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The electronic structure of different phosphorus carbide solid phases with stoichiometry P_4C_3 is studied using first-principles density-functional calculations; the lowest energy phase is cubic defect zinc-blende with graphitic phases much higher in energy.

Recently there has been much interest in doped diamond-like carbon (DLC) for use in electronic devices. Most previous studies have concentrated on N as a dopant,^{1,2} but a possible alternative dopant to nitrogen is phosphorus. Incorporation of up to 1% P into DLC films reduced the resistivity by 6–7 orders of magnitude, with no apparent change in the amorphous nature of the carbon films.³ Capacitively-coupled radio frequency (RF) plasma deposition has been used to produce P-doped DLC films,^{4,5} using PH_3 as a dopant gas producing films with P contents estimated to be ≈ 11 at.%, with increases in room temperature conductivity of nearly five orders of magnitude. Golzan *et al.*⁶ have suggested that in films doped with $\approx 3\%$ P, the dopant destabilises the tetrahedral network in favour of an sp^2 bonded network.

Recent work at Bristol,^{7,8} studied the effect of doping DLC with much larger amounts of phosphorus. Films were deposited with P:C ratios of up to 3:1, but were still essentially hard and amorphous in nature with an optical band gap of 2.1–2.6 eV. With such high P content it is no longer valid to call these films ‘doped DLC’—instead, they have been termed ‘amorphous phosphorus carbide’. For many semiconductor applications, however, crystalline materials are preferred, but to date, very little is known about the properties of potential crystalline phases of phosphorus carbide. There continues to be, of course, much work on the analogous carbon nitrides—in particular C_3N_4 —due to its high bulk modulus and its potential as an ‘ultrahard’ material.

We have thus started a comprehensive search for stable forms of phosphorus carbide phases with structural formulae P_4C_3 and PC —by analogy with the widely studied carbon nitride phases C_3N_4 and CN . In this first paper we report results of calculations for P_4C_3 . There are of course many possible forms but we have restricted ourselves to eight. These include the five possible structures suggested for C_3N_4 by Teter and Hemley,⁹ which comprise α , β , cubic, and pseudocubic structures, and one hexagonally-closed-packed graphitic form. The remaining three are a defect wurtzite structure, a face-centred cubic graphitic form differing from that of Teter and Hemley⁹ only in the stacking of the layers, and a further graphitic modification with the alternative vacancy ordering suggested by Mattesini *et al.*¹⁰

Calculations in this work were carried out using (i) plane-wave density functional theory (DFT) calculations in the generalized gradient approximation (GGA) as implemented in the CASTEP code¹¹ (ii) periodic numerical atomic orbitals density functional theory (DFT),^{12, 13} as implemented in the SIESTA code.¹⁴ Again GGA was used, with the exchange-correlation functional due to Perdew, Burke and Ernzerhof.¹⁵ Only the valence electrons are considered throughout, the core

electrons in the SIESTA calculations being replaced by norm-conserving scalar pseudopotentials¹⁶ factorized in the Kleinman–Bylander form.^{17,18} In the CASTEP calculations we used the ultra-soft Vanderbilt potentials.¹⁹ We have checked that the results are well converged with respect to the real space grid, Brillouin zone sampling, basis set and geometry relaxation parameters. Full details of the energy cutoffs, basis sets and other technical details are available in the supplementary information.[†] We performed two sets of CASTEP calculations. In the first, space-group symmetry was maintained and in the second all symmetry constraints were removed. No symmetry constraints were applied in the SIESTA runs.

Fig. 1 shows the structure of the P_4C_3 phase with the lowest energy from all sets of calculations, the pseudocubic based on a defect-zinc blende structure. Further details of energies and optimized structures are given in the supplementary information.[†] It is clear that P_4C_3 is predicted to have totally different structure and properties from C_3N_4 , since the pseudocubic form is very high in energy⁹ for C_3N_4 . Phases low in energy for C_3N_4 are high in energy for P_4C_3 . These include the α , β , and cubic forms, all of which contain eight-membered rings; indeed when symmetry constraints were removed, all of these led to very distorted, symmetry-broken solutions. CPC bond angles in the high-energy α , β , and cubic phases are all considerably larger (typically between 110° and 115°) from those in the pseudocubic phase ($\approx 104^\circ$) which are closer to the bond angle in, *e.g.*, $P(CH_3)_3$ (99°). The hexagonal defect wurtzite structure,²⁰ only ≈ 0.3 eV per formula unit higher in energy than the pseudocubic, is the next lowest in energy, again with CPC bond angles $\approx 104^\circ$. This is not inconsistent with the known molecular chemistries of N and P, where P shows a much more marked preference than N for tetrahedral coordination. The suggestions

