

Point Defects in Two-Dimensional γ -Phosphorus Carbide

Andrey A. Kistanov^{†,}, Vladimir R. Nikitenko[‡], Oleg V. Prezhdo^{‡,§}*

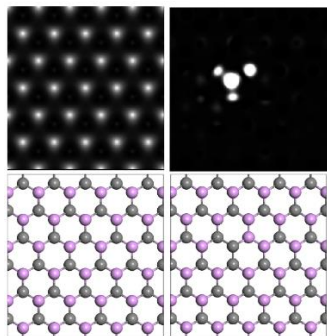
[†]Nano and Molecular Systems Research Unit, University of Oulu, 90014 Oulu, Finland

[‡]National Research Nuclear University MEPhI, 115409 Moscow, Russia

[§]Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States

ABSTRACT: Defects are inevitably present in two-dimensional (2D) materials and usually govern their various properties. Here a comprehensive density functional theory-based investigation of 7 kinds of point defects in a recently produced γ allotrope of 2D phosphorus carbide (γ -PC) is conducted. The defects, such as antisites, single C or P, and double C and P and C and C vacancies, are found to be stable in γ -PC, while the Stone–Wales defect is not presented in γ -PC due to its transition metal dichalcogenides-like structure. The formation energies, stability, and surface density of the considered defect species as well as their influence on the electronic structure of γ -PC is systematically identified. The formation of point defects in γ -PC is found to be less energetically favourable than in graphene, phosphorene, and MoS₂. Meanwhile, defects can significantly modulate the electronic structure of γ -PC by inducing hole/electron doping. The predicted scanning tunneling microscopy images suggest that most of the point defects are easy to distinguish from each other and that they can be easily recognized in experiments.

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KEYWORDS: first-principles calculations; nanomaterials; defect engineering; phosphorus carbide; scanning tunneling microscopy

Over the past decade, two-dimensional (2D) materials have become common building blocks in various branches of science and industry.^{1,2} Complex theoretical and advanced experimental studies allow obtaining new atomically thin structures, including hybrid structures of already discovered 2D materials.³⁻⁷ Specifically, the structural similarity of graphene and phosphorene has allowed the theoretical prediction⁸⁻¹⁰ of a new family of 2D phosphorus carbide (PC) materials consisting of carbon and phosphorus. Later, the experimental discovery^{11,12} of 2D PC allotropes has been achieved by combining the theoretical predictions and previous experimental observations indicating that different ratios of PH₃/CH₄ gases during the radio frequency plasma deposition process lead to different atomic ratios of P/C, producing different structures in phosphorus carbide.¹³ Depending on the geometry of their structure these 2D PC allotropes can vary from metallic to semi-metallic to wide bandgap semiconducting.^{9,14,15}

One of the most extraordinary allotropes of 2D PC, γ -PC with a unique γ -InSe-like structure, has not been considered until recently. The first investigation on γ -PC has been reported by Claeysens et al.,¹⁶ who have considered stability and electronic structure of the bulk form of γ -PC. Later, theoretical studies have proposed an atomically thin γ -PC layer.^{10,17} γ -PC can be distinguished from other PC allotropes by its superior structural stability, resistance to deformation, ultrahigh conductivity,¹⁰ and excellent ability to recover upon interaction with environmental molecules.¹⁷ Further, monolayer γ -PC is also predicted to show semiconducting behaviour with a direct bandgap of ~2.60 eV.¹⁰ Despite the recent emergence, 2D allotropes of PC have already showed extremely high potential for applications in optoelectronics,¹⁸ lithium-ion batteries,¹⁰ single-photon source,¹¹ high-performance field-effect transistors,¹² and gas- and bio-sensors.¹⁷

It is commonly accepted that all 2D layered materials host structural defects such as point defects,¹⁹⁻²² which are usually generated by ion/electron irradiation or by mechanical damage of the material.²³ Defects strongly influence material structure and properties, and therefore

need to be accounted for in applications.²⁴⁻²⁶ Similar to other 2D materials, γ -PC surfaces may contain structural defects, which may affect performance of γ -PC-based devices. However, to our knowledge, no comprehensive studies have focused on typical point defects in γ -PC up to date. Thus, the influence of point defects on the characteristics of γ -PC in applications is unknown. In this work, *ab initio* electronic structure and molecular dynamics calculations are used to systematically study the geometry, stability, and electronic properties of typical point defects in γ -PC. Theoretical guidance on the experimental routes of detection of these defects in γ -PC is provided.

