
**FULLERENES
AND ATOMIC CLUSTERS**

Phonon Spectrum of Double-Wall Carbon Nanotubes

G. S. Ivanchenko and N. G. Lebedev

Volgograd State University, ul. Prodol'naya 30, Volgograd, 400062 Russia

e-mail: genaivanchenko@yandex.ru, nikolay.lebedev@volsu.ru

Received January 12, 2006

Abstract—The results of studying the phonon spectra of carbon nanotubes within the framework of the periodic-cluster model are presented. Special attention is paid to the phonon spectrum of double-wall nanotubes. It is shown that the spectrum is separated into two subbands corresponding to the acoustic and optical vibrational modes. A specific feature of the phonon dispersion curves is their “doublet” character. The spectrum has an acoustic mode corresponding to longitudinal oscillations of the two walls of a double-wall carbon nanotube with respect to each other.

PACS numbers: 61.46.Fg, 63.22.+m

DOI: 10.1134/S1063783406120183

1. INTRODUCTION

The phonon modes of carbon nanotubes (CNTs) [1, 2] have been found using techniques similar to those developed for calculating their electronic properties [1–7]. Since the unit cell of a CNT contains $2N$ atoms, the total number of degrees of freedom is $6N$. To find IR and Raman active modes, group theory has been used [8, 9]. The vibrational representation can be expanded in irreducible representations of the point group corresponding to a given CNT. Thus, for (n, n) CNTs of D_{nh} symmetry (for which the number n is even and $n/2$ is odd), the vibrational representation can be expanded in the following irreducible representations [1, 3]:

$$\begin{aligned} \Gamma^{\text{vib}} = & 4A_{1g} + 2A_{1u} + 4A_{2g} + 2A_{2u} + 2B_{1g} + 4B_{1u} \\ & + 2B_{2g} + 4B_{2u} + 4E_{1g} + 8E_{1u} + 8E_{2g} + 4E_{2u} \quad (1) \\ & + \dots + 8E_{(n/2-1)g} + 4E_{(n/2-1)u}. \end{aligned}$$

(If $n/2$ is even, the coefficients 8 and 4 of the E -type irreducible representations in the second line are permuted.)

For example, for (6, 6) CNTs, we have $N = 12$ (the number of degrees of freedom is 72) and formula (1) gives 48 different normal modes, since the last two terms in Γ^{vib} are missing for $n/2 - 1 = 2$. At the center of the Brillouin zone, one A_{2u} mode, one E_{1u} mode, and one A_{2g} mode have zero frequencies, since these modes correspond to translations along the tube axis or perpendicular to it or to rotations around this axis.

In order to determine the IR active and Raman active modes, we can use the relevant character tables [8, 9]. For a D_{nh} group, the A_{2u} and E_{1u} modes are IR active and the A_{1g} , E_{1g} , and E_{2g} modes are Raman active. Thus, at the center of the Brillouin zone, the phonon spectrum has 8 frequencies of IR active modes ($A_{2u} + 7E_{1u}$) and

16 frequencies of Raman active modes ($4A_{1g} + 4E_{1g} + 8E_{2g}$). It is important that the number of IR active and Raman active modes is independent of the CNT diameter. This statement is also valid for the other classes of CNTs. However, the frequencies of these modes change with the CNT diameter.

For armchair CNTs with D_{nd} symmetry (n is odd), analogous studies have shown that there are 7 frequencies of IR active modes and 15 frequencies of Raman active modes. The phonon spectra of zigzag CNTs with D_{nh} or D_{nd} symmetry likewise have 7 IR active and 15 Raman active mode frequencies.

Chiral CNTs belong to the C_n point groups, for which the vibrational representation contains the following irreducible representations [1, 3]:

$$\Gamma^{\text{vib}} = 6A + 6B + 6E_1 + 6E_2 + \dots + 6E_{(N/2-1)g}. \quad (2)$$

In this case, the A and E_1 modes are IR active and the A , E_1 , and E_2 modes are Raman active. There is a substantial difference between (n, n) and $(n, 0)$ CNTs, on the one hand, and chiral CNTs, on the other hand. In the first case, the band folding shifts the M point to the center of the Brillouin zone (the Γ point), whereas in chiral CNTs the M point is never superimposed on the Γ point. Therefore, the scatter in the IR and Raman frequencies for (n, n) and $(n, 0)$ CNTs should be greater than that for chiral CNTs.

The vibrational mode frequencies of a single-wall CNT can be calculated from the spectrum of a two-dimensional graphene layer using the equation [1, 3]

$$\omega_{1D}(\mathbf{k}) = \omega_{2D}(k\mathbf{K}_2 + \mu\mathbf{K}_1), \quad \mu = 0, 1, 2, \dots, N-1,$$

where ω_{1D} is a vibrational mode frequency for a one-dimensional CNT, ω_{2D} is a mode frequency for a two-dimensional graphene layer, \mathbf{k} is the wave vector in the

\mathbf{K}_2 direction in the reciprocal space along the CNT axis, and μ enumerates the wave vectors along direction \mathbf{K}_1 normal to the CNT axis.

