Effects of single vacancy on electronic properties of blue-phosphorene nanotubes

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Keywords: DFT, nanotubes, blue-phosphorene

Abstract
We investigate the electronic properties of blue-phosphorene nanotubes using density functional theory first-principle calculations, taking into account, in particular, the presence of atom vacancies in the structure. The study considers both zigzag and armchair achiral conformation and reports on the structure and the electron energy states of the nanostructure. Compared to pristine blue-phosphorene nanotubes, which exhibit values of the fundamental bandgap between one and two electron-volts. For atomic single vacancies, the incorporation of spin-polarization helps to identify the induction of localized mid-gap states in the blue phosphorene nanotubes. The difference of energy between the highest near-valence and lower near-conduction localized states is, approximately, of 0.5 eV. Also the increase of the single vacancies concentration leads to the formation of additional bands that change the energy gap of the system.

1. Introduction

Nanotubes (NTs) are a kind of one-dimensional (1D) materials with atomic layer thickness that have attracted much attention in comparison with their bulk counterparts due to their unique properties, which provide for prospective applications encompassing microelectronics, photovoltaics, gas sensing, electrochemical sensing, infrared photodetection, photocatalyst and biomedics, for example [1–10].

Among the novel two-dimensional (2D) materials that can be manipulated and transformed into single- or multi-walled NTs, there are the two -black and blue- phosphorus allotropes named as phosphorenes. The theoretical premise for this kind of phosphorus-based nanosystems appeared in the article by Seifert et al back in 2000 [11], and other theoretical studies followed in later years (see, for instance, [12]). But the largest number of reports on phosphorene nanotubes (PNTs) have come out in recent times [13–32]. The vast majority of these works correspond to theoretical first-principle investigations (including density functional theory (DFT) calculations), covering a wide spectrum of physical and chemical properties. To expand on just a few examples regarding NTs made of black-phosphorus (PNTs), we can mention the investigation of the electronic properties of black PNTs made by Yu and collaborators [15]. They found that the armchair PNTs have semiconducting properties along the axial direction and that compressive strain can significantly improve the carrier mobility. Besides, Sorkin and Zhang studied the effect of monovacancies and divacancies on the mechanical properties of black PNTs [24]. According to their findings, divacancies in armchair (AC) PNTs and monovacancies in zigzag (ZZ) PNTs possess the lowest vacancy formation energy, which decreases with the tube diameter in AC PNTs and increases in ZZ PNTs.

In the case of blue phosphorene, a semiconductor layered system put forward by Zhu and Tománek in 2014 [33], the corresponding nanotubes (BPNTs) have also attracted some interest in the last years. In their work of [27], Aierken et al showed that blue phosphorene is better suited to make small NTs. Montes and collaborators found the BPNTs to be semiconductors with a sensitive indirect band gap that allows flexible tuning. This band gap turns out to be very sensitive to the tube diameter [28]. On the other hand, authors of [29] performed first
principle calculations of electronic structure and carrier mobilities in BPNTs, whilst in [30] they study the adsorption of CO, CO₂, NH₃, NO, and NO₂ molecules on AC and ZZ BPNTs, on the basis of the same kind of microscopic calculations. These nanotubes are found to surpass the gas sensing performance of other 1D materials. More recently, Ju et al. investigated the electronic structure and related properties of BPNTs using first-principle calculations to explore their photocatalytic activities. They show that the value of the strain energy of BPNTs with diameters larger than 8 Å is very close to that of carbon NTs, indicating that these structures are stable. Due to the properties of the energy spectrum, the BPNTs reveal as promising candidates for photocatalytic activity, showing potential for application in visible light photocatalysis for overall water splitting. It is also worth mentioning the DFT study of structural, elastic, electronic and dielectric properties of blue phosphorus nanotubes reported by Hao and collaborators [32].

Despite of great deals of theoretical efforts, there are still certain untreated aspects regarding the BPNTs. One of them is the effect of single atom vacancies on the electronic features of these nanosystems. Thus, in the present work we are aimed at investigating such an influence and will report on the properties of the energy states in presence of vacancy sites in the BPNT structure. Our study is based on first-principle DFT calculations. The reader will find some remarks on the methodology employed in the next section of the article. Then, section 3 will contain the presentation and discussion of the obtained results and, finally, the conclusions of the work will appear in section 4.

