

ARTICLES

Heteroatomic Nanotubes with Quasi-One-Dimensional Superlattice Structure

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We have fulfilled modeling of molecular and electronic structure of nanotubes $B_xN_xC_y$ ($x \geq 0, y \geq 0$) with various atom dispositions in the hexagonal lattice points on cylinder surfaces. Electronic spectra of such systems with a quasi-one-dimensional superlattice structure have been investigated in the topological and valence approximations. We suppose that these nanotubes consist of alternating carbon and boron nitride ring-like or chain-like structures. We have demonstrated that these systems with different extent of minizones in the electronic spectrum can be produced by means of a change of belt-like fragment width. Quasi-localized states were found in C_{2m} symmetry nanotubes.

1. Introduction

A few years ago Iijima obtained tube carbon forms with diameters comparable with C_{60} fullerene dimensions (~ 10 Å) by an arc synthesis method.¹ This work stimulated multiple theoretical and experimental studies aimed at the creation of carbon materials composed of nanotube graphite forms, at modeling nanotube growth mechanisms, and also at the investigation of their properties (see ref 2 and references therein). Note though that Iijima was not the first to draw attention to cylinder structure carbon modifications—thread-like graphite forms have been known for quite a long time.^{3,4}

Since there is a boron nitride modification with a layered structure similar to that of graphite,⁵ it is natural to suppose that tubular forms of boron nitride can exist as well as nanotubes of mixed chemical composition consisting of carbon, nitrogen, and boron atoms. Such systems have been recently synthesized by Stephan and colleagues and Zettl's group⁶ by an electric arc method. Analysis of the structure of the energy loss spectrum of obtained samples allowed us to conclude that $B_xN_xC_y$ nanotubes were formed as well as boron nitride forms. These data stimulated investigations aimed at modeling the electronic spectrum of various tubular modifications of carbon boron nitrides—nanotubes consisting of periodically repeating fragments of various atomic composition.^{7–9}

This work presents results of energy zone calculations of nonhelical nanotubes $B_xN_xC_y$ ($x \geq 0, y \geq 0$) by the method of crystal orbitals in the π -electron Huckel approximation and in the valence approximation by the EHT (a program¹⁰ that was used). The spectrum structure of these nanotubes is investigated depending on the composition of the repeating fragments consisting of alternating ring-like or cycle-like carbon fragments and boron nitride fragments for the case when the period of such original quasi-one-dimensional superlattices is comparable with bond lengths. Such types of BN–C structures (a nanotube

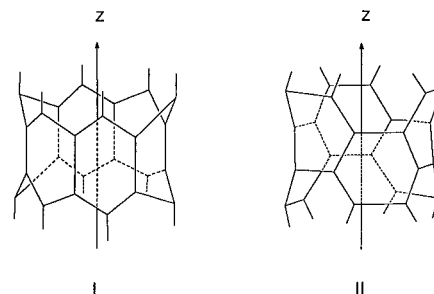


Figure 1. Fragments of first (I) and second (II) class of nanotubes with six rings in a translated cell.

quantum “dot”—a carbon conductive fragment in a dielectric BN nanotube and periodic BN–C nanotubes) were discussed in ref 11.

2. Nanotubes of a Homogeneous Structure: C_{2n} and B_nN_n

Each tubular graphene system is characterized by its diameter and by a helix step in the case of helical nanotubes.² All nonhelical nanotubes that are further analyzed are divided into two classes according to the orientation of hexagons to the main symmetry axis of the cylinder surface. Two bonds of each hexagon are parallel to the cylinder axis in the first class of systems (I) denoted as $(n, 0)$ nanotubes. Two bonds of each hexagon are perpendicular to the axis in the second class of systems (II)— (m, m) nanotubes. Topology of such a class of nanotubes is completely defined by the order of the main symmetry axis. All atoms of the systems are supposed to lie on a cylinder surface. Using the AM1 method,¹² we have optimized the geometry of $C_{24}H_{12}$ molecules, the carbon skeleton of which coincides with repeating fragments of $(6, 0)$ or $(3, 3)$ nanotubes (Figure 1). The calculations have shown that C–C bond lengths differ slightly for both nanotube classes and are equal to about 1.43 Å. Moreover, we have found that all six-sided cycles are not planar and have a “bath” conformation (Figure 1). Such geometry has been used in all the following calculations of the carbon nanotube electronic structure in the

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[®] Abstract published in *Advance ACS Abstracts*, December 15, 1996.

