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N.B.: When citing this work, cite the original article.

Original Publication:

Gueorgui Kostov Gueorguiev, Zs Czigany, Andrej Furlan, Sven Stafström and Lars Hultman, Intercalation of P atoms in Fullerene-like CP_x, 2011, CHEMICAL PHYSICS LETTERS, (501), 4-6, 400-403.

<http://dx.doi.org/10.1016/j.cplett.2010.11.024>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-66312>

Intercalation of P atoms in Fullerene-like CP_x

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Abstract

The energy cost for P atom intercalation and corresponding structural implications during formation of Fullerene-like Phosphorus carbide (FL- CP_x) were evaluated within the framework of Density Functional Theory. Single P atom interstitial defects in FL- CP_x are energetically feasible and exhibit energy cost of 0.93–1.21 eV, which is comparable to the energy cost for experimentally confirmed tetragon defects and dangling bonds in CP_x . A single P atom intercalation event in FL- CP_x can increase the inter-sheet distance from 3.39–3.62 Å to 5.81–7.04 Å. These theoretical results are corroborated by Selected Area Electron Diffraction characterization of FL- CP_x samples.

1. INTRODUCTION

Predictive *Ab-initio* simulations constitute a valuable tool for designing new materials by addressing the detailed relation between structure and properties. Led by this idea, we developed the Synthetic Growth Concept (SGC) based on the Density Functional Theory (DFT) [1, 2] for simulations of film formation during vapor phase deposition. SGC treats structural evolution by sequential steps of atomic rearrangement where each step is assigned according to the previous relaxed states. This enables a variety of precursors for nanostructured compounds to be systematically addressed for their interaction when they form condensed phases. The structural patterns thus formed are relevant to the film formation and eventually to the assessment of material's properties [2].

Currently, carbon-based nanostructured materials attract intense research interest due to the rich diversity of their structural and bonding features leading to a plethora of mechanical, electronic, optical, and chemical characteristics useful for applications [3, 4]. By employing SGC we introduced a new class of carbon-based materials which can be unified by the term Fullerene-Like (FL) carbon-based solid compounds alloyed with N and P. Currently, fullerene-like Carbon Nitride (FL-CN_x) is one of the most promising industrially applied CN_x compounds with outstanding mechanical properties [5]. Employing SGC, we predicted FL phosphorus-carbide (FL-CP_x) [6, 7], and successfully guided its deposition by magnetron sputtering. The SGC predictions for remarkable mechanical properties of FL-CP_x – high hardness and high elasticity, were also confirmed by experiments [8, 9].

The structural and electronic properties of P-doped graphene-like systems have been theoretically addressed also by other researcher groups. At the same level of theory as the

SGC, Melchor *et al.* investigated the bonding of atomic P to graphene systems, hydrocarbons and fullerene cages and concluded that the bonding of P atoms both induces and enhances curvature in such structures [10]. Recently, Garcia *et al.* confirmed the strong local curvature and the increased local reactivity for P-doped graphene sheets [11] - both of these findings key features defining the FL-CP_x properties [6].

While C-P compounds have been previously produced as amorphous thin film material over a wide range of P:C composition ratios up to 3 [12, 13]; the P-containing Carbon-based systems which are closest to the FL-CP_x with respect to their composition are the P-doped diamond-like carbon (P-DLC) films [14–16] with P content typically reaching 10–11 at.%. P-DLC thin films are electrically conducting at room temperature and exhibit significant mechanical hardness. However, compared to DLC compounds, the FL-structure thin films in general, and the FL-CP_x in particular, possess a superior resiliency to mechanical deformation based on their unique super-elasticity [5, 8, 17].

Due to the importance of FL compounds for applications such as protective coatings where the water absorption plays a significant role, applying SGC, also the density of dangling bonds in FL-CN_x and FL-CP_x (as well as their amorphous counterparts), was addressed [18-20].

In the present work, we report the energy cost obtained by SGC for P atoms intercalated in FL-CP_x and discuss how such interstitial defects influence the conformations with short-range order typical for this compound. These theoretical findings are corroborated by characterization results obtained for FL-CP_x by Selected Area Electron Diffraction (SAED) [21] and high-resolution transmission electron microscopy imaging [8, 21].