Figure 1a-f shows the geometry of perfect γ -PC and the most common typical point defects found to be stable in γ -PC. These are antisite defect (AD), single vacancy of a C atom (SV_C), single vacancy of a P atom (SV_P), double vacancy of one C atom and one P atom (DV_{CP}), and double vacancy of two P atoms (DV_{CC}). It should be noted that, differently from graphene-like 2D materials, the Stone–Wales (SW) defects are not formed in transition metal dichalcogenides (TMDs) due to the polar nature of chemical bonds with trigonal symmetry.²⁷ Here we found that γ -PC that possesses a TMDs-like structure is also free of SW defects (Section 1 in SI and Figure S1 and movie 1). As shown in Figure 1b, AD occurs by exchanging the positions of neighbouring C and P atoms. Two kinds of SV defects can be produced by removing the C or P atom from γ -PC, as shown in Figures 1c and d, respectively. There are five kinds of divacancy (DV) defects in γ -PC. The first is the DV_{CP} defect which is created when two neighbouring atoms (one C atom and one P atom) are removed from the γ -PC surface (Figure 1e). DV_{CC} is formed when two C atoms are removed from the γ -PC surface (Figure 1f). The remaining DV defects formed when two C or P (DV_{PP}) atoms are removed from the surface or from the plane perpendicular to the surface are found to be unstable in γ -PC or leading to its destruction. More specific changes in the geometry of γ -PC induced by point defects are show in Figure S2 and are discussed in Section 2 in supporting information (SI).

The *ab initio* molecular dynamics (AIMD) simulations are performed to check the thermal stability of the considered defects in γ -PC. The initial states at the time $t = 0.0$ ps for the performed calculations are set to optimized geometric structures of defect-containing γ -PC. It is predicted that only AD, SV_C , SV_P , DV_{C+P} , and DV_{CC} are stable in γ -PC at 400 K for times longer than 2.0 ps (detailed information is presented in Section 3 in SI, and Figures S3-S7 and movies 2-6). In all the remaining cases the vacancies rather annihilate, as in the case of the SW defect, or lead to the disintegration of the γ -PC structure, as in the case of the DV_{PP} defect (movie 7).

The stability of the considered point defects in γ -PC is also considered in terms of their formation energy E_{form} , which is calculated as

$$E_{\text{form}} = E_{\text{perfect}} - E_{\text{defect}} - N_C \cdot E_C - N_P \cdot E_P \quad (1)$$

where E_{perfect} and E_{defect} are the total energies of perfect and defect-containing γ -PC, E_C and E_P are the energies of a single carbon and phosphorus atom, and N_C and N_P correspond to the number of the removed carbon and phosphorus atoms.

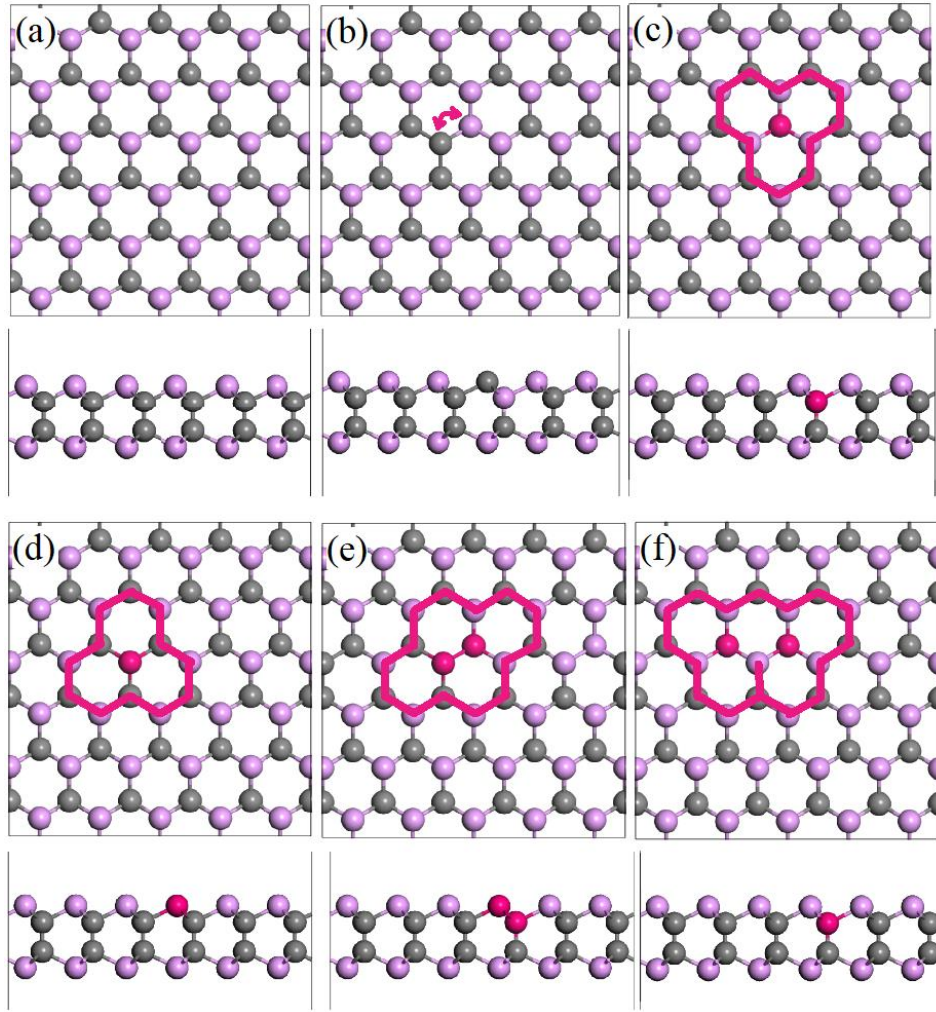


Figure 1. The schematic top and side views of (a) perfect and (b) AD⁻, (c) SV_C⁻, (d) SV_P⁻, (e) DV_{CP}⁻, and (f) DV_{CC}⁻-containing γ -PC. The area of the considered point defects is marked by the pink lines. The carbon, phosphorus, and vacant atoms are colored in gray, violet, and pink.

