

Absorption of BN nanotubes under the influence of a perpendicular electric field

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We calculate the optical absorption spectra of prototype (6,6) and (9,9) BN nanotubes in the presence of a perpendicular electric field. This model mimics a gated BN nanotube device. Even though the band-gap of the tubes decreases strongly as a function of the electric field strength, the absorption spectrum of the pure tubes remains remarkably constant up to high field-strength. We show that, in contrast, the levels which are responsible for defect-mediated photo-luminescence are shifted by the electric field. We address the use of BN nanotubes for optoelectronic applications.

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1 Introduction

Contrary to carbon nanotubes, boron nitride nanotubes (BNNTs), have a large band-gap of more than 6 eV, independently of radius and chirality [1]. Recently, the potential of bulk hexagonal BN for ultra-violet lasing has been demonstrated [2]. It is a logical next step trying to build lasing or opto-electronic devices with BN nanotubes. In this respect, it is interesting to know if the optical properties can be tuned in a controlled way. It has been shown theoretically [3, 4] that the band gap of BNNTs can be reduced by applying an electric field perpendicular to the tube axis. This decrease of the gap is due to the Stark-Effect, i.e., the charge densities of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) become spatially separated on opposite sides of the tube [3]. Even though the gap is reduced considerably, the effect of an electric field on the optical absorption spectrum was found to be less pronounced [5] (for light polarization parallel to the tube axis which gives the dominant contribution to the averaged light-scattering cross Section). The calculations of Ref. [5] have been performed on the level of the random-phase approximation, i.e., neglecting the effects of electron–electron and electron–hole correlation (excitonic effects). These effects, however, have been shown to strongly dominate the optical spectra of BNNTs [6, 7]. We investigate therefore in this paper, how the transverse electric field changes the excitonic nature of the absorption spectrum. Furthermore, we discuss the influence of the electric field on the impurity levels that may lead to defect-mediated luminescence [8].

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2 Methodology

The calculations of the optical absorption spectra proceed in three steps. We first calculate the wavefunctions of the valence band states and a large number of conduction band states using density functional theory (DFT) in the local-density approximation (LDA) using the Perdew–Zunger exchange–correlation functional [9]. These calculations have been done using the Quantum-ESPRESSO package [10]. Core electrons are replaced by norm-conserving pseudo-potentials generated by the scheme of von Barth and Car [11]. The wavefunctions are expanded in plane waves with an energy cutoff at 40 Rydberg. We use a periodic supercell where the closest distance between neighboring tubes is 10.6 Å. The transverse electric field is introduced by a sawtooth potential commensurate with the supercell geometry. The optimized geometry of the tube was only calculated without the external electric field, i.e., potential changes in the geometry induced by the field are neglected.

The second and third step are analogous to the recent work on excitonic effects in BN nanotubes [6, 7]: We use the GW-approximation [12, 13] to calculate the quasi-particle energies (“true” single-particle excitation energies). Effects of electron–hole attraction (excitonic effects) are included by solving the Bethe–Salpeter (BS) equation [12]. These calculations are performed with the code SELF [14].

For the present exploratory calculations we have chosen the (9,9) BN tube which has a diameter of 12.5 Å, at the lower limit of the diameter range of experimentally produced single-walled BNNTs. For the investigation of excitonic effects, we have chosen – due to reasons of numerical feasibility – the (6,6) BN tube which has a diameter of 8.3 Å. Note that this latter tube is only 0.3 Å larger in diameter than the (10,0) tube that was investigated in Ref. [5]. The effect of an electric field should thus be practically the same.

3 Results and discussion

Figure 1 shows the band-structure of the (9,9) BNNT for different values of the external electric field. We note that the gap for this tube is indirect because the “nearly-free electron” (NFE) state [15] at Γ is lower in energy than the conduction band minimum at the direct gap which is situated at $2/3$ between Γ and X. However, for larger diameter armchair tubes, the NFE state is higher in energy and the onset of absorption is thus determined by the value of the direct gap (i.e., we do not need to consider phonon mediated absorption for indirect gap materials here). Figure 1 demonstrates that the band-gap becomes strongly reduced through the application of a perpendicular electric field as shown in previous works [3–5].

