Rock-salt SnS and SnSe: Native Topological Crystalline Insulators

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Unlike time-reversal topological insulators, surface metallic states with Dirac cone dispersion in the recently discovered topological crystalline insulators (TCIs) are protected by crystal symmetry. To date, TCI behaviors have been observed in SnTe and the related alloys Pb1–xSnxSe/Te, which incorporate heavy elements with large spin-orbit coupling (SOC). Here, by combining first-principles and ab initio tight-binding calculations, we report the formation of a TCI in the relatively lighter rock-salt SnS and SnSe. This TCI is characterized by an even number of Dirac cones at the high-symmetry crystal surfaces perpendicular to the (110) mirror plane. We find that both SnS and SnSe have an intrinsically inverted band structure and the SOC is necessary only to open the bulk band gap. The bulk band gap evolution upon volume expansion reveals a topological transition from an ambient pressure TCI to a topologically trivial insulator. Our results indicate that the SOC alone is not sufficient to drive the topological transition.

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Since the discovery of Z2 topological insulators (TIs) [1, 2], band topological properties in condensed matter physics have attracted increasing interest as a new physical paradigm, which also shows great promise for potentially revolutionary applications in quantum computing and spintronics. TIs possess a non-trivial time-reversal Z2 topological invariant and the topological characteristics are manifested by the presence of an odd number of linearly dispersing Dirac cones at the crystal surfaces. These surface metallic states are due to large spin-orbit coupling (SOC) and are protected by time-reversal symmetry [1, 2].

In 2011, Liang Fu proposed a theoretical model for an alternative class of topological states, named topological crystalline insulators (TCIs), in which the gapless surface states are protected not by time-reversal symmetry but by crystal symmetry [3, 4]. Up to now, the only reported TCIs are the narrow band gap semiconductor SnTe and the related alloys Pb1–xSnxSe/Te [5–7]. Very recently, Barone et al. have theoretically predicted that a suitable combination of applied pressure and alloying can turn rock-salt lead chalcogenides, such as PbSe, PbTe, and PbS, into TCIs [10]. The most prominent feature of this class of TCIs is the presence of an even, not odd as in TIs, number of Dirac cones which lay on surface terminations oriented perpendicular to the mirror symmetry planes. It is shown that the necessary conditions for the band inversions to occur in all these TCIs are (i) a strongly asymmetric hybridization between cation (anion) s and anion (cation) p states and (ii) a sizable SOC strength, similarly in time-reversal TIs [11–18]. Large SOC is recognized to be a crucial ingredient to form possible TCIs also in pyrochlore oxides A2Ir2O7, where A is a rare-earth element [19]. However, TCIs can be considered as the counterpart of TIs in materials without SOC [3]. Thus, it is of fundamental importance to seek a manifestation of the non-trivial crystalline topology in materials composed of constituents with lighter mass and thus smaller SOC, for which the SOC effect is detached from the formation of TCIs.

In this Letter, through first-principles calculations along with Wannier functions based ab initio tight-binding (TB) modeling, we report that rock-salt SnS and SnSe are both TCIs in their native phase without any alloying or applied strain/pressure. We find that their inverted band order is induced by chemical bonding and crystal field, whereas the SOC effect is only to open the bulk band gap. This non-trivial topological state is substantiated by the emergence of an even number of Dirac cones at the high-symmetry crystal surfaces perpendicular to the (110) mirror symmetry plane. We also demonstrate that a topological transition occurs to a trivial insulator upon volume expansion.

First-principles calculations based on density func-
tional theory (DFT) are performed in the generalized gradient approximation (GGA), following the Perdew-Burke-Ernzerhof parametrization scheme [20], with the projected augmented wave method as implemented in the Vienna Ab initio Simulation Package (VASP) [21, 22]. The energy cutoff is set to be 500 eV. The TB matrix elements are calculated by projection onto maximally localized Wannier orbitals [23, 24], using the VASP2WANNIER90 interface [26].

