



# Electronic and optical properties of pure and doped boron-nitride nanotube

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## ABSTRACT

Band structure of the carbon doped zigzag boron nitride nanotubes (BNNTs) is calculated by a simple tight-binding model. It was found that the doping effect of B-substituted and N-substituted BNNT is different and carbon substitution for either boron or nitrogen in BNNTs reduces the band gap. Investigations show the dependence of band gap to the axial magnetic and transverse electric fields for C-doped BNNTs. The applied high electric field causes transition from semiconductor to conductor in C-doped BNNTs. The band gap of C-doped BNNTs oscillates as a function of magnetic flux with period  $\phi$  in the magnetic fields. Influence of C-doping on the absorption spectrum is also discussed in this paper.

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## 1. Introduction

The discovery of carbon nanotubes (CNTs) has provided opportunities for obtaining quasi one-dimensional nano material [1]. Carbon nanotubes have received remarkable research interests due to their excellent electronic [2], thermal [3], structural and mechanical properties [4,5]. Single walled carbon nanotubes (SWCNTs) could be metallic or semiconducting depending on their diameter and chirality and they are used as nanotube devices [6,7].

Theoretical studies predicted that honeycomb-BN might form a boron-nitride nanotube (BNNT) similar to CNT, and in fact it has been successfully synthesized [8,9]. Boron-nitride nanotubes have a similar structure as CNTs, while their electronic properties are quite different from CNTs, however they exhibit only semiconducting properties independent of their chirality and diameter [10,11].

Carbon has successfully been doped into BNNTs [12–16]. Carbon doping was predicted to continuously tune BNNTs' electronic structure. Golberg et al. prepared a series of BNNTs doped with carbon (they can also be called BCN) by controlling a reaction time, the detailed chemical composition analysis revealed that the tubes may be homogeneous BCNNTs or phase separated BN–CNTs depending on the synthesis conditions [17].

Recently, the grafting of polymer chains on nanotubes has attracted increasing attention as it can potentially be used to enhance the solubility of nanotubes and in the development of novel nanotube-based devices, ab initio calculation results suggest that trans-polyacetylene is easily formed on carbon-doped BNNT [18]. Carbon atom substitution instead of boron may add an extra electron, while carbon atom substitution instead of nitrogen can yield an

electron hole. Zhao and Dai, in their theoretical results show the possibility of transforming the insulating BNNT into a n-type or a p-type semiconductor by carbon-doping for the case of carbon substituting for boron or nitrogen atom respectively [19]. The conductivity of BNNTs might be improved as the result of forming electron or hole. To improve the conductivity of BNNT, one-carbon doping is theoretically effective, especially for a boron atom substituted by a carbon atom [20]. The width of band gap decreases from 5.5–6.0 eV to about 1.5 eV (for B substituted) or about 4.0 eV (for N substituted) [20]. Delocalization of the extra  $\pi$  electron in boron substituted BNNT decreases the band gap, giving a narrow-gap semiconductor, while carbon substituting nitrogen provides a wide-gap semiconductor because of the localization of the electron hole [20]. The carbon induced magnetization in BNNT is experimentally accessible and the system can be potentially very useful in future technology [21].

In this paper, by using tight binding model, we study the electronic structure, band gap modulation in the external axial magnetic and perpendicular electric fields and optical properties of carbon doped single wall BNNTs with zigzag chirality. This paper completes the research of Ref. [22].

## 2. Method

We map the tubes to a one dimensional system by dividing them to similar unit cells along their length. For zigzag single wall tubes each unit cell includes  $4n$  atoms. Each unit cell includes  $2n$   $\alpha$ -type and  $2n$   $\beta$ -type atoms for zigzag BNNT, where  $\alpha$  and  $\beta$  show the boron and nitrogen type atoms for zigzag BNNTs.

