Structure and electron bands of phosphorus allotropes

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The small difference between the rhombohedral phosphorus lattice (A-7 phase) and the simple cubic phase as well as between phosphorene and the cubic structure is used in order to construct their quasiparticle band dispersion. We exploit the Peierls idea of the Brillouin zone doubling, which has been previously employed in consideration of semimetals of the V period and IV-VI semiconductors. In the common framework, individual properties of phosphorus allotropes are revealed.

PACS numbers: 73.20.AT, 73.22.-f, 74.20.Pq

Introduction—

In the last decade much progress in study of the graphene monolayer has been achieved. Graphene turned out to be a material with remarkable properties: the universal optical conductivity $e^2/4\hbar$, light transmittance giving the fine–structure constant, the Coulomb renormalization of the Fermi velocity. However, absence of a band gap does not permit to use graphene in field effect transistor devices. This is the reason to seek other two dimensional materials with sizable gap and high mobilities. One of such promised substances becomes phosphorene, i.e. a monolayer of black phosphorus.

The element phosphorus belongs to the same period of the periodic table as semimetals As, Sb, and Bi and contains two 3s and three 3p valent electrons. There exist at least three phosphorus allotropes: simple cubic, rhombohedral (bismuth A-7 symmetry), and orthorhombic (A-17). At 4.5 GPa, the structure changes from A-17 to A-7, which transforms to the sc one at 10 GPa. There are two phase transformations also at 137 and 262 GPa.

The cubic allotrope possesses one remarkable property - it becomes a superconductor with maximum $T_c = 9.5$ K under pressure 32 GPa, and the high temperature of the superconducting transition was explained in the Ref. by the electron-phonon coupling.

The orthorhombic black phosphorus (BP) is the most stable allotrope of the element. It is a layered material with each layer forming a puckered surface. Anisotropic optical response with a high mobility of carriers promises BP as viable linear polarizers for applications.

Recently, the success was achieved in fabricating field-effect transistors based on few-layer BP. Comparing to graphene, BP has an advantage possessing a quasiparticle band gap. The band gap value of monolayer (0.9–1.7 eV in various calculations) tends to smaller values (0.1–0.36 eV) in bulk BP. The calculations within the local-orbital method or modern first-principal ones give the different values of the minimum band gap. That is the direct gap at the $\Gamma$ point or the indirect band between the valence-band maximum at the $Z$ point and the conduction-band minimum at $\Gamma$. Sometimes, the variations in the band gap value are explained by the many-particle correlation effects. According to Ref. , the self-energy correction enlarges the band gap from 0.8 to 2 eV, however, the optical absorption peak is reduced to 1.2 eV, that can be broadly tuned by changing the number of stacked layers.

The spin-orbit interaction $\Delta_{so}$ is pointed out as a possible source of contradictions in the calculations of the band structure. Because the spin-orbit interaction is proportional to the ion charge squared and $\Delta_{so}=1.2$ eV in bismuth, we can estimate the spin-orbit value for BP as $\Delta_{so} \approx 0.04$ eV, i.e. much smaller in comparison with the interesting energy of the order of 0.2 eV in BP. Therefore, the spin-orbit coupling cannot noticeably change the quasiparticle band structure in phosphorus.

The structure of BP consists of two puckered surfaces. One such the surface is shown in Fig. Each atom is connected with the nearest-neighbors by three bonds. There are two bonds of $2.16$ Å and one bond of $2.21$ Å, two bond angles are $103.7^\circ$ and one bond angle is $98.1^\circ$. There are four atoms in the unit cell, and we have to obtain twelve bands for the $p_i$ orbitals, $i = x, y, z$, hybridized weakly with the $s$ bonds.

If we set all the bonds be equal and all the angles be equal to $90^\circ$, we obtain two planes of atoms with the simple cubic arrangement instead of one puckered phosphorene layer. Then we have to take the small difference between the cubic arrangement and phosphorene into account. The corresponding deformation is known as a Peierls distortion and was employed for the evaluation of the electron dispersion in bismuth as well as in IV-VI compounds. The similar procedure used for construction of the phonon spectrum is known as folding.

