1. INTRODUCTION

With the preparation of carbon nanotubes [1] there has been much theoretical interest in these [2, 4] and related boron–nitrogen substituted species, both polymers [3, 5] and cages [6]. Although, for C nanotubes under suitable circumstances, zero-energy band gaps can occur (see also [7] for effects on the gap of varying tubular boundary conditions and finite size effects), the various investigations of BN alternant polymers seem always to give substantial band gaps of ≳ 5 eV, presumably because of the electronegativity difference between B and N atoms. Indeed, within the context of the simple Hückel π-electron model this large HOMO–LUMO gap result has been established [5] for all BN alternants, whether molecules, nanotubes or infinite sheets.

The question remains as to what will happen to HOMO–LUMO gaps on partial substitution of C by B and N. That is, will the gap be proportionate to the fraction of carbon atoms replaced by B and N? or will there be a more subtle dependence on the replacement pattern? If patterns are important, then just which patterns might give small band gaps is to be considered, especially for the circumstance of substantial BN content. The question is addressed as to whether such a gap is zero (whence metallic behavior is expected) or just small (whence semiconductive behavior is expected).

Here we begin with a first-principles density functional study of a planar CBN network, for which the associated band gap (≈ 0.2 eV) is quite small in comparison to the fraction of C present. Thereafter we rationalize this in terms of a simple argument based on the Hückel model, and thereby provide a general criterion to design such small HOMO–LUMO gap alternant carborazenes. This insight is used to point out several other small-gap carborazenes.

2. DENSITY FUNCTIONAL ENERGY BANDS USING LDA FOR AN ORDERED HEXAGONAL LAYER OF BCN

While the earlier work on BN was carried out using the Hückel approximation, we demonstrate that in application to a perfect hexagonal layer of CBN it is important to transcend this method when calculating the electronic bands, and in particular when evaluating and locating (in wave-vector k space) the minimum HOMO–LUMO energy gap. For present purposes, we have therefore adopted an ab initio density functional theory (DFT), based on a potential V(r) with the appropriate periodicity for the ordered CBN lattice in Fig. 1(a). In the present work the potential V(r) is expressed as the sum of a Hartree part $V_{\text{Hartree}}(\vec{r})$, determined by the nuclear framework plus the ground-state electronic density $n(\vec{r})$, and an exchange-correlation potential $V_{\text{xc}}(\vec{r})$. The latter has presently to be approximated and we have utilized the so-called local density approximation (LDA) for $V_{\text{xc}}(\vec{r})$, which then is similarly determined by the electron density $n(\vec{r})$. The electron–ion interaction has been described by norm-conserving non-local pseudopotentials and the electronic wave functions have been expanded in plane waves with an energy cutoff of 40 Ry to ensure convergence in forces and energy eigenvalues. For details of the ab initio pseudopotential methods see Ref. [8]. The planar CBN geometry considered here has not been structurally optimized; instead, we have taken a fixed average bond length of 1.42 for the three bonds present in the structure (this is equivalent to a graphene sheet where, out of each three carbon atoms, two are substituted by B
and N respectively). We note that structural relaxation is not relevant for the present work in which we wish to address the errors in the Hückel method to describe the HOMO–LUMO gap of compounds.

The energy-band dispersion relations $E(\mathbf{k})$ have then been calculated within the Brillouin zone (BZ) shown in Fig. 2, in which the symmetry points used in Fig. 3 are labelled in analogy with the symmetry points corresponding to a hexagonal graphitic unit cell. We indicate that the present BZ is obtained by direct folding of the graphitic one due to the larger unit cell in CBN as compared to graphite or BN sheets.

Focussing on the energy bands around the chosen zero of energy in Fig. 3 (the top of the valence band), we see that there is a small HOMO–LUMO energy gap of $\sim 0.2$ eV. It does not occur, however, at the central $\Gamma$ point in the BZ of Fig. 2, but is rather displaced slightly from this $\mathbf{k}$ value. We can understand this position of the HOMO–LUMO transition by noticing that the CBN unit cell consists of two hexagons, as compared to BN or graphite unit cells (folding of the BZ), and that neither BN nor graphite have the top of the valence band at $\Gamma$ (indeed, it is at the $K$ point), and the bottom of the conduction band for BN is at $M$ within LDA [3] and at $\Gamma$ within a GW quasiparticle calculation [9]. The small value of the band gap is connected with the global reduction of the ionicity of the CBN network as compared to BN (band gap of 5.5 eV). The energy gap evidently is a potential-sensitive quantity, in contrast to graphite where

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**Fig. 1.** Atomic configuration of (a) a single CBN sheet showing the perfect hexagonal unit-cell having 12 atoms and (b) a (6,0)-CBN tubule obtained by rolling the planar sheet, having a unit cell of 48 atoms. For the single sheet the two-dimensional translational lattice vectors are indicated ($a_1$ and $a_2$). All first-neighbor distances are fixed to 1.42 Å as in a pure graphene sheet. Black circles denote N atoms whereas large (small) dashed circles denote C (B) atoms. Both the sheet and the tubule are small band-gap semiconductors with $\sim 0.2$ and 0.08 eV gaps respectively.

