**Topology on a new facet of bismuth**

The MIT Faculty has made this article openly available. *Please share* how this access benefits you. Your story matters.

| Citation       | Hsu, Chuang-Han et al. “Topology on a new facet of bismuth.” Proceedings of the National Academy of Sciences of the United States of America 116 (2019): 13255-13259 © 2019 The Author(s) |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| As Published   | 10.1073/pnas.1900527116                                                                                                                                                                           |
| Publisher      | Proceedings of the National Academy of Sciences                                                                                                                                                   |
| Version        | Final published version                                                                                                                                                                           |
| Citable link   | https://hdl.handle.net/1721.1/124469                                                                                                                                                              |
| Terms of Use   | Article is made available in accordance with the publisher’s policy and may be subject to US copyright law. Please refer to the publisher’s site for terms of use.                                       |
Topology on a new facet of bismuth

Chuang-Han Hsu1,a,b,1, Xiaoting Zhou1,c, Tay-Rong Changd,d,1, Qiong Ma1, Nuh Gedik2, Arun Bansil1, Su-Yang Xu2,2, Hsin Lin2,b, and Liang Fu2,a,2

*Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore 117542; 1Department of Physics, National Cheng Kung University, Tainan 701, Taiwan; 2Center for Quantum Frontiers of Research & Technology (QFort), Tainan 701, Taiwan; 3Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139; 4Department of Physics, Northeastern University, Boston, MA 02115; and 5Institute of Physics, Academia Sinica, Taipei 11529, Taiwan

Edited by Philip Hofmann, Department of Physics and Astronomy, Aarhus University, and accepted by Editorial Board Member Angel Rubio May 20, 2019 (received for review January 10, 2019)

Bismuth-based materials have been instrumental in the development of topological physics, even though bulk bismuth itself has been long thought to be topologically trivial. A recent study has, however, shown that bismuth is in fact a higher-order topological insulator featuring one-dimensional (1D) topological hinge states protected by threefold rotational and inversion symmetries. In this paper, we uncover another hidden facet of the band topology of bismuth by showing that bismuth is also a first-order topological crystalline insulator protected by a twofold rotational symmetry. As a result, its (110) surface exhibits a pair of gapless Dirac surface states. Remarkably, these surface Dirac cones are “unpinned” in the sense that they are not restricted to locate at specific k points in the (110) surface Brillouin zone. These unpinned 2D Dirac surface states could be probed directly via various spectroscopic techniques. Our analysis also reveals the presence of a distinct, previously uncharacterized set of 1D topological hinge states protected by the twofold rotational symmetry. Our study thus provides a comprehensive understanding of the topological band structure of bismuth.

Significance

We uncover the presence of a new topological crystalline insulator (TCI) state in bismuth, which is protected by a twofold rotational symmetry. In contrast to the recently discovered higher-order topological phase in bismuth, the present TCI phase hosts unpinned Dirac cone surface states that could be accessed directly through photoemission experiments. Our study provides a comprehensive understanding of the rich topological electronic structure of bismuth.

Author contributions: H.L. designed research; C.-H.H., X.Z., T.-R.C., Q.M., N.G., A.B., S.-Y.X., H.L., and L.F. performed research; C.-H.H., X.Z., T.-R.C., S.-Y.X., H.L., and L.F. analyzed data; C.-H.H., A.B., S.-Y.X., H.L., and L.F. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission. P.H. is a guest editor invited by the Editorial Board.

This open access article is distributed under Creative Commons Attribution-NonCommercial-NoDerivatives License 4.0 (CC BY-NC-ND).

