Inversion symmetry breaking induced triply degenerate points in orderly arranged PtSeTe family materials

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Abstract

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\textit{k} paths exactly with \textit{C}_3v\ symmetry allow to find triply degenerate points (TDPs) in band structures. The paths that host the type-II Dirac points in PtSe\textsubscript{2} family materials also have the \textit{C}_3v\ spatial symmetry. However, due to Kramers degeneracy (the systems have both inversion symmetry and time reversal symmetry), the crossing points in them are Dirac ones. In this work, based on symmetry analysis, first-principles calculations, and \textit{k} · \textit{p} method, we predict that PtSe\textsubscript{2} family materials should undergo topological transitions if the inversion symmetry is broken, i.e. the Dirac fermions in PtSe\textsubscript{2} family materials split into TDPs in PtSeTe family materials (PtSSe, PtSeTe, and PdSeTe) with orderly arranged S/Se (Se/Te). It is different from the case in high-energy physics that breaking inversion symmetry \textit{I} leads to the splitting of Dirac fermion into Weyl fermions. We also address a possible method to achieve the orderly arranged in PtSeTe family materials in experiments. Our study provides a real example that Dirac points transform into TDPs, and is helpful to investigate the topological transition between Dirac fermions and TDP fermions.

Keywords: topological semimetal, triply degenerate point, Dirac fermion

(Some figures may appear in colour only in the online journal)
anti-chiral effect of the chiral Landau level [27], and novel quantum oscillations [28] also make the type-II Dirac/Weyl semimetals significant compared with the type-I Dirac/Weyl ones.

Whether the band crossings in Dirac/Weyl semimetals are type-I or type-II, they are all fourfold/twofold degenerate points. Moreover, condensed matters also allow for the existence of other types of unconventional quasi-particle excitations such as three-, six-, or eightfold degenerate points [29–33]. The triply degenerate points (TDPs) residing at high symmetry points in reciprocal spaces result from non-degenerate bands cross double-degenerate ones, so it is necessary for the little groups of k paths to connect one and two dimensional irreducible representations. Hence in most-so-far discovered TDP materials (tungsten carbide (WC)-type structure materials [30, 32–34], NaCu3Te2 [35, 36], simple half-Heusler [37, 38], and metal diborides [39]), the k paths that host TDPs mostly have C3v symmetry.

TDPs in the condensed matters can be viewed as intermediate topological phases between Dirac points and Weyl points. PtSe2 family materials (PtSe2, PtTe2, and PtTe2) with D3h point group symmetry (figure 1(a)) were recently predicted by theories [18] and confirmed by angle-resolved photoemission spectroscopy (ARPES) in experiments (see [22] and [23] for PtSe2, [19] and [23] for PtTe2, and [20, 21] and [23] for PtTe2) to be type-II topological Dirac materials. Γ−A (Δ) paths that host the type-II Dirac points in PtSe2 family materials also have the C3v spatial symmetry. However, the materials have both inversion symmetry I and time reversal symmetry T. Thus the two non-degenerate bands are degenerate due to Kramers degeneracy. If the inversion symmetry I is broken, the Kramers degeneracy along Γ−A path is generally broken, and TDPs can exist under this symmetry condition. It is natural to consider the chalcogen substitution in PtSe2 family materials to break the inversion symmetry I. In this work, we focus on the PtSSe, PtSeTe, and PdSeTe, which have been previously synthesized in experiments [40, 41]. In order to simplify calculation and catch main physics, we further consider the orderly arranged ones as shown in figure 1(b). Therefore, the little groups of Γ−A (Δ) path merely has the C3v spatial symmetry without T·I symmetry.

In the following main text, taking PtSeTe as a representation, we propose that the Dirac fermions in PtSe2 family materials split into TDPs in orderly arranged PtSeTe family materials (PtSSe, PtSeTe, and PdSeTe) by breaking inversion symmetry I, and we analyze the mechanism of the topological transitions in two family materials. Furthermore, the phonon stabilities of PtSeTe family materials are studied, and a possible synthesis method is also addressed.

