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Stability and electronic structure of phosphorus nanotubes

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Abstract. – First-principles density-functional theory (DFT) calculations of single-walled phosphorus nanotubes constructed from the black-phosphorus (b-P) layered allotrope show that their strain energies per atom for radii above 0.6 nm are comparable to the strain energies predicted for experimentally observed single-walled carbon nanotubes with radii of 0.5 nm. Our DFT calculations further predict that the nanotube structures are energetically more stable than the corresponding strips for radii larger than 0.55 nm, suggesting that the synthesis of phosphorus nanotubes (PNTs) could be possible. We find that polarized basis sets including d functions are necessary for accurate treatment of the strain energy, and these basis sets lead to strain energies per atom substantially larger than DFT strain energies of single-walled carbon nanotubes at similar diameters. We have also found that all the PNTs studied are semiconducting regardless of their helicity, in contrast with the band structures of carbon nanotubes. The band gaps increase and converge to the value of the band gap of a black-phosphorus single puckered layer, 1.8 eV, as the radius is increased. For a fixed radius, the band gaps increase when increasing the chiral angle. Our DFT calculations are in very good qualitative and quantitative agreement with earlier density-functional tight-binding calculations of black-phosphorus single puckered layers and nanotubes.

Introduction. – Carbon nanotubes are the most commonly studied form of a family of nanostructures that can be constructed from layered crystalline materials. The geometry of all these nanostructures can be understood in terms of the underlying structure of a graphite sheet. Since the discovery of carbon nanotubes [1], the synthesis of different non-carbon nanotubes has been reported: B$_x$C$_y$N$_z$ [2–6], MoS$_2$ and WS$_2$ [7–9], NiCl$_2$ [10], vanadium oxide [11], InS [12], bismuth [13], ZnS [14] and single crystals of GaN nanotubes [15]. Many of these nanotubes have phases consisting of layered structures and hence, it has been proposed that maybe other materials forming stable layered structures can have nanotube counterparts as the graphite has the carbon nanotubes. Previous theoretical results of BN [16,17], BC$_3$ [18], BC$_2$N [19], GaN [20], B [21], GaSe [22] and black-P [23] nanotubes have suggested that the synthesis of these nanotubes could be possible.
Seifert and Hernández [23] examined zigzag and armchair phosphorus nanotubes (PNTs), based on the black-phosphorus allotrope, using atomistic simulations based on a density-functional tight-binding method. They found that PNTs based on the graphitic-like orthorhombic black phosphorus are energetically stable and that all of these PNTs were semiconductor nanotubes, with the band gap tending to the band gap of a b-P monolayer in the asymptotic limit of infinite diameter.

We are interested in the strain and exfoliation energies, as well as the electronic structure of PNTs. We have done DFT calculations on all PNTs (zigzag, armchair and chiral nanotubes) with radii between 0.25 and 0.8 nm. We have used a LDF method described elsewhere [24,25] that considers the helical symmetry of the nanotubes to calculate their electronic structure, using local Gaussian-type orbitals within a one-dimensional band structure approach [26,27]. We have used the Gaspar-Kohn-Sham (GKS) [28,29] and the Perdew-Zunger (PZ) [30] exchange-correlation functionals. We have carried out calculations using the 3-21G basis set and with the corresponding polarized basis set 3-21G*.

Description of the geometric structure. – Orthorhombic black-phosphorus is the most stable form of phosphorus under normal conditions and it has a layered structure. In a single layer, the P atoms are arranged in a honeycomb network similar to that of a graphene layer, but with the two atoms in the unit cell “puckered” into two alternate layers. Every P atom in a puckered layer has four $sp^3$ hybrid orbitals, which form three $\sigma$ bonds with their nearest neighbors in the alternate lattice and a lone electron pair. Puckering of the layers minimizes the repulsion between the lone electron pairs of the neighboring P atoms. Experimentally [31], every P atom has three nearest neighbors in the layer at distances 2.224, 2.224 and 2.244 Å, and two different bond angles of 102 and 96.5 degrees. The puckering width, $P_w$, between the two planes of atoms is 1.2 Å. In fig. 1 we show the top and lateral views of the structure of a single puckered b-P sheet.

The conformation of specific carbon and black-phosphorus nanotubes can be described with a pair of integer indexes ($n_1, n_2$), that define a rollup vector $R = n_1R_1 + n_2R_2$, [25,32,33], where $R_1$ and $R_2$ are primitive lattice vectors of the honeycomb graphitic-like lattice. The real lattice vector $R$ maps upon rolling up the sheet into the circumference of the nanotube. The PNTs are constructed by rolling up a single puckered graphitic-like sheet of b-P with a P-P bond distance of 2.23 Å for the three bonds, the average of the experimental P-P bond
lengths, and a puckering width $P_w$ of 1.2 Å. We have not optimized the geometry of these nanostructures, and all results are in terms of these unrelaxed geometries.