1 C.-H.H., X.Z., and T.-R.C. contributed equally to this work.

2 To whom correspondence may be addressed. Email: nilnish@gmail.com, suyangxu@mit.edu, or liangfu@mit.edu.

1 Topological crystalline insulator | bismuth | topological hinge states | electronic structure

Bismuth is well known for its peculiar physical properties. It was long considered to be the stable element with the highest atomic mass, but relatively recent experiments have shown that bismuth is in fact weakly radioactive (1). It is a semimetal with a vanishingly small carrier density (10^17 cm^-3) but an exceptionally high electron mobility (10^6 cm^2 s^-1 V^-1) (2–5). As a result, the ultratetragonality regime is reached in bismuth at a magnetic field as small as 9 T, beyond which a number of correlated electron states have been observed (4–7). Because of bismuth’s large spin–orbit coupling, bismuth-based materials have also played a fundamental role in topological physics (8, 9). A bismuth–antimony alloy (Bi1−xSb) was the first experimental realization of a 3D topological insulator (TI) (10). The Bi2X3 family supports the prototypical TI state with a single surface Dirac cone (11–14). Doped Bi2X3 gives rise to the quantum anomalous Hall effect (15) and unconventional nematic superconductivity (16, 17). Na3Bi is a 3D Dirac semimetal (18, 19). Despite being a crucially important chemical component in many topological materials, pure bismuth has long been thought to be topologically trivial. However, distinct from an atomic band insulator, bismuth does have an even number of band inversions (10, 20). The existence of these band inversions implies that bismuth cannot be smoothly connected to an atomic band insulator without undergoing closing of its band gap. This suggests that the band topology of bismuth must be far from being trivial (8, 9, 20–22).

Theoretical advances on topological crystalline insulators (TCIs) (21) have greatly expanded the topological classification of band insulators beyond the Z2 TIs (8, 9). After the success of theoretical prediction and experimental realization of the mirror-symmetry–protected TCIs (20–35), two novel TCI phases, rotational-symmetry–protected TCIs (36) and higher-order TIs (37–43), have been theoretically proposed recently. Rotational-symmetry–protected TCIs are predicted to harbor “unpinned” Dirac surface states in that the surface normal to an N-fold rotational axis (N = 2, 4, 6) can host N Dirac cones whose Dirac points appear at generic k points in the surface Brillouin zone. In contrast, higher-order TIs are generated through the consideration of higher-order bulk-boundary correspondence. For instance, a 3D second-order TI supports 1D topological hinge states in a rotational symmetry-preserving rod. It is important to note that the first-order and higher-order topologies are not mutually exclusive. In particular, a TCI could support both topological 2D surface states and 1D hinge states. Thus, strictly speaking, a pure higher-order TI should refer to the TCIs that do not show the presence of topological surface states. Beyond these new TCI phases, another important theoretical advance is the development of methods to systematically diagnose topological invariants in terms of the symmetry eigenvalues of the electronic states (44–51). In this connection, Song et al. (47) and Khalaf et al. (48) found that, when certain additional symmetry Y is present, topological invariants of TCIs protected by symmetry X can be inferred from the Y-related symmetry eigenvalues of the energy bands. Such proposals of symmetry indicators and topological quantum chemistry have facilitated first-principles studies of new topological materials (52–58). Building upon these theoretical advances, a recent work (41) showed that pure bismuth hosts a second-order band topology that is protected by threefold rotational and inversion symmetries. As a result, it supports 1D topological hinge
states in a crystal whose shape preserves the threefold rotational and inversion symmetries. Here we show that the band topology of bismuth is even richer in that it also hides a first-order TCI state, which is protected by its twofold rotational symmetries, resulting in a pair of unpinned topological Dirac surface states on its (110) surface. We also reveal the presence of a distinct, previously uncharacterized set of 1D topological hinge states protected by twofold rotational symmetry.

Results

First-principles calculations were carried out using the VASP package (59, 60). An ultrasoft pseudopotential and the generalized-gradient approximation were applied in the self-consistency process. The experimental crystal structure of Bi was used (61) in the calculations. A Wannier-basis–based tight-binding model, where the s and p orbitals of Bi were included, was obtained via the Wannier90 package (62).

Bismuth crystalizes in a rhombohedral structure (61). Its space group and point group are $R3m$ ($\#166$) and $D_{3d}$, respectively. Each layer in this structure forms a buckled honeycomb lattice. The three principle lattice vectors ($a_{i}=\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$, $a_{2}=\left(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right)$, and $a_{3}=\left(0, 0, 1\right)$) are expressed in the Cartesian coordinates. (B) The bulk Brillouin zone. The principle reciprocal space vectors ($b_{1}$, $b_{2}$, and $b_{3}$) and high-symmetry points are noted. (C) Band structure of bismuth including spin-orbit coupling. The red and green circles represent positive and negative parity eigenvalues, respectively.

