PHYSICAL REVIEW B VOLUME 49, NUMBER 7 15 FEBRUARY 1994-I

Theory of graphitic boron nitride nanotubes

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(Received 2 November 1993)

Based upon the similarities in properties between carbon- and BN-based (BN=boron nitride) materials, we propose that BN-based nanotubes can be stable and study their electronic structure. A simple Slater-Koster tight-binding scheme has been applied. All the BN nanotubes are found to be semiconducting materials. The band gaps are larger than 2 eV for most tubes. Depending on the helicity, the calculated band gap can be direct at Γ or indirect. In general, the larger the diameter of the nanotube the larger the band gap, with a saturation value corresponding to the calculated local-density-approximation band gap of hexagonal BN. The higher ionicity of BN is important in explaining the electronic differences between these tubes and similar carbon nanotubes.

The recent discovery[1] and large-scale synthesis[2] of graphitic carbon nanotubes has stimulated great interest because of their potentially useful electronic and mechanical properties.[3–6] Nanotubes are often coaxially arranged to form a needle with a diameter of a few nanometers. The spacing between tubes is very close to the interlayer distance in graphite. Because the interaction between tubes is van der Waals, the electron transfer from tube to tube is small. Theoretically, there is an infinite number of possible atomic structures for the graphitic tubules. Each structure can be obtained by rolling a graphite sheet and is uniquely specified by its diameter and the degree of the helical arrangement of the hexagons. Previous theoretical studies have shown that depending on diameter and chirality the tube is either metallic or semiconducting.[3–5] This different behavior can be qualitatively explained in terms of the two dimensional graphite band structure and the discrete wave vectors allowed by boundary conditions in the tubes.

Here we propose that similar to carbon, III-V compounds found in the hexagonal graphite structure could also lead to microscopic tubular structures. The III-V material most closely related to C is boron nitride (BN), which, like carbon, is found in both sp^2- and sp^3-bonded structures. Stoichiometric combinations of C, B, and N can be used to create graphitic hybrids of graphite and BN.[7] We expect that BN tubes will grow in weakly-interacting coaxially arranged tubes similar to carbon nanotubes. Because of the large ionicity of BN and large band gap ($\sim$ 5.8 eV in the hexagonal phase[8]), the corresponding tubes may be more uniform in electronic properties than carbon tubes. This could be technologically advantageous because samples containing many different sizes and structures of tubes could be grown with predictable bulk properties. In recent experiments, a turbostratic tubular form of BN with a diameter on the order of a micrometer has been produced[9] from boron nitride's amorphous phase. Boron nitride nanotubes with a high degree of crystallinity in the tube walls have not been reported, however.

In this paper we study the electronic properties of BN nanotubes obtained by bending a BN graphitic sheet. The similarities and differences with carbon nanotubes are discussed. Since the higher ionicity of BN leads to the opening of a band gap in the hexagonal structure compared to semimetallic graphite, the BN tubes are expected to be one dimensional semiconductors. Novel physical and device characteristics could be obtained from the corresponding normal and doped structures.

We carry out the calculations using a simple *s-p* Slater-Koster tight binding (TB) (Ref. 10) method with first- and second-nearest-neighbor interactions. The parameters have been fit to reproduce the main features of the pseudopotential plane-wave local-density-approximation (LDA) band structure calculation for hexagonal BN. The distance dependence of the parameters has been incorporated following Harrison's universal TB scaling[11] to take into account the differences in bond lengths between the nanotubes and the planar structure. Following the notation of Ref. 3, we study the tubes (n_1, n_2) where the chirality and diameter are uniquely specified by the vector $c_h = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ which connects two equivalent sites, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of the graphite sheet. The tube diameter d is defined as $d = \mid c_h \mid /\pi = a\sqrt{3(n_1^2 + n_2^2 + n_1 n_2)}/\pi$, where a=1.45 Å is the in-plane B-N distance for the hexagonal BN sheet. No distortion of bond angles exists other than that caused by the cylindrical curvature of the tube. In this way, the curvature of the tube induces a shortening of the nearest-neighbor distance. The nonchiral tubes correspond to $(n_1, 0)$, where n_1 means that the circumference of the tube holds n_1 hexagons. In the (n_1, n_1) tubes the number of atoms in the unit cell is the same as for the $(n_1, 0)$ tube but the tube radius is larger. For a given n_1, the smallest unit cell corresponds to tubes with $n_2 = 0$ or $n_2 = n_1$.