We used this equation to calculate the dependence of the frequencies of IR active and Raman active modes on the CNT radius. The frequencies were calculated at the center of the Brillouin zone, since only the modes close to this point are Raman active and IR active in the first-order spectra.

2. PHONON SPECTRUM OF SINGLE-WALL CARBON NANOTUBES

The phonon spectrum of single-wall CNTs has been calculated using the methods of classical mechanics (Hamiltonian formalism) in the graphite layer approximation [10]. A geometrical model of a single-wall CNT is schematically represented in Fig. 1. The positions of neighboring atoms of the crystal lattice are assumed to be nonidentical (sites A are connected only to sites B and vice versa). The radius vectors of sites of the A and B sublattices are

$$\mathbf{r}_{ij}^A = i\Delta_1 + j\Delta_2, \quad \mathbf{r}_{ij}^B = \mathbf{r}_{ij}^A + \Delta_3,$$

where Δ_s are the basis translation vectors of the graphite layer ($s = 1, 2, 3$).

The generalized momenta of atoms of both types can be written as

$$\mathbf{p}_{ij}^A = \dot{\mathbf{p}}_{ij}^A m, \quad \mathbf{p}_{ij}^B = \dot{\mathbf{p}}_{ij}^B m.$$

In the harmonic approximation, the Hamiltonian of a single-wall CNT can be written in the form

$$\begin{aligned} \hat{H} = & \sum_{i,j} \left(\frac{(p_{ij}^A)^2}{2m} + \frac{(p_{ij}^B)^2}{2m} \right) + \frac{\mathcal{N}}{2} \sum_{i,j} [(\mathbf{r}_{ij}^A - \mathbf{r}_{i-1,j}^B)^2 \\ & + (\mathbf{r}_{ij}^A - \mathbf{r}_{i-1,j+1}^B)^2 + (\mathbf{r}_{ij}^B - \mathbf{r}_{ij}^A)^2 + (\mathbf{r}_{ij}^B - \mathbf{r}_{i+1,j}^A)^2 \\ & + (\mathbf{r}_{ij}^B - \mathbf{r}_{i+1,j-1}^A)^2 + (\mathbf{r}_{ij}^B - \mathbf{r}_{ij}^A)^2], \end{aligned} \quad (3)$$

where m is the mass of a carbon atom and \mathcal{N} is the coupling constant for neighboring carbon atoms.

Using this Hamiltonian, we write the equations of motion for the atoms

$$\dot{\mathbf{p}}_{ij} = -\frac{\partial}{\partial \mathbf{q}_{ij}} \hat{H},$$

and search for the solution to these equations in the form of plane waves

$$r_{ij}^A = A \exp(i\omega t - ikr_{ij}^A), \quad r_{ij}^B = B \exp(i\omega t - ikr_{ij}^B).$$

After substituting these expressions into the equations of motion, we obtain a system of linear algebraic equations. The solvability condition of this system gives a dispersion equation

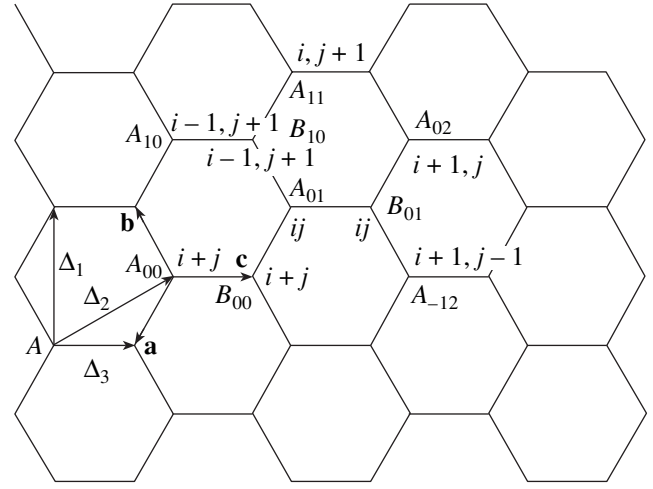


Fig. 1. Geometrical model of a single-wall CNT.

