Superconductivity in two-dimensional phosphorus carbide (β₀-PC)†

Bao-Tian Wang, Peng-Fei Liu, Tao Bo, Wen Yin, Olle Eriksson, Jijun Zhao and Fangwei Wang

Two-dimensional (2D) boron has been predicted to show superconductivity. However, intrinsic 2D carbon and phosphorus have not been reported to be superconductors, which has inspired us to study the superconductivity of their mixture. Here we performed first-principles calculations for the electronic structure, phonon dispersion, and electron–phonon coupling of the metallic phosphorus carbide monolayer, β₀-PC. The results show that it is an intrinsic phonon-mediated superconductor, with an estimated superconducting temperature \( T_c \) of ≈ 13 K. The main contribution to the electron–phonon coupling is from the out-of-plane vibrations of phosphorus. A Kohn anomaly on the first acoustic branch is observed. The superconducting related physical quantities are found to be tunable by applying strain or by carrier doping.

Introduction

Owing to the developments of atomic techniques, such as molecular beam epitaxy, atomic layer deposition, pulsed laser deposition, magnetron sputtering, etc., many two-dimensional (2D) or layered superconductors have been synthesized successfully. Superconductivity can be remarkably robust in the 2D limit with respect to the corresponding parent bulk materials. The fascinating phenomena of competition between charge density waves, the Kohn anomaly, and strong spin–orbit coupling for superconductivity in 2D systems have attracted much attention.

Since the well-known discovery of graphene through mechanical exfoliation, various 2D-monolayer carbon and phosphorus materials have been successfully obtained. Both graphene and phosphorene can be manipulated to be superconductors through carrier doping, strain, metal decorating/intercalating, and/or ‘magic’ angle twisting. However, until now, no superconducting properties have been experimentally observed or theoretically predicted for these famous 2D materials in their intrinsic forms. This fact stimulated our interest to seek a superconducting state in one of their compounds, i.e., 2D phosphorus carbide (PC).

Recently, various allotropes of 2D-monolayer PC were theoretically predicted to be stable through a particle-swarm optimization method and density functional theory (DFT). Subsequently, few-layer 2D black PC was synthesized successfully via a novel carbon doping technique. Among all reported 2D PCs, the graphene-like β₀-PC exhibits metallic character and has been verified as being stable at the DFT level. Therefore, it is necessary to verify whether this newly reported phase exhibits superconductivity or not.

Methods

The calculations were performed at the DFT level, employing the local density approximation and norm-conserving pseudo-potentials as implemented in the QUANTUM-ESPRESSO (QE) package. The plane-waves kinetic-energy cutoff was set as 100 Ry and the structural optimization was performed until the forces on the atoms were less than 10 meV Å⁻¹. Monolayer PC was simulated with a vacuum thickness of 20 Å, which was enough to decouple the adjacent layers. An unshifted Brillouin-zone (BZ) \( k \)-point mesh of \( 16 \times 6 \) and a Hermitian–Gaussian smearing method were adopted for the electronic charge density calculations. The phonon modes were computed within density-functional perturbation theory on a \( 8 \times 3 \) \( q \) mesh.

Results and discussion

Optimized phosphorus carbide (β₀-PC) monolayer crystallizes in a polar orthorhombic structure with the space group \( Pmn2_1 \).
Monolayer $\beta_0$-PC, Fig. 1a, the alternating arrangement of P and C atoms renders Fig. 1b. Monolayer $\beta_0$-PC exhibits intrinsic metallic features via unconventional $\pi-\pi$ interactions which delocalize the lone pair electrons of the P atoms and bring about imperfect $sp^3$- and $sp^3$-hybridized states for monolayer $\beta_0$-PC. Apparently, such characteristics give rise to metallic behavior for monolayer $\beta_0$-PC, and accordingly favor a superconducting sheet.