2. Calculation details

The first-principles calculations based on density functional theory (DFT) were performed using QUANTUM-ESPRESSO package [42]. Ultrasoft pseudo-potentials and general gradient approximation (GGA) according to the PBE functional were used. The energy cutoff of the plane wave (charge density) basis was set to 50 Ry (500 Ry). The Brillouin zones were sampled with a $12 \times 12 \times 8$ k-points mesh. The lattice constants and ion positions were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm. Convergence thresholds on total energy and forces for ionic minimization were set as $1.0 \times 10^{-5}$ and $1.0 \times 10^{-4}$ (in atomic units) per atom, respectively. All of band structure calculations were cross-checked by VASP codes [43, 44], and the results are consistent with each other. Phonon spectra were calculated using density functional perturbation theory (DFPT) [45] with a $6 \times 6 \times 4$ $q$-points mesh. Low-energy effective Hamiltonians were studied by $k \cdot p$ method with invariant theory.

3. Results and discussion

3.1. Character table of C3v

Character table for point group C3v is shown in table 1, and Mulliken symbols $(A_1, A_2, E)$ for some irreducible representations are also listed. According to the table:

$$
\begin{align*}
A_1 \otimes D^{1/2} &= \Gamma_4, \\
A_2 \otimes D^{1/2} &= \Gamma_4, \\
E \otimes D^{1/2} &= \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_6,
\end{align*}
$$

where $D^{1/2}$ is the representation matrix of spin. From equation (1), we can see that $A_1/A_2$ state transfers into $\Gamma_4$, while $E$ state splits into $\Gamma_4$, $\Gamma_5$, and $\Gamma_6$ states when spin orbit coupling (SOC) effects are considered. $\Gamma_5$ and $\Gamma_6$ transfer into each other under the time reversal operator $T$:

$$
\begin{align*}
TT_5 &= -\Gamma_6, \\
TT_6 &= \Gamma_5,
\end{align*}
$$

and the matrix of time reversal operator for the bases of $(\Gamma_5, \Gamma_6)$ is

$$
D(T) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} K.
$$

Figure 1. Crystal structures of (a) PtSe2 and (b) PtSeTe. (c) Brillouin zone of PtSe2 and PtSeTe. (c) Brillouin zone is equivalent to A point, and lies beneath $\Gamma$ point. (d) Illustration of TDPs near A point. Orange and blue dots in (c) and (d) stand for TDPs originating from $\Delta_4$ band crossing $\Delta_5$ and $\Delta_6$ bands, respectively.
Table 1. Character table for double point group $C_3v$.

| $C_{3v}/3m$ | $I$ | $\bar{I}$ | $2C_3$ | $2\bar{C}_3$ | $3\sigma_v$ | $3\sigma_l$ | Bases |
|------------|-----|-------|--------|-------------|-------------|-------------|--------|
| $\Gamma_1/\Lambda_1$ | 1 | 1 | 1 | 1 | 1 | 1 | $z$ |
| $\Gamma_2/\Lambda_2$ | 1 | 1 | 1 | 1 | $-i$ | $-i$ | $S_z$ |
| $\Gamma_5/\Lambda_4$ | 2 | $-i$ | 1 | $-i$ | 0 | 0 | $(x, y)$ |
| $\Gamma_6$ | 1 | $-i$ | $-i$ | $-i$ | 1 | 1 | $(i|3/2, -3/2| - |3/2, 3/2|)$ |

Note. Data are from [54]. $I$ means identity, $S_z$ stands for the $z$ component of an axial vector ($S = r \times p$).

Figure 2. (a) Band structure of PtSe$_2$. $\Delta_{3,4,6}$ means degenerate $\Delta_3$ and $\Delta_6$ bands, and $D$ point denotes position where Dirac cone locates along $\Gamma' - A$ path. (b) Band structure of PtSeTe. Insets are zoomed in pictures near $A$ and $T1$ points. (c) Three dimensional band structure of PtSeTe, where $K$ is complex conjugate operator. These two states are Kramers pair, and they are degenerate at time reversal symmetry point. Along the $\Gamma' - A$ ($\Delta$) path, we prefer $\Delta_4$, $\Delta_5$, and $\Delta_6$ instead of $\Gamma_4$, $\Gamma_5$, and $\Gamma_6$.

