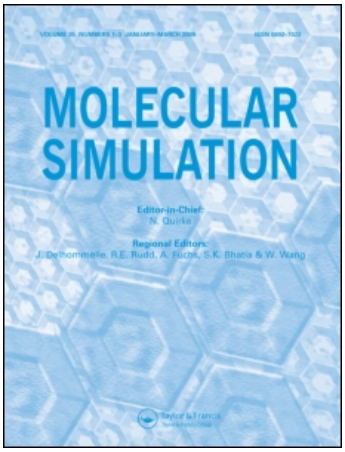

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Electronic energy band structure of uniaxially deformed (5,5) armchair carbon nanotube

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Semiempirical molecular orbital calculations of the (5,5) armchair carbon nanotube give the Kekule structure in its ground state with two essentially different bonds (the bond lengths difference is 0.003 nm). This is a result of the Peierls distortions leading to tripled (compared with undistorted case) translational period. When the armchair nanotube is elongated, two first order deformational structural phase transitions are predicted. The first one at the elongation of 5% leads to doubling of a translational period (instead of tripling at smaller elongations). The second one at the elongation of 13% leads to the quinoid type structure. The dependence of the electronic energy-band structure of the (5,5) carbon nanotube on elongation is investigated using the tight binding approximation. The transition from narrow-gap semiconductor to metal is predicted at the elongation of 5%, indicating that the uniaxially deformed armchair carbon nanotube at greater elongation (more than 5%) remains metallic at all temperatures.

Keywords: carbon nanotubes; Kekule structure; tight binding approximation; deformations; structural transitions

PACS: 73.63.Fg; 73.22.−f; 61.46.Fg

1. Introduction

The studies of electronic and elastic properties of carbon nanotubes (CNTs) are actually related to perspectives of their applications in nanoelectronic devices [1] and in composite materials [2].

The present paper is devoted to a theoretical investigation of the possible structural phase transitions of an armchair CNT controlled by the expansion on the example of the (5,5) CNT. The semi-empirical method of molecular orbitals modified for one-dimensional periodic structures [3] with the parametric method 3 (PM3) parametrisation of Hamiltonian [4] has been applied to calculate the formation enthalpy and structure of the uniaxially deformed (5,5) nanotube. Previously, the method was used to calculate the Kekule structure of the ground state in the case of the (5,5) nanotube [5]. The adequacy of the PM3 parametrisation of Hamiltonian has been demonstrated [6] by calculation of bond lengths of the C_{60} fullerene with the I_h symmetry: the calculated values of bond lengths coincide with the experimental ones within the experimental accuracy of 10^{-4} nm.

PM3 method is well suited [7] for geometrical structure optimisation but not for electronic structure calculations. Moreover, being a numerical method, it is not adequate for exploring qualitative trends. Therefore, we combine PM3 atomic structure calculations of the (5,5) CNT with tight binding [8] electronic structure calculations to investigate qualitative features in the electronic energy band structure of the uniaxially deformed armchair (5,5) CNT.

2. Deformational structural transitions in the (5,5) CNT

The Kekule structure of the ground state of the (5,5) nanotube is shown in Figure 1(a). From the geometrical point of view, this structure is possible for all armchair (n,n) nanotubes. The Kekule structure of an armchair CNT is a result of Peierls distortions [8–10]. There are three energetically equivalent atomic structures corresponding to the ground state that are shown in Figure 1(a). The transition state between these minima is shown in Figure 1(c). The calculated energy difference between the ground state and the transition state of the (5,5) CNT is 3 meV per one carbon atom. This corresponds to $\sim$30 K Peierls transition temperature.

Since the translational period of a deformed nanotube *a priori* is not known, we use a computational cell of 120 carbon atoms to take into account both the possibilities of tripling or doubling of the translational period of a deformed CNT. Born–von Karman periodic boundary conditions along the nanotube axis (the y-axis) were used to optimise the structure of the infinite CNT. The structure of the (5,5) nanotube is calculated for different elongations (all other geometrical parameters have been optimised) $\varepsilon = (l - l_{eq})/l_{eq}$, where l is the length of the computational cell, and l_{eq} is the length of this cell, corresponding to the elongation $\varepsilon = 0$.

