Direct observation of spin-polarized surface states in the parent compound of a topological insulator using spin-resolved-ARPES spectroscopy in a Mott-polarimetry mode

D. Hsieh, L. Wray, D. Qian, Y. Xia, Y.S. Hor, R.J. Cava, and M.Z. Hasan

Joseph Henry Laboratories, Department of Physics, Princeton University, Princeton, NJ 08544, USA

Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

Princeton Center for Complex Materials, Princeton University, Princeton, NJ 08544, USA

(Dated: January 11, 2010)

We report high-resolution spin-resolved photoemission spectroscopy (Spin-ARPES) measurements on the parent compound Sb of the recently discovered 3D topological insulator Bi$_{1-x}$Sb$_x$ \cite{D. Hsieh et al., Nature 452, 970 (2008)}. By modulating the incident photon energy, we are able to map both the bulk and (111) surface band structure, from which we directly demonstrate that the surface bands are spin polarized by the spin-orbit interaction and connect the bulk valence and conduction bands in a topologically non-trivial way. A unique asymmetric Dirac surface state gives rise to a k-splitting of its spin polarized electronic channels. These results complement our previously published works on this materials class and re-confirm our discovery of topological insulator states in the Bi$_{1-x}$Sb$_x$ series.

PACS numbers:

Topological insulators are a new phase of quantum matter that are theoretically distinguished from ordinary insulators by a $Z_2$ topological number that describes its bulk band structure \cite{2, 3, 9–11}. They are characterized by a bulk electronic excitation gap that is opened by spin-orbit coupling, and unusual metallic states that are localized at the boundary of the crystal. The two-dimensional (2D) version, known as the quantum spin Hall insulator \cite{4–6}, is commonly understood as two copies of the integer quantum Hall effect \cite{7} where the spin-orbit coupling acts as a magnetic field that points in a spin dependent direction, giving rise to counter propagating spin polarized states \cite{8} on the 1D crystal edge. Three-dimensional topological insulators on the other hand have no quantum Hall analogue. Its surface states, which are necessarily spin polarized, realize a novel 2D metal that remains localized even in the presence of disorder \cite{2, 3, 9–11}. For these reasons, they have also been proposed as a route to dissipationless spin currents which, unlike current semiconductor heterostructure based spintronics devices, do not require an externally applied electric field.

Recent photoemission \cite{12} and theoretical results \cite{2, 10} suggest that single crystals of insulating Bi$_{1-x}$Sb$_x$ ($0.07 \leq x \leq 0.22$) alloys realize a 3D topological insulator. The non-trivial $Z_2$ invariant that characterizes Bi$_{1-x}$Sb$_x$ is inherited from the bulk band structure of pure Sb \cite{2, 10}, therefore, although Sb is a bulk semimetal, its non-trivial bulk band topology should be manifest in its surface state spectrum. Such a study requires a separation of the Fermi surface of the surface states of Sb from that of its bulk states over the entire surface Brillouin zone (BZ), as well as a direct measurement of the spin degeneracy of the surface states. To date, angle-resolved photoemission spectroscopy (ARPES) experiments on low lying states have only been performed on single crystal Sb with fixed He Ia radiation (apart from our previous work on this), which does not allow for separation of bulk and surface states \cite{13}. Moreover the aforementioned study, as well as ARPS experiments on Sb thin films \cite{14}, only map the band dispersion near $\bar{\Gamma}$, missing the band structure near $\bar{M}$ that is critical to determining the $Z_2$ invariant \cite{12}. In this work, we have performed spin- and angle-resolved photoemission experiments on single crystal Sb(111). Using variable photon energies, we successfully isolate the surface from bulk electronic bands over the entire BZ and map them with spin sensitivity. We show directly that the surface states are gapless and spin split, and that they connect the bulk valence and conduction bands in a topologically non-trivial way.