TABLE 1: Basic Energy Characteristics of Carbon and Heteroatomic Class I and Class II Nanotubes Obtained by EHT^a

I				II			
n	$-E/n$	Δ	E_F	n	$-E/n$	Δ	E_F
C ₂₄ , 6 cycles	70.70	0.0	-10.19	C ₂₄ , 6 cycles	70.57	0.0	-9.89
C ₂₈ , 7 cycles	70.81	1.03	-10.84				
C ₃₂ , 8 cycles	70.87	0.84	-10.65	C ₃₂ , 8 cycles	70.78	0.0	-10.46
C ₃₆ , 9 cycles	71.00	0.00	-10.51	C ₃₆ , 9 cycles	70.02	0.0	-10.65
B ₁₂ N ₁₂ , 6 cycles	71.75	5.32	-12.52	B ₁₂ N ₁₂ , 6 cycles	71.69	6.08	-12.42
B ₁₄ N ₁₄ , 7 cycles	71.80	5.57	-12.51				
B ₁₆ N ₁₆ , 8 cycles	81.83	5.73	-12.50				
B ₁₈ N ₁₈ , 9 cycles	71.85	5.89	-12.50				
Al ₁₂ N ₁₂ , 6 cycles	68.96	7.16	-13.33	Al ₁₂ N ₁₂ , 6 cycles	68.95	6.56	-13.32

^a Number of atoms in a unit cell is equal to n . E/n is the average value of total energy per an atom. E_F is the Fermi level, and Δ is the gap. All are in units of eV.

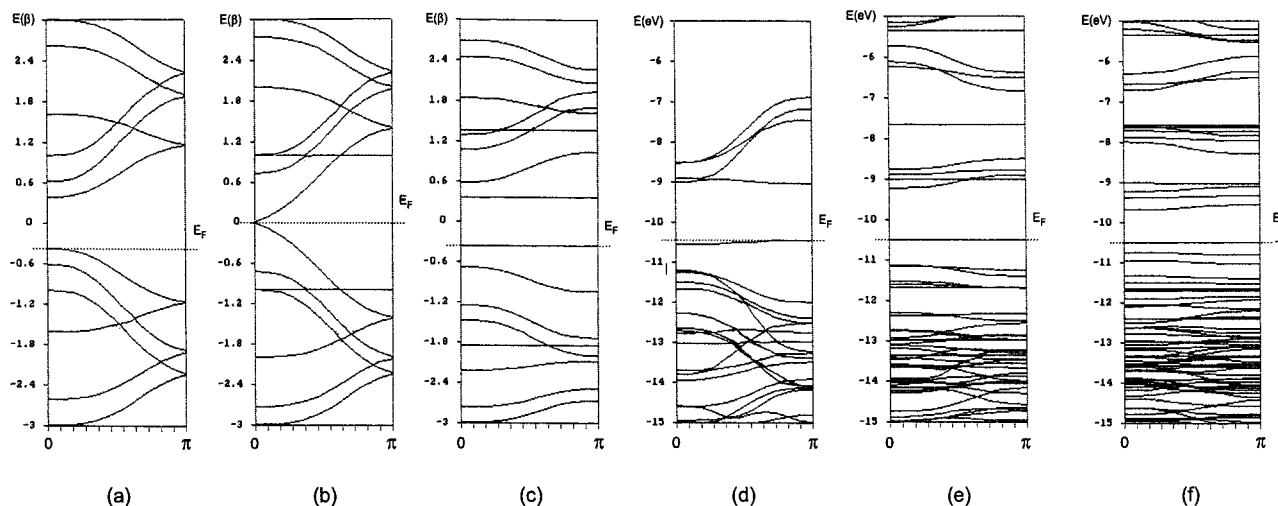


Figure 2. Dispersion curves of nanotubes: the topological spectra of a C₂₀ tube of C_{5v} symmetry (a); a C₂₄ tube of C_{6v} symmetry (b); a B₆N₆C₁₂ tube (c); the valence spectra of a B₆N₆C₁₂ tube (d); a B₁₂N₁₂C₂₄ tube (e); a B₁₂N₁₂C₄₈ tube (f).

valence approximation. Furthermore, the trial calculations have proved that the valence spectrum character of both C and BN (1.46 Å bond length) nanotubes is practically the same while all bond lengths change simultaneously in the range of ± 0.03 Å. Therefore, calculations for heteroatomic nanotubes have been performed using the same geometry as that of carbon.

