Confinement Effect Driven Quantum Spin Hall Effect in Monolayer AuTe$_2$Cl

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Based on first-principles calculations, we predict that the monolayer AuTe$_2$Cl is a quantum spin Hall (QSH) insulator with a topological band gap about 10 meV. The three-dimensional (3D) AuTe$_2$Cl is a topological semimetal that can be viewed as the monolayer stacking along b axis. By studying the energy level distribution of $p$ orbitals of Te atoms for the bulk and the monolayer, we find that the confinement effect driven $p_y^− - p_z^+$ band inversion is responsible for the topological nontrivial nature of monolayer. Since 3D bulk AuTe$_2$Cl has already been experimentally synthesized, we expect that monolayer AuTe$_2$Cl can be exfoliated from a bulk sample and the predicted QSH effect can be observed.

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INTRODUCTION

Two-dimensional (2D) topological insulators (TIs), known as quantum spin Hall (QSH) insulators are characterized by a topological nontrivial bulk gap and gapless helical edge states protected by time-reversal symmetry from backscattering at the sample boundaries [1–3]. Because of their potential applications in semiconductor spintronics, they have recently attracted great attention in condensed matter physics [4]. For example, the QSH effect can be achieved in an exfoliated, monolayer TI layers along a certain crystal orientation while the QSH effect at room temperature. In spite of those progresses, desirable materials preferably with high feasibility of experimental realization are still extremely scarce and deserve to explore in experiment and theory.

Recently, the catalogue of topological electronic materials greatly enriches the number of new topological materials, which has listed all 3D TIs and topological semimetals (TSMs) based on symmetry indicators [13–15], and inspires the enthusiasm for the study of new topological materials. As we know, some 3D TIs and TSMs are closely related to 2D QSH insulators [16]. They can be built up by stacking 2D QSH insulating layers along a certain crystal orientation while the QSH effect can be achieved in an exfoliated, monolayer TI and TSM. A well-studied example is transition metal dichalcogenides 1T’-MX$_2$ (M = W, Mo and X = S, Se, Te) [17]. This is a new way to search for new layered materials from the catalogue of topological electronic materials and study the two-dimensional topological nature to achieve QSH effect.

In this paper, we study the structure and electronic properties of bulk and monolayer AuTe$_2$Cl. We find that the bulk AuTe$_2$Cl is a TSM with a band inversion along $Γ − Y$ direction. While the monolayer is a QSH insulator with a $p_y^− - p_z^+$ band inversion at the $Γ$ point in the 2D BZ. This band inversion is driven by the confinement effect, which eliminates the coupling between $p_y$ orbitals along $y$ direction and pulls down the anti-bonding state $p_y^−$ below the Fermi level and the bonding state $p_z^+$.

Its topological nontrivial nature is demonstrated through the Wannier center evolution and surface density of state (DOS) calculations. Therefore, we present a new way of exploring 2D QSH insulators from 3D TSMs. We expect the predicted AuTe$_2$Cl monolayer and its QSH effect can be realized in future experiments.

METHODS

First-principles calculations based on density functional theory (DFT) are carried out by the Vienna ab initio simulation package (VASP) [18–20]. The exchange-correlation functional is treated within the local-density approximation (LDA) [21]. A self-consistent field method (tolerance 10$^{-5}$ eV/atom) is employed in conjunction with plane-wave basis sets of cutoff energy of 500 eV. Atomic structure optimization is implemented until the remnant Hellmann-Feynman forces on the ions are less than 0.01 eV/Å. We use 11 $×$ 11 $×$ 7 and 11 $×$ 1 $×$ 7 $Γ$-centered $k$-meshes to sample the BZ of bulk and monolayer systems, respectively. The vacuum layer is set to 15 Å to minimize artificial interaction between layers. SOC is considered for all calculations. For monolayer, we also perform hybrid functions calculations to correct
FIG. 1: (a) The crystal structure of bulk AuTe$_2$Cl. It has a layered orthorhombic structure and $d$ is the distance of two adjacent layers. (b), (c) are the side view and top view of the AuTe$_2$Cl monolayer, respectively. The red star in (b) denotes an inversion center. (d) The 3D Brillouin zone for the bulk and the 2D BZ for the monolayer with high symmetry $k$ points labeled. (e) The total DOS and projected DOS for bulk AuTe$_2$Cl. (f) The projected band structure for the three $p$ orbitals of Te in the bulk AuTe$_2$Cl. The size of the red squares, green circles and blue diamonds represent the weight of $p_x$, $p_y$ and $p_z$ orbitals, respectively.

its band structure [22]. The maximum localized Wannier functions are constructed by using the Wannier90 package [23]. The topological properties are calculated by using Wanniertools [24].

