Title
Time-reversal-protected single-Dirac-cone topological-insulator states in Bi2Te3 and Sb2Te3: Topologically Spin-polarized Dirac fermions with pi Berry's Phase

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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$_1$-xSbx [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 in the bulk and robust conducting states along the edges. Although Sb$_2$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.

The surging number of interesting experimental proposals involving odd Dirac cone surface metals [11, 15, 10, 17, 18] has ignited a search for the most elementary form of a topological insulator, namely one with a large bulk 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 [8, 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 (hv), 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 Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. 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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Advanced Light Source in Lawrence Berkeley National Laboratory. The typical energy and momentum resolution was 15 meV and 1% of the surface Brillouin zone (BZ) respectively. Single crystals of Bi$_{2-x}$Mn$_x$Te$_3$ were grown by melting stoichiometric mixtures of elemental Bi (99.999 %), Te (99.999 %) and Mn (99.95 %) at 800°C overnight in a sealed vacuum quartz tube. The crystalline sample was cooled over a period of two days to 550°C, and maintained at the temperature for 5 days. The same procedure was carried out with Sb (99.999 %) and Te (99.999 %) for Sb$_2$Te$_3$ crystals. Samples were cleaved in ultra high vacuum (UHV) at pressures better than $5 \times 10^{-11}$ torr at 15 K. Our calculations were performed using the linear augmented-plane-wave method in slab geometry using the WIEN2K package [22]. Generalized gradient approximations of Perdew, Burke, and Ernzerhof [23] was 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 35x35x1 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 $k_T$ in the surface Brillouin zone (BZ), where $k_T$ satisfies $k_T = -k_T + \mathbf{G}$.
and $G$ is a surface reciprocal lattice vector $[2]$. Our theoretical calculations on $\text{Bi}_2\text{Te}_3$ (111) show that it is a SOC induced bulk band insulator, and that a single surface Dirac cone that encloses $k_F = \bar{\Gamma}$ only appears when SOC is included (Fig. 1(b)). To determine whether single crystalline $\text{Bi}_2\text{Te}_3$ 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 $\text{Bi}_2\text{Te}_3$, 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 $\bar{\Gamma}$ (Fig. 1(f)), in accordance with $\text{Bi}_2\text{Te}_3$ being a topological insulator.

Our theoretical calculations show that stoichiometric $\text{Bi}_2\text{Te}_3$ is a bulk indirect gap insulator (Fig. 1(b)). The bulk valence band maximum (VBM) in $\text{Bi}_2\text{Te}_3$ 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 $[25, 26]$. 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 $\text{Bi}_2\text{Te}_3$ 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 $k_z = 0.27 \text{ Å}^{-1}$, whose maximum rises to an energy $\delta$ closest to $E_F$ ($\delta = -150 \pm 50 \text{ meV}$) when $h\nu = 35 \text{ eV}$ (Fig. 2(d)). Using the free electron final state approximation, the VBM is located at $(0.27, 0, 0.37) \text{ Å}^{-1}$, in agreement with calculations. ARPES scans taken in the vicinity of the $d$-point $(0.17, 0, 0.37) \text{ Å}^{-1}$, which is traversed directly when $h\nu = 38 \text{ eV}$, 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 ($>150 \text{ meV}$) measured using tunneling $[27]$ and optical techniques $[28]$. We note that because ARPES is only sensitive to the topmost quintuple layer (Fig. 3(a)) at our sampled photon energies $[29]$, 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 $\text{Bi}_2\text{Te}_3$, we performed time dependent ARPES experiments. Our results show that the binding energy of the $\text{Bi}_2\text{Te}_3$ surface Dirac node exhibits a pronounced time dependence, increasing from $E_B \sim -100 \text{ meV}$ 8 minutes after cleavage to $E_B \sim -130 \text{ meV}$ at 40 minutes (Fig. 3(c)-(e)), in agreement with a previous report $[21]$. 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 $[20, 27]$. Unlike previous calculations $[20]$, 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 $\bar{\Gamma}$ as the surface band merges with the bulk bands and becomes short-lived $[6, 7, 29]$. The slow dynamics of the band bending process suggests that charge accumulation at the surface is coupled to a much slower surface lattice relaxation $[21]$. The system is likely to be significantly delayed in achieving equilibrium by lo-
K relaxation time scale to be accessed. ARPES valence band (Fig. 3(f)-(h)), allowing a wider range of the intrinsic re-
here that band bending can be slowed by up to 10 fold
tration through Mn for Bi substitution, we demonstrate
[9, 27]. By systematically increasing the defect concen-
from site defects, which are prominent in such materials
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from site defects, which are prominent in such materials
[8] [27]. By systematically increasing the defect concen-
from site defects, which are prominent in such materials
106803 (2007).

