Symmetry-dependent topological phase transitions in PbTe layers

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Abstract

By stacking PbTe layers there is a non-monotonic topological phase transition as a function of the number of monolayers. Based on first principles calculations we find that the proper stacked crystal symmetry determines the topological nature of the slab. While a single PbTe monolayer has a nontrivial phase, external pressure can induce topological phase transition in bulk PbTe. Between these two limits, where finite size effects are inherent, we verified that, by applying an external pressure, odd stacking layers can be tuned easily to a topological phase, while even stacking keeps a larger band gap, avoiding band inversion. The quite distinct behavior for odd/even layer is due to the symmetry of the finite stacking. Odd layers preserve the bulk symmorphic symmetry with strong surface hybridization, while even layers belong to a nonsymmorphic group symmetry. Nonsym-morphism induces extra degeneracy reducing the hybridization, thus protecting band inversion, postponing topological phase transitions.

1. Introduction

Topological insulators (TI) form a quantum phase of matter, where metallic states arise on the borders and are protected by some symmetry. The first materials predicted in this class were protected by time reversal symmetry [1]. Recently it has been proposed TIs protected by crystal symmetry [2]. This topological crystalline insulator (TCI) phase was predicted in a real material SnTe [3], and promptly observed experimentally [4], following many other IV–VI compounds [5–9]. PbSe, PbTe and PbS three-dimensional (3D) bulk materials are trivial insulators, but pressure can be used to turn them in TI [10–12]. On the other hand, free standing monolayers composed by these materials are two-dimensional (2D) TCIs [13, 14].

The stacking of IV–VI monolayers formed by precursor bulk TCI materials have been largely studied [14–20]. Odd and even stacking of layers formed by TCI bulk materials show topological phase transitions and a non-monotonic progression on their energy band gaps. In fact odd and even stacking can present different space crystal symmetry. As this is the symmetry that protects the topological phase in these systems, odd/even can also present distinct topological phases. While odd stacking preserves the bulk symmorphic symmetry, even stacking present a nonsymmorphic symmetry. Nonsym-morphism by itself is already of great interest since it induces extra degeneracies [21], and it must be present in the lately proposed topological order Hourglass fermions [22, 23].

Stacking of layers composed by a trivial precursor 3D bulk material can be interesting due to the connection of nano-size effects with non trivial topological phases. In this work we investigate topological properties due to finite size effects of stacked layers formed from the trivial bulk PbTe. Nanostructure formed by PbTe is interesting to be investigated, since its 3D bulk is trivial, while the monolayer is a 2D TCI system [13, 14]. Based on electronic structure calculations we verify that for odd stacking, due to the hybridization there is a compensation on the nano-size effects reducing the band gap. On the other hand, for nonsymmorphic even stacking the symmetry-locked degeneracy keeps a larger band gap. More interesting, we verified that a feasible hydrostatic pressure can support topological phase for all odd stackings, while for nonsymmetric even stacking, the topological phase can only be reached for a large number of layers.
2. Methodology

The PbTe nanostructures have been investigated using a density functional calculation (DFT) as implemented in the VASP code \[24, 25\]. The exchange-correlation functional is described by the general gradient approximation \[26\]. Interactions between electrons and ionic core are described by fully relativistic PAW pseudopotentials that include spin–orbit (SO) interactions \[27\]. Wave functions are expanded in orthogonal plane waves basis set with an energy cutoff of 450 eV. A Monkhorst–Pack \[28\] grid of \(4 \times 4 \times 1\) \((4 \times 4 \times 4)\) is employed to describe the Brillouin zone and obtain the charge density of the layers (bulk). In all calculations a vacuum region of 12 Å in the perpendicular direction of the layers is used to reduce the interaction between periodic images.

3. Results and discussion

Bulk PbTe, a rock salt structure, is an insulator material with small direct band gap \(0.19\) eV. The SO effect is quite strong in lead chalcogenides, particularly for PbTe our calculation energy band gap is reduced from 0.83 to 0.11 eV, by including SO interactions. The smaller band gap obtained here as compared to the experimental one is due to the DFT approach. The strong SO effect is not enough to invert the band gap, so bulk PbTe is a trivial insulator, where the valence band maximum is composed mostly by \(p\) orbitals of Te atoms and the conduction band minimum by \(p\) orbitals of Pb atoms. However, if external pressure is applied to reduce the volume, we observe a band inversion that occurs when PbTe is compressed to \(91\%\) of the equilibrium volume \(V_0\), making PbTe a nontrivial insulator. Similar calculation has been performed by Barone et al\[10\] where they obtained also a topological phase transition due to pressure. The phase transition takes place due to the enhancement of \(sp\) hybridization, pushing the \(p\) states around the Fermi level provoking a band inversion.