The following phases with different symmetries of the structure have been found for the uniaxial deformation of the (5,5) CNT: the phase A with the Kekule structure and

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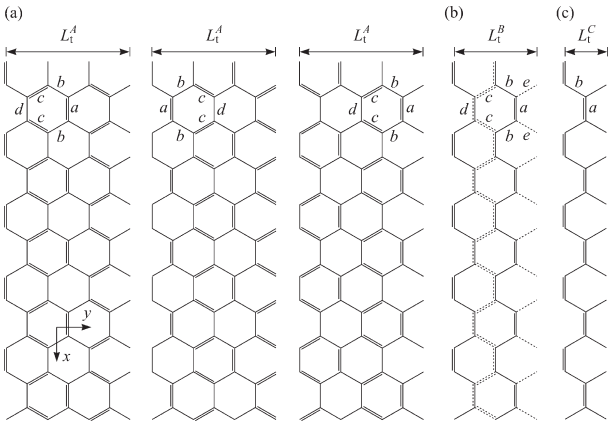

Figure 1. (a), (b) and (c) are the schemata of the evolvements of the elementary cells of the (5,5) nanotube for the phases *A*, *B* and *C*, respectively; (c) corresponds also to the transition state of the phase *A*. Translational periods $L_t^C = L_t^B/2 = L_t^A/3 = L_t = a_0\sqrt{3}$, if all bond lengths are equal to a_0.

the triple translational period L_t^A at small elongations ε, the phase *B* with the double translational period L_t^B at intermediate ε and the phase *C* with the quinoid type structure and the ordinary translational period L_t^C at large ε (Figure 1).

The calculated dependence of the non-equivalent bond lengths with respect to ε is shown in Figure 2. The abrupt change in the nanotube structure at the critical elongation values ε_c, where the formation enthalpies of the phases coincide ($\varepsilon_c = 5\%$ for the phases *A* and *B* and $\varepsilon_c = 13\%$ for the phases *B* and *C*), means that at zero temperature both structural phase transitions between the phases *A* and *B* and the phases *B* and *C* are the first order transitions with respect to the elongation ε (control parameter).

3. Electronic structure of the deformed (5,5) CNT

In the tight binding approximation [8], the band structure of armchair CNTs with all equal bonds has two half-filled bands intersecting at the Fermi level. They are shown

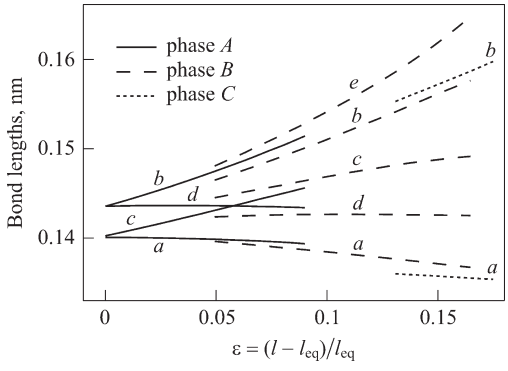

Figure 2. The dependence of the non-equivalent bond lengths on the elongation ε. Bonds notation corresponds to Figure 1.

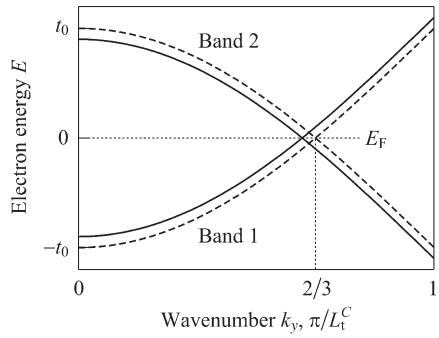

Figure 3. The half-filled bands 1 and 2 intersecting at the Fermi level ($E = 0$) of armchair nanotubes with quinoid structure for the case $t_a = 1.1t_0$, $t_b = t_0$ and $L_t^C = a_0\sqrt{3}$. Dashed lines are for the equal bonds $a = b = a_0$.

in Figure 3. When dimerisation of quinoid type (c) in Figure 1 occurs, these bands become [9]

$$E_{1,2}(k_y) = \pm t_a[1 - 2(t_b/t_a)\cos(k_y L_t^C/2)], \qquad (1)$$

where t_a, t_b are resonance integrals for bonds *a* and *b*, L_t^C is the translational period of the CNT (for the phase *C*), k_y is the one-dimensional wavenumber of an electron along the CNT axis. In this case, the nanotube remains metallic.