We now focus on the vibrational properties and electron-phonon coupling (EPC) in $\beta_0$-PC. Fig. 2a shows the phonon dispersion over the whole BZ. The absence of imaginary modes clearly indicates that $\beta_0$-PC is dynamically stable. Our results agree well with one recent calculation$^{35}$ by Rajbanshi et al., who used a finite displacement method in obtaining phonon spectra. From the decomposition of the phonon spectrum with respect to C and P atomic vibrations, as indicated in Fig. 2a, we found that the main contribution to the acoustic branches below 150 cm$^{-1}$ was the phosphorus out-of-plane P$_z$ vibrations. The interaction between P and C atoms contributes to the intermediate-frequency region from 150 to 634 cm$^{-1}$. Similar to that in Li-decorated monolayer graphene$^{26}$ and 2D Cu-benzenehexathial (Cu-BHT), here, the in-plane modes of the C atoms occupy the high frequencies above 860 cm$^{-1}$. The vertical vibrations of the C atoms are lower than their horizontal modes.$^{50}$

The phonon density of state (PhDOS), the Eliashberg electron-phonon spectral function $\chi^2 F(\omega)$, and the cumulative frequency-dependent EPC function $\lambda(\omega)$ are displayed in Fig. 2b and c. Here, $\chi^2 F(\omega)$ and $\lambda(\omega)$ are calculated by

$$\chi^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{q\nu} \gamma_{q\nu} \delta(\omega - \omega_{q\nu})$$

and

$$\lambda(\omega) = 2 \frac{\int \chi^2 F(\omega) \omega d\omega}{\int_0^{\infty} \omega d\omega},$$

where $N(E_F)$ is the electronic density of state at the Fermi level and $\gamma_{q\nu}$ is the phonon linewidth. We find that the low-frequency phonons, mainly associated with out-of-plane P$_z$ modes, are key...
to achieving a high EPC in $\beta_0$-PC as they account for 1.08 (73%) of the total EPC ($\lambda = 1.48$). As shown in Fig. 2e, the 1st to 4th peaks of the $x^2F(\omega)$ are responsible for this part. The 5th and the 6th peaks are responsible for the out-of-plane C$_z$ modes and are associated with an EPC strength of 0.23 (16%). Similar to graphene$^{18}$ and 2D Cu-BHT,$^{50}$ the EPC induced by high-frequency phonons is almost negligible. Specifically, the high-frequency phonons, mainly the C$_\text{xy}$ modes, only contribute 0.06 (4%) of the total EPC. Overall, our calculated EPC value of 1.48 clearly makes the 2D $\beta_0$-PC an intermediate to strong conventional superconductor.

The Fermi surface contour of $\beta_0$-PC is shown in Fig. 3a, where one electron pocket centered at the $Y$ point can be seen. Away from the $I$ point and along $S-X-S$, a hole arc is observed. Along $Y-S$ and near the $S$ point, the electron pocket crosses with the hole arc. Given the electronic states of the P and C atoms at the Fermi level, the out-of-plane phonon vibrations couple strongly with the 2D $\pi$-electron hybridization of P-$p_z$ and C-$p_z$.

As a result, the distribution of $\lambda_\text{q}$ ($\lambda_\text{q} = \frac{\gamma_\text{q}}{\pi h N(E_F) \omega_\text{log}}$) for the first transverse acoustic (TA) branch in BZ should overlap with the electronic Fermi surface. As shown in Fig. 3b, an arc-type distribution of $\lambda_\text{q}$ is observed and is believed to strongly couple with the electron pocket near the $Y$ point. On combination of Fig. 3b with Fig. 3c, one can find that the largest value of the EPC appears at the $q_1 = (0,0.36)$ point along $I-Y$ on the first TA branch. This Kohn anomaly$^{34,52}$ or softening of the phonon mode yields significant coupling between electrons and acoustic phonons, with a very low frequency of ~8 cm$^{-1}$. The phonon Kohn anomaly here is due to anomalous screening of the electrons around the Fermi energy. As indicated in Fig. 1b and 3a and b, the largest value of the EPC and the Fermi surface appear spontaneously at the $q_1$ point. The Kohn anomaly indicates that the P atoms are easily moved along the $a_1$ direction. This means that a phase transition from $\beta_0$-PC to $\alpha_0$-PC may occur, consistent with the binding energy results in a previous DFT study.$^{50}$

Using our calculated Eliashberg spectral function $x^2F(\omega)$ and $\lambda$, we calculated the logarithmic average frequency defined as $\omega_\text{log} = \exp \left[ \frac{1}{2} \int_0^\infty d\omega x^2F(\omega) \log \omega \right]$ to be 118.0 K. Using a typical value of the effective screened Coulomb repulsion constant $\mu^* = 0.1$, the superconducting transition temperature $T_c$ can be estimated, according to Bardeen–Cooper–Schrieffer (BCS) theory,$^{53}$ using the Allen–Dynes modified McMillan equation$^{54,55}$

$$T_c = \frac{\omega_\text{log}}{1.2} \exp \left[ \frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right].$$

