MgTa$_2$N$_3$: A reference Dirac semimetal

QuanSheng Wu,$^{1,2,3,} ^*$ Christophe Piveteau,$^3$ Zhida Song,$^4$ and Oleg V. Yazeyev$^{1,2,} ^{†}$

$^1$Institute of Physics, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
$^2$National Centre for Computational Design and Discovery of Novel Materials MARVEL, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
$^3$Institut für Theoretische Physik, ETH Zürich, 8093 Zürich, Switzerland
$^4$Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Science, Beijing 100190, China

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We present a prediction of the Dirac semimetal (DSM) phase in MgTa$_2$N$_3$ based on first-principles calculations and symmetry analysis. In this material, the Fermi level is located exactly at the Dirac point without additional Fermi surface pockets. The band inversion associated with the Dirac cone involves the $d$ orbitals of two structurally inequivalent Ta atoms with octahedral and trigonal prismatic coordination spheres. We further show that the lattice symmetry breaking can realize topological phase transitions from the DSM phase to a triple nodal point semimetal, Weyl semimetal or topological insulator. The topologically protected surface states and the non-protected Fermi arc surface states are also studied.

Three-dimensional topological Dirac semimetals (DSMs)$^{1–3}$ are materials realizing a novel state of quantum matter described by the massless Dirac equation. The four-component Dirac spinor is composed of two two-component Weyl fermions of opposite chirality. Under magnetic field applied parallel to the electric field $\vec{E} \parallel \vec{B}$, charge is predicted to flow between the Weyl nodes resulting in negative magnetoresistance, a phenomenon known as the Adler-Bell-Jackiw anomaly$^4$. Furthermore, the mirror anomaly$^5$ was predicted in DSMs. Although the degeneracy of the Dirac point (DP) is not protected in topological sense due to its zero net Chern number, it can still be protected by the space group symmetries, e.g. $C_{4v}$ and $C_{6v}$ and non-symmorphic symmetries$^6,7$, and therefore referred to as the symmetry-protected degeneracy. Several materials realizing such symmetry-protected DSM phase have been proposed theoretically$^{1–3,8–10}$ and confirmed experimentally$^{1,11,12}$. Notable examples of DSMs are Na$_3$Bi and Cd$_3$As$_2$ with DPs protected by $C_{6v}$ and $C_{4v}$ rotation symmetries, respectively. However, Na$_3$Bi oxidizes in air easily while arsenic is poisonous thus limiting applications of Cd$_3$As$_2$. Therefore, searching for new 3D DSMs that are stable at ambient conditions and are less toxic is of both fundamental and technological importance.

In this work, we report an investigation of a new predicted Dirac semimetal MgTa$_2$N$_3$. By means of first-principles calculations and symmetry analysis we address the electronic structure and topological properties of this material. We further predicted some properties of the topological phase that can be measured experimentally and show how different topological phase transitions can be attained by breaking crystalline symmetries.

The synthesis of MgTa$_2$N$_3$ was reported by Brokamp and Jacobs in 1991$^{13}$. The crystal structure of MgTa$_2$N$_3$ belongs to space group $P6_3/mcm$ with lattice constants $a = 5.205$ Å and $c = 10.425$ Å. It consists of alternating layers of Ta atoms with trigonal prismatic and octahedral coordination spheres (below referred to as tri-Ta and oct-Ta, respectively), similar to numerous ABX$_2$ layered oxides$^{14}$, oxynitrides, and nitrides such as ScTa$_2$N$_2$.$^{15}$ Two Mg atoms substitute two Ta atoms in the octahedral layer, suggesting the (Ta$_{oct}$)$_2$(Mg$^{2+}$)$_4$(Ta$_{tri}$)$_6$N$_2$I$_2$ ionic picture with $d^0$ and $d^6$ electronic configurations of oct-Ta and tri-Ta, respectively (Figs. 1(a–c)).

