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Band-gap tunability of a (6,0) BN nanotube bundle under pressure: *Ab initio* calculations

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Ab initio calculations were performed to study the structural transformation on a boron nitride nanotubes bundle under pressure. Several bundles of boron nitride nanotubes, disposed into a hexagonal arrangement, were studied between which the (6,0) zigzag configuration was chosen to be detailed here. Upon compression the hexagonal arrangement as well as the circular cross section of the tubes were preserved up to a critical pressure value. At this pressure value the tubes deform to an oval cross section and the bundle shape diverge from the original hexagonal symmetry. The percent difference volume suffers a discontinuity with pressure demonstrating the discontinuous nature of the structural transition. The energy gap undergoes a continuous decrease up to the pressure of collapse of the tubes. The tunability of the gap is a fundamental requirement for engineering electronic nanodevices widening the perspectives for boron nitride nanotube applications.

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Boron nitride nanotubes, BNNTs, have been considered ideal for several device applications in the nanoscale domain, owing not only to their unique electronic structure[1] but also to their high chemical inertness,[2] thermal stability,[3] and excellent mechanical properties. In the emerging field of spintronic at the nanoscale, nanomaterials such as C/BN systems have been suggested as suitable candidate for functional magnetic devices, as C-BN hybrid structures exhibit substantial collective magnetism.[4] BNNTs are inherently noncytotoxic[5,6] and can be surface functionalized with biological species with no risk to their use in living organisms, opening the opportunity of their use for therapeutic or diagnostic applications. Likewise, the biocompatibility associated to the magnetic properties of BNNTs containing Fe catalysts stimulated investigations on the feasibility for their use as nanovectors for targeted drug delivery.[7] As filler in polymeric composites, BNNTs can improve mechanical properties and thermal conductivity of a polymer while preserving its dielectric properties.[8,9] Some outstanding applications especially in nanoelectrical devices were recently proposed, either as inorganic compound nanowire-nanotube hybrid systems[10] or insulating/conducting nanocables outer shells, with carbon nanotubes inside.[11] The C/BN cable is a high-strength material similar to pure carbon nanotube and under tensile deformation was predicted to retain the basic electronic characteristics (metallic for the inner and dielectric for the outer shell).[12] Even though there is a number of perspective frontier use of BNNTs, electronic and photonic applications were believed inviable due to the stability of their energy gap on diameter and/or chirality.[1] The ability to engineer the band-gap energy of the isolated BN tube, either by applying a transverse electric field or a transverse deformation, has been considered in some recent investigations using first-principles pseudopotential density-functional theory (DFT) calculations.[13,14] In one way it was found that different diameter BNNTs show a reduction in the band gap under an external electric field. However, to reduce the band gap from 4 to 0.4 eV required about 2.5 V/nm and no prediction for the structure of the tube was given for such a high-field strength.[13] Another work predicted that in zigzag BN nanotubes the gap can be decreased while the armchair BN nanotubes were found to be insensitive to radial deformations.[14] This selective behavior between zigzag and armchair nanotubes was attributed to the different characteristics of states near the gap. In crystalline bundles, on the other hand, a more recent calculation shows that the charge transfer per B atom in the bundled (8,8) BNNT increases as a function of the decrease in the intertube separation.[15] Based on this result it is possible to infer that compressing the bundle should produce considerable effects on its electronic properties, in contrast with the predictions for isolated tubes. Modifications of the electronic properties through the functionalization of BN nanotubes have mainly focused on the B-N-C system through the control of a C content.[16,17] Alternatively, doped BN nanotubes obtained through chemical modification would also be a prospective object for tailoring the electronic properties. Nevertheless, high chemical inertness of BNNT prevents them from stable functionalization. A stable fluorination of BN nanotubes was achieved recently and resulted on the resistivity to be decreased by about three orders of magnitude as compared to that of the undoped tube.[18] However, the fluorine doped BN nanotubes were found to posses a morphology with considerably disordered walls when examined with the use of electron transmission microscopy techniques. A cleaner method for band-gap engineering relies on the application of an external pressure that combined with the lack of chemical reactivity is a promising means for BN-based electronic nanodevice applications. This method should serve for tuning the gap with no side effects on the tube symmetry structure or compromising the tube walls. Even though a work developed by some of us reports predictions of the changes on the electronic and structural properties of a wide diameter tube[19] subjected to hydrostatic pressure, its focus was not, particularly, the band-gap tuning.