The calculated E_f of the considered stable defects in γ -PC is presented in Table 1. According to Table 1, E_f of AD is the lowest among the considered defects. The SV_P defect has a ~ 1.9 times lower E_f (5.48 eV) compared to the SV_C defect (10.39 eV). For comparison, E_f of SV in graphene is 7.5 eV,²⁸ and E_f of SV in phosphorene is ~ 1 -2 eV.²⁹ For the most common TMDs material, MoS₂, E_f of the SV defects varies from 2.12 (sulfur vacancy) to 6.20 eV (molybdenum vacancy).³⁰ Therefore, the formation of SVs in γ -PC is less favorable compared to that in phosphorene and MoS₂, and is similar to that in graphene. Among DVs, DV_{CP} has the lowest $E_f = 13.80$ eV, while E_f of DV_{CC} is much higher and is equal to 18.87 eV. For comparison, E_f of DV in graphene²⁸ is ~ 8 eV, E_f of DV in phosphorene²⁹ is ~ 2 -3 eV, and E_f of

DV in MoS₂³⁰ is ~4 eV. Thus, the formation of the DVs in γ -PC is much less favorable energetically than in graphene, phosphorene, and MoS₂.

Table 1. The calculated formation energy E_f (eV) of point defects in γ -PC.

	AD	SV _C	SV _P	DV _{CP}	DV _{CC}
γ -PC	1.28	10.39	5.48	13.80	18.87
graphene ²⁸	-	7.5		8	
phosphorene ²⁹	-	1-2		2-3	
MoS ₂ ^{30,31}	5.77, 5.79	2.12, 6.20		4	

Further, the surface density of defects in γ -PC, at a finite temperature, is evaluated (detailed information is presented in Section 4 in SI). It is found that point defects in γ -PC have much lower surface densities compared to phosphorene²⁹ and MoS₂,³² while the surface density of some defects such as DVs in graphene²⁹ is slightly higher than in γ -PC (Figure S8 in SI). This also confirms that the creation of point defects in γ -PC is less energetically favorable than in phosphorene²⁹ and MoS₂,³² but may be more energetically favourable than in graphene.²⁹ The obtained results may indicate high structural stability of γ -PC, as defects usually lead to faster degradation of 2D surfaces.²⁹ On the other hand, the estimated comparably low thermodynamic probability of point defect formation in γ -PC can be much higher during manufacturing, as it is common for most 2D materials,³³ since synthesis may be governed by kinetic factors. Furthermore, the defects concentration in γ -PC can be controlled by means of defect engineering.³⁴

The simulated scanning tunnelling microscopy (STM) images of perfect and defect-containing γ -PC are obtained to facilitate differentiation of point defects in γ -PC experimentally. Based on the expected STM characterization methods, both a constant height mode, which is faster but useful only for relatively smooth surfaces, and a constant current mode that measures irregular surfaces with high precision, but is more demanding, are considered. The STM images of the perfect γ -PC and γ -PC containing point defects are presented in Figure 2 (constant height mode) and Figure S9 (constant-current mode at a +1.0 V

bias). Most defects correlate with their defective atomic structures and are easy to recognize. For instance, the AD in γ -PC can be easily recognized in both types of STM images, because it appears as one middle bright spot surrounded by smaller bright spots (Figure 2b and Figure S9b), which are contributed by the unoccupied states from the carbon and phosphorus atoms at the defect site. The STM image at the +1.0 V bias gives a clear view of the of the SV_C defect with three bright spots and three grey lines connecting phosphorus atoms (Figure S9c). The SV_P defect in γ -PC (Figure 2d) is also easy to recognize, it is presented by nine bright spots, which are contributed by three carbon atoms around the defect core. The DV_{CP} defect (Figure 2e) show similar STM images as the SV_C defect (Figure 2c) with bright spot. To distinguish between these defects in the experiments advanced methods are needed. In particular, it is possible to differentiate these two defects at the +1.0 V bias by comparing their atomic structures and STM images (Figures S9c and e). The DV_{CC} defect in γ -PC can be distinguished by comparing the atomic structures and STM images (Figure 2f and Figure S9f).

