Electronic States of BCN Alloy Nanotubes in a Simple Tight-Binding Model

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Electronic states are calculated in boron carbonitride (BCN) alloy nanotubes with a simple tight-binding model. Random replacement of carbon atoms with boron and nitrogen (B-N) ones in metallic carbon nanotubes mainly causes level broadening and the nanotubes remain metallic. On the other hand, the energy gap of boron nitride (BN) nanotubes always survives under random substitution of B-N atoms by carbon ones while it becomes smaller than the original gap. Further, the optical gap does not correspond well with the band gap of the density of states in nanotubes with high B-N concentration. This can be understood in terms of localized states associated with carbon impurities in a BN nanotube.

Keywords: graphite, carbon nanotube, boron, nitrogen, BN

§1. Introduction

Recently, boron carbonitride (BCN) nanotubes were synthesized by electrical arc discharge,1,2) pyrolysis methods,3) and bias-assisted hot filament chemical vapor deposition.4,5) The structure of the obtained BCN nanotubes was studied by scanning electron microscopy and transmission electron microscopy and their electronic states were investigated by photoluminescence.4,5) In this paper, we consider BCN nanotubes of random atomic configurations, which we call BCN alloy nanotubes, and elucidate electronic states with a simple tight-binding model.

Carbon nanotubes are two-dimensional (2D) graphite sheets rolled into cylinders.6) Calculations of the electronic structure within a tight-binding model and an effective-mass approximation show that a nanotube becomes a metal or a semiconductor depending on its chiral vector.7–11) Boron nitride (BN) nanotubes were synthesized more recently.12,13) In graphitic BN, the high ionicity of BN leads to the opening of a band gap in contrast to the vanishing gap and semimetallic behavior in graphite. Therefore, BN nanotubes are all expected to be one-dimensional (1D) semiconductors. Their electronic structure was calculated in a tight-binding model,14) in local density approximation, and within a quasi-particle approach.14–16) The results showed that the band structure can be obtained in a manner similar to that in carbon nanotubes except in tubes with extremely small diameters.

In contrast, there is little information on BCN nanotubes. So far, there exist some pioneering works on the stable structure of BC3 and BC2N,17,18) and several interesting properties are predicted for those nanotubes.19,20) In this paper we consider BCN alloy nanotubes composed of randomly distributed boron, carbon, and nitrogen atoms. Boron or nitrogen doped carbon nanotubes are attracting attentions as possible 1D heterostructures toward new devices.21) The present study is expected to provide information on electronic properties of such heterostructures.

For simplicity, we shall confine ourselves to the case that the concentration of boron and nitrogen (B-N) atoms is same and consider three different models of BCN nanotubes having different configurations. We calculate electronic states of finite-length nanotubes in a tight-binding model and obtain the density of states and the optical absorption spectra. In §2 the model and method of calculation are discussed. The numerical results are presented in §3 and discussed in §4. A summary and conclusion are given in §5.

§2. Model and Method

2.1 Tight-Binding Model

In 2D graphite having a honeycomb lattice, a unit cell contains two carbon atoms denoted as A and B as shown in Fig. 1 (a). The first Brillouin zone is shown in Fig. 1 (b). There are two independent corner points called K and K'. In graphitic BN, all carbon atoms at A sites are replaced by boron and those at B sites by nitrogen. In BCN alloys, carbon, boron, and nitrogen atoms occupy A or B sites at random with possible restrictions dependent on methods of their synthesis. In this paper we consider only π energy bands because they are most important for the determination of electronic properties.

In a nearest-neighbor tight-binding model, the equation of motion for the amplitude ψA(RA) and ψB(RB) at an A site located at RA and a B site located at RB, respectively, is give by

\[ [ε − ε_A(R_A)] \psi_A(R_A) = - \sum_{l=1}^{3} γ_{R_A,R_A−τ_l} ψ_B(R_A−τ_l), \]

\[ [ε − ε_B(R_B)] \psi_B(R_B) = - \sum_{l=1}^{3} γ_{R_B,R_B+τ_l} ψ_A(R_B+τ_l), \]

(2.1)

where εA(RA) and εB(RB) are the local site energy at A and B sites, respectively, and the vectors τ1, τ2, and τ3 connect three nearest-neighbor A and B sites as shown in Fig. 1 (a).