2. Model and calculation details

As mentioned, there is a possibility to modify the geometric and electronic structure of BPNTs by inducing structural defects in them. The formation of single vacancies (SV), double vacancies (DV), and Stone-Wales (SW) has already been studied in BPMLs [34]. It is shown that the formation energies are lower than those corresponding to graphene monolayer with several structural defects. In this work, we are taking into account the effects of SVs in the electronic structure of BPNTs. We consider two different types of SVs in our calculation, the so called type-A (SV-A) and type-B (SV-B). Accordingly, we will have two non-equivalent atoms in the BPNTs (see figure 1).

The calculation of structural and electronic properties is performed within the framework of DFT, as it is implemented in the ab initio SIESTA package [35], using a 1 × 1 × 5 supercell. Localized double-ζ, single-polarized atomic orbitals are employed as basis set, together with norm-conserving pseudopotentials. The exchange-correlation functional used corresponds to the generalized gradient approximation (GGA) [36]. All structures are relaxed through the FIRE minimization algorithm, until the forces on the atoms are smaller than 0.04 eV/Å [37]. The Brillouin zone sampling is carried out via a Monkhorst-Packk-grid of 1 × 1 × 10 for unit cells and 1 × 1 × 2 for supercells. In order to gain further inside on the influence of vacancies, the study is carried out with and without the inclusion of collinear spin-polarization.

With the results at hand, we shall present the outcome for structural and geometric parameters as well as the energy dispersion relations of BNPTs. These structures can be seen as rolled up blue-phosphorene monolayers (BPML). The BPML can be twined on different directions, in a way a similar to liked to the case of carbon nanotubes [38]. Here, we considered the so-called achiral nanotubes, in which the rolling line goes along the zigzag or armchair direction of the BPML. Then, the unit cell of the BPNTs is determined by the chiral and translation vectors, given respectively by \( \tilde{C}_h = \tilde{m}_1 + \tilde{m}_2 \) and \( \tilde{T} = u\tilde{a}_1 + v\tilde{a}_2 \); where \( \tilde{a}_1 \) and \( \tilde{a}_2 \) are the vectors of the BMPL unit cell. The geometric and electronic structure of BPNTs is characterized by a couple of indices, \((m,n)\). In accordance, for achiral zigzag blue-phosphorene nanotubes (ZBPNTs) \( n = 0 \), while for armchair blue-phosphorene nanotubes (ABPNTs) \( m = n \). As \( m \) and \( n \) increase, the diameter of the BPNTs augments. Unlike carbon nanotubes, the BPNTs has two radii, determined by the buckling of phosphorus atoms in the original BPML. The buckling and the rolling of BPNTs induces a strong sp³ hybridization, which could lead in a change of the electronic properties of the resulting NTs.

3. Results and discussion

3.1. Geometric structure

The table 1 contains the values of the main geometric and structural parameters of the structures investigated: internal and external radii, \( R_1 \) and \( R_2 \), and the average bond length \( \bar{P} \). For pristine BPNTs one may notice that, as long as the radius growth, the average bond length decreases, for both zigzag and armchair nanotubes, achieving values of 2.295 and 2.284 Å, respectively. For comparison, in the case of the BPML, we obtain a \( P = \bar{P} \) bond length of 2.274 Å. So, for (14, 0) and (14, 14) BPNTs, the \( P = \bar{P} \) bonds are only 0.02 Å bigger. The difference between the mayor and minor radii, for each nanotube, is of about 1.286 Å, which is the value of the buckle in BPML. These results indicate that BPNTs retain some of the structural properties of the BPML.
addition, the reader may notice that the presence of any of two kinds of SVs produces only slight changes in the calculated bond lengths, compared to their values in the pristine case. For small radii, the greatest differences appear in the case of zigzag BPNTs whereas for larger values of the radius, the bigger separations from the pristine $P - P$ occur in armchair BPNTs.