Our calculated value of $T_c$ is 13.35 K, comparable with that predicted in 2D boron.$^{56,57}$

Superconductivity has been rarely predicted for intrinsic 2D-monolayer systems. In Table 1 we have listed the superconductive parameters of $\mu^*$, $N(E_F)$, $\omega_\text{log}$, $\lambda$, and $T_c$ for some typical 2D phonon-mediated superconductors. All these systems have been predicted to show superconductivity without the external conditions of high pressure, strain, carrier doping, metal decorations/intercalations, and/or functional groups. It is clear that the $T_c$ of $\beta_0$-PC is larger than that of 2D boron ($\gamma$ sheet),$^{59}$ TiSi$_4$,$^{61}$ Li$_2$B$_7$,$^{62}$ Mo$_2$C,$^{58}$ and Cu-BHT,$^{50}$ while it is smaller than that of $\beta_2$C$_6$,$^{60}$ and $\beta_3$C.$^{56}$ Among these systems, $\beta_0$-PC exhibits the largest value of $\lambda$ but holds a relatively small value of $\omega_\text{log}$. The vertical vibrations of the P atoms in $\beta_0$-PC play a role in EPC similar to that of the S atoms in Cu-BHT.$^{50}$

We note that 2D boron sheets have been successfully grown on a Ag(111) substrate.$^{63,64}$ The growth of $\beta_0$-PC on different substrates may also be realized in experiments. In one recent calculation$^{55}$ it was found that strain can modulate the electronic structure and phonon spectrum of $\beta_0$-PC. We wanted to know here the effect of strain on the superconductivity, as it is already known to be critical for graphene and phosphorene.$^{18,22}$ Under a tensile equibiaxial strain of $0% \leq \varepsilon \leq 3\%$, where $\varepsilon = \frac{\Delta L}{L_0} \times 100\%$, the atomic structures are fully relaxed. Most of our calculated phonon dispersions are positive. These results agree well with a previous study,$^{15}$ where $\beta_0$-PC was found to be dynamically stable up to 9.1% strain. We show in Fig. 4a the phonon dispersions together with the magnitude of the EPC $\lambda_\text{q}$ under strains of 2% and 3%. We find that the Kohn anomaly point under a strain of 2% (with some imaginary frequencies) is moved from near the $Y$ point along $I-Y$ (under strains of 0% and 1%) to near the $X$ point along $I-X$. The EPC $\lambda_\text{q}$ at the Kohn anomaly point is extremely large. Upon further tensile strain up to 3%, the Kohn anomaly point over the whole BZ disappears; the phonon frequencies below 300 cm$^{-1}$

<table>
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<tr>
<th>Compounds</th>
<th>$\mu^*$</th>
<th>$N(E_F)$</th>
<th>$\omega_\text{log}$</th>
<th>$\lambda$</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
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<tr>
<td>B$<em>2$/C$</em>{20}$/C$_{21}$</td>
<td>0.1</td>
<td>314.8</td>
<td>0.92</td>
<td>19.2</td>
<td>60</td>
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<tr>
<td>B (3 sheet)</td>
<td>0.05</td>
<td>5.85</td>
<td>262.2</td>
<td>0.52</td>
<td>6.7</td>
<td>59</td>
</tr>
<tr>
<td>B (5 sheet)</td>
<td>0.1</td>
<td>8.12</td>
<td>425</td>
<td>0.69</td>
<td>14</td>
<td>57</td>
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<tr>
<td>TiSi$_4$</td>
<td>0.1</td>
<td>0.59</td>
<td>5.8</td>
<td>61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_2$B$_7$</td>
<td>0.12</td>
<td>462.8</td>
<td>0.56</td>
<td>6.2</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>0.1</td>
<td>0.63</td>
<td>5.9</td>
<td>58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-BHT</td>
<td>0.1</td>
<td>51.8</td>
<td>1.16</td>
<td>4.3</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>$\beta_0$-PC</td>
<td>0.1</td>
<td>7.27</td>
<td>118.0</td>
<td>14.8</td>
<td>13.35</td>
<td>This work</td>
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Table 1 The superconductive parameters of $\mu^*$, $N(E_F)$ (in unit of states per spin per Ry per cell), $\omega_\text{log}$ (in K), $\lambda$ and $T_c$ (in K) for some intrinsic 2D-monolayer-phonon-mediated superconductors.
are strengthened while those above 300 cm⁻¹ are lowered; the EPC \( \lambda_{qv} \) becomes small.

