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Energetics and electronic properties of BN nanocones with pentagonal rings at their apexes

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Abstract. The geometric structures, energetics and electronic properties of the recently discovered BN nanocones are investigated using first-principles calculations based on the density-functional theory. We have proposed one particular structure for BN nanocones associated with the 240° disclination, derived by the extraction of four 60° segments, presenting as characteristic four pentagons at the apex and termination in two atoms. The cones are simulated by three clusters containing 58 B plus N atoms and additional 12 H atoms to saturate the dangling bonds at the edge. The most stable configuration is obtained when the two terminating atoms are one B and one N. For the cases where the two terminating atoms are of the same kind, the tip with B atoms is determined to have lower binding energy than with N atoms. The local densities of states of these BN nanocones are investigated and sharp states are found in the regions close (below and above) to the Fermi energy.

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1 Introduction

Carbon nanocones were observed by the first time in 1992 as caps at the ends of the nanotubes [1] just after the discovery of nanotubes and also as free-standing structures two years latter [2]. Since that time, similar structures with B and N instead of C atoms have been proposed [3] and also experimentally observed [4–6].

Cones can be built departing in specific ways from a flat surface resulting in one or more topological defects located at their apexes. The localization and the number of these defects determine both the disclination angles of the cones and their electronic properties [7,8]. Whereas, for carbon cones the most common such defects are known to be pentagonal rings, for BN nanocones the situation is not well established, involving propositions with square [9], pentagons and even octagons [10]. Here, one must regard to the fact that an exact analogy between C and BN is not possible because, for instance, a pentagonal ring formed entirely by B and N atoms will present at least one homonuclear bond. Even-membered rings, in particular squares, have been thought to be the preferred defects because they do not necessitate the inclusion of B–B or N–N bonds, which are weaker than B–N bonds [11]. Nevertheless, the simple substitution of pentagons by squares could not be the best solution, because the new structure configurations, with squares, could result energetically unfavorable when compared with those with pentagons [12]. In this sense, the study of the structural and electronic properties of BN nanocones is a rich and low explored field of materials science.

2 Methodology

The disclination angles of the cones can be seen as resulting from the remotion of segments from a flat sheet. For the case of carbon nanocones Krishnan *et al.* [7] demonstrated that the disclination of a cone is associated with the number of pentagons at the tip. In particular, for BN cones, Bourgeois *et al.* [5] showed that the cones with 240° disclination are the sharper ones with the presence of B–N bonds only. By generating this cone from the extraction of one continuum segment of 240°, only hexagons will result and the tip will be composed of two two-coordinated atoms. Although the absence of homonuclear bonds, the unavoidable dangling bonds of the two-coordinated atoms at the tip make this structure not favourable energetically. The same disclination can also be derived by the extraction of two separated segments of 120° each, resulting one square, two pentagons and two hexagons at the apex. This structure presents as characteristic steric frustration due to the square rings [12]. Finally, an original nanocone with 240° disclination arises from a planar

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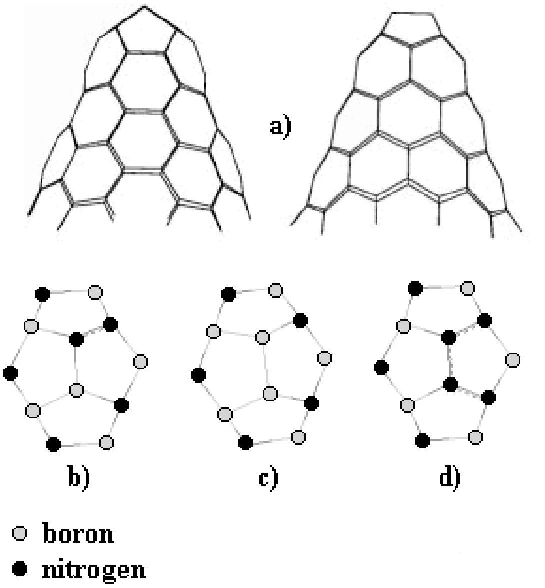

Fig. 1. (a) BN nanocone in two lateral views, rotated by 90° one from another, presenting four pentagons at their apex and termination in two atoms, as seen for a top view in (b) for B–N termination, in (c) for B–B, and in (d) for N–N terminations.

hexagonal sheet when four 60° segments originating from adjacent hexagonal centers are cut out of the plane and the severed edges of the segments are rejoined.

The comparison in terms of total energies among the three possibilities above, for carbon nanocones, showed that the one obtained with the extraction of four 60° segments is the most stable one [13]. Although not totally conclusive, our calculations [13], together with Rogers *et al.* results [12], should be seen as an indication that the same could be true for BN nanocones. In this way, we have proposed a BN nanocone structure with 240° disclination, derived by the extraction of four 60° segments, presenting as characteristic odd-membered rings with four pentagons and two three-coordinated atoms at the apex, as a plausible candidate to be the most stable structure.

The particular cap morphology adopted in this study with all atoms being three-coordinated and the apex consisting of four pentagons sharing two atoms (B–N, B–B, or N–N) is presented in Figure 1. As seen in Figure 1, the apexes present two (Fig. 1b) or three (Figs. 1c and 1d) homonuclear bonds. Similar studies with other disclinations, like 300° [2,4,6], are still under investigation.

