Pressure induced topological quantum phase transition in Sb$_2$Se$_3$

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Based on the first-principles band structure calculations, we investigate the effects of hydrostatic pressure on the conventional insulator (CI) Sb$_2$Se$_3$ and predict that it undergoes a topological quantum phase transition from a CI to a non-trivial topological insulator at a critical pressure value. The pressure induced topological quantum phase transition is confirmed by calculating the evolution of the bulk energy gap as a function of pressure, the inversion of energy band structure and the $Z_2$ topological invariant as well as the existence of the Dirac-like topological surface states. Our predictions can be tested by both spectroscopy and transport experiments.

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I. INTRODUCTION

Over the years, there have been significant theoretical and experimental efforts from condensed matter and materials physics communities to understand and identify the topological quantum phase transition (TQPT) as well as different topological phases of matter$^{1,2}$. These topological phases can be characterized by various kinds of topological properties such as topological invariants, non-trivial topological protected edge/surface states and/or unusual elementary excitations in the bulk or surface. A more recent promising realization of topological phases of matter is the time reversal invariant (TRI) topological insulators (TIs)$^{3,4}$. The TIs in two$^{5,6}$ or three$^{7,18}$ dimensions have a bulk energy band gap, like a conventional insulator (CI), but have a conducting gapless edge or surface states protected by time reversal symmetry. According to Kramer’s theorem, the edge or surface states consisting of an odd number of massless Dirac cones are robust against TRI perturbations, while those states consisting of an even number of massless Dirac cones are not protected. This even-odd effect is the key reason why TIs are characterized by a $Z_2$ topological invariant$^{19,20}$. Interestingly, a uniaxial pressure in Sb$_2$Se$_3$ induced TQPT has been proposed theoretically$^{21}$. But it is very hard to realize experimentally that is because of the layer structure of Sb$_2$Se$_3$ resulting a van der Waals-type coupling between each quintuple layers (QLs). Thus, both the theoretical and experimental studies of control parameters induced TQPT are still awaiting.

Recently, Bera et al.$^{20}$ observed a hydrostatic pressure induced transition in Sb$_2$Se$_3$ using Raman spectroscopy and obtained a bulk energy band gap closing at the critical pressure value using the first-principles calculations. That work indicated this system undergoes a TQPT from a CI phase to a non-trivial TI one with reversal of parity of electronic bands passing through a metallic state at the transition point by tuning the pressure. However, the mechanism of the hydrostatic pressure induced TQPT observed by Raman spectroscopy$^{20}$ remains unclear. From the viewpoint of the band structure calculations in a well-understood framework, to undergo such a TQPT, four criteria must be satisfied: (i) The bulk energy gap must be closed when the TQPT occurs; that is, when the pressure reaches the critical value $P_c$, the bulk energy gap should vanish. (ii) The conduction and valence bands cross, forming a “band inversion” at the TRI $k$ point in the Brillouin Zone (BZ) at a pressure above $P_c$. (iii) The $Z_2$ topological invariant should have a different number in the two phases divided by the bulk energy gap closing point. (iv) The gapless Dirac-like topological surface states inside the bulk energy gap only exist in one phase, while the other one does not exist. It is important to note that the criterion (iii), that the $Z_2$ topological invariant changed, suffices to understand the nature of occurring a TQPT and it also implies the others criteria based on the context of band theory and the idea of the bulk-surface correspondence of the TIs$^{21}$.

In this paper, we theoretically study the hydrostatic pressure induced TQPT in Sb$_2$Se$_3$ motivated by aforementioned discussions of four fundamental criteria, as well as the mechanism for TQPT based on the first-principles calculations. Our results show that when the pressure is increased to the critical value, the bulk energy gap is closed accompanied by the TQPT occurring. Our results also predict that a “band inversion” appears at the TRI $\Gamma$ point in the BZ at a pressure value above $P_c$, which is attributed to the pressure induced enhancement of the crystal field splitting, resulting in the crossing be-
The pressure dependent optimized lattice constants and the internal coordinates of the Sb$_2$Se$_3$, where the Se2 site is set to be at the origin (0, 0, 0), the two Sb sites are at (±µ, ±µ, ±µ), and two Se1 sites are at (±ν, ±ν, ±ν), defined in the unit of primitive translation vectors, as shown in (a).

The structure of this paper is as follows. In Sec. II, we present the theoretical results and discussions. Finally, in Sec. III we summarize our main conclusions.

II. RESULTS AND DISCUSSIONS

The first-principles calculations implemented in the VASP code, the plane wave basis method, and the ultrasoft pseudopotential method with generalized gradient approximation (USPP-GGA) exchange correlation potential have been used. Additionally, the spin-orbit coupling is also included through all over the calculations. A 500 eV cutoff in the plane wave expansion and a 12 × 12 × 12 Monkhorst-Pack k-grid are chosen to ensure the calculation with an accuracy of 10$^{-5}$ eV, and all structures (lattice constants as well as internal coordinates) were optimized until forces on individual atoms were smaller than 0.005 eV/Å to obtain sufficient accuracy throughout the calculations.

