Exploring topological phase transition in Pt$_2$Hg$_{1-x}$Tl$_x$Se$_3$

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Abstract

The transition from trivial to non-trivial phase in two-dimensional materials are called a topological phase transition (TPT). The Berry phase, non-local string order parameter, and edge states define the topological nature of the system. A newly discovered jacutingaite material Pt$_2$HgSe$_3$ is a layered material which occurs naturally in the form of minerals. The material can be exfoliated and was predicted as a quantum spin Hall insulator. Here, on the basis of density functional theory and tight-binding calculations, we explore Pt$_2$Hg$_{1-x}$Tl$_x$Se$_3$ ($x = 0.25, 0.50, 0.75, 1$) to understand the electronic and topological properties. We start with the parent material Pt$_2$HgSe$_3$ wherein Hg is replaced partially with $x$ amount of Tl, to tune the topological phases. From the electronic structure calculations, Pt$_2$HgSe$_3$ is found to be a non-trivial semimetal in it’s bulk. Upon electron doping, the material transforms to strong topological metallic phase. The topological Z$_2$ invariant calculation shows TPT in Pt$_2$Hg$_{1-x}$Tl$_x$Se$_3$ with weak topological insulating state (0;001) for $x$=0, to strong topological metal (1;000) for $x$=1, respectively.

Keywords


1 Introduction

Topological concept in material science has a crucial role in condensed matter and materials science. Topological notion not only enhances the understanding of various physical phenomena, but also play an important role in the development and innovation in materials science [1]. The study of topological properties is thriving research area due to its promising applications in electronics and quantum computing. Topology and topological invariants plays a significant role in understanding and classification of new states of matter in material science. By using the concepts of mirror Chern number, chern number and topological invariant (Z$_2$) we can explain the properties and different behaviors exhibited by various quantum Hall systems, topological insulators (TIs), topological semimetals
such as Dirac, Weyl and nodal line.

The surface or edge effects in topological materials are found to change in several properties such as in electronic, optical, transport, magnetic, etc. [2,3] and can be detected using transmission electron microscopy. Two-dimensional (2D) quantum spin Hall insulator (QSHI) are characterized by a gapless helical edge states with small electronic band gap in it’s bulk. Though they resists interaction and disorder extending up to room temperature, the study related to QSHI are limited [4,5]. Topological features of the materials can be identified by calculating the $Z_2$ invariant. $Z_2$ consists of four components: $\nu_0; \nu_1, \nu_2, \nu_3$ based on which the material can be distinguished whether they are strong or weak topological materials. For instance, when $\nu_0 = 1$; and any of its $\nu_1, \nu_2, \nu_3$ are either 0 or 1, the material are called strong topological insulator/metal, but, if $\nu_0 = 0$ and any other invariants ($\nu_1, \nu_2, \nu_3$) are non-zero, they are called weak topological material.

Among several group of materials, Pt$_2$HgSe$_3$ is one of the natural mineral of platinum group belonging to jacutingaite family discovered in 2008 [6] and successfully synthesized in 2012 [7–10]. This material has been cleaved to its monolayer and from crystal structure and computational calculations, it was reported to be a QSHI with a band gap of $\sim$0.15 eV (0.5 eV) at the Dirac point [11]. QSHI to quantum anomalous Hall (QAH) phase was also observed in monolayer of Pt$_2$HgSe$_3$ by chemical functionalization [12].

In materials belonging to topological materials, topological phase transition (TPT) can be achieved by chemical functionalization, applying magnetic and electric field, pressure and doping, etc. TPT has been observed in bilayer of jacutingaite when perpendicular electric field was applied wherein the bilayer changes from a normal insulator to QSHI [13]. Likewise, unconventional superconductivity was observed in monolayer of Pt$_2$HgSe$_3$ by electron and hole doping along with other exotic property such as QSHI [14]. Monolayer of Pt$_2$HgSe$_3$ has also been studied recently in which the material loses its symmetric behavior due to presence of ferromagnetic substrate (NiB$_2$). Charge transfer takes place at the interface resulting in spin degeneracy band gap of $\sim$134.2 meV and valley dependent global gap of 58.8 meV, respectively [15]. Further, it was noticed that lattice defect can shift the Fermi level (EF) above the van Hove singularity in Pt$_2$HgSe$_3$, and thus can potentially serve as an effective means to regulate doping effect [16].

Band inversion is one of the key parameter that dictates the nontrivial property and is associated with a bulk topological invariant. Further, calculation of parities in the Brillouin zone (BZ) of occupied bands at the time reversal invariant momentum (TRIM) are used in determining the topological invariant of the system following inversion symmetry [17]. Thus, in inversion symmetric system, a material with strong spin-orbit coupling (SOC) strength is required to flip the maximum of the valence band to the minimum of conduction band with opposite parities at the TRIM point. This allows to change the phase from normal insulator (NI) to topological insulator (TI). In topological band inversion, band gap is denoted by a negative sign to distinguish it from a trivial band gap in an even topological invariant scenario. TI to NI phase transition was observed also by nonmagnetic substitution [18–20]. While the overall idea of such a transition seems intuitive, specifics are yet unknown. Therefore we can expect that the band gap of a TI would decrease linearly on substitution of a lighter element with weaker SOC strength. The traditional interpretation of nonmagnetic doping phase transition behavior in TIs has been challenged by the low concentration ($x$), say about 5% in (Bi$_1$–$_x$In$_x$)$_2$Se$_3$ system. The low concentration of $x$ in a linear band-closure system, has been carried out by several experimental groups [20,21].