To be rigorous, many parameters are necessary because of the presence of three different atoms. However, in order to focus on the study of effects of randomness, we...
apply further simplification. First, the transfer integral is assumed to be uniform regardless of atomic configurations, i.e., \( \gamma_{RA, RB} = \gamma_0 \). It may not be so appropriate for quantitative description because the bond lengths change between different atoms.\(^{14-16} \)

Second, the local site energy at boron and that of nitrogen are assumed to be symmetric around that of carbon. In fact, the energy of atomic nitrogen are assumed to be symmetric around that of carbon.\(^{22} \)

Furthermore, considering that their absolute values are close to \( \gamma_0 \sim 3 \) eV, we shall assume for simplicity \( U_B = +\delta, U_C = 0, \) and \( U_N = -\delta \) with \( \delta = 2\gamma_0 \). In the present model, the transfer integral \( \gamma_0 \) is a unique parameter characterizing energy scale, and the band gap of a BN sheet is given by \( 2\gamma_0 \). We carried out numerical calculations for sets of parameters closer to known values in several atomic configurations and found no qualitative difference in the density of states and the dynamical conductivity.

The present model is certainly too simple in describing details of the electronic states. For example, the difference in the ionicity of three atoms requires a self-consistent determination of the charge transfer, which may cause a shift of a local site energy depending on its environment. The present simple model should be considered as a lowest order approximation of BCN alloy nanotubes giving essential but qualitative features of electronic properties.

In this model the energy bands of a BN sheet are easily calculated as

\[
\epsilon_{\pm}(k) = \pm \gamma_0 \sqrt{\left( \frac{\delta}{\gamma_0} \right)^2 + \sum_{l=1,3} \exp(i\mathbf{k} \cdot \mathbf{\tau}_l)^2}. \quad (2.2)
\]

They have a minimum gap of \( 2\delta \) at \( \mathbf{K} \) and \( \mathbf{K}' \) points and maximum and minimum energies \( \pm \gamma_0\sqrt{1 + (\delta/3\gamma_0)^2} \) at \( \mathbf{k} = 0 \), showing that effects of nonzero \( \delta \) are strongest in the vicinity of the band gap but relatively weak at the top and the bottom as long as \( \delta/\gamma_0 \ll 1 \). A comparison with the \( \pi \) bands obtained in more elaborate methods\(^{14-16} \) shows that the model can describe essential features and is sufficient for the present purpose.

The structure of a nanotube is specified by the chiral vector \( \mathbf{L} \) given by

\[
\mathbf{L} = n_n a + n_b b \equiv (n_n, n_b)a, \quad (2.3)
\]

with integer \( n_n \) and \( n_b \) where \( a \) is the lattice constant given by \( a = 2.46 \) Å giving the bond length \( a/\sqrt{3} = 1.42 \) Å in the 2D graphite. Zigzag nanotubes have \( \mathbf{L} = (n, 0)a \) and armchair nanotubes have \( \mathbf{L} = (2n, n)a \) with integer \( n \). It is possible to choose the primitive translation vectors \( \mathbf{a}_1 = a \) and \( \mathbf{a}_2 = a + b \). For this choice armchair nanotubes have a chiral vector \( \mathbf{L} = n\mathbf{a}_1 + n\mathbf{a}_2 \) and therefore they are frequently called \( (n, n) \) nanotubes. It is straightforward to obtain the band structure of a BN nanotube by imposing periodic boundary conditions in the circumference direction \( \mathbf{L} \).

### 2.2 Optical Absorption

There are two different configurations in optical absorption in nanotubes, the (electric-field) polarization parallel to the axis and perpendicular to the axis. In the case of carbon nanotubes, the dynamical conductivity and selection rules describing such different polarizations were discussed in detail.\(^{23,24} \) The results showed that sharp absorption peaks disappear for light perpendicular to the axis because their intensity is transferred to that of interband plasmon modes and absorption peaks are observable mainly for polarization parallel to the axis. Recent experiments gave results in agreement with this prediction.\(^{25,26} \) Because the situation is expected to be same in BN and BCN nanotubes, we shall consider the absorption for light polarized parallel to the axis.