2. COMPUTATIONAL DETAILS

The recursion model developed for the purposes of SGC [1, 2] has been applied to the FL-CP_x compound in order to investigate if P intercalation defects are feasible. For this purpose relaxed, curved, cross-linked, and cage-like model systems typical for FL-CP_x [6] were investigated. In addition, previous knowledge about precursor selection for FL-CP_x film formation [7] was taken into account.

Following a scheme similar to our previous works [6, 7, 20] involving simulation of film growth events within the SGC, geometry optimizations and cohesive energy (E_{coh}) calculations were performed at the Generalized Gradient Approximation (GGA) to DFT level of theory. Different possible interstitial locations for single P atoms between the short and curved graphene-like FL-CP_x sheets were investigated and compared to alternative P incorporation at substitutional sites in the graphene network.

The cohesive energy E_{coh} of a model system is trivially defined as the energy required for breaking the system into isolated atomic species, i.e.,

$$E_{\text{coh}} = E_{\text{total}} - \sum_i E_{i,\text{total}}^{\text{isolated}},$$

where i represents the index of summation over all constituent atoms. Regarding E_{coh} , the term “model system” also includes its weakly bound fragments and/or individual atoms if present.

The size of model systems adopted (estimated by the number of C and P atoms these systems contain) is, in average, comparable or larger than the size of the models used by others for similar material systems and properties addressed at a similar level of theory [10, 11].

The feasibility of an intercalation defect is directly related to its energy cost defined as the difference in the cohesive energies $|\Delta E_{coh}|$ between a pair of model systems: one containing the interstitial defect and the other – entirely analogous but without intercalation.

All simulations were carried out by using the GAUSSIAN 03 program [22] with the 6-31G* basis set and by employing the Perdew–Wang 91 hybrid functional [23]. This functional is known to provide an accurate description of the structural and electronic properties of fullerene-like thin films [1, 2, 6, 20] and systems with prevailing covalent bonding [24–26]. In order to ensure that the results reported here do not depend on the exchange correlation functional and the basis set adopted, test calculations employing the B3LYP [27] hybrid exchange correlation functional and the cc-pVTZ basis set augmented with diffuse functions were also carried out.

3. RESULTS AND DISCUSSION

3.1 Theoretical Modeling

FL-CP_x model systems containing structural features typical for this compound such as cage-like formations and tetragon defects, as well as cross-linked and interlocked graphene sheets [6] were considered in their variants with and without single interstitial P atoms, respectively. Also configurations containing a very low concentration of substitutional P atoms at C sites were considered.

The prevalence of interstitial defects was simulated by letting the model systems containing an intercalated P atom evolve: allowing for randomly perturbed atomic

positions followed by subsequent geometry relaxation, in the sense of SGC as applied in Refs. [1, 2, 6].

Our simulation results clearly indicate that P atom intercalation in conformations consisting of nearly plane graphene sheets without inter-locking is energetically unlikely. For example, in such systems containing very low concentrations (≤ 1 at. % P) of substitutional P atoms at C sites, the geometry relaxation procedure normally results in ejection of the interstitial P atom from the space between the graphene sheets. Thus, the energy cost for P intercalation can be discussed quantitatively only for model systems able to accommodate an interstitial defect, i.e., a system retaining a single P atom at an interstitial (as opposed to substitutional) site after relaxation. Such “susceptive” to P-intercalation conformations proved to be the curved/inter-locked configurations (containing ≥ 10 at. % P) perceived as most typical for FL-CP_x [6].

