Dirac-semimetal phase diagram of two-dimensional black phosphorus

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Abstract
Black phosphorus (BP), a layered van der Waals material, reportedly has a band gap sensitive to external perturbations and manifests a Dirac-semimetal phase when its band gap is closed. Previous studies were focused on effects of each perturbation, lacking a unified picture for the band-gap closing and the Dirac-semimetal phase. Here, using pseudospins from the glide-reflection symmetry, we study the electronic structures of mono- and bilayer BP and construct the phase diagram of the Dirac-semimetal phase in the parameter space related to pressure, strain, and electric field. We find that the Dirac-semimetal phase in BP layers is singly connected in the phase diagram, indicating the phase is topologically identical regardless of the gap-closing mechanism. Our findings can be generalized to the Dirac semimetal phase in anisotropic layered materials and can play a guiding role in search for a new class of topological materials and devices.

1. Introduction
Two-dimensional (2D) materials have attracted much attention in applications and theories, since graphene was found to be easily producible through mechanical exfoliation. Graphene now becomes the typical example for the 2D Dirac semimetal with the linear band structure and high mobility. However, without a band gap, graphene has a limitation in applications for optical or switching devices. On the other hand, another group of 2D materials, such as transition-metal dichalchogenides, have intermediate band gaps and show applicability to electronic devices. Recently, black phosphorus (BP) [1], an allotrope of phosphorus, gains lots of attention as a new 2D layered system [2–4]. BP has a thickness-dependent band gap varying from 0.3 eV for the bulk [5–8] up to 2 eV for the monolayer [6, 9–11], and it is remarkable with the emergence of the Dirac-semimetal phase [12–21] and the quantum Hall effect at low temperature [22].

BP has a layered puckered-honeycomb structure, as shown in figure 1 [23–25]. The interlayer interaction is mainly van der Waals interaction [26, 27], which makes the bulk sample easily cleaved to few-layered 2D samples. BP layers have strong in-plane anisotropy in the atomic structure, resulting in anisotropic electrical conduction [4, 7, 8, 28–30]. The band gap of BP is controllable by various external parameters such as pressure [5, 6, 8, 17, 18, 31], electric field [14, 16, 32, 33], and potassium doping [12, 13]. Very recently, BP is found to become a Dirac semimetal when its gap is closed [12–18], making a strong contrast with other 2D semiconducting materials. Electronic structures of BP have been studied successfully by tight-binding methods [6, 34, 35], density-functional methods [12–16, 18, 27, 28, 31, 32, 34, 35], and the GW method [34, 35]. However, a unified picture for the band-gap closing method and the Dirac-semimetal phase in BP layers is still lacking.

In this work, we investigate key ingredients of BP to obtain a unified picture for the band-gap closing and the Dirac-semimetal phase. The gap-closing condition is obtained in the parameter space of Hamiltonian that is related to pressure, strain, and electric field. From the glide-reflection (GR) symmetry of BP, pseudospins are derived, which guarantee a massless Dirac Hamiltonian when the band gap is closed. In each layer, the band gap can be closed by reducing the anisotropy of the intralayer hopping, while the interlayer coupling narrows the band gap in multilayer BP. We also find intra- and interlayer potential differences have opposite effects so that a perpendicular electric field does not decrease the band gap in the monolayer while it reduces the gap in the multilayer. Obtained phase diagrams show that the Dirac semimetal phase in BP layers is topologically identical regardless of the
gap–closing method despite some difference in detailed electronic band structures.

2. Monolayer BP

2.1. Microscopic Hamiltonian

Each BP layer has four P atoms in the unit cell, as indexed in figure 1. For a tight-binding model, one orbital per P atom can describe the electronic structure near the band gap [35]. In [35], a tight-binding model with one orbital per P atom was constructed, with 15 hopping parameters fitted to the GW band dispersions near the band gap. In our present study, we construct a simpler Hamiltonian, including only the three largest hopping parameters, which are the nearest-neighbor intralayer hopping energies, \( t_{xz} = -1.486 \text{ eV} \) and \( t_{ac} = 3.729 \text{ eV} \), along the zigzag and armchair directions, respectively, and the nearest-neighbor interlayer hopping energy \( t_z = 0.524 \text{ eV} \). We neglect the other smaller hopping parameters in order to make our model simple enough for analytic analysis. Although our model uses the three values for the nearest-neighbor hopping parameters to describe pristine BP systems, our major findings are valid independently of their detailed values.

