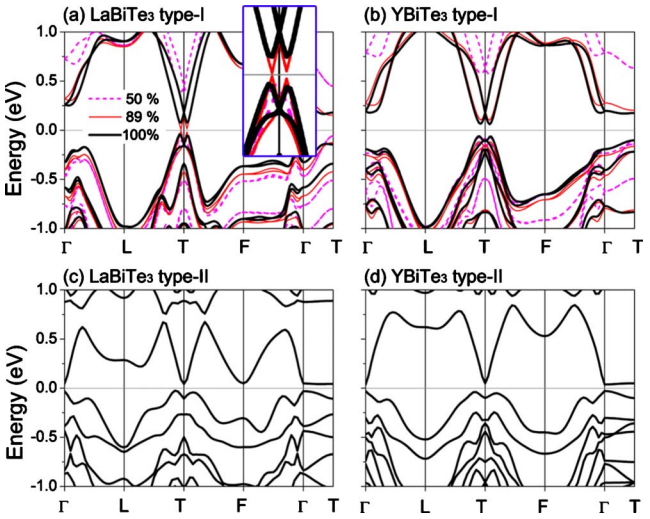

FIG. 2. (Color online) Band structures for (a) $LaBiTe_3$ and (b) $YBiTe_3$ of type-I structures, and (c) $LaBiTe_3$ and (d) $YBiTe_3$ of type-II structures. The strengths of spin-orbit coupling (SOC) are tuned to be 50% (dashed purple lines), 89% (thin red lines), and 100% (thick black lines) respectively, in (a) and (b). The Fermi energy is set to zero. The energy gap decreases to zero and reopens as SOC increases from zero to 100% for $LaBiTe_3$, showing a clear band anticrossing feature. The Dirac-type level crossing at 89% SOC is highlighted in the inset. (e) Brillouin zone for this class of materials. The four inequivalent time-reversal-invariant points are $\Gamma(0;0;0)$, $L(\pi;0;0)$, $F(\pi;\pi;0)$, and $T(\pi;\pi;\pi)$. The surface Brillouin zone is projected from the 3D bulk Brillouin zone into the plane of the atomic layer.

separated in different atomic layers are more stable than those with La and Bi mixed in the same atomic layer. There are two structures which have lowest energy. Because the energy differences between the two configurations are very small, in the following we will study both of them separately. (i) Type-I structure consists of stacking quintuple layers along [111] direction, each of which is ordered as Te-La-Te-Bi-Te, as shown in Fig. 1(a). This structure is inversion asymmetric. (ii) Type-II structure consists of stacking pairs of quintuple layers along [111] direction, ordered as Te-La-Te′-La-Te and Te-Bi-Te″-Bi-Te. This structure is inversion symmetric. The experimental lattice constants and optimized atomic coordinates for the two structures are listed in Table I.

III. TYPE-I STRUCTURE

We start by computing the band structures for $LaBiTe_3$, $YBiTe_3$, $LaSbTe_3$, and $YSbTe_3$ in the type-I crystal structure. As examples, Fig. 2 shows the results for $LaBiTe_3$ and $YBiTe_3$. Both of them have similar band gap 0.12 eV around the T point. The band gap of $YBiTe_3$ is close to the previous experimental value[35] $0.18\sim0.23$ eV. As mentioned above, due to the lack of inversion symmetry, the parity criteria for

TABLE I. The experimental lattice parameters (Ref. 28) a and c of hexagonal lattice in unit of angstrom, the theoretically optimized atomic positions and band gaps. Type-II structure has twice the length of type-I along c axis (see Fig. 1) and thereafter has double atoms. The atomic coordinate is $(0,0,z_0c)$ in the rhombohedral primitive unit cell. We listed z_0 values for all atoms. These Te atoms as inversion centers of type-II are marked as Te′ and Te″. The energy gap(E_g) is in unit of eV.

