Ab initio study of topological surface states of strained HgTe

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Abstract – The topological surface states of mercury telluride (HgTe) are studied by ab initio calculations assuming different strains and surface terminations. For the Te-terminated surface, a single Dirac cone exists at the Γ-point. The Dirac point shifts up from the bulk valence bands into the energy gap when the substrate-induced strain increases. At the experimental strain value (0.3%), the Dirac point lies slightly below the bulk valence band maximum. A left-handed spin texture was observed in the upper Dirac cone, similar to that of the Bi\(_2\)Se\(_3\)-type topological insulator. For the Hg-terminated surface, three Dirac cones appear at three time-reversal–invariant momenta, excluding the Γ-point, with non-trivial spin textures.

Introduction. – Topological insulators (TIs) constitute a new quantum state of matter that is attracting much attention in condensed-matter physics for both its fundamental interest and its potential applications [1–4]. Mercury telluride (HgTe) is a prototype of a TI material with an inverted band structure [5,6] that distinguishes it from a normal insulator. However, its conduction and valence bands are degenerate at the Fermi surface because of the cubic symmetry, inducing a zero energy gap. Breaking the cubic symmetry can open a band gap and realize a true TI in two ways. One is by reducing the dimensions from three to two in thick CdTe/HgTe/CdTe quantum wells (QWs) [5]. This is the first experimentally realized TI system [6], which is also called the quantum spin Hall effect. The other way is by using an external strain [7–9] (e.g., from the CdTe substrate) to induce a three-dimensional (3D) TI. Two-dimensional (2D) HgTe QWs have been extensively studied as a model system for phenomena including edge state conductance [10], spin polarization [11], and even direct imaging [12]. In contrast, 3D HgTe has not been explored as fully as other 3D TIs such as Bi\(_2\)Se\(_3\) [13,14]. Although quantum Hall measurements and angle-resolved photoemission spectroscopy (ARPES) [9,15] recently verified the existence of topological surface states (TSSs), the surface state dispersion above the Dirac point and the helical spin texture have yet to be explored. This is plausible for two reasons: i) in experiments, strained HgTe samples, which are not easily fabricated, are usually hole-doped, which hinders the access of ARPES to unoccupied surface states; ii) in theory, the requirement of thick slab models significantly increases the computational cost of ab initio calculations.