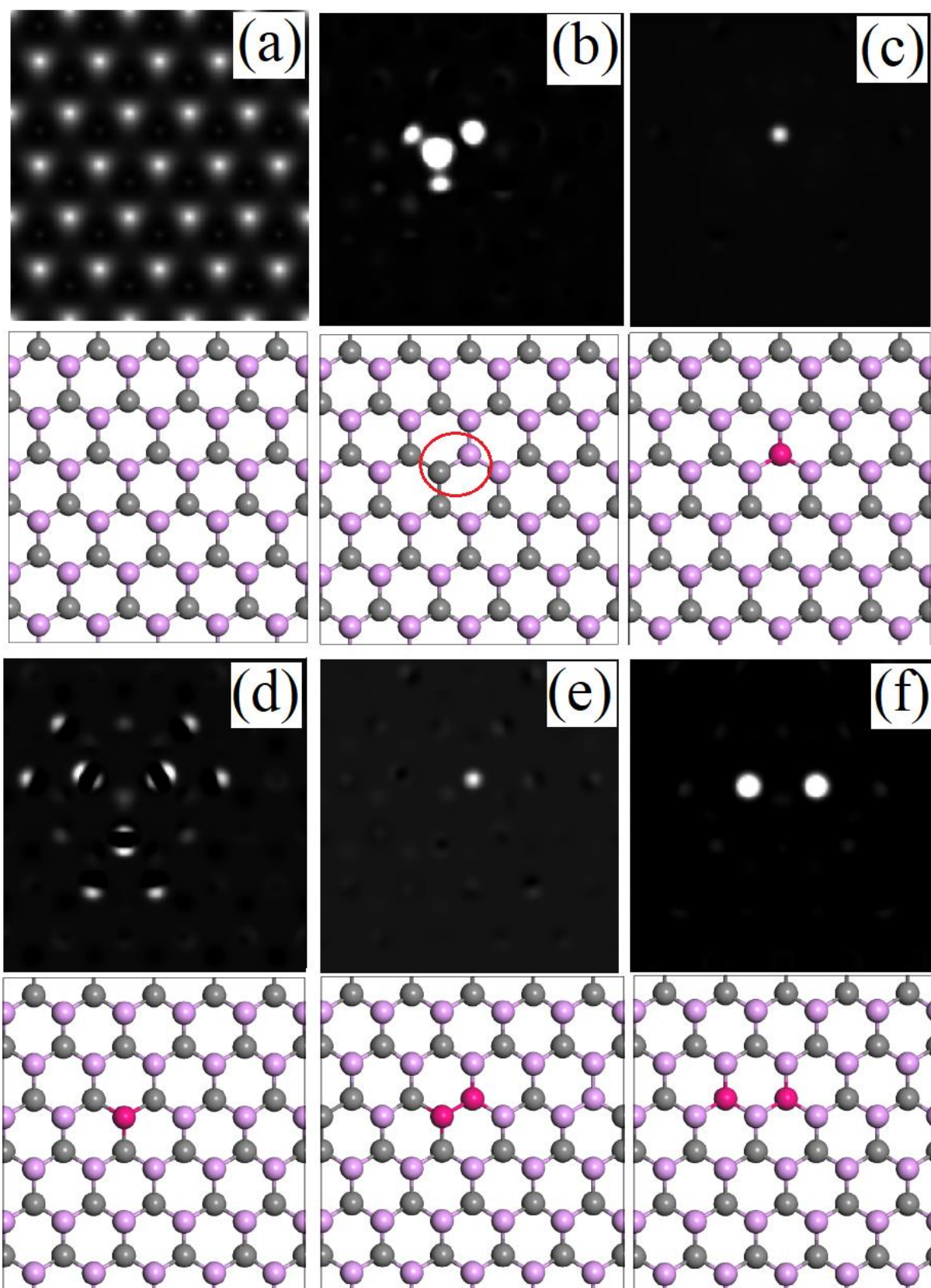


Figure 2. The STM images at a constant height mode (the upper panels) and the geometry (the lower panels) of (a) perfect and (b) AD-, (c) SV_C^- , (d) SV_P^- , (e) DV_{CP}^- , and (f) DV_{CC}^- -containing γ -PC. The carbon, phosphorus, and vacant atoms are colored in gray, violet, and pink.

It has been proven that the local electronic properties of 2D materials may change substantially around the defect sites due to breaking of the lattice periodicity.³⁵⁻³⁷ Figures 3a-f show the band structure plots of (a) perfect and (b) AD-, (c) SV_C-, (d) SV_P-, (e) DV_{CP}-, and (f) DV_{CC}-containing γ -PC. There is a significant realignment of bands in the band plots of vacancy-containing γ -PC, and there are non-zero states at the Fermi level in the cases of SV_C and SV_P. These newly formed localized states in the bandgap of the host γ -PC can be attributed to the dangling bond states due to defects in γ -PC, similarly to those in phosphorene^{29,38} MoS₂.^{30,36}

Perfect γ -PC is found to be a semiconductor with an indirect bandgap of 1.51 eV according to the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional under the generalized gradient approximation (GGA) (Figure 3a), and 2.58 eV according to the hybrid exchange–correlation functional of Heyd–Scuseria–Ernzerhof (HSE) (Figure S10 in SI). This is in a good agreement with the previous studies.^{10,17} Considering the lower computational load, the GGA method is used in further calculations. More detailed discussion on the bandgap calculations techniques can be found in Section 6 in SI. It should be noted that the bandgap of perfect γ -PC is larger than those of phosphorene (~0.91 eV GGA value and 1.88 eV HSE value)^{29,38} and MoS₂ (1.8 eV HSE value).³⁴