There are two main geometric differences between carbon and phosphorus nanotubes. First, the nearest-neighbor bond distance is 1.44 Å for carbon nanotubes and 2.23 Å for PNTs. The second difference arises from the puckering of the underlying b-P layer compared to the flat graphene layer. Because of this puckering the phosphorus atoms in the PNTs are at two different radii, whose difference is the puckering width. In fig. 2 we show two views of the structure of a (10,0) PNT, with the puckering and the corresponding two different radii. The rollup vector $R$ maps to the circumference of a cylinder with radius

$$r = \frac{a \sqrt{n_1^2 + n_2^2 + n_1 n_2}}{2\pi},$$

where $a$ is the lattice spacing of the appropriate honeycomb lattice. For the PNTs, the lattice parameter $a$ is 3.26 Å. We have chosen the innermost radius to equal the radius generated by the rollup vector, with the outside atoms at a radius $r + P_w$, because the unrelaxed PNTs have the lowest total energies with this internal radius. Throughout this paper we will refer to the average nanotube radius for the PNTs, defined as the average of the inner and outer radii.

Conformational energetics. – In fig. 3(a) we compare the strain energies of phosphorus and carbon single-walled carbon nanotubes for radii between 0.25 and 0.8 nm, obtained using the GKS functional. The strain energy was defined as the difference between the energy per atom of the finite radius nanotube and the energy per atom in the asymptotic limit of infinite radius. The strain energies are expected to fit very well to a curve of the type $a/r^2$, where $r$ is the average nanotube radius [34,35].

Our initial calculations using the 3-21G basis set and the GKS functional resulted in strain energies for the PNTs smaller than that of comparable diameter carbon nanotubes. Including polarization functions by using the 3-21G* basis set substantially increased the calculated strain energies, however. We carried out analogous comparative calculations for CNTs using uncontracted 11s7p1d (polarized) and 7s3p (unpolarized) basis sets for carbon. These calculations resulted in only very small differences between the strain energies for the two carbon basis sets, and we do not depict the polarized basis results for CNTs in fig. 3(a). The 3d orbitals of the C atom are unoccupied but are high-lying and therefore, the addition of 3d-type functions leads to negligible changes in energy. However, in the PNTs the 3d orbitals are low-lying and therefore, the addition of 3d-type functions in the basis has a large effect in the bonding and strain energy.
I. Cabria et al.: Phosphorus nanotubes

Fig. 3 – Strain energies of carbon and phosphorus nanotubes (a) as a function of the average nanotube radius obtained using the GKS functional and the two basis sets for the P atoms, and strain energies of PNTs (b) obtained using the GKS and PZ functionals and the two basis sets.

Because these are variational calculations, the addition of 3d-type functions will lower the calculated total energies of the PNTs at all radii compared to the unpolarized basis. We observed, however, that the stabilization resulting from adding 3d-type functions increased with increasing PNT radius, with a maximum in the asymptotic limit of infinite radius. This trend results in the larger calculated strain energies for PNTs when 3d-type functions are included. This effect on the total energy does not appear related to any changes in the band gaps, because no systematic differences were observed in the band gaps using the two basis sets as a function of nanotube radius.

We also examined the effect of using the GKS and PZ density functionals, and depict a summary of our results in fig. 3(b). These energies depend on the type of functional, but this dependence is less important than the dependence on the basis. The largest relative difference due to the type of functional is about 16% and corresponds to the smallest radius; the difference decreases when increasing the radius. The polarized basis increases the strain energies using both types of functionals, and the magnitude of that increase, about a factor of two, is practically independent of the type of functional.

Single-walled carbon nanotubes have been experimentally observed with radii as small as 0.5 nm. At these radii, we would predict strain energies per carbon of roughly 0.1 eV. Our first-principles results indicate that phosphorus nanotubes would have similar strain energies per atom at a radius greater than 0.6 nm. This critical radius and also the numerical values of the strain energies obtained using the polarized basis are in very good agreement with the calculations done by Seifert and Hernández [23] using the PZ functional. These results indicating comparable strain energies to carbon nanotubes suggest that formation mechanisms for PNTs are possible, but do not tell us whether PNTs once formed would be stable against spontaneous breakdown by “unzipping” or other relaxation mechanisms for relieving the strain energy.

The exfoliation energy can be defined as the difference between the total energies per atom of a nanotube and the corresponding strip, essentially by unzipping the nanotube. In fig. 4 we present the relative strain energies for the unrelaxed geometries. The strain energy of a nanotube can be expressed as $E_s = C/r^2$ [34, 35], where $r$ is the radius, and the total
energy per atom of a strip, also called edge energy, as $E_e = b/r$ [36,37]. We have fitted the total energies per atom to those expressions. It can be seen in fig. 4 that PNTs are energetically more stable than their corresponding b-P strips when their radii are larger than the critical radius, $r_c = C/b = 0.55\, \text{nm}$. The calculations of the strips were spin-unrestricted ones. Convergence problems and computational resources limited the largest strip for which we could obtain results to a size corresponding to a PNT radius of 0.48\, \text{nm}.