One-electron energy levels can be calculated in the π -electron Huckel approximation for homoatomic class I tubes if a two-atomic fragment is chosen as a cell just as in the case of a graphite layer. In this case energy levels are presented in the form^{2,13}

$$\lambda_{\pm}(C-C) = \alpha_C \pm \beta |1 + e^{ik} + e^{-i\varphi}| \quad (1)$$

where $-\pi \leq k \leq \pi$ is a wave vector, $\varphi = 2\pi j/n$, $j = 0, \dots, n-1$, n is the order of the main symmetry axis, and $\beta < 0$ is the resonance integral. The value of the Coulomb integral α_C is taken as the origin of the energy scale. In particular, it follows from (1) that the gap in π -electron spectra of a carbon ($n, 0$) nanotube is zero only in the case when the order of the main axis is a multiple of 3.

In the case of BN tubes when B and N atom positions in the points of a cylinder hexagon lattice alternate, the formulas for one-electron energy levels are also simple functions of such levels $\lambda_{\pm}(C-C)$ of a similar carbon system.¹⁴⁻¹⁷ Thus, they can also be put in the analytic form⁹

$$\lambda_{\pm}(BN) = 0.5(\alpha_B + \alpha_N \pm ((\alpha_B - \alpha_N)^2 + 4\lambda_{\pm}^2(C-C))^{1/2}) \quad (2)$$

where $\alpha_{N(B)}$ are the Coulomb integral of a N(B) atom. It follows from the formula that tubular alternant boron nitrides have a

gap Δ , which is not less than $|\alpha_N - \alpha_B|$. Using the values¹⁸ $\alpha_B = -1.0\beta$, $\alpha_N = 1.5\beta$ ($\beta \approx -2.4$ eV, $\beta_{B-N} \approx \beta$), we get $\Delta = -2.5\beta \approx 6$ eV.

From here on we consider nanotubes of the C_{nv} symmetry, which consist of alternating ring-like or cycle-like fragments of carbon atoms and similar fragments of boron nitride. Repeating fragments of such systems consist of a sufficiently large number of atoms. Therefore, it is difficult to find analytical formulas similar to (1) and (2) for the dispersion curves of considered tubes in the general case even in the π -approximation. To compare spectra of nanotubes of various chemical composition, we have chosen repeating fragments containing an identical number of atoms. Such a choice allows us to study the structure of the spectrum of the analyzed system in more detail as well as the structure of some crystal orbitals.

The results of spectrum calculations in the topological and valence approximations are qualitatively the same. Thus, dispersion curves are overlapped in the domain of the Fermi level, forming a metal spectrum (Table 1) in the case of carbon (m, m) nanotubes regardless of the number of six-membered cycles in a cell. A semimetal spectrum is observed for the class I tubes when the number of cycles in a translated ring is a multiple of 3 (see ref 2). In all other cases there is a gap (about $1.0|\beta|$ for the simple Huckel method and ~ 0.9 eV for the EHT (Table 1, parts a and b of Figure 2)). Parts a–c of Figure 2 present electronic spectra calculated only in the topological approximation, since their character coincides with the spectrum character in the valence approximation, but they are much simpler, since there are fewer dispersion curves in them.