Our first-principles band-structure calculations are performed within the density functional theory framework using VASP (Vienna Ab initio Simulation Package)$^{16,17}$. The approach relies on all-electron projector augmented wave (PAW) basis sets$^{18}$ combined with the generalized gradient approximation (GGA) with exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE)$^{19}$ and the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional$^{20}$. Both PBE and HSE06 calculations predict the existence of Dirac point degeneracies in the band structures when spin-orbit coupling (SOC) is taken into account. The PBE functional calculations, however, show the presence of an additional Fermi surface pocket at the $M$ point that could be caused by the underestimated correlation effect. In the rest of the paper the Heyd–Scuseria–Ernzerhof (HSE06)$^{20}$ hybrid functional will be used to take into account the non-local potential. Detailed comparison of the results obtained using PBE and HSE06 functionals is presented in the Appendix A. The cutoff energy for the plane wave expansion was set to 500 eV and a $k$-point mesh of $8 \times 8 \times 6$ was used in the bulk calculations. The WannierTools code$^{22}$ was used to investigate the topological properties and calculate the Landau levels (LLs) based on the maximal localized Wannier functions tight-binding model$^{23}$ that was constructed by using the Wannier90 package$^{24}$ with Ta 5$d$ atomic orbitals as projectors. The surface state spectra are calculated using the iterative Green’s function method$^{22,25}$. The total and atom-projected density of states (DOS) calculated without taking into consideration the spin-orbit coupling are shown in Fig. 1(c). A direct band gap
of 21 meV is seen at the Γ point. The states of Mg are located entirely above the Fermi level showing the fully ionic character of Mg$^{2+}$ ions. The 2$s$ states of N atoms are located between $-21$ eV to $-17$ eV. The energy range between $-11$ eV and $-4$ eV is dominated by the 2$p$ states of N atoms and a fraction of Ta $d$ states. Above the energy of $-4$ eV, the $d$ states of oct-Ta are located above the Fermi level and there is a peak originating from tri-Ta states between $-4$ eV to $0$ eV, which is consistent with the suggested $d^0$ and $d^2$ electronic configurations of oct-Ta and tri-Ta ions.

The band structure of MgTa$_2$N$_3$ calculated without taking SOC into account is shown in Fig. 1(f). The valence band maximum (VBM) and the conduction band minimum (CBM) are located at the Γ point. The VBM is composed of the $d_{z^2}$ orbitals of tri-Ta atoms and belongs to the $B_{2u}$ irreducible representation of the $D_{6h}$ point group$^{26}$. The CBM is mainly composed of the $d_{x^2-y^2}$ orbitals of oct-Ta atoms and belongs to the $E_{2g}$ irreducible representation of $D_{6h}$.$^{26}$ The spin-orbit coupling splits the $E_{2g}$ representation into $E_{5/2,g}$ and $E_{3/2,g}$ representations resulting in the separation of the 4-fold degenerate bands into pairs of 2-fold degenerate bands, eventually leading to band inversion between the $E_{5/2,u}$ and $E_{3/2,g}$ bands (see Fig. 1(g)). Along the Γ–A direction, two bands close to the Fermi level belong to the $E_{3/2}$ and $E_{5/2}$ irreducible representations of the little group of $C_{6v}$.$^{26}$ According to the Schur’s lemma the two bases belonging to two different irreducible representations are orthogonal to each other, hence the two bands cross without opening a gap resulting in a Dirac point band degeneracy. In MgTa$_2$N$_3$ the two DPs are located at (0, 0, ±0.203$^{2}$).

From the DOS and symmetry analysis it follows that the two energy bands forming the Dirac cones, referred to as the $E_{5/2}$ and $E_{3/2}$ bands hereafter, are composed of atomic orbitals of either oct-Ta or tri-Ta atoms belonging to the two distinct layers in the crystal structure. The weights of the oct-Ta and tri-Ta $d$ orbitals in the Dirac cone band in the $k_x$ – $k_z$ plane are shown in Fig. 2(a). One can also see that the Dirac cone is anisotropic in the $k_x$ – $k_z$ plane according to the

![Diagram](image)

**FIG. 2.** (a) Dirac cone band dispersion showing the orbital weights of the tri-Ta and oct-Ta ions. (b) Landau levels calculated for magnetic field $\vec{B}$ applied parallel to the $c$ axis.
difference of the lattice constants \( a \) and \( c \). The calculated Fermi velocities of the Dirac fermion charge carriers\(^{21}\) are \( v_x = v_y = 2.8 \text{ eV} \cdot \text{Å} \), \( v_z(E_{5/2}) = 0.95 \text{ eV} \cdot \text{Å} \), \( v_z(E_{3/2}) = 2.38 \text{ eV} \cdot \text{Å} \). These Fermi velocities are comparable to that in \( \text{Na}_2\text{B}^{31,27,28} \), but smaller than in \( \text{Cd}_3\text{As}_2^{12,29,30} \).

In the \( k_x \) direction, the weights are symmetrical as \( \rho_\sigma(k_x,k_y,k_z) = \rho_\sigma(-k_x,k_y,k_z) \), where \( \rho_\sigma(k) = \sum_\nu \langle \psi_\nu(k) | \varphi_\sigma \rangle \langle \varphi_\sigma | \psi_\nu(k) \rangle \), \( \psi_\nu \) is the Bloch wave function and \( \varphi_\sigma \) is the \( d \) orbital atomic of tri-Ta or oct-Ta atoms. Along the \( k_z \) direction, the weight is larger for tri-Ta \( d \) orbitals close to the \( \Gamma \) point in the upper half of the conical intersection, while the opposite is true in the lower cone. It is worth mentioning that larger weights of tri-Ta orbitals are due to the fact there three times as many tri-Ta atoms than the oct-Ta atoms in the crystal structure of \( \text{MgTa}_2\text{N}_3 \).