In Fig. 1 a-c three pairs of relaxed systems denominated System A, B, and C, are displayed. System A (Fig. 1a), consisting of two FL-CP_x graphene-like sheets illustrates that P atoms are stable within a graphene sheet inducing, in this case, pentagon defects with increased local curvature and C-P bond lengths of about 1.86 Å which is in agreement with the value of ~1.85 Å for the C-P bond lengths in P-doped graphene sheets obtained by Garcia *et al.* [11]. For comparison, the C-C bond length in graphene is ~1.42 Å [3]. System B (Fig. 1b), composed of a cross-linked model sub-system coupled to a highly curved cage-like conformation, emphasizes other typical features observed during structural evolution and relaxation of FL-CP_x. These features, directly related to the tetrahedral bonding configuration preferred by P, are tetragon defects incorporated in graphene sheets, cage-like structures seeded by tetragons as well as cross-linkages

between P-containing graphene sheets [6]. System C (Fig. 1c) is a combination of a typical FL-CP_x graphene-like sheet, not dissimilar to those in Fig. 1a, and an incomplete onion-like fragment. Onion-like conformations may be frequent in FL-CP_x also at relatively low P content (≤ 10 at. %) [6], and for seek of completeness they should be taken into account in simulations of events involving FL-CP_x structural relaxations such as the P atom intercalation studied in this work.

Systems A, B, and C resulted from following the simulation patterns established within the SGC approach [1, 2, 6]. By considering alternative and competing chains of bonding events, sets of model systems representative for the CP_x were built up. In order to achieve an adequate description of the real CP_x material also CP_x sample characterization data such as bonding details, absence of P-segregation, etc. [8], were taken into account when selecting the above mentioned CP_x model systems.

Each of the pairs A, B and C, consists of two variants of the given model system - without (left panels), and with (right panels) an intercalated P atom. Table 1 shows the PW91/6-31G* energy costs ΔE_{coh} for an interstitial defect matching each of the pairs of systems A, B and C, respectively. In parentheses, also the energy costs for the same defect incorporated in the same systems but at the B3LYP/cc-pVTZ level of theory are listed. Since no significant differences with respect to the Perdew–Wang 91 results were found and in order to keep the present energy values numerically comparable to previously published results [6, 20] the discussion below refers to the PW91/6-31G* energy costs.

For each one of these model systems a variety of similar conformations incorporating an interstitial P atom can result from the geometric relaxation procedures,

only the pairs of systems corresponding to the lowest energy cost for an interstitial defect are shown in Fig. 1. As seen from Table 1, the energy costs for a single P-atom intercalation in a typical FL-CP_x system vary in the range 0.93 – 1.21 eV. Such energy cost values are comparable to that for a tetragonal defect in FL-CP_x (0.84 – 1.33 eV) [6, 7] and slightly higher than the average energy cost for a dangling bond and/or a vacancy defect (0.62 – 1.04 eV) [20] for the same compound and at the same level of theory. Taking into account that:

(i) Energy cost values of around $\Delta E_{\text{coh}} \sim 1$ eV for different kind of defects are considered feasible in wide range of C-based nanostructured compounds obtained under energetic synthesis conditions such as fullerenic clathrates and other covalent cluster-assembled solids [3] as well as CN_x [2, 18].

(ii) Tetragon defects are not only a likely type of defects in FL-CP_x but, actually, they are perceived as being of fundamental importance for understanding the prevailing close-ordered structure of this compound: tetragon defects were reliably predicted theoretically [6] and their existence is in excellent agreement with FL-CP_x sample characterization results [8, 9];

(iii) Dangling bond defects do occur frequently in FL-CP_x thin films as shown by both theoretical modeling and experimental measurements of water uptake on the surface FL-CP_x samples [19, 20],

The cohesive energy results listed in Table 1 suggest that single P-atom interstitial defects are energetically feasible in FL-CP_x, since importantly, the short-range ordered structure typical for this compound (and corresponding to P concentration between ~5 and ~15 at. %) with highly curved graphene fragments, tetragon defects, cage-like

conformations and nano-onions [6, 8, 9] is a decisive structural factor contributing to the low energy cost for P atom intercalation in FL-CP_x.