Early experimental characterizations [27–29] have found that both SnS and SnSe crystallize in low temperatures Pnma GeS-type orthorhombic phases [30] and that at high temperatures two metastable orthorhombic Cmcm TII-type [31] and rock-salt cubic NaCl-type phases [29] (Fig. 1) exist. Here, we focus on the rock-salt structure, which has been shown to be stable under epitaxial growth of SnSe and SnS on a NaCl substrate with lattice constants $a_{\text{SnSe}} = 5.99$ Å [28] and $a_{\text{SnS}} = 6.00$ Å [28] and 5.80 Å [31], respectively. Our first-principles calculations find that the optimized lattice constants are $a_{\text{SnS}} = 6.05$ Å and $a_{\text{SnSe}} = 5.85$ Å for SnSe and SnS, respectively, in good agreement with the experimental values.

To quantify the topological feature, we shall evaluate the mirror Chern number. We first calculate the Berry curvature $\Omega^m(k) = \nabla_k \times A^m(k)$ on the (T10) mirror symmetry plane in the BZ. Here, $A^m(k) = i \sum_n \langle u^m_n(k) | \nabla_k | u^m_n(k) \rangle$ is the Berry connection, $u^m_n(k)$ is the $n$-th eigenstate at momentum $k$ and with mirror eigenvalue $m (= \pm \hat{z})$ of the TB model described below, and the sum is over all occupied bands. The results of the component $\Omega^m_{\pm}(k)$ perpendicular to the (T10) mirror plane are shown in Fig. 2 for SnSe with both experimental and expanded lattice constants. We find that the main contributions are from momenta close to $L$ and that $\Omega^m_{\pm}(k) = -\Omega^m_{\mp}(k)$. We evaluate the mirror Chern number $c_M = (n_{+} - n_{-})/2$, where $n_m = \int \Omega^m(k) \cdot dS$, and find that $c_M = -2$ (0) for SnSe with the experi-

**FIG. 1:** (color online) (a) SnM (M = S and Se) rock-salt lattice structure and (b) face cubic centered (FCC) Brillouin zone (BZ). Two dimensional BZ projected onto the (001), (110), and (111) surfaces are also shown in (b). These three surfaces are all perpendicular to the (110) mirror symmetry plane.

**Bulk band structure.** The calculated bulk band structures along the high symmetry lines around $L$ in the Brillouin zone (BZ) are shown in Fig. 2(a)–(d), and for comparison the results for those of the isostructural TCI SnTe are also plotted in Fig. 2(e) and (f) [32, 33]. The band structures of SnS, SnSe, and SnTe display similar features, which are summarized as follows: (i) Without SOC, all compounds have a gapless three dimensional (3D) Dirac cone located in the vicinity of the high symmetry $L$ point along the $L$-$W$ line; (ii) Level anticrossing occurs once SOC is included and the 3D Dirac cone is broken with opening a finite band gap; (iii) The top of the valence band and the bottom of the conduction band at and near $L$ are primarily composed of Sn $p$-like and S/Se/Te $p$-like states, respectively; (iv) The parity of the top (bottom) of the valence (conduction) band at $L$ is odd (even); (v) The band character around $L$ remains unchanged upon including SOC. These features already indicate that rock-salt SnS and SnSe are TCIs just like SnTe [34]. It should be emphasized here that, unlike TIs [11–18], the inverted band order is found to be driven not by SOC but solely by chemical bonding and crystal field [see Fig. 2(j)].