Spin-integrated ARPES measurements were performed with 14 to 30 eV photons on beam line 5-4 at the SSRL and at ALS BL-12 at higher photon energies. Spin resolved ARPES measurements were performed at the SIS beam line at the SLS using the COPHEE spectrometer \cite{13} with a single 40 kV classical Mott detector and a photon energy of 20 eV. The typical energy and momentum resolution was 15 meV and 1% of the surface BZ respectively at beam line 5-4, and 80 meV and 3% of the surface BZ respectively at SIS using a pass energy of 3 eV. High quality single crystals of Sb and Sb$_{0.9}$Bi$_{0.1}$ were grown by methods detailed in \cite{12}. Cleaving these samples in situ between 10 K and 55 K at chamber pressures less than 5 \times 10$^{-11}$ torr resulted in shiny flat surfaces, characterized by low energy electron diffraction to be clean and well ordered with the same symmetry as the bulk [Fig. 1(a) & (b)]. This is consistent with photoelectron diffraction measurements that show no substantial structural relaxation of the Sb(111) surface \cite{10}. Band calculation was performed using the full potential linearized augmented plane wave method in film geometry as implemented in the FLEUR program and local density approximation for
FIG. 1: Experimental separation of bulk from surface electron states in Sb using ARPES. (a) Schematic of the bulk BZ of Sb and its (111) surface BZ. The shaded region denotes the momentum plane in which the following ARPES spectra were measured. (b) LEED image of the in situ cleaved (111) surface exhibiting a clear hexagonal symmetry. (c) Select MDCs at the Fermi level taken with photon energies from 14 eV to 26 eV in steps of 2 eV, taken in the TXLU momentum plane. Peak positions in the MDCs were determined by fitting Lorentzians (red curves). (d) Experimental 3D bulk Fermi surface near H (red circles) and 2D surface Fermi surface near Γ (open circles) determined by matching the fitted peak positions from (c) to calculated constant υ contours (black curves). Theoretical hole Fermi surface calculated in situ cleaved (111) shown for comparison.

The Fermi surface of Sb(111) is composed of a series of de Haas-van Alphen (dHvA) oscillations, which are a direct measure of the Fermi surface geometry. These oscillations are observed in the magnetic field dependence of the electrical resistivity of a metallic sample. The oscillations are due to the quantization of the electron cyclotron orbit area and are proportional to the area of the Fermi surface. The dHvA oscillations in Sb(111) are observed to be strongly anisotropic, with the electron and hole Fermi surfaces being distinctly different. The electron Fermi surface is composed of a single hole pocket centered at the K point, while the hole Fermi surface is composed of a pair of electron pockets centered at the L point. The electron and hole Fermi surfaces are separated by a gap, which is due to the presence of a single valence band in Sb.

The ARPES spectra shown in FIG. 1 are a direct measurement of the Fermi surface. The spectra are obtained by plotting the intensity of photoelectrons as a function of the momentum transfer to the sample. The momentum transfer is determined by the angle of incidence and the photon energy of the incoming light. The spectra reveal the presence of a single hole pocket centered at the K point, which is consistent with the theoretical calculation. The hole pocket is centered at the K point and is composed of a pair of electron pockets centered at the L point. The electron and hole Fermi surfaces are separated by a gap, which is due to the presence of a single valence band in Sb.

The ARPES spectra also reveal the presence of a pair of spin-split surface bands that become degenerate at the surface Kramers pair, which crosses the Fermi level at the surface. These bands are due to the presence of the three-dimensional spin-orbit interaction in Sb.

The ARPES spectra are consistent with the theoretical calculation of the Fermi surface in Sb(111). The theoretical calculation is based on the electronic structure of Sb, which is obtained from first-principles calculations.

The ARPES spectra also reveal the presence of a pair of spin-split surface bands that become degenerate at the surface Kramers pair, which crosses the Fermi level at the surface. These bands are due to the presence of the three-dimensional spin-orbit interaction in Sb.

The ARPES spectra are consistent with the theoretical calculation of the Fermi surface in Sb(111). The theoretical calculation is based on the electronic structure of Sb, which is obtained from first-principles calculations.
FIG. 3: Large spin splitting of surface states on Sb(111). (a) Experimental geometry of the spin resolved ARPES study. At normal emission ($\theta=0^\circ$), the sensitive $y'$-axis of the Mott detector is rotated by $45^\circ$ from the sample $\Gamma$-$\bar{M}$ ($\parallel x$) direction, and the sensitive $z'$-axis of the Mott detector is parallel to the sample normal. Spin up and down are measured with respect to these two quantization axes. (b) Spin integrated ARPES spectra along the $\bar{M}$-$\bar{\Gamma}$-$\bar{M}$ direction taken using a photon energy $h\nu = 22$ eV. The momentum splitting between the band minima is indicated by the black bar and is approximately $0.03\,\AA^{-1}$. (c) Momentum distribution curve of the spin integrated spectra at $E_B = -30$ meV (shown in (b) by white line) using a photon energy $h\nu = 20$ eV, together with the Lorentzian peaks of the fit. (d) Measured spin polarization curves (symbols) for the $y'$ and $z'$ components together with the fitted lines using the two-step fitting routine. Even though the measured polarization only reaches a magnitude of around ±0.4, similar to what is observed in thin film Bi(111) [20], this is due to a non-polarized background and overlap of adjacent peaks with different spin polarization. The fitted parameters are in fact consistent with 100% polarized spins. (e) Spin resolved spectra for the $y$ component based on the fitted spin polarization curves shown in (d). (f) The in-plane and out-of-plane spin polarization components in the sample coordinate frame obtained from the spin polarization fit. The symbols refer to those in (c).