Band structures along the high-symmetry lines obtained numerically from our model are shown in figures S1 and S2 in supplemental material for mono- and bilayer BP, respectively (stacks.iop.org/TDM/4/025071/mmedia). When compared with the tight-binding band structures using the 15 parameters [35], our band structures have some difference in detailed features. For example, band structures along the XS line are not dispersive in our results while they are in [35]. Moreover, similarly to the tight-binding model in [35], our tight-binding model contains only one orbital per P atom, so it does not reproduce some of the valence and conduction bands which are actually present in BP but away from the band gap. In the case of pristine BP, these neglected bands are safely away from the band gap, but some strong perturbation may shift these bands substantially towards the band gap, as shown in figure 2(d) of [14], for instance. In such a case, our model may not describe the realistic situation properly, and one needs to employ a theoretical framework with multiple orbitals per P atom. Despite these shortcomings, our model is a good starting point to develop a unified picture for the band–gap closing and the Dirac-semimetal phase in BP systems.

For the monolayer BP, our tight-binding Hamiltonian is

\[
H_{\text{1}} = \sum_k \Psi_k^\dagger \hat{H}_k \Psi_k
\]

\[
\Psi_k = \begin{bmatrix} e^{-i\vec{k}\cdot \vec{r}_{\text{1}}^{\text{1}}} c_{\text{1}, \vec{k}} & e^{-i\vec{k}\cdot \vec{r}_{\text{1}}^{\text{2}}} c_{\text{1}, \vec{k}} & e^{-i\vec{k}\cdot \vec{r}_{\text{2}}^{\text{1}}} c_{\text{2}, \vec{k}} & e^{-i\vec{k}\cdot \vec{r}_{\text{2}}^{\text{2}}} c_{\text{2}, \vec{k}} \end{bmatrix},
\]

\[
\hat{H}_k = \begin{bmatrix} \mu_x + 2t_{xz} \cos \frac{k_{\text{ac}}}{2} & 0 & t_{ac} & 0 \\ 0 & \mu_x + 2t_{xz} \cos \frac{k_{\text{ac}}}{2} & 0 & t_{ac} \\ t_{ac} & 0 & \mu_x - 2t_{xz} \cos \frac{k_{\text{ac}}}{2} & 0 \\ 0 & t_{ac} & 0 & \mu_x - 2t_{xz} \cos \frac{k_{\text{ac}}}{2} \end{bmatrix},
\]

where \( c_{\text{1}, \vec{k}} \) and \( c_{\text{2}, \vec{k}} \) are the electron creation (annihilation) operator of the orbital at the \( \vec{r}_{\text{1}}^{\text{1}} \) and \( \vec{r}_{\text{2}}^{\text{1}} \) in the unit cell with the momentum \( \vec{k} \), and \( a \) and \( b \) are the unit-cell lengths along the zigzag (\( x \)) and armchair (\( y \)) directions, respectively. \( d_i \) is the \( y \)-coordinate difference of the first and second atoms. We also introduce a puckering potential energy, \( \mu_y \), which can be controlled by an electric field perpendicular to the BP plane.

BP has a glide-reflection (GR) symmetry with respect to the plane at the middle of the zigzag chain as shown by the red dotted plane in figure 1. This symmetry exists regardless of the number of layers and even with perpendicular electric fields that generate nonzero intra- and interlayer potential differences. As the GR operator commutes with Hamiltonian, it is the Dirac-cone protecting nonsymorphic symmetry [36] of gap-closed mono- and multilayer BP.