The occurrence of band inversion at an even number of $k$ points (i.e., four equivalent $L$ points) and the fact that this band inversion is not driven by SOC are suggestive of the formation of a crystal-symmetry driven non-trivial topological state. In order to provide further support, let us study the evolution of the band gap as a function of the lattice constant. It is an obvious fact that any insulator is topologically trivial in the atomic limit. Therefore, the occurrence of inverted band order implies that the band gap has to close and re-open by progressively increasing the lattice constant. This behavior is indeed found in Fig. 2(i): The band gap $E_g$ at $L$ closes with increasing the lattice constant and then re-opens with the opposite band character, i.e., the parity as well as the main contributing weight of the constituent atoms being reversed for the top of the valence band and the bottom of the conduction band [Fig. 2(d) and (h)]. These results clearly demonstrate that a topological phase transition from a topologically non-trivial to a trivial states occurs with increasing the lattice constant. Note that a similar behavior is found even without including SOC [Fig. 2(c) and (g)], indicating that SOC has indeed no influence in determining the band character around $L$. The evolution of the band character is schematically drawn in Fig. 2(j).
FIG. 2: (color online) (a-h): Electronic band structures obtained by first-principles calculations for SnS (a,b), SnSe (c,d,g,h), and SnTe (e,f) with and without SOC. The size of red dots in (a)-(h) is proportional to the amount of contributing weight in each band from S (a,b), Se (c,d,g,h), or Te (e,f) atoms. In (a)-(f), the experimental lattice constant \(\alpha\) (indicated in the figures) is used \(\frac{\sqrt{2}}{2}\), whereas in (g) and (h) an expanded lattice constant is used. The irreducible representations of the bands closest to Fermi energy (set to be 0) are also indicated \(\frac{\sqrt{2}}{2}\).

(j) A schematic energy level diagram around \(L\): (I) atomic limit, (II) including hybridization with a large lattice constant, (III) with the experimental lattice constant, and (IV) inclusion of SOC. The band is inverted already in (III) without SOC. Here \(E_F\) stands for Fermi energy. The signs (+, −) denote the parities of the corresponding \(p\)-like orbitals.

expected to exist only on surfaces which are perpendicular to the \((\bar{T}10)\) mirror symmetry planes \(\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}\).

To prove these expectations, we shall now compute the band dispersions for the \((001), (110)\) and \((111)\) surfaces [see Fig. 4 (b)] using the \textit{ab initio} TB model. The \textit{ab initio} TB model is constructed by downfolding the bulk energy bands, obtained by first-principles calculations, using maximally-localized Wannier functions (MLWFs). As the bulk energy bands near Fermi energy are predominantly formed by hybridized \(p\)-like Sn and S/Se orbitals, the MLWFs are derived from atomic \(p\)-like orbitals and the TB parameters are determined from the MLWFs overlap matrix. The SOC is considered here in the atomic form:

\[
H_{SO}^{p}(\lambda) = \frac{\lambda}{2} \begin{bmatrix}
0 & 0 & -i & 0 & 0 & 0 \\
0 & 0 & 0 & i & -1 & 0 \\
i & 0 & 0 & 0 & 0 & -i \\
0 & -i & 0 & 0 & -i & 0 \\
0 & -1 & 0 & i & 0 & 0 \\
1 & 0 & i & 0 & 0 & 0
\end{bmatrix}
\]

with \(p\)-like orbital bases \(\{|p_x, \uparrow\}, |p_x, \downarrow\}, |p_y, \uparrow\}, |p_y, \downarrow\}, |p_z, \uparrow\}, |p_z, \downarrow\}\rangle\), where arrows indicate electron spins. The SOC parameter \(\lambda\) for Sn, Se, and S are taken from experimental spectral data, i.e., \(\lambda_{Sn}=0.27\) eV, \(\lambda_{Se}=0.22\) eV, and \(\lambda_{S}=0.05\) eV, respectively [38]. The quality of the TB parameterization is successfully assessed in Fig. 4, where the TB bulk band structures are compared with the corresponding first-principles results.