By using a single  $\pi$  orbital, the Hamiltonian matrix elements of this system can be described as [23]:

$$H_{\alpha_p, \beta_q} = \sum_i \epsilon_i^{\alpha_p \beta_q}(\mathbf{F}) \delta_{\alpha_p \beta_q} + \sum_{ij} t_{ij}^{\alpha_p \beta_q}(\mathbf{B}) e^{i\mathbf{k} \cdot \mathbf{r}_{ij}^{\alpha_p \beta_q}} \quad (1)$$

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The hopping integral  $t_{ij}^{\alpha_p\beta_q}$  is defined by

$$t_{ij}^{\alpha_p\beta_q} = \langle \phi^{(\alpha)}(\mathbf{r}-\mathbf{r}_i^{\alpha_p}) | H | \phi^{(\beta)}(\mathbf{r}-\mathbf{r}_j^{\beta_q}) \rangle, p, q = 1, \dots, 2n \quad (2)$$

where  $i$  and  $j$  indexes indicate Bravais lattice sites of this 1D system and  $\mathbf{r}_i^{\alpha_p}$  shows position of  $p$ th  $\alpha$  type atoms in site  $i$  and  $\phi^{(\alpha)}(\mathbf{r}-\mathbf{r}_i^{\alpha_p})$  is the  $\pi$  orbital wave function of  $p$ th  $\alpha$ -type atom of the site  $i$ .  $\epsilon_i^{\alpha_p\beta_q}(F)$  is the on-site energy for  $p$ th  $\alpha$ -type atom in the presence of the electric fields.

The Hamiltonian obtained from Eq. 1 is diagonalized at different  $k$ -points to obtain the band structure and the corresponding Bloch orbitals in the 1D Brillouin zone. In this study the NT unit cell is used as a cylindrical segment with length  $T$  where  $T$  is the NT transition vector. The 1D lattice constant for zigzag tube is  $T = 3a_0$  where  $a_0 = 1.45$  is B–N distance [24,25]. The one dimensional wave vector  $k_z$  takes values in the first Brillouin zone  $(-\pi/T) \leq k_z \leq (\pi/T)$ .

The density of states (DOS) is given by the imaginary part of the Green's function [26]

$$\text{Dos}(E) = -\frac{1}{\pi} \text{Im} \int_{-\pi}^{\pi} \frac{dk}{E - E_k + i\epsilon} \quad (3)$$

where  $E_k$  is the spectrum of eigen energies of the Hamiltonian.

Applying the electric field perpendicular to the nanotube axis leads to add an electric potential to the on-site energy of different atoms. For simplicity, we consider that the hopping integral of the tube is not affected by the electric field. The on-site energies of C, B and N atoms in the absence of the electric fields are  $-0.7$ ,  $3.2$  and  $-1.45$  eV, respectively [27]. In this study the maximal strength of applied effective electric field is about  $0.5$  V/Å.

We followed a single  $\pi$  band tight binding approach and we used Peierls phase approximation to consider the magnetic field which an extra phase added to the Hamiltonian terms in the tight binding model. In the presence of uniform axial magnetic field, the hopping integral modifies by the phase factor [28–30],

$$t_{ij}^{\alpha_p\beta_q}(B) = t_{ij}^{\alpha_p\beta_q} e^{i\frac{2\pi}{\Phi} \int_{\mathbf{r}_i^{\alpha_p}}^{\mathbf{r}_j^{\beta_q}} \vec{A}(\vec{r}) \cdot d\vec{r}} \quad (4)$$

where  $\vec{A}(\vec{r})$  is the vector potential defined as in gauge  $\vec{A}(\vec{r}) = (1/2)(\vec{B} \times \vec{r})$  and  $\Phi = h/e$  is the magnetic quantum flux.

For the C-doped BNNTs the nearest neighbors hopping integral is  $-2.45$  eV for B–N,  $-2$  eV for C–B and  $-2.9$  eV for C–N [27].