The band structure calculation of the Kekule distorted CNT is reduced in the tight binding approximation to the diagonalisation of the six-order matrix [10]. We assume that the dependence of the resonance integral on the C—C bond length a_{C-C} is [11]:

$$t = (a_0/a_{C-C})^2 t_0, \qquad (2)$$

where $a_0 = 0.142$ nm and $t_0 = 2.6$ eV are the bond length and the resonance integral for the undistorted CNT [12,13], respectively.

The two-dimensional primitive cells of the armchair CNT for the phases *A* and *B* are shown in Figure 4. These primitive cells are used for writing down the Hamiltonian matrixes for the phases *A* and *B*.

The Hamiltonian matrix for the case of four non-equal bonds of the armchair CNT (corresponding to the Kekule structure of the phase *A*) taking into account only first nearest-neighbour atom interaction is obtained as:

$$\begin{array}{c} \\ \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \beta_1 \\ \beta_2 \\ \beta_3 \end{array} \begin{array}{c} \begin{array}{cccccc} \alpha_1 & \alpha_2 & \alpha_3 & \beta_1 & \beta_2 & \beta_3 \end{array} \\ \begin{pmatrix} 0 & 0 & 0 & t_a e^{-i\boldsymbol{k}\boldsymbol{r}_1} & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_2} & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_3} \\ 0 & 0 & 0 & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_3} & t_d e^{-i\boldsymbol{k}\boldsymbol{r}_4} & t_c e^{-i\boldsymbol{k}\boldsymbol{r}_5} \\ 0 & 0 & 0 & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_2} & t_c e^{-i\boldsymbol{k}\boldsymbol{r}_6} & t_d e^{-i\boldsymbol{k}\boldsymbol{r}_4} \\ t_a e^{i\boldsymbol{k}\boldsymbol{r}_1} & t_b e^{i\boldsymbol{k}\boldsymbol{r}_3} & t_b e^{i\boldsymbol{k}\boldsymbol{r}_2} & 0 & 0 & 0 \\ t_b e^{i\boldsymbol{k}\boldsymbol{r}_2} & t_d e^{i\boldsymbol{k}\boldsymbol{r}_4} & t_c e^{i\boldsymbol{k}\boldsymbol{r}_6} & 0 & 0 & 0 \\ t_b e^{i\boldsymbol{k}\boldsymbol{r}_3} & t_c e^{i\boldsymbol{k}\boldsymbol{r}_5} & t_d e^{i\boldsymbol{k}\boldsymbol{r}_4} & 0 & 0 & 0 \end{pmatrix} \end{array}, \qquad (3)$$

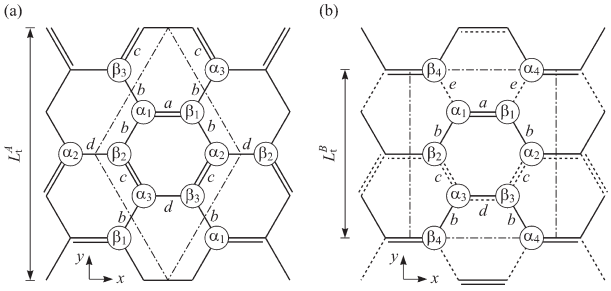

Figure 4. The two-dimensional primitive cells (dash-dotted lines) of deformed armchair nanotube: (a) for phase *A*, (b) for phase *B*. The coordinate system *x*, *y* is used for calculations of the Hamiltonian matrixes (3) and (4).

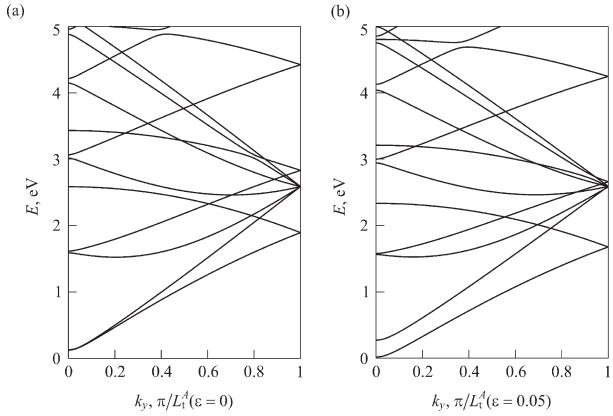

Figure 5. Band structure of the (5,5) CNT for the phase *A* near Fermi level ($E = 0$) at elongations: (a) $\varepsilon = 0$, and (b) $\varepsilon = 0.05$. Only conduction bands are shown. The valence bands are the same with opposite sign.