FIG. 4: Topologically non-trivial surface states of Sb(111). (a) Calculated surface state band structure for freestanding 20 bilayer Sb(111) slabs together with an ARPES intensity map of Sb(111) along the $\Gamma$-$\bar{M}$ direction taken with $h\nu = 22$ eV photons. Green curves show the calculated bulk bands along the $k_z$ direction projected onto the $(111)$ plane. (b) ARPES intensity map at $E_F$ in the $k_{xx}$-$k_{yy}$ plane taken with $h\nu = 20$ eV photons. (c) Schematic picture showing that the gapless spin polarized surface bands (red and blue lines) connect the projected bulk valence and conduction bands (shaded regions) and are thus topologically non-trivial. The surface resonances (dashed green lines) do not connect the bulk valence and conduction bands and are thus topologically trivial. (d) Schematic of the surface Fermi surface topology of Sb(111) showing the pockets formed by the pure surface states (un-filled) and the surface resonances (filled green). The purely surface state Fermi contours enclose only the one surface TRIM located at $\bar{\Gamma}$.

Curves (EDCs) in Fig. 2(a)-(c), but can be clearly observed in the MDCs shown in Fig. 1c) especially on the positive $k_z$ side. Centered about the $\bar{M}$ point, we also observe a crescent shaped envelope of weak intensity that does not disperse with $k_z$ [Fig. 2(d)-(f)], pointing to its surface origin. Unlike the sharp surface states near $\bar{\Gamma}$, the peaks in the EDCs of the feature near $\bar{M}$ are much broader ($\Delta E \sim 80$ meV) than the spectrometer resolution (15 meV). The origin of this diffuse ARPS signal is not due to surface structural disorder because if that were the case, electrons at $\bar{\Gamma}$ should be even more severely scattered from defects than those at $\bar{M}$. In fact, the occurrence of both sharp and diffuse surface states originates from a k dependent coupling to the bulk as discussed later.

To extract the spin polarization vector of each of the surface bands near $\bar{\Gamma}$, we performed spin resolved MDC measurements along the $\bar{M}$-$\bar{\Gamma}$-$\bar{M}$ cut at $E_B = -30$ meV for maximal intensity, and used the two-step fitting routine developed in [24]. The Mott detector in the COPHEE instrument is mounted so that at normal emission it is sensitive to a purely out-of-plane spin component ($z'$) and a purely in-plane ($y'$) spin component that is rotated by $45^\circ$ from the sample $\Gamma$-$\bar{M}$ direction [Fig. 3(a)]. Each of these two directions rep-
represents a normal to a scattering plane, defined by the electron incidence direction on a gold foil and two detectors mounted on either side that measure the left-right asymmetry $A_{y,z}(R)$, which is 0.03 Å$^{-1}$ resolved spectra for each of the fitted peaks $P$ shown in Fig. 3(c), and fit the calculated polarization spectrum to measurement. The spin resolved spectra for the $y$ component derived from the polarization fit is shown in Fig. 3(e), given by $I^y_P = \sum_{y=1}^2 I(1 \pm P^y)/6 + B/6$, where $B$ is a background and $P^y$ is the fitted $y$ component of polarization. There is a clear difference in $I^y_P$ and $I^z_P$ at each of the four MDC peaks indicating that the surface state bands are spin polarized. Each of the pairs $l_0/11$ and $r1/r2$ have opposite spin, consistent with the behavior of a spin split Kramers pair, and the spin polarization of these bands is reversed on either side of $\bar{\Gamma}$ in accordance with time reversal symmetry [Fig. 3(f)]. Similar to Au(111) [21] and W(110)-(1×1)H [13], the spin polarization of each band is largely in-plane consistent with a predominantly out-of-plane electric field at the surface. However unlike the case in Au(111), where the surface band dispersion is free electron like and the magnitude of the Rashba coupling can be quantified by the momentum displacement between the spin up and spin down band minima [21], the surface band dispersion of Sb(111) is highly non-parabolic. A comparison of the $k$-separation between spin split band minima near $\bar{\Gamma}$ of Sb(111) [Fig. 3(b)] with those of Bi(111) [17], which are 0.03 Å$^{-1}$ and 0.08 Å$^{-1}$ respectively, nevertheless are consistent with the difference in their atomic $p$ level splitting of Sb(0.6 eV) and Bi(1.5 eV) [23]. Therefore, despite Sb having a similar atomic spin-orbit coupling strength to Au(0.5 eV), the $k$ splitting between spin polarized surface bands near $E_F$ is greater in Sb due to its unique dispersion. This could also be due to the nature of spin-polarized photoemission and detection methods.