3.2. Band structure of PtSe$_2$ and PtSeTe

PtSe$_2$, PtTe$_2$, and PdTe$_2$ belong to transition metal dichalcogenides with $D_{3d}$ point group and time reversal symmetry $T$. Each has a layered structure with one transition metal atom and two $X$ ($X = Se, Te$) atoms located at $(0,0,0)$, $(1/3, 2/3, z_x)$, and $(2/3, 1/3, -z_x)$ sites, respectively (figure 1(a)). The band structure of PtSe$_2$ with SOC effects is shown in figure 2(a). Because $\Gamma' - A$ path processes the $C_{3v}$ and $T \cdot I$ symmetries, $\Delta_3$ (basis: $(|3/2, -3/2| - i|3/2, 3/2|)$) and $\Delta_6$ (basis: $(i|3/2, -3/2| - |3/2, 3/2|)$) bands are degenerate (Kramers degeneracy, denoted as $\Delta_{3,6}$), and they cross double-degenerate $\Delta_4$ (basis: $(|1/2, 1/2|, |1/2, -1/2|)$) band, forming the Dirac points. Therefore, the Dirac points in PtSe$_2$ are protected by $C_{3v} \otimes Y'$ symmetry ($Y' = \{I', T \cdot I\}$, $I'$: identity). Furthermore, the Dirac cones are tilted along $\Gamma' - A$ path, which connect the electronic and hole pockets, and called type-II Dirac cones. Due to similar crystal structure, the band structures of PtSe$_2$, PtTe$_2$, and PdTe$_2$ resemble each other [18, 23, 46]. Though the Dirac points are far away from Fermi energy, theory [19] and experiment [47] have shown that it is possible to tune the Dirac points to the Fermi energy by doping Ir in PtTe$_2$ (i.e. Pt$_{1-x}$Ir$_x$Te$_2$). Tight-binding mode predicted that the type-II Dirac cones can be transformed into type-I ones by controlling inter-layer hopping [23]. DFT calculations also revealed that external pressure can manipulate the type-II and type-I Dirac points in PtSe$_2$, PtTe$_2$, and PdTe$_2$ [46].

Table 2. Experimental and optimized lattice constants of PtSSe, PtSeTe, and PdSeTe (in Å).

|          | PtSSe | PtSeTe | PdSeTe |
|----------|-------|--------|--------|
| $a_{\text{Expt.}}$ | 3.59  | 3.89  | 3.90  |
| $c_{\text{Expt.}}$ | 5.06  | 5.11  | 4.98  |
| $a_{\text{Opt.}}$ | 3.66  | 3.91  | 3.96  |
| $c_{\text{Opt.}}$ | 5.04  | 5.07  | 4.98  |

Note. Experimental data are from [40] and [41].

When one Se layer in PtSe$_2$ is replaced by one Te layer, and Se and Te layers are and orderly arranged as shown in figure 1(b), then the inversion symmetry $I$ is absent in PtSeTe, so its spatial symmetry is reduced from $D_{3d}$ to $C_{3v}$. (Here $D_{3d} = C_{3v} \otimes C_1$, $C_1 = \{I, I\}$). The optimized lattice constants of PtSeTe are in agreement with the experiments as shown in table 2. $\Gamma' - A$ path still has the $C_{3v}$ spatial symmetry, but no $T \cdot I$ symmetry. In this case, the $\Delta_5$ and $\Delta_6$ bands are not degenerate at all, then the split $\Delta_3$ and $\Delta_4$ bands cross $\Delta_5$ band, forming two TDPs, as shown in figure 2(b). Near the TDPs, the splitting energy of the $\Delta_3$ and $\Delta_6$ bands (split $E$) is about 9 meV. As expected, there is another pair of TDPs along $\Gamma' - A$' line (figure 2(b)). The position of these two pairs of TDPs in the reciprocal space are $(0, 0, \pm 0.368)$ and $(0, 0, \pm 0.370)$ (in crystal coordinate), respectively. While at the $\Gamma'$ and $A$ points, the $\Gamma_5$ and $\Gamma_6$ states are degenerate again, due to possessing the $T$ symmetry at these points (figure 2(b) inset). The splitting energy of the $\Delta_5$ and $\Delta_6$ bands is small along $\Gamma' - A$ line, but the splitting of the two band surface can be a large value on $k_y - k_x$ plane (figure 2(c)), so the separation on this plane of these two bands is easier to be detected by experiments. $\Delta_4$ band surfaces are also split on this plane (figure 2(c)), also due to Kramers degeneracy breaking.
can be classified as the black and makes irreducible representations −symmetry. So