**Band gaps.** – We have studied the electronic structure and band gap of PNTs with radii between 0.25 and 0.8\, \text{nm}, using two different energy density functionals and two basis sets. The band gap has a weak dependence on the type of density energy functional. The PZ band gap is always larger than the GKS band gap, with a relative difference of between 2 and 12\%. The band gaps obtained with the 3-21G* basis are, in general, larger than those obtained with the 3-21G basis, with a relative difference ranging between $-11$ and 26\%.

We have found that all the PNTs (zigzag, armchair and chiral) studied here are semiconducting, in contrast with the CNTs, whose electronic nature (semiconductor, quasimetallic or metallic) depends on the helicity of the nanotube. The band gap increases with the radius and tends to 1.8\, \text{eV} when the radius tends to infinite, in agreement with earlier calculations of a b-P puckered single layer: Asahina et al. [38,39] and Takao et al. [40,41] found a band gap between 1.3 and 1.8\, \text{eV}. Goodman et al. [42] reported a band gap of 1.3\, \text{eV}.

Similar results were also found for the band gaps of PNTs by Seifert and Hernández [23], although they obtained a band gap of 1.99\, \text{eV} for the b-P single puckered layer. However, they did not study chiral nanotubes and the dependence of the band gaps on the radius and chiral angle. The band gaps of the zigzag PNTs have a rough dependence on the average radius $r$ of the form $E_g^\infty - a/r$, as can be seen in fig. 5(a). The band gaps of the armchair and chiral PNTs also increase when increasing the radius and their analytical dependence on $r$ seems to
Fig. 5 – Band gaps of zigzag phosphorus nanotubes with a radius between 0.25 and 0.8 nm obtained with the polarized basis and the PZ functional, as a function of the average nanotube radius \( r \) (a), and band gaps of armchair and chiral PNTs with \( 3 \leq n_1 \leq 41 \) and \( n_2 = 1 \rightarrow 4 \) as a function of \( \theta_c \) (b). In (a) the solid line is the fitting curve \( E_{g}^{\infty} - a/r \), where \( E_{g}^{\infty} = 1.79 \) eV and \( a = 0.41 \) eV nm.

be similar to that of the zigzag nanotubes, but more complex. In the infinite radius limit, the band gaps of all the PNTs tend to 1.8 eV, regardless of their helicity.

In fig. 5(b) we have plotted the band gaps of these nanotubes as a function of the chiral angle \( \theta_c \). This angle is given by \( \tan \theta_c = (\sqrt{3}n_2/(2n_1 + n_2)) \) for a \((n_1, n_2)\) PNT and is situated between 0 (zigzag) and 30 degrees (armchair nanotubes). In general, the band gaps increase as a function of \( \theta_c \) for nanotubes with a given radius. We have also calculated the band gaps of some chiral nanotubes with radii larger than 0.8 nm and smaller than 2.3 nm, with \( 3 \leq n_1 \leq 41 \) and \( n_2 = 1 \rightarrow 4 \), belonging to the \( C_1 \) symmetry group. The gaps of PNTs with the same value for the integer index \( n_2 \) increase monotonically when \( \theta_c \) decreases and lie along curves that are linear in the vicinity of \( \theta_c = 0 \), with the slopes of these curves inversely proportional to \( n_2 \). When the chiral angle tends to zero, the band gaps of all the curves tend to 1.8 eV, the band gap of the b-P layer.

**Conclusions.** – In summary, we have found that the strain energies of PNTs with radii larger than 0.6 nm are lower than the strain energies of observed single-walled CNTs with radii of 0.5 nm. The strain energies of PNTs are larger than those of CNTs when a polarized basis including \( d \) functions is used in the calculations. The present theoretical exfoliation energies indicate that PNTs are more stable than their corresponding strips for radii larger than 0.55 nm. All these results mean that PNTs with sufficiently large radii could be stable. All PNTs are semiconductors, regardless of their helicity, in contrast with the CNTs, whose band gap is strongly dependent on the helicity. The band gaps tend to 1.8 eV when the radius tends to infinite, in agreement with former calculations of a b-P puckered single layer. The band gaps of zigzag PNTs have a dependence on the radius \( r \) of the form \( E_{g}^{\infty} - a/r \). The band gaps of armchair and chiral nanotubes also increase with the radius, but their dependence on the radius is more complex. Finally, the band gaps also depend on the chiral angle, although the differences due to this angle decrease rapidly when increasing the radius and the band gap tends to 1.8 eV when the chiral angle tends to zero.
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