Under strain the overall band structure (shown in Fig. 4b) is shifted downward, and the \( N(E_F) \) (Fig. 4c) is decreased firstly to \(~ 7.1 \) states per spin per Ry per cell \( (\varepsilon = 2\%) \) and is then increased to \(~ 7.3 \) \( (\varepsilon = 3\%) \). Normally, the superconducting related physical quantities of \( \omega_{\text{log}} \) and \( T_c \) should increase or decrease monotonically along with applied strain. However, in our case, \( \omega_{\text{log}} \) decreases firstly to \(~ 90 \) K \( (\varepsilon = 1\%) \) and then increases to 182.8 K at \( \varepsilon = 3\% \) (Fig. 4c); \( \lambda \) and \( T_c \) increase firstly and then decrease (Fig. 4d). The abnormal behaviors of these physical quantities are tightly related to the existence of the Kohn anomaly point under strains of 0–2% where the EPC strengths are extremely enlarged. Under \( \varepsilon = 3\% \) without the Kohn anomaly point, \( \beta_{0\text{-PC}} \) still exhibits the superconducting properties of \( \lambda = 1.01 \) and \( T_c = 13.03 \) K. So, the superconducting behavior in \( \beta_{0\text{-PC}} \) is robust.

Charge carrier doping can also modulate the electronic structure and the phonon spectra of materials. In our present study, the carrier doping was simulated using a jellium model, whereby the excess/defect electronic charge was our present study, the carrier doping was simulated using a jellium model, whereby the excess/defect electronic charge was drawn proportional to the magnitude of the EPC \( \lambda_{qv} \) for strains of 2% and 3%, respectively. The red circles have been reduced 20-fold. (b) Band structures. The Fermi energy level is set at zero. (c) \( \omega_{\text{log}} \) and \( N(E_F) \) and (d) \( T_c \) and \( \lambda \) under strain. The lines in (c and d) are only visual guides.

Under the conditions of the hole doping, as indicated in Fig. 5, the Kohn anomaly point near the \( Y \) point along \( \Gamma-Y \) is still evident. The phonon frequencies below 300 cm⁻¹ are slightly lowered, and those above 300 cm⁻¹ are slightly raised. As a result, the EPC \( \lambda_{qv} \) on the first acoustic branch is still large and the total \( \lambda \) is only reduced to 1.43 and 1.07 at doping levels of 0.1 and 0.2 h per cell, respectively. The overall band structures are shifted upward and \( N(E_F) \) is increased to \(~ 7.6 \) and 8.0 states per spin per Ry per cell, \( \omega_{\text{log}} \) is increased to 120 and 174 K, and \( T_c \) is modulated to 13.09 and 13.47 K. These results indicate that hole doping, although changing the electronic structure and phonon spectrum of \( \beta_{0\text{-PC}} \) to some extent, induces limited effects on the superconducting transition temperature.

High-quality graphene and MoS₂ have been successfully grown on substrates experimentally without substantially affecting their crystal structures. Thus, one would expect that \( \beta_{0\text{-PC}} \) could also be fabricated or transferred on some other potential substrates. Here, we recommend the use of Cr₂AlC as a substrate to fabricate \( \beta_{0\text{-PC}} \) since the hexagonal lattice constant of Cr₂AlC is equal to 2.857 Å. This value matches well with the \( a_2 \) of graphene-like \( \beta_{0\text{-PC}} \). Theoretically, the h-BN substrate has been predicted to enhance the superconducting transition temperature of Li-decorated graphene while the Ag(111) substrate may effectively suppress the \( T_c \) of \( \beta_{12} \) borophene. Thus, the effects of the substrate on the superconductivity are indeterminate and experiments are needed to clarify them.

**Conclusions**

In summary, we have investigated the structure, electronic structure, phonon spectrum, EPC, and superconducting properties of...
monolayer phosphorus carbide ($\beta_0$-PC) using first-principles calculations. We predicted that this intrinsic monolayer material, the first example within the 2D carbon and phosphorus families, is an intermediate conventional superconductor. The out-of-plane $P_2$ vibrations together with the lone pair electrons of P-$P_2$ play a dominant role for the EPC. The superconducting behavior in $\beta_0$-PC is robust, and even under conditions of tensile equibiaxial strain or electron doping the Kohn anomaly point is suppressed. Our findings provide a new choice in realizing 2D superconductors and will inspire further efforts in this field.

Conflicts of interest
There are no conflicts to declare.

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References