Figure 2(b) shows the weighted Landau levels (LLs) formed from the energy bands upon applying magnetic field along the \( c \) axis. It is known that the two zeroth LLs could lead to the chiral anomaly. The upward and downward parabolic curves are mostly associated with the atomic orbitals of oct-Ta and tri-Ta, respectively. The LLs provide a way of studying the layer-resolved features.

Since the crystal symmetries protect the Dirac points in \( \text{MgTa}_2\text{N}_3 \), it is important to address possible topological phase transitions realized upon breaking these symmetries. Here, we consider breaking only the spatial symmetries while preserving the time-reversal symmetry. One qualitative approach to this question consists in studying the compatibility relationships of the two irreducible representations \( E_{3/2} \) and \( E_{5/2} \) when deducing the little group \( C_{6v} \) of the DP. The corresponding subduction table\(^{26}\) is shown in Table I. From this table, we can divide the possible ways of symmetry breaking into two groups, with and without inversion symmetry. In presence of inversion symmetry all energy bands are doubly degenerate according to the Kramers theorem, hence only the DSM or topological insulator (TI) phases can be realized. Table I shows that \( C_3 \) and inversion symmetries are sufficient to protect the DP degeneracy. Breaking the \( C_3 \) symmetry results in the transition of DSM into the TI phase. Without inversion symmetry, the double degeneracy can be lifted by breaking the \( C_3 \) and mirror symmetries. We distinguish three types of symmetry breaking referred to as types A, B and C. Type-A symmetry breaking preserves the \( C_3 \) symmetry while breaking the vertical mirror \( \sigma_v \) symmetry or the \( \sigma_d \) symmetry, resulting in the \( C_{3v} \) group. The two-dimensional representation \( E_{3/2} \) splits into one two-dimensional representations \( E_{1/2} \) and \( E_{3/2} \), while \( E_{5/2} \) changes into the two-dimensional representation \( E_{1/2} \). Eventually, the DPs splits into two triple nodal points (TNPs)\(^{31–37}\). Type-B symmetry breaking preserves the \( C_3 \) symmetry while breaking all mirror symmetries \( \sigma_v \) and \( \sigma_d \), thus resulting in the \( C_6 \) group or the \( C_3 \) group upon further breaking the \( C_2 \) symmetry. The two two-dimensional representations \( E_{3/2} \) and \( E_{5/2} \) split into four different one-dimensional representations resulting in the separation of DPs into four symmetry-protected Weyl points. Type-C symmetry breaking eliminates the \( C_3 \) symmetry resulting in the \( C_{2v} \) group or the \( C_s(C_2) \) group upon further breaking the \( C_2(\sigma_v) \) symmetry. Here, the \( E_{3/2} \) and \( E_{5/2} \) representations split into the same representations, leading to the strong TI phase. It is worth mentioning that \( C_3 \) symmetry is not sufficient for protecting a DP, and the presence of inversion or six vertical mirror symmetries is required. This is at odds with the conclusion of Ref. 2 where it is claimed that the \( C_3 \) symmetry is sufficient to protect the DPs.

In order to get a quantitative insight, we build a universal \( 4 \times 4 k \cdot p \) model for the point groups in the first row of Table I. Here, we only list matrix elements up to quadratic term in the diagonal matrix elements and up to linear term of \( k_z \) in the off-diagonal matrix elements

\[
H(k) = \epsilon_0(k) + \begin{pmatrix}
M(k) + B_1(k) & B_2(k) & A_1(k) & A_1(k)
M(k) & B_3(k) & A_2(k) & A_2(k)
M(k) & B_1(k) & A_2(k) & A_2(k)
M(k) & B_3(k) & A_1(k) & A_1(k)
\end{pmatrix}
\]

