Electronic Structures and Surface States of Topological Insulator Bi$_{1-x}$Sb$_x$

Hai-Jun Zhang$^1$, Chao-Xing Liu$^2$, Xiao-Liang Qi$^3$, Xiao-Yu Deng$^1$, Xi Dai$^1$, Shou-Cheng Zhang$^3$ and Zhong Fang$^1$

$^1$ Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China;
$^2$ Department of Physics, McCullough Building, Stanford University, Stanford, CA 94305-4045;
$^3$ Center for Advanced Study, Tsinghua University, Beijing, 100084, China and Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

(Dated: March 13, 2009)

We investigate the electronic structures of the alloyed Bi$_{1-x}$Sb$_x$ compounds based on first-principle calculations including spin-orbit coupling (SOC), and calculate the surface states of semi-infinite systems using maximally localized Wannier function (MLWF). From the calculated results, we analyze the topological nature of Bi$_{1-x}$Sb$_x$, and found the followings: (1) pure Bi crystal is topologically trivial; (2) topologically non-trivial phase can be realized by reducing the strength of SOC via Sb doping; (3) the indirect bulk band gap, which is crucial to realize the true bulk insulating phase, can be enhanced by uniaxial pressure along $c$ axis. (4) The calculated surface states can be compared with experimental results, which confirms the topological nature; (5) We predict the spin-resolved Fermi surfaces and showed the vortex structures, which should be examined by future experiments.

PACS numbers: 71.15.Dx, 71.18.+y, 73.20.At, 73.61.Le

I. INTRODUCTION

In an ordinary insulator, the valence and conduction bands are separated by an energy gap, making it electrically inert. Therefore, the ordinary insulator is not sensitive to the change of boundary condition. Recently a new class of insulator, namely topological insulator (TI), is proposed. TI also has a bulk energy gap, which is usually generated by spin-orbit coupling (SOC); however it is different from the ordinary insulator in the sense that topologically protected gapless states, robust against disorder, appear at the edge or surface of a finite sample within the bulk energy gap. Thus the TI has conducting channels along its edge or surface. The quantum spin Hall (QSH) insulator, such as HgTe/CdTe quantum well, is an example of two-dimensional (2D) TI. The conducting edge channels of HgTe/CdTe quantum wells have been theoretically predicted and experimentally observed. From the theoretical point of view, the TI can be distinguished from the ordinary insulator by the Z$_2$ topological invariant, and the existence of gapless spin-filtered edge states on the sample boundary is guaranteed for TI. The edge states come in Kramers’s doublets, and time reversal (TR) symmetry ensures the crossing of their energy band at time reversal invariant momenta (TRIM). Since these band crossings on the edge are protected by TR, they can not be removed by any perturbation respecting the TR symmetry, such as non-magnetic impurities. It is expected that the robust gapless spin-filtered surface(edge) states have novel applications in spintronics.

Besides the 2D QSH insulator, the TI can also exist in three dimensional (3D) material. Similar to the edge states in 2D QSH insulator, in 3D TI, topological surface state protected by TR, which can be described by odd number of Dirac points, emerges at the surface of the finite 3D sample. Compared with the 2D TI, the 3D TI and its surfaces can be readily investigated by ARPES and STM experiments. The 3D TI also displays the remarkable topological magneto-electric effect. Therefore searching for realistic 3D TI is now becoming an attractive and challenging subject.

It was first suggested that the semiconducting alloy of bismuth and antimony (Bi$_{1-x}$Sb$_x$) is an example of such 3D TI. Based on the tight-binding (TB) model of Liu and Allen, Fu and Kane developed a theory to analyze the topological nature of the surface state in Bi$_{1-x}$Sb$_x$ alloy. Experimentally, Hsieh et al. observed the surface states by high-momentum-resolution angle-resolved photoemission spectroscopy (ARPES), and demonstrated the topological nature of the surface states by counting the number of the Fermi surface crossings from the zone center to the boundary. However, clear discrepancies exist between the theory and the experiment about the surface states, although their final conclusions are consistent with each other. On the other side, the surface states of pure Bi or Sb have been intensely studied experimentally and theoretically but there are still fewer careful studies of their alloy. Therefore, in this paper, we present a systematic study of the surface states of Bi$_{1-x}$Sb$_x$ alloy, based on quantitative first principle calculations. We show that pure Bi is topologically trivial because the SOC is too strong. The effective role of Sb doping is to reduce the strength of SOC and revert the band ordering at L point of the Brillouin Zone(BZ). Finally strong topological insulator can be reached by Sb doping. By constructing the maximally localized Wannier function (MLWF) from the ab-initio schemes, we calculate the surface states of semi-infinite system, and analyze the shape of Fermi surfaces as well as the spin-resolved local density of states. These results are compared with the experiment of Hsieh et al. In addition, although direct band gap exists in Bi$_{1-x}$Sb$_x$ system, indirect band gap can be only realized for a very narrow
doping range, and the material has long been regarded as typical semi-metallic system. In order to make the bulk material insulating completely, based on our calculations, we predict that an efficient way to enhance the indirect band gap is to apply uniaxial pressure along the c-axis.