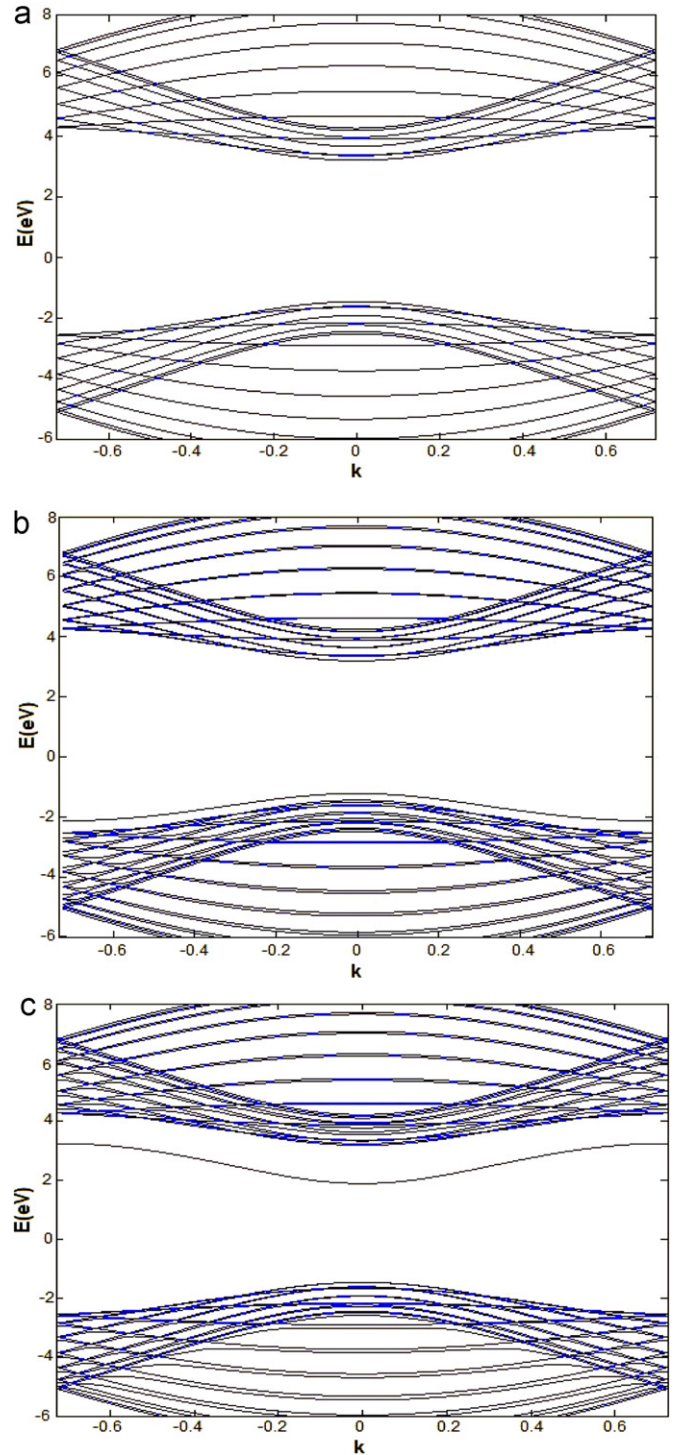
In order to compute the optical absorption spectrum within the TB model, the momentum matrix elements  $c(k)|P|v(k)$  need to be computed between the valence band states  $|v(k)$ , and the conduction band states  $|c(k)$ . Dresselhaus and Dresselhaus [31], Smith [32] and several others [33] have argued that one can replace  $P$  by  $m_0/\nabla_k H(k)$  ( $m_0$  is the free-electron mass) [34], leading to the expression

$$c(k)|P|v(k) = \left(\frac{m_0}{\hbar}\right) \langle c(k) | \nabla_k H(k) | v(k) \rangle \quad (5)$$