**Fig. 2.** Two-dimensional Brillouin zone corresponding to the CBN unit cell shown in Fig. 1(a) (inner rectangle) related to the Brillouin zone for graphite and BN sheets (outer hexagon). The high symmetry points and directions as used in Fig. 3 to plot the band structure are also labelled. The reciprocal lattice vectors ($b_1$ and $b_2$) are along the lines $\Gamma J$ and $\Gamma M$ respectively.
the semimetallic character of a single layer arises from symmetry arguments. We should stress here that the minimized CBN structure corresponds to a slight change of the perfect hexagons shown in Fig. 1(a), made by shortening the C–N length as compared to the larger B–C length. This leads to a bigger unit cell and, by folding and breaking of symmetry, to a slightly larger gap close to the centre of the BZ.

From our previous studies of tubular forms made of inorganic structures such as BN [3], BC₃ [11] and C₂BN [10] that have layered structures, as found experimentally [12–14], we have concluded that, generally, inorganic compounds exhibiting a layered phase will likely form tubular structures [4]. On the basis of this and the computed stability of the layered CBN structure we can conclude that CBN-tubular forms could be experimentally realizable. In Fig. 1(b) is shown a typical tubular CBN structure corresponding to the (6,0)-tubule obtained by rolling the single CBN sheet in such a way that we have six hexagons around the tubule circumference. We indicate that the LDA band structure of the tubules is well described by folding of the band structure of the single CBN sheet shown in Fig. 3 for large diameter tubes. In contrast, the small diameter tubes do show hybridization effects ($\sigma^*-\pi^*$) introduced by the curvature of the tubule that leads to a reduction of the band gap. This is the case for the (6,0)-CBN tubule where we have obtained a gap of $\sim 0.06$ eV, whereas the gap is absent in a Hückel-type calculation (see below). This hybridization effect has also been shown to occur in small diameter carbon nanotubes [15] and to become less important as the size of the tubule increases.

Before going on to compare and contrast these energy bands with those of related materials, it is worth noting that, as in Ref. [15], we have also carried out Hückel calculations of the electronic band structure. These have been made, however, with Hückel parameters chosen very specifically so that $\alpha_C - \alpha_N = \alpha_B - \alpha_C$, which is akin, in the above language of DFT, to a particular choice of charge transfer in constructing the density $n(\mathbf{r})$, and hence the periodic potential $V(\mathbf{r})$. One then obtains a zero energy gap, but we stress that this is a potential-sensitive result, and not a consequence of layer symmetry as is known to be the case for the touching $\pi$-bands of a single graphitic layer. For example, two models as different in philosophy as tight-binding and free-electron network models [16, 17] lead to the same conclusion of zero energy gap in the $\pi$-bands of a single graphitic layer. Evidently our carborazene Hückel model can only be trusted to indicate no more than that a band gap is small.

The conclusion from the present DT study, therefore, is that a single, ordered, hexagonal layer of CBN and tubules is semiconducting, with an energy gap of a few tenths of an eV. Below, we shall first compare and contrast the present findings for this new material with

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Fig. 3. Energy band structure obtained in an LDA calculation for the single CBN sheet of Fig. 1(a). The band gap is not located at the center of the BZ and is $\sim -0.2$ eV (see text for details).

Fig. 4. Three structural models for the C₂BN monolayer. In each case the unit cell shown contains eight atoms. Structure I is metallic whereas the other two are semiconducting. In both type I and type II the bottom of the conduction and top of the valence bands do have $\pi$ character. This is not the case for type II where the top of the valence band has also $\sigma$ character. This indicates that only the first two could be modelled within the simple Hückel $\pi$-electron model if the charge transfer parameters are carefully chosen.
the known electronic structures of related carbon–boron–nitride materials.