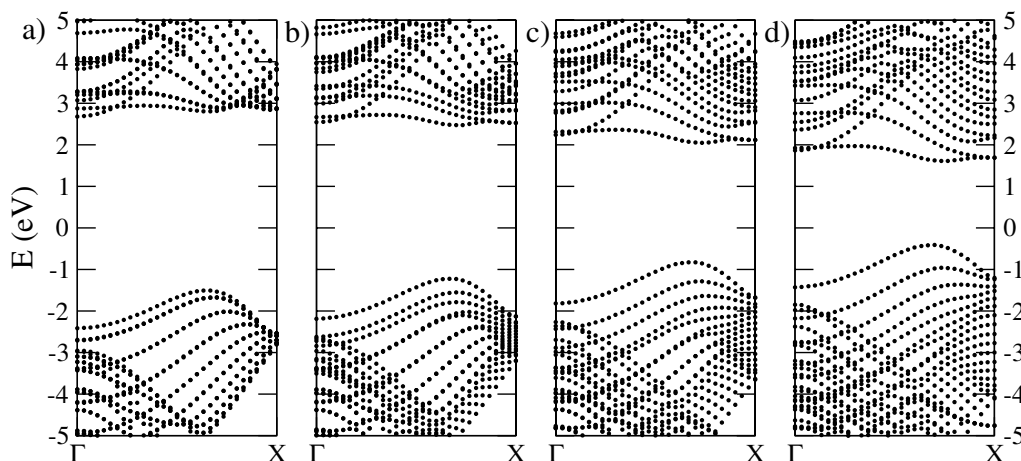


Fig. 1 Calculated band structure of a (9,9) BN nanotube, a) without external electric field, b) $E = 0.1$ V/Å, c) $E = 0.2$ V/Å, d) $E = 0.3$ V/Å.

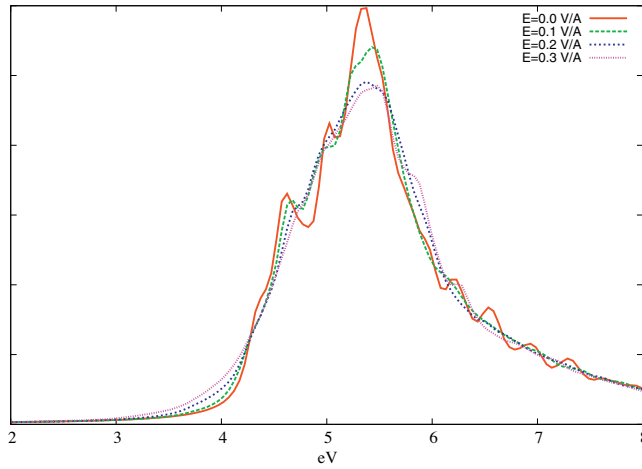


Fig. 2 (online colour at: www.pss-b.com) Optical spectrum, calculated in the random-phase approximation, of the (9,9) BN nanotube for different values of a perpendicular homogeneous electric field. The light-polarization is parallel to the tube axis.

Figure 2 shows the optical spectra that result from the band-structures of Fig. 1 in the random-phase approximation. In this approximation, the effects of electron–electron and electron–hole correlation are neglected and the spectrum is calculated according to Fermi’s golden rule:

$$\varepsilon_2(\omega) \propto \int_{\text{IBZ}} dk \sum_{v,c} |D_{vk,ck}|^2 \delta(\varepsilon_{ck} - \varepsilon_{vk} - \omega), \quad (1)$$

where the integral is performed over the first Brillouin zone, v and c denote valence and conduction bands, respectively. $D_{vk,ck}$ denotes the dipole matrix element between two states with energies ε_{ck} and ε_{vk} , respectively. We only show here the absorption spectra for light polarization parallel to the tube axis as this contribution dominates the total absorption cross section. (The contribution of perpendicularly polarized light is strongly suppressed by depolarization effects below 7 eV [16].) The main peak at 5.3 eV in the spectrum corresponds to the maximum in the joint density of states for transitions between the π and π^* bands of the BN single sheet at M . The fine structure below this peak in the spectrum without electric field is caused by optical transitions between states around the Van-Hove singularities in the 1D density of states. These singularities are due to the formation of one dimensional subbands in the tubes (see Fig. 1a). We used a sampling of 30 k-points in the irreducible Brillouin-zone in order to make sure that this fine-structure is not an artefact due to insufficient k-point sampling. With increasing electric field, the fine-structure is washed out. This effect is due to the splitting of the bands that are degenerate at zero electric field. The main peak around 5.3 eV remains almost constant. With increasing electric field, the onset of absorption is shifted towards lower energies. However, due to the spatial separation of occupied and unoccupied states on different sides of the tube, the spectral weight at the onset of absorption is very weak. Therefore, the overall spectrum remains remarkably stable as a function of the electric field. This is in agreement with the findings of Ref. [5].

The main result of this paper is the inclusion of quasi-particle and excitonic effects on the absorption spectra shown in Fig. 3. For comparison with experimental data, we present the data with a broadening of 0.1 eV in the left panel. For a theoretical discussion, we also present the spectra with a very fine broadening of 0.01 eV, in order to better discern the distinct excitonic peaks. A set of 10 k-points in the irreducible Brillouin zone has been used for these calculations. The effect of the electric field is a shift of oscillator strength from the dominant excitonic peak to the higher lying excitonic peaks. Nevertheless, as in the case of the RPA spectra, the overall structure of the spectrum remains constant. We note that the