In the process of absorption of incident on the nanotube electromagnetic radiation, electron is excited from occupied states ( $v$ ) into empty states ( $c$ ). In the random-phase approximation and neglecting the local field corrections, the imaginary part of the dielectric function for direct dipole transitions and radiation polarized in the  $z$ -direction is given as a function of the photon energy [35,36].

$$\epsilon_2(\omega) = C \left(\frac{1}{\omega^2}\right) \sum_k \sum_{cb,vb} |\langle c(k) | \nabla_k H(k_z) | v(k) \rangle|^2 \delta(E_{c,v,k} - \omega) \quad (6)$$

where  $\omega$  represents the photon energy of the incident radiation and,  $E_{c,v,k} = E_{c,k} - E_{v,k}$ , is the inter-band excitation energy, where  $E_{c,k}$  ( $E_{v,k}$ ) are the energies of the conduction (valence) bands. Also,



**Fig. 1.** (a) Calculated band structure of the (15,0) BNNT, (b) calculated band structure of the (15,0)BNNT with a nitrogen atom substituted by carbon, and (c) calculated band structure of the (15,0) BNNT with a boron atom substituted by carbon  $(-\pi/T) \leq k \leq (\pi/T)$ .

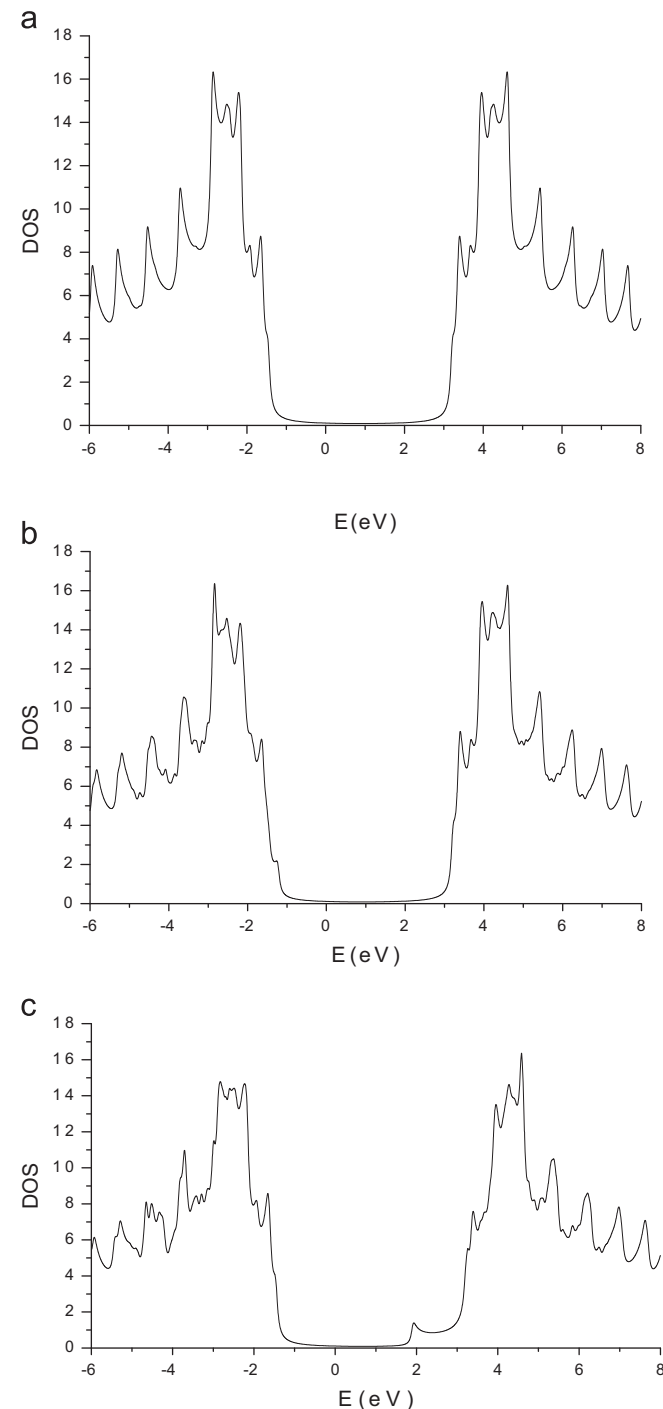
$vb$  and  $cb$  denote the valence and conduction bands, respectively. We have set  $C=1$  in all the cases to obtain the absorption spectra in arbitrary units.