Figure 4(a) shows the full ARPES intensity map from $\bar{\Gamma}$ to $\bar{M}$ together with the calculated bulk bands of Sb projected onto the (111) surface. Although the six-fold rotational symmetry of the surface band dispersion is not known a priori due to the three-fold symmetry of the bulk, we measured an identical surface band dispersion along $\bar{\Gamma}$-$\bar{\Gamma}$-$\bar{\Gamma}$. The spin-split Kramers pair near $\bar{\Gamma}$ lie completely within the gap of the projected bulk bands near $E_F$ attesting to their purely surface character. In contrast, the weak diffuse hole like band centered near $k_x = 0.3$ Å$^{-1}$ and electron like band centered near $k_x = 0.8$ Å$^{-1}$ lie completely within the projected bulk valence and conduction bands respectively, and thus their ARPES spectra exhibit the expected lifetime broadening due to coupling with the underlying bulk continuum [20]. Figure 4(b) shows the ARPES intensity plot at $E_F$ of Sb(111) taken at a photon energy of 20 eV, where the bulk band near $H$ is completely below $E_F$ [Fig. 2(b)]. Therefore this intensity map depicts the topology of the Fermi surface due solely to the surface states. By comparing Figs 4(a) and (b), we see that the inner most spin polarized V-shaped band produces the circular electron Fermi surface enclosing $\bar{\Gamma}$ while the outer spin polarized V-shaped band produces the inner segment ($0.1 \bar{A}^{-1} \leq k_x \leq 0.15 \bar{A}^{-1}$) of the six hole Fermi surfaces away from $\bar{\Gamma}$. Previous ARPES experiments along the $\bar{\Gamma}$-$\bar{M}$ direction [13] show that this outer V-shaped band merges with the bulk valence band, however the exact value of $k_x$ where this occurs along the $\bar{\Gamma}$-$\bar{M}$ direction is unclear since only occupied states are imaged by ARPES. The outer segment of the six hole pockets is formed by the hole like surface resonance state for $0.15 \bar{A}^{-1} \leq k_x \leq 0.4 \bar{A}^{-1}$. In addition, there are electron Fermi surfaces enclosing $\bar{M}$ and $\bar{M}'$ produced by surface resonance states at the BZ boundaries. Altogether, these results show that in a single surface BZ, the bulk valence and conduction bands are connected by a lone Kramers pair of surface states [Fig. 4(c)].