To predict full effects of pressure on the distinguished electronic properties and estimate the collapse pressure for a bundle of single-walled BNNTs with smaller diameter tubes, a (6,0) zigzag configuration is considered here. The study focus on the structural characterization and electronic properties by means of an *ab initio* calculation. The circular cross section of the tubes is preserved upon application of pressure up to a critical value when this form is observed to collapse to oval. After this collapse the hexagonal arrangement of the tubes in the bundle is transformed into a deformed hexagon elongated in a certain direction. A discontinuous change in the percent differential volume is observed to occur at this critical pressure that is also correlated with the cohesive energy. Besides being a first insight in understanding the stability of bundled BNNTs the results suggest the possibility of tuning their electronic properties. This possibility is handy to overcome the wide band-gap limitation inherent to BN nanotubes in order to serve several perspective applications of BNNT bundles to electronic nanodevices.

First-principles DFT[20] calculations were performed to study the structure, energetic, and electronic properties of the BNNT bundle under pressure. The SIESTA code was used[21] and full self-consistent calculations were performed by solving the Kohn Sham equations.[22] The generalized gradient approximation of Perdew-Burke-Ernzerhof[23] was employed to the exchange and correlation functional. In all calculations the double zeta basis set plus polarization function was used to represent the valence electrons.[24] The interaction between ionic cores and valence electrons is described by norm-conserving pseudopotentials,[25] in the Kleinamn-Bylander form.[26] A cutoff of 120 Ry for the grid integration was used to represent the charge density. The Brillouin zone was sampled by eight k points generated according to the Monkhorst-Pack scheme.[27] The (6,0) zigzag nanotubes bundle was built by taking a hexagonal prism as its unit cell. At the center of each periodically repeated unit cell 24 atoms were settled with the nanotube axis perpendicular to the basal hexagonal plane of the unit cell. At atmospheric pressure a separation between the centers of nanotubes in neighboring cells was assumed in the bundle, corresponding to the tube diameter plus 3.33 Å, the latter representing the distance between hexagonal planes in BN bulk. For each value of the external hydrostatic pressure a complete conjugated gradient optimization of the atomic coordinates and the lattice parameters was performed. The optimization was interrupted when the changes both on the atomic forces and on the stress components were lesser than 0.05 eV/Å and $4 \times 10-4$ eV/Å^3, respectively. A stepwise monotonically increasing hydrostatic pressure was applied to the BNNTs bundle after equilibrium under atmospheric conditions. The pressure was increased from 0 to the pressure of breakdown of the system in 30 stages for the (6,0) tubes bundle. The cohesive energy was calculated as

$$E_c = E_0 - E_P, \tag{1}$$

where E_0 is the total energy of the bundle with no pressure applied and E_P is the total energy of the bundle when the applied pressure value is P.

A detailed discussion the (6,0) zigzag BNNTs bundle will be considered next. The relaxed structure of these bundles is shown in Figs. 1(a)–1(d) for an external hydrostatic pressure of 0, 22.0, 23.0, and 25.0 GPa, respectively.

In the low-pressure range, $P<22$ GPa, the nanotubes maintain their original form (as observed at atmospheric pressure) with a circular cross section as shown in Figs. 1(a) and 1(b). At a certain critical pressure value, P_c, the tubes turn to an oval cross-section form and for higher pressures, $P>22$ GPa, the nanotubes oval form cross section evolve gradually to a more closed oval form [see Figs. 1(c) and 1(d)]. For pressure values $P>25.0$ GPa the (6,0) bundle was observed to suffer a breakdown to a set of planes of hexagonal BN. To help the analysis of this structural change, the parameters **a** and **b** were defined as the distances from the next neighboring tubes, as shown in Fig. 1(a). The parameters **a** and **b** diminish with the increase in the pressure applied to the (6,0) BNNTs bundle up to the critical pressure, $22\text{ GPa}<P_c<23$ GPa, when a discontinuity occurs. Increasing further the pressure up to the breakdown value, the rate of variation in the parameters **a** and **b** decreases.

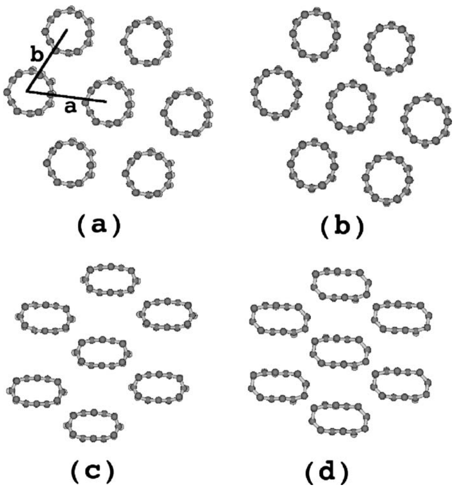

FIG. 1. Optimized structure representation for the zigag (6,0) BNNTs bundle under pressure (a) 0 GPa, (b) 22.0 GPa, (c) 23.0 GPa, and (d) 25.0 GPa.