Furthermore, we have calculated the valence electron spectra of real alternant systems obtained with both classes of carbon

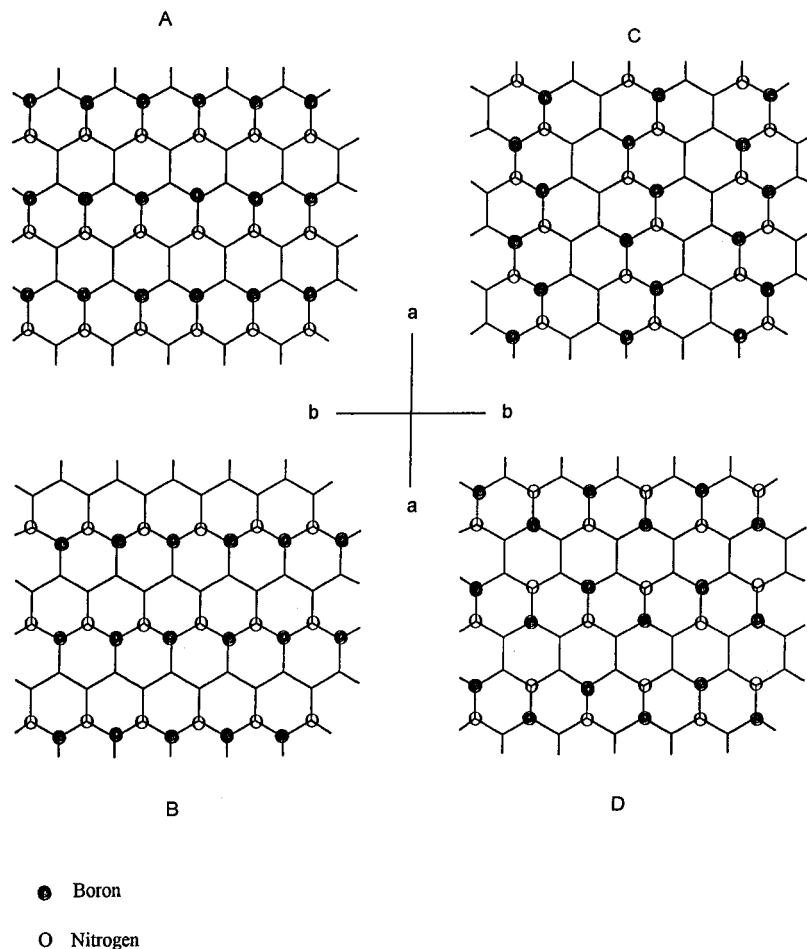


Figure 3. Four variants of C, N, and B atom positions in mixed atomic composition nanotubes. Rolling over of the strip in the direction $a-a$ ($b-b$) causes formation of class I (II) nanotubes. Open and closed symbols distinguish between B and N atoms.

nanotubes by a change of all C atoms in them for B and N atoms. Calculations in the topologic and valence approximations have shown, according to formula 2, that such a change causes the appearance of a wide gap in the spectra of nanotubes of both the I and II classes (see Table 1; we have used the value of $\beta_{B-N} = 0.9\beta$). We have fulfilled an additional analysis that proved the dispersion curves determining the gap correspond to the wave functions built on π -orbitals of the heteroatoms.

In the case of a change of the cycle number from 6 to 9 in the repeating fragment of the first class of BN nanotubes, the gap Δ found in the valence approximation increases from 5.3 to 5.9 eV. In the case of the second class of BN nanotubes, the gap is slightly more than 6 eV. These estimates correspond to experimental optical absorption data for hexagonal boron nitride ($\Delta = 5.8$ eV¹⁹).

Analysis of data presented in Table 1 allows us to conclude that in all considered cases the first class of nanotubes is more stable than the second class. The difference between their total energy values (per atom) is ~ 0.1 eV for pure carbon nanotubes and ~ 0.06 eV for BN nanotubes, and only for AlN nanotubes is the difference very small.²⁰

3. Nanotubes of a Mixed $B_nN_nC_{2n}$ Composition

Now we are going to discuss the one-electron structure of nanotubes containing carbon atoms as well as boron and nitrogen atoms. Repeated fragments of such nanotubes are described by a formula $B_nN_nC_{2n}$ and differ only in the positions of the atoms. Figure 3 depicts four possible variants, A–D, of their arrangements in a graphite-like strip. The class I tubes are obtained when such a strip is rolled over in the direction $a-a$,

TABLE 2: Basic Energy Characteristics of Class I and Class II $B_nN_nC_{2n}$ Nanotubes Obtained by EHT^a