Table 1. Two possible topological states for the symmetry indicator $Z_{2,2,2,4}=\{0,0,0,2\}$ (47)

| $n_{I_{I_{000}}}^{\bar{1}0}$ | $n_{M_{110}}^{\bar{1}0}$ | $n_{2}$ |
|--------------------------|----------------------|--------|
| (0,0,0,0)                | 1                    | 0      |
| (0,0,0,0)                | 0                    | 2      |
| (0,0,0,0)                | 1                    | 1      |

$\left(\nu_{0}^{\bar{1}10};\nu_{2}^{\bar{1}10}\nu_{3}^{\bar{1}10}\right)$ are the $Z_{2}$ invariants for 3D $Z_{2}$ TIs. $n_{I_{I_{000}}}^{\bar{1}0}$ is a $Z_{2}$ invariant for the twofold rotational symmetry $Z_{110}$. $n_{M_{110}}^{\bar{1}0}=1$ corresponds to a rotational-symmetry-protected TCI, which features two unpinned Dirac surface states on the (110) surface. $n_{M_{110}}^{\bar{1}0}$ is the mirror Chern number for mirror plane $M_{110}$ and is a $Z_{2}$ invariant. $n_{M_{110}}^{\bar{1}0}=N$ features N Dirac surface states. Finally, $n_{2}$ is the $Z_{2}$ classified inversion (7) protected TCI index. $n_{2}=1$ features the hinge state in a 3D finite geometry preserving $I$.
As expected, we found two sets of surface Dirac cones, whose Dirac points are located at \((\pm 0.01 \pi, \mp 0.269 \pi)\) of \((k_x, k_z)\) axes indicated in Fig. 1B. These are generic \(k\) points, which are related only by the twofold rotational symmetry \(Z_2^{110}\). The calculated surface states along the \(k\) paths passing through the Dirac points (DPs) (Fig. 2E and F) directly show the presence of gapless Dirac surface states. Interestingly, these unpinned Dirac fermions are of type II (64) in that the velocities of the two surface bands that cross possess the same sign. By contrast, along the path \(T - \Gamma - L_1\) that does not go through the DP, the surface states are gapped (Fig. 2D). To further confirm the nontrivial nature of these states, we studied the Wannier points. For this purpose, it is helpful to rearrange the Fu–Kane formula (63) (Eq. 1) as

\[
(-1)^{\nu_0} = (-1)^\frac{1}{2} \sum_{k \in \text{TRIMs}} n_{k^-} \\
= (-1)^\frac{1}{2} \sum_{i = 1}^{N_{\text{TRIMs}}} C_{2,i}^{+} \pm \frac{1}{2} \sum_{i = 1}^{N_{\text{TRIMs}}} C_{2,i}^{-} \\
= (-1)^{\nu(+) + \nu(-)},
\]

where \(\nu_0\) is the strong TI (STI) index, and \(n_{k^-}\) is the number of occupied bands with negative parity eigenvalue. For space group \(\# \text{166}, \) only TRIMs \(\{1, T, L_1, F_1\}\) are invariant under one of the three \(C_2^{2±(1,2,3)}\) axes. However, states at the other pairs of \(\{L_2, L_3\}\) and \(\{F_2, F_3\}\) can be linearly combined into states invariant under \(C_2^{1±}\). Thus, the occupied bands can be separated into two subspaces according to their respective \(C_2\) eigenvalues \((\pm)\), which are \(\{C_{2,+}\}\) and \(\{C_{2,-}\}\) (Eq. 2). This rearrangement may lead to new topology beyond the \(Z_2\) TI state, but it can be made only when the system is \(Z_2\) trivial \((\nu_0 = 0)\). From Eq. 3, we see that \(\nu(+) + \nu(-) = 1\) in other words, the band structure in each \(C_2\) subspace can be viewed as a strong TI. The hybridization between the two strong TI surface states in the presence of the \(2_{110}\) rotational symmetry thus leads to the pair of unpinned Dirac surface states on the \((110)\) surface.

With the preceding discussion in mind, we computed the surface band structure throughout the \((110)\) surface BZ (Fig. 2).
A bismuth rods (Fig. 3) protected by charge centers (WCCs) (65–67) Rashba bands due to the double band inversions.

The calculated band structures (Fig. 2) show that these helical states are localized on the edges shared by adjacent side surfaces, further confirming that these are topological hinge states.

Finally, we show that the $2_{110}$ rotational-symmetry-protected topology sheds light on the large Rashba surface states observed on the (111) and (001) surfaces (2, 3). The double bulk band inversion at $\Gamma$ also leads to a pair of surface Dirac cones on the (111) and (001) surfaces. However, as (111) and (001) surfaces do not respect $2_{110}$, these Dirac cones are gapped, which naturally gives rise to the Rashba surface bands (Fig. 4). Note that since the Rashba surface states are nontopological, they can be created or removed by adjusting the surface potential (69).