The real part of the dynamical conductivity describing absorption for electric field parallel to the axis is given by the Kubo formula,

\[
\sigma_{yy}(\omega) = \frac{\pi \epsilon^2}{hLA} \sum_{\alpha, \beta} \frac{(|\beta|\omega|\alpha|)^2(f_\alpha - f_\beta)}{\omega_\alpha - \omega_\beta}\delta(\omega - \omega_\alpha + \omega_\beta), \quad (2.4)
\]

where \( A \) is the tube length, \( \alpha \) and \( \beta \) denote eigen states, \( \omega_\alpha \) and \( \omega_\beta \) are their energies, and \( f_\beta \equiv f(\hbar\omega_\beta) \) is the Fermi distribution function. We calculate the conductivity at zero temperature throughout this paper. In this expression exciton effects are completely neglected although they can be important because of 1D nature of the nanotube.\(^{27} \) The velocity operator is calculated by \( \hat{v} = (1/\hbar)[\hat{r}, \hat{H}] \), where \( \hat{H} \) is the Hamiltonian and \( \hat{r} \) is the position operator.

### 2.3 BCN Alloy Nanotubes

In the following we shall confine ourselves to tubes containing the same number of B-N atoms for simplicity. We generate finite-length tubes using three different methods so as to clarify effects of correlations in the atomic configurations. In the first method, which will be called method I in the following, we start with a BN nanotube and replace equal amount of B-N atoms by carbon atoms at random. In the second method (method II), we start with a carbon nanotube and replace carbon atoms by equal amount of B-N atoms at random. In the third method (method III), we generate nanotubes by method II under the condition that nearest neighbor sites of a boron atom can never be occupied by a boron atom and those of a nitrogen atom can never be occupied by a nitrogen atom, either.

In the method III, there is practically an upper limit of the concentration of B-N atoms, because sample generation becomes increasingly difficult with the concentration. Accordingly, in the method III, we shall stop the attempt to generate nanotubes in which more than 70 % of carbon sites are replaced by B-N atoms.

Nanotubes generated by the method I are expected to describe actual systems obtained by doping of carbon atoms into BN nanotubes. Those obtained by the methods II and III are same and expected to be realized when equal amount of B-N atoms are doped into carbon nanotubes and their concentration is sufficiently small. Important difference between II and III appears when the concentration becomes large and the probability of occupation of two nearest neighbor sites by boron or nitrogen atoms becomes appreciable. In actual
systems, the bond of boron-boron (or nitrogen-nitrogen) is unfavorable.\textsuperscript{17,18} Such correlations are not taken into account in the method II but in the method III.

We specify the composition rate of a BCN alloy nanotube by the concentration $\rho$ of B-N atoms. Therefore, nanotubes with $\rho = 0$ represent pure carbon nanotubes in all the methods. The tube with $\rho = 1$ becomes a BN nanotube in the method I, while it does not in the method II.

2.4 Virtual-Crystal Approximation

In a virtual-crystal approximation (VCA) we shall assume the same local site energy $\varepsilon_A$ for A sites and $\varepsilon_B$ for B sites. In nanotubes constructed by the methods II and III, the A and B sites are occupied by equal amount of B-N atoms and therefore we have $\varepsilon_A = \varepsilon_B = 0$. This shows that the band structure of these nanotubes remains same as that of the corresponding carbon nanotubes in VCA.

In nanotubes constructed by the method I, boron atoms occupy only A sites and nitrogen atoms B sites. Then, we have $\varepsilon_A(R_A) = +\rho \delta$ and $\varepsilon_B(R_B) = -\rho \delta$. Obviously, this model describes a carbon nanotube when $\rho = 0$ and a BN nanotube when $\rho = 1$. In this approximation the electronic states of nanotubes with given concentration $\rho$ can easily be calculated by replacement of $\delta$ by $\rho \delta$. Therefore, the band gap of a nanotube with structure giving metallic CN is given by $E_g = 2\rho \gamma_0$ independent of the circumference. For a tube with a structure giving semiconducting CN, the gap becomes slightly larger because of the deviation of the wave vector corresponding to the band gap from K and K’ points.