The (001) surface of HgTe for ARPES measurement [9,15] was usually obtained by sputtering of an Ar ion beam. The resultant surface exhibits a roughness of the order of \(\sim 2\) nm, as revealed by AFM measurements [15]. In these experiments, no signature of surface reconstructions (e.g., the Brillouin zone folding) has been observed by ARPES and low-energy electron diffraction (LEED), even though the as-grown HgTe (001) surface was reported to show a \((2 \times 2)\)-type reconstruction with Hg termination by STM and other surface-sensitive techniques [16]. This discrepancy is probably due to different techniques to prepare the surface. Due to the 0.3% larger lattice constant of the substrate CdTe than HgTe, in-plane strain is induced to HgTe thin films, which is expected to open the bulk energy gap. On both strained [15] and unstrained [9,17] surfaces, TSSs with linear dispersion were revealed by ARPES, wherein the Dirac point lies at the zone center and slightly below the top of the valence bands. The TSSs are known to exist inside the inverted bulk energy gap. For example, TSSs with a single Dirac-cone-type dispersion emerge in the bulk energy gap that is formed by the inverted lowest conduction band (LCB) and highest valence band (HVB) in Bi\(_2\)Se\(_3\) [13]. However, it is
not so simple in HgTe [5], because LCB and the second highest valence band get inverted and LCB and HVB are degenerate with, as a consequence, a zero energy gap. The LCB, HVB, the second and third highest valence bands are usually called $\Gamma_{8}$-light hole, $\Gamma_{8}$-heavy hole, $\Gamma_{6}$ and $\Gamma_{7}$ bands, respectively, according to the symmetry of wave functions. The degeneracy of $\Gamma_{8}$-light hole and $\Gamma_{8}$-heavy hole bands is due to the cubic lattice symmetry. Without external strain, TSSs should exist between $\Gamma_{6}$- and $\Gamma_{8}$-light hole bands and thus overlap with the bulk $\Gamma_{8}$-heavy hole state [8], indicating that the surface Dirac point is submerged in the valence bands. When strain increases and gradually opens the bulk energy gap, this Dirac point will shift continuously from the valence bands into the energy gap. This scenario was once demonstrated by Chu et al. with the $k$-$p$ Kane model, wherein the strain was applied as a parameter [18]. In order to describe TSSs in a more realistic way, Wannier-function–based tight-binding methods (refs. [8] and [19] and references therein) and ab initio calculations with slab models [20] have been performed for non-strain and large-strain cases. Although it takes the surface charge redistribution and $c(2 \times 2)$ reconstruction into account, the ab initio calculation induces unwanted trivial surface states at the Fermi level that were not observed in ARPES [9,15] and magneto-optical studies [21], and did not illustrate the evolution of the Dirac point with respect to the strain. Because of the roughness of the surface cleaved in ARPES as mentioned above, it is not surprising that ARPES results cannot be well reproduced by ab initio calculations, which employ an ordered surface configuration with the supercell setup. The Wannier function calculations on a semi-infinite surface only concentrated on the large-strain case demonstrating the Dirac-type TSSs, which are similar to those from the Kane model and close to ARPES. In this sense, the Wannier function method with proper boundary conditions (i.e. Te termination, as we will see) is the optimal choice to simulate TSSs on the rough surface of HgTe, because it adopts more realistic materials parameters than the $k$-$p$ method, and simpler boundary conditions for a rough surface than the ab initio method. In addition, previous Wannier function and ab initio calculations are all based on the local density approximation (LDA) of the density-functional theory (DFT). However, LDA is known to overestimate the band inversion and yields an incorrect band order ($\Gamma_{6}$, which influences the energy position of TSSs. Therefore, optimized functionals are necessary to reproduce the correct bulk band structure of HgTe as well as TSSs.

In this paper, we studied the TSSs of strained HgTe as a 3D TI and focused on their spin textures by using maximally localized Wannier functions (MLWFs) [23] extracted from ab initio DFT calculations, which enables us to simulate large surface models. We went beyond LDA by employing the hybrid functional method [24,25] to obtain the correct band ordering, i.e. $\Gamma_{7} < \Gamma_{6} < \Gamma_{8}$. The evolution of surface states was demonstrated with respected to the in-plane strain. The way of surface terminations can sensitively affect the dispersion of TSSs. The helical spin textures of the Dirac-type surface states were revealed, where the upper Dirac cone exhibits a left-hand chirality with a Berry phase $\pi$.

Methods. – Ab initio calculations were performed using DFT as implemented in the Vienna ab initio simulation package (VASP) [26,27]. Spin-orbit coupling was included in the band structure calculations. The LDA was employed for the exchange-correlation functionals to optimize the lattice structures. In the band structure calculations and MLWF projections, we went beyond the LDA and adopted the hybrid functional method [24,25]. We studied the HgTe (001) surface that was grown in recent experiments [9]. Our optimized equilibrium lattice constant was 6.438 Å, which is close to the experimental value of 6.461 Å [ref. (28)]. On the basis of the optimized cubic lattice (fig. 1(a)), we adopted the primitive tetragonal unit cell (fig. 1(b)) to simulate the (001) surface. For the (001) orientation with the substrate-induced strain $\epsilon$, the strain tensor components are given by $\epsilon_{xx} = \epsilon_{yy} = \epsilon, \epsilon_{zz} = -2\epsilon C_{12}/C_{11}$ and $\epsilon_{ij} = 0$ for $i,j = x, y, z$, where $C_{12}$ and $C_{11}$ are elastic stiffness constants and $C_{12}/C_{11} = 0.68$ for HgTe [29]. We investigated the electronic structures in the strain range $0 \leq \epsilon \leq 3\%$, in which the substrate-induced strain is equivalent to $\epsilon = 0.3\%$ according to experiment [9]. For each strain value, we extracted the corresponding MLWFs from the bulk calculations and then calculated the surface states, where the Bloch wave functions were projected to the Hg-s and Te-p orbitals.