PtSeTe along a double-degenerate energy level (from illustrated in figure 4. Se/Te atoms locate in the trigonal four steps are required to understand TDPs in PtSeTe, as both for PtSe2 and PtSeTe, Pt-
orbits. Additionally,
in figure 3(b). Therefore, the bands forming the Dirac points

Figure 3. Orbital resolved bands (fat-bands) of (a) PtSe2 and (b) PtSeTe along Γ – A path.

In high-energy physics, breaking time reversal T or inversion symmetry I can lead to the splitting of Dirac fermion into Weyl fermions. However, in condensed matter physics, fermions are constrained by the crystal symmetries rather than by the Lorentz invariance. The symmetry group of any k path of any symmorphic system can be described by magnetic point group. C3v ⊗ I′ can be classified as the black and white magnetic point group of 3m [48]. Therefore, though PtSe2 family materials are non-magnetic, their Γ – A paths can be labeled by black and white magnetic point group 3m. Anti-unitary operator T · I makes irreducible representations ∆5 and ∆6 of C3v degenerate. The symmetries of Γ – A paths in orderly arranged PtSeTe family materials belong to original point group 3m (C3v), without anti-unitary T · I symmetry. So the magnetic point groups of the Γ – A path of two kinds of material are different.

The orbital resolved bands of PtTe2 along the Γ – A path are shown figure 3(a). The upper ∆4 band is mainly composed by Se-pz orbits, while the ∆5+6 and the lower ∆4 bands are mainly composed by Se-py + px orbits. So is PtSeTe, as shown in figure 3(b). Therefore, the bands forming the Dirac points or TDPs are mainly composed by Se/Te-p orbitals. Additionally, both for PtSe2 and PtSeTe, Pt-d and Se-e-p orbitals show hybridization in the ∆5 and ∆6 bands near the A points. Starting from the atomic orbitals of Se/Te, the following four steps are required to understand TDPs in PtSeTe, as illustrated in figure 4. Se/Te atoms locate in the trigonal crystal field, and every p atomic energy level transforms into a double-degenerate E energy level (from px and py orbits) and non-degenerate A1 energy level (from pz orbit) under crystal field splitting (CFS) as shown in figure 4(I). The interatomic hopping transforms the atom energy levels into A1 and E bands along the Γ – A path. The out-of-plane pz orbits usually have much larger the hopping than in-plane px and py orbits along the Γ – A path [23], so the A1 band is more dispersive than the E one, and they cross each other as shown in figure 4(II). When SOC is considered, the A1 band transforms into the ∆4 one, and the E band transforms into ∆4 and ∆5+6 bands. Furthermore, the ∆4 band originating from A1 band crosses the ∆5+6 band forming type-II Dirac point in PtSe2 or PtTe2 (figure 4(III)). When the inversion symmetry is broken, the ∆5+6 band splits into ∆4 and ∆6 ones, and one Dirac point transforms into two TDPs as shown in figure 4(IV). So the TDPs in PtSeTe can be explained by the evolution of Se/Te-p orbital energy levels as a result of CFS, interatomic hopping, SOC effects, and inversion symmetry breaking.

3.3. k · p derivation

To further investigate the nature of TDPs in PtSeTe, we constructed a low-energy effective Hamiltonian using k · p method. The little group of A point is C3v ⊗ I′ (I′ = {I, T}). There are two generators of C3v, including a threefold rotational symmetry C3v (−x/2 − √3y/2, √3/2 − y/2, z) and mirror symmetry σyz(−x, y, z). Consequently, the related symmetry representation matrices under the bases of {∆4, ∆5, ∆6} are given by

\[
D(C_{3v}) = \begin{pmatrix}
0 & e^{i\pi/3} & 0 \\
0 & e^{-i\pi/3} & 0 \\
-1 & 0 & -1
\end{pmatrix}, \quad (4)
\]