(1)

where \( \epsilon_0(k) = C_0 + C_1 k_x^2 + C_2 (k_x^2 + k_y^2) \), \( k_{\pm} = k_x \pm ik_y \), \( A_1, A_2 \) are the linear combinations of \( k_x \) and \( k_z \), and \( M(k) = M_0 - M_1 k_z^2 - M_2 (k_x^2 + k_y^2) \). \( M_0, M_1 > 0 \) is the condition of band inversion along the \( \Gamma - A \) direction. The details of construction can be found in the Appendix B. Under the \( D_{6h} \) or \( C_{6v} \) groups that preserve the \( C_3, \sigma_v \) and \( \sigma_d \) symmetries, all linear terms of \( k_z \) vanish as \( B_1(k_z) = B_2(k_z) = B_3(k_z) = D_1(k_z) = D_2(k_z) = 0 \), resulting in two Dirac points at \( k_{DP} = (0, 0, \pm \sqrt{M_0/M_1}) \). For the type-A symmetry breaking, only

| \( \Gamma \) | \( C_{6v} \) | \( C_{3v} \) | \( D_{6h} \) | \( D_{3h} \) | \( C_{6v} \) | \( C_{3v} \) | \( D_{6h} \) | \( D_{3h} \) |
|---|---|---|---|---|---|---|---|---|
| \( \text{irrep.} \) | \( E_{3/2} \) | \( E_{5/2} \) | \( E_{3/2} \) | \( E_{5/2} \) | \( E_{1/2} \) | \( E_{3/2} \) | \( E_{5/2} \) | \( E_{1/2} \) |
| Phase | Dirac | Dirac/| Triplet | Weyl | Dirac/ | Weyl | TI | TI or Weyl | Weyl |
$B_1(k_z) = B k_z$ or $B_2(k_z) = B k_z$ are present, resulting in two pairs of TNPs at $k_{TNPs} = \pm (0, 0, B \pm \sqrt{B^2 - 16 M_0 M_1})$. For the type-B symmetry breaking, only $B_1(k_z) = B k_z$ and $B_1'(k_z) = B' k_z$ are present. There are four pairs of WPs located at $k_{WPs} = \pm (0, 0, B_0 \pm B)$ with $B_0 = B' \pm B$. For the type-C symmetry breaking, the coupling terms between the two bands forming the Dirac cone are $D_1(k_z) = D_2(k_z) = D k_z$, which leads to a finite effective mass and results in the Hamiltonian characteristic of a strong TI phase.

We now address the topological properties of MgTa$_2$N$_3$. The evolution of hybrid Wannier charge centers (WCCs) in the time-reversal invariant planes $k_z = 0$ and $k_z = \pi / c$ is shown in Figs. 4(a) and 4(b), respectively. The corresponding $Z_2$ numbers are 1 and 0, indicating that band inversion between $E_{3/2}$ and $E_{5/2}$ bands along the $\Gamma - A$ direction is topologically non-trivial. The non-trivial $Z_2$ number at $k_z = 0$ plane is expected to result in one surface Dirac cone at the $\Gamma$ point on the side surfaces, e.g. the (010) surface shown in Fig. 4(c). The space group of the (010) surface is $Pmma$ (No. 28), whose generators are the two-fold rotation $C_2y$ with axis along the $y$ direction and the glide symmetry $G_y = \{ \sigma_x \}$ of the (001) surface. The latter symmetry leads to the hourglass surface states (SSs) along the $\Gamma - A$ direction. The calculated momentum-resolved surface density of states along the high-symmetry line in the 2D BZ is shown in Fig. 4(e). The hourglass dispersion of the SSs is shown in the inset of Fig. 4(f), while Fig. 4(g) shows the iso-energy plot of the SS spectrum at the Fermi energy $E - E_F = 0$. One can observe the following two features: first, the presence of a long Fermi arc linking the two DPs; and second, the double degeneracy of bands at the 2D BZ boundary due to the glide symmetry $G_y$.

The DPs discussed here could be considered as the combination of two WPs with opposite chirality. According to the linking rules the Fermi arc surface state should connect WPs of different chirality, hence in a DSM the Fermi arc could originate and terminate at the same DP or link together two different DPs. However, such Fermi arcs are not topologically protected as discussed in Refs. 10, 44, and 45. The degeneracy can be lifted along the $\Gamma - A$ direction if the corresponding term is present, and our symmetry analysis (see Appendix B) shows that such term naturally exists for the side surface of MgTa$_2$N$_3$. The observed splitting is shown in Fig. 4(f). In order to observe the “unprotected” Fermi arc states we plot the iso-energy surface-state spectrum at $E - E_F = 0.05$ (Fig. 4(h)). Fig. 4(i) provides the details of the surface states that reveal a “candlelight” shaped Fermi arcs that originate and terminate at the same Fermi pocket. The lack of connection between the “candlelight” Fermi arcs and other states is shown in Fig. 4(j), which covers the momentum range indicated by the cyan box in Fig. 4(h).