where t_a, t_b, t_c, t_d are the resonance integrals corresponding to the bonds *a*, *b*, *c*, *d*, respectively; $\boldsymbol{k} = k_x\boldsymbol{e}_x + k_y\boldsymbol{e}_y$ is the electron wavevector; $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ are the unit vectors of the coordinate system; $\boldsymbol{r}_1 = \alpha_1\beta_1 = a\boldsymbol{e}_x$, $\boldsymbol{r}_2 = \alpha_1\beta_2 = \alpha_3\beta_1 = -b_x\boldsymbol{e}_x - b_y\boldsymbol{e}_y$, $\boldsymbol{r}_3 = \alpha_1\beta_3 = \alpha_2\beta_1 = -b_x\boldsymbol{e}_x + b_y\boldsymbol{e}_y$, $\boldsymbol{r}_4 = \alpha_3\beta_3 = \alpha_2\beta_2 = d\boldsymbol{e}_x$, $\boldsymbol{r}_5 = \alpha_2\beta_3 = -c_x\boldsymbol{e}_x - c_y\boldsymbol{e}_y$, $\boldsymbol{r}_6 = \alpha_3\beta_2 = -c_x\boldsymbol{e}_x + c_y\boldsymbol{e}_y$ are the vectors of bonds between α_i and β_i atoms.

The diagonalisation of matrix (3) with the PM3 derived bond lengths of the (5,5) CNT (Figure 2) and a standard zone-folding procedure [8] taking into account circumferential quantisation gives electronic energy-band structure shown in Figure 5. The valence bands are the same as the conduction bands with the opposite sign because we neglect overlap integral. For the Kekule structure of the undeformed ($\varepsilon = 0$) nanotube with bond lengths $a = c = 0.140\,\text{nm}$ and $b = d = 0.143\,\text{nm}$ the bandgap $E_g = 0.24\,\text{eV}$ appears between the valence and the conduction bands at $k_y = 0$ (Figure 5(a)). The scanning tunneling microscope measurements [14] of electron density of states show $E_g = 0.11\,\text{eV}$ for the armchair (7,7) CNT at liquid helium temperature. The diagonalisation of (3) for $\boldsymbol{k} = 0$ gives for the bandgap $E_g = 2(t_d - t_c)$, i.e. almost linear dependence on ε according to Figure 2 and Equation (2). At the elongation of $\varepsilon = 0.05$ the structural phase transition occurs, and the bandgap becomes zero for the phase *B* due to the double translational period of this phase (Figure 1(b)).

For the phase *B*, the primitive cell contains eight atoms (Figure 4(b)). The Hamiltonian matrix for the case of five non-equal bonds of the armchair CNT (the phase *B*) has the form

$$
\begin{array}{c}
\\
\alpha_1\\ \alpha_2\\ \alpha_3\\ \alpha_4\\ \beta_1\\ \beta_2\\ \beta_3\\ \beta_4
\end{array}
\begin{array}{c}
\begin{array}{cccccccc} \alpha_1 & \alpha_2 & \alpha_3 & \alpha_4 & \beta_1 & \beta_2 & \beta_3 & \beta_4 \end{array}\\
\begin{pmatrix}
0 & 0 & 0 & 0 & t_a e^{-i\boldsymbol{k}\boldsymbol{r}_1} & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_2} & 0 & t_e e^{-i\boldsymbol{k}\boldsymbol{r}_3}\\
0 & 0 & 0 & 0 & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_4} & t_d e^{-i\boldsymbol{k}\boldsymbol{r}_5} & t_c e^{-i\boldsymbol{k}\boldsymbol{r}_6} & 0\\
0 & 0 & 0 & 0 & 0 & t_c e^{-i\boldsymbol{k}\boldsymbol{r}_7} & t_d e^{-i\boldsymbol{k}\boldsymbol{r}_5} & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_2}\\
0 & 0 & 0 & 0 & t_e e^{-i\boldsymbol{k}\boldsymbol{r}_8} & 0 & t_b e^{-i\boldsymbol{k}\boldsymbol{r}_4} & t_a e^{-i\boldsymbol{k}\boldsymbol{r}_1}\\
t_a e^{i\boldsymbol{k}\boldsymbol{r}_1} & t_b e^{i\boldsymbol{k}\boldsymbol{r}_4} & 0 & t_e e^{i\boldsymbol{k}\boldsymbol{r}_8} & 0 & 0 & 0 & 0\\
t_b e^{i\boldsymbol{k}\boldsymbol{r}_2} & t_d e^{i\boldsymbol{k}\boldsymbol{r}_5} & t_c e^{i\boldsymbol{k}\boldsymbol{r}_7} & 0 & 0 & 0 & 0 & 0\\
0 & t_c e^{i\boldsymbol{k}\boldsymbol{r}_6} & t_d e^{i\boldsymbol{k}\boldsymbol{r}_5} & t_b e^{i\boldsymbol{k}\boldsymbol{r}_4} & 0 & 0 & 0 & 0\\
t_e e^{i\boldsymbol{k}\boldsymbol{r}_3} & 0 & t_b e^{i\boldsymbol{k}\boldsymbol{r}_2} & t_a e^{i\boldsymbol{k}\boldsymbol{r}_1} & 0 & 0 & 0 & 0
\end{pmatrix}
\end{array}, \qquad (4)
$$