FIG. 4: Evidence for a topologically non-trivial band
structure and spin-Dirac cone in Sb$_2$Te$_3$ : (a) Calculated band structure along the K-Γ-M cut of the Sb$_2$Te$_3$(111)
BZ. Bulk band projections are represented by the shaded areas. The bulk (surface) band structure results with spin-orbit
coupling (SOC) are presented in blue (red lines) and that
without SOC in green (black lines). (b) Schematic of the sin-
gle surface Dirac cone in Sb$_2$Te$_3$ based on calculations. (c)
Enlargement of low energy region (shaded box in (a)) near Γ.
(d) Second derivative image of the bulk valence bands along
Γ-M and (e) Γ-K at $k_z = -0.77$ Γ – Z. The superposed SOC
calculation (orange dots) has been rigidly shifted upwards by
300 meV to match the data.

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from site defects, which are prominent in such materials
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(Fig. 3(f)-(h)), allowing a wider range of the intrinsic re-
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106803 (2007).
\[3\] J. E. Moore and L. Balents. Phys. Rev. B 75 121306(R)

spectra (Fig. 3(i)) of Bi$_{1.95}$Mn$_{0.05}$Te$_3$ taken over a 15
hour period show that the positions of the valence band
edges shift downward by a total energy of around 100
meV, which we take as a measure of the total magnitude
of band bending Δ.

Having identified the topological insulator Bi$_2$Te$_3$, we
proceed to investigate whether similar topological ef-
cets can take place in a non bismuth based compound.
Figure 4(a) shows the calculated electronic structure of
Sb$_2$Te$_3$, which, like Bi$_2$Te$_3$, exhibits a bulk insulating
band structure that is strongly influenced by SOC and
a single Dirac cone on its (111) surface. By comparing
our SOC calculations with the experimentally measured
bulk valence bands, it is clear that there is good agree-
ment 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 intrin-
sic 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 depen-
dence of the bands is observed. Recently, we came across
independent work on the Bi$_2$(Sn)Te$_3$ (Sn-doping 31) se-
ries that finds a single Dirac cone on the surface. Single
spin-Dirac cone and Berry’s phase on these classes of ma-
terials were first presented in 8 [also see 31].

In conclusion, our first-principles theoretical predic-
tions 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 topolog-
ically nontrivial Z$_2$ (Time-Reversal-Protected nature and
the absence of backscattering are guaranteed by the odd
number of spin-polarized crossings as the character of Z$_2$
topology) surface states. Our direct observation of single
Dirac cones in these materials and the systematic meth-
ods demonstrated to control the Dirac fermion dynamics
on these highly non-trivial surfaces point to new opportu-
nities 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$_2$S$_3$) were presented in two
talks : Direct Determination of Topological Or-
der:Topological Quantum Numbers and Berry’s Phase
from Spin-Texture Maps of Spin-Orbit Insulators. See
http://online.itp.ucsb.edu/online/mottentrals07/hasan/
(2007) and http://online.itp.ucsb.edu/online/qspinhall_08/hasan/
(2008).
[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.
[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/motterials07/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)