I	$-E/n$	Δ	E_F	II	$-E/n$	Δ	E_F
A _{aa}	70.13	0.57	−10.21	A _{bb}	70.04	1.14	−9.90
B _{aa}	70.38	1.42	−10.45	B _{bb}	70.32	1.31	−11.15
C _{aa}	70.42	0.86	−10.83	C _{bb}	70.31	0.88	−10.28
D _{aa}	70.14	0.44	−10.56	D _{bb}	70.04	0.65	−10.07

^a n is the number of atoms in a unit cell. E/n is the average value of total energy per an atom. E_F is the Fermi level, and Δ is the gap. All are in units of eV.

and the class II tubes are obtained when the rolling direction is $b-b$. Variants B and C contain pure carbon chains as well as chains of alternating boron and nitrogen atoms. Note that both kinds of chains are *trans*-forms in variant B while they are *cis*-forms in variant C. There are no such chains in variant A, but two kinds of *trans*-form chains can be found in it: ...B–C–B–C... and ...N–C–N–C.... All chains in variant D contain carbon atoms as well as nitrogen and boron atoms.

We have calculated electronic spectra of eight $B_nN_nC_{2n}$ nanotubes in the valence approximation. Each such system contains six hexagons in a ring that is a repeating fragment of a tube. This results in a sixth-order axial symmetry of the tube. Results of the calculations are presented in Table 2. The table indicates that in this case too the class I nanotubes are more stable than similar nanotubes of the second class. Moreover, existence of ...–C–C–C–C–... chains and also of ...–N–B–N–B–... chains in the B and C variants evidently provides for additional stabilization compared to the A and D variants. Table 2 also confirms that the gap of $B_nN_nC_{2n}$ nanotubes substantially depends on the mutual position of C, B, and N atoms.

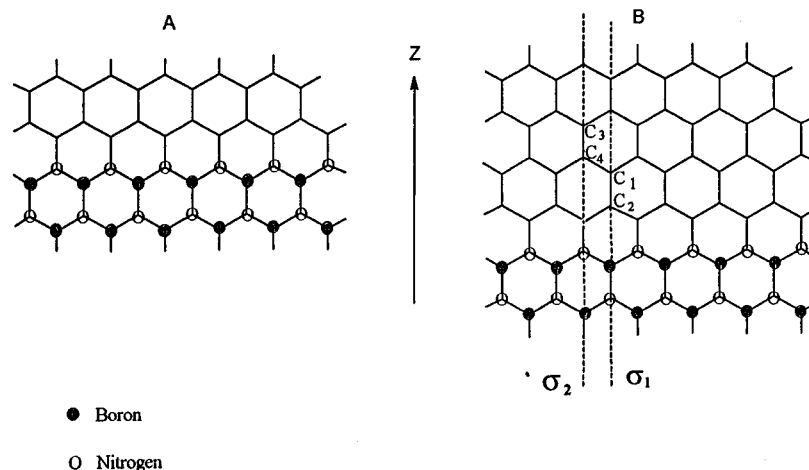


Figure 4. Structure of a B₁₂N₁₂C₂₄ repeating fragment (a); structure of a B₁₂N₁₂C₄₈ repeating fragment (b). Symbols σ₁ and σ₂ designate symmetry planes. Open and closed symbols distinguish between B and N atoms.

As it could be predicted on the basis of general physical properties of quantum superlattices,²¹ introduction of a conducting carbon layer between dielectric BN nanotube fragments results in the appearance of alternating forbidden and permitted minizones in the nanotube spectrum. The number of such minizones increases with the width of the C-ring (parts d–f of Figure 2), while the relative width of these minizones decreases. In the interval from 6 to 12 eV there are two minizones above the Fermi level ($E_F \approx -10.5$ eV) and two below E_F for a B₁₂N₁₂C₂₄ tube, and five zones above the Fermi level and six below E_F for a B₁₂N₁₂C₄₈ tube.