Essentially, a good dopant should have a shallow defect level and reach optimal solubility in its host material, however, performance of the device is significantly impacted by a few basic doping constraints. For instance, it was discovered that n-type and p-type doping in ZnO were challenging [22]. Consequently, bipolar doping issues arise in numerous large band gap semiconductors, wherein dopants of either the n-type or p-type semiconductor can be introduced, rather than both [23]. Therefore, materials’ qualities such as carrier density, mechanical strength, and magnetism are found to change through doping or alloying method [24]. Here, by means of electron doping to Hg site in Pt$_2$HgSe$_3$ we report that with increase in doping concentration the material undergoes topological phase transition.

2 Crystal Structure and Computational Details

The crystal structure of Pt$_2$HgSe$_3$ is shown in Figure 1 and belongs to space group P-3m1 (space group number 164). The crystal consist of 12 atoms in a unit cell with two structural formula unit (Z = 2). Unit cell of Pt$_2$HgSe$_3$ jacutingaite has two distinct position of platinum denoted as Pt1 and Pt2. Six selenium atoms encircle Pt1, while the Pt2 are connected to Hg atoms positioned at the middle of a planar square of selenium atoms (see Fig. 1). The lattice parameters of Pt$_2$HgSe$_3$ used for our calculations are $a = 7.3477$ Å and $c = 5.2955$ Å with lattice angles $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$ and $\gamma = 120^{\circ}$. The corresponding atomic positions are [0, 0, 0] for Pt1, [-1/2, 0, 0] for Pt2, [1/3, -1/3, 0.3507] for Hg and
We perform the density functional theory (DFT) calculations both in the scalar and full-relativistic mode using the full-potential local orbital code (FPLO) version 22.00-62 [25]. Doping effects has been considered in $\text{Pt}_2\text{Hg}_{1-x}\text{Tl}_x\text{Se}_3$ (x = 0.25, 0.50,0.75 and 1) by means of virtual crystal approximation (VCA) method implemented in the FPLO code. The standard generalized-gradient approximation (GGA) in the parametrization of Perdew, Burke, and Ernzerhof (PBE) [26] has been used for the exchange-correlation potential. A 16×16×16 k-mesh grid was used in the irreducible BZ for the self-consistent calculations. The energy and charge convergence criteria are set to $10^{-8}$ Hartree and $10^{-6}$ C, respectively.

Figure 1: Crystal structure of jacutingaite $\text{Pt}_2\text{HgSe}_3$ having hexagonal crystal system.

3 Results and Discussion

Electronic Structure: Here we show the results for the parent material $\text{Pt}_2\text{HgSe}_3$ and the end material $\text{Pt}_2\text{TlSe}_3$. From the total and partial density of states (DOS) shown in Figure 2a for $\text{Pt}_2\text{HgSe}_3$, it can be observed that the major contribution are from Se-4p orbitals hybridizing with the inequivalent Pt-5d, and Hg-6s orbitals extending in the valence region from -1 eV upto the conduction region, with a crossover at $E_F$. Band structure for the parent material $\text{Pt}_2\text{HgSe}_3$ is shown in Fig. 2b within scalar and full-relativistic (with SOC) mode. Without SOC, the two Dirac crossing were observed at K and H close to $E_F$. With the application of SOC, Dirac points at high symmetry points are gapped with a band gap of $\sim$30.3 meV at point H as shown in Fig. 2b (inset) followed by band inversion revealing the topological semimetallic behavior. Moving on to the electronic structure of the end material $\text{Pt}_2\text{TlSe}_3$, which results from an electron doping via VCA, the total and partial DOS in the valence and conduction region are found to change abruptly. As seen in Fig. 2c, total DOS at $E_F$ is found to increase significantly giving rise to metallic state. The main reason for accumulation of large DOS at $E_F$ is due to the electron occupancy. The total DOS in $\text{Pt}_2\text{TlSe}_3$ is mainly contributed by Se-4p with substantial contribution from Pt-5d and Tl-6s orbitals.

The orbital-resolved electronic band structure of $\text{Pt}_2\text{TlSe}_3$ shows that the major contribution at and around $E_F$ are from Se- 4p$_{x,y,z}$, Pt-5d$_{yz}$ and Tl-6s states. Furthermore, it is interesting to note that electron and hole pocket increases along the $\Gamma$ - A - L – H path in the BZ with increase in Tl doping (see Fig. 2 (b,d)).