2.2. Pseudospin representation

Using the GR symmetry, the Hamiltonian (1) is block-diagonalized by a pseudospin representation (see supplemental material):

\[
\hat{H}_{k,1} = (D + 2 t_{xz} \cos \frac{k_{\text{ac}}}{2}) \sigma_x + t_{ac} \sin \frac{k_{\text{ac}}}{2} \sigma_y,
\]

\[
\hat{H}_{k,2} = (D - 2 t_{xz} \cos \frac{k_{\text{ac}}}{2}) \sigma_x - t_{ac} \sin \frac{k_{\text{ac}}}{2} \sigma_y,
\]

with

\[
D = \sqrt{t_x^2 + t_{ac}^2 \cos^2 (k_{b}/2)}.
\]

Here, \( \sigma_x \) and \( \sigma_y \) are Pauli matrices with respect to the pseudospinors. Energy bands from \( \hat{H}_{k,1} \) and \( \hat{H}_{k,2} \) are

\[
E_{k,1,\pm} = \pm \sqrt{(D + 2 t_{xz} \cos \frac{k_{\text{ac}}}{2})^2 + t_{ac}^2 \sin^2 \frac{k_{b}}{2}},
\]

\[
E_{k,2,\pm} = \pm \sqrt{(D - 2 t_{xz} \cos \frac{k_{\text{ac}}}{2})^2 + t_{ac}^2 \sin^2 \frac{k_{b}}{2}},
\]

respectively. Because \( D \gg 0 \) and \( t_{xz} < 0 \), the energy gap is determined by \( \hat{H}_{k,1} \).
Figure 2 shows our tight-binding band structures for different parameters. As seen in figure 2(a), pristine monolayer BP has a direct band gap at \( \Gamma \) in the Brillouin zone (BZ). Near \( \Gamma \), the Hamiltonian \( \hat{H}_{k1} \) in (2) can be approximated as

\[
\hat{H}_{k1} \approx \left( \frac{1}{2} E_g + \frac{\hbar^2 k_x^2}{2 m_x} + \frac{\hbar^2 k_y^2}{2 m_y} - \frac{\hbar^2 v_x^2 k_x^2}{E_g} + \hbar v_y k_y \right),
\]

where the energy gap \( E_g = 2 \sqrt{\mu_x^2 + t_{ac}^2 + 4 t_{zz}^2} \), the zigzag effective mass \( \mu_y = -2 \hbar^2 (t_{zz} m_x^2) \), the armchair effective mass \( m_y = -\hbar^2 E_g \sqrt{\mu_x^2 + t_{ac}^2 + t_{zz}^2 m_x^2} \), and the armchair velocity \( v_y = t_{ac} b (2 \hbar) \). The expression (4) is valid for positive or negative \( E_g \). For zero \( E_g \), all \( k^2 \sigma_x \) terms should be neglected together with \( E_g \). The band dispersions in \( \Gamma Y \), that is, the armchair direction from \( \Gamma \), are

\[
E_{k1,a} \approx \pm \sqrt{E_g^2/4 + |t_{ac}| b^2 k_y^2/(2 \mu_x^2 + t_{ac}^2)},
\]

which are hyperbola whose asymptotic lines are

\[
E = \pm \sqrt{t_{ac}^2 b^2 |t_{ac}|/(2 \mu_x^2 + t_{ac}^2)} \ k_y.
\]

2.3. Band-gap closing criterion and 2D Dirac Hamiltonian

Monolayer BP is a honeycomb lattice in the sense that every P atom has three nearest neighbors. In the honeycomb lattice, an energy gap exists if the absolute values of the hopping energies to the three nearest neighbors cannot form a triangle [37–40]. In the case of pristine BP, \( \mu_c = 0 \) and there is a finite energy gap of \( E_g = 1.514 \text{ eV} > 0 \). This nonzero band gap is consistent with the triangular criterion, that is, monolayer BP is semiconducting because the hopping energy along the armchair direction is greater than twice the absolute value of the hopping energy along the zigzag direction.

If \( t_{ac} \) decreases or \( |t_{ac}| \) increases, \( E_g \) will decrease. Thus, a way to modify the energy gap in BP layers is to apply pressure or strain which can change bond angles and bond lengths and thereby the intralayer hopping energies.