\[
D(\sigma_{yz}) = \begin{pmatrix}
i & 0 & 0 \\
0 & i & 0 \\
0 & 0 & -i
\end{pmatrix}, \quad (5)
\]

\[
D(T) = \begin{pmatrix}
0 & 1 & 0 \\
-1 & 0 & 0 \\
0 & 1 & 0
\end{pmatrix}K, \quad (6)
\]
According to invariant theory:

\[ D(R)H(k)D(R)^{-1} = H(Rk), \]

where \( R \) is a symmetry operator. The \( 4 \times 4 \) effective Hamiltonian that considers first-order \( k \) terms for off-diagonal matrix elements and second-order \( k \) terms for diagonal matrix elements is:

\[ H_{\text{eff}}(q) = \varepsilon_0(q) \]
\[ + \begin{bmatrix} M(q) & iCq_+ & Aq_- & -A^*q_- \\ -iCq_- & M(q) & -Aq_+ & -A^*q_+ \\ A^*q_- & -A^*q_+ & -M(q) + Bq_z & 0 \\ -Aq_+ & -Aq_- & 0 & -M(q) - Bq_z \end{bmatrix}. \]

(8)

where \( \varepsilon_0(q) = C_0 + C_1 q_z^2 + C_2 (q_x^2 + q_y^2) \), \( M(q) = M_0 - M_1 q_z^2 - M_2 (q_x^2 + q_y^2) \), \( \mathbf{q} = \mathbf{k} - \mathbf{A}, q_\pm = q_x + iq_y \), and \( q_- = q_x - iq_y \). \( \mathbf{A} \) is a complex number, while \( B \) and \( C \) are real numbers. \( Bq_z \), exists in \( H_{33} \) and \( H_{44} \), and this term makes \( \Delta_5 \) and \( \Delta_6 \) bands split. We can get the eigenvalues along the \( \Gamma - A \) path:

\[ E_{\Delta_4} = C_0 + C_1 q_z^2 + M_0 - M_1 q_z^2, \]
\[ E_{\Delta_5} = C_0 + C_1 q_z^2 - M_0 - M_1 q_z^2 + Bq_z, \]
\[ E_{\Delta_6} = C_0 + C_1 q_z^2 - M_0 - M_1 q_z^2 - Bq_z. \]

(9) (10) (11)

According to equations (10) and (11), \( \Delta_5 \) and \( \Delta_6 \) states are degenerate at \( A \) point (\( q_z = 0 \), i.e. \( \Delta_5 \) and \( \Delta_6 \)), coinciding with the DFT results. The \( \Delta_4 \) and \( \Delta_5 \) bands cross at \( q_z = \left( -B \pm \sqrt{B^2 + 16M_0M_1} \right) / 4M_1 \), while the \( \Delta_4 \) and \( \Delta_6 \) bands cross at \( q_z = \left( B \pm \sqrt{B^2 + 16M_0M_1} \right) / 4M_1 \). If the mirror symmetry of PtSeTe is broken (such as applying magnetic field along \( z \) direction), the symmetry of \( \Gamma - A \) path transforms from \( C_{4v} \) into \( C_s \), and \( H_{11} \) and \( H_{22} \) will also process linear \( q \) terms. Hence, the \( \Delta_4 \) band splits, and each TDP transforms into two Weyl points when the mirror symmetry is broken.

The \( k \cdot p \) model bands along the \( \Gamma - A \) path are shown in figure 5(a). According to equations (10) and (11), the splitting energy of \( \Delta_4 \) and \( \Delta_5 \) bands \( \Delta E(q) = 2Bq_z \) (see figure 5(b)), so \( B \) determines the splitting between the \( \Delta_5 \) and \( \Delta_6 \) bands. \( \Delta E \) originates from the second-order interaction between the \( J_z = \pm 3/2 \) (\( \Delta_{5} \) and \( \Delta_{6} \)) states and the metal cation (Pt) \( d \) core levels [35, 49]. According to [35], \( \Delta E(q) \) can be changed by varying \( p - d \) hybridization of metal and anion atoms. To reveal the effect of \( p - d \) hybridization on the splitting, we performed a hypothetical experiment that applying positive and negative pressure on PtSeTe to change the lattice constants by using DFT calculations, and we found that positive (negative) pressure does increase (decrease) \( \Delta E_m \) (see figure 5(c)).