The paper is organized as follows. In sec. II we discuss the crystal structure and symmetry of Bi$_{1-x}$Sb$_x$. In Sec. III we study the transition between the topological non-trivial and trivial phases, and present a schematic phase diagram as a function of SOC. In Sec. IV we develop an accurate method based on ML WF to obtain the surface Green Function, and study the topologically non-trivial surface states of Bi$_{1-x}$Sb$_x$. In Sec. V we provide a brief discussion and conclusion.

II. STRUCTURE AND SYMMETRY

Bi and Sb have the same rhombohedral A7 crystal structure with space group $R\bar{3}m$. The A7 structure can be regarded as a distorted fcc NaCl structure. For fcc NaCl structure, there are two sets of sublattice, say Bi-1 for Na sites and Bi-2 for Cl sites, which both form the fcc structure. In such fcc structure, Bi-1 and Bi-2 sublattices are equivalent and we can shift Bi-1 sublattice by $(1/2,0,0)$, or $(0,1/2,0)$, or $(0,0,1/2)$ of cubic structure to obtain Bi-2 sublattice. Along (111) direction of fcc structure, Bi triangle layers are stacked with the sequence of ABCABCABC· · · , where A, B and C denote three different atomic positions for triangle plane, as shown in Fig.1. Without distortions, there exist two kinds of space-inversion center. One is located at the Bi layer center and each Bi sublattice is space-inverted to itself (called type-I inversion), while the other one is located at the middle way of two Bi layers and each Bi sublattice is space-inverted to another sublattice (called type-II inversion).

Starting from fcc NaCl structure, two steps are required to obtain rhombohedral A7 structure. One is the stretching along cubic (111) direction, while the second is the relative shift of inter-Bi-layer distances along (111) direction, or in other words dimerization of two Bi layers. The second step breaks the type-I inversion symmetry, but preserve the type-II inversion. Therefore, after distortions, the inversion symmetry can only transfer the atoms from one sublattice to the other, which is very important for our following discussion.

The Brillouin Zone(BZ) of fcc structure and rhombohedral A7 structure are shown in Fig.2. For fcc structure, there are four equivalent L points, which are located at $L_1=(\pi,\pi,\pi)$, $L_2=(\pi,-\pi,\pi)$, $L_3=(\pi,\pi,-\pi)$ and $L_4=(\pi,-\pi,-\pi)$ of BZ. After two kinds of distortions along cubic (111) direction, the fcc structure changes to the rhombohedral A7 structure, which breaks the equivalence between $L_1$ (which is denoted as T point in BZ of rhombohedral A7 structure) and $L_{2,3,4}$.

III. EFFECT OF ALLOYING AND PHASE DIAGRAM

Although pure Bi and Sb have been studied extensively, the alloyed system is not carefully considered yet. In this section, we will present a simple TB model by taking the strength of SOC $\lambda$ and dimerization $\Delta d$ as two key parameters to describe the effect of alloying. Based on this TB model, we obtained a schematic phase diagram for the topological nature of the compounds, which is instructive for us to understand the main physics. Then in the next section, surface states of alloyed system will be studied from accurate ab-initio calculations based on virtual crystal approximation (VCA).
A. Effect of Alloying