In this work, we have taken the Peierls idea as a starting point in constructing an effective low-energy Hamiltonian for phosphorus allotropes. Within the common framework, the electron dispersion is evaluated in an explicit form for the sc, A-7 allotropes, and phosphorene.

Electron band-dispersion for a semimetal with the rhombohedral lattice and two atoms in the unit cell—
Here we consider the electron dispersion of the sc and A-7 lattices for the elements of the V group, starting from the tight-binding approximation and using the Peierls idea of the unit-cell doubling. There are one atom in the unit cell of the sc lattice and two atoms in the A-7 unit cell. The correct Bloch functions of the zeroth approximation are constructed from the Wannier orbitals \( p_i(\mathbf{r}) \) as a sum over the lattice sites \( n \) and atoms \( A \) in the unit cell as

\[
\psi_i(\mathbf{r}) = \sum_{n,A} e^{i\mathbf{k}\cdot\mathbf{r}_n^{A}} p_i(\mathbf{r} - \mathbf{r}_n^A),
\]

where \( i = x, y, z \) numerates the \( p_i \) orbitals. We assume that the \( s \) orbitals are located more deeply and are separated well from the \( p_i \) bands.

In the sc lattice, an atom with the coordinates \((000)\) has six nearest neighbors at the distance \( a \) in \( \pm(100), \pm(010), \) and \( \pm(001) \) sites and twelve next-nearest neighbors in the sites like \((110)\). The electron–lattice interaction \( H_0 \) of cubic symmetry gives the following matrix elements between the first neighbors

\[
\xi_{xx} = \xi_0 \cos k_x a + \xi_1 (\cos k_y a + \cos k_z a)
\]

and between the next-nearest neighbors

\[
\eta_{xy} = \eta_0 \sin k_x a \sin k_y a,
\]

\[
\eta_{xx} = \eta_1 \cos k_y a \cos k_z a + \eta_2 \cos k_x a (\cos k_y a + \cos k_z a).
\]

Here the hopping integrals are

\[
\xi_0 = 2 \langle p_x(000)|H_0|p_x(100) \rangle, \\
\xi_1 = 2 \langle p_x(000)|H_0|p_x(010) \rangle, \\
\eta_0 = -4 \langle p_x(000)|H_0|p_y(011) \rangle, \\
\eta_1 = 4 \langle p_x(000)|H_0|p_x(011) \rangle, \\
\eta_2 = 4 \langle p_x(000)|H_0|p_x(110) \rangle,
\]

and the arguments of the \( p_i \) orbitals indicate the atom coordinates where these orbitals are centered. The remaining matrix elements are given by cyclic permutation of the indices. In Fig. 2 the electron dispersion is shown for the sc lattice with \( \xi_0 = 4 \text{ eV} \), \( \xi_1 = -1 \text{ eV} \), \( \eta_0 = -0.2 \text{ eV} \), \( \eta_1 = \eta_2 = 0.2 \text{ eV} \). If the interatomic distance \( a \) is short enough and the nearest hopping integrals \( \xi_0 \) and \( \xi_1 \) have a typical atomic values, such the crystal should be a good metal. Then three valent electrons can occupied only half places in these three bands degenerate twice in the spin. It is not surprising that phosphorus becomes a superconductor under pressure, when it displays the sc structure.