Our analysis gives insight into the origin of Rashba bands on bismuth's (111) and (001) surfaces, which have been observed experimentally (2, 3, 69), in terms of the underlying symmetries and the double band inversions in the band topology of bismuth.

In summary, we have investigated topological properties of the bulk and surface band structures of bismuth. We show that bismuth is a TCI with multiple nontrivial topological invariants. In the first order, bismuth features unpinned Dirac surface states on the (110), (011), and (101) surfaces that are protected by their twofold rotational symmetries. These unpinned Dirac surface states would be amenable to direct imaging via photoemission spectroscopy. In the second order, bismuth features two sets of independent topological helical hinge states. The first set is protected by the twofold rotational symmetries whereas the second set is protected by the inversion symmetry. Our study thus provides a comprehensive picture of the rich band topology of bismuth, which is arguably the most important element involved in the field of topological materials.

Note Added in Proof. After we completed our study, we became aware of refs. 54 and 55, which also propose bismuth as a potential TCI. Our analysis, however, uniquely identifies bismuth as a rotational-symmetry-protected TCI.

**ACKNOWLEDGMENTS.** T.-R.C. and X.Z. were supported by the Young Scholar Fellowship Program from the Ministry of Science and Technology (MOST) in Taiwan, under a MOST grant for the Columbus Program MOST108-2636-M-006-002, National Cheng Kung University, Taiwan, and National Center for Theoretical Sciences, Taiwan. This work was supported partially by the MOST, Taiwan, Grant MOST107-2627-E-006-001. This research was supported in part by Higher Education Sprout Project, Ministry of Education to the Headquarters of University Advancement at National Cheng Kung University (NCKU). H.L. acknowledges Academia Sinica, Taiwan, for the support under Innovative Materials and Analysis Technology Exploration (AS–IMATE-107–11). L.F. was supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Division of Materials Sciences and Engineering under Award DE–SC0018945. The work at Northeastern University was supported by the US DOE, Office of Science, BES Grant DE–FG02–07ER46352, and benefited from Northeastern University's Advanced Scientific Computation Center and the National Energy Research Scientific Computing Center (NERS) supercomputing center through DOE Grant DE–AC02–05CH11231. N.G. and S.-Y.X. acknowledge support from the Science and Technology Center for Integrated Quantum Materials, NSF Grant DMR–1231319.

---

1. P. De Marcillac, N. Coron, G. Dambier, J. Leblanc, J.-P. Moallic, Experimental detection of $\alpha$-particles from the radioactive decay of natural bismuth. Nature 422, 876–878 (2003).
2. P. Hofmann, The surfaces of bismuth: Structural and electronic properties. Prog. Surf. Sci. 81, 191–245 (2006).
3. C. R. Ast, H. Höchst, Fermi surface of Bi (111) measured by photoemission spectroscopy. Phys. Rev. Lett. 87, 176702 (2001).
4. K. Behnia, L. Balicas, Y. Kopelevich, Signatures of electron fractionalization in ultraquantum bismuth. Science 317, 1729–1731 (2007).
5. L. Li et al., Phase transitions of Dirac electrons in bismuth. Science 321, 547–550 (2008).
6. B. E. Feldman et al., Observation of a nematic quantum Hall liquid on the surface of bismuth. Science 354, 316–321 (2016).
7. M. T. Randeria et al., Ferroelectric quantum Hall phase revealed by visualizing Landau level wavefunction interference. Nat. Phys. 14, 796–800 (2018).
8. M. Zahid Hasan, C. L. Kane, Colloquium: Topological insulators. Rev. Mod. Phys. 82, 3045–3067 (2010).
9. X.-L. Qi, S.-C. Zhang, Topological insulators and superconductors. Rev. Mod. Phys. 83, 1057–1110 (2011).
10. D. Hsieh et al., A topological Dirac insulator in a quantum spin Hall phase. Nature 452, 970–974 (2008).
11. Y. Xia et al., Observation of a large-gap topological-insulator class with a single Dirac cone on the surface. Nat. Phys. 5, 398–402 (2009).
12. H. Zhang et al., Topological insulators in Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ with a single Dirac cone on the surface. Nat. Phys. 5, 438–442 (2009).
13. D. Hsieh et al., A tunable topological insulator in the spin helical Dirac transport regime. Nature 460, 1101–1105 (2009).
14. Y. L. Chen et al., Experimental realization of a three-dimensional topological insulator, Bi$_2$Te$_3$. Science 325, 178–181 (2009).
15. C.-Z. Chang et al., Experimental observation of the quantum anomalous Hall effect in a magnetic topological insulator. Science 340, 167–170 (2013).
16. K. Matano, M. Kriener, K. Segawa, Y. Ando, G.-q. Zheng, Spin-rotation symmetry breaking in the superconducting state of Cu$_2$Bi$_2$Se$_3$. Nat. Phys. 12, 852–854 (2016).
17. S. Yonezawa et al., Thermodynamic evidence for nematic superconductivity in Cu$_2$Bi$_2$Se$_3$. Nat. Phys. 13, 123–126 (2017).
18. Z. Wang et al., Dirac semimetal and topological phase transitions in A$_3$Bi (A=Na, K, Rb). Phys. Rev. B 85, 195320 (2012).
19. Z. K. Liu et al., Discovery of a three-dimensional topological Dirac semimetal, Na$_3$Bi: Science 343, 864–867 (2014).