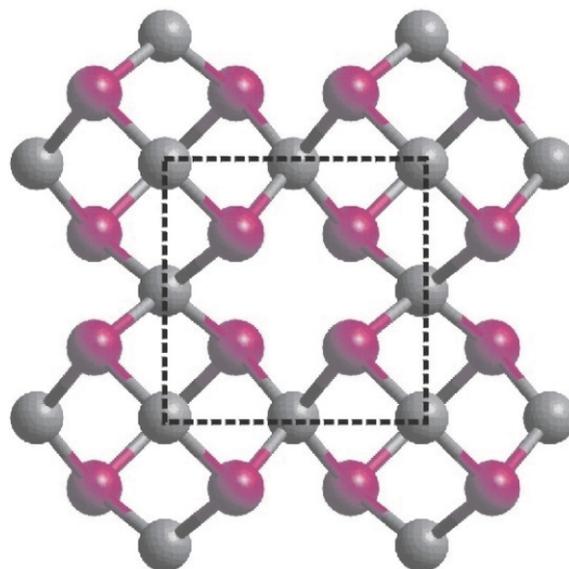


Fig. 1 Crystal structure of the pseudocubic phase of P_4C_3 . Dark grey and crimson spheres denote carbon and phosphorus atoms respectively. The dashed black line denotes the unit cell.

[†] Electronic supplementary information (ESI) available: CASTEP and SIESTA calculations. See <http://www.rsc.org/suppdata/cc/b2/b207743b/>

of Golzan *et al.*²¹ thus remain puzzling, though their remarks do relate to doped tetrahedral amorphous carbon, rather than the periodic structures studied here.

Graphitic forms for P_4C_3 are higher in energy than diamond-like forms, unlike for C_3N_4 where these lie lowest in energy.⁹ Once again, this is in line with the well-known preference of P and other second row elements for single, rather than multiple, bond formation. In order to generate graphitic forms, two carbon atoms in graphite must be replaced by a single N atom, which thus generates a carbon vacancy. There is more than one possible vacancy ordering¹⁰ and we have considered two: the hexagonal unit cell proposed by Teter and Hemley,⁹ a rhombohedral distortion of which gives the pseudocubic form considered earlier, and the orthorhombic form proposed by Mattesini *et al.*¹⁰ (see Fig. 2). Calculated energies show these two structures to be close in energy. The layers in the orthorhombic form show considerably more distortion from the ideal flat graphitic structure than the hexagonal, with a short interplanar P–P distance. When the constraint of AA stacking of the layers is removed, the symmetry is lowered from orthorhombic to triclinic (P112). Graphitic C–P bond lengths (typically ≈ 1.76 Å in the CASTEP calculations) are shorter than the single C–P bonds in the pseudocubic phase, as expected (typically ≈ 1.86 Å in the CASTEP calculations).

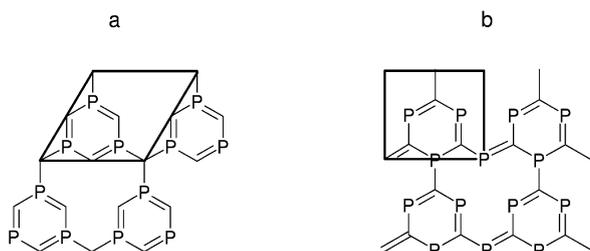


Fig. 2 Possible vacancy orderings for graphitic P_4C_3 . (a) Hexagonal unit cell⁹ (b) Orthorhombic unit cell¹⁰

The calculated bulk modulus of the resulting lowest-energy pseudocubic phase, obtained by a fit of the calculated E vs. V curve to the Birch–Murnaghan equation of state, is 158 GPa and 161 GPa for the CASTEP and SIESTA calculations, respectively. This is substantially lower than an estimate due to Lim *et al.*²² (230 GPa), and much lower than the bulk modulus of diamond (442 GPa) and that calculated⁹ for pseudocubic- C_3N_4 (448 GPa). The value is comparable to that of MgO or Fe and it is worth bearing in mind bulk moduli for so-called ‘hard’ materials,²³ such as Al_2O_3 (246 GPa), SiC (226 GPa) and Si_3N_4 (249 GPa). At the DFT level P_4C_3 , unlike C_3N_4 , also appears to be metallic, though we caution that band gaps are commonly underestimated by DFT. We have also carried out periodic Hartree–Fock calculations on P_4C_3 which lead to very similar conclusions as reported here as regards structure, but indicate an insulating state. Further work is required here.

A marked contrast with C_3N_4 is the polarity of the individual bonds. While C–N is polarized $C^{\delta+}-N^{\delta-}$, C–P bonds possess

the reverse polarity $C^{\delta-}-P^{\delta+}$, as confirmed by the calculated Mulliken populations. For example, calculated CASTEP values for the pseudocubic phase are -0.90 (C) and $+0.67$ (P); for the graphitic phase the bond is slightly more polar, as would be expected for the more electronegative sp^2 hybridised carbon.

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