Topological Properties: We extend our study to understand the topological properties in jacutingaite materials. As is well-known, four independent topological invariants, (i.e., $Z_2 = \nu_0$; $\nu_1$ $\nu_2$ $\nu_3$) proposed by Fu and Kane [27] is given by

$$(-1)^{\nu_0} = \prod_{n_i = 0,1} \delta n_1 \delta n_2 \delta n_3$$

$$(-1)^{\nu_0} = \prod_{n_i \neq 0,1; n_i = 1} \delta n_1 \delta n_2 \delta n_3$$

Connecting it with the bulk band structures of $\text{Pt}_2\text{HgSe}_3$ and $\text{Pt}_2\text{TlSe}_3$ (see Fig. 2 (b, d), it reveals that at each k-point the conduction band and the valence band are gapped. This allows us to define $Z_2$ index [28]. Basing on this, we perform $Z_2$ invariant calculations. Note that, for 3D systems, odd $Z_2$ ($\nu_0 = 1$) index signify strong TI, whereas for even $Z_2$ ($\nu_0 = 0$) index with odd indices for the other three ($\nu_1$ $\nu_2$ $\nu_3$) characterizes the signature of weak TIs. Thus $Z_2$ index indicates the distribution of gapless surface states at TRIM in the BZ of 2D surface. Two fold degenerate four occupied bands between energy range -1 to 0.8 eV are used to calculate the
$Z_2$ invariants by using FPLO code [25]. Our calculation shows that $Z_2$ index is [0;001] for Pt$_2$HgSe$_3$ and [1;000] for Pt$_2$TlSe$_3$. This clearly suggest that the parent material Pt$_2$TlSe$_3$ is a weak TI while the end material Pt$_2$TlSe$_3$ is a strong TI. $Z_2$ invariants for different values of x concentration in Pt$_2$Hg$_{1-x}$Tl$_x$Se$_3$ are also summarized in Table 1.

In a crystal lattice with inversion symmetric system, Wannier charge center (WCC) are used to calculate $Z_2$ index. Yu and co-workers recently predicted the topological transition in Sb$_2$Mg$_3$ by calculating the $Z_2$ invariant which was based on U(2N) non-Abelian Berry connection [29,30]. For this, the number of crossing to any horizontal reference line and evolution of WCC in k-space in a random direction are used to calculate the topological invariant. With odd number of crossings to a reference gives rise to $Z_2 = 1$, confirming the topological phase of system. Likewise, an even number of crossing to the reference line will characterize $Z_2 = 0$, indicating a trivial phase of system. Following this we computed the WCC.

From our calculations of $Z_2$ for the highest occupied molecular orbital, represented by band number 88 for Pt$_2$HgSe$_3$, and band number 82 for Pt$_2$TlSe$_3$, we observed a horizontal reference line (blue line) that intersects the WCC (see Fig. 3). It is interesting to note that the intersection are odd numbers (say one crossing for Pt$_2$HgSe$_3$ and three crossings for Pt$_2$HgSe$_3$ which confirms that the two jacutingaite are topological materials.

![Figure 2: Density of states (a,c) and band structures (b,d) of Pt$_2$HgSe$_3$ (left) and Pt$_2$TlSe$_3$ (right). Blue and red colors in Fig. b represents scalar-relativistic and full-relativistic for Pt$_2$HgSe$_3$.](image)

Table 1: Calculation of $Z_2$ invariants.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\nu_0; \nu_1 \nu_2 \nu_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_2$HgSe$_3$</td>
<td>0.001</td>
</tr>
<tr>
<td>Pt$<em>2$Hg$</em>{0.25}$Tl$_{0.75}$Se$_3$</td>
<td>0.001</td>
</tr>
<tr>
<td>Pt$<em>2$Hg$</em>{0.5}$Tl$_{0.5}$Se$_3$</td>
<td>0.001</td>
</tr>
<tr>
<td>Pt$<em>2$Hg$</em>{0.75}$Tl$_{0.25}$Se$_3$</td>
<td>0.001</td>
</tr>
<tr>
<td>Pt$_2$TlSe$_3$</td>
<td>1.000</td>
</tr>
</tbody>
</table>
Figure 3: Wannier centers and reference line for band 88 of \( \text{Pt}_2\text{HgSe}_3 \) (top) and band 82 of \( \text{Pt}_2\text{TlSe}_3 \) (bottom).

4 Conclusion

We studied the electronic and topological properties of \( \text{Pt}_2\text{Hg}_{1-x}\text{Tl}_x\text{Se}_3 \) by means of density functional theory and tight-binding calculations using FPLO code [25]. Topological invariants \( Z_2 \) are computed by taking Wannier function as a Bloch function. \( \text{Pt}_2\text{HgSe}_3 \) is found to be a weak topological semimetal while \( \text{Pt}_2\text{TlSe}_3 \) is predicted as a strong topological metal. This is confirmed by the odd number of intersection from the Wannier charge center. Thus a topological phase transitions are noted in \( \text{Pt}_2\text{Hg}_{1-x}\text{Tl}_x\text{Se}_3 \) with weak topological insulating state (0;001) for \( x=0 \), to strong topological metal (1;000) for \( x=1 \), respectively.

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Conflict of Interest

The authors claims that there is no conflict of interest.

References