At high pressure from 40 to 80 kbar, phosphorus has the rhombohedral structure (A-7 phase). This structure can be formed from the sc phase by a small relative displacement of two face-centered sublattices. Thus, in the unit cell, we get two atoms shown in Fig. 3 by the cross and empty circles and obtained from the atoms at the \((000)\) and \((111)\) sites in the cubic phase. In the A-7 phase, their rhombohedral coordinates become \( \pm(0.25-u, 0.25-u, 0.25-u) \) with \( u \) equal to several percents. For bismuth and rhombohedral phosphorus, such a distortion is on the order of 5–10%. For instance, in bismuth, the angles between bonds become 57° instead of

![FIG. 1. (Color online) Structure of phosphorene. a) 3D representation; the A and B atoms belong to two planes constituting a puckered monolayer phosphoren (see text). b) Top view; the \( a_1, a_2 \) box shows the unit cell with four atoms.](image)

![FIG. 2. (Color online) Three electron bands for a metal with a simple cubic lattice; the degenerate band is shown in a thick line.](image)
60° in the sc phase. The Peierls distortion results in the doubling of the unit cell volume. The primitive vectors for the face-centered lattice are

\[ a_i = a(011), \quad a(101), \quad a(110), \]

and the primitive vectors for the reciprocal lattice write

\[ \mathbf{Q}_i = \pi(-1,1,1)/a, \quad \pi(1,-1,1)/a, \quad \pi(1,1,-1)/a. \]

The Peierls distortion can be represented as a result of the electron–lattice interactions of the rhombohedral symmetry \( D_{3d} \), first, due to the sublattice shift

\[ U(r) = \mathbf{u} \cdot \nabla(V_A(r) - V_B(r)) \equiv \mathbf{u} \cdot \mathbf{O} \quad (5) \]

in the (111) direction and second, because of the deformation

\[ E(r) = \varepsilon_{ij} \mathbf{O}_{ij}(r). \quad (6) \]

affecting the angles between the bonds and described by the tensor \( \varepsilon_{ij} \).

The Hamiltonian for the face-centered lattice with two atoms in the unit cell obtains the form

\[ H(k) = \begin{pmatrix} A & iU \\ -iU & A_Q \end{pmatrix}, \quad (7) \]

where \( A \) is the \( 3 \times 3 \) matrix given by the matrix elements in Eqs. \( (2)-(4) \). The matrix \( A_Q \) is obtained from \( A \) by the substitution \( k \rightarrow k + Q_1 + Q_2 + Q_3 \). The additional contributions to the matrix \( A \) appears from the interaction \( E(r) \), Eq. \( (9) \), and has the matrix elements

\[ E_{xy} = e_0 + e_1 (\cos k_x a + \cos k_y a) + e_2 \cos k_z a, \]

with the hopping integrals

\[ e_0 = \varepsilon_{xy} \langle p_x(000)|O_{xy}|p_y(000) \rangle, \]
\[ e_1 = \varepsilon_{xy} \langle p_x(000)|O_{xy}|p_y(100) \rangle, \]
\[ e_2 = \varepsilon_{xy} \langle p_x(000)|O_{xy}|p_y(001) \rangle. \quad (8) \]

The Hamiltonian of Eq. \( (7) \) gives six bands shown in Fig. 3. In this case, we get a semimetal with holes at the \( T \) point and electrons at the \( L \) point as it should be in bismuth. The following values of the hopping integral are taken (in eV): \( \xi_0 = 4, \xi_1 = -1, u_1 = 0.2, u_2 = 0.25, u_3 = 0.3, \eta_0 = -0.3, \eta_1 = 0.15, \eta_2 = -0.1 \). The parameters of Eq. \( (8) \) are set to zero. Another set of parameters can produce a semiconductor with the narrow band-gap. The largest hopping integrals \( \xi_0 \) and \( \xi_1 \) have approximately the similar values for semimetals of the \( V \) period and for the \( IV-VI \) semiconductors [20, 21]. The values of \( e_0, e_1, e_2, u_1, u_2, \) and \( u_3 \) parameters must do not exceed 0.1\( \xi_0 \), because they are proportional to the Peierls weak distortion. The spin-orbit interaction should be included for antimony and bismuth, where it is of the same order as the Peierls distortion.