In Figure 2 we present a schematic reconstruction of SV-A and SV-B, together with the formation energy, which is obtained from the expression $E_{\text{Formation}} = E_{\text{BPNT-SV}} - N E_{P}$, where $E_{\text{BPNT-SV}}$ is the total energy of the BPNTs with a SV, $N$ is the number of phosphorus atoms in the SV-BPNT, and $E_{P}$ is the energy of one phosphorus atom in the structure. Our results for the formation energies in ABPNTs with SV-A lie within the range from 2.31 eV to 1.43 eV, with the lower value corresponding to the biggest ABPNT considered. By observing the figure 2, one notices that the behavior of the formation energies in the SV-B situation is similar to that of SV-A, with small differences that amount nearly 0.1 eV. When the spin-polarization is included, the formation energies only show little change, as observed from figure 2. In BPMLs, the formation energy for a SV is found to be 2.38 eV [34], which is smaller than the value of formation energies found for graphene monolayers. According to our results, for small BPNTs, the SV formation energies are close to the reported result for the

Table 1. Calculated geometric and structural parameters for zigzag and armchair blue-phosphorene nanotubes. The average value of the internal radius, $R_1$, external radius, $R_2$, and phospherene bond length are presented for the cases of pristine nanotubes ($P - P$), type-A vacancy ($P - P - VA$), and type-B vacancy ($P - P - VB$). All distances are measured in Å.

| System          | $R_1$ (Å) | $R_2$ (Å) | $P - P$ (Å) | $P - P - VA$ (Å) | $P - P - VB$ (Å) |
|-----------------|-----------|-----------|-------------|-----------------|-----------------|
| (7, 0)/(7, 7)   | 3.256/5.816 | 4.524/7.087 | 2.318/2.299 | 2.319/2.298     | 2.312/2.298     |
| (8, 0)/(8, 8)   | 3.746/6.667 | 5.016/7.941 | 2.311/2.294 | 2.312/2.297     | 2.310/2.297     |
| (9, 0)/(9, 9)   | 4.249/7.531 | 5.520/8.805 | 2.307/2.290 | 2.308/2.294     | 2.307/2.295     |
| (10, 0)/(10, 10)| 4.769/8.457 | 6.031/9.729 | 2.304/2.290 | 2.305/2.292     | 2.304/2.295     |
| (11, 0)/(11, 11)| 5.265/9.289 | 6.537/10.563| 2.301/2.287 | 2.302/2.292     | 2.302/2.293     |
| (12, 0)/(12, 12)| 5.790/10.193| 7.061/11.467| 2.298/2.288 | 2.299/2.291     | 2.298/2.292     |
| (13, 0)/(13, 13)| 6.315/11.047| 7.585/12.322| 2.295/2.286 | 2.296/2.290     | 2.296/2.294     |
| (14, 0)/(14, 14)| 6.795/11.909| 8.067/13.184| 2.292/2.284 | 2.293/2.289     | 2.293/2.289     |
However when the nanotube radius increases, the SV formation energies decreases; thus suggesting that SV formation is more likely for wider ABPNTs.

Something different takes place in the case of the formation energies of ZBPNTs, as can be seen from the corresponding curves appearing in rightmost panel of figure 2. First, we analyze the SV-A case. In this case, the value of $E_{\text{Formation}}$, for the smallest - (7, 0) - NT is even lower than the corresponding BPML one, and the inclusion of spin-polarization only raises it a little. Already for the second smaller ZBPNT considered [the (8, 0) one], this quantity approaches the SV-A value in the monolayer and, shows a smooth increasing tendency that reverts only in the case of the widest ZBPNT; the one labeled as (14, 0). It is worth noticing that the increment of SV-A $E_{\text{Formation}}$ due to the inclusion of spin-polarization is much more notorious in this achiral zigzag geometry.