As noticeable from Fig. 1 a-c, in any case of the model systems A, B, and C, the intercalated P atom leads to a considerably larger distance between the modified/deformed CP_x graphene planes in comparison to the situation without an intercalation event. Both the “inter-sheet” distances in absence, and in presence of an intercalated P atom, for each of the relaxed FL-CP_x model systems A, B, and C, respectively, are listed in Table 1. In absence of an intercalated P atom, the “inter-sheet” distance in FL-CP_x is in the range 3.39 – 3.62 Å which, in average, is comparable, although slightly larger, than the inter-sheet distance in pure graphite ~3.35 Å [3]. After a single P-intercalation event this distance increases significantly to 5.81 – 7.04 Å (see Fig. 1). This behavior is due to the fact that, as usual in case of intercalation events, the equilibrium geometry after a single atom intercalation is reached at the account of locally enlarged inter-“sheet” distance. This also leads to local changes in the curvature/deformation of the graphene-like sheets adjacent to the intercalation site. The considerable extent of the *local* increment of the inter-sheet distances (from 67% in the case of System A to 94% for System B) resulting from intercalation of a single P atom in FL-CP_x should be interpreted in the context of the large atomic radius of P atom (about 46% larger than the atomic radius of C).

Since FL-CP_x is a compound with strongly inter-locked graphene sheets with elements of nano-onions [8, 9], most FL-CP_x model systems do not exhibit conventional graphene sheets. In model systems like System B and System C (Fig. 1b, and c) the term “inter-sheet distance” actually corresponds to a distance between adjacent close-ordered

FL-CP_x structural conformations, which is just the closest possible FL-CP_x analogue to the conventional “inter-sheet” distance observed in different graphene-like compounds structurally closer to pure multilayer graphene.

3.2 Experimental results

The CP_x films were investigated in a Philips CM20 electron microscope operated at 200 kV. The SAED patterns were recorded on imaging plates, which have broad linear range in intensity (20 bit grayscale resolution). The SAED patterns processed here were taken at 1 m camera length. The SAED patterns consisted of diffuse rings typical for amorphous materials. The diameters of the diffuse amorphous rings were determined with ProcessDiffraction software [28].

The patterns can be grouped in two types of structures [9]: the lower P content CP_x films ($x < 0.1$) and higher P content films ($x \geq 0.1$). A typical example for the diffraction pattern of the lower P content films is the film sputtered at 300 °C at 9 mTorr working pressure (Fig. 2a). This film exhibits a similar graphitic short range order like CN_x [21] having rings at ~ 1.2 Å and ~ 2.1 Å like all other amorphous C allotropes including FL-CN_x [21]. However, in addition to those rings there is a weak ring at ~ 3.9 Å, which is different from the expected ~ 3.5 Å typical of the FL-CN_x structure (corresponding to graphite 0002 reflection). Our calculations indicate that P incorporation into the carbon sheets (also for P substitution) increases the inter-sheet distance up to ~ 3.6 Å, while the observed experimental increase to ~ 3.9 Å is by $\sim 8\%$ higher than the theoretical prediction.

Even more remarkable are the higher P content films like CP_{0.1} deposited at 300 °C at 3 mTorr working pressure which exhibit rings at ~ 1.7 Å, ~ 2.7 Å and ~ 6 Å (Fig. 2b). These

values for carbon based compounds were first reported in Ref. 8. The rings at $\sim 1.7 \text{ \AA}$ and $\sim 2.7 \text{ \AA}$, can be explained by the highly curved FL fragments of CP_x [6] showing similar appearance to electron scattering of C_{20} molecule or C_{20} molecule fragments [21]. The broad ring at $\sim 6 \text{ \AA}$ is related to the average spacing of these highly curved FL fragments like the 3.5 \AA ring of FL-CN_x corresponding to the average spacing of the FL basal plane fragments [21]. Since the highly curved fragments in FL-CP_x are rather small compared to the basal plane fragments in FL-CN_x , the 6 \AA ring is consequently broader. This broad ring of $\text{FL-CP}_{0.1}$ at $\sim 6 \text{ \AA}$ is in good agreement with the inter sheet distance of $5.81\text{-}7.04 \text{ \AA}$ calculated for P intercalated CP_x domains.