§3. Results

3.1 Numerical Calculation

We calculate electronic states of finite-size nanotubes by numerically diagonalizing the Hamiltonian in the tight-binding model introduced in the previous section, adopting periodic boundary conditions along the axis direction. The results are used for the calculation of the density of states and the dynamical conductivity. We shall take an average of results for about 50 different concentrations of B-N atoms. This shows that the band structure of these nanotubes becomes less than 0.02 in units of $1/(\gamma_0 \sqrt{2} a^2)$. These band edges are denoted by arrows in Fig. 2. In contrast, tubes constructed by method II and III have no gap and always become metallic.

Except for the energy gap mentioned above, random B-N doping causes level broadening and the density of states shows no characteristic dependence on methods of low B-N concentration. For method II, peak structures typical for 1D systems completely vanishes due to level broadening by further B-N doping. On the other hand, correlations in atomic configurations tend to generate local ordering of B-N atoms to form B-N bonds with the increase of $\rho$ in nanotubes both for method I and for method III. The structures appearing in the energy range away from zero ($\varepsilon/\gamma_0 < -1.5$ and $\varepsilon/\gamma_0 > +1.5$) manifest such local atomic ordering and correspond well to those of BN nanotubes.

Figure 2 shows the density of states of tubes with $L = (10,0)a$. Here, the histograms at $\rho = 0\%$ show the density of states of the finite-size semiconducting carbon nanotube. Basically, random B-N doping causes level broadening as seen in the previous case and peak structures reflecting 1D systems appear away from zero energy for method I and III where correlations in atomic configurations are taken into account. Energy gaps are also explained by the level broadening and the correlations as shown in the following.

The energy gaps of tubes with $L = (9,0)a$ and $(10,0)a$ given above are compared with the results of VCA in Fig. 4. In $(9,0)$ nanotubes, there is no energy gap without B-N doping. The gap grows with the increase of the B-N concentration for method I, while it remains zero with any B-N concentrations for method II and III. We can see that VCA explains these results qualitatively. Accurately, the numerical results are always smaller than the VCA results except at $\rho = 0\%$ and $\rho = 100\%$ and therefore exhibit a large “bowing” behavior.

On the other hand, the $(10,0)$ nanotube has an energy gap with no B-N doping. For method I, the gap increases as in the case for $(9,0)$ nanotubes. This is again in qualitative agreement with VCA and numerical results also show the bowing behavior. For method II, level broadening makes the energy gap disappear with high B-N concentration, while the gap survives and remains constant with nonzero concentrations for method III.
This shows the importance of local ordering of B-N atoms.

3.3 Optical Absorption

Figure 5 shows the dynamical conductivity of tubes with \( L = (9, 0) \) a. For \( p = 0 \% \) a Drude contribution given by a delta-function is present at \( \omega = 0 \) in carbon nanotubes but is not included in the figure. The nonzero optical band gap appears in BCN nanotubes constructed by method I and becomes larger as the B-N concentration increases, which shows qualitative agreement with the VCA result. In Fig. 5(a), arrows indicate the band gap determined by the density of states, and it is clear that the absorption edge is shifted considerably to higher energy side than the density-of-states band edge in tubes with intermediate values of the B-N concentration. The deviation is particularly apparent for \( p \sim 90 \% \).

This is due to the fact that states lying below the conduction band consist mainly of those occupying closely spaced carbon atoms substituting boron sites and those lying above the valence band consist of carbon atoms occupying nitrogen atoms. These states are localized spatially and their mutual overlap is negligible when the concentration of carbon atoms is low, leading to an extremely small matrix element for the interband optical transition. This will become clear when we look at actual wave functions in the next section.

In tubes constructed by methods II and III, the Drude-like absorption between the states near the fundamental gap appears even at the low doping concentration \( p = 10 \% \). In this regime, extra B-N atoms act as scatterers and therefore tend to broaden transitions and cause the appearance of a Drude tail. In the case of high B-N concentrations this low energy peak is more pronounced, while in tubes with intermediate values of the B-N concentration the Drude-like absorption between the states near the fundamental gap remains noticeable. This behavior is particularly apparent for \( p \sim 90 \% \).

The dynamical conductivity of tubes with \( L = (10, 0) \) a is shown in Fig. 6. In tubes I, the behavior is similar to that of tubes with \( L = (9, 0) \) a shown in Fig. 5 except for the presence of a semiconducting gap in carbon nanotubes. There is again a considerable deviation between the absorption edge and the band edge denoted by arrows.