**Electron band dispersion for phosphorene**

Now we apply the Peierls doubling to phosphorene. In the simple case of doubling, we obtain the unit cell with two atoms instead of one atom. However, we have now four atoms in the unit cell of phosphorene. Let three \( p_i \) bonds in phosphorene be equal to one another and the angles between the bonds be equal to 90°. Thus, we obtain two parallel planes with one atom \( A \) under another atom \( B \) in these two planes at the distance \( a \). The distance between the nearest atoms in the plane is also equal.
to a. Instead of one monolayer phosphorene, we have two parallel planes with two atoms A and B in the unit cell and with the translation symmetry only in x and y directions (see, Fig. 1). Therefore, the vector \( \mathbf{k} \) has only two component \( x \) and \( y \). Instead of one matrix in the rhombohedral case, Eqs. (2)-(4), we have to combine the matrix \( A \), connecting the nearest and next-nearest neighbors of the A type, the matrix \( B = A \), connecting the neighbors of the B type, and the matrix \( A_B \), connecting the atoms of the A and B type. We obtain the low-energy Hamiltonian in the form of the \( 6 \times 6 \) matrix

\[
A(k) = \begin{pmatrix}
A & A_B \\
A_B^\dagger & A
\end{pmatrix}
\]

The hopping integrals of the cubic Hamiltonian \( H_0 \) between the \( p_i \) orbitals centered on two atoms A and B:

\[
\begin{align*}
A_{xx} &= \xi_0 \cos k_x a + \xi_1 \cos k_y a + \eta_2 \cos k_x a \cos k_y a, \\
A_{yy} &= \xi_0 \cos k_y a + \xi_1 \cos k_x a + \eta_2 \cos k_x a \cos k_y a, \\
A_{zz} &= \xi_1 (\cos k_x a + \cos k_y a) + \eta_1 \cos k_x a \cos k_y a, \\
A_{xy} &= A_{yx} = \eta_1 \sin k_x a \sin k_y a, \\
A_{xz} &= A_{zx} = A_{yz} = A_{zy} = 0, \\
A_{Bxx} &= 0.5\eta_1 \cos k_y a + \eta_2 \cos k_x a (\cos k_y a + 0.5), \\
A_{Byy} &= 0.5\eta_1 \cos k_x a + \eta_2 \cos k_y a (\cos k_x a + 0.5), \\
A_{Bzz} &= 0.5\xi_0 + \eta_1 \cos k_x a \cos k_y a + 0.5\eta_2 (\cos k_x a + \cos k_y a), \\
A_{Bxy} &= 0.5i\eta_0 \sin k_x a, A_{Byx} = 0.5i\eta_0 \sin k_y a, \\
A_{Bxz} &= -A_{Bzx}, A_{Bzx} = -A_{Byz}, A_{Bzy} = A_{Byx} = 0
\end{align*}
\]

with \( \xi \) and \( \eta \) having the same meaning as in Eq. (4).

If two primitive vectors of the cubic lattice in the \( x, y \) plane are denoted as \( a(10) \) and \( a(01) \), then the lattice with the doubling unit cell has the primitive vectors \( \mathbf{a}_1 = a(1,1) \) and \( \mathbf{a}_2 = a(-1,1) \). The primitive vectors of the reciprocal lattice are

\[
Q_1 = \pi(1,1) / a, \quad Q_2 = \pi(-(1,1) / a)
\]