It should be noticed that it is the bundle structure, rather than the isolated tube, that is mostly affected in the pressure range $P<22$ GPa. The unit-cell parameters in the plane perpendicular to the tube axis decrease while for $P>P_c$ the angle between them change producing a large geometric deformation toward a well distorted hexagon. The angle between the parameters of the unit cell playing a crucial hole in the structural configuration makes it difficult to draw conclusions on the changes in the weak interaction among the tubes in the bundle based on intertube distances. In order to give a more complete description, the percent difference in cell volume compared to the equilibrium volume at zero pressure is calculated.

In Fig. 2(a) the percent relative volume versus pressure is plotted and in Fig. 2(b) the percent relative volume dependence on the cohesive energy is shown. A decrease in relative volume was observed to take place for pressures up to 22.0 GPa. At this value a strong discontinuity is observed. A further decrease in percent relative volume is observed for higher pressures up to the value at which the rupture of the bundles was observed to occur. The cohesive energy decreases with the increase in pressure with a discontinuity separating the two distinguished regimes occurring at $E=-3.2$ eV.

Comparison with the plots of percent volume difference points to the discontinuity to represent the limit value of cohesive energy possible to attain for the (6,0) BN nanotube

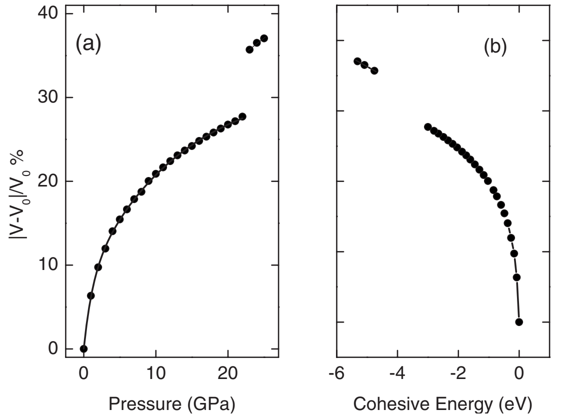

FIG. 2. Magnitude of percentage difference in relative volume with (a) pressure and (b) cohesive energy for the (6,0) BNNTs bundle.

bundle prior to collapse. This discontinuity indicates that the structural phase transition, described as the departure from the circular cross-section form, is first order.

In order to explore the possible effects of pressure on the electronic properties the band structures were calculated for this set of nanotubes. Figure 3 represents the electronic band structure of the (6,0) BNNTs bundle for $P=0$, 10.0, 20.0, 22.0, 23.0, and 25.0 GPa.

The band-structure changes, in the low pressures regime ($P<22.0$ GPa), are mainly manifested by the downshift of the lowest lying conduction bands and upshift of the upper lying valence bands near the Γ point, the qualitative pattern being relatively well preserved for great steps of pressure. In the high-pressure regime ($P>22.0$ GPa), on the other hand, a generalized dispersion of electronic states is observed, giving rise to a completely new pattern each time the pressure is changed, even if the pressure step is as small as 1 GPa, as can be seen in the figure. It is most probably the decrease in the unit-cell volume of the bundle that drives the displacement of the lowest conduction band and the highest valence band toward the Fermi level diminishing the energy gap for any pressure below P_c, as the isolated tubes are not deformed significantly. The overall effect of pressure in the band-gap energy is represented in Fig. 4. It can be observed in low-pressure regime a reduction in band-gap energy from 2.3 eV for $P=0.0$ GPa to 0.5 eV for $P=22.0$ GPa, allowing to predict that the (6,0) bundle band-gap energy can be tuned in a wide range from the visible to the infrared region of the spectrum. At this point it is desirable to compare the above described results with those obtained for higher diameter tubes, such as the zigzag (16,0), (12,0), and (8,0) BNNTs bundles, for instance. For this purpose the energy gap versus pressure plots for these bundles were also included in the figure. Considering the complete set of bundles, the band-gap energy range between 4.1 and 0.5 eV, for pressures increasing up to $P=22.0$ GPa.