In tubes II the gap becomes smaller with the B-N concentration and disappears beyond a critical concentration, while in tubes III the gap remains nonzero for the whole concentration range. This behavior is in agreement with that of the density of states. Further, the difference between the absorption edge and the band edge is not appreciable in tubes II and III.

Similar calculations can be made for thicker nanotubes such as \( L = (20, 0) \) a, etc. They show that essential features of the results are independent of the nanotube radius except in nanotubes with quite small doping concentration of B-N atoms where the band gap is determined by boundary conditions along the circumference direction.

§4. Discussion

A BN nanotube doped with a single carbon atom has a localized bound state in the band gap near the conduction band bottom when a boron is replaced by a carbon and near the valence band top when a nitrogen is replaced by a carbon. This bound-state formation corresponds to the long band tail in the density of states in tubes with a high B-N concentration and the considerable difference between the optical and density-of-states band-gap.

The bound state is localized near the carbon atom which replaces a boron or nitrogen site, and the binding energy in a nanotube is almost equal to that in a sheet unless the tube radius is so small. In an effective-mass approximation the binding energy in a BN sheet is analytically given by \( \varepsilon_B = \varepsilon_c \exp\left[-\left(\sqrt{\frac{3\pi^2}{2\gamma}}\right)^\delta\right] \) with \( \varepsilon_c \) being a cut-off energy. For the choice \( \varepsilon_c \sim (3\pi^2/8)\gamma_0^2/\delta \), this gives \( \varepsilon_B/\gamma_0 \sim 0.16 \) for \( \delta/\gamma_0 = 1 \). The details are given in Appendix A. The binding energy can be calculated numerically with a tight-binding model and becomes \( \varepsilon_B/\gamma_0 = 0.200 \) for \( \delta/\gamma_0 = 1 \). Further, it can be estimated also from local density of states in a finite-size nanotube, which gives \( \varepsilon_B/\gamma_0 = 0.20 \) for a (10, 0) tube.

The band edges are strongly perturbed at larger concentration of carbon atoms. Figure 7 shows an example for a state at the top of the valence band and the bottom of the valence band in a (9, 0) tube with \( p = 90 \% \) (10 \% carbon) constructed by method I. In the figure the wave function is shown by a circle around at each lattice site with a radius proportional to its squared absolute value. For the valence-top state the wave function is localized in a region where nitrogen sites are mostly occupied by carbons and for the conduction-bottom state it is localized in a region where boron sites are mostly occupied by carbons. Those regions are spatially far apart and therefore the oscillator strength between these states vanishes.

When the energy moves away from the conduction-bottom or the valence-top, wavefunctions gradually extend in space and can have spatial overlap with other states. Then, transition matrix elements can be nonzero and optical absorption becomes possible. This is the reason why the energy gap in the density of states is smaller than the optical gap.

Boron and nitrogen atoms, at low concentration, act as short-range repulsive and attractive scatterers in a carbon nanotube. Their effects have been studied in a tight-binding model,\(^{28-31}\) in the effective-mass approximation,\(^{32}\) and also from first-principles.\(^{33}\) They cause the appearance of quasi bound states near the edge of the valence bands and the first excited conduction bands and give rise to a resonance scattering at these energies. Therefore, it is easily understood that B-N atoms can be regarded as scatterers and contribute mainly to the broadening of the density of states when their concentration is low.

§5. Summary and Conclusion

We have considered finite-size BCN alloy nanotubes containing equal amount of B-N atoms and calculated energy levels and dynamical conductivity corresponding to interband optical absorption. Three methods I, II, and III have been introduced for generation of alloy
nanotubes. We have employed a simple tight-binding model consisting of $\pi$ orbitals.

Clearly, random atomic configurations cause level broadening. However, correlations in atomic configurations due to the ionicity can generate characteristic structures in the density of states reflecting local atomic ordering. In particular, there exists nonzero band gap in BCN nanotubes which are constructed by doping carbon atoms into BN nanotubes, or by method I.

It has turned out that the optical band gap does not correspond well with the gap of the density of states in nanotubes with high B-N concentration. This can be understood in terms of localized states lying below the edge of the conduction band and those above the top of the valence band associated with carbon impurities in a BN nanotube.