In order to take into account the effect of alloying, certain kinds of approximation have to be introduced. The first step, which is conventionally followed, is to assume the uniform distribution and neglect the disorder effects. However, this approximation is not sufficient. To further simplify our understanding, we emphasize the following factors: (1) Sb is located just on top of Bi in the periodical table, therefore they have the same number of valence electrons and form the same A7 crystal structure. (2) Even 30% Sb alloying into Bi will only modify the lattice parameters by around 1%. These factors: (1) Sb is located just on top of Bi in the periodical table, therefore they have the same number of valence electrons and form the same A7 crystal structure. (2) Even 30% Sb alloying into Bi will only modify the lattice parameters by around 1%. Therefore, we believe the strongest effect of Sb alloying into Bi is to reduce the SOC strength, and we can neglect the effect coming from the change of lattice parameters. Following this strategy, we construct a simple TB model to understand the main physics.

We consider one s and three p orbitals of each Bi atoms, together with the two sublattices and two spin degree of freedom, and totally there are 16 orbitals, denoted as $|s^1_1\rangle$, $|s^2_1\rangle$, $|p^1_{1x}\rangle$, $|p^1_{1y}\rangle$, $|p^1_{1z}\rangle$, $|p^2_{1x}\rangle$, $|p^2_{1y}\rangle$, $|p^2_{1z}\rangle$, $|s^1_2\rangle$, $|s^2_2\rangle$, $|p^1_{2x}\rangle$, $|p^1_{2y}\rangle$, $|p^1_{2z}\rangle$, $|p^2_{2x}\rangle$, $|p^2_{2y}\rangle$, $|p^2_{2z}\rangle$. Here z axis is taken along the (111) direction of fcc structure or the (001) direction of hexagonal cell and subscript number denotes different sublattice. The hopping parameters are defined in Fig.4 with the expression

$$V_{pp\sigma} = V_{pp\sigma} (1 + \alpha (\Delta d - \Delta d_0))$$

$$V_{pp\pi} = V_{pp\pi} (1 + \beta (\Delta d - \Delta d_0))$$

$$V_{ss\sigma} = V_{ss\sigma} (1 + \gamma (\Delta d - \Delta d_0))$$

$$V_{sp\sigma} = V_{sp\sigma} (1 + \delta (\Delta d - \Delta d_0))$$

for the first nearest-neighbour (NN) hopping,

$$V'_{pp\sigma} = V'_{pp\sigma} (1 - \alpha (\Delta d - \Delta d_0))$$

$$V'_{pp\pi} = V'_{pp\pi} (1 - \beta (\Delta d - \Delta d_0))$$

$$V'_{ss\sigma} = V'_{ss\sigma} (1 - \gamma (\Delta d - \Delta d_0))$$

$$V'_{sp\sigma} = V'_{sp\sigma} (1 - \delta (\Delta d - \Delta d_0))$$

for the second NN hopping and

$$V''_{pp\sigma} = V''_{pp\sigma}$$

$$V''_{pp\pi} = V''_{pp\pi}$$

$$V''_{ss\sigma} = V''_{ss\sigma}$$

$$V''_{sp\sigma} = V''_{sp\sigma}$$

for the third NN hopping. Here the parameters $V_m$, $V_m'$, and $V_m''$ are taken from the Liu-Allen model, where $m$ is $pp\sigma$, $pp\pi$, $ss\sigma$ or $sp\sigma$, respectively. Since the intra-layer Bi-Bi distance is larger than inter-layer Bi-Bi distance, $V_m$ and $V_m'$ are larger than $V_m''$. Linear dependence of $\Delta d$ due to the dimerization is assumed and $\Delta d_0$ is for the experiment structure of pure Bi. When $\Delta d = 0$, this system has no dimerization, leading to $V_m = V_m''$. Then a set of linear equations is obtained, which can be used to determine the value of the parameters $\alpha$, $\beta$, $\gamma$ and $\delta$. Besides the hopping terms, the atomic SOC with parameter $\lambda$ is also taken into account. Therefore, the final Hamiltonian is given as the function of two variables $\Delta d$ and $\lambda$, with the form