A nanoscale 2D system composed by a free standing monolayer of PbTe, showed in figure 1, presents a nontrivial topological phase. Our calculated equilibrium lattice parameter for bulk PbTe is \(6.56\) Å, and for the monolayer \(6.36\) Å. This reduction in the lattice parameter strengthen the \(sp\) hybridization, that, together with SO interactions, result in a band gap inversion without any external effect. In figures 2(a), (b) we can see that the SO interactions put the Te \(p\) orbitals in the conduction band and the Pb \(p\) orbitals in the valence band, opposite characters as found in bulk PbTe. Our results substantiate that PbTe monolayer is a 2D TCI material, in agreement with previous calculations in 2D lead chalcogenides \[13, 14\].

By stacking \(N\) PbTe layers along the [001] direction as shown in figure 3 we can have odd or even number of layers. For odd stacking the system preserves the same symmetry as the bulk and the monolayer PbTe. While for even number of layers the pure point group symmetry is not enough to describe the system, there are fractions of translation symmetry to be included. Odd/even stackings belong to different space group symmetries. In fact odd stackings present a nonsymmorphic symmetry. The consequences of the nonsymmorphism are more interesting on the electronic properties, where extra topological protections have been shown in 2D TCIs \[16, 29\].

Let us starting with the nonsymmorphic bilayer \((N = 2)\), where the calculated equilibrium lattice parameter is \(6.45\) Å, a value between the bulk and the monolayer parameter. The bilayer presents larger band gap, \(0.51\) eV, as compared to the monolayer, \(0.26\) eV (see figure 2). As the stacking enlarge the band gap, the SO interaction does not induce a band inversion, and the bilayer is a trivial insulator as can be seen in figures 2(c), (d). At the M

\[\text{Figure 1. Lattice structure and Brillouin zone used here for PbTe monolayer. Blue spheres represent Pb atoms and gray spheres represent Te atoms. For this cell, the bulk L point is projected into 2D M point.}\]
point of 2D Brillouin zone (projected from the L point of the bulk) the electronic states are at the least fourfold degenerate, due to the nonsymmorphic symmetry.

For the symmorphic trilayer ($N = 3$) we have a reduction on the band gap as compared to the bilayer, 0.11 eV and 0.86 eV with and without SO interaction, respectively. Those values are quite close to the bulk PbTe band gaps. However this reduction is not enough to change the bands, so trilayer PbTe is still within a trivial phase. By increasing the number $N$ of layers, as we can see from figure 4, the evolution of the energy band gaps is non-monotonic. While for symmorphic odd stacking the band gap is almost constant, for nonsymmorphic even stacking the band gap varies with the number of layers. Odd and even systems have to be analyzed separately, according to its spatial crystal symmetry.

Focusing on the symmorphic odd stackings, we can see a phase transition (with a gap closing) between 1 and 3 layers. For $N = 1$ it is a TCI system, and for $N \geq 3$ they are all trivial systems. A small oscillation of the band gap can be seen for odd stacking in figure 4. For the nonsymmorphic even stacking, the confinement effects affect strongly the electronic structure. The band gap is enlarged as compared to the symmorphic symmetry, and it decreases monotonically as the number of even layers increases. We also observe a small oscillation of the band

**Figure 2.** Band structure of PbTe monolayer ((a) and (b)) and PbTe bilayer ((c) and (d)). Blue circles represent projection onto Pb $6p$ orbitals, while red circles projection onto Te $5p$ orbitals. The Fermi level is set to zero.

**Figure 3.** Lattice structure of PbTe few layers. For odd number of layers, like $N = 3$, the system is symmorphic, the same symmetry as the bulk and monolayer of PbTe. For even number of layers, like $N = 2$, the system presents a nonsymmorphic symmetry. Blue and gray spheres represent Pb and Te atoms.
gap for even stacking, but no phase transition for these nonsymmorphic systems. The results are similar to those of Wan et al [11] calculations for PbS stacking, where odd/even present different trends on the band gap as a function of the number of layers.