Sb$_2$Se$_3$ is assumed to have a rhombohedral crystal structure with space group $D_{3d}^1(R3m)$, similar to that of Bi$_2$Se$_3$ and shown in Fig. 1(a). This system contains QLs ordered in a Se1-Sb-Se2-Sb-Se1 sequence along the c-axis, and the primitive translation vectors $t_{1,2,3}$ are: $t_1 = (-a/2, -\sqrt{3}a/6, c/3)$, $t_2 = (a/2, -\sqrt{3}a/6, c/3)$, and $t_3 = (0, \sqrt{3}a/3, c/3)$, respectively, where $a$ and $c$ are lattice constants in the hexagonal cell. The internal coordinates of atoms Se1, Se2, and Sb are set to be at the (±ν, 0, 0), $(0, \sqrt{3}a/3, c/3)$, respectively, where $a$ and $c$ are shrinked with increasing pressure.

Within the high pressure phase, the crystal structure will change and the TIs could become conductors or CIs. The issue of the structure stability of Sb$_2$Se$_3$ will be left to be addressed in future studies. Those optimized results are all shown in Fig. 1(b). At ambient pressure $P=$ 0 GPa the optimized lattice constants for Sb$_2$Se$_3$ are consistent with previous results. From Fig. 1(b), we notice that the lattice constants $a$ and $c$ are shrunk with increasing pressure, as one expects intuitively. However, the internal coordinate of the Sb atom increases with higher pressures, which seems to be counterintuitive. This feature can be understood from the binding energy consideration: the coupling is strong between two atomic layers within one QL, while the coupling between QLs, which is predominately a van der Waals-type interaction, is much weaker. Consequently, the lattice coordinate of the Sb atom increases to minimize the total energy.

Next, we turn to discuss the relationship between pressure and the bulk energy gap, as shown in Fig. 2. The calculated bulk energy gap for Sb$_2$Se$_3$ at ambient pressure is 0.31 eV, which is in good agreement with previous predictions.
The spin-orbit coupling is taken into account in (b) and (d). FIG. 3: (Color online) Energy band structure for Sb$_2$Se$_3$ under pressures of P= 0 GPa (a)-(b) and P= 3.0 GPa (c)-(d). The spin-orbit coupling is taken into account in (b) and (d). The dashed line indicates the Fermi level.

The spin-orbit coupling is unable to induce the band inversion even under a high pressure value and it cannot explain the Raman experimental results$^{20}$ either. To explore the mechanism of TQPT, we start from the crystal field splitting without considering the spin-orbit coupling effect. According to the point-group symmetry, the $p_x$ orbital is split from the $p_x$ and $p_y$ orbitals and the latter of the two orbitals remains degenerate on the Sb and Se atoms. Due to such splitting, the energy levels around the Fermi energy forming the valence and the conduction bands exhibit a large energy gap. This gap is much larger than the energy scale of the spin-orbit coupling at ambient pressure (comparing with Fig. 3(a) and (b)). When the pressure is applied, the crystal structure will be squeezed. As a result, the level splitting is enhanced and the bulk energy gap between the top of valence band and the bottom of conduction band at Γ point is gradually reduced. If the pressure is increased enough, the valence band and the conduction band will cross to form a semi-metallic state, see Fig. 3(c). In Fig. 3(c), there are two accidental degenerate states appearing around the Γ point, which are not protected by time reversal symmetry. Thus, if we take the spin-orbit interaction into account, these accidental degenerate states will be broken and a non-trivial TI is realized (see Fig. 3(d)).

To firmly confirm that the TQPT is induced by pressure, we further calculate the $Z_2$ topological invariant. Because of the existence of the spatial inversion symmetry in Sb$_2$Se$_3$, the calculation of the $Z_2$ topological invariant can be dramatically simplified by the so-called “parity method”$^{27}$. Accordingly, the $Z_2$ topological invariant of Sb$_2$Se$_3$ under pressure can be obtained from the wave function parities at the eight TRI k points defined as

$$
\Gamma_i = (n_1 n_2 n_3) = \frac{1}{2} (n_1 \mathbf{G}_1 + n_2 \mathbf{G}_2 + n_3 \mathbf{G}_3),
$$

where $G_j$ are

| $\delta_1$ | $\delta_2$ | $\delta_3$ | $\delta_4$ | $\delta_5$ | $\delta_6$ | $\delta_7$ | $\delta_8$ |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 0 GPA    | +1       | +1       | +1       | +1       | +1       | +1       | (0;000)  |
| 0.8 GPA  | +1       | +1       | +1       | +1       | +1       | +1       | (0;000)  |
| 1.2 GPA  | -1       | +1       | +1       | +1       | +1       | +1       | (1;000)  |
| 3 GPA    | -1       | +1       | +1       | +1       | +1       | +1       | (1;000)  |

suggesting that the new phase in Sb$_2$Se$_3$ under high pressure is a non-trivial TI phase. Therefore, we demonstrate that the pressure induced phase transition is indeed a TQPT from a CI phase to a non-trivial TI one.