RESULTS AND DISCUSSION

The bulk compound AuTe$_2$Cl has been synthesized in experiment [25–27], which adopts a layered orthorhombic structure ($D_{2h}$ point group) and lattice constant $a = 4.02$ Å, $b = 11.87$ Å, $c = 8.77$ Å with the nonsymorphic space group $Cmcm$ (No. 63), as shown in Fig. 1(a). For each layer, a pair of Te atoms is joined to neighboring Au atoms and forms a Au-Te-Te-Au corrugated net, which is sandwiched by the upper and lower Cl atoms. Therefore, each Au atom is coordinated with four Te atoms and, likewise, each Te atom is coordinated with four Au atoms. The bond length of Au-Te and Te-Te covalent bond are 2.67 Å and 2.78 Å, respectively. The short bond length indicates that strong covalent bonds are formed and, are responsible for the in-plane crystal stability. The interaction along $b$ axis are mainly contributed by the Te-Te bond (3.2 Å) between two adjacent layers [see $d$ in Fig. 1(a)]. The Te-Te bonds along $b$ axis are much weaker than the covalent bonds in the $xz$ plane, which means it is experimentally possible to exfoliated monolayer AuTe$_2$Cl from bulk samples [see Figs. 1(b) and 1(c)].

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From the projected density of states (PDOS) of bulk AuTe$_2$Cl shown in Fig. 1(e), we observe that the most important orbitals within the energy window from $-1.2$ to 2.0 eV are the Te $p$ orbitals. The Au $d$ orbitals and Cl $p$ orbitals mainly contribute to the states below $-1.2$ eV, and the Au $s$ orbitals are responsible for the peak at 3.4 eV. From these observation, we can understand the electronic transfer and chemical bonding as follows. Each Au atom donates a $5s$ electron to the Cl $3p$ empty orbitals, which lowers the total energy and keeps the PDOS of these orbitals away from the Fermi level. The band structure of bulk system in Fig. 1(f) reveals a semimetal character, where the valence band is partially empty resulting in a hole pocket along $\Gamma-Y$, while the conduction band is partially filled resulting in an electron pocket along $X-M$. This has been confirmed in transport experiments [27].

When the SOC is neglected, there is a Dirac point along $\Gamma-Y$ direction at 0.25 eV above the Fermi level formed by the $p_x$ and $p_z$ band crossing. When SOC is considered, a topological nontrivial gap about 7 meV is opened up. The parities of $(p_x, p_y, p_z)$ orbitals at $\Gamma$ (and $Y$) point are $(-, -, +)$, respectively, as shown in Fig. 1(f). For the
covalent bonding between \( p \) orbitals, the bonding state has the positive parity and the anti-bonding state has the negative parity. Therefore, the \( p_z \) orbitals are bonding states and the \( p_x, p_y \) orbitals are anti-bonding states near the Fermi level. We notice that the \( p_y \) orbitals have a stronger dispersion along \( \Gamma-Y \) direction compared with \( p_x \) and \( p_z \) orbitals, which is mainly due to the relatively strong hopping between \( p_y \) orbitals along \( y \)-direction.

Now we focus on the topological properties of monolayer system. Due to relatively strong coupling of \( p_y \) orbitals in the \( y \) direction, when bulk \( \text{AuTe}_2\text{Cl} \) is exfoliated to the monolayer, the confinement effect should be considered. We simulate the transform from bulk to monolayer by increasing the adjacent layer distance \( d \). Fig. 2(a) exhibits the evolution of conduction band minimum (CBM) of \( p_x \) and \( p_y \) orbitals, and valence band maximum (VBM) of \( p_z \) orbitals at \( Y \) point with increasing \( d \). It demonstrates that the CBM of the \( p_x \) orbitals rapidly falls below the \( p_x \) orbitals and the Fermi level. While the CBM of \( p_x \) and the VBM of \( p_z \) orbitals rise slightly. When \( d > 4.2 \) Å, the energy levels of three \( p \) orbitals reach stationary values, indicating vanishing of the interlayer coupling along \( y \) direction. Moreover, when the \( d \) is large enough, the band dispersion along \( \Gamma-Y \) disappears, which means the system reach its monolayer limit. Hence the topological nature is determined by the \( \Gamma \) point in the 2D BZ.

To illustrate the band inversion process in the monolayer \( \text{AuTe}_2\text{Cl} \) explicitly, we start from the Te \( p \) orbitals and consider the effect of chemical bonding and confinement effect for bulk and monolayer \( \text{AuTe}_2\text{Cl} \). This is schematically depicted in the three stages in Fig. 2(b).