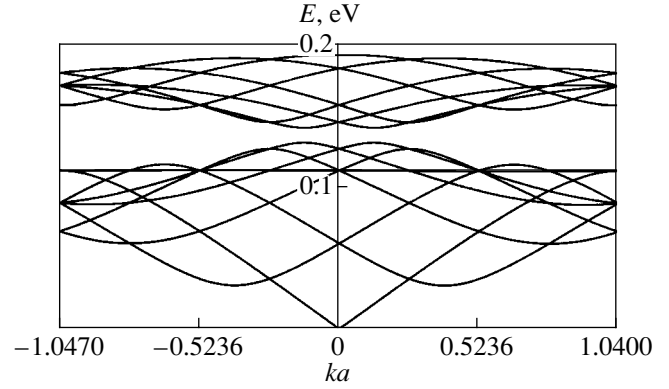


Fig. 2. Phonon spectrum of a single-wall (8, 0) CNT.

$$\begin{aligned} & (\omega^2 - 6\omega_0^2)^2 - 4\omega_0^4 [3 + 2\cos(\sqrt{3}ak_x) \\ & + 2\cos\left(\frac{3}{2}ak_x + \frac{\sqrt{3}}{2}ak_y\right) \\ & + 2\cos\left(\frac{3}{2}ak_x - \frac{\sqrt{3}}{2}ak_y\right)] = 0. \end{aligned} \quad (4)$$

The solutions of this equation are

$$\omega_{1,2}^2 = 6\omega_0^2 \pm 2\sqrt{\mu}, \quad (5)$$

where

$$\begin{aligned} \mu = & 1 + 4\cos^2\left(\frac{\sqrt{3}}{2}ak_y\right) \\ & + 4\cos\left(\frac{3}{2}ak_x\right)\cos\left(\frac{\sqrt{3}}{2}ak_y\right). \end{aligned}$$

In order to obtain the dispersion relations for a CNT, we use cyclic boundary conditions. If N is the number

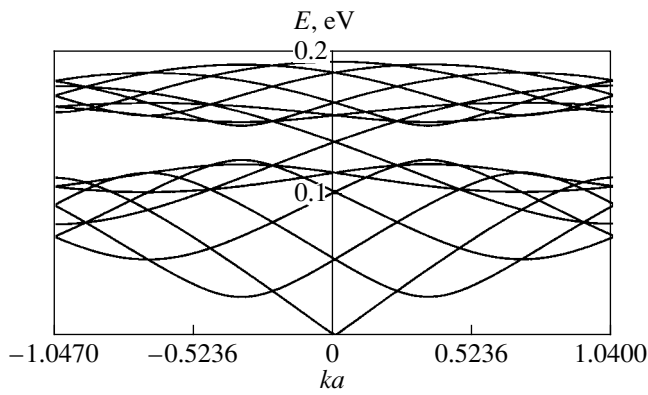


Fig. 3. Phonon spectrum of a single-wall (9, 0) CNT.

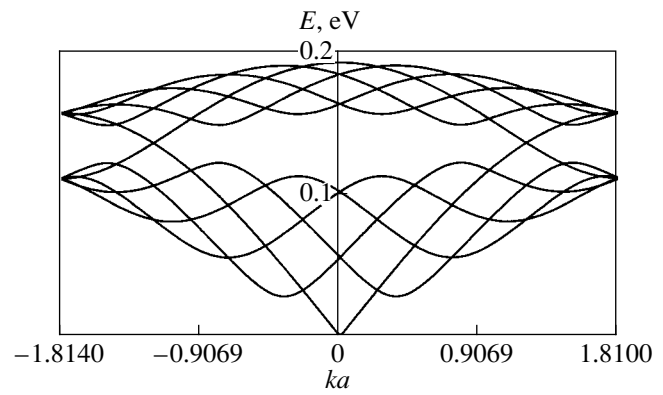


Fig. 4. Phonon spectrum of a single-wall (5, 5) CNT.

of hexagons forming the perimeter of the CNT, then we have

$$r_{ij}^4 = r_{i+N,j}^A,$$

and the boundary conditions assume the form

$$\frac{3}{2}k_x a + \frac{\sqrt{3}}{2}k_y a = 2\pi \frac{n}{N}. \quad (6)$$

The boundary conditions along the CNT axis can be found in a similar manner. If M is the number of hexagons along the CNT axis, then the cyclic boundary conditions are

$$\frac{3}{2}k_x a - \frac{3\sqrt{3}}{2}k_y a = 2\pi \frac{m}{M}. \quad (7)$$

Using these boundary conditions, we can express k_x and k_y as

$$k_x = \frac{\pi}{a} \left(\frac{n}{N} + \frac{m}{3M} \right), \quad k_y = \frac{1}{\sqrt{3}a} \left(\frac{n}{N} - \frac{m}{M} \right). \quad (8)$$

Figures 2–4 show phonon dispersion curves for different single-wall CNTs. These curves have branches of acoustic and optical vibrations, and the phonon spectrum is separated into two subbands. For a semiconductor CNT (Fig. 2), the phonon spectrum has a band gap of about 0.02 eV. For conducting CNTs (Figs. 3, 4), the phonon spectrum does not have a band gap.

The results obtained agree well with the available data on the phonon spectra of single-wall CNTs [11].