Encouraged by this quantitative agreement, let us finally compute the surface band structures by adopting
three slabs for the (001), (110), and (111) surfaces with thickness of 89, 89, and 239 atomic layers, respectively. The results of the TB calculations are summarized in Fig. 5. These results show clearly that the (001), (110), and (111) surfaces with the experimental lattice constants posses metallic states with opposite mirror eigenvalues which cross each other forming a massless Dirac cone. It have been shown [5, 9] that the rock-salt TCIs with the mirror Chern number \( c_M = -2 \) guarantees the presence of two pairs of counter-propagating, spin-resolved surface states with opposite mirror eigenvalues along all symmetrically equivalent \( \Gamma-X \) lines in the (100) surface, and only one pair in the (110) surface [Fig. 5 (b)]. Indeed, both SnS and SnSe surfaces follow this symmetry consideration, displaying four equivalent Dirac cones in the (001) surface [Fig. 5 (a) and (e)] and two Dirac cones in the (110) surface [Fig. 5 (b) and (f)]. Instead, similarly to the case of SnTe [5], four Dirac cones are found in the (111) surface, one at \( \Gamma \) and other three at \( M \), as shown in Fig. 5 (c), (d), (g), and (h).

In addition, as already shown in Fig. 5 (a) and Fig. 4 for the lattice constants larger than 6.10 Å for SnS and 6.37 Å for SnSe, the band character changes and the systems undergo a topological transition towards a trivial insulator. This is clearly reflected also in the surface band structures computed for SnSe with the lattice constant \( a = 6.5 \) Å in Fig. 5 (i)-(l): the Dirac cones disappear and a broad spectral feature develops on the top (bottom) of the valence (conduction) band with a finite band gap, a typical behavior of an ordinary trivial insulator. These results unambiguously demonstrates that rock-salt SnSe and SnS represent the features of TCI.

In conclusion, using first-principles calculations together with \textit{ab initio} tight-binding model analyses, we have revealed that rock-salt SnS and SnSe represent a prime example of topological crystalline insulators at ambient pressure without incorporating heavy elements. We have shown that in both systems an even number of symmetry-protected Dirac cones emerge in the (100), (110), and (111) surfaces perpendicular to the \((110) \) mirror symmetry plane. We have also shown that the spin-orbit coupling is still important to open the band gap in the bulk phases although it is not necessary to drive the topologically non-trivial state with the inverted band order, as proposed in the original theory [5]. We have also demonstrated that a topological transition occurs toward a trivial insulator upon volume expansion. Finally, we emphasize that the onset of the topological crystalline insulating state in SnS and SnSe is not dependent on alloying, strain, pressure, or any electronic structure engineering, but SnS and SnSe are both topological crystalline insulators in their native phase.