The above triangular criterion is modified when an external electric field is applied. We define a gap-closing parameter including the puckering potential energy \( \beta_1 \),

\[
\beta_1 \equiv \frac{t_{ac}}{2t_{zz} \sqrt{1 + \frac{\mu_c^2}{t_{ac}^2}}}
\]

Then, monolayer BP has a finite energy gap when \( \beta_1 > 1 \), as in the case of the pristine monolayer (figure 2(a)), and the gap vanishes when \( \beta_1 \leq 1 \). It is clear from the formula (6) that any perpendicular electric field always increases \( \beta_1 \) since it generates finite \( \mu_c \). Moreover, as \( \beta_1 \) is already bigger than 1 for pristine monolayer BP, any perpendicular electric field cannot close the band gap of monolayer BP. Reduction of \( \beta_1 \) can be achieved only by changing the ratio of \( t_{ac} \) and \( t_{zz} \), for example, by applying a strain in one direction. At the moment of the
gap closing (\(\beta_1 = 1\)), the band gap is zero at \(\Gamma\) and the Hamiltonian \(\hat{H}_{k,1}\) becomes

\[
\hat{H}_{k,1} \approx \frac{\hbar^2 k_x^2}{2m_x} + \hbar v_x k_y \sigma_y
\]

which results in a linear dispersion in the armchair direction (\(\Gamma Y\)), and quadratic one in the zigzag direction (\(\Gamma X\)) (figure 2(b)). Here the \(\Gamma\) point is a semi-Dirac point \([41, 42]\) corresponding to a merged point of two Dirac points \([42–44]\).

When \(\beta_1 < 1\), monolayer BP is metallic, with the valence and conduction bands touching each other at finite momenta \((\pm k_D, 0)\) in the \(\Gamma X\) line (figure 2(c)). From the analytic form of \(E_{k,1,\pm}\) in (3) and the band-crossing condition \(E_{k,1,+} = E_{k,1,-}\) at \((k_D, k_D) = (k_D, 0)\), we obtain

\[
k_D = \frac{2}{a} \cos^{-1} \beta_1
\]

Near the crossing point, \((k_D, 0)\), the Hamiltonian \(\hat{H}_{k,1}\) can be written as a massless Dirac particle,

\[
\hat{H}_{k,1} \approx \hbar v_x (k_x - k_D) \sigma_x + v_y k_y \sigma_y
\]

where \(v_x = -(t_{szat} a) \sin(k_Da/2) = -(t_{szat} a) \sqrt{1 - \beta_1^2}\). Thus, \((\pm k_D, 0)\) are Dirac points with anisotropic linear bands \(E_{\pm}(k_x) = \pm \hbar \sqrt{v_x^2 (k_x - k_D)^2 + v_y^2 k_y^2}\). Perpendicular electric field can generate \(\mu_z\) which re-opens the gap if it is large enough to make \(\beta_1 > 1\). Now the phase diagram is constructed according to (6) in the parameter space of \((t_{ac}, \mu_z)\) (figure 2(d)).

2.4. Chiral pseudospins and possibility of topological phase transition

The pseudospin representations of the conduction- and valence-band states are \(\frac{1}{\sqrt{2}} (1, e^{i\phi})\) and \(\frac{1}{\sqrt{2}} (1, -e^{i\phi})\), respectively, when the Hamiltonian \(\hat{H}_{k,1}\) in (2) is expressed as \(\hat{H}_{k,1} = E_{k,1,\pm} (\cos \phi \sigma_x + \sin \phi \sigma_y)\). Then, the expectation value of the pseudospin vector, \(\langle \sigma \rangle\), for a conduction-band state is \(\langle \sigma \rangle = \langle \sigma_x, \sigma_y, \sigma_z \rangle = (\cos \phi, \sin \phi, 0)\), which lies in the \(xy\)-plane in our representation. Figure 3 shows the calculated \(\langle \sigma \rangle\) of the conduction and valence bands. We find that the \(y\)-component of \(\langle \sigma_y \rangle\) of each band always changes the sign by the reflection across the \(x\)-axis, that is

\[
\langle \sigma_y(k_x, k_y) \rangle = -\langle \sigma_y(-k_x, -k_y) \rangle
\]

in the semiconducting phase (figure 3(a)) as well as the semi-Dirac (figure 3(b)) and Dirac-semimetal (figures 3(c)) phases. This sign-reversal reduces the back scattering of charge carriers moving along the armchair direction, enhancing their mobility even at the semiconducting phase, unless impurities or defects produce very abrupt potential. After the gap closing, the pseudospin becomes chiral around the Dirac points (figure 3(c)), enhancing the mobility in all directions.