3. SIMILARITIES AND DIFFERENCES BETWEEN HEXAGONAL CBN AND RELATED MATERIALS, ESPECIALLY C$_2$BN

It is instructive to compare and contrast (below) the above discussion of the electronic band structure of CBN with that of related materials which have been treated earlier. We have already discussed the zero energy gap in a single graphitic layer. It is well known that in a BN layer the electronegativity difference measured by the difference between the Hückel parameters $\alpha_B$ and $\alpha_N$ leads to a large gap. This is known from experiments to be 5.5 eV. DFT plus LDA calculations are semiquantitative only, giving a gap of ~4 eV which is within the typical error of LDA calculations for quasiparticle excitations. However many-body calculations embodying the self-energy in the so-called GW approximation [18] correctly reproduce the experimental band-gap and energy dispersion for the BN sheet [9].

But the comparison we shall stress below is with a C$_2$BN ordered layer with rather different geometrical structures, referred to as I and II in the earlier calculations of Liu et al. [19], where I is computed to be metallic and II is a medium gap semiconductor. Structure II is the most stable one and will therefore be the main focal point of the ensuing discussion (we reproduce the geometrical structures of Ref. [19] in Fig. 4). One can think of building a layer of structure II using essentially parallel zig-zag chains of first C-atoms (compare to polyacetylene, but without dimerization) and then of alternating B and N atoms (BN zig-zag chain). The former chain will have a zero energy gap and the latter a non-zero gap. Interaction of one C zig-zag chain with the neighboring BN chains will remove the electronic degeneracies, opening an energy gap for the two-chain building block. Calculations confirm such a picture, and Liu et al. [19] find a HOMO–LUMO gap for structure II of ~2 eV. We expect the many-body calculations using the GW method to increase this energy gap somewhat.

Returning to the structures studied by Liu et al. [19], these workers investigated various possible geometries of the C$_2$BN monolayer (see Fig. 4). These were chosen on the grounds of exhibiting basic bonding features; namely near-neighbor coordination and symmetry properties. Of the three geometries chosen, the electronic energy band structures show that phase I is a metal, whereas models II and III are semiconducting with indirect band gaps of 1.6 and 0.5 eV respectively. C$_2$BN-II was found to be the energetically favoured phase.

As to a brief note on methodology, the three possible atomic arrangements for the monolayer considered for C$_2$BN were studied by Liu et al. using a first-principles pseudopotential approach with a localized basis for the wave functions. These workers point out that the phase with the lowest total energy has a nearest-neighbor environment optimizing the chemical bond energy by maximizing the number of C–C and B–N bonds. They have emphasized the intimate relation between symmetry and the conducting properties of the different monolayers studied. Inversion symmetry permits metallic behavior as in phase I. But the absence of inversion symmetry in phases II and III has, as a consequence, the opening of a gap, with semiconducting behavior. As mentioned already, the stable phase can be viewed, following Miyamoto et al. [10], as built up of alternating zig-zag chains, and the B–C bonds are energetically less favourable than C–C or B–N neighbors.

Having dealt at some length with DFT results for CBN, and comparison and contrast with possible geometrical structures of C$_2$BN, we now turn to some further comments on Hückel-theoretic predictions, despite the shortcomings exposed by our DFT calculations on CBN.

4. SMALL-GAP C$_2$BN STRUCTURES: COMMENTS ON HÜCKEL RESULTS

For the simple tight-binding Hückel model with substitution of C by BN, the criterion to keep a zero band gap is quite simple. If the non-bonding orbital for the pure-C case does not occupy all of the sites and one situates all the B and N atoms on the unoccupied sites, then this pure-C eigenorbital remains so for the substituted material. Further, with equal symmetrically related substitution by B and N with Hückel parameters $\alpha_C - \alpha_N = \alpha_B - \alpha_C$, the eigenvalue spectrum is symmetric about $\epsilon = \alpha_C$, so that the position for non-bonding orbitals remains unchanged (from what it is for the pure-C species). Thus we have a sufficient condition for retention of a Hückel gap of zero, namely that all BN substitution is to take place in a symmetric fashion at sites which are unoccupied in one pure-C non-bonding eigenorbital.

Now, to identify the maximally substituted carborane C$_2$BN which has a Hückel gap of zero, we need the nonbonding Hückel molecular orbitals for graphite (or for carbon nanotubes, one might consider). In fact, for either type of structure the non-bonding orbitals are much the same, when represented on a (unit-like) cell to be repeated so as to cover the whole extended structure.