where t_a, t_b, t_c, t_d and t_e are the resonance integrals corresponding to the bonds *a*, *b*, *c*, *d* and *e*, respectively; $\boldsymbol{r}_1 = \alpha_1\beta_1 = \alpha_4\beta_4 = a\boldsymbol{e}_x$, $\boldsymbol{r}_2 = \alpha_1\beta_2 = \alpha_3\beta_4 = -b_x\boldsymbol{e}_x - b_y\boldsymbol{e}_y$, $\boldsymbol{r}_3 = \alpha_1\beta_4 = -e_x\boldsymbol{e}_x + e_y\boldsymbol{e}_y$, $\boldsymbol{r}_4 = \alpha_2\beta_1 = \alpha_4\beta_3 = -b_x\boldsymbol{e}_x + b_y\boldsymbol{e}_y$, $\boldsymbol{r}_5 = \alpha_2\beta_2 = d_x\boldsymbol{e}_x$, $\boldsymbol{r}_6 = \alpha_2\beta_3 = -c_x\boldsymbol{e}_x - c_y\boldsymbol{e}_y$, $\boldsymbol{r}_7 = \alpha_3\beta_2 = -c_x\boldsymbol{e}_x + c_y\boldsymbol{e}_y$, $\boldsymbol{r}_8 = \alpha_4\beta_1 = -e_x\boldsymbol{e}_x - e_y\boldsymbol{e}_y$ are the vectors of bonds between atoms.

The diagonalisation of matrix (4) with the PM3 derived bond lengths and zone-folding procedure [8] gives the electronic energy band structure for the phase *B* which is shown in Figure 6. In this case, the CNT remains metallic, however, the electron Fermi wavenumber k_F shifts. The results of the electron Fermi wavenumber k_F calculations for different elongations ε of the phase *B* are presented in Figure 7. The value of k_F increases with

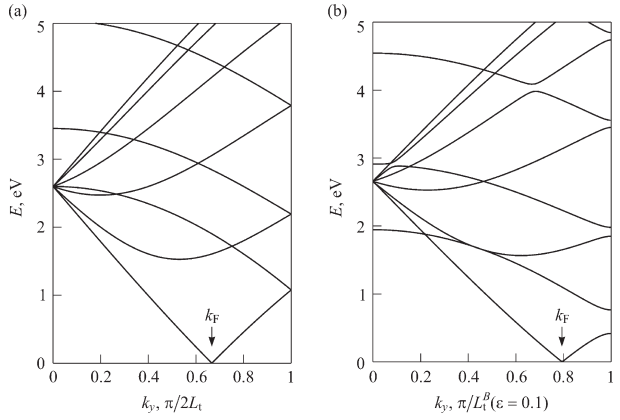

Figure 6. Band structure of the (5,5) nanotube for phase *B*: (a) undistorted nanotube (all equal bonds) with artificially doubled period, (b) at elongation $\varepsilon = 0.1$.