It is interesting we analyze the topological properties by applying an external hydrostatic pressure on the PbTe layers, since the bulk PbTe changes its topological phase under pressure [10]. In particular for a trilayer, as shown in figure 5, we observe that the fundamental band gap is already inverted for a reduction of the volume to 91% of the free standing equilibrium volume $V_0$. In fact the topological phase transition occurs for a volume of 0.93$V_0$, while for bulk PbTe this transition occurs for a volume of 0.91$V_0$ [10]. For $N = 5$ the trivial to topological phase occurs for a volume of 0.92$V_0$. And for all other $N \geq 7$ symmorphic odd PbTe stacking the band inversion takes place for pressure of volume 0.91$V_0$, the same as the bulk PbTe transition. In figure 6 we plot the energy band gap as a function of the number of layers for the critical volume 0.91$V_0$. We observe that all symmorphic stackings belong to the TCI phase. On the other hand, for nonsymmorphic even number of PbTe stacking, the trivial to topological phase only takes place for a large number of layers, $N \geq 16$. This postponing topological phase transition is due to the nonsymmorphic symmetry. Nonsymmorphism presents fractions of translation symmetry inducing extra degenerate states, hampering band inversions.

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**Figure 4.** Energy band gap as a function of number of PbTe layers $N$ along the [001] direction. Open (filled) symbols represent band gap without (with) SO interaction. Circles (squares) are for even (odd) layer stacking. The full (dashed) horizontal line is the bulk PbTe band gap with (without) SO interaction.

**Figure 5.** Band structure of PbTe trilayer ($N = 3$). In (a) is the band for optimized lattice parameter (volume $V_0$), and (b) is for an external pressure reducing the volume to 91% of $V_0$. Blue circles represent projection onto Pb 6p orbitals, while red circles projection onto Te 5p orbitals. Fermi level is set to zero.
By comparing the evolution of the band gap for pressured systems of figure 6 with those of free standing of figure 4, we see that the topological phase due to the compressed strain is reached for systems where the non-pressured band gaps are close to the equilibrium volume of bulk PbTe band gap. As the confinement effects are negligible for symmorphic odd stackings, keeping the band gaps close to the PbTe bulk band gap (see figure 4), by reducing the volume to 0.91\( V_0 \), all of them become TCI materials. On the other hand, as the band gaps for nonsymmorphic even stackings are more sensitive with the number \( N \) of PbTe layers, the phase transition only occur for a large number of layers. Usually the effects of pressure in trivial systems enlarge the band gap, as observed for nonsymmorphic stacking with \( N \leq 14 \) in figure 6. If the band gap is reduced due to the pressure, it may belong to a non-trivial phase, as is the case for \( N \geq 16 \).

4. Conclusions

In summary we show that, while bulk 3D PbTe is a trivial material and a monolayer is a 2D TCI system, few layers of PbTe present a non-monotonic evolution of the band gap, but they are still all trivial when free standing. Moreover by applying an external hydrostatic pressure, odd stacking layers can be tuned easier to a topological phase than even stacking layers. As odd and even belong to different spatial crystal symmetry, the confinement effects act different on each system. Few odd layers enhance the \( sp \) hybridization leading to a faster band gap inversion. While the energy band gap for even nonsymmorphic stacking is quite enlarged for few layers, avoiding a band inversion, even if pressure is applied. Based on electronic structure calculations, we verified that all odd PbTe stackings become TCI systems when subject to a pressure of volume 0.91\( V_0 \), the same pressure as the bulk PbTe transition. On the other hand by keeping the same external pressure, the topological phase transition for even stacking only takes place for 16 layers or more. The difference on the topological phase transition for odd/even stacking can be understood by the difference on the crystal symmetry. While odd layers preserve the bulk symmorphic symmetry, even layers belong to a nonsymmorphic symmetry, which protects degenerate states, reducing the hybridization, thus avoiding band inversion and delaying the topological phase transition.

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Figure 6. Energy band gap as a function of number of PbTe layers \( N \) for an external pressure reducing the volume to 91% of the free standing layers. Negative values for the band gaps means topological non trivial phase.
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