According to Figure 3b, the AD leads to a downward shift of the valence and conduction bands and appearance of defect states in the fundamental bandgap of γ -PC, 0.45 eV below the Fermi level. However, AD-containing γ -PC remains a semiconductor with almost the same indirect bandgap of 1.47 eV. Similar behavior is common for MoS₂ in the presence of ADs.³⁰ To understand the effect of concentration of ADs on the band structure of γ -PC, two ADs in are considered the same simulation cell, i.e. the AD concentration increased two times (Figure S16 in SI). Additional defect states appear below the Fermi level in the fundamental bandgap of γ -PC. On the other hand, there is no significant readjustment of bands in γ -PC which remains a semiconductor with the host bandgap of 1.47 eV. Considering the predicted low concentration

of defects in γ -PC, we expect a minor influence of the defect concentration, particularly the concentration of the AD, on the electronic properties of γ -PC. For the SV_c defect, removal of a carbon atom from perfect γ -PC creates unpassivated phosphorus atoms and dangling bonds in the defect core which lead to the formation of unoccupied localized states in the γ -PC fundamental bandgap, as shown in Figure 3c. A partially occupied defect-induced band, which crosses the Fermi level, appears at about 0.34 eV above the valence band maximum (VBM) of the host γ -PC. According to Figure 3d, in case of the SV_P defect, the valence bands are greatly upshifted, while partially occupied defect band located at about 0.25 eV above the VBM crosses the Fermi level. This suggests easy generation of hole states in γ -PC (p -type conductivity) even upon moderate thermal excitations, which is similar to the behavior of phosphorene with a single vacancy defect.³⁸

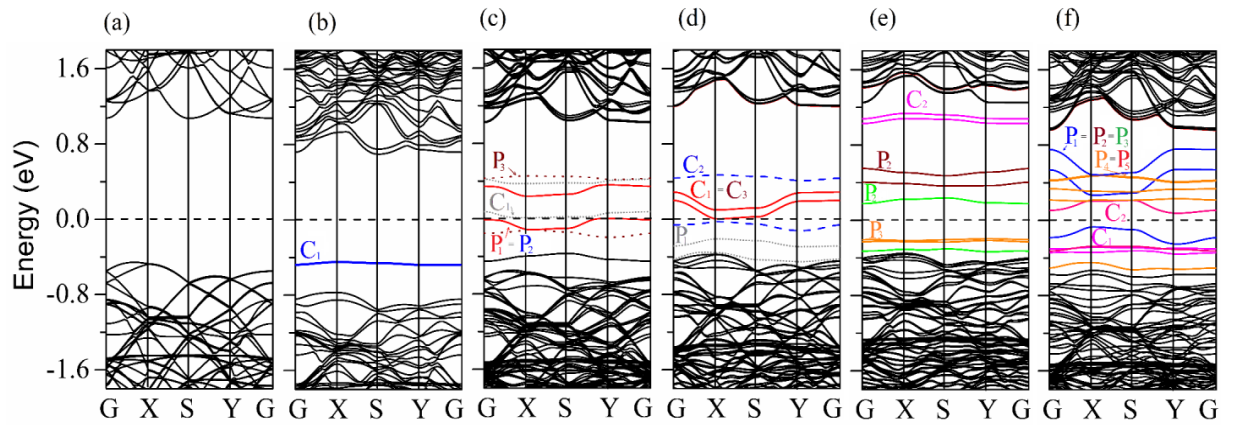


Figure 3. The band structure of (a) perfect and (b) AD⁻, (c) SV_c ⁻, (d) SV_P ⁻, (e) DV_{CP} ⁻, and (f) DV_{CC} ⁻-containing γ -PC. The Fermi level is marked by the black dashed line and is set to zero. The in-gap states are labelled according to Figure 5.

Based on Figure 3e, defect states with nearly flat band dispersion for the DV_{CP} defect reside inside in the fundamental bandgap of γ -PC. Although DV_{CP} containing γ -PC exhibits a significant readjustment of the band lines, it still has a bandgap of 1.45 eV (0.37 eV including in-gap states). In addition, the valence and conduction bands become flatter, and as a result, the conduction band minimum (CBM) of the host γ -PC shifts from the S point (for perfect γ -PC) to the Y point, and the VBM of the host γ -PC shifts from the X point (for perfect γ -PC) to the

vicinity of the Y point. This change in the band structure, signifying the possibility of an indirect-to-direct bandgap transition in γ -PC in the presence of the DV_{CP} defect, may affect the optical emission efficiency of γ -PC. Importantly, as shown above, it may be hard to distinguish the SV_C and DV_{CP} defects in an STM image. As these defects induce remarkably different changes in the band diagram of host γ -PC, they may be distinguished from each other via photoemission spectroscopy techniques.³⁹ The band structure of DV_{CC} -containing γ -PC is shown in Figure 3f. Partially occupied defect bands are mixed with the valence bands of the host γ -PC and are located at about 0.07 eV below the Fermi level. In addition, there are defect bands located 0.07 eV above the Fermi level. Therefore, both n - and p -type conductivity is possible in γ -PC.