### 3. Result

In this paper first we obtain band structure (BS) and density of state (DOS) for carbon doped (15,0) boron nitride nanotube. Thus

that we substituted a carbon atom instead of boron or nitrogen atom in unit cell of BNNT and we obtained the results for both states (for boron or nitrogen substituted).

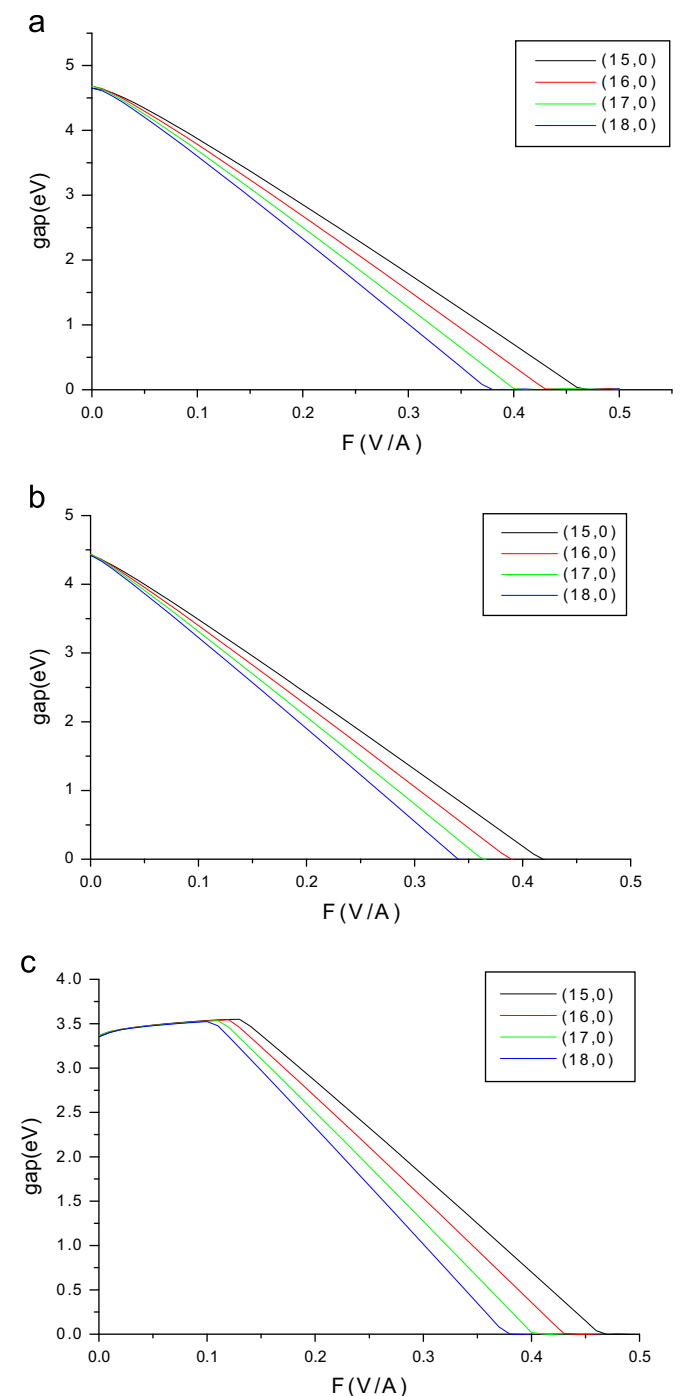
BS and DOS show that substitution of carbon atom creates a single band and one peak in band gap in the BS and DOS, respectively (Figs. 1 and 2). If carbon atom substitutes instead of boron this band is formed near conduction band and if it substitutes instead of nitrogen, this band is formed near the valance band. Due to the presence of this new band, band gap of BNNT reduces. This reduction is 0.23 eV or 1.3 eV when carbon atom substitutes instead of nitrogen or boron, respectively.



