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A Density Functional Theory (DFT) of optical properties of Boron and Nitrogen doped Single Wall carbon Nanotubes

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Abstract : The optical properties of (8,0) single wall carbon nanotubes (SWCNTs) alloyed with boron (B) and nitrogen (N) are investigated using relaxed carbon-carbon (C-C) bond length ab-initio density functional theory (DFT) calculations in the long wavelength limit. The electronic band structure as well as the Fermi energy is modified by this doping to single walled carbon nanotube systems. In N-doped case, the Fermi energy shows a maximum (7.522 eV) at 75% doping while with boron (B) doped system, a minimum is observed at 53% doping concentration. It is observed that the magnitude of the static dielectric constant essentially depends on the nitrogen and boron doping concentration as well as the direction of polarization. The reflectivity at normal incidence vanishes at some particular concentration of N. However, with B doping, we have not observed this phenomenon. With increase of N doping concentration, the peak of the loss function is seen to shift to higher frequency. All these factors may shed light on the

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nature of collective excitations in boron-carbon-nitrogen (B-C-N) nanotubules and other nanotube composite systems.

Keywords: Carbon Nanotube, doping, abinitio DFT calculations, optical properties

1. Introduction

Owing to their unique one-dimensional structure, carbon nanotubes (CNTs) possess unusual physical, chemical and mechanical properties. Quite naturally, CNTs have been attracted the attention of theoretical and experimental research groups [1-3]. The electronic properties of single walled carbon nanotubes (SWCNTs) depend strongly on size and chirality. However, in experimental synthesis of the CNTs, the above properties cannot be easily tailored. But there have been quite a few attempts to control the properties by incorporating extrinsic foreign atom doping. In most of these dopings, the natural choices have been boron (B) or N, due to two specific reasons. Firstly, both B and N have atomic radii similar to C. Secondly, B and N-doped CNTs can either be p-type or n-type CNTs [4], similar to the usual semiconducting materials, resulting in several important applications in nano-electronic devices [5]. These substitutions in CNT significantly modify the chemical binding configuration, physical and chemical properties in comparison to pure CNTs. Besides, these substitutions in nanotubes strongly modify the electronic band structure and hence the optical properties as it depend on the band structure. The effect of both n- and p-type doping in SWCNTs have been reviewed recently in the literature [6-9].

In this paper we would like to investigate the optical properties of (8,0) BC and CN nanotubes as a function of frequency under the action of a uniform electric field with various polarization direction through relaxed C-C bond length ab-initio DFT. The plan of this paper is as follows: in Section 2, we give a brief description of the numerical methods we have employed. In Section 3, we discuss the simulation results. Finally, in Section 4, we draw the conclusions of this study.

2. Numerical Methods

An extensive account of the numerical computation dealing with various aspects has been described in our earlier work [10-12] associated with B doped system and N-doped systems [13-14]. Here we briefly summarize some of the salient features of this computation. In this numerical simulation, the imaginary part of the dielectric function has been computed by using first order time dependent perturbation theory. In the simple dipole approximation used in Cambridge Serial Total Energy Package (CASTEP) code [15], the imaginary part is given by

$$\varepsilon_2(q \rightarrow 0_{\vec{u}}, \hbar\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{k,V,C} \left| \langle \psi_k^C | \vec{u} \cdot \vec{r} | \psi_k^V \rangle \right|^2 \delta(E_k^C - E_k^V - E) \quad (1)$$

Ω and ε_0 represent respectively the volume of the super-cell and the dielectric constant of the free space; \vec{u}, \vec{r} respectively represent the polarization vector of the incident electric field and position vector. The dielectric constant describes the typical causal response, the real ε_1 and imaginary part of it are connected by Kramers-Kronig transform. In computing the imaginary part of the above dielectric function, typically [$\frac{1}{2}$ (total number of electrons +4)] number of bands were taken.

For the exchange and correlation term in DFT, the generalized gradient approximation (GGA) as proposed by Perdew et. al. [16] is adopted. The standard norm-conserving pseudo-potential in reciprocal space is invoked for the optical calculation. Compared to the standard local density approximation (LDA) (with appropriate modifications) used mostly in electronic band structure calculation, the optical properties of the system are normally standardized by *spin un-polarized* GGA. A cutoff energy of 550 eV for the grid integration was adopted for computing the charge density of the doped system. For BZ integration along the tube axis, we have used 6 Monkhorst [17] k-points. The smearing broadening in computing the optical properties was kept fixed at 0.5 eV. The atomic positions are relaxed until the forces on the atoms are less than 0.01 eV/Å. The typical convergence was achieved till the tolerance in the Fermi energy is 0.1×10^{-6} eV. The geometrical structure of impure system was built by replacing one of the C atom(s) in the

hexagonal ring by N atom(s). The preferred B as well as N sites were chosen having lowest total energy. These results are in agreement with the prediction made for N-doped (n,0) SWNT systems [18].