The density of states resolved in space known as local density of states (LDOS), computed for peripheral atoms in the defect core and for atoms far from the defect core are significantly different, which suggests that the states are renormalized greatly in the defect core. Therefore, to better understand the changes in the band structure of γ -PC due to the presence of point defects in terms of the contribution of each atom within the defect core, LDOS plots for these atoms are evaluated, as shown in Figure 4. The states introduced by the AD are mainly contributed by the C_1 atom and with a minor contribution from the P_1 atom (Figure 4a). The changes depicted at the band structure diagram of SV_C -containing γ -PC (Figure 3c) arise mainly from the P_1 , P_2 , P_3 , and C_1 atoms (Figure 4b). Similarly, the defect-induced states in the band structure of SV_P -containing γ -PC (Figure 3d) mainly originate from the C_1 , C_2 , C_3 , and P_1 atoms (Figure 4c). In the case of DV_{CP} -containing γ -PC (Figure 4d), the $P1-3$ (major contribution) and $C1-3$ atoms (minor contribution) surrounding the defect have partially occupied/unoccupied states contributing into the valence/conduction bands of the host γ -PC (Figure 3e). The $P1-5$ and $C1-2$ atoms (Figure 4e) are responsible for the in-gap states appearing at the band structure plot of the DV_{CC} -containing γ -PC (Figure 3f). An additional discussion of the impact of each atom in the defect core on the electronic structure of

defect-containing γ -PC is presented in Section 7 in SI, which presents projected density of states (PDOS) and provides information on the contributions of the different orbitals of the considered atoms.

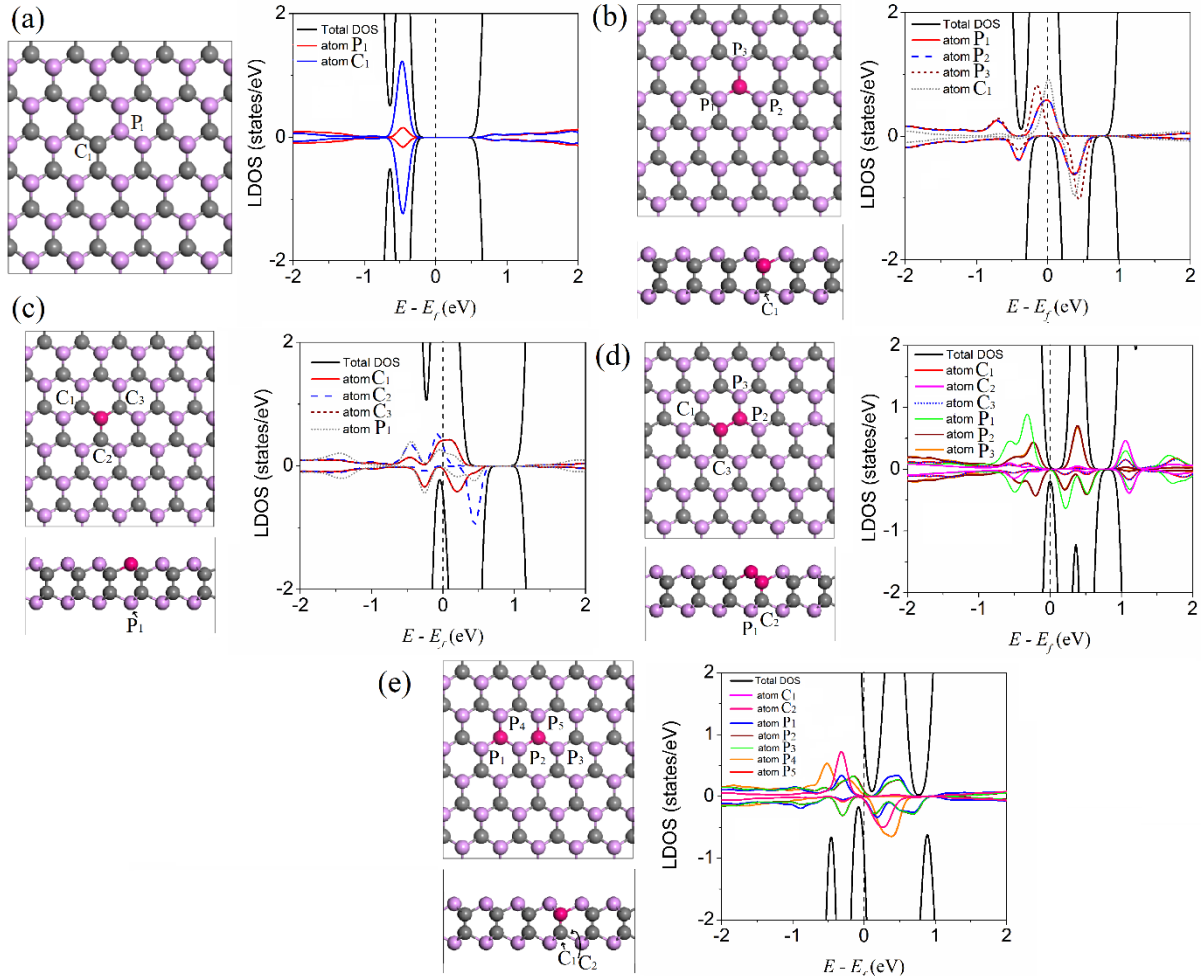


Figure 4. Defect geometry with atoms in the defect core labelled by numbers (left panel) and LDOS of atoms in the defect core (right panel) for (a) AD^- , (b) SV_C^- , (c) SV_P^- , (d) DV_{CP}^- , and (e) DV_{CC}^- -containing γ -PC. The Fermi level is marked by the black dashed line and is set to zero.

