Time-reversal-protected single-Dirac-cone topological-insulator states in Bi$_2$Te$_3$ and Sb$_2$Te$_3$: Topologically Spin-polarized Dirac fermions with $\pi$ Berry’s Phase

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We show that the strongly spin-orbit coupled materials Bi$_2$Te$_3$ and Sb$_2$Te$_3$ (non-Bi Topological insulator) and their derivatives belong to the $Z_2$ (Time-Reversal-Protected) topological-insulator class. Using a combination of first-principles theoretical calculations and photoemission spectroscopy, we directly show that Bi$_2$Te$_3$ is a large spin-orbit-induced indirect bulk band gap ($\delta \sim 150$ meV) semiconductor whose surface is characterized by a single topological spin-Dirac cone. The electronic structure of self-doped Sb$_2$Te$_3$ exhibits similar $Z_2$ topological properties. We demonstrate that the dynamics of surface spin-only Dirac fermions can be controlled through systematic Mn doping, making these materials classes potentially suitable for exploring novel topological physics. We emphasize (theoretically and experimentally) that the Dirac node is well within the bulk-gap and not degenerate with the bulk valence band.

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Topological insulators are a new phase of quantum matter that host exotic Dirac electrons at their edges owing to a combination of relativistic and quantum entanglement effects [1]. They were recently proposed [2,3,4] and shortly afterwards discovered in the Bi$_{1-x}$Sbx [6,7] and Bi$_2$Se$_3$ [8,9] materials. In these systems, spin-orbit coupling (SOC) gives rise to electrically insulating states in the bulk and robust conducting states along the edges. In contrast to graphene, which has four Dirac cones (2 doubly degenerate cones at the K and K’ points in momentum space) [10], the remarkable property of topological edge states is that their dispersion is characterized by an odd number of non-degenerate Dirac cones. Such odd spin-Dirac cone edge metals exhibit a host of unconventional properties including a fractional (half-integer) quantum Hall effect [2,5,11] and immunity to Anderson localization due to spin-texture and $\pi$ Berry’s phases on their surfaces [2,6,7,8,12]. The $\pi$ Berry’s phase and topological spin-textures were observed in several topological insulators and parent materials such as Bi-Sb, pure-Sb (pure Antimony), Bi$_2$Se$_3$ and Bi$_2$Te$_3$ by Xia et.al. [8] and Hsieh et.al. [2] by spin-resolved measurements. Interesting physics may also occur at the interface between a topological insulator and an ordinary ferromagnet or superconductor, where electromagnetic responses that defy Maxwell’s equations [11,13,14], and excitations that obey non-Abelian statistics [15,16] are theoretically expected.

The surging number of interesting experimental proposals involving odd Dirac cone surface metals [11,15,16,17,18] has ignited a search for the most elementary form of a topological insulator, namely one with a large bulk band gap and a single surface Dirac cone. Although Bi$_{1-x}$Sbx has a room temperature direct band gap ($\delta > 30$ meV) [6], a small effective mass of its bulk electrons is known to cause the system to form conducting impurity bands even in high purity samples [19], which dominate over conduction through the surface states. More importantly, Bi$_{1-x}$Sbx has multiple surface states of both topological and non-topological origin [6], which makes isolating any transport signal from a single topological surface state particularly challenging. More recently, angle-resolved photoemission spectroscopy (ARPES) [8] and theoretical [13,20] evidence suggest that Bi$_2$Se$_3$ is a large band gap ($\sim 300$ meV) single spin-Dirac cone topological insulator. In this Letter, we report a bulk and surface ARPES investigation of single crystals of Bi$_2$Te$_3$, Bi$_{2-x}$MnxTe$_3$ and Sb$_2$Te$_3$. Remarkably, we find that their electronic structures are in close agreement with our topological SOC calculations, and a spin-Dirac cone is realized on their (111) surfaces. We emphasize (theoretically and experimentally) that the Dirac node is well within the bulk-gap and not degenerate with the bulk valence band. Although Sb$_2$Te$_3$ is found to have stable bulk states, we show that the Fermi energy of Bi$_2$Te$_3$ is time dependent, which has also been observed with ARPES in hole doped Bi$_2$Te$_3$ samples [21], and can be controlled via Mn doping. Using a synchrotron light source with a variable photon energy ($h\nu$), we show that the bulk-like states of Bi$_{2-x}$MnxTe$_3$ (x=0) are insulating with the valence band maximum lying around 150 meV below $E_F$, realizing a large band gap topological insulator with tunable surface dynamics that can be used in future transport based searches for novel topological physics.