3. Discussion and Results

Before we discuss the optical properties, the typical ball and stick model of (8,0) BC nanotubes is shown in figure 1. The typical computational super cell used here (which include typically four units of CNT) is the 3d triclinic crystal ($a=18.801 \text{ \AA}$, $b= 19.004 \text{ \AA}$, $c= 4.219 \text{ \AA}$ and angles $\alpha = \beta = 90^\circ, \gamma = 120^\circ$) having P1 symmetry.

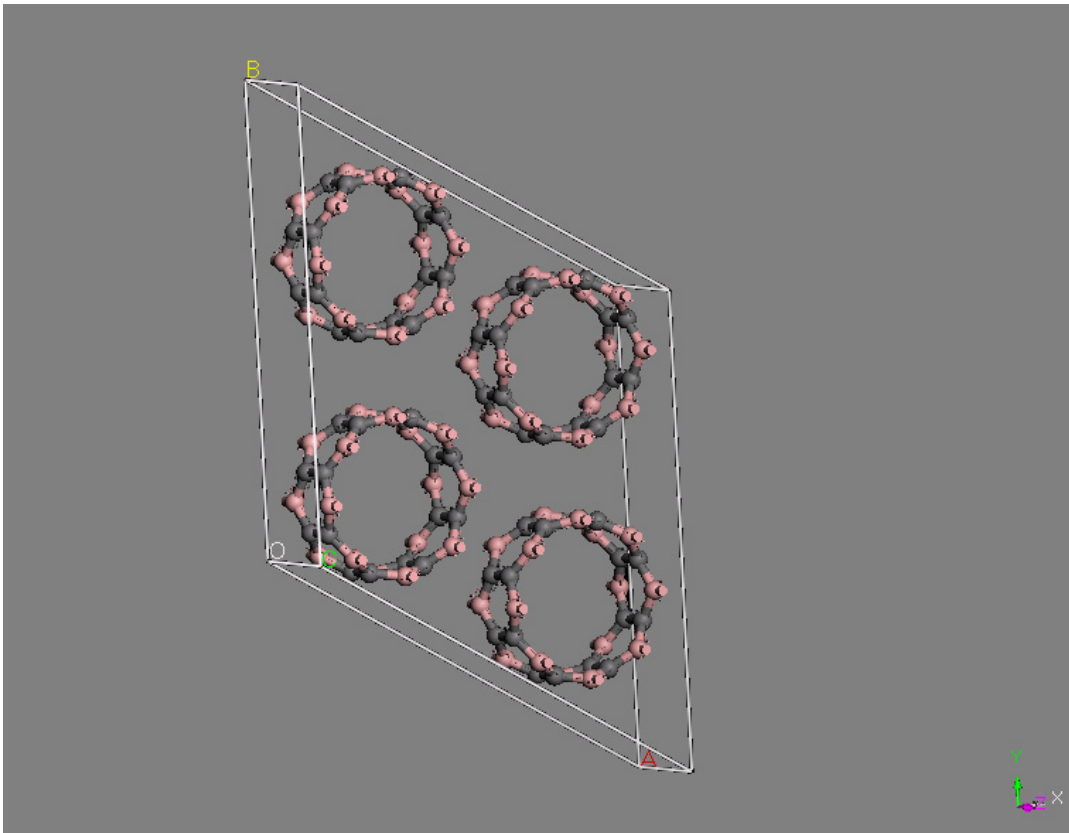


Figure (1) : Ball and stick model of (8,0) BC tube in 3d triclinic structure

The partial density of states (PDOS) of (8,0) CN system is shown in Figure 2. In this figure the Fermi energy is indicated by the dashed line. The figure indicates a series of spikes in the whole spectrum of band energy and these are nothing but the characteristic

van Hove singularity typical feature of low dimensional condensed matter systems. The low temperature scanning tunneling spectroscopy (STS) measurement can be used to verify the position of the spikes. For pure (8,0) we found [10] the Fermi energy 6.028 eV with band gap at Γ point (most symmetric point in the BZ) as 0.48 eV (the energy cut-off used in the above calculation was 470 eV). The Fermi energy for CN nanotubes turns out to be 7.22 eV.