BP has weak spin–orbit coupling (SOC) and the first-principles calculation showed that SOC takes place as \(\hat{H}_{\text{SOC}} = \lambda_{\text{SOC}} \hat{S}_x \sigma_y\) in the low-energy effective Hamiltonian \([13]\), where \(\lambda_{\text{SOC}}\) is a constant and \(\hat{S}_x\) is the \(x\)-component of the real spin. Since this term does not break the GR symmetry, the Dirac point in semimetallic BP layers is still protected and only shifted in the \(k_y\)-direction. To open a band gap at the Dirac point, we need a mass term, which adds a \(\sigma_z\) term to (9). If the mass term is simply a constant times \(\sigma_z\), BP layers become a trivial insulator. However, if one can introduce, for example, a momentum-dependent mass term like

\[
H_m = \lambda_m \sin(k_x a) \sigma_z
\]

it generates a topologically nontrivial energy gap at the Dirac point \([45]\). Realization and control of such perturbation in BP is of great interest because it will enable a topologically trivial-to-nontrivial phase transition.
3. Bilayer BP

3.1. Microscopic Hamiltonian

Now we consider bilayer BP. We generalize the operator $c_{i,k}$ to $c_{i,k,p}$ where $j = 1, 2$ indicates the first and second layer in the bilayer, and similarly $\hat{\Psi}_k$ to $\hat{\Psi}_{k,p}$. Then, the Hamiltonian of the bilayer is

$$ H = \sum_k [\hat{\Psi}^\dagger_k (\hat{H}_k + \mu_l) \hat{\Psi}_{k,1} + \hat{\Psi}^\dagger_{k,2} (\hat{H}_k - \mu_l) \hat{\Psi}_{k,2} $$

$$ + \hat{\Psi}^\dagger_{k,1} \hat{\Psi}_{k,2} + \hat{\Psi}^\dagger_{k,2} \hat{\Psi}_{k,1}], $$

(12)

where $\hat{H}_k$ is the intralayer Hamiltonian (1), $\mu_l$ is half of the difference in the average potentials of the two layers, and $\hat{\Psi}_{k,p}$ is due to the interlayer hopping. We assume that the first layer is placed on top of the second layer so that the third and fourth P atoms of the first layer are the nearest neighbors of the second and first P atoms of the second layer, respectively, as shown in figure 1. Then, $\hat{\Psi}_{k,p}$ is a $4 \times 4$ matrix $\left(\begin{array}{cc} 0 & \hat{\rho}_k \\ \hat{\rho}_k^\dagger & 0 \end{array}\right)$ with $\hat{\rho}_k = 2t_2 \cos(k_b/2)\hat{\sigma}_h - \sin(k_b/2)\hat{\sigma}_v$ and $\hat{\sigma}_h$, $\hat{\sigma}_v$ are Pauli matrices. The interlayer coupling $t_{1,2}$ is due to the interlayer hopping. We generalize the operator $\hat{\Psi}_k$ to $\hat{\Psi}_{k,p}$.

3.2. Band-gap closing criterion

Figures 4(a)–(e) show our tight-binding band structures of bilayer BP. Due to the GR symmetry of the lattice, the band-gap closing occurs at a point in the $\Gamma X$ line in BZ [46]. For $k_z = 0$, one can exploit the GR symmetry and obtain the lowest conduction-band energy $E_c$ and the highest valence-band energy $E_v$ in the $\Gamma$ as

$$ E_{c,v}(k_x) = \pm 2t_2 \cos(k_a/2) \pm \sqrt{P_{k_z}^2 - 2Q_{k_z}}, $$

(13)

where $+$ and $-$ are for conduction band and valence band, respectively, $P_{k_z} = 2t_2^2 \cos^2(k_a/2) + t_{2z}^2$, and $Q_{k_z} = t_2^2 \cos^2(k_a/2) + t_{2z}^2 + t_{1z}^2 \cos^2(k_a/2) - \mu_l t_{1z}^2$. Then the Dirac point $k_D$ is determined by the condition $E(k_D) = E_c(k_D)$. For the simplicity, we neglect $\mu_l$ since $\mu_l$ has a smaller value than $\mu_l$ at an applied electric field.