ARPES measurements were performed with 28 to 45 eV linearly polarized photons on beam line 12.0.1 at the
in ultra high vacuum (UHV) at pressures better than 5×10⁻¹¹ torr at 15 K. Our calculations were performed with the linear augmented-plane-wave method in slab geometry using the WIEN2K package. Generalized gradient approximations of Perdew, Burke, and Ernzerhof were used to describe the exchange-correlation potential. Spin-orbit coupling was included as a second variational step using scalar-relativistic eigenfunctions as basis. The surface was simulated by placing a slab of six quintuple layers in vacuum using optimized lattice parameters from [24]. A grid of 35×35×1 points were used in the calculations, equivalent to 120 k-points in the irreducible BZ and 2450 k-points in the first BZ.

The most basic 3D topological insulator supports a single Dirac cone on its surface ([Fig. 1(a)], with the Dirac node located at a momentum \( k_F \) in the surface Brillouin zone (BZ), where \( k_F \) satisfies \( k_F = -k_F + \mathbf{G} \).
and \( \mathbf{G} \) is a surface reciprocal lattice vector. Our theoretical calculations on Bi\(_2\)Te\(_3\) (111) show that it is a SOC induced bulk band insulator, and that a single surface Dirac cone that encloses \( \mathbf{k}_F = \mathbf{\Gamma} \) only appears when SOC is included (Fig. 1(b)). To determine whether single crystalline Bi\(_2\)Te\(_3\) is a topological insulator as predicted, we first mapped its high energy valence bands using ARPES. Figure 1(c) and Figure 2 show that the measured bulk band structure is well described by SOC calculations, suggesting that the electronic structure is topologically non-trivial. A more direct probe of the topological properties of Bi\(_2\)Te\(_3\), however, is to image its surface states. Figure 1(d) and (e) show that the surface states are metallic and are characterized by a single Dirac cone crossing \( E_F \), in agreement with theory (Fig. 1(b)). Moreover, the density of states at \( E_F \) is distributed about a single ring enclosing \( \mathbf{\Gamma} \) (Fig. 1(f)), in accordance with Bi\(_2\)Te\(_3\) being a topological insulator.

Our theoretical calculations show that stoichiometric Bi\(_2\)Te\(_3\) is a bulk indirect gap insulator (Fig. 1(b)). The bulk valence band maximum (VBM) in Bi\(_2\)Te\(_3\) lies at the b-point in the \( \Gamma Z L \) plane of the three-dimensional bulk BZ (Fig. 2(b)), giving rise to VBM in each of six such mirror planes in agreement with previous proposals. The VBM exhibits an indirect gap with the conduction band minimum (CBM) above \( E_F \), which is located at the d-point in the \( \Gamma Z L \) plane. In order to establish whether Bi\(_2\)Te\(_3\) is a bulk insulator as predicted, we performed a series of ARPES scans along the cuts shown by red lines in Figure 2(a) (displaced along \( k_x \) by varying the incident photon energy) that traverse the locations of the VBM and CBM in the bulk BZ. All \( h\nu \)-dependent scans were taken more than an hour after cleavage to allow the band structure to stabilize (see Fig. 3). Figures 2(c)-(h) show a series of ARPES band dispersions along momentum cuts in the \( k_x-k_z \) plane taken using photon energies of 31 eV, 35 eV and 38 eV respectively. The Dirac cone near \( E_F \) shows no dispersion with \( h\nu \), supporting its surface state origin. In contrast, a strongly \( h\nu \) dispersive hole-like band is observed near \( k_x = 0.27 \) Å\(^{-1}\), whose maximum rises to an energy \( \delta \) closest to \( E_F \) (\( \delta = -150\pm50 \) meV) when \( h\nu = 35 \) eV (Fig. 2(d)). Using the free electron final state approximation, the VBM is located at (0.27, 0, 0.37) Å\(^{-1}\), in agreement with calculations. ARPES scans taken in the vicinity of the d-point (0.17, 0, 0.37) Å\(^{-1}\), which is traversed directly when \( h\nu = 38 \) eV, do not measure any signal from the CBM, showing that \( E_F \) lies in the bulk band gap. This is consistent with the size of the indirect band gap (> 150 meV) measured using tunneling and optical techniques. We note that because ARPES is only sensitive to the topmost quintuple layer (Fig. 3(a)) at our sampled photon energies, the measured energy of the bulk band edge \( \delta \) may differ from the true bulk value due to band bending effects that are commonly observed in semiconductors.