4. Quasi-Localized States of C_{2m} Symmetry Nanotubes

Note another interesting fact about all modifications of the first class ($n, 0$) of nanotubes with an even order symmetry main axis ($n = 2m$). There are dispersion curves independent of the wave vector (straight lines parallel to the abscissa in Figure 2) in their electronic spectra computed both in the topological and in the valence approximations. In the case of pure carbon and BN (or AlN) systems, the existence of such dispersion curves should not influence considerably the physical properties of nanotubes, since the energies of the curves lie in the conductivity zone. They correspond to so-called resonance states. But in the case of B_nN_nC_{2m} nanotubes these curves determine the gap boundary and the Fermi level goes along one of them (see parts c–f of Figure 2, where spectra of C_{6v} symmetry tubes are shown). Parts c and d of Figure 2 present spectra of a B₆N₆C₁₂ tube (variant B, a – a , Figure 3). Two dispersion curves inside the gap are straight lines, since the topological approximation does not take into account the long-range interactions (Figure 2c), while similar curves have a slight curvature in the valence approximation (Figure 2d) due to a weak overlapping of atomic orbitals located on non-neighboring atom pairs. But the curves considered become straight lines in the valence approximation if heteroatom chains are also divided by a wide belt of carbon atoms blocking their interaction. This could be seen from parts e and f of Figure 2 where electronic spectra of the nanotubes B₁₂N₁₂C₂₄ and B₁₂N₁₂C₄₈ are shown. Figure 4 depicts structures of elementary cells of these tubes.

The described peculiarity of spectra is connected with symmetry properties of a nanotube. If it has an even order symmetry axis, planes containing the axis are divided into two types. The first includes all σ₁ planes in which “vertical” C₁–C₂ and B–N bonds are contained (Figure 4). The second type consists of σ₂ planes going through C₃–C₄, C–N, and C–B bonds. Thus, if a nanotube one-electron wave function belong-

ing to an irreducible representation of a C_{nv} symmetry group is antisymmetrical with respect to all σ₁ planes, then such a function is built on atomic orbitals of atoms forming C₃–C₄, C–N, and C–B bonds. In turn, the wave function antisymmetrical with respect to σ₂ planes of the nanotube is built on atomic orbitals of atoms forming C₁–C₂ and B–N bonds. In both cases the bonds are arranged far away from each other, so we can ignore their interaction. Therefore, there are straight dispersion lines corresponding to noninteracting C–C, B–C, B–N, and C–N bonds among dispersion curves of one-electron spectra of discussed nanotubes with an even order symmetry main axis.

If a nanotube has a symmetry axis of an odd order, all symmetry planes containing it belong to the same type. Thus, there is no irreducible representation of a tube symmetry group antisymmetrical with respect to all σ planes. Correspondingly, there are no independent bonds and all dispersion curves of such nanotubes differ from straight lines.

5. Conclusion

We have discussed examples of structures of nanotube quasi-one-dimensional quantum superlattices constructed of conducting carbon and dielectric boron nitride fragments. It would be natural to suppose that a nanotube of isolated C quantum dots with a discrete electronic spectrum can be obtained by an increase of the BN fragment length in the C–BN structure. We have demonstrated the possibility of generating minizones in the spectra of such systems. One can vary the widths of these zones by varying the relative widths of C and BN fragments. Note that the appearance of minizones and separate levels should also be expected in phonon spectra of these nanotube structures. Such exotic spectra should manifest themselves first of all in nonlinear volt–ampere characteristics and high-frequency electrical and optical properties of these one-dimensional superlattices.

Acknowledgment. This work was supported by the ISTC (Project N 079), ISF (Project N M41300), and Russian Federal Scientific and Technical Program “Actual directions in condensed medium physics”, the direction being “fullerenes and atomic clusters”.

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- (20) We have also investigated tubular forms of aluminum nitride using 1.96 Å Al–N bond length. Thus, the AlN tube diameter is 1.37 times larger than that of a corresponding carbon nanotube. The calculation has shown that the spectrum gap of AlN nanotubes is greater than that of BN nanotubes; it equals ~7 eV (Table 1). The spectra of C–AlN nanotubes should be qualitatively the same as those of C–BN nanotube superlattices. But to calculate them, it is necessary to know their structure in detail. These C–AlN superlattices should be considerably strained because of a difference in C–C and Al–N bond lengths.
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