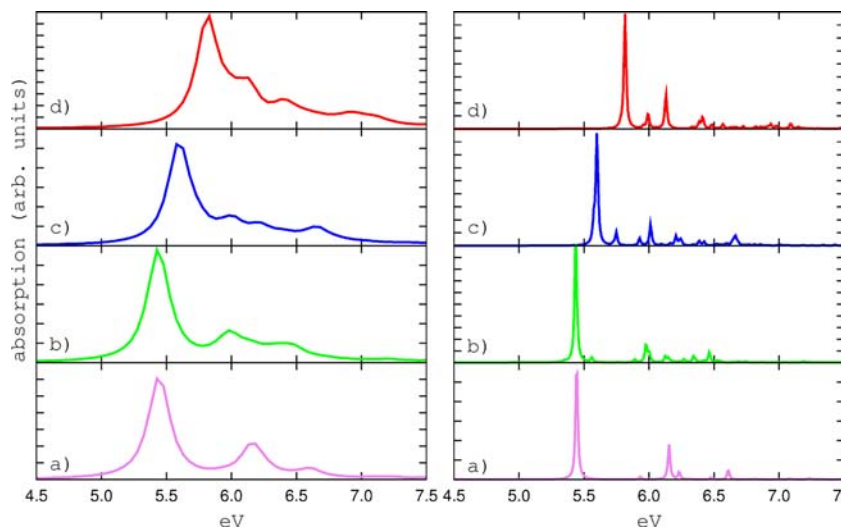


Fig. 3 (online colour at: www.pss-b.com) Optical spectrum including quasi-particle and excitonic effects of the (6,6) BN nanotube for different values of a perpendicular homogeneous electric field: a) no electric field, b) 0.1 V/Å, c) 0.2 V/Å, d) 0.3 V/Å. The light-polarization is parallel to the tube axis. Left panel: 0.1 eV broadening, right panel: 0.01 eV broadening.

blue shift of the spectrum for higher field-strength is due to an enhanced value of the GW gap correction and not due to a weaker excitonic binding energy. However, further convergence studies with respect to the intertube-distance are needed. (For the case of zero-electric field, we verified in Ref. [6] that the spectrum is almost independent of the intertube distance: increasing the amount of vacuum increases the GW-gap correction. At the same time the excitonic binding energy increases, leaving the main absorption peak at the same position.) In principle, a cutoff of the Coulomb-potential between neighboring tubes should be used [17, 18].

For pure BN nanotubes, we can thus conclude that the optical absorption spectra are very little affected by an electric field. This situation may, however, change for luminescence spectra. Peaks around 4 eV in the luminescence spectra [8] are related to defect levels. Possible candidates are vacancies or carbon substitutions. As an example, we have calculated the influence of the electric field on the acceptor level that is due to the replacement of a nitrogen atom by a carbon atom. We have performed the calculation in a large supercell, containing one carbon substitution in 252 atoms. Figure 4a shows the density of states of the pure (9,9) BNNT, calculated within DFT-LDA. Adding the carbon impurity in panel b) intro-

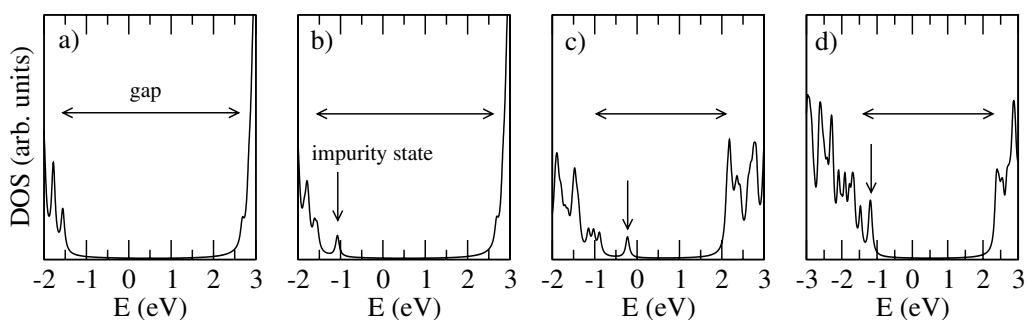


Fig. 4 Density of states of a) a pure (9,9) BN nanotube, b) a tube with a carbon impurity atom, c) with a C atom and a perpendicular E-field of 0.2 V/Å, d) with a C atom on the opposite side and an E-field of 0.2 V/Å. The light-polarization is parallel to the tube axis.

duces an impurity level at about 0.5 eV above the valence band edge. Depending on the orientation of the carbon impurity with respect to the direction of the electric field, this impurity level can move up or down with respect to the valence and conduction band edges (Fig. 4c and d). Photoluminescence may involve transitions from the conduction band to the impurity level and from the impurity level to the valence band. Defect mediated luminescence spectra may thus be more sensitive to the influence of an electric field than the spectra of pure BNNTs.

4 Conclusion

In conclusion, we have shown that the optical spectra of BN nanotubes are quite robust to the application of external fields. Furthermore, we have shown that the external field affects the defect energy levels due to carbon impurities. Those defects gives rises to luminescence in the visible as well as modification of the shape of the main absorption peak shown in Fig. 3. Therefore an external electric field can be used as tool to discriminate the photoemission due to exciton recombination in pure systems with respect to the one due to defects. BN nanotubes may thus be very good candidates for tunable nanoscale optoelectronic devices in the UV regime.

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