The \( k \cdot p \) model bands along the \( \Gamma - A \) path are shown in figure 5(a). According to equations (10) and (11), the splitting energy of \( \Delta_4 \) and \( \Delta_5 \) bands \( \Delta E(q) = 2Bq_z \) (see figure 5(b)), so \( B \) determines the splitting between the \( \Delta_5 \) and \( \Delta_6 \) bands.

\[ \Delta_4 \text{ and } \Delta_5 \text{ bands keeping only linear order terms for matrix elements is as follows:} \]
\[
H_{\Delta_4, \Delta_5} = \eta \mathbf{p} z + \begin{bmatrix} \alpha p_z & i\beta p_+ & \gamma p_- \\ -i\beta p_- & \alpha p_z & -\gamma p_+ \\ \gamma^* p_+ & -\gamma^* p_- & -\alpha p_z \end{bmatrix},
\]

(12)

where \( \mathbf{p} = \mathbf{q} - \mathbf{q}_{T \Gamma} = (p_x, p_y, p_z) \), \( \alpha, \beta \) and \( \eta \) are real numbers, and \( \gamma \) is a complex number.

The \( 2 \times 2 \) Hamiltonian of the crossing point of \( \Delta_{4 \uparrow} \) and \( \Delta_{5} \) is:

\[
H_{\Delta_{4 \uparrow}, \Delta_{5\downarrow}} = \eta p_z + \begin{bmatrix} \alpha p_z & \gamma p_- \\ \gamma^* p_+ & -\alpha p_z \end{bmatrix},
\]

(13)

and the effective Hamiltonian of the crossing point of \( \Delta_{4 \downarrow} \) and \( \Delta_{5\downarrow} \) is:

\[
H_{\Delta_{4 \downarrow}, \Delta_{5\downarrow}} = \eta p_z + \begin{bmatrix} \alpha p_z & -\gamma p_+ \\ -\gamma^* p_- & -\alpha p_z \end{bmatrix}.
\]

(14)

Any \( 2 \times 2 \) Hermitian matrix can be expanded by the Pauli matrices and the identity matrix.
According to [6], the chirality of a 2

\[ \chi = \text{sgn} [\text{det}(V)] \],

so

\[ \chi(\Delta_4, \Delta_5) = -\chi(\Delta_4, \Delta_5). \] (20)

Similarly, the 3x3 effective Hamiltonian around the TDP by \( \Delta_4 \) and \( \Delta_6 \) bands is:

\[ H = \sum_i \sigma_0 v_{0i} p_i + \sum_{ij} v_{ij} p_i \sigma_j, \] (15)

where \( \sigma_0 \) is a 2x2 identity matrix, \( i,j = x,y,z \), \( \sigma_j \) are one of three Pauli matrices. So equation (13) can be rewritten as:

\[ H_{\Delta_4, \Delta_5} = \eta p_x \sigma_0 + p_x \sigma_x \sigma_0 + p_x \gamma \sigma x \]

\[ + p_y \gamma y \sigma y - p_\gamma y \sigma y + p_\gamma y \sigma y, \] (16)

and equation (14) can be rewritten as:

\[ H_{\Delta_4, \Delta_5} = \eta p_x \sigma_0 + p_x \sigma_x - p_x \gamma \sigma x \]

\[ + p_y \gamma y \sigma y + p_\gamma y \sigma y + p_\gamma y \sigma y, \] (17)

where \( \gamma_R \) and \( \gamma_I \) are the real and imaginary part of \( \gamma \), respectively. So

\[ V_{\Delta_4, \Delta_5} \equiv [v_{ij}]_{\Delta_4, \Delta_5} = \begin{bmatrix} \gamma_R & -\gamma_I \\ \gamma_I & \gamma_R \end{bmatrix}, \] (18)

\[ V_{\Delta_4, \Delta_5} \equiv [v_{ij}]_{\Delta_4, \Delta_5} = \begin{bmatrix} -\gamma_R & \gamma_I \\ \gamma_I & \gamma_R \end{bmatrix}, \] (19)