**Fig. 2.** (a) Calculated DOS of the (15,0) BNNT, (b) calculated DOS of the (15,0) BNNT with a nitrogen atom substituted by carbon, and (c) calculated DOS of the (15,0) BNNT with a boron atom substituted by carbon (with  $s = 0.05$ ).

The degeneracy of BNNT is lost due to the substitution of carbon atom on the boron and nitrogen sites, which leads to create new peaks in the density of states (Fig. 2). The substitution of carbon atom instead of nitrogen has less effect on band gap because on-site energy of carbon atom is near to nitrogen atom.

Also we investigated the modifications of band gap of C-doped BNNTs by applying electric field. Our calculations show that the pure BNNTs band gap decreases linearly to the zero by increasing the electric field strength. All BNNTs have similar behavior for the gap reduction and by increasing their diameter, the rate of the gap reduction increases, these changes have been plotted for BNNTs



**Fig. 3.**  $E_g$  in term of electric field strength  $F$  for: (a) BNNTs for different radius, (b) BNNTs with a N atom substituted by carbon, and (c) BNNTs with a B atom substituted by carbon.

with different radius in Fig. 3. The figure shows that applying high electric field causes transition from semiconductor to conductor in BNNTs [37].

The calculations show that if carbon atom substitutes instead of nitrogen, band gap decreases linearly to the zero by increasing the strength of electric field. But in the case of substitution of carbon on the boron site, band gap increasing linearly to the maximum value and then decreases to zero by increasing the strength of electric field, increasing of band gap at first is similar to behavior of the carbon NTs in electric fields (the band gap for

CNTs increases at first and decreases later (metallic) or first hold constant and then decreases (semiconductor) [23]).

Also we investigated the modifications of C-doped BNNTs band gap in the presence of magnetic fields. The results show that the band gap of C-doped BNNTs oscillates as a function of magnetic flux, as parabolic and has a symmetric behavior as  $E(\theta/\theta_0) = E(1-(\theta/\theta_0))$  [38]. The period of this oscillation is  $\theta_0$  in both situation (for boron or nitrogen substituted) and similar to the pure BNNT. All BNNTs (pure and C-doped) remain semiconductor in any magnetic field (Fig. 4).

We calculated the absorption spectrum of C-doped (15,0) BNNT for parallel polarization of light with NT axel. In the absorption spectrum, each peak is the corresponding with the energy difference between occupied and unoccupied Von Hove