With the exception of the (11, 0) zigzag configuration, for which a significant decrease of $E_{\text{Formation}}$ is detected, the SV-B formation energy also depicts an initial growth with the NT size. This time, the (7, 0) geometry gives a very low value that indicates that the appearance of such kind of vacancy is highly favorable for this narrow NT and even for the second smaller (8, 0) one. But the further widening of the ZBPNT causes a rather strong increase of $E_{\text{Formation}}$ towards the vicinity of the BPML value; and pretty above when the spin-polarization is taken into account. The growing tendency shows a continuation after the particular fall corresponding to the (11, 0) case and, similar to the ABPNT case, starts a fall in the case of the wider, (14, 0) configuration. These results clearly point at a strong dependence of the formation energy on the geometry of the BPNT. Besides, it becomes apparent that including spin-polarization can be crucial when looking for a right description of vacancy formation in achiral ZBPNTs.

Going over to the structural issue, it is possible to say that despite the BPNTs show noticeable differences in single vacancy formation, the changes in the $P - P$ bond lengths for SV-A and SV-B can be considered to be negligible. This suggests that the SV effects are, actually, of local nature and circumscribe to the immediate vicinity of the defective atom.

### 3.2. Electronic structure

In order to have an idea of the energy spectrum of the structures under study, one may need to look at the total density of states (DOS). In the figure 3 we show the DOS corresponding to BPNTs of several diameters for both zigzag and armchair configurations. In comparison with BPML, the DOS for BPNTs has several Van Hove singularities near to the top of the valence band and the bottom of the conduction band. This suggests that the $sp^3$ hybridization due to the rolling onto BPNTs induces a stack of Van Hove singularities in the DOS of these systems, indicating a rich band structure dispersion for BPNTs.

To analyze the electronic properties of BPNTs, we display in figures 4 and 5 the energy band structures of ZBPNT (14, 0) and ABPNT (14, 14), respectively. In both cases, the energy dispersion relations are obtained for a $1 \times 1 \times 5$ supercell, such that the Brillouin zone is folded. The band structures depicted in figures 4(a) and 5(a) correspond to pristine BPNTs. It can be noticed that, for the ZBPNT, the conduction and valence band edges show a very little dispersion that suggest the possible presence of localized states. However, in the case of the ABPNT, the band structures shows a parabolic dispersion near $\Gamma$-point for conduction bands together with quasi-flat valence bands. These characteristics of (14, 0) and (14, 14) BPNTs band structures are observed for all studied cases, and are consistent with previous reports.[28]
The effects of SVs on the electronic states of BPNTs can also be studied from their band structure. In figures 4(b)–(c) and 5(b)–(c), we are presenting the electron dispersion relations of (14, 0) and (14, 14) BPNTs, respectively, which are calculated taking into account the presence SV-A (b) and SV-B (c). In all cases, the presence of vacancies pulls electron states from the conduction and valence bands towards the gap regions, so they become spatially localized mid-gap states.

Interestingly, the calculation performed without the inclusion of spin-polarization would induce such mid-gap states just at the Fermi level, either for zigzag or armchair nanotubes, for both the SV-A and SV-B BPNT configurations. However, when the spin-polarization is incorporated, such mid-gap states appear below and above the Fermi level, for both vacancy types, in the ZBPNTs and ABPNTs. Actually, one may observe in figures 4(b), (c) and 5(b), (c) that a difference of energy between the vacancy-related states within the original gap
arises, thanks to the splitting associated to spin-polarization. It turns out that, for all BPNTs considered, the system behaves as a ferromagnetic, with a magnetic moment equal to $1 \mu_B$. This magnetic moment is mainly induced by the dangling bonding around phosphorus vacancies. For SV-A and SV-B in ZBPNTs, the induced mid-gap states are dispersionless, as expected, indicating their local nature. In the case of ABPNTs, the mid-gap states show a small dispersion, which relates with the smaller size of the translation vector in this geometry, that is approximately the half of the ZBPNT translation vector one.