Because the vectors \( \mathbf{k} \) and \( \mathbf{k} + Q_1 \) are equivalent in the Brillouin zone after doubling in the direction \( Q_1 \) (this is the \( x \) direction in phosphorene, see Fig. 1), we have to join the matrices \( A(k) \) and \( A(k + Q_1) \) into the \( 12 \times 12 \) matrix. Thus, we get the low-energy effective Hamiltonian for four atoms with the \( p_i \) orbitals in the unit cell in the form of Eq. (11), where the matrix \( A_Q \) is obtained from the matrix of Eqs. (11) and (12) with the replacement \( \cos k_x a, \cos k_x a \rightarrow -\cos k_x a, -\cos k_x a \). The \( U \) matrix has the form

\[
U(k) = \begin{pmatrix}
UA & 0 \\
0 & UA
\end{pmatrix}
\]

with the matrix elements of the orthorhombic Hamiltonian in Eq. (6):

\[
\begin{align*}
UA_{xx} &= u_1 \sin k_x a + u_2 \sin k_y a, \\
UA_{yy} &= u_1 \sin k_y a + u_2 \sin k_x a, \\
UA_{zz} &= u_2 (\sin k_x a + \sin k_y a), \\
UA_{xy} &= UA_{yx} = u_3 (\sin k_x a + \sin k_y a), \\
UA_{xz} &= UA_{zx} = u_3 \sin k_x a, \\
UA_{yz} &= UA_{zy} = u_3 \sin k_y a
\end{align*}
\]

The Hamiltonian of Eq. (13) has the orthorhombic symmetry \( C_{2h} \), as well as the Hamiltonian in Eq. (5). The corresponding matrix elements

\[
\begin{align*}
E_{xy} &= e_0 + e_1 (\cos k_x a + \cos k_y a), \\
E_{yz} &= e_0 + e_1 \cos k_y a + e_2 \cos k_x a, \\
E_{xz} &= e_0 + e_1 \cos k_x a + e_2 \cos k_y a
\end{align*}
\]

are added to the matrix \( A \).

The band structure for phosphorene is shown in Fig. 5 with the following values of the hopping integrals (in eV): \( \xi_0 = 4.1, \xi_1 = -1.0, \eta_0 = 0.1, \eta_1 = 0.3, \eta_2 = -0.1, u_1 = 0.4, u_2 = 0.09, u_3 = -0.1, e_0 = 0.2, e_1 = 0.25, e_2 = 0.15 \). This set gives a semiconductor with the minimal quasi-particle band gap at the \( \Gamma \) point \( \varepsilon_g = 0.46 \) eV. All the energies at \( \Gamma \) are expressed in terms of the above hopping integrals (see Supplemental Material at [23]). The band dispersion is more flat along the \( \Gamma - M \) direction than in the \( \Gamma - X \) and \( \Gamma - Y \) directions. The effective masses of holes do not coincide with the masses of electrons [22], because their dispersions are described by rather independent equations. At the \( \Gamma \) point, the conduction band is determined by the matrix \( A(k) \) in Eqs. (11), (12) and the valence band corresponds to the matrix \( A(k + Q_1) \). The matrix elements between them are the terms with \( u_i \), Eqs. (13) and (14). The last elements vanish at the \( \Gamma \) point and should be expanded in \( k_x, k_y \) in order to find the effective masses. Using the foregoing set of parameters, we obtain for the inverse effective masses \( m^{-1} \) the
sum of two terms $a^2(\xi_0 + \xi_1)/\hbar^2 \pm a^2 u_1^2/\hbar^2 \varepsilon_2$ for electrons and holes, correspondingly. Here, the first term plays a main role. Thus, we estimate the masses as $m \simeq 0.5m_0$.

Summary—

At 4.5 GPa, the phosphore structure changes from the orthorhombic (A-17) to rhombohedral (A-7, of bismuth type), which transforms to the sc one at 10 GPa. The structure of the orthorhombic and rhombohedral phases differs slightly from the more symmetrical sc structure. Therefore, their quasiparticle dispersion can be obtained in the framework of the general Peierls idea of the doubling distortion. We show that in agreement with experiments, the low energy Hamiltonian constructed in accordance with the Peierls method gives the dispersion of a metal for the sc phase, of a semimetal or a narrow gap semiconductor for the A-7 phase, and of a semiconductor for phosphorene. Because of the small gap at different points in the Brillouin zone ($\Gamma$, $X$, and $Y$), phosphorene can be transformed from direct band gap semiconductor to indirect semiconductor or semimetal with the compression or in the multilayer structures.