	Type-I				Type-II			
	$LaBiTe_3$	$YBiTe_3$	$LaSbTe_3$	$YSbTe_3$	$LaBiTe_3$	$YBiTe_3$	$LaSbTe_3$	$YSbTe_3$
a	4.39	4.46	4.24	4.47	4.39	4.46	4.24	4.47
c	30.20	31.65	30.40	30.32	60.40	63.30	60.80	60.64
Te(Te′/Te″)	0.0	0.0	0.0	0.0	0.0/0.5	0.0/0.5	0.0/0.5	0.0/0.5
Te	0.20876	0.22243	0.20426	0.21850	±0.10604	±0.10764	±0.10702	±0.10839
Te	−0.20893	−0.21228	−0.21136	−0.21306	±0.39572	±0.38883	±0.39790	±0.39076
Bi(Sb)	0.40274	0.40161	0.40102	0.40156	±0.19922	±0.19873	±0.19846	±0.19801
La(Y)	−0.39938	−0.39416	−0.40111	−0.39582	±0.29951	±0.30219	±0.29913	±0.30120
E_g	0.12	0.12	0.15	0.28	0.07	0.07	0	0.10

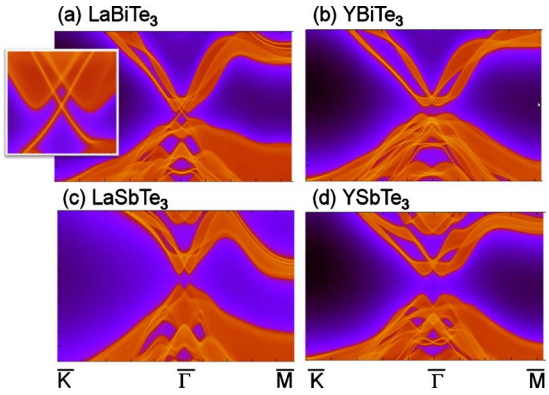

FIG. 3. (Color online) The band dispersion for an semi-infinite surface of (a) $LaBiTe_3$, (b) $YBiTe_3$, and (c) $LaSbTe_3$ and $YSbTe_3$ of type-I structures. The inset of (a) highlights the surface states near the Dirac cone.

topological insulators[10] does not apply. Alternatively, we study the evolution of conduction and valence bands by tuning the SOC strength artificially. Without SOC, any insulator must be topologically trivial so that a topological insulator phase can be identified by studying the topological phase transition at some critical SOC strength.[8] A Dirac-type level crossing between valence and conduction bands separate the topologically trivial and nontrivial phases.[8,36] The continuous tuning of SOC is obtained by changing the speed of light c in the VASP package. As shown in Fig. 2(a), upon the increase in SOC strength, the band gap of $LaBiTe_3$ decreases and vanishes on a ring in Brillouin zone (BZ) near T at 89% SOC and opens again, which indicates a topological phase transition[37] and suggests that $LaBiTe_3$ is a topologically nontrivial insulator with full SOC strength. In contrast, the band gap remains finite upon turning on SOC for $YBiTe_3$, which is thus a topologically trivial insulator. We perform the same calculations for $LaSbTe_3$ and $YSbTe_3$, and find both of them are topologically trivial insulators.

The existence of topological surface states is one of the most important physical consequence of the TIs. To further confirm the topological nature of the proposed materials and study the detailed features of the surface states, we obtain the dispersion of surface states based on *ab initio* method. We construct tight-binding Hamiltonian of the semi-infinite system with maximally localized Wannier functions (Refs. 38 and 39) basis for $LaBiTe_3$ family materials and then apply the standard Green function's iteration method[40,41] to obtain the surface density of states. The detail of this method can be found in Ref. 36. In Fig. 3 we can see clearly that the topological surface states form a single-Dirac cone at the $\bar{\Gamma}$ point in 2D BZ within the bulk gap for $LaBiTe_3$ while no such surface states are observed for $YBiTe_3$, $LaSbTe_3$, and $YSbTe_3$. This result determines the topologically nontrivial nature of $LaBiTe_3$ without any doubt. From this calculation, we can further obtain the Fermi velocity for $LaBiTe_3$ to be 4.0×10^5 m/s, similar to that of Bi_2Se_3.[12]