When, for a hexagonal carbon network, any nonbonding orbitals are present there are four, with their representations on our cell being as shown in Fig. 5. Then, for the nonbonding orbital (of Fig. 5(iii) or (v)) with a maximum number of sites which are unoccupied, we substitute these with B and N at these empty sites to obtain the sought-after zero band gap for C$_2$BN structure(s) at a minimum value of $s$. Evidently for this minimum $s = 1$, with the distribution of B and N as uniform as possible, one obtains...
a unique unit cell for the CBN structure as indicated in Fig. 1(a). Evidently too, for the case of a nanotube, in order that these unit cells, when repeated, fully cover the tubule surface one needs valence structural parameters $t_\perp$ and $t_\parallel$ such that $t_\parallel - t_\perp$ is divisible by 3, a criterion which is well known [20] from the study of unsubstituted nanotubes. Here $t_\perp$ and $t_\parallel$ are the integral multiples of two ring-center to ring-center basis vectors at 120° to one another that constitute the minimal lattice-vector displacements in the tubule, quite analogously to graphite.

The C$_2$BN structures of the preceding section may also be considered from our Hückel-theoretic view. Evidently the structure I of Fig. 4 satisfies our criterion for the occurrence of a non-bonding orbital, in fact two of them, associated with both Fig. 5 (iii) or (v). On the other hand our criterion is not satisfied for structures II or III, so these should exhibit larger band gaps — in agreement with the earlier mentioned computations of Liu et al. [19]. However, now we see the conductive properties due not only to inversion symmetry but also due to the pattern of substitution of B and N for C. Indeed, one may readily imagine other small band-gap C$_2$BN structures, based, say, on substitutions in the unoccupied sites of the non-bonding orbitals of Fig. 5 (iv) or (vi) (where none of the substituted sites would be adjacent).

In Fig. 6 we present some Hückel results for the occupied partial density of states on each atom (C, B and N) for the two-dimensional CBN sheet and (6,6), (9,3) and (12,0) tubules. Only half the energy range for
the e-energy is shown, since there is a symmetry about 0: the plots for $p_c(-\epsilon) = p_c(\epsilon)$ while $p_d(-\epsilon) = p_d(\epsilon)$. We can see that the main features of the density of states for the tubules are already present in the planar sheet with slight changes in intensity and with some transitions missing that are not allowed by symmetry in the tubules (folding arguments). Moreover, the lowest mass of bands is high in density on N sites while the highest mass of bands is high in density on B sites, whereas the intermediate set of bands is more pronouncedly localized on the C sites. The folding of the two-dimensional electronic structure describes well the Hückel results because there are no curvature-induced hybridization effects (as in the \textit{ab initio} LDA calculations presented above).

5. SUMMARY

Density functional calculations have been presented for a hexagonal ordered CBN layer. The main conclusions are that (i) a small electronic energy gap of $\sim 0.2$ eV exists and (ii) the minimum electronic energy gap occurs away from the center of the two-dimensional Brillouin zone. This situation is contrasted with that in the most stable geometrical structure for an ordered C$_6$BN layer, studied by Liu et al. [19]. These latter workers find a wide HOMO–LUMO energy gap of $\sim 2$ eV. This can be expected to increase somewhat in a full many-electron treatment of the self-energy problem.

Some comments are finally added as to predictions of Hückel theory for C$_6$BN. It is found that this provides insight for some qualitative aspects of these results, and a simple structural criterion for small band-gap carbonarazenes is enunciative. However, it is emphasized that, for more quantitative detail, more sophisticated methodology is needed, as with the DFT results presented here. We stress the limitations of the Hückel approach when it is applied to potential-sensitive properties as opposed to symmetry-determined features. The small energy gap, and its position in the two-dimensional BZ for the hexagonal layer of CBN, are potential sensitive and therefore require the careful DFT study presented here. This situation contrasts with that for a single graphite layer, or a layer of BN, where in the latter case the substantial energy gap is directly \textit{driven} by the large electronegativity difference between B and N. For the case of C$_6$BN, also referred to here in relation to the study in Ref. [19], bonding considerations favouring B–N and C–C nearest-neighbor bonds appear to single out successfully the stable geometrical structure and to lead to a wide energy-gap material.

From the present study, the ordered CBN layer appears to offer promising electrical characteristics as a narrow energy-gap semiconductor. We have also discussed the electronic properties of tubular forms of CBN that, for large diameter tubes, are well described within a band-folding picture. This compound adds to the now large family of synthesized and proposed composite nanotubes: BN, BC$_x$, BC$_2$N, CN, C$_3$N$_4$, WS$_2$; and MoS$_2$ [12].

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