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

where $H_{11} = H_{22}$, $H_{12} = H_{21}^\dagger$ are $8 \times 8$ matrices. $H_{11}$ includes intra-sublattice hopping and on-site SOC interaction, while $H_{12}$ represents inter-layer hopping. Since the Hamiltonian has the type II inversion symmetry at T and L points, a unitary transformation is applied here to rewrite the Hamiltonian in the new basis with unambiguous parity, the odd parity basis, $\frac{1}{\sqrt{2}}(|s^1_1\rangle - |s^2_2\rangle)$, $\frac{1}{\sqrt{2}}(|p^1_{1x}\rangle + |p^1_{2x}\rangle)$, $\frac{1}{\sqrt{2}}(|p^1_{1y}\rangle + |p^2_{1y}\rangle)$, $\frac{1}{\sqrt{2}}(|p^1_{1z}\rangle + |p^2_{1z}\rangle)$ and the even parity basis, $\frac{1}{\sqrt{2}}(|s^1_1\rangle + |s^2_2\rangle)$, $\frac{1}{\sqrt{2}}(|p^1_{1x}\rangle - |p^1_{2x}\rangle)$, $\frac{1}{\sqrt{2}}(|p^1_{1y}\rangle - |p^2_{1y}\rangle)$, $\frac{1}{\sqrt{2}}(|p^1_{1z}\rangle - |p^2_{1z}\rangle)$. With the new basis, the Hamiltonian is changed to be $\tilde{H}$,

$$\tilde{H} = \begin{pmatrix} \tilde{H}_{11} & 0 \\ 0 & \tilde{H}_{22} \end{pmatrix}$$

which is block diagonal, because the odd and even parity states will not mix in a system with space-inversion symmetry.

B. Phase Diagram

The topological nature of the system can be determined from the parity of the occupied bands at TRIM. The band gap for Bi$_{1-x}$Sb$_x$ is near T and L points, therefore here we focus on one T and three L points in BZ. The parity of the occupied bands for T and L points can be easily obtained since the eigen states of $\tilde{H}_1$ have odd parity while those of $\tilde{H}_2$ have even parity. In Fig.5 the energy levels of six p bands for both L and T points are plotted as a function of $\Delta d$, where two different values of $\lambda$ are chosen, $\lambda = 1.5$ corresponding to the value of Bi and $\lambda = 0.5$ corresponding to the value of Sb. Three lowest levels of total six p bands should be occupied, namely the conduction band and valence band are the third lowest band and fourth lowest band respectively, which have opposite parities. When increasing the dimerization parameter $\Delta d$, at T point the band gap increases rapidly and there is no leveling crossing between the conduction band and valence band, while at L point, the band gap is quite small and the sequence of conduction band and
valence band can even change with $\lambda = 0.5\text{eV}$. When $\Delta d = \Delta d_0$, as indicated by the dashed line in Fig. 3, the occupied valence bands for Bi ($\lambda = 1.5\text{eV}$) and Sb ($\lambda = 0.5\text{eV}$) have different parities at L point but the same at T point, therefore we conclude the topological natures of Bi and Sb are different. This result is the same as that of Fu and Kane, in which they claim that $Z_2$ invariants $(v_1: v_{11} v_{12} v_{13})$ are (0:000) for Bi, which is topologically trivial, but (1;111) for Sb, which corresponds to topological non-trivial phase.

By determining the gap closing line of the conduction and valence band at L points, we can obtain the phase diagram of the alloy Bi$_{1-x}$Sb$_x$ as a function of SOC parameter $\lambda$ and dimerization parameter $\Delta d$, as shown in Fig. 4. Since the topological nature of the system can only be changed by closing bulk gap, in the magenta region, the system should have the same non-trivial topological behavior to Sb, while in the green region, it should be trivial insulator, which is same to Bi. It can be also understood from the parity analysis that the Bi is topologically trivial because both L and T points have reverted bands ordering, namely parity are -1 for both L and T. However, by reducing the SOC strength (i.e. Sb doping), the parity of L is recovered to be +1 while T remains to be -1, therefore topological non-trivial system is realized. In the next section, accurate simulation from ab-initio calculations will be presented.

FIG. 3: (color online) Energy bands are plotted as a function of the dimerization parameter ($\Delta d$) with SOC parameter $\lambda$ taken as 1.5eV and 0.5eV. (a) and (b) are for T point, while (c) and (d) for L point. The blue lines denote the states with parity +1 while the red ones are the states with parity −1. The dashed line represents $\Delta d = \Delta d_0$.