IV. TYPE-II STRUCTURE

The band structures for $LaBiTe_3$ and $YBiTe_3$ of type-II are shown in Figs. 2(c) and 2(d). Their band gaps are 0.07 eV near the Γ point, smaller than those of type-I structures. Due to inversion symmetry, we can follow the parity criteria proposed by Fu and Kane[10] to calculate $\mathbb{Z}_2$ topological index. The product of the parities of the Bloch wave functions is determined for the occupied bands at all time-reversal-invariant momenta $\Gamma(0,0,0), L(\pi,0,0), F(\pi,\pi,0), T(\pi,\pi,\pi)$ in BZ. For $LaBiTe_3$, we find that the product of parities at Γ is "+" and those at L,F,T are all "–." Thus $LaBiTe_3$ is topological nontrivial with $\mathbb{Z}_2$ index (1;000). For $YBiTe_3$ and $YSbTe_3$, we find that the products of parities at Γ,L,F,T are all "–" so that both of them are topologically trivial with $\mathbb{Z}_2$ index (0;000). In addition, $LaSbTe_3$ is found to be a semimetal. For both type-I and -II structures, it is noted that the states near Fermi energy are partially composed by La/Y $5d_{z^2}$ as well as Bi/Sb $6p_z$ and Te $5p_z$ orbitals.

V. DISCUSSION

In summary, our *ab initio* calculation has verified that $LaBiTe_3$ is a strong topological insulator while $YBiTe_3$, $LaSbTe_3$, and $YSbTe_3$ are trivial materials. This can be qualitatively explain by the fact that $LaBiTe_3$ has the strongest SOC among these four compounds due to heavy La and Bi elements. The substitution of La in $LaBiTe_3$ with even heavier rare-earth elements will open a wide platform to study various topological nontrival behaviors. It is found that many isostructural stoichiometric compounds similar to $LaBiTe_3$ also exist in the family of ternary rare earth chalcogenides,[28] such as LnBiTe$_3$ (with Ln standing for La,Ce,Pr,…,Lu or Y) and LnSbTe$_3$, many of which have intrinsic magnetic moments due to the localized f electrons (e.g., Pr, Sm, or Gd). Since the strong correlation effect induced by f electrons cannot be properly taken into account in the current GGA calculations, we will leave the detailed study of these materials for the future work but discuss the possible states induced by strong electron correlation. First, if the coupling between magnetic moments is ferromagnetic, quantum anomalous Hall effect may emerge in thin films or heterostructures of LnBiTe$_3$ when the band structure is normal for one spin while inverted for the other, similar to the proposals in $Hg_{1-x}Mn_xTe$ (Ref. 42) and $Bi_{2-x}Fe_xSe_3$.[27] Second, if the magnetic coupling is ferromagnetic within one atomic layer but antiferromagnetic between two neighboring atomic layers, the dynamical axion field may be realized, which is proposed as a novel optical modulators device.[6] The recently proposed topological Kondo insulator[43] may also exist in this class of materials due to the existence of f electrons. Besides the topological insulators the newly proposed materials have another important potential application. As we have shown, some materials in this family are trivial insulators such as $YBiTe_3$ and $YSbTe_3$. Due to their similarity with the Bi_2Te_3 family, the trivial insulators in this family are natural candidates of barrier materials for thin films or quantum wells of the TIs in the Bi_2Te_3 family and the $LaBiTe_3$ family. Especially, $YBiTe_3$(a=4.46 Å)-$LaBiTe_3$(a=4.39 Å) and $YBiTe_3$-Bi_2Te_3(a=4.3835 Å) (Ref. 44) pairs have the best-matched lattice constants. Such a barrier material may help protecting a clean surface of TI and greatly

improve the surface condition in transport experiments, which is a main difficulty in the current experiments.