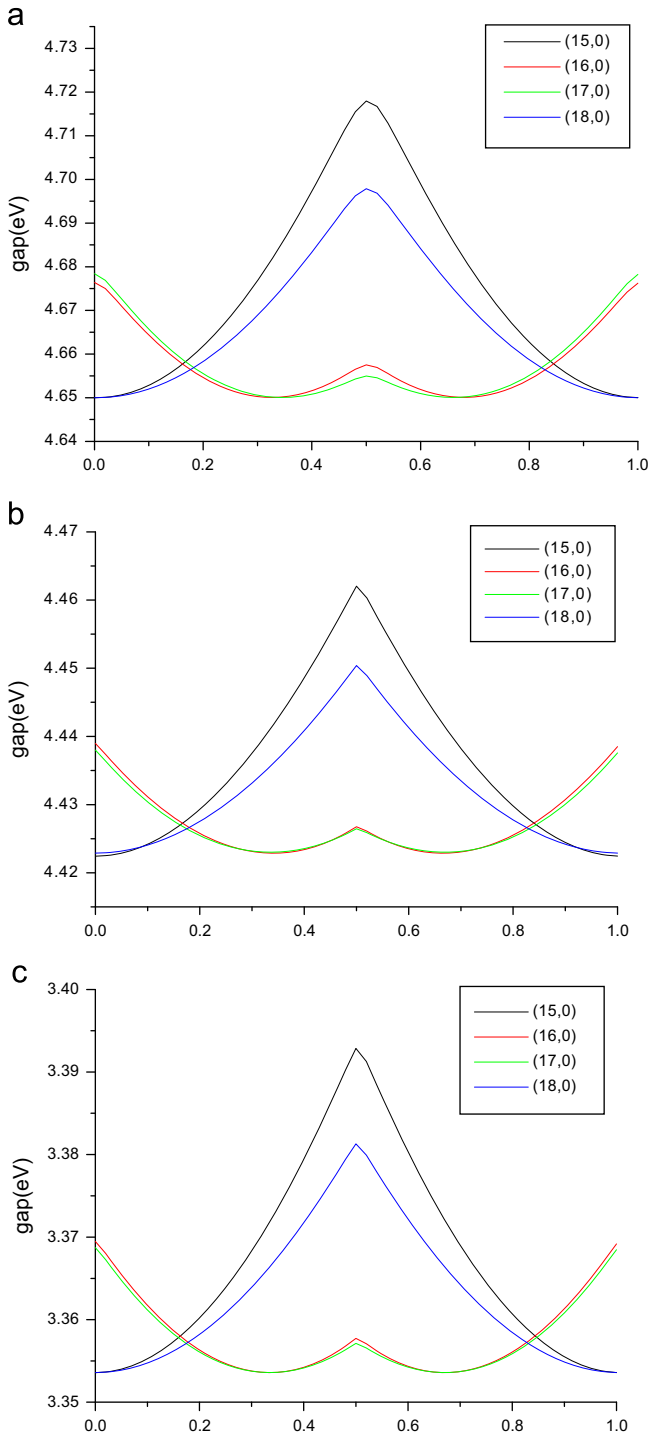


Fig. 4. Eg in term of magnetic field strength  $\theta/\theta_0$  for: (a) BNNTs for different radius, (b) BNNTs with a nitrogen atom substituted by carbon, and (c) BNNTs with a boron atom substituted by carbon.