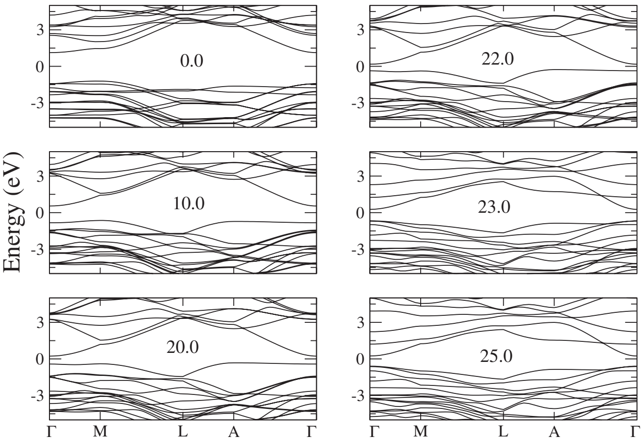

FIG. 3. Band structure for zigzag (6,0) BNNTs bundle under pressure. The pressure values are given in the figure in units of GPa. The Fermi level is localized in 0 eV.

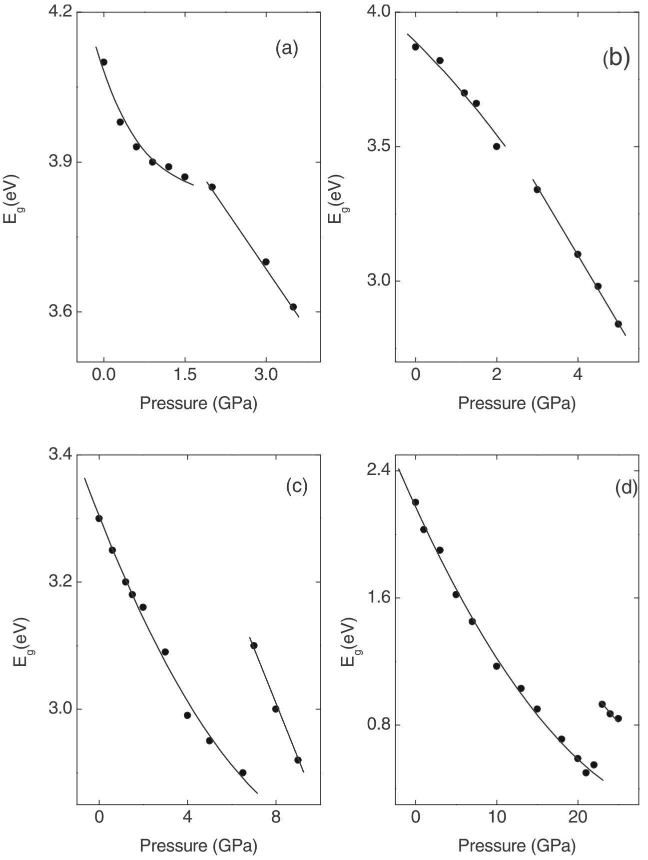

FIG. 4. Band gap versus pressure for the zigzag (a) (16,0); (b) (12,0); (c) (8,0); and (d) (6,0) BNNTs bundles.

The comparison also leads to the conclusion that there is a clear decrease in collapse pressure with increasing BN nanotube diameter. There appears to be an inverse proportionality between collapse pressure and tube diameter, the mathematical expression for this law depends on a range of diameters to be investigated. Calculations for a set of other diameter tubes are on their way and will be reported in a future publication. Most remarkable, is the tunability of the energy band gap that will allow to overcome the major drawback in applications of the wide band-gap BN nanotubes in nanodevice electronics. The possibility of band-gap tuning in the range ~ 4.1 eV$<E_g<\sim 0.5$ eV for different zigzag BN nanotubes gives rise to further potentially useful variations in device applications. It should be noticed that the structural phase transition in the BNNTs bundles studied here differ from the case of CNTs in the sense that a single discontinuous transformation occurs. The deformation of CNTs was found to occur either as a first-order transformation or a second order, depending on the tube diameter.[28] Moreover, the CNTs were predict to deform with a gradual change to "racetrack" and "peanut" shapes as pressure increases[28] while BNNTs deform to an oval cross section that elongates further with the increase in pressure above the critical value. This comparison indicates a remarkable difference between the elastic response of these two systems on compression.

In summary, *ab initio* calculations were carried out for a bundle zigzag (6,0) BNNTs arranged into a hexagonal symmetry cell, subjected to hydrostatic pressures. Below a critical pressure value all tubes preserve their structural form with a circular cross section. In accordance with our results, the BNNTs suddenly collapse to form tubes of oval cross section and the hexagonal arrangement elongates. The transformation is first order as indicates the discontinuous behavior of the percent difference volume. The effect of diameter on collapse pressure was found to be an inversion dependence. The electronic properties change considerably upon compression of the tubes with the energy gap diminishing gradually with the applied pressure. The ability to modify the BNNTs electronic properties upon application of an external pressure opens new possibilities for the future of electronic nanodevices.

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