20. J. C. Y. Teo, L. Fu, C. L. Kane, Surface states and topological invariants in three-dimensional topological insulators: Application to Bi$_{1−x}$Sb$_x$: Phys. Rev. B 78, 045425 (2008).

21. L. Fu, Topological crystalline insulators. Phys. Rev. Lett. 106, 106802 (2011).

22. T. H. Hsieh et al., Topological crystalline insulators in the SnTe material class. Nat. Commun. 3, 982 (2012).

23. H. Weng, J. Zhao, Z. Wang, Z. Fang, X. Dai, Topological crystalline Kondo insulator in mixed valence ytterbium borides. Phys. Rev. Lett. 112, 016403 (2014).

24. B. J. Wieder et al., Wallpaper fermions and the nonsymmorphic Dirac insulator. Science 361, 246–251 (2018).

25. Z. Wang, A. Alexandradinata, R. J. Cava, B. Andrei Bernevig, Hourglass fermions. Nature 532, 189–194 (2016).

26. Y. Tanaka et al., Experimental realization of a topological crystalline insulator in SnTe. Nat. Phys. 8, 800–803 (2012).

27. P. Dziawa et al., Topological crystalline insulator states in Pb$_{1−x}$Sn$_x$Se. Nat. Mater. 11, 1023–1027 (2012).

28. S.-Y. Xu et al., Observation of a topological crystalline insulator phase and topological phase transition in Pb$_{1−x}$Sn$_x$Te. Nat. Commun. 3, 1192 (2012).

29. Y. Okada et al., Observation of Dirac node formation and mass acquisition in a topological crystalline insulator. Science 341, 1486–1499 (2013).

30. I. Zeljkovic et al., Mapping the unconventional orbital texture in topological crystalline insulators. Nat. Phys. 10, 572–577 (2014).

31. T. Liang et al., Evidence for massive bulk Dirac fermions in Pb$_{1−x}$Sn$_x$Se from Nernst and thermopower experiments. Nat. Commun. 4, 2696 (2013).

32. X. Li, Q. Niu, Topological phase transitions in thin films by tuning multi-valley boundary-state couplings. Phys. Rev. B 85, 241411 (2017).

33. K. Chang et al., Discovery of robust in-plane ferroelectricity in atomic-thick SnTe. Science 353, 274–278 (2016).

34. P. Sessi et al., Robust spin-polarized midgap states at step edges of topological crystalline insulators. Science 354, 1269–1273 (2016).

35. T. Liang et al., A pressure-induced topological phase with large Berry curvature in Pb$_{1−x}$Sn$_x$Te. Sci. Adv. 3, e1602510 (2017).

36. C. Fang, L. Fu, Rotation anomaly and topological crystalline insulators. arXiv:1709.01929 (6 September 2017).

37. Z. Song, Z. Fang, C. Fang, (d = 2)-dimensional edge states of rotation symmetry protected topological states. Phys. Rev. Lett. 119, 246402 (2017).

38. F. Schindler et al., Higher-order topological insulators. Sci. Adv. 4, eaat0346 (2018).

39. E. Khalaf, Higher-order topological insulators and superconductors protected by inversion symmetry. Phys. Rev. B 97, 205136 (2018).

40. A. Matsugatani, H. Watanabe, Connecting higher-order topological insulators to lower-dimensional topological insulators. Phys. Rev. B 98, 205129 (2018).