FIG. 4: (color online) The phase diagram of the system with two variables: the dimerization parameter $\Delta d$ and SOC parameter $\lambda$. In the magenta region, the parity of L and T points are +1 and -1, respectively, in other words, the system is in the topological non-trivial phase with $Z_2$ invariants (1;111). In the green region, however, the parity of L and T points are all -1, i.e, it is topological trivial with $Z_2$ invariants (0:000). Pure Bi locates in the trivial region and Sb locates at topological non-trivial region. The experimental $\Delta d$ of Bi and Sb are almost the same.

IV. AB-INITIO CALCULATIONS AND SURFACE STATES

A. ab-initio Method and Surface Green Function

The ab-initio calculation is carried out by our BSTATE (Beijing Simulation Tool for Atom Technology) code with plane wave pseudo-potential method. The generalized gradient approximation(GGA) of PBE-type is used for the exchange-correlation potential. Especially in Bi’s pseudo-potential, we take into account 5d pseudo-electrons as the valence band by ultra-soft pseudo-potential scheme. The $k$-mesh is taken as $12 \times 12 \times 12$ and the cut-off energy is 340.0eV for the self-consistent calculation. For pure Bi, the optimized lattice parameters are $a = 4.669\text{Å}, c = 12.1506\text{Å}$, and $d = 0.2341\text{Å}$, which are in good agreement with previous calculations.

To take into account the effect of alloying, virtual crystal approximation (VCA) is necessary. There are several ways to do this, particularly in the pseudo-potential approach, the simple linear combination of Sb and Bi pseudo-potentials can be used, and the corresponding pseudo-potential of alloyed virtual atom is regenerated by solving the atomic problem again. Unfortunately, this procedure is not accurate enough for our purpose here. As already suggested by previous studies, such VCA procedure can be used for those states far away from the Fermi level, however for those states very close to the Fermi level, the error bar is big. The system we study here (Bi$_{1-x}$Sb$_x$) is very sensitive to the $p$ orbitals, such VCA pseudo-potential can not give sufficient accuracy. In order to have an accurate VCA scheme, we need to consider the particularity of our system. As we already
explained in the last section, the alloyed Bi$_{1-x}$Sb$_x$ have the same crystal structure and almost the same structure parameters. The main effect of Sb alloying is to tune the SOC strength, $\lambda$. Therefore we may have a simple yet accurate VCA scheme. Here we take Bi’s parameters for simplicity and tune $\lambda$ in Bi’s pseudo-potential to simulate the doping parameter $x$ of the alloyed Bi$_{1-x}$Sb$_x$. In such a way, since we do not need to solve the atomic problem again, the pseudo-potential is accurate enough.

We are interested in the surface states of the semi-infinite system, a method based on maximally localized Wannier function (MLWF) is developed to calculate the surface states of semi-infinite system. The ab-initio MLWF method can be regarded as an exact TB method with its parameters calculated from ab-initio self-consistent electronic structure calculations. First, the semi-infinite Bi$_{1-x}$Sb$_x$ system can be divided into two parts: the bulk part and the surface part. The bulk part Hamiltonian is constructed with the MLWFs from bulk Bi$_{1-x}$Sb$_x$ ab-initio calculations, while the surface part Hamiltonian is constructed with MLWFs from Bi$_{1-x}$Sb$_x$ film with slab calculations. With these MLWFs’ hopping parameters, iterative method is adopted to solve the surface Green function of the semi-infinite system $G_{nn}^{\lambda l, l\alpha} (k_{||}, \epsilon + i\eta)$, where $n$ and $l$ denote the super-cell along $z$ direction and the atomic bilayer plane within one super-cell respectively. $\alpha$ gives the orbital index in one atomic bilayer and $k_{||}$ is a good quantum number in semi-infinite system.