Before discussing the results for the BN nanotubes, it is informative to compare the LDA band structures of hexagonal BN and graphite. In Fig. 1 the *ab initio* pseudopotential band structure within the LDA for hexagonal BN is given. This has been calculated with a plane wave basis set up to a cutoff energy of 50 Ry. The crystal electron-ion potential for BN can be expressed in terms of a symmetric part, $V_s = (V_N + V_B)/2$, and an anti-

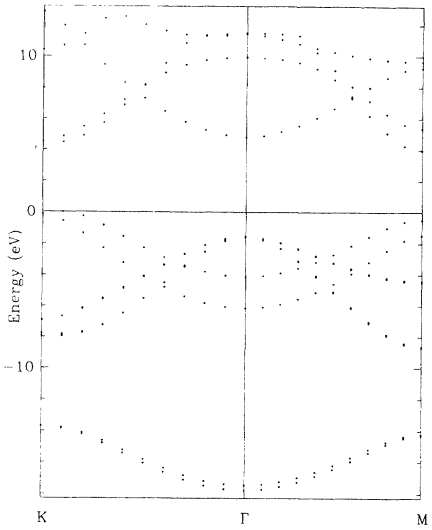

FIG. 1. The two dimensional LDA band structure for hexagonal BN along $K-\Gamma-M$. The system shows an indirect band gap $K-M$ of 4 eV.

symmetric part, $V_a = (V_N - V_B)/2$. Due to the similar full valence bandwidths of cubic (hexagonal) BN and diamond (graphite),[12] we expect the symmetric part of the potential is similar for carbon and BN. Then, differences in the band structures stem from the antisymmetric part of the crystal potential. The degree of ionicity can be inferred by the gap at K (4.6 eV), where the corresponding states in graphite are degenerate. In our LDA calculation the band gap is indirect ($K-M$) with a value of 4 eV. As compared to graphite, some of the bands are no longer degenerate reflecting the important antisymmetric splitting (clearly seen at the Γ point for the π derived bands).

From previous studies of carbon nanotubes within TB and LDA approaches[13] we know that TB results agree with the LDA for large radii tubes. Since some tubes can only be calculated within TB at present due to the large number of atoms per unit cell [for example the unit cell of the (6,5) tube consists of 380 atoms], the TB gap values should be seen as predictions to be tested in the regime where LDA calculations are possible. For small tubes, however, there are large discrepancies due to the strong hybridization of the antibonding σ^* and π^* conduction bands induced by curvature. Tight-binding calculations do not accurately describe this hybridization because the parameters are usually fit to the dispersion of the highest valence and lowest conduction bands. This interaction may be smaller in more ionic compounds because of charge transfer, localization of charge, and the fact that some carbon degeneracies are broken by symmetry. Thus, one should keep in mind the limitations of the present method when studying small tubes where hybridization effects could have a strong influence on the electronic structure.

Based on our TB calculation, all the BN tubes are semiconducting compared to carbon nanotubes which can be either semiconducting or metallic. As stated earlier, this arises from the effect of BN's ionicity (potential antisymmetry) on the structure factor which was responsible for the gap closure in graphite. Because we have fit our parameters to *ab initio* LDA calculations where it is expected that the band gap is underestimated, we anticipate an underestimation of the band gap values for the BN nanotubes (the LDA band gap of hexagonal BN is 4 eV whereas the experimental value is 5.8 eV).

In Fig. 2 we give the evolution of the band gaps for $(n,0)$ and (n,n) tubes as a function of n. In calculations for carbon nanotubes[3–5] the (n,n) tubes are all metallic, whereas the $(n,0)$ tubes oscillate between metals and small- to medium-gap semiconductors. In the BN tubes, the calculated value of the band gap ranges from less than 1 eV to around 4 eV and saturates at the calculated (TB) band gap for hexagonal BN as n and the radius increase.[14] The fact that the band gap reduces with the size of the tube can be qualitatively explained in terms of the evolution of the fundamental band gap in hexagonal BN under pressure. The calculated band gap in hexagonal BN decreases as external pressure increases (lattice constant is reduced)[12] and is opposite to what happens in cubic BN. For a given n the (n,n) nanotube has a bigger band gap than the $(n,0)$ nanotube because it has a larger radius [the ratio between the (n,n) and $(n,0)$ radius is $\sqrt{3}$, independent of n].