4. CONCLUSIONS

Ab-initio simulations carried out within the DFT-based Synthetic Growth Concept show that P atom intercalation in FL-CP_x (with typical P concentration 5 - 15 at. %) is feasible under energetic synthesis conditions, P atoms being stabilized at interstitial sites as a result of simulation procedures consisting in sequential addition of precursor species to model systems representative for CP_x and subsequent relaxations. The energy cost for a single P atom intercalation event in FL-CP_x is in the range 0.93 - 1.21 eV, which is comparable to the energy cost for tetragon defects and dangling bonds, both experimentally confirmed in CP_x . While substitutional P atoms at C sites in the graphene sheets introduce sheet curvature and consequently increases the inter-sheet distances to $\sim 3.4 - 3.6 \text{ \AA}$, a single P-atom intercalation event leads to considerably larger inter-sheet distance of $5.81 - 7.04 \text{ \AA}$, the exact value depending on the local structure. These

theoretical predictions for inter-sheet distances agree with SAED patterns obtained from characterization of FL-CP_x samples. In particular, the calculated inter-sheet distances in P-intercalated FL-CP_x successfully explain the SAED ring at ~ 6 Å which can be seen as a specific diffraction fingerprint for FL-CP_x with higher (x≥0.1) P-content.

ACKNOWLEDGEMENTS

G.K.G. gratefully acknowledges support by the Swedish Research Council (VR). L.H. acknowledges support by the European Research Council (ERC).

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Table 1. PW91 energy costs ΔE_{coh} and changes in the inter-sheet distances for introducing a single interstitial defect in each of the relaxed FL-CP_x model systems A, B, and C, displayed in Fig. 1 a, b, and c, respectively. In parentheses, also the energy costs for the same configurations but at the B3LYP/cc-pVTZ level of theory are listed. $\Delta E_{\text{coh}} = |E_{\text{coh}}(\text{model system containing an intercalated P atom}) - E_{\text{coh}}(\text{analogous model system, but without intercalation})|$. For comparative purposes, the PW91 energy costs for a dangling bond defect [20] and for a tetragonal defect [6] in FL-CP_x are provided.

FL-CP _x	ΔE_{coh} , eV	Inter-sheet distance, Å	
		No intercalation	Intercalated P-atom
System A	0.93 (0.77)	3.47 (3.61)	5.81 (5.91)
System B	1.07 (0.88)	3.39 (3.66)	6.46 (6.31)
System C	1.21 (1.08)	3.62 (3.88)	7.04 (6.81)
Dangling bond (typical)	0.62-1.04	-	-
Tetragon defect	0.84-1.33	-	-

Figure Captions

Figure 1: Relaxed FL-CP_x model systems, each one in its two variants - without (left panels), and with (right panels) an intercalated P atom: (a) System A, consisting of two FL-CP_x sheets; (b) System B, composed of a cross-linked model sub-system coupled to a highly curved cage-like conformation; (c) System C is a combination of an onion-like fragment and a typical FL-CP_x sheet.

Figure 2: Selected area electron diffraction patterns of CP_x films deposited at 300 °C and: (a) 9 mTorr; (b) 3 mTorr working gas pressure.