In general, the spin degeneracy of surface bands on spin-orbit coupled insulators can be lifted due to the breaking of space inversion symmetry. However Kramers theorem requires that they remain degenerate at four special time reversal invariant momenta (TRIM) on the 2D surface BZ, which for Sb(111) are located at $\bar{\Gamma}$ and three $\bar{M}$ points rotated by 60° from one another. According to recent theory, there are a total of four $Z_2$ topological numbers $\nu_0(\nu_1\nu_2\nu_3)$ that characterize a 3D spin-orbit coupled insulator’s bulk band structure [3, 4, 11]. One in particular ($\nu_0$) determines whether the spin polarized surface bands cross $E_F$ an even or odd number of times between any pair of surface TRIM, and consequently whether the insulator is trivial ($\nu_0=0$) or topological ($\nu_0=1$). An experimental signature of topologically non-trivial surface states in insulating Bi$_{1-x}$Sb$_x$ is that the spin polarized surface bands traverse $E_F$ an odd number of times between $\bar{\Gamma}$ and $\bar{M}$ [2, 12, 19]. Although this method of counting cannot be applied to Sb because it is a semimetal, since there is a direct gap at every bulk
k-point, it is meaningful to assume some perturbation, such as alloying with Bi \[27\] that does not significantly alter the spin splitting [Fig. 3], that pushes the bulk valence H and conduction L bands completely below and above \(E_F\) respectively without changing its \(Z_2\) class. Under such an operation, it is clear that the spin polarized surface bands must traverse \(E_F\) an odd number of times between \(\bar{\Gamma}\) and \(\bar{M}\), consistent with the 1;(111) topological classification of Sb. This conclusion can also be reached by noticing that the spin-split pair of surface bands that emerge from \(\bar{\Gamma}\) do not recombine at \(\bar{M}\), indicative of a “partner switching” \[9\] characteristic of topological insulators.

In conclusion, we have mapped the spin structure of the surface bands of Sb(111) and shown that the purely surface bands located in the projected bulk gap are spin split by a combination of spin-orbit coupling and a loss of inversion symmetry at the crystal surface. The spin polarized surface states have an asymmetric Dirac like dispersion that gives rise to its \(k\)-splitting between spin up and spin down bands at \(E_F\). The large splitting could be due to the nature of spin-polarized photoemission and detection methods and may or may not be intrinsic in nature however, this does not affect our conclusions regarding the topological band aspects of the system. The topologically non-trivial surface band structure makes Sb(111) an especially appealing candidate for an unusual 2D Dirac protected free fermion system that exhibits antilocalization \[9\].

We thank F. Meier, H. Dil, J. Osterwalder for technical assistance and C.L. Kane for theoretical discussion.

[1] C.L. Kane & E.J. Mele, Phys. Rev. Lett. 95, 146802 (2005).
[2] L. Fu and C.L. Kane, Phys. Rev. B 76, 045302 (2007).
[3] J.E. Moore and L. Balents, Phys. Rev. B 75, 121306(R) (2007).
[4] C.L. Kane & E.J. Mele, Phys. Rev. Lett. 95, 226801 (2005).
[5] B.A. Bernevig et al., Science 314, 1757 (2006).
[6] M. König et al., Science 318, 766 (2007).
[7] F.D.M. Haldane, Phys. Rev. Lett. 61, 2015 (1988).
[8] C. Wu et al., Phys. Rev. Lett. 96, 106401 (2006).
[9] L. Fu et al., Phys. Rev. Lett. 98, 106803 (2007).
[10] S. Murakami, New J. Phys. 9, 356 (2007).
[11] R. Roy, arXiv:cond-mat/0604211 (2006).
[12] D. Hsieh et al., Nature 452, 970 (2008).
[13] K. Sugawara et al., Phys. Rev. Lett. 96, 046411 (2006).
[14] H. Höcht and C.R. Ast, J. Electron Spectrosc. Relat. Phenom. 137, 441 (2004).
[15] M. Hoesch et al., J. Electron Spectrosc. Relat. Phenom. 124, 263 (2002).
[16] S. Bengió et al., Surface Science 601, 2908 (2007).
[17] Yu. M. Koroteev et al., Phys. Rev. Lett. 93, 046403 (2004).
[18] M. Hochstrasser et al., Phys. Rev. Lett. 89, 216802 (2002).
[19] J. Teo, L. Fu and C.L. Kane, arXiv:0804.2664v1 [cond-mat.mes-hall] (2008).
[20] T. Hirahara et al., Phys. Rev. B 76, 153305 (2007).
[21] M. Hoesch et al., Phys. Rev. B 69, 241401(R) (2004).
[22] X. Gonze et al., Phys. Rev. B 44, 11023 (1991).
[23] L.M. Falicov and P.J. Lin, Phys. Rev. 141, 562 (1965).
[24] F. Meier et al., Phys. Rev. B 77, 165431 (2008).
[25] Y. Liu and E. Allen, Phys. Rev. B 52, 1566 (1995).
[26] E. Kneedler, K.E. Smith, D. Skelton and S.D. Kevan, Phys. Rev. B 44, 8233 (1991).
[27] B. Lenoir et al., Fifteenth International Conference on Thermoelectrics (Pasadena, California) 113 (IEEE, New York, 1996).