In summary, based on first-principles calculations and effective model analysis we predicted an ideal Dirac semimetal phase in MgTa$_2$Ta$_3$, a material that has been synthesized previously. The Dirac cone band degeneracies are composed of two atomic $d$ orbitals originating from two distinct layers of Ta atoms with different coordination. We then analyzed possible topological phase transitions that can be realized by breaking lattice symmetries. It was found that the Dirac semimetal phase
can be transformed into a number of distinct topological phases, namely the triple nodal point metal, Weyl semimetal, strong topological insulator, without breaking the time-reversal symmetry. In practice, such symmetry breaking can be realized by strain along different directions or alloying. The topologically protected surface states as well as the Fermi arcs lacking such protection were studied in detail. We point out that the “candlelight” shaped unprotected Fermi arcs can be detected in ARPES measurements.

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Note: Another work addressing the same material appeared when the present manuscript was in preparation. Our work was presented at the APS March meeting 2018 prior to the publication of Ref. 46.

Appendix A: Comparison of the PBE and HSE06 band structures

In the main text, we discuss the results obtained using the HSE06 hybrid functional. Here, we provide the band structures obtained using the PBE functional for comparison (see Fig. 4). At the $M$ point, there is an additional hole pocket which is absent in the hybrid functional calculations. The PBE band structure without SOC is metallic in contrast to the gapped band structure in the HSE06 calculations. The open-source code PyProcar is used to generate the weighted band structures shown in Figs. 4(c) and 4(d).

$$H(k) = H_0(k) + H'(k)$$  \hspace{1cm} (B1)

with $H_0(k)$

$$H_0(k) = \begin{pmatrix}
\epsilon_0(k) + M(k) & 0 & 0 \\
0 & \epsilon_0(k) - M(k) & 0 \\
0 & 0 & \epsilon_0(k) + M(k)
\end{pmatrix},$$  \hspace{1cm} (B2)

where $\epsilon_0(k) = C_0 + C_1 k_z^2 + C_2 (k_x^2 + k_y^2)$ and $M(k) = M_0 - M_1 k_z^2 - M_2 (k_x^2 + k_y^2)$.

$D_{6h}$. The little group of MgTa$_2$N$_3$ for the $\Gamma$ point is $D_{6h}$, hence the constructed $k \cdot p$ model is

$$H'_{D_{6h}}(k) = \begin{pmatrix}
0 & 0 & i F k_z k_x^2 & i A k_+ \\
0 & 0 & i F k_z k_y^2 & -i A k_-
\end{pmatrix},$$  \hspace{1cm} (B3)

where $k_\pm = k_x \pm i k_y$, $i$ is the imaginary unit. This $k \cdot p$ model is the same as that of Na$_3$Bi at the $\Gamma$ point.
FIG. 4. (a),(b) The calculated band structures of MgTa$_2$N$_3$ within the PBE function calculations (a) without and (b) with SOC. (c) Projected band structure with the weights of oct-Ta $d_{x^2} + d_{xy}$ orbitals indicated. (d) Projected band structure with the weights of tri-Ta $d_{z^2}$ orbitals indicated.

TABLE II. Subduction table for the little group at the $\Gamma$ point and the compatible relation of its irreducible representations $E_{3/2,u}$ and $E_{5/2,u}$ composing the Dirac cone. This table is the simplified version of Table 35.9 in Ref. 52.

| $D_{6h}$ | $D_{3d}$ | $D_{3d}$ | $D_6$ | $D_3$ | $D_{2h}$ | $C_2v$ | $C_{6h}$ |
|--------|--------|--------|-------|------|--------|-------|--------|
| $E_{3/2,u}$ | $E_{5/2}$ | $E_{3/2}$ | $E_{5/2}$ | $E_{3/2}$ | $E_{5/2}$ | $E_{3/2}$ | $E_{5/2}$ |
| $E_{5/2,u}$ | $E_{1/2}$ | $E_{1/2}$ | $E_{1/2}$ | $E_{1/2}$ | $E_{1/2}$ | $E_{1/2}$ | $E_{1/2}$ |
| $C_{6v}$ | $C_{3v}$ | $C_6$ | $C_3$ | $C_{2v}$ | $C_{2v}$ | $S_6$ | $S_6$ |

up to a unitary transformation. The Dirac points occur only when $M_0 M_1 > 0$, which is the condition for band inversion. The parameters obtained by fitting the energy bands to the result of first-principles calculations are $C_0 = -0.0336$ eV, $C_1 = 2.9058$ eV Å$^2$, $C_2 = -3.8226$ eV Å$^2$, $M_0 = -0.1098$ eV, $M_1 = -7.3012$ eV Å$^2$, $M_2 = -15.5233$ eV Å$^2$, $A = 2.9129$ eV Å.