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Appendix A: Effective-Mass Approximation

It is straightforward to extend an effective-mass approximation for 2D graphite\cite{34,11} to that for a BN sheet. The Schrödinger equation for states in the vicinity of K and K’ points is given by

$$H F(r) = \varepsilon F(r) \quad (A1)$$

with

$$H = \begin{pmatrix} \delta & \gamma(k_x - i k_y) & 0 & 0 \\ \gamma(k_x + i k_y) & -\delta & 0 & 0 \\ 0 & 0 & \delta & \gamma(k_x + i k_y) \\ 0 & 0 & \gamma(k_x - i k_y) & -\delta \end{pmatrix},$$

and

$$F(r) = \begin{pmatrix} F_K(r) \\ F_{K'}(r) \end{pmatrix}, \quad \text{(A3)}$$

where

$$F_K(r) = \begin{pmatrix} F_B^K(r) \\ F_B^{K'}(r) \end{pmatrix}, \quad F_{K'}(r) = \begin{pmatrix} F_B^{K'}(r) \\ F_B^K(r) \end{pmatrix}. \quad \text{(A4)}$$

In the above, $k = -\frac{i}{\hbar}, \gamma = (\sqrt{3}/2) a \gamma_0$, and $F(r)$ is an envelope function.

In the presence of a scatterer at an A site $r_i^A$ with short range potential with strength $-u$, the effective potential has been calculated to be\cite{35}

$$U = \begin{pmatrix} 1 & 0 & e^{i \phi} & 0 \\ 0 & 0 & 0 & 0 \\ e^{-i \phi} & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} u \delta(r - r_i^A), \quad \text{(A5)}$$

with $\phi = (K' - K) \cdot r_i^A + \eta$, where $\eta$ is the chiral angle defined in Fig. 1 (a). A similar effective Hamiltonian can be obtained for an impurity at a B site.

For states in the vicinity of the bottom of the conduction band, i.e., $\varepsilon = +\delta$, the above matrix Hamiltonian is reduced to a $2 \times 2$ matrix

$$H' = \begin{pmatrix} \hbar^2 k_f^2/2m^* & 0 \\ 0 & \hbar^2 k_f^2/2m^* \end{pmatrix} - u \begin{pmatrix} 1 & e^{i \phi} \\ e^{-i \phi} & 1 \end{pmatrix} \delta(r - r_i^A), \quad \text{(A6)}$$

where the effective mass is given by $m^* = \hbar^2 \delta/\gamma^2$ and the energy origin is chosen at the band edge.

The wave function is expanded into a Fourier series as

$$F(r) = \sum_k \left( \begin{array}{c} C_k^K \\ C_k^{K'} \end{array} \right) e^{i kr}, \quad \text{(A7)}$$

where $C_k^K$ and $C_k^{K'}$ are coefficients to be determined.

The equation for the coefficients is easily obtained as

$$0 = \begin{pmatrix} I + \frac{u}{\hbar^2} \sum_{k'} \left[ \varepsilon' - \frac{\hbar^2 k_f^2}{2m^*} \right] - u \begin{pmatrix} 1 & e^{i \phi} \\ e^{-i \phi} & 1 \end{pmatrix} \right] \sum_k \left( \begin{array}{c} C_k^K \\ C_k^{K'} \end{array} \right), \quad \text{(A8)}$$

where $I$ is a $2 \times 2$ unit matrix and $\varepsilon'$ is defined as $\varepsilon - \delta$. Consequently, the condition for the presence of nontrivial solution gives a single localized level with negative energy given by

$$\varepsilon' = -\varepsilon_c \exp \left[ -\frac{(m^* u)^2}{\hbar^2} \right], \quad \text{(A9)}$$

where $\varepsilon_c$ is a cut-off energy. In the case of a carbon impurity, we have $u = (\sqrt{3}/2) a \gamma_0$. Then, the binding energy $\varepsilon_B$ appearing in the discussion is given by $|\varepsilon'|$.