Results and discussion. – The bulk band structure of HgTe is shown in figs. 2(a)–(d). The strain-free lattice is a zero-gap semimetal, in which the conduction and valence bands are degenerate at the $\Gamma$-point. An energy gap opens with increasing strain. The direct energy gap at the $\Gamma$-point ($E_{\Gamma}$) is 25 meV at the experimental strain $\epsilon = 0.3\%$. It agrees very well with the value obtained from the $k$-$p$ theory [9,15]. We note that the indirect energy gap is much smaller than $E_{\Gamma}$, only 4 meV for this strain. Both unstrained and strained lattices preserve the band inversion and thus host TSSs. One can see that the

![Fig. 1: (Colour on-line) (a) Zinc blende crystal structure of HgTe in a cubic unit cell. White and green balls represent Hg and Te atoms, respectively. The dashed lines indicate a tetragonal unit cell. (b) Tetragonal unit cell. Substrate-induced strains are applied in-plane tensile strains and a uniaxial compressive strain. (c) Te atoms on the top of the T-terminated surface form a 1D chain along the [110] direction.](image-url)

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band order related to $\Gamma_8$, $\Gamma_6$ and $\Gamma_7$ is correctly obtained, consistently with recent calculations [30,31]. Hence, we believe that hybrid functionals give more accurate band structures than the LDA does for HgTe.

To demonstrate the surface states, we calculated the local density of states (LDOS) using the Green’s function method: LDOS $(k,E)=\frac{-1}{\pi} \text{Im} G_{00}(k,E)$. On the semi-infinite surface, $G_{00}$ is the Green’s function projected from the 3D bulk to the top layer [32], which is constructed from the tight-binding Hamiltonian based on MLWFs. The surface band structures are shown in figs. 2(e)–(h). Without strain, there are already two types of TSSs. One locates at the boundary of low conduction bands in energy; their linear dispersion extends clearly from the $\Gamma$-point to higher momentum in the 2D Brillouin zone. This indicates that these TSSs are well separated from the bulk states in real space, so that they can be distinguished by recent ARPES measurements [9,15,17]. We note that it might be necessary to take these two types of surface states into account when interpreting future ARPES and transport experiments.