Arguably, the density of vacancies is the fundamental quantity to determine the electronic behavior of the BPNTs with such kind of defects. This is specially observed in the case of ABPNTs, where the increase of the SV concentration causes the induction of additional bands that transform the system into a smaller gap semiconductor. The figure 6 illustrates this phenomenon. There, we are presenting the calculated electronic band structure of a $(10, 10)$ ABPNT using a $1 \times 1 \times 10$ supercell (with a size twice larger than the previously employed in the work), including spin-polarization. Results for both single A (figure 6(a)) and B (figure 6(c)), and double A (figure 6(b)) and B (figure 6(d)) vacancies are depicted. First, it is possible to notice that, under this supercell configuration, the dispersion of the mid-gap states almost disappears in the SV-A case, and is very small in some of the mid-gap states of the SV-B. This confirms our assertion in the precedent paragraph regarding the influence of the translation vector size. However, when this larger supercell accommodates a second vacancy of the same type, one may clearly observe that the interaction between the neighbor vacancies leads to the formation of new bands, clearly differentiated by the spin polarization, within the original energy band gap. Accordingly, as mentioned above, the ABPNT turns into a small gap—bipolar—magnetic semiconductor.

Finally, in figure 7 we have depicted the variation of the main energy band-gap, calculated as a function of the size of the BPNTs, together with and energy difference between the lowest conduction-like and the highest valence-like mid-gap states induced by SV types A and B, $\Delta E_{\text{mid-gap}}$. For the sake of comparison, we include the results of [29], which correspond to the calculation of the gap for some armchair and zigzag BPNT sizes. Our results are pretty close from the quantitative point of view and show similar qualitative behavior to those of [29]. On the other hand, it is possible to verify that, for the case of single vacancies, the $\Delta E_{\text{mid-gap}}$ corresponds to the difference between spin-up and spin-down state energies. As noticed, for SV-A there is only a little change of the value of $\Delta E_{\text{mid-gap}}$ as long as the diameter of the NT augments, with the sole exception of the $(14, 0)$ ZBPNT. On the other hand, the SV-B produces a slight increase of the $\Delta E_{\text{mid-gap}}$ with the increment of ABPNT size. But rather important variations can be noticed for the ZBPNT case. The reason for this phenomenon could be behind the fact—revealed in the analysis of the $(14, 0)$ case—of a stronger modification of the energy band structure corresponding to the presence of the type-B atom vacancy.

4. Summary and conclusions

In this work we have investigated the electronic properties of armchair and zigzag blue-phosphorene nanotubes, with and without single atom vacancies, via first-principle DFT calculations. Two different types of vacancies have been taken into account.
From the structural point of view, the formation of blue-phosphorene nanotubes does not entail a significant modification of the typical buckling length appearing in blue-phosphorene monolayers. Some alterations of the value of the phosphorus-phosphorus atomic bond length are found in the systems with single vacancies, compared to the pristine nanotube case. These differences largely depend on the size of the nanostructure.

**Figure 6.** Calculated band structure of (10, 10) armchair blue-phosphorene nanotube, using a supercell with a size twice larger than the one used to generate previous figures, and including spin-polarization: (a) with type-A single vacancy per cell, (b) with type-A double vacancy per cell, (c) with type-B single vacancy per cell, (d) with type-B double vacancy per cell.

**Figure 7.** The fundamental band-gap for armchair and zigzag blue-phosphorene nanotubes and difference of energy between lowest conduction and highest valence mid-gap states in armchair and zigzag with single vacancy.
Formation energies of type-A and type-B single vacancies in armchair achiral blue-phosphorene nanotubes show an overall decreasing tendency with the increment of the radius, with small quantitative differences between them disregarding the inclusion or the absence of spin-polarization in the calculations.

From the results for electronic structure it is possible to conclude that, while the pristine blue-phosphorene nanotubes are non-polar moderate-gap semiconductors, the presence of vacancies introduces mid-gap states, however the increase of the vacancies density transforms the system into a small gap magnetic bipolar semiconductor. This condition is revealed only when the calculation takes into account the spin-polarization effect. Otherwise, the structures investigated appeared as metallic systems.

In our opinion, the features exhibited by the electronic and structural properties of the blue-phosphorene-single-vacancy complex could be of interest for the development of new devices such as gas sensors or spin-tronic nanodevices.

Acknowledgments

Authors thanks COLCIENCIAS to financial support of this research by contract 120680864729. MEMR thanks Universidad de Medellín for kind hospitality during sabbatical stay 2019–2020, and to Mexican CONACYT for support through Grant CB–2017–2018 No. A1–S-8218.

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