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[1] M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010).
[2] X. L. Qi and S. C. Zhang, Rev. Mod. Phys. 83, 1057 (2011).
[3] L. Fu, Phys. Rev. Lett. 106, 106802 (2011).
[4] Also see R.-J. Slager, A. Mesaros, V. Juričić, and J. Zaanen, Nature Phys. 9, 98 (2013).
[5] T. H. Hsieh, H. Lin, J. Liu, W. Duan, A. Bansil, and L. Fu, Nature Comms. 3, 982 (2012).
[6] P. Dziawa, B. J. Kowalski, K. Dybko, R. Buczko, A. Szczepanakowska, M. Szot, E. Lusakowska, T. Balasubramanian, B. M. Wojek, M. H. Berntsen, O. Tjernberg, and T. Story, Nature Mater. 11, 1023 (2012).
[7] Y. Tanaka, Z. Ren, T. Sato, K. Nakayama, S. Souma, T. Takahashi, K. Segawa, and Y. Ando, Nature Phys. 8, 800 (2012).
[8] S. Y. Xu, C. Liu, N. Alidoust, D. Qian, M. Neupane, J. D. Denlinger, Y. J. Wang, H. Lin, L. A. Wray, R. J. Cava, A. Marcinkova, E. Morosan, A. Bansil, and M. Z. Hasan, Nature Comms. 3, 1192 (2012).
[9] J. Liu, W. Duan, and L. Fu, arXiv:1304.0430.
[10] P. Barone, T. Rauch, D. D. Sante, J. Henk, I. Mertig, and S. Picozzi, Phys. Rev. B 88, 045207 (2013); P. Barone, D. D. Sante, and S. Picozzi, arXiv:1308.1288.
[11] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature Phys. 5, 398 (2009).
[12] H. Zhang et al., Natrue Phys. 5, 438 (2009); C. X. Liu, X. L. Qi, H. Zhang, X. Dai, Z. Fang, and S. C. Zhang, Phys. Rev. B 82, 045122 (2010).
[13] H. Z. Lu, W. Y. Shan, W. Yao, Q. Niu, and S. Q. Shen, Phys. Rev. B 81, 115407 (2010).
[14] J. G. Analytis, J. H. Chu, Y. Chen, F. Corredor, R. D. McDonald, Z. X. Shen, and I. R. Fisher, Phys. Rev. B 81, 205407 (2010).
[15] D. Xiao, Y. Yao, W. Feng, J. Wen, W. Zhu, X.-Q. Chen, G. M. Stocks, and Z. Zhang, Phys. Rev. Lett. 105, 096404 (2010).
[16] Y. Sun, X.-Q. Chen, S. Yunoki, D. Li, and Y. Li, Phys. Rev. Lett. 105, 216406 (2010).
[17] Y. Sun, X.-Q. Chen, C. Franchini, D. Li, S. Yunoki, Y. Li, and Z. Fang, Phys. Rev. B 84, 165127 (2011).
[18] Y. Chen, Front. Phys. 7, 175 (2012).
[19] M. Kargarian and G. A. Fiete, Phys. Rev. Lett. 110, 156403 (2013).
[20] J. P. Perdew, K. Burke, and M. Ernzerho, Phys. Rev. Lett. 77, 3865 (1996).
[21] G. Kresse and J. Hafner, Phys. Rev. B 48, 13115, (1993).
[22] G. Kresse and J. Furthmüller, Comp. Mater. Sci. 6, 15 (1996).
[23] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
[24] I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).
[25] A. A. Mostofi, J. R. Yates, Y. S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. 178, 685 (2008).
[26] C. Franchini, R. Kovik, M. Marsman, S. S. Murthy, J. He, C. Ederer, and G. Kresse, J. Phys.: Condens. Matter 24, 235602 (2012).
[27] P. M. Nikolic, Brit. J. Appl. Phys. 16, 1075 (1965).
[28] A. N. Mariano and K. L. Chopra, Appl. Phys. Lett. 10, 282 (1967).
[29] L. S. Palatnik and V. V. Levitin, Doklady Akademii Nauk SSSR 96, 975-978 (1955).
[30] T. Chattopadhyay, J. Pannetier, and H. G. Von Schnering, J. Phys. Chem. of Solids 47, 879 (1986).
[31] B. F. Bilenkii, A. G. Mikolaichuk, and D. M. Freik, Phys. Status Solidi K5, 1968).
[32] For the lattice constant of SnTe, see R. Marx and K. J. Range, J. Less-Common Met. 155, 49 (1989).
[33] Although not shown for clarity, the same irreducible representations are assigned to the bands of SnS and SnTe. Note that the origin of the symmetry operations is set to Sn atom.
[34] One of the important quantitative differences is that the band gap $E_g$ of SnSe ($E_g$ $\sim$ 0.202 eV) seems larger than SnTe ($E_g$ $\sim$ 0.172 eV). However, more careful study beyond GGA is required for better quantitative comparison.
[35] J. C. Y. Teo, L. Fu, and C. L. Kane, Phys. Rev. B 78, 045426 (2008).
[36] L. Fu, C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 98, 106803 (2007).
[37] S. Safaei, P. Kacman, and R. Buczko, Phys. Rev. B 88, 045305 (2013).
[38] K. Wittel and R. Manne, Theor. Chim. Acta 33, 347 (1974).