The adopted tool for the full survey of the geometric structure optimization, energetics and electronic properties of the nanocones is the density-functional theory with the B3LYP exchange-correlation functional [14] and single-valence basis set, as implemented in the TURBOMOLE code [15].

The selected nanocones are simulated by clusters containing 58 B and N atoms, where the dangling bonds of the atoms at the cone edge are saturated by 12 H atoms. The starting atomic coordinates of the cone's apexes were generated according to the concepts of designability presented by Treacy and Killian [16].

3 Results and discussion

The obtained average distances for the atoms around the apexes are 1.48 Å, 1.68 Å, and 1.50 Å for the cones terminating in B–N, B–B, and N–N bonds, respectively. In the nanocone central region the average distance results around 1.46 Å and close to the edge (H atoms) 1.45 Å is obtained. These numbers are comparable with 1.43 Å for B–N bonds in nanotubes and 1.56 Å for c–BN.

In terms of energetics, the binding energies of the different cone terminations are calculated according to the following equation

$$E_{\mathrm{b}}[\mathrm{B}_x\mathrm{N}_y] = E_{\mathrm{T}}[\mathrm{B}_x\mathrm{N}_y] - xE_{\mathrm{T}}[\mathrm{B}] - yE_{\mathrm{T}}[\mathrm{N}] \tag{1}$$

where $E_{\mathrm{b}}[\mathrm{X}]$ ($E_{\mathrm{T}}[\mathrm{X}]$) is the binding (total) energy for X. This calculation shows that the cone terminating in B and N atoms (Fig. 1b) is the most stable and it is assumed as the zero reference for binding energy. The binding energies for the two other possibilities indicate that the apex with three B–B homonuclear bonds (Fig. 1c) is more stable than that with three N–N bonds (Fig. 1d), resulting 0.49 eV and 3.43 eV above the reference, respectively. The relative differences in binding energies reflect the changes induced by the occurrence of homonuclear bonds. We conclude that in general, contrasting with results previously obtained by Rogers *et al.* [12] for BN cages, the cones with dominant B–B bonds should be more stable than those with dominant N–N bonds.

For BN nanotubes with pentagons at their apexes we expect that the pentagonal rings determine all essential features of the electronic structure at the tips. The study of the densities of states (DOS) for the three different nanocone terminations allows us to understand the relation between the structural and electronic properties of these systems. The calculated DOS for the regions near the apexes show sharp resonant states in the gap region. Taking the DOS of the graphitic-like BN sheet as reference (Fig. 2a) we observe in Figure 2 that for the cone terminating in a B–N bond two levels appear, one doubly occupied close to the top of the valence band and another one non-occupied close to the bottom of the conduction band (Fig. 2b). For the case of the cone terminating in a B–B bond, a non-occupied level (acceptor state) appears above the Fermi energy (E_{f}), as shown in Figure 2c. The N–N terminating cone, on the other hand, introduces a doubly occupied level (donor state) close to E_{f} (Fig. 2d).

This variation in the occupation and energy of the apex-levels could be explored to build scanning tunneling probe tips with pre-determined DOS features just by tailoring the BN nanocone' apex atoms. On the other hand, the DOS at the tip, observable by scanning tunneling spectroscopy [18], can be used to discriminate among different tip structures, with the charge densities associated with states near E_{f} (corresponding to the DOS at the particular position and energy) being proportional to the current observed in the experiment.

The electronic and structural properties of nanocones are crucial pre-requisites for understanding the role of terminating caps in the physical behavior of contacts between

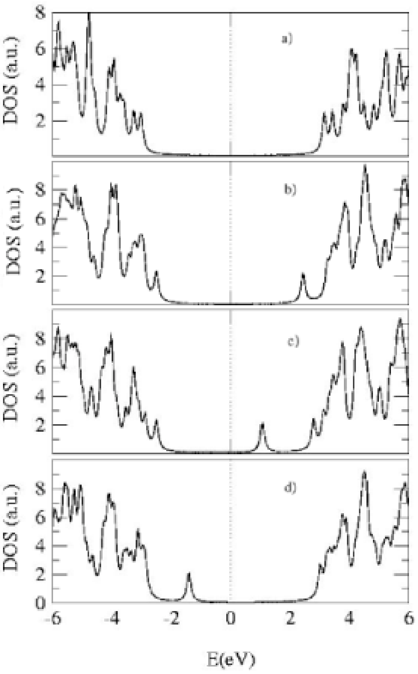

Fig. 2. Densities of states for the (a) BN plane sheet and three different BN nanocones, with (b) B–N, (c) B–B, and (d) N–N bonds at the tip apexes.

nanotube-based nanodevices. Similar results concerning the sharp resonant states dominating the electronic structure in the region close to E_f were previously obtained for C nanocones by Charlier and Rignanese [8]. BN nanocones with pentagons at the tips are alternatively proposed as good candidates for electron field emitters [17] and also for nanoprobes in scanning tunneling microscopy [18].

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