The charge density of states (DOS) and spin DOS are related to the surface Green function with the expression

$$N_{\nu}^\parallel (k_{||}, \epsilon) = -\frac{1}{\pi} \text{Im} \sum_{\alpha} G_{nn}^{\lambda l, l\alpha} (k_{||}, \epsilon + i\eta)$$

and

$$S_{n,\sigma}^l (k_{||}, \epsilon) = -\frac{1}{\pi} \text{Im} \sum_{\alpha, \beta} c_{nn}^{\lambda l, \beta\alpha} (k_{||}, \epsilon + i\eta) O_{\beta\alpha}^\sigma,$$

respectively, where $\hat{s}^\sigma$ is the spin($s_x, s_y, s_z$) operator. When $n = 0$, $l = 0$, $N_{\nu}^0 (k_{||}, \epsilon)$ and $S_{0,\sigma}^0 (k_{||}, \epsilon)$ give the local DOS and local spin DOS at the surface and in the following we use $N(k_{||}, \epsilon)$ and $S_\sigma(k_{||}, \epsilon)$ for short.

### B. Surface State and Fermi surface

The local DOS $N(k_{||}, E)$ at the surface is plotted for two different SOC parameters, $\lambda = 1.28$eV and $\lambda = 1.1$eV for the topologically trivial and non-trivial situations respectively. In Fig. 4 with $\lambda = 1.1$eV, developing from the $\bar{\Gamma}$ point, there exists two surface bands connected to the $\bar{M}$ point, which are denoted as $\Sigma_1$ and $\Sigma_2$ respectively. At $\bar{M}$ point, $\Sigma_2$ band returns to valence band while $\Sigma_1$ band merges into the conduction band. Therefore, those surface states cross the Fermi energy five times in total (odd number), which indicates the topologically non-trivial nature of this phase. On the contrary, in Fig. 5 for $\lambda = 1.28$eV, both $\Sigma_1$ and $\Sigma_2$ bands return to the valence band at $\bar{M}$ point, and they cross the Fermi level four times (even number). This indicates that the system is topological trivial.

The shape of the Fermi surface for the two different phases is plotted in Fig. 7 and Fig. 8. There are one $\bar{\Gamma}$ point and three $\bar{M}$ points in the surface BZ, and they are all TRIM. The main difference between Fig. 7 and Fig. 8 is around the $\bar{M}$ point. For both cases, the $\bar{\Gamma}$ point is enclosed by one Fermi arc, however, the $\bar{M}$ point is different: it is enclosed by one Fermi arc at $\lambda = 1.28$eV, and it is not for $\lambda = 1.1$eV. Therefore by counting the total number of TRIM enclosed by Fermi surface in the BZ, it is even number for $\lambda = 1.28$eV (one $\bar{\Gamma}$ plus three $\bar{M}$), and odd number for $\lambda = 1.1$eV (only one $\bar{\Gamma}$ point).

Here we compare our results with that from TB analysis and that from experiment. As shown in Fig 9(a),
we find five crossing points between the surface bands and the Fermi energy along the line from $\bar{\Gamma}$ to $\bar{M}$, this is the same to those observed in the experiment of Hsieh et al (Fig. 9), however in a simple TB model, the number of crossing is three (Fig 9 (b)). A small discrepancy is found between our ab-initio calculation and the experiment of Hsieh et al near $\bar{M}$ point, as shown in Fig 9 (a) and (d). In the experiment of Hsieh et al, a third surface band $\Sigma_3$ appears near $\bar{M}$ point and be degenerate with $\Sigma_1$ band at $\bar{M}$ point, however in our calculation, there is no such band and $\Sigma_1$ band will go up and merge with the conduction band. This discrepancy may come from additional trivial surface states, as suggested in Fig 9 (c). This discrepancy remains to be justified by future studies.

In addition to the energy resolution, we are also able to calculate the spin-resolved surface states. As an example, we carry out this calculation for the semi-infinite Bi$_{1-x}$Sb$_x$ system’s blow surface, and show the spin-resolved surface state in Fig. 10. The spin orientation of the surface states at the Fermi level is plotted for

### FIG. 7: (color online) Left panel: The Fermi surface plot for $\lambda = 1.1\text{eV}$. The black hexagonal region is the 2D BZ of [111] surface for A7 structure. $\bar{\Gamma}$ is enclosed by a hexagonal electron pocket. There are other six hole pockets and six electron pockets surrounding. Right panel: The region framed by red rectangle in the left panel is zoomed in. We can clearly see that the outest six small electron pocket don’t enclose $\bar{M}$.

### FIG. 8: (color online) Left panel: The Fermi surface plot for $\lambda = 1.28\text{eV}$, which is similar to Fig. 4 except that the outest six electron pockets enclose the $\bar{M}$ point. Right panel: The region framed by red rectangle in the upper panel is zoomed in.