In calculations of the above surface band structure, we adopted the Te layer as the top layer of the semi-infinite surface. It is also possible to have a Hg layer as the outer surface. However, the Te-terminated model provides a surface band structure that is much closer to that obtained experimentally using ARPES than that of the Hg-terminated one, as we will see in fig. 3. Actually, our fully ab initio calculations based on a slab model with either Te or Hg terminations, which take surface charge self-consistency into account, yield several trivial dangling bond states at the Fermi energy, which is different from ARPES measurements. As mentioned above, the surface measured by ARPES is very rough and possibly terminated by Te and Hg mixed surfaces, rather than atomically smooth. However, either the Wannier function or ab initio slab calculations cannot directly simulate a fully disordered surface. The alternative solution is to find a proper boundary condition that is close to the realistic surface. For example, hydrogen atoms are employed to terminate the surface dangling bonds in recent ab initio calculations with LDA [26]. But it did not give a clear feature as to where the Dirac cone locates and how it reacts to strain. Our Wannier function results agree much better with experiments than the ab initio calculations. In this sense, the direct truncation of hopping in the tight-binding scheme is a proper, although not perfect, boundary condition for the rough surface of HgTe. But one drawback of the current method is that the effect of the smooth surface setup still exists. As illustrated by fig. 1(c), the surface Te atoms are interconnected by the second layer of Hg atoms to form a nearly 1D chain along the [110] direction. Therefore, the calculated TSSs are more dispersive along the $\Gamma$-$Y$ direction than along the $\Gamma$-$X$ direction. However, the dispersion of TSSs in ARPES is very isotropic in the surface Brillouin zone [9,15,17], because of the randomness of the surface structure. In addition, the effect of surface charge redistribution (such as surface band bending) was not taken into account in the current study, which may affect the exact position of the Dirac point but will not change our main conclusions.
The Te- and Hg-terminated surfaces can act as typical examples to illustrate the robustness and flexibility of TSSs. We constructed two slab models which are 239 atomic layers thick (∼38 nm) with top and bottom surfaces. One slab is terminated by Te on both surfaces, and the other is terminated by Hg. To exhibit a simple Dirac cone with a large bulk energy gap, we adopted the MLWFs from 3% strained bulk HgTe. The slab Hamiltonians were directly diagonalized to obtain the band structures (see fig. 3). Take the Te-terminated surface as an example. Although it behaves approximately isotropically at smaller strains (figs. 2(a)–(c)), the surface state of the Dirac cone exhibits considerable anisotropy when it shifts inside the bulk gap at a large strain due to the chain-like surface structure (fig. 3(a)). The top and bottom surfaces are connected by the $C_4$ rotation with an addition mirror ($xy$ plane) operation. Thus, the 1D chain along $y$ on the top surface corresponds to a chain along $x$ on the bottom surface. As a consequence, one can observe two pairs of non-degenerate TSSs in the band structure of fig. 3, wherein one pair is due to the top surface and the other pair is due to the bottom surface. We highlighted the TSSs on the top surface by solid red lines and those on the bottom surface by dashed gray lines in fig. 3. In fig. 3(b), one can see that the $\Gamma$-$X$ dispersion of the top TSSs is equivalent to the $\Gamma$-$Y$ dispersion of the bottom TSSs, because the 1D Te chains from the top and bottom surfaces are perpendicular to each other. Further, the Te-terminated surface exhibits a single Dirac cone at the $\Gamma$-point as in fig. 2(a), whereas the Hg-terminated surface shows three Dirac cones at other time-reversal–invariant $k$-points, $Y$, $M$, and $X$. This indicates that the energy dispersion of the TSSs responds quite flexibly to local surface potential modifications, whereas the existence of TSSs is always protected by the underlying topology of the bulk band structure. We note that the surface states of the Hg-terminated surface are similar to those in previous calculations in refs. [8] and [19]. For the Te surface, one can observe a left-handed spin texture in the upper Dirac cone. For the Hg surface, there exist two right-handed ($X$ and $Y$) vortices and one left-handed ($M$) vortex. Because an odd number of Dirac cones exist on either the Te or Hg surface, an electron always obtains a non-trivial Berry phase, $\pi$ or $-\pi$, due to the spin vortices when it circles around the Fermi surface, showing a topological feature. In addition, one can find that the Te-terminated surface exhibits the same left-handed spin texture as $\text{Bi}_2\text{Se}_3$ [33,34].

Conclusions. – In summary, we studied the TSSs on the (001) surface of strained HgTe. The position and number of Dirac points are sensitive to whether the surface terminates in Te or Hg atomic layers. The Te-terminated surface exhibits a simple Dirac cone at the $\Gamma$-point, whereas the Hg-terminated surface has three Dirac points, at the $X$, $Y$, and $M$ points. On the basis of our calculations for different strain values, we expect that the Dirac point lies slightly below the bulk valence band maximum for the substrate-strained HgTe in previous experiments. The HgTe surface supplies a simple model to demonstrate the modification of the energy dispersion of TSSs by the surface boundary condition. Regardless of the surface termination, the spin textures of the Dirac cones carry a Berry phase $\pi$, which indicates a topological feature.

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