$D_{3d}$. By breaking the horizontal mirror symmetry $\sigma_h$, the vertical mirror symmetries $\sigma_{e1}$, $\sigma_{e2}$, $\sigma_{e3}$ and the $C_6$ rotation symmetry, $D_{6h}$ deduces to the $D_{3d}$ group. The $k \cdot p$ model is therefore

$$H'_{D_{3d}}(k) = \begin{pmatrix}
0 & iB_{k_z} + iG_{k_z}k_x^2 & D_2 k_zk_+ + iF_{1}k_zk_x^2 & iA_{1} + D_1 k_z^2 \\
-iB_{k_z} - iG_{k_z}k_x^2 & 0 & iF_1 k_zk_x^2 & -iA_{1} - D_1 k_z^2 \\
D_2 k_zk_+ + iF_{1}k_zk_x^2 & iA_{1} + D_1 k_z^2 & 0 & iF_2 k_zk_x^2 \\
-iA_{1} - D_1 k_z^2 & iF_1 k_zk_x^2 & -iF_2 k_zk_x^2 & 0
\end{pmatrix}.$$
In this $k$-$p$ model the energy bands along $\Gamma-A$ are double degenerate and the Dirac cone is not split. Although $C_{3v}$ is the maximum subgroup of $D_{3d}$ and $D_{3h}$, there are certain differences. The difference is the $PT$ symmetry which is the combination of inversion and time-reversal symmetries. The little group of the $k$ point along $\Gamma-A$ is $C_{3v}$ plus the $PT$ symmetry when the little group of the $\Gamma$ point is $D_{3d}$. All the bands become double degenerate. Hence, breaking the inversion symmetry and the vertical mirror symmetries wouldn’t lift the degeneracy of the Dirac point. This confirms that breaking all vertical mirror symmetries but keeping other vertical mirror symmetries $\sigma_{d1}, \sigma_{d2}, \sigma_{d3}$ (or $\sigma_{v1}, \sigma_{v2}$, $\sigma_{v3}$) are the keys for the reaching the triple nodal point phases.

$C_{6h}$. This group can be obtained from $D_{6h}$ by breaking all vertical mirror symmetries and the two-fold rotation symmetries in the $xy$ plane. The inversion symmetry is preserved. The $k$-$p$ model is

$$H'_{C_{6h}}(k) = \begin{pmatrix}
0 & 0 & A_1 k_- + F_1 k_z k_+^2 & -A_1 k_+ + F_1 k_z k_-^2 \\
0 & 0 & A_2 k_- + F_2 k_z k_+^2 & -A_2 k_+ + F_2 k_z k_-^2 \\
A_1 k_- + F_1 k_z k_+^2 & A_2 k_- + F_2 k_z k_+^2 & 0 & 0 \\
-A_1 k_- + F_1 k_z k_-^2 & -A_2 k_- + F_2 k_z k_-^2 & 0 & 0
\end{pmatrix}. \tag{B4}$$

There is no term that can break the degeneracy of the Dirac point. This confirms that breaking all vertical mirror symmetries wouldn’t lift the degeneracy of the Dirac point in the presence of both inversion symmetry and the $C_3$ symmetry.

$S_6$. In $D_{6h}$, $S_6$ is the smallest subgroup that has both inversion symmetry and the $C_3$ symmetry but lacks mirror symmetry. The $k$-$p$ model is

$$H'_{S_6}(k) = \begin{pmatrix}
0 & 0 & A_1 k_- + F_1 k_z k_+^2 & -A_1 k_+ + F_1 k_z k_-^2 \\
0 & 0 & A_2 k_- + F_2 k_z k_+^2 & -A_2 k_+ + F_2 k_z k_-^2 \\
A_1 k_- + F_1 k_z k_+^2 & A_2 k_- + F_2 k_z k_+^2 & 0 & 0 \\
A_2 k_- + F_2 k_z k_-^2 & -A_1 k_- + F_1 k_z k_-^2 & 0 & 0
\end{pmatrix}. \tag{B4}$$

The difference between $S_6$ and $C_{3h}$ is the presence of horizontal mirror symmetry $\sigma_h$ and the $C_{2z}$ rotation symmetry in the latter. In this $k$-$p$ model, the presence of inversion symmetry and the $C_3$ symmetry is sufficient for protecting the Dirac point.