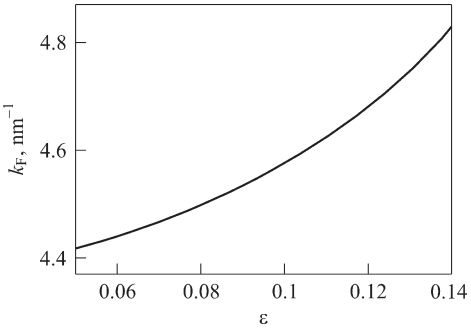

Figure 7. Dependence of Fermi wavenumber k_F on elongation ε in (5,5) nanotube for phase *B*.

elongation. This effect can be used for tuning the electrical properties of a CNT (for example tunneling current [15]) via deformation in nanoelectromechanical devices [16].

4. Conclusion

The atomic structure of the (5,5) carbon nanotube is calculated for its quasistatic expansion up to the elongation of 20%. Two first order structural phase transitions with the change in the atomic structure symmetry are revealed at the nanotube expansion. It is shown that for the elongation greater than 5% the structure of the CNT corresponds at any temperature to the metallic phase without the Peierls gap in the electron spectrum. We believe that the narrow gap semiconductor to metal phase transition at CNT elongation can be used for elaboration of nanotube-based stress nanosensors.

Acknowledgements

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References

[1] M.J. O'Connell (ed.), *Carbon Nanotubes: Properties and Applications*, Taylor & Francis, New York, 2006.
[2] S. Rul, F. Lefèvre-schlick, E. Capria, Ch. Laurent, and A. Peigney, *Percolation of single-walled carbon nanotubes in ceramic matrix nanocomposites*, Acta Mater. 52 (2004), pp. 1061–1067.
[3] J.J.P. Stewart, *MNDO cluster model calculations on organic polymers*, New Polymeric Mater. 1 (1987), pp. 53–61.
[4] J.J.P. Stewart, *Optimization of parameters for semiempirical methods. I method*, J. Comput. Chem. 10 (1989), pp. 209–220; J.J.P. Stewart, *Optimization of parameters for semiempirical methods. II applications*, J. Comput. Chem. 10 (1989), pp. 221–264.
[5] N.A. Poklonski, E.F. Kislyakov, O.N. Bubel', and S.A. Vyrko, *Quantum-chemical calculations of Peierls distortions in (5,5) carbon nanotube*, in *The 6th International Conference on the Science and Application of Nanotubes*, Gothenburg (Sweden), 2005.
[6] O.N. Bubel', S.A. Vyrko, E.F. Kislyakov, and N.A. Poklonski, *Totally symmetric vibrational modes of fullerene* C_{60}, JETP Lett. 71 (2000), pp. 506–508.
[7] N.A. Poklonski, E.F. Kislyakov, Nguyen Ngoc Hieu, O.N. Bubel', S.A. Vyrko, A.M. Popov, and Yu.E. Lozovik, *Uniaxially deformed (5,5) carbon nanotube: structural transitions*, Chem. Phys. Lett. 464 (2008), pp. 187–191.
[8] R. Saito, G. Dresselhaus, and M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.
[9] K. Okahara, K. Tanaka, H. Aoki, T. Sato, and T. Yamabe, *Band structures of carbon nanotubes with bond-alternation patterns*, Chem. Phys. Lett. 219 (1994), pp. 462–468.
[10] N.A. Viet, H. Ajiki, and T. Ando, *Lattice instability in metallic carbon nanotubes*, J. Phys. Soc. Japan 63 (1994), pp. 3036–3047.
[11] W.A. Harrison, *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond*, Dover Publications, New York, 1989.
[12] J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, and C. Dekker, *Electronic structure of atomically resolved carbon nanotubes*, Nature 391 (1998), pp. 59–62.
[13] T.W. Odom, J.-L. Huang, P. Kim, and C.M. Lieber, *Atomic structure and electronic properties of single-walled carbon nanotubes*, Nature 391 (1998), pp. 62–64.
[14] M. Ouyang, J.-L. Huang, C.L. Cheung, and C.M. Lieber, *Energy gaps in "metallic" single-walled carbon nanotubes*, Science 292 (2001), pp. 702–705.
[15] N.A. Poklonski, Nguyen Ngoc Hieu, E.F. Kislyakov, S.A. Vyrko, A.I. Siahlo, A.M. Popov, and Yu.E. Lozovik, *Interwall conductance in double-walled armchair carbon nanotubes*, Phys. Lett. A 372 (2008), pp. 5706–5711.
[16] Yu.E. Lozovik and A.M. Popov, *Properties and nanotechnological applications of nanotubes*, Phys. Usp. 50 (2007), pp. 749–761.