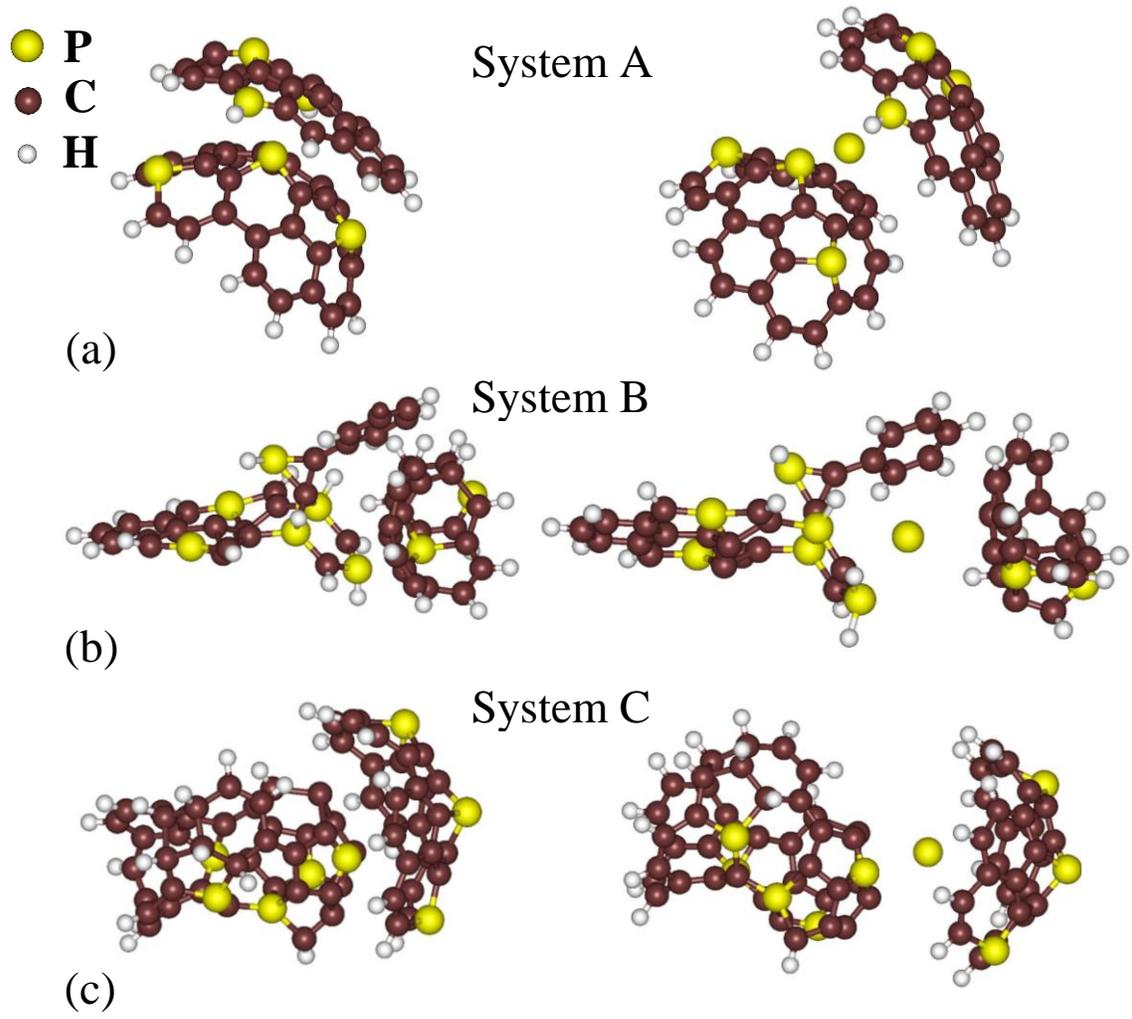


Figure 1

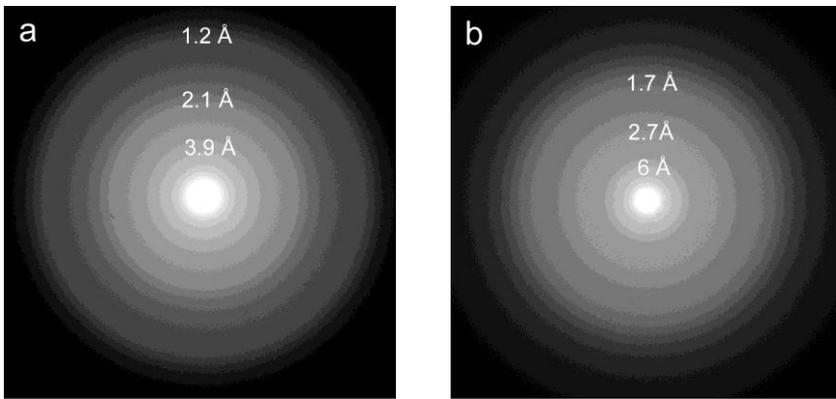


Figure 2