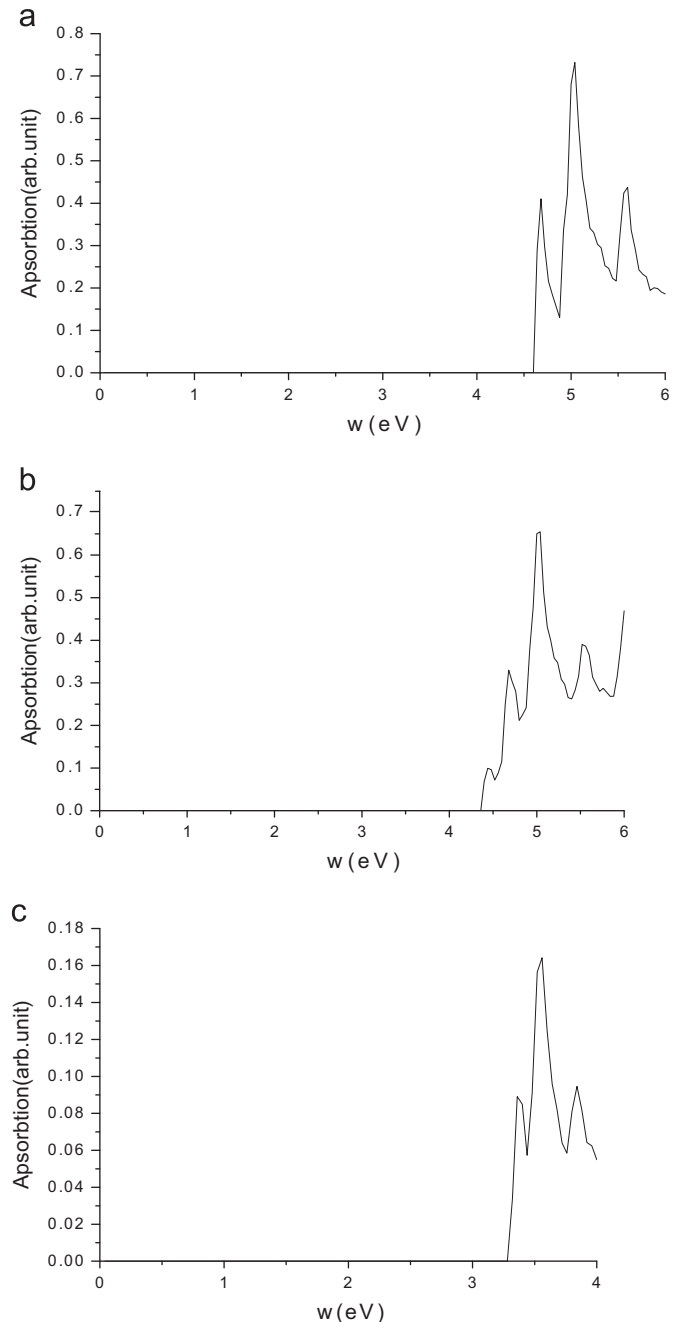


Fig. 5. Absorption spectrum for: (a) the (15,0) BNNT, (b) the (15,0) BNNT with a nitrogen atom substituted by carbon, and (c) the (15,0) BNNT with a boron atom substituted by carbon.

singularities (VHSs) in the 1D electronic DOS. By interring carbon in BNNTs optical gap decreases, too. This can be understood in terms of localized states lying below the edge of the conduction band or above the top of the valence band associated with carbon impurity in a BNNT [39]. Also, because of reduction of peak's height in DOS (first peaks near Fermi level) the intensity of absorption peaks decrease (first peaks), especially for substitution boron (Fig. 5).

#### 4. Conclusions

We show that substitution of one carbon atom instead of boron or nitrogen creates a single band and one peak in band gap in the BS and DOS, respectively. Due to the presence of this new band, band gap of BNNT reduced, this reduction is 0.23 eV or 1.3 eV when carbon atom substitutes instead of nitrogen or boron, respectively.

We show that by interring carbon in BNNTs, the degeneracy breaks in the band structure which leads to create new peaks in the density of states. We have investigated the dependence of band gap modifications to the axial magnetic and transverse electric fields for one carbon doped BNNTs and compared them with pure BNNTs. Our calculations show that when carbon atom substitutes instead of nitrogen, band gap decreases linearly to the zero by increasing the strength of electric field. But in the case of substitution of carbon on the boron site, band gap increasing linearly to the maximum value and then decreases to zero by increasing the strength of electric field, increasing of band gap at first is similar to behavior of the CNTs in electric fields. The results show that the band gap of C-doped BNNTs oscillates as a function of magnetic flux, as parabolic and has a symmetric behavior as  $E(\phi/\phi_0) = E(1 - (\phi/\phi_0))$ . The period of this oscillation is  $\phi_0$  in both situations (for boron or nitrogen substituted), similar to the pure BNNTs. The absorption spectrum of C-doped (15,0) BNNT for parallel polarization of light with NT axel show that optical gap and the intensity of absorption peaks (first peaks) decrease by adding carbon atom, especially for substitution boron. The substitution of carbon atom instead of nitrogen has less effect on properties of BNNTs because of on-site energy of carbon is near to nitrogen.

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