In order to investigate the effects of semiconductor band bending on the surface Dirac cone on Bi\(_2\)Te\(_3\), we performed time dependent ARPES experiments. Our results show that the binding energy of the Bi\(_2\)Te\(_3\) surface Dirac node exhibits a pronounced time dependence, increasing from \( E_B \sim -100 \) meV 8 minutes after cleavage to \( E_B \sim -130 \) meV at 40 minutes (Fig. 3(c)-(e)), in agreement with a previous report. Such behavior has been attributed to a downward band bending near the surface (Fig. 3(b)) that is caused by the breaking of inter-quintuple layer van der Waals Te(1)-Te(1) bonds (Fig. 3(a)), which creates a net electric field near the surface upon crystal termination. Unlike previous calculations, our calculated position of the Dirac node lies in the bulk band gap (Fig. 1(b)), which corroborates our experimental finding that the intensity is strongest near the Dirac node and drastically weakens away from \( \Gamma \) as the surface band merges with the bulk bands and becomes short-lived. The slow dynamics of the band bending process suggests that charge accumulation at the surface is coupled to a much slower surface lattice relaxation. The system is likely to be significantly delayed in achieving equilibrium by lo-
Laxation time scale to be accessed. ARPES valence band (Fig. 3(f)-(h)), allowing a wider range of the intrinsic resistance through Mn for Bi substitution, we demonstrate [9, 27]. By systematically increasing the defect concentration along both the $k_x$ (Fig. 4(d)) and $k_y$ (Fig. 4(e)) directions, showing that the bulk electronic structure of Sb$_2$Te$_3$ is consistent with having topologically non-trivial bulk properties. However, due to a high level of intrinsic doping that is typical of these compounds [8, 9], the Fermi energy of naturally grown Sb$_2$Te$_3$ lies in the bulk valence band continuum and thus does not cut through the surface states. Unlike Bi$_2$-$x$Mn$_x$Te$_3$, no time dependence of the bands is observed. Recently, we came across independent work on the Bi$_2$(Sn)Te$_3$ (Sn-doping [31]) series that finds a single Dirac cone on the surface. Single spin-Dirac cone and Berry’s phase on these classes of materials were first presented in [8] [also see 31].

In conclusion, our first-principles theoretical predictions and calculations and photoemission results show that Bi$_2$Te$_3$ and Sb$_2$Te$_3$ possess bulk band structures where the insulating gap originates from a large spin-orbit coupling term, and such insulators support topologically non-trivial $Z_2$ (Time-Reversal-Protected nature and $Z_2$ topology) surface states. Our direct observation of single Dirac cones in these materials and the systematic methods demonstrated to control the Dirac fermion dynamics on these highly non-trivial surfaces point to new opportunities for spintronic and quantum-information materials research.

Note Added: The experimental data pre-existed the theoretical calculations. The surface-state data and spin-ARPES methods were presented at two KITP conference proceedings (BiSb, Bi$_2$Te$_3$, Sb$_2$Te$_3$, pure Sb and Bi$_2$Se$_3$) were presented in two talks: Direct Determination of Topological Order:Topological Quantum Numbers and Berry’s Phase from Spin-Texture Maps of Spin-Orbit Insulators. See http://online.itp.ucsb.edu/online/motterials07/hasan/ (2007) and http://online.itp.ucsb.edu/online/qspinhall08/hasan/ (2008).