Another difference between these two types of tubes is that the $(n,0)$ tubes are direct gap semiconductors (Γ to Γ) whereas the (n,n) tubes are indirect gap ($\Delta-\Gamma$) materials. This is related to the metallic character of the equivalent carbon tubes. Band overlap in the C tubes occurs at a point along the Γ to X direction which corresponds to the K point of the two dimensional Brillouin zone of graphite. For BN, due to the antisymmetry of the crystal ionic potential an opening of the band gap at this point is expected. To see this effect more clearly, in Fig. 3 we have plotted the TB band structure for the $(10,0)$ and $(10,10)$ tubes along the $\Gamma-X$ direction for the valence and conduction bands near the Fermi level. The different dispersion of the conduction and valence bands for these two tubes can be traced back to the two dimensional hexagonal BN band structure (the tube band

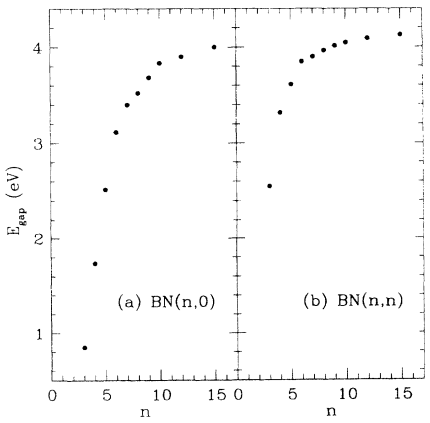

FIG. 2. Dependence of the TB band gap for (a) $(n,0)$ and (b) (n,n) BN nanotubes as a function of n. The $(n,0)$ tubes have direct gaps ($\Gamma-\Gamma$) whereas the (n,n) tubes are indirect ($\Delta-\Gamma$).

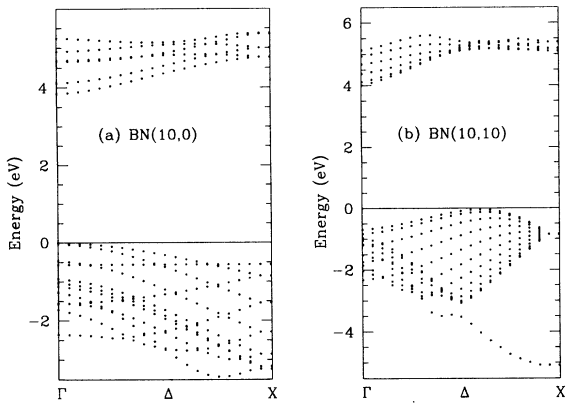

FIG. 3. TB band structure along the $\Gamma - X$ direction for (a) the (10,0) and (b) the (10,10) BN nanotubes. The diameters of these tubes are 8 Å and 13.8 Å, respectively.

structure resembles this somewhat if the tube diameter is not extremely small) using the same kind of arguments as have been used in explaining band structures for carbon nanotubes.[4]

In Fig. 4 we give the results of the evolution of the band gap for (n_1, n_2) nanotubes with fixed n_1 (4, 6, and 10) as a function of n_2 (chiral angle), to study the influence of the chiral angle on the band gap. In general, increasing the chiral angle increases the band gap. For the small n_1 tubes there is a nearly linear increase with n_2 while the slope reduces as we increase n_1 and becomes nearly constant for the $(10, n_2)$ tubes. The change in band gap for the $(10, n_2)$ tubes is about 0.2 eV which is within the error of the TB description, compared with a change of about 2 eV for the $(4, n_2)$ nanotubes. This effect is more accurately attributed to an increase in radius for the (n_1, n_2) tubes with respect to n_2 than to chirality, however. In each series, the increase in radius from $(n_1, 0)$ to (n_1, n_1) is a factor of $\sqrt{3}$. For smaller tubes, an increase in radius changes the gap significantly while the gap of larger tubes saturates (see Fig. 2). Thus, the band gap of (n_1, n_2) tubes with small n_1 should be expected to change significantly more with respect to n_2 than larger (n_1, n_2) tubes.