This research was initiated by V. Brazhkin who called the author’s attention to the problem of phosphorene. We acknowledge the Russian Foundation for Basic Research (grant No. 13-02-00244A) and the SIMTECH Program, New Centure of Superconductivity: Ideas, Materials and Technologies (grant No. 246937).

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Supplemental Material for “Structure and electron bands of phosphorus allotropes”

BAND ENERGIES IN PHOSPHORENE AT THE $\Gamma$ POINT

At the $\Gamma$ point, the matrix $U(k)$, Eqs. (14-15), vanishes and the band energies are determined by the eigenvalues of two matrices, $A(k = 0)$, Eqs. (11-12), and $A(Q_1)$. In addition, the matrix $A_B$ in Eq. (12) takes the diagonal form with the elements $A_{Bxx} = A_{Byy} = 0.5\eta_1 + 1.5\eta_2$, $A_{Bzz} = 0.5\xi_0 + \eta_1 + \eta_2$. Therefore, we can find three elements of the eigenfunction $(\varphi_4, \varphi_5, \varphi_6)$ from the first three eigen-equations, given by the matrix of Eq. (11), and substitute them in the second three eigen-equations. As a result, we get the equation determining the energies at the $\Gamma$ point in the form

$$
\begin{vmatrix}
  d_{11} & d_{12} & d_{13} \\
  d_{12} & d_{11} & d_{13} \\
  d_{13} & d_{13} & d_{33}
\end{vmatrix} = 0,
$$

where

$$
\begin{align*}
    d_{11} &= A_{Bxx} - \frac{(A_{xx} - \varepsilon)^2 + A_{xy}^2}{A_{Bxx}} - \frac{A_{zz}^2}{A_{Bzz}}, \\
    d_{12} &= -2A_{xy} \frac{A_{xx} - \varepsilon}{A_{Bxx}} - \frac{A_{zz}^2}{A_{Bzz}}, \\
    d_{13} &= -A_{xz} \left[ \frac{A_{xx} + A_{xy} - \varepsilon}{A_{Bxx}} + \frac{A_{zz} - \varepsilon}{A_{Bzz}} \right], \\
    d_{33} &= A_{Bzz} - \frac{(A_{zz} - \varepsilon)^2}{A_{Bzz}} - 2A_{xz}^2.
\end{align*}
$$

(S2)

The equation (S1) is reduced to two equations

$$
\begin{align*}
    d_{11} - d_{12} &= 0 \quad \text{and} \quad (d_{11} + d_{12})d_{33} - 2d_{13}^2 = 0. \quad \text{(S3)}
\end{align*}
$$

The first quadratic equation gives two band energies

$$
\varepsilon_{1,2} = A_{xx} - A_{xy} \pm A_{Bxx}
$$

(S4)

The second equation of the fourth order also can be solved giving the energies

$$
\begin{align*}
    \varepsilon_{3,4} &= 0.5(A_{xx} + A_{xy} + A_{zz} + A_{Bxx} + A_{Bzz}) \pm 0.25(2(A_{xx} + A_{xy} - A_{zz} + A_{Bxx} - A_{Bzz})^2 + 2A_{xz}^2)^{1/2}.
\end{align*}
$$

(S5)

and $\varepsilon_{5,6}$ obtained with changing the sigh at $A_{Bxx}$ and $A_{Bzz}$. The same set of parameters as in Fig. 5 give for the $\varepsilon_1 + \varepsilon_6$ energies (in eV): 2.35, 2.29, 3.78, -4.06, 3.96, 0.36.

Other six bands at the $\Gamma$ point have the opposite parity. Their energies are given in Eqs. (S4) and (S5) with changing the sigh of $\xi_0$ and $\xi_1$. We obtain (in eV): -3.07, -2.69, -0.10, -3.3151, 4.74, -3.68.