Stage I represents the chemical bonding process between Te atoms. As analysed above, the states around the Fermi energy are mainly contributed by bonding states of Te \( p_x \) orbitals with positive parity \( \xi = +1 \) and anti-bonding states of \( p_x \) and \( p_y \) orbitals with negative parity \( \xi = -1 \). At this stage, the bonding states have lower energy below Fermi level and the anti-bonding states have higher energy above the Fermi level. In stage II, the energy levels have changed mainly due to hopping along \( y \) direction. The band inversion occurs between the \( p_x \) orbitals with parity \( \xi = -1 \) and the \( p_x \) orbitals with parity \( \xi = +1 \). Stage III represents the rearrangement of energy levels driven by the confinement effect. Since \( p_y \) orbitals have larger hopping constants along the \( y \) direction, the confinement effect will influence \( p_y \) orbitals much stronger than the \( p_x \) and \( p_z \) orbitals, and pulls down the \( p_y \) orbitals below the Fermi level. As a result, the band inversion happens between the bonding state of \( p_z \) orbitals and the anti-bonding state of \( p_y \) orbitals in the monolayer \( \text{AuTe}_2\text{Cl} \).

In order to obtain a stable monolayer structure, the lattice parameters and ions positions are fully optimized in the LDA calculation. The total energy with respect to the lattice constants are given in Fig. 2(c). The lowest total energy corresponds to \( a = 4.02 \) Å and \( c = 8.32 \) Å. The LDA band structure of monolayer \( \text{AuTe}_2\text{Cl} \) is shown in Fig. 3(a). In the absence of SOC, the monolayer \( \text{AuTe}_2\text{Cl} \) shows semimetal feature with a Dirac point located on the \( \Gamma-X \) path in the 2D BZ, which confirms the band inversion at \( \Gamma \) point. When the SOC is considered, the Dirac point is gapped out. Our LDA results suggest that the monolayer \( \text{AuTe}_2\text{Cl} \) is very close to a insulating state. The overlap between the CBM and VBM is about 27 meV. We further perform the hybrid functional calculations using the HSE06 functional. The HSE06 band structure exhibits a positive band gap about 10 meV at the Fermi level, as shown in Fig. 3(b). This means when interlayer distance \( d \) is increased, the system undergoes a topological semimetal to topological insulator phase transition.

Since monolayer \( \text{AuTe}_2\text{Cl} \) has inversion symmetry, the \( Z_2 \) topological invariant can be determined by the parities of all occupied bands at the four time-reversal-invariant-momentum (TRIM) points. According to Fu-Kane formula, \((-1)^v = \prod_i \delta_i \) with \( \delta_i = \prod_{m=1}^{N_i} \xi_{2m}(\Gamma_i) \). Here \( v \) is the \( Z_2 \) number and \( \xi_{2m}(\Gamma_i) \) is the parity of the \( 2m \)th occupied band at TRIM point \( \Gamma_i \) [31]. For monolayer \( \text{AuTe}_2\text{Cl} \), the calculated \( \delta_i \) for four TRIM points \( \Gamma, \ Y, \ X \) and \( \bar{U} \) are given by \(-, - , - , + \), respectively.
FIG. 3: Results for the monolayer AuTe₂Cl. (a), (b) are the band structures from LDA and hybrid functional calculations, respectively. In each case, the p orbitals of Te are projected out. (c) The Wannier center evolution in the y-direction with the SOC calculation. The reference dash line crosses the evolution line once which indicates a topological nontrivial band structure. (d) The surface DOS along X – Γ of the 2D BZ. The red topological edge states are clearly visible.

Hence the Z₂ number ν = 1, which demonstrates that it is a topological nontrivial insulator. The topological nontrivial nature can also be confirmed by the calculated Wannier center evolution as shown in Fig. 3(c). The reference dash line crosses the evolution line an odd number of times in the y-direction. We also calculate the edge spectrum in Fig. 3(d), in which pair of gapless edge states connects the conduction bands and the valence bands. From all these compelling evidences, we thus conclude that the monolayer AuTe₂Cl is a QSH insulator with a topological band gap about 10 meV. It should be noted that the 3D bulk AuTe₂Cl has been experimentally synthesized. We expect the monolayer system can be exfoliated from its 3D counterpart, or from molecular beam epitaxy growth method.

In summary, we predict that the monolayer AuTe₂Cl is a QSH insulator with a topological band gap about 10 meV. The nontrivial band topology stems from the band inversion between pₓ anti-bonding state and pₓ bonding state of Te atoms at Γ point. This band inversion is driven by the confinement effect when 3D bulk system is exfoliated to monolayer thickness. Since bulk AuTe₂Cl has been experimentally synthesized, we expect the experimental realization of monolayer AuTe₂Cl and the predicted QSH effect are also very promising. Our work demonstrates how 2D QSH insulators can be designed from 3D layered TSMs or TIs. This may further promote the exploration of 2D TIs.

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