Some changes in the results for small tubes should be expected due to hybridization effects which are beyond the scope of the method applied here. For these tubes an *ab initio* LDA calculation will be needed in order to study the stability, hybridization, and charge transfer effects in these tubes. A word of caution has to be given with respect to the study of these small nanotubes $(4, n_2)$, where the diameter ranges from 3.2 Å ($n_2 = 0$) to 5.6 Å ($n_2 = 4$). Taking into account that the interlayer distance in hexagonal BN is 3.34 Å, a strong interaction between diametrically situated atoms is expected, which could lead to a destabilization of the tubular structure. As is found for carbon nanotubes,[13] a reduction of the radius of the tubes is expected because of this interaction.

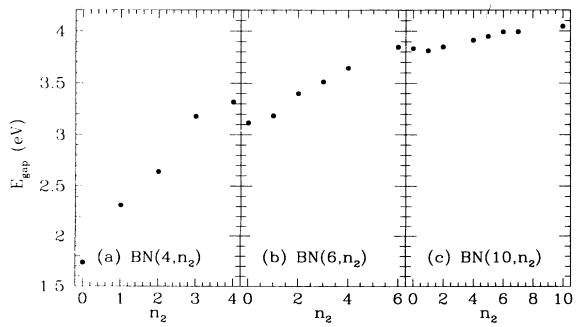

FIG. 4. Evolution of the calculated TB band gap for (n_1, n_2) BN nanotubes as a function of n_2 for (a) $n_1 = 4$, (b) $n_1 = 6$, and (c) $n_1 = 10$. For large n, the gap is fairly independent of n_2.

For carbon nanotubes there is no agreement on the growth mechanism, although different proposals exist in the literature.[15] The growth mechanism, stability, and structure of the BN nanotubes proposed in the present work also needs to be addressed both experimentally and theoretically. One way to obtain more insight into these properties is to apply the total energy *ab initio* LDA pseudopotential method and find the minimum energy structure of these tubes. Due to the different size of B and N atoms in the nanotube and the reduction of the B-N nearest neighbor distance, a buckling structure on the tube walls is expected. Preliminary LDA supercell calculations[16] confirm this idea together with the shrinking of the tube radius. How this buckling influences the electronic and transport properties is an open question.

Other topics to be addressed in future work are the optical and electronic properties of doped BN nanotubes. Substitutional doping with carbon could be compared with tubes obtained by bending sheets of hexagonal BC_2N. Hexagonal BC_2N can be either metallic or semiconducting depending on whether the structure possesses inversion symmetry.[7] Electronic and elastic properties intermediate to those of carbon and BN nanotubes are expected for BC_2N tubes.

Finally, the capillarity induced filling of BN tubes may be significantly different than in the carbon tubes. It has been possible to dope carbon nanotubes with lead.[17] The semimetallic character of graphite leads to a lot of intercalation compounds whereas insulating BN has a very limited intercalation chemistry. As a result, capillarity filling in BN tubes may be more difficult than in C tubes.

In conclusion, we have presented a study of the electronic structure of BN nanotubes within a simple TB scheme. All the tubes are semiconductors with band gaps increasing with diameter and rapidly saturating at the hexagonal BN value. Tubes with radii larger than 6 Å are calculated to be wide band gap semiconductors with a very small dependence on the chirality. At present and until a growth mechanism is controlled, it is difficult to say which tubes will have the most interesting properties (mechanical, transport, or electronic). Experimental characterization and data on BN nanotubes are needed in order to compare their structural and electronic properties with carbon nanotubes.

This work was supported by National Science Foundation Grant No. DMR91-20269 and by the Director Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. A.R. was supported by a Fullbright-MEC grant. We would like to thank X. Blase, S. P. Lewis, S. G. Louie, Y. Miyamoto, and E. L. Shirley for helpful discussions.

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