41. F. Schindler et al., Higher-order topology in bismuth. Nat. Phys. 14, 918–924 (2018).

42. Z. Wang, B. J. Wieder, J. Li, B. Yan, B. Andrei Bernevig, Higher-order topology, monopole nodal lines, and the origin of large Fermi arcs in transition metal dichalcogenides $X\text{Se}_2$ ($X=$ Mo, W). arXiv:1806.11116 (28 June 2018).

43. C. Yue et al., Symmetry enforced chiral hinge states and surface quantum anomalous Hall effect in magnetic axion insulator Bi$_2$$_2$Sn$_2$Se$_3$: arXiv:1807.01414 (4 July 2018).

44. B. Bradlyn et al., Topological quantum chemistry. Nature 547, 298–305 (2017).

45. J. Kruthoff, J. de Boer, J. van Wezel, C. L. Kane, R.-J. Slager, Topological classification of crystalline insulators through band structure combinatorics. Phys. Rev. X 7, 041069 (2017).

46. H. Chun Po, A. Vishwanath, H. Watanabe, Symmetry-based indicators of band topology in the 230 space groups. Nat. Commun. 8, 50 (2017).

47. Z. Song, T. Zhang, Z. Fang, C. Fang, Quantitative mappings between symmetry and topology in solids. Nat. Commun. 9, 3530 (2018).

48. E. Khalaf, H. Chun Po, A. Vishwanath, H. Watanabe, Symmetry indicators and anomalous surface states of topological crystalline insulators. Phys. Rev. X 8, 31070 (2017).

49. Z. Song, T. Zhang, C. Fang, Diagnosis for nonmagnetic topological semimetals in the absence of spin-orbital coupling. Phys. Rev. X 8, 031069 (2018).

50. B. Bradlyn et al., Band connectivity for topological quantum chemistry: Band structures as a graph theory problem. Phys. Rev. B 97, 035138 (2018).

51. J. Cano et al., Building blocks of topological quantum chemistry: Elementary band representations. Phys. Rev. B 97, 035139 (2018).

52. X. Zhou et al., Topological crystalline insulator states in the Ca$_2$As family. Phys. Rev. B 98, 241104 (2018).

53. F. Tang, H. Chun Po, A. Vishwanath, X. Wan, Efficient topological materials discovery using symmetry indicators. Nat. Phys. 15, 470–476 (2019).

54. F. Tang, H. Chun Po, A. Vishwanath, X. Wan, Comprehensive search for topological materials using symmetry indicators. Nature 566, 486–489 (2019).

55. T. Zhang et al., Catalogue of topological electronic materials. Nature 566, 475–479 (2019).

56. M. G. Vergniory et al., A complete catalogue of high-quality topological materials. Nature 566, 480–485 (2019).

57. B. Bradlyn et al., Beyond Dirac and Weyl fermions: Unconventional quasiparticles in conventional crystals. Science 353, aar5037 (2016).

58. C.-H. Hsu et al., Purely rotational symmetry-protected topological crystalline insulator $\alpha = \text{Bi}_{2}\text{Br}_4$: 2D Mater. 6, 031004 (2019).

59. G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

60. G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).

61. P. Cukca, C. S. Barrett, The crystal structure of Bi and of solid solutions of Pb, Sn, Sb and Te in Bi. Acta Crystallogr. 15, 865–872 (1962).

62. A. A. Mostofi et al., Wannier90: A tool for obtaining maximally-localised Wannier functions. Comput. Phys. Commun. 178, 685–699 (2008).

63. L. Fu, C. L. Kane, Topological insulators with inversion symmetry. Phys. Rev. B 76, 045302 (2007).

64. A. A. Soluyanov et al., Type-II Weyl semimetals. Nature 527, 495–498 (2015).

65. R. Yu, X. Liang Qi, A. Bernevig, Z. Fang, X. Dai, Equivalent expression of $\tilde{Z}_2$ topological invariants for band insulators using the non-Abelian Berry connection. Phys. Rev. B 84, 075119 (2011).

66. M. Tahernejad, K. F. Garrity, D. Vanderbilt, Wannier center sheets in topological insulators. Phys. Rev. B 89, 115102 (2014).

67. A. Alexandradinata, X. Dai, A. Bernevig, Wilson-loop characterization of inversion-symmetric topological insulators. Phys. Rev. B 89, 155114 (2014).

68. R. Resta, Manifestations of Berry's phase in molecules and condensed matter. J. Phys. Condens. Matter 12, R107–R143 (2000).

69. G. Bian et al., Band topology and dichotomic signature of bismuth. arXiv:1710.00908 (2 October 2017).