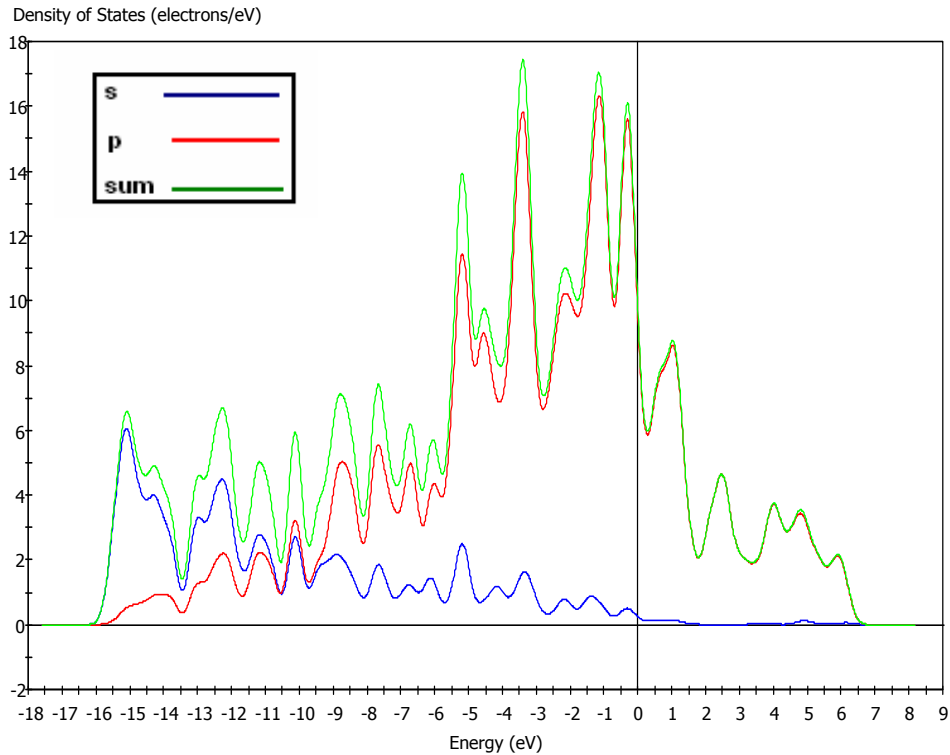


Figure 2. Partial density of states (PDOS) of (8,0) BC SWCNT

With this brief introduction to the density of states of (8,0) BC, we now move on to the discussion of the optical properties of (8,0) BC and CN SWCNTs. In figure 3, we show the variation of real as well as imaginary part of the dielectric constant of BC and CN for parallel polarization of the electromagnetic field as a function of frequency. It is seen that the static dielectric constant of CN SWCNT is strikingly larger compared to BC case. This is due to the large free charge carriers in CN system.