### FIG. 9: Schematic picture for the comparison of the surface bands obtained from (a) our ab-initio calculation, (b) TB model (from the work of Teo et al) and (d) ARPES experiment results. In ARPES experiment, an additional $\Sigma_3$ surface band (dotted line in (d)) becomes degenerate with $\Sigma_2$ band at $\bar{M}$ point. This additional band may come from the hybridization between the topological surface states and the other trivial surface states, as suggested by the red dotted line in (c).

### FIG. 10: (color online) The spin resolved Fermi surface for the semi-infinite Bi$_{1-x}$Sb$_x$’s below surface, whose normal is along -$z$ direction. The arrow in (a) indicates $(S_x, S_y)$; different colors in (a) and (b) represent $S_z$ along different directions. The red color means that the $S_z$ is along the +z direction; the blue color means that the $S_z$ is along the -$z$ direction. The three pieces of Fermi surface $F_1$, $F_2$ and $F_3$ are marked in Fig 7 $\lambda$ is taken as 1.1eV here.
three regions of 2D BZ with $\lambda = 1.1eV$. Clearly, vertex structure is found for the electron pocket around $\Gamma$ point ($F_1$), which confirms the topological nature of surface state. Because below surface’s normal is along the $-z$ direction, we can confirm that the chirality of the vertex structure around $\Gamma$ is left-handed and agrees with the recent spin-resolved ARPES experiment.

C. Indirect Band Gap

In the above discussions, we call Bi$_{1-x}$Sb$_x$ bulk as “insulator” because there exists a direct band gap between the conduction and the valence bands. Unfortunately, Bi$_{1-x}$Sb$_x$ is actually a semi-metal (not true insulator) for most of the doping range $x$, namely there exists finite overlap between the conduction band bottom (CBB) and the valence band top (VBT). If we define the true gap $E_g$ (indirect gap) as the energy difference between the CBB and the VBT, $E_g$ is negative for most of the $x$, and it is positive only for $0.07 < x < 0.22$.

On the other hand, to identify the TI nature, except the parity arguments as discussed above, it is crucially important to have a full bulk gap throughout the BZ. Therefore, a serious question for Bi$_{1-x}$Sb$_x$ is “can we make the indirect gap $E_g$ as positive as possible?”, or in other words, “can we widen the range of doping $x$ where system is truly insulating?”. Here we will show that applying the uniaxial pressure is an efficient way to open up the indirect band gap $E_g$.

Fig.11 shows the calculated indirect band gap $E_g$ as function of $c/a$ ratio with fixed volume. The $c/a$ ratio can be tuned either by $c$-axis pressure or by forming thin-film matched to substrate with different lattice parameters. For both sides of the topological phases ($\lambda = 1.28eV$ or $1.1eV$), a broad positive $E_g$ region can be obtained by reducing $c/a$ ratio slightly (around 3% reduction from its experimental value $c/a=2.6$). For both $\lambda = 1.28eV$ and $\lambda = 1.1eV$, the CBB is located at L point, however the VBT is located at T point for $\lambda = 1.28eV$, and at H$_1$ point (around T point in the mirror plane) for $\lambda = 1.1eV$. Despite of the different positions of VBT, the effect of $c$-axis pressure is always to raise the energy levels round L point, and lower the levels around the T point. For $\lambda = 1.1eV$, energy level at H$_1$ point goes lower, and energy level at H$_2$ point near the L point in the mirror plane goes upper. Therefore the positive indirect band gap is realized as schematically illustrated in the insets of Fig.11.

V. CONCLUSIONS

As a summary, we develop a method to study the alloyed Bi$_{1-x}$Sb$_x$ system and present a phase diagram to describe the topological nature of the system. We show that Bi is topologically trivial because the SOC is too strong. By alloying with Sb, the effective SOC strength is reduced and the topologically non-trivial phase is realized. By accurate ab-initio calculations and MLWF, we calculate the surface states of semi-infinite system. The results are compared with recent experiments. We predict the spin-resolved Fermi surface which can be tested by spin resolved ARPES. Finally, we suggest an efficient way to tune the indirect band gap by uniaxial pressure, such that true bulk insulating state can be realized for a broad doping range.