According to [6], the chirality of a 2x2 Hamiltonian

\[ \chi = \text{sgn} [\text{det}(V)], \]

so

\[ \chi(\Delta_4, \Delta_5) = -\chi(\Delta_4, \Delta_5). \] (20)

Similarly, the 3x3 effective Hamiltonian around the TDP by \( \Delta_4 \) and \( \Delta_6 \) bands is:

\[ \chi_{\Delta_4, \Delta_6} = \eta' p_z + \begin{bmatrix} \alpha' p_z & i\beta' p_z & \gamma' p_z \\ -i\beta' p_z & \alpha' p_z & \gamma' p_z \\ \gamma' p_z & \gamma' p_z & -\alpha' p_z \end{bmatrix}, \] (21)

where \( \alpha', \beta', \) and \( \gamma' \) are real numbers and \( \gamma' \) is a complex number. Using similar method, we can prove that one TDP formed by \( \Delta_4 \) and \( \Delta_6 \) bands can also be viewed as two Weyl points with opposite chirality. Moreover, the results are invariant with the values of above \( k \cdot p \) parameter. These results are similar with the TDPs induced by breaking time reversal symmetry in centrosymmetric system [50].

3.5. PtSSe and PdSeTe

Having examined PtSeTe, now we move on to PtSSe and PdSeTe. Optimized lattice constants of PtSSe, and PdSeTe are shown in table 2, experimental ones are also given, and they coincide with each other. We find that the Dirac points in PtSe2 and PdTe2 also transform into the TDPs in orderly arranged PtSSe and PdSeTe (see figure 6). There is no imaginary frequency in the calculated phonon spectra of the three orderly arranged compounds as shown in figure 7, indicating that the compounds are all stable and could be synthesized.
in reality. Previous study have shown that S and Se can be orderly arranged in $1\overline{7}$-TaS$_2$, Se$_3$ [51]. Mono to several layers high-quality PtSe$_2$ samples have been grown by molecular beam epitaxy (MBE) method [52, 53]. Therefore, MBE could be a promising method to synthesize the orderly arranged PtSeTe, PtSSe, and PdSeTe by one-by-one atomic layer growing sequence.

Like the type-II Dirac points in PtSe$_2$ family materials, the TDPs in PtSeTe family materials are all far away from the Fermi level, so they are difficult to be observed by electrical transport in experiments (charge-carrier doping may move the TDPs to the Fermi level). However, the TDPs in PtSeTe family materials could be detected by ARPES in experiments, just like the case of the type-II Dirac point in the PtSe$_2$ family materials [19–23].

4. Conclusion

Due to $C_3\nu \otimes \bar{I}$' symmetry, $\Delta_5$ and $\Delta_6$ bands degenerate in PtSe$_2$ family materials. By breaking $I$ symmetry, Kramers degenerate $\Delta_5$ and $\Delta_6$ bands split, therefore each Dirac cone in PtSe$_2$ family materials transform into two TDPs in orderly arranged PtSeTe, PtSSe, and PdSeTe where the $\Gamma - A$ paths only preserve $C_3\nu$ symmetry. Unlike the high-energy physics, breaking the inversion symmetry $I$ of PtSe$_2$ family materials leads to the splitting of Dirac fermion into TDPs rather than Weyl fermions. The splitting energy $\Delta E$ of $\Delta_5$ and $\Delta_6$ bands can be manipulated by $p - d$ hybridization of metal and anion atoms. Each TDP can be regard as two Weyl points with opposite chirality. These three materials are stable in phonon spectra and very possible to be grown in experiments, such as using MBE method. If orderly arranged PtSe$_2$ family materials are synthesized, they will provide real examples, in which Dirac points transform to TDP points, and can help us to investigate the topological transition between Dirac fermions and TDP fermions. Further experimental verification and theoretical studies need to be carry out.

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RCX carried out all the calculations and wrote the paper with assistance from PLG and JGS. CHC performed the symmetry analysis and checked $k \cdot p$ calculation and paper writing. WJL planned and integrated the research, and revised the manuscript. YPS supervised the project.

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