$C_3$. $C_3$ is the maximum subgroup of $S_3$ after breaking inversion symmetry but keeping the $C_3$ symmetry. The $k$-$p$ model is

$$H'_{C_3}(k) = \begin{pmatrix}
B_1 k_z & B_2 k_z & (A_1 + D_1 k_z) k_- + F_1 k_z k_+^2 & (A_2 + D_2 k_z) k_- + F_2 k_z k_+^2 \\
B_2 k_z & -B_1 k_z & (A_1 + D_1 k_z) k_+ + F_1 k_z k_-^2 & (A_2 + D_2 k_z) k_+ + F_2 k_z k_-^2 \\
(A_1 + D_1 k_z) k_+ + F_1 k_z k_-^2 & (A_2 + D_2 k_z) k_+ + F_2 k_z k_-^2 & 0 & 0 \\
(A_1 + D_1 k_z) k_- + F_1 k_z k_+^2 & (A_2 + D_2 k_z) k_- + F_2 k_z k_+^2 & 0 & 0
\end{pmatrix}. \tag{B5}$$

The $B_1 k_z$, $B_2 k_z$ and $B' k_z$ terms lift the degeneracy of the two-fold degenerated bands. However, there are no
hybridization linear terms involving \( k_z \) between the two blocks. Therefore, the Dirac points will split into four pairs of Weyl points.

\[
H'_{C_6}(k) = \begin{pmatrix}
B_1 k_z & 0 & 0 & (A_2 + D_3 k_z) k_+ \\
0 & -B_1 k_z & (A_2 - D_3 k_z) k_+ & 0 \\
0 & (A_2 - D_3 k_z) k_- & B' k_z & A_3 k_- \\
(A_2 + D_3 k_z) k_- & 0 & A_3 k_+ & -B' k_z
\end{pmatrix}.
\]  

(B6)

The \( B_1 k_z \) and \( B' k_z \) terms lift the degeneracy of the two-fold degenerated bands. However, there are no hybridization linear terms involving \( k_z \) between the two blocks. Therefore, the Dirac points will split into four pairs of Weyl points as in the case of \( C_3 \) group.

\[
H'_{D_3}(k) = \begin{pmatrix}
0 & B_1 k_z & A_1 k_- + F_1 k_z k_2^2 & -A_1 k_+ F_1 k_z k_2^2 \\
B_2 k_z & 0 & B_2 k_z & A_2 k_- + F_2 k_z k_2^2 \\
A_1 k_- + F_1 k_z k_2^2 & A_2 k_- + F_2 k_z k_2^2 & 0 & B' k_z \\
-1k_+F_1 k_z k_2^2 & A_2 k_- - F_2 k_z k_2^2 & 0 & B' k_z
\end{pmatrix}.
\]  

(B7)

The \( B_2 k_z \) and \( B' k_z \) terms lift the degeneracy of the two-fold degenerated bands. There are no hybridization linear terms involving \( k_z \) between the two blocks. Hence, the Dirac points will split into four pairs of Weyl points as in the cases of \( C_3 \) and \( C_6 \) groups.

\[
H'_{D_6}(k) = \begin{pmatrix}
B_1 k_z & 0 & iF_1 k_z k_2^2 & i(A_1 + D_1 k_z) k_+ \\
0 & -B_1 k_z & -i(A_1 - D_1 k_z) k_+ & iF_1 k_z k_2^2 \\
-iF_1 k_z k_2^2 & i(A_1 - D_1 k_z) k_+ & 0 & B' k_z \\
-i(A_1 + D_1 k_z) k_- & -iF_1 k_z k_2^2 & 0 & A_3 k_+
\end{pmatrix}.
\]  

(B8)

The \( B_1 k_z \) and \( B' k_z \) terms lift the degeneracy of the two-fold degenerated bands, but there are no hybridization linear terms involving \( k_z \) between the two blocks. The Dirac points will split into four pairs of Weyl points as in the cases of \( C_3 \), \( C_6 \) and \( D_3 \) groups.

\[
H'_{D_6}(k) = \begin{pmatrix}
0 & 0 & 0 & F_1 k_z k_2^2 \\
0 & 0 & 0 & (A_1 + iD_1 k_z) k_- \\
F_2 k_z k_2^2 & (A_1 - iD_1 k_z) k_+ & 0 & -iA_3 k_+
\end{pmatrix}.
\]  

(B9)

Like the \( k \cdot p \) models of \( D_{6h}, D_{3d}, C_{6v} \) and \( S_6 \) groups, the Dirac points are retained in \( C_{6v} \) even without the inver-
sion symmetry due to the presence of 6 vertical mirror symmetries $\sigma_{v1}, \sigma_{v2}, \sigma_{v3}, \sigma_{d1}, \sigma_{d2}$ and $\sigma_{d3}$.

$$H'_{C_3}(k) = \begin{pmatrix}
B_1 k_z & 0 & 0 \\
0 & -B_1 k_z & 0 \\
-i(A_1 + D_1 k_z) k_- + F_1 k_z k_z^2 & -i(A_2 - D_2 k_z) k_- - iF_2 k_z k_z^2 & (A_1 + D_1 k_z) k_- + F_1 k_z k_z^2 \\
-i(A_1 + D_1 k_z) k_- + iF_1 k_z k_z^2 & (A_2 - D_2 k_z) k_- - iF_2 k_z k_z^2 & 0 \\
(A_1 + D_1 k_z) k_- + F_1 k_z k_z^2 & i(A_1 + D_1 k_z) k_- + iF_1 k_z k_z^2 & -iA_3 k_- \\
i(A_2 - D_2 k_z) k_- + iF_2 k_z k_z^2 & 0 & 0
\end{pmatrix} \cdot (A_1 + D_1 k_z) k_- + F_1 k_z k_z^2. \quad (B10)$$

The double degenerate $E_{3/2}$ band splits into two non-degenerate bands while the double degenerate $E_{5/2}$ band is not affected. Eventually, the Dirac points transform into two pairs of triple nodal points.