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[1] X. Qi and S. Zhang, Phys. Today **63**(1), 33 (2010).
[2] J. Moore, Nature (London) **464**, 194 (2010).
[3] M. Hasan and C. Kane, arXiv:1002.3895 (unpublished).
[4] X.-L. Qi, T. L. Hughes, and S.-C. Zhang, Phys. Rev. B **78**, 195424 (2008).
[5] X. Qi, R. Li, J. Zang, and S. Zhang, Science **323**, 1184 (2009).
[6] R. Li, J. Wang, X.-L. Qi, and S.-C. Zhang, Nat. Phys. **6**, 284 (2010).
[7] L. Fu and C. L. Kane, Phys. Rev. Lett. **100**, 096407 (2008).
[8] B. A. Bernevig, T. L. Hughes, and S. C. Zhang, Science **314**, 1757 (2006).
[9] M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. Molenkamp, X.-L. Qi, and S.-C. Zhang, Science **318**, 766 (2007).
[10] L. Fu and C. L. Kane, Phys. Rev. B **76**, 045302 (2007).
[11] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature (London) **452**, 970 (2008).
[12] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nat. Phys. **5**, 438 (2009).
[13] Y. Xia *et al.*, Nat. Phys. **5**, 398 (2009).
[14] Y. L. Chen *et al.*, Science **325**, 178 (2009).
[15] B. Yan, C.-X. Liu, H.-J. Zhang, C.-Y. Yam, X.-L. Qi, T. Frauenheim, and S.-C. Zhang, EPL **90**, 37002 (2010).
[16] Y. Chen, Z. Liu, J. Analytis, J. Chu, H. Zhang, S. Mo, R. Moore, D. Lu, I. Fisher, S. Zhang, Z. Hussain, and Z. Shen, arXiv:1006.3843 (unpublished).
[17] T. Sato, K. Segawa, H. Guo, K. Sugawara, S. Souma, T. Takahashi, and Y. Ando, arXiv:1006.2437 (unpublished).
[18] S. Chadov, X. L. Qi, J. Kübler, G. H. Fecher, C. Felser, and S. C. Zhang, Nature Mater. **9**, 541 (2010).
[19] H. Lin, L. A. Wray, Y. Xia, S. Xu, S. Jia, R. J. Cava, A. Bansil, and M. Z. Hasan, Nature Mater. **9**, 546 (2010).
[20] H. Lin, R. Markiewicz, L. Wray, L. Fu, M. Hasan, and A. Bansil, arXiv:1003.2615 (unpublished).
[21] S. Xu, L. Wray, Y. Xia, R. Shankar, A. Petersen, A. Fedorov, H. Lin, A. Bansil, Y. Hor, D. Grauer, R. Cava, and M. Hasan, arXiv:1007.5111 (unpublished).
[22] M. Klintenberg, arXiv:1007.4838 (unpublished).
[23] W. Feng, J. Ding, D. Ixiao, and Y. Yao, arXiv:1008.0056 (unpublished).
[24] H. Jin, J. Song, A. Freeman, and M. Kanatzidis, arXiv:1007.5480 (unpublished).
[25] Q. Liu, C.-X. Liu, C. Xu, X.-L. Qi, and S.-C. Zhang, Phys. Rev. Lett. **102**, 156603 (2009).
[26] Y. S. Hor *et al.*, Phys. Rev. B **81**, 195203 (2010).
[27] R. Yu, W. Zhang, H. Zhang, S. Zhang, X. Dai, and Z. Fang, Science **329**, 61 (2010).
[28] O. Madelung, U. Rössler, and M. Schulz, *Ternary Compounds and Organic Semiconductors*, Landolt-Börnstein, Group III, Condensed Matter Vol. 41E (Springer, Berlin, 2000), pp. 471–477.
[29] S. Raghu, X. Qi, C. Honerkamp, and S. Zhang, Phys. Rev. Lett. **100**, 156401 (2008).
[30] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[31] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[32] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[33] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[34] Z. Fang and K. Terakura, J. Phys.: Condens. Matter **14**, 3001 (2002).
[35] P. Rustamov, F. Sadygov, Z. Melikova, M. Alidzhanov, and M. Ali-Zade, Inorg. Mater. **15**, 607 (1979).
[36] H.-J. Zhang, C.-X. Liu, X.-L. Qi, X.-Y. Deng, X. Dai, S.-C. Zhang, and Z. Fang, Phys. Rev. B **80**, 085307 (2009).
[37] S. Murakami, New J. Phys. **9**, 356 (2007).
[38] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).
[39] I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B **65**, 035109 (2001).
[40] M. P. L. Sancho, J. M. L. Sancho, and J. Rubio, J. Phys. F: Met. Phys. **14**, 1205 (1984).
[41] M. P. L. Sancho, J. M. L. Sancho, J. M. L. Sancho, and J. Rubio, J. Phys. F: Met. Phys. **15**, 851 (1985).
[42] C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Phys. Rev. Lett. **101**, 146802 (2008).
[43] M. Dzero, K. Sun, V. Galitski, and P. Coleman, Phys. Rev. Lett. **104**, 106408 (2010).
[44] O. Madelung, U. Rössler, and M. Schulz, *Bismuth Telluride* (Bi_2Te_3) *Crystal Structure, Chemical Bond, Lattice Parameters (Including Data for Related Compounds)*, Landolt-Börnstein, Group III, Condensed Matter (Springer, Berlin, 1998).