It should be noted that the energy of the bound state is inevitably dependent on the cut-off energy because the localized state is constructed by many of eigenstates situated away from the K and K points. The cut-off is determined roughly by the condition that the wave vectors lie in the first Brillouin zone and therefore $\varepsilon_c \approx \hbar^2 k_f^2/2m^*$ with $k_f \sim \pi / a$. This gives $\varepsilon_c \sim (3\pi^2/8) \gamma_0^2 / \delta$. Because of the explicit dependence on the cut-off, the obtained binding energy may be used for the purpose to show the qualitative dependence on the parameters such as $\delta/\gamma_0$.

The energy bands of a nanotube is obtained by imposing periodic boundary conditions in the circumference direction. For the envelope functions the conditions read\cite{11}

$$F_K(r + L) = \exp \left( -\frac{2\pi i}{3} \nu \right) F_K(r), \quad \text{(A10)}$$

$$F_{K'}(r + L) = \exp \left( +\frac{2\pi i}{3} \nu \right) F_{K'}(r), \quad \text{(A10)}$$

where $\nu = 0$ or $\pm 1$ given by

$$n_a + n_b = 3N + \nu, \quad \text{(A11)}$$

with integer $N$. Therefore, the energy bands in the vicinity of a K point are given by

$$\varepsilon_K^* = \pm \sqrt{\nu c(n)^2 + k^2 + \delta^2 / \gamma^2} \approx \pm \left( \delta + \frac{\hbar^2}{2m^*} [\nu c(n)^2 + k^2] \right), \quad \text{(A12)}$$

with $\nu c(n)^2 + k^2$.
with
\[
\kappa_n(n) = \frac{2\pi}{L} (n - \nu) \frac{1}{3}.
\]  \hspace{1cm} (A13)

The bands in the vicinity of a K' point are obtained by replacing \(\nu\) by \(-\nu\) in the above expressions.

References


Figure Captions

Fig. 1 (a) The coordinates systems of a 2D graphite and graphitic BN sheet. The vectors \(\vec{r}_1\), \(\vec{r}_2\), and \(\vec{r}_3\) are vectors connecting nearest neighbor A and B sites. The vectors \(a\) and \(b\) with length \(a\) are primitive translation vectors. The vector \(L\) is the chiral vector and \(\eta\) is the chiral angle. (b) The first Brillouin zone of a 2D graphite and graphitic BN sheet.

Fig. 2 Calculated density of states of zigzag BCN alloy nanotubes \((L/a = 9)\) and \((A/a = 50\sqrt{3})\) and the results of VCA (dashed lines). (a) Method I. (b) Method II. (c) Method III. The arrows indicate the band edge.

Fig. 3 Calculated density of states of zigzag BCN alloy nanotubes \((L/a = 10)\) and \((A/a = 50\sqrt{3})\).

Fig. 4 The band gap of BCN alloy nanotubes and as a function of the boron and nitrogen concentration. (a) \(L/a = (9,0)\) and (10,5). (b) \(L/a = (10,0)\). The VCA results are shown by dashed lines.

Fig. 5 Calculated dynamical conductivity of \((9,0)\) BCN alloy nanotubes \((L/a = 9)\) and \((A/a = 50\sqrt{3})\) and the results of VCA (dashed line). (a) Method I. (b) Method II. (c) Method III. The arrows indicate the band gap determined by the density of states.

Fig. 6 Calculated dynamical conductivity of \((10,0)\) BCN alloy nanotubes \((L/a = 10)\) and \((A/a = 50\sqrt{3})\).

Fig. 7 The square of the absolute value of the wave function for \(\rho = 90\%\) in \((9,0)\) BCN nanotube created by method I. The left shows that of a state at the top of the valence band and the right the bottom of the conduction band. Filled tetragons denote boron sites occupied by a carbon and empty tetragons nitrogen sites occupied by a carbon in the shaded regions with width \(5\sqrt{3}a\) and mutual distance \(30\sqrt{3}a\).
Fig. 1

(a) [Diagram of the unit cell with labels A, B, and A, and arrows indicating directions x, y, and z.]

(b) [Diagram of the Brillouin zone with points Γ, K, and K' and the direction k_x and k_y.]

Fig. 2

(a) (9,0) Method I

(b) (9,0) Method II

(c) (9,0) Method III

Energy (units of $\gamma_0$) vs. Density of States (units of $2/(\gamma_0^3a^2)$)
Fig. 3

Fig. 4
Fig. 5

Fig. 6
Fig. 7