$D_{2h}$. $D_{2h}$ is the subgroup of $D_{6h}$ obtained by breaking $C_3$ rotational symmetry. The vertical mirror symmetries $\sigma_x$ and $\sigma_y$, the horizontal mirror symmetry $\sigma_z$ and inversion symmetry are preserved. The corresponding $k \cdot p$ model is

$$H'_{D_{2h}}(k) = \begin{pmatrix}
0 & 0 & Bk_z & A_1 k_- + A_2 k_+ \\
0 & 0 & A_1 k_- + A_2 k_+ & -Bk_z \\
Bk_z & A_1 k_- + A_2 k_+ & 0 & 0 \\
A_1 k_- + A_2 k_+ & -Bk_z & 0 & 0
\end{pmatrix}. \quad (B11)$$

Since there are many high-order terms of $k$, here we only list the linear terms of $k$. The $PT$ symmetry protects the double degeneracy of each band. However, the $C_3$ symmetry breaking introduces the $Bk_z$ hybridization term between the $E_{3/2}$ and $E_{5/2}$ bands. Such hybridization will open a gap at the Dirac point, thus transforming the Dirac semimetal into a topological insulator.

$C_{2v}$. $C_{2v}$ is the subgroup of $D_{2h}$ obtained by breaking inversion symmetry. Vertical mirror symmetries $\sigma_x$ and $\sigma_y$ are preserved. The corresponding $k \cdot p$ model is

$$H'_{C_{2v}}(k) = \begin{pmatrix}
0 & iB_1 k_- + iB_2 k_- & iBk_z + \Delta & iA_1 k_- + iA_2 k_+ \\
-iB_1 k_- + iB_2 k_- & 0 & -iA_1 k_- + iA_2 k_- & iBk_z + \Delta \\
-iBk_z + \Delta & -iA_1 k_- + iA_2 k_- & 0 & iB_1 k_- + iB_2 k_- \\
-iA_1 k_- + iA_2 k_- & -iBk_z + \Delta & -iB_1 k_- + iB_2 k_- & 0
\end{pmatrix}. \quad (B12)$$

There is an additional constant hybridization term $\Delta$ between the $E_{3/2}$ and $E_{5/2}$ bands as in the case of $D_{2h}$ group. The gap of the Dirac point will be opened, leading to the strong topological insulator phase.

$$H'_{C_2}(k) = \begin{pmatrix}
B_3 k_z & iB_1 k_- + iB_2 k_- & iBk_z + \Delta & iA_1 k_- + iA_2 k_+ \\
-iB_1 k_- + iB_2 k_- & -B_3 k_z & -iA_1 k_- + iA_2 k_- & iBk_z + \Delta \\
-iBk_z + \Delta & iA_1 k_- + iA_2 k_- & B_3 k_z & iB_1 k_- + iB_2 k_- \\
-iA_1 k_- + iA_2 k_- & -iBk_z + \Delta & -iB_1 k_- + iB_2 k_- & -B_3 k_z
\end{pmatrix}. \quad (B13)$$

The breaking of the mirror symmetries $\sigma_x$ and $\sigma_y$ allows the presence of the $B_3 k_z \sigma_z$ term in the diagonal part.
The $B_{3g} \cdot \sigma_x$ term lifts the double degeneracies of $E_{3/2}$ and $E_{5/2}$ bands. Accidental Weyl points could be realized in this little group.

Appendix C: $k \cdot p$ model for the (010) surface at the $\Gamma$ point

As mentioned in the main text, the space group of the (010) surface is $Pma2$ (No. 28), whose generators are $\mathbf{a}$ and $\mathbf{c}$ in this little group.

At the $\Gamma$ point, the bands are double degenerate. Along the $k_z$ direction, $k_z \sigma_x$ lifts the degeneracy. As a result, the surface energy bands split along $\Gamma - A$ as shown in Fig. 4(f) of the main text.

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The supplementary material contains the comparison of band structures obtained using PBE and HSE06 functionals and describes effective $k \cdot p$ models at the $\Gamma$ point in presence of various symmetry-breaking distortions.

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