VI. ACKNOWLEDGMENTS

We acknowledge the support from Prof. N. Marzari for solving problems related to the construction of MLWF. This work is supported by the National Science Foundation of China, the Knowledge Innovation Project of the Chinese Academy of Sciences, and the 973 project of the Ministry of Science and Technology of China. XLQ and SCZ are supported by the US Department of Energy, Office of Basic Energy Sciences under contract DE-AC02-76SF00515.

---

1. C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 146802 (2005).
2. B. A. Bernevig, T. L. Hughes, and S.C. Zhang, Science 314, 1757 (2006).
M. Konig, H. Buhmann, L. W. Molenkamp, T. Hughes, C.-X. Liu, X.-L. Qi, and S.-C. Zhang, J. Phys. Soc. Jpn 77, 031007 (2008).
4 L. Fu, C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 98, 106803 (2007).
5 J. E. Moore and L. Balents, Phys. Rev. B 75, 121306 (2007).
6 X.-L. Qi, T. L. Hughes, and S.-C. Zhang, Phys. Rev. B 78, 195424 (2008).
7 M. Konig, S. Wiedmann, C. Brune, A. Roth, H. Buhmann, L. W. Molenkamp, X.-L. Qi, and S.-C. Zhang, Science 318, 766 (2007).
8 L. Fu and C. L. Kane, Phys. Rev. B 76, 045302 (2007).
9 X. Dai, T. L. Hughes, X.-L. Qi, Z. Fang, and S.-C. Zhang, Phys. Rev. B 77, 125319 (2008).
10 D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature 452, 970 (2008).
11 J. C. Y. Teo, L. Fu, and C. L. Kane, Phys. Rev. B 78, 045426 (2008).
12 H. Zhang, C. Liu, X. Qi, X. Dai, Z. Fang, and S. Zhang, Arxiv: cond-mat/0812.1622 (2008).
13 Y. Xia, L. Wray, D. Qian, D. Hsieh, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, et al., Arxiv: cond-mat/0812.2078 (2008).
14 Q. Liu, C.-X. Liu, C. Xu, X.-L. Qi, and S.-C. Zhang, arxiv: cond-mat/0808.2244 (2008).
15 Y. Liu and R. E. Allen, Phys. Rev. B 52, 1566 (1995).
16 K. Sugawara, T. Sato, S. Souma, T. Takahashi, M. Arai, and T. Sasaki, Phys. Rev. Lett. 96, 046411 (2006).
17 P. Hofmann, Progress in Surface Science 81, 191 (2006).
18 C. R. Ast and H. Höchst, Phys. Rev. Lett. 90, 016403 (2003).
19 Y. M. Koroteev, G. Bihlmayer, J. E. Gayone, E. V. Chulkov, S. Blügel, P. M. Echenique, and P. Hofmann, Phys. Rev. Lett. 93, 046403 (2004).
20 C. R. Ast and H. Höchst, Phys. Rev. B 67, 113102 (2003).
21 T. Hirahara, T. Nagao, I. Matsuda, G. Bihlmayer, E. V. Chulkov, Y. M. Koroteev, P. M. Echenique, M. Saito, and S. Hasegawa, Phys. Rev. Lett. 97, 146803 (2006).
22 Z. Fang and K. Terakura, Journal of Physics: Condensed Matter 14, 3001 (2002).
23 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
24 N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
25 I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).
26 M. P. L. Sancho, J. M. L. Sancho, and J. Rubio, Journal of Physics F: Metal Physics 14, 1205 (1984).
27 M. P. L. Sancho, J. M. L. Sancho, J. M. L. Sancho, and J. Rubio, Journal of Physics F: Metal Physics 15, 851 (1985).
28 D. Hsieh, Y. Xia, L. Wray, D. Qian, A. Pal, J. H. Dil, J. Osterwalder, F. Meier, G. Bihlmayer, C. L. Kane, et al., Science 323, 919 (2009), 10.1126/science.1167733.
29 A. Nishide, A. A. Taskin, Y. Takeichi, T. Okuda, A. Kakizaki, T. Hirahara, K. Nakatsuji, F. Komori, Y. Ando, and I. Matsuda, Arxiv: cond-mat/0902.2251 (2009).