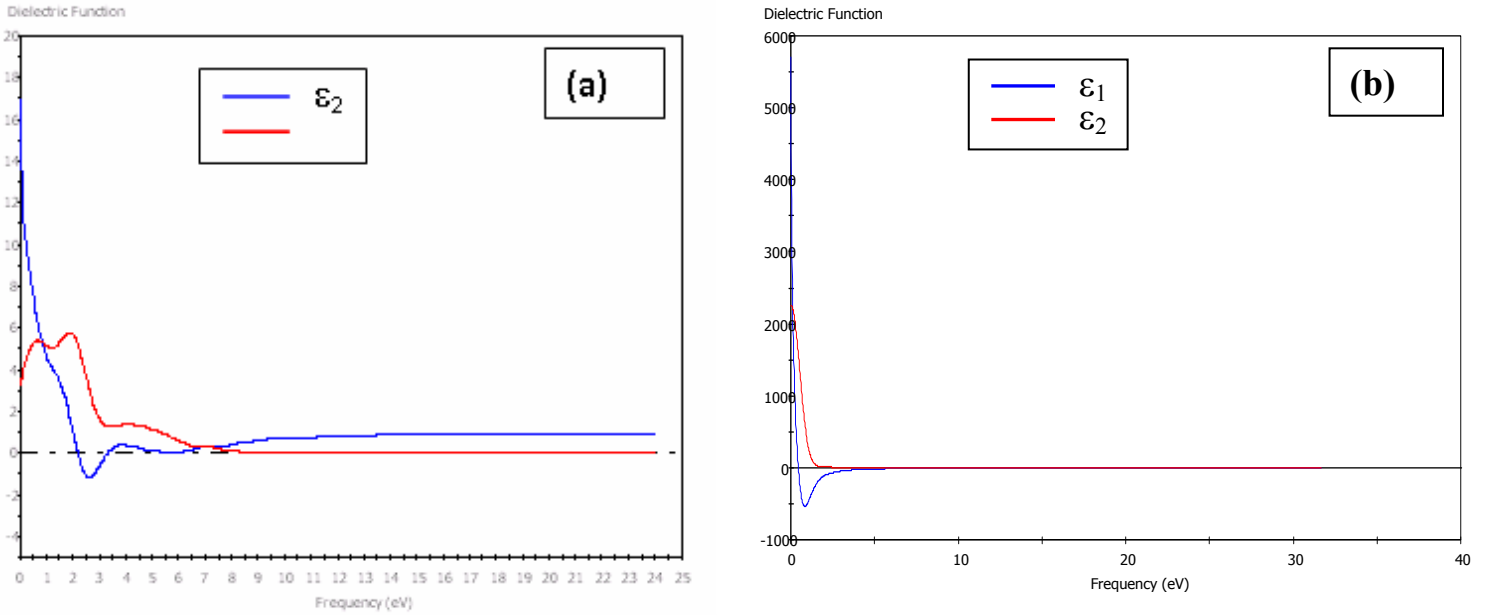


Figure 3. Variation of dielectric constant with frequency for (a) BC and (b) CN in parallel polarization.

To show the anisotropy in the optical properties, we have also computed the reflectivity and the loss function of (8,0) CN system for parallel and perpendicular polarization. The reflectivity $R(\omega)$ of any media at normal incidence is calculated from the refractive indexes via the relations (as implemented in CASTEP [15]) given by

$$R(\omega) = \left(\frac{1 - \sqrt{\epsilon(\omega)}}{1 + \sqrt{\epsilon(\omega)}} \right)^2, \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (6)$$

In figure 4, we depict the reflectivity of the CN system as a function of frequency in the two polarization cases. It is seen from the figure that the reflectivity is bounded by the unity in both cases.

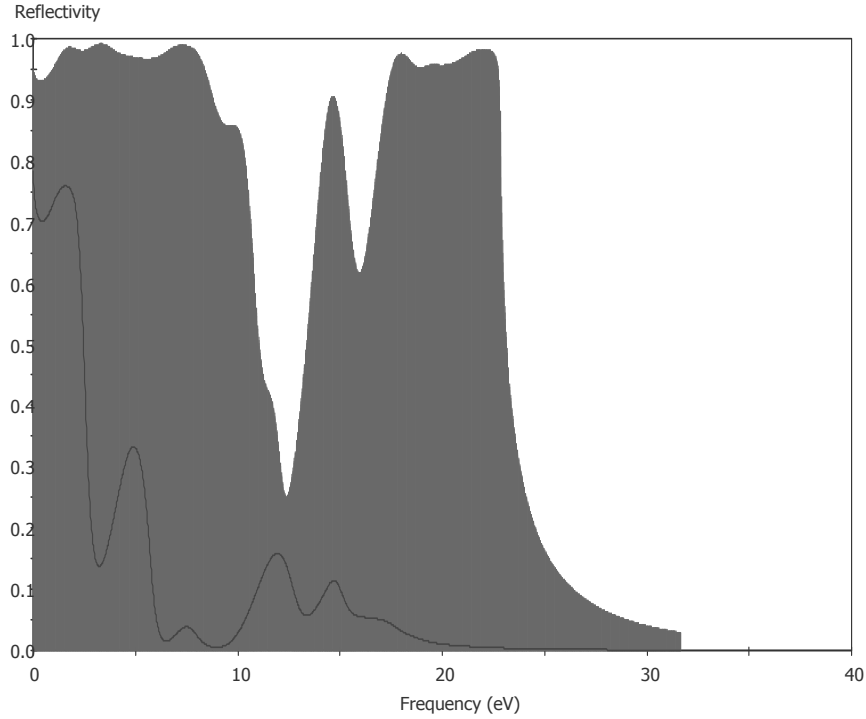


Figure (4) : The shaded one is for parallel polarization while the unshaded for perpendicular polarization of (8,0) CN carbon nanotubes.

The imaginary part of the reciprocal of the total (real plus imaginary) dielectric constant, being a function of frequency generally peaks at the plasma frequency. The loss function, which is a direct measure of the collective excitations of the systems, is calculated from $\text{Im}[-1/\varepsilon(q, \omega)]$ at $q \rightarrow 0$ limit. A straightforward algebra reveals that

$$\text{Im}[-1/\varepsilon(q, \omega)] = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}. \text{ At the plasma frequency, the above expression attains}$$

the higher value when $\varepsilon_1 \rightarrow 0$ and $\varepsilon_2 < 1$. In figure 5, we show this loss function as function of frequency in the two polarization cases.