To further understand the influence of point defects on the electronic structure of γ -PC, the electron localization function (ELF) of defect-containing γ -PC is calculated. The value of the ELF maps reflects the degree of charge localization in the real space. The value ranges between 0 and 1, where 0 represents a free electronic state, while 1 represents a perfect localization. The isosurface value of 0.70 is adopted in Figure 5, in which the ELF maps for AD^- , SV_C^- , SV_P^- , DV_{CP}^- , and DV_{CC}^- -containing γ -PC are presented. In all cases, in the area far

away of the defect, the electrons are localized at the C-C and C-P bonds and P atoms, while C atoms are free of the electrons. In case of AD-containing γ -PC (Figure 5a) the electrons are clearly packed together at the C_1 atom, while the P_1 atom become empty of electrons. In addition, slight localization of electrons is observed at two P-P bonds of the P_1 atom in the defect core. It can be concluded that the C_1 atom forms strong sp^2 bonds with neighboring C atoms, while the P_1 atom has unpassivated dangling bonds. That can explain the formation of empty states within the original bandgap of γ -PC, as it is shown at the band structure plot in Figure 3b. According to Figure 5b, in case of the SV_C defect, the charge simply redistributes from the removed C atom to the neighboring P_1 , P_2 , P_3 , and C_1 atoms. As indicated in Figure 5c, the presence of the SV_P defect leads to an increase of the charge localization at the C_2 - P_1 bond and the C_2 atom in the defect core. That indicates a strong covalent chemical bonding between the C_2 atom in the defect core and the P_1 atom right below the absent P atom. Strong electron redistribution is observed in the DV_{CP} -containing γ -PC (Figure 5d). A full depletion of electrons from the C_1 - P_1 and C_3 - P_1 bonds and their almost full depletion from the C_2 - P_1 bond in the defect core are found. In addition, a strong electron localization at the P_1 atom located right below the absent P atom and the C-C bond of the C_1 atom is also found. Therefore, the C_1 - P_1 and C_3 - P_1 bonds of the P_1 atom, are broken and the C_2 - P_1 bond of the P_1 atom is nearly broken. Consequently, the presence of the DV_{CP} defect leads to the formation of a hole in the γ -PC layer. As indicated in Figure 5e, the DV_{CC} defect in γ -PC leads to an increase of electron localization at the P_1 - P_5 , C_1 , and C_2 atoms and the P-P and C-P bonds of the P_6 atom, while there are no localized electrons at the P_6 atom itself. The increase in the electron localization at the bonds of the P_6 atom indicates the formation of a strong covalent chemical bonding between the P_6 and P_2 , and P_6 and C_3 atoms.