We now proceed to elaborate the mechanism of the pressure induced TQPT. It is known from the atomic physics that the spin-orbit coupling strength is proportional to $Z^4$ (where $Z$ is the atomic number; $Z=51$ for Sb and 34 for Se). As we have shown above, the spin-orbit coupling strength in Sb$_2$Se$_3$ is not strong enough to induce the band inversion at ambient pressure. Therefore, the spin-orbit coupling is unable to induce the band inversion even under a high pressure value and it cannot explain the Raman experimental results$^{20}$ either. To explore the mechanism of TQPT, we start from the crystal field splitting without considering the spin-orbit coupling effect. According to the point-group symmetry, the $p_x$ orbital is split from the $p_x$ and $p_y$ orbitals and the latter of the two orbitals remains degenerate on the Sb and Se atoms. Due to such splitting, the energy levels around the Fermi energy forming the valence and the conduction bands exhibit a large energy gap. This gap is much larger than the energy scale of the spin-orbit coupling at ambient pressure (comparing with Fig. 3(a) and (b)). When the pressure is applied, the crystal structure will be squeezed. As a result, the level splitting is enhanced and the bulk energy gap between the top of valence band and the bottom of conduction band at Γ point is gradually reduced. If the pressure is increased enough, the valence band and the conduction band will cross to form a semi-metallic state, see Fig. 3(c). In Fig. 3(c), there are two accidental degenerate states appearing around the Γ point, which are not protected by time reversal symmetry. Thus, if we take the spin-orbit interaction into account, these accidental degenerate states will be broken and a non-trivial TI is realized (see Fig. 3(d)).

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$$

where $G_j$ are

| $\delta_1$ | $\delta_2$ | $\delta_3$ | $\delta_4$ | $\delta_5$ | $\delta_6$ | $\delta_7$ | $\delta_8$ |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 0 GPA    | +1       | +1       | +1       | +1       | +1       | +1       | (0;000)  |
| 0.8 GPA  | +1       | +1       | +1       | +1       | +1       | +1       | (0;000)  |
| 1.2 GPA  | -1       | +1       | +1       | +1       | +1       | +1       | (1;000)  |
| 3 GPA    | -1       | +1       | +1       | +1       | +1       | +1       | (1;000)  |
Ants are ~1,000 for Sb\(_2\) and CI. The calculated parities:

- non-trivial TI with either strong TI or weak TI, variants
- not. The combination of these four independent invariants indicates a non-trivial strong TI, while

\[ \nu \] choice of primitive reciprocal lattice vectors

- taken over all of the occupied bands in independent invariants.

\[ \nu \] band index due to the Kramers degeneracy

- \( k \) band and the TRI

\[ \nu \] points and are also listed

\[ \nu \] of all TRI

\[ \nu \] functions (\( \Phi \)) can be obtained by multiplying

\[ \nu \] face. The red regions indicate bulk energy gaps while the

\[ \nu \] Green’s function. Comparing with Fig. 4(a) and (b), one can see the topological surface states, which form a single Dirac cone at \( \Gamma \) point, only exist at the pressure \( P = 3 \) GPa. This concludes a non-trivial TI nature and agrees well with the bulk parity analysis and band structures calculations.

III. CONCLUSION

In conclusion, we have performed the first-principles calculations for the effect of hydrostatic pressure on the Sb\(_2\)Se\(_3\) and predicted that there is a TQPT occurring at the critical value \( P_c \approx 1 \) GPa. To verify the TQPT, we firstly calculate the evolution of bulk energy gap as a function of pressure and observe the bulk energy gap closing-reopening transition. Secondly, the band structure calculations show that there is a “band inversion” appearing at the \( \Gamma \) point in the BZ at a pressure value above \( P_c \), which is attributed to the pressure induced enhancement of crystal field splitting, resulting in the crossing of the conduction and valence bands. Thirdly, the calculated \( Z_2 \) topological invariant indicates that a CI phase (0; 000) and non-trivial strong TI phase (1; 000) are separated by the critical pressure value \( P_c \). Finally, the calculated Dirac-like topological surface states only exist in the non-trivial strong TI phase (1; 000) region. These results can be compared directly with experimental spectroscopy techniques, such as angle-resolved photoemission spectroscopy and scanning tunneling microscopy, and transport measurements. Its verification by future experiments will be a firm step towards understanding and realizing TQPT in real materials.

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