[1] C. Day, Physics Today 62, 12 (2009).
[2] L. Fu, C. L. Kane and E. J. Mele. Phys. Rev. Lett. 98, 106803 (2007).
[3] J. E. Moore and L. Balents. Phys. Rev. B 75 121306(R).
(2007).

[4] R. Roy. arXiv:cond-mat0604211v2 (2006).

[5] S.-C. Zhang, Physics 1, 6 (2008); C.L. Kane, Nature Phys. 4, 348 (2008).

[6] D. Hsieh et al. Nature (London) 452, 970 (2008).

[7] D. Hsieh et al., Science 323, 919 (2009); D. Hsieh et al., Nature (London) 460, 1101 (2009).

[8] Y. Xia et al., Nature Phys. 5, 398 (2009).

[9] Y. S. Hor et al. Phys. Rev. B 79, 195208 (2009).

[10] K. S. Novoselov et al. Nature (London) 438, 197 (2005).

[11] X.-L. Qi, T. L. Hughes and S.-C. Zhang, Phys. Rev. B 78, 195424 (2008).

[12] A. P. Schnyder, S. Ryu, A. Furusaki and A. W. W. Ludwig, Phys. Rev. B 78, 195125 (2008).

[13] A. Essin, J. E. Moore and D. Vanderbilt, Phys. Rev. Lett. 102, 146805 (2009).

[14] M. Franz, Physics 1, 36 (2008).

[15] L. Fu and C. L. Kane. Phys. Rev. Lett. 102, 216403 (2009).

[16] A. R. Akhmerov, J. Nilsson and C. W. J. Beenakker. Phys. Rev. Lett. 102, 216404 (2009).

[17] Y. Ran, Y. Zhang and A. Vishwanath. Nature Phys. 5, 298 (2009).

[18] B. Seradjeh, J. E. Moore and M. Franz. Phys. Rev. Lett. 103, 066402 (2009).

[19] B. Lenoir, M. Cassart, J.-P. Michenaud, H. Scherrer and S. Scherrer. J. Phys. Chem. Solids. 57, 89 (1996).

[20] H. Zhang et al. Nature Phys. 5, 438 (2009).

[21] First observation of linear Dirac bands in Bi$_2$Te$_3$ were reported by H.-J. Noh et al. Europhys. Lett. 81, 57006 (2008). No spin-polarization or pi Berry’s phase, critical for proving topological order were observed here.

[22] P. Blaha et al. Computer code WIEN2K. Vienna University of Technology, Vienna (2001).

[23] J.P. Perdew, K. Burke, & M. Ernzerhof Phys. Rev. Lett. 77, 3865-3868 (1996).

[24] G. Wang, & T. Cagin Phys. Rev. B 76, 075201 (2007).

[25] S. J. Youn and A. J. Freeman. Phys. Rev. B 63, 085112 (2001).

[26] S. K. Mishra, S. Satpathy and O. Jepsen. J. Phys: Condens. Mat. 9, 461 (1997).

[27] S. Urazhdin et al. Phys. Rev. B 69, 085313 (2004).

[28] G. A. Thomas et al. Phys. Rev. B 46, 1553 (1992).

[29] S. Hüfner. Photoelectron Spectroscopy. Springer, Berlin (1995).

[30] Y.L. Chen et al. arXiv:0904.1829v1 [ScienceExpress, 11-June, 2009].

[31] The surface-state data (BiSb, Bi$_2$Te$_3$, pure Sb, Sb$_2$Te$_3$ and Bi$_2$Se$_3$) and the unique spin-ARPES methods were presented at the KITP conference proceedings in (2007, 2008): http://online.itp.ucsb.edu/online/mottentials07/hasan/ (2007) and http://online.itp.ucsb.edu/online/qspinhall_m08/hasan (Direct Determination of Topological Order:Topological Quantum Numbers and Berry’s Phase from Spin-Texture Maps of Spin-Orbit Insulators)