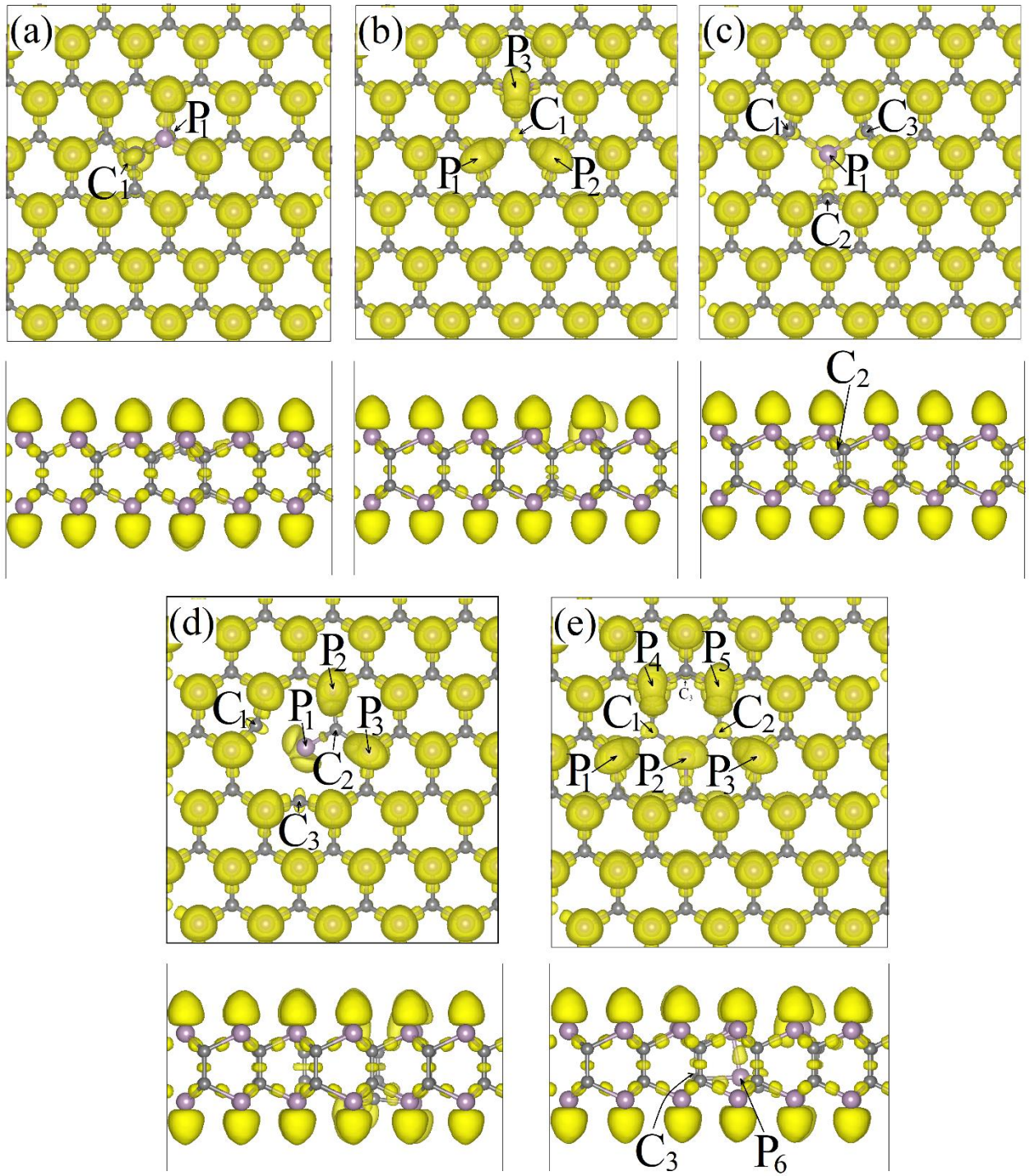


Figure 5. The ELFs for (a) AD⁻, (b) SV_c⁻, (c) SV_p⁻, (d) DV_{cp}⁻, and (e) DV_{cc}⁻-containing γ -PC. The isosurface value is set to 0.7.

In summary, density-functional theory (DFT) and *ab initio* molecular dynamics calculations have been used for the systematic study of the geometry, stability, and electronic structure of typical point defects in γ -PC. It is found that the Stone-Wales defect is unlikely to form in γ -PC due to its TDMs-like structure. Nevertheless, γ -PC may host a wide variety of

other point defects, such as antisites, SVs, and DVs. All these defects (except DV_{PP}) are found to be highly stable in γ -PC at the temperature of 400 K. The energy input required for the formation of single and double vacancies is comparable to that for graphene and is ~2 times higher than that for phosphorene and MoS₂. The simulated scanning tunnelling microscopy images have shown the possibility of the identification of the considered point defects in γ -PC in experiments. The predicted stable defects also impose significant changes in the electronic structure of γ -PC, which allows their identification via photoemission spectroscopy techniques. Despite the predicted comparably low concentration of point defects in γ -PC, it may be possible to control hole/electron doping in γ -PC by defect-engineering as in graphene and phosphorene.⁴⁰ This reported work provides valuable insights into the influence of point defects on the electronic properties of γ -PC, facilitates their identification in experiments, and widens potential applications of γ -PC.

Methods

The spin-polarized DFT-based simulations were used in this work as implemented in the Vienna Ab initio Simulation Package.⁴¹ The PBE GGA⁴² and HSE06⁴³ functionals were adopted for the geometry optimization and electronic structure calculations of perfect γ -PC. In electronic structure calculations of defect-containing γ -PC the GGA PBE functional was used. The geometries of all structures were fully optimized until the total energy and all forces on the atoms converged to less than 10⁻⁸ eV and 0.01 eV/Å, respectively. The cutoff energy for plane waves was set to 400 eV. The calculated lattice parameters of γ -PC were found to be $a = 3.09$ Å and $b = 5.35$ Å. The considered supercell of γ -PC was composed of 5×3 unit cells (60 C and 60 P atoms). The concentration of SVs is 0.83% (one C/P-defect per 120 atoms) and the concentration of DVs is 1.67% (two C/P-defects per 120 atoms). The periodic boundary conditions were applied for the two in-plane transverse directions while the vacuum depth of 15 Å was introduced to the direction perpendicular to the surface plane to avoid artificial

interactions in the considered supercells. AIMD calculations⁴⁴ were conducted at 400 K to verify the thermal stability of defects in γ -PC. The AIMD simulations lasted 2 ps or longer, and were carried out with a 1.0 fs time step. The temperature was controlled by the Nose–Hoover thermostat.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.XXXX.

AIMD results on the stability of the SW[−], AD[−], SV_C[−], SV_P[−], DV_{CP}[−], DV_{CC}[−], and DV_{PP}[−]-containing γ -PC (Figures S1, S3-S6 and Movies 1-7); the geometry of defects in γ -PC (Figure S2); the comparison of the surface density of the defects in γ -PC, graphene, phosphorene, and MoS₂ (Figure S8); the STM images of AD[−], SV_C[−], SV_P[−], DV_{CP}[−], and DV_{CC}[−]-containing γ -PC (Figure S9); the comparison of the electronic structure calculations using the GGA PBE and HSE06 methods (Figure S10); the partial density of states of atoms in the defect core of defect-containing γ -PC (Figures S11-S15).

AUTHOR INFORMATION

Corresponding Authors

*E-mail: andrey.kistanov@oulu.fi

Notes

The authors declare no competing financial interest.

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