When $\beta_2 = 0$, we define the gap-closing parameter $\beta_2$ of bilayer BP as

$$ \beta_2 = \frac{-2t_{2z}^2 (t_{2z}^4 + \mu_l^2) - t_{1z}^2 \mu_l^2 - \sqrt{F}}{8t_{2z}^2 (t_{2z}^2 - t_{1z}^2)}, $$

(14)

with $F = 4t_2^2 t_{2z}^4 (t_{2z}^4 + 4t_{1z}^2 \mu_l^2 - 3t_{2z}^2 \mu_l^2) + t_{1z}^4 \mu_l^4$. When $\beta_2 > 1$, bilayer BP is semiconducting with a direct band gap at $\Gamma$. When $\beta_2 < 1$, bilayer BP is metallic with Dirac points at $(\pm k_D, 0)$ given by

$$ k_D = (2/a) \cos^{-1} \beta_2, $$

(15)

In the case of pristine bilayer, $\beta_2 > 1$ so that it is semiconducting, as shown in figure 4(a). Here, due to the interlayer coupling $t_{1,2}$, the gap is smaller than that in the monolayer.

3.3. Band-gap closing methods and Dirac-semimetal phase diagram

The interlayer potential energy difference $2\mu_l$, which can be generated by applied electric field, decreases the energy gap of bilayer BP. As shown in figures 4(b) and (e), the increase of $\mu_l$ can close the band gap and induce the Dirac-semimetal phase. This is in contrast with the puckering potential energy $\mu_l$ that acts against the gap closing although $\mu_l$ is also generated by an electric field.
Figures 4(d) and (e) show the band-gap closing by reducing the armchair-hopping and by increasing the interlayer hopping, respectively. Compared with these bands, the field-induced band structure in figure 4(c) displays non-monotonous dispersions of the conduction and valence bands in the IY line, where a minimum of their band-energy difference occurs away from Γ.

In bilayer BP, the interlayer coupling $t_{\perp}$ decreases $\beta_2$ of (14), making the Dirac point appear more easily in bilayer than monolayer. Since the GR symmetry exists in multilayer BP, $t_{\perp}$ does not mix different pseudospins of each layer, but it widens each band, resulting in a smaller band gap in a thicker BP layer. When the band gap is closed, the band dispersions from Γ to Y in figure 4(e) are monotonous similarly to the case of the armchair-hopping reduction (figure 4(d)), in contrast with the non-monotonous behavior in figure 4(c), as mentioned above. Applied pressure can contribute to the band-gap reduction and closing since it enhances the interlayer coupling by decreasing the interlayer distance.

From (14), we obtained the phase diagram of Dirac semimetal for bilayer BP in the three-dimensional parameter space of $(t_{\perp}, \mu, t_{ac})/t_{ab}$ as shown in figure 4(f). Here the parameters $t_{ac}, \mu$, and $t_{\perp}$ are changeable by strain, pressure, and electric fields, as discussed above. We find that the region for the Dirac-semimetal phase is topologically identical regardless of the gap-closing method.

4. Conclusion

We obtained a unified picture on the Dirac-semimetal phase of BP layers. Phase diagrams are obtained for mono- and bilayer BP in the parameter space of the Hamiltonian. Phase-controlling parameters are identified to be (i) the anisotropy of the intralayer hopping, which can be changed by pressure or strain, (ii) the interlayer hopping, which can be enhanced by pressure, and (iii) the interlayer potential energy difference, which can be generated by electric fields. Pseudospins, originating from the glide-reflection symmetry of BP, exist even in the semiconducting phase and assure the Dirac-semimetal phase when the band gap is closed. The Dirac-semimetal phase in BP layers is singly connected in the parameter space, indicating it is of the same kind regardless of the gap-closing method. Our findings can be generalized to the Dirac-semimetal phase in anisotropic layered materials and can play a guiding role in search for a new class of topological materials and devices.

Acknowledgments

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