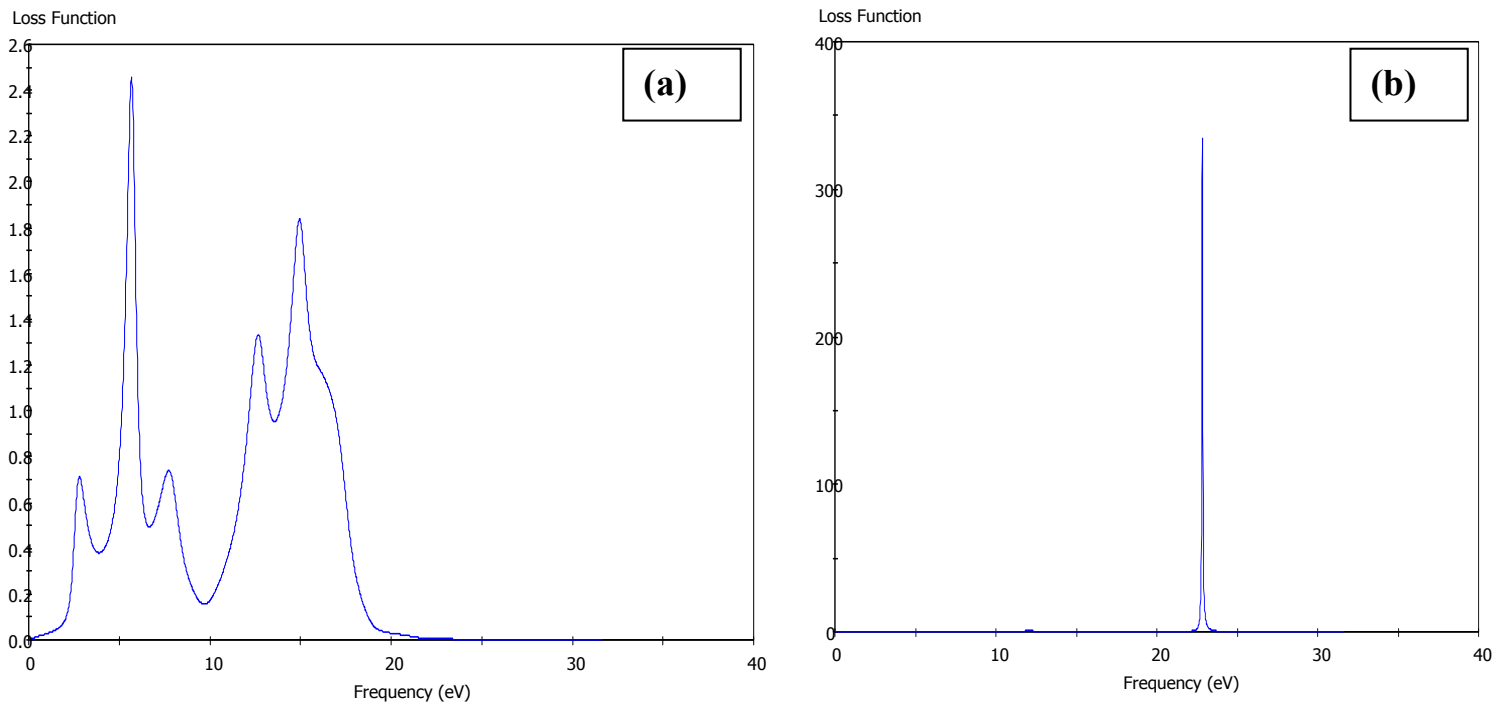


Figure (5) : The loss function as a function of frequency for (a) Perpendicular Polarization and (b) parallel polarization of (8,0) CN SWCNT.

The anisotropy in parallel and perpendicular polarization is clearly revealed in figure 5. Moreover, in parallel polarization, there exists a unique peak corresponding to a collective excitation of π electrons whose magnitude is appreciably higher than that of perpendicular polarization.

4. Conclusions

From the first principles relaxed C-C bond length DFT calculation of the optical property of (8,0) BC and CN SWCNT systems, we have observed significant changes in the optical behavior for different polarizations. The behavior of the static dielectric constant of CN system is higher compared to BC system due to enhanced metallic character. This is also reflected from the study of the loss function of CN system in perpendicular and parallel polarization. A significant anisotropic behavior is also noticed in CN system for

parallel as well as perpendicular polarizations. It will be interesting to compare these theoretical predictions with experimental results.

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