3. PHONON SPECTRUM OF DOUBLE-WALL NANOTUBES

The phonon spectrum of double-wall CNTs has been calculated using the above method [12]. A geometrical model of a double-wall CNT is schematically represented in Fig. 5. The positions of neighboring atoms of the crystal lattice are assumed to be nonidentical (sites A are connected only to sites B and vice versa). The neighboring layers of a double-wall CNT

are assumed to correspond to the $ABAB$ packing type (Fig. 5a). In this case, the radius vectors of the sites of the A and B sublattices of one single-wall CNT and of the C and D sublattices of the other single-wall CNT can be written as

$$\begin{aligned} \mathbf{r}_{ij}^a &= i\Delta_1 + j\Delta_2, & \mathbf{r}_{ij}^b &= \mathbf{r}_{ij}^a + \Delta_3, \\ \mathbf{r}_{ij}^c &= \mathbf{r}_{ij}^b + \Delta_4, & \mathbf{r}_{ij}^d &= \mathbf{r}_{ij}^c + \Delta_3. \end{aligned}$$

The generalized momenta of atoms of both types are

$$\mathbf{p}_{ij}^a = \dot{\mathbf{q}}_{ij}^a m, \quad \mathbf{p}_{ij}^b = \dot{\mathbf{q}}_{ij}^b m, \quad \mathbf{p}_{ij}^c = \dot{\mathbf{q}}_{ij}^c m, \quad \mathbf{p}_{ij}^d = \dot{\mathbf{q}}_{ij}^d m.$$

In the harmonic approximation, the Hamiltonian of a double-wall CNT can be written in the form

$$\begin{aligned} \hat{H} &= \frac{1}{2m} \sum_{i,j} [(p_{ij}^a)^2 + (p_{ij}^b)^2 + (p_{ij}^c)^2 + (p_{ij}^d)^2] \\ &+ \frac{1}{2} \sum_{i,j} \{ \mathcal{N}_0 [(r_{ij}^a - r_{ij}^b)^2 + (r_{ij}^a - r_{ij-1}^b)^2 \\ &+ (r_{ij}^a - r_{i+1,j-1}^b)^2 + (r_{ij}^c - r_{ij}^d)^2 + (r_{ij}^c - r_{ij-1}^d)^2 \\ &+ (r_{ij}^c - r_{i+1,j-1}^d)^2] + \mathcal{N}_1 (r_{ij}^c - r_{ij}^b)^2 \\ &+ \mathcal{N}_2 [(r_{ij}^d - r_{ij+1}^a)^2 + (r_{ij}^d - r_{i-1,j+1}^a)^2 \\ &+ (r_{ij}^d - r_{i-1,j+2}^a) + (r_{ij}^d - r_{ij}^b)^2 + (r_{ij}^d - r_{ij+1}^b)^2 \\ &+ (r_{ij}^d - r_{i-1,j+1}^b)^2] \}, \end{aligned} \quad (9)$$

where m is the mass of a carbon atom and \mathcal{N}_0 , \mathcal{N}_1 , and \mathcal{N}_2 are the coupling constants for different bonds between carbon atoms in the graphite layers and between the layers, respectively.

Using this Hamiltonian, by analogy with the single-wall CNT case, we write the equations of motion of atoms and seek a solution in the form of plane waves. We arrive at a system of homogeneous linear algebraic equations and, solving this system, obtain the following

dispersion equation describing the phonon spectrum of a double-wall CNT:

$$\begin{aligned}
 & 2(\omega_0^6 - \omega_2^2(3\omega_2^2 + \omega_1^2)\omega_0^2 + \omega_2^4(-\omega_1^2 + \omega^2))\omega_0^2 \\
 & \times \left(2\cos\left(\frac{3}{2}k_x a_0\right) \left(\cos\left(\frac{3}{2}k_x a_0\right) \right. \right. \\
 & \quad \left. \left. + \cos\left(\frac{3}{2}\sqrt{3}k_y a_0\right) \right) - 1 \right) \\
 & + 2\omega_0^8(2\cos(\sqrt{3}k_y a_0)(\cos(3k_x a_0) \\
 & \quad + \cos(\sqrt{3}k_y a_0)) - 1) \\
 & + (20\omega_0^8 + 12(-6\omega_2^2 - \omega_1^2 + 2\omega^2)\omega_0^6 \\
 & + (-90\omega_2^4 + 6(4\omega^2 - 7\omega_1^2)\omega_2^2 - 4\omega^2(-\omega_1^2 + \omega^2))\omega_0^4 \\
 & + 2(-18\omega_2^4 + (18\omega^2 - 21\omega_1^2)\omega_2^2 + 2\omega^2\omega_1^2)\omega_2^2\omega_0^2 \\
 & - 2(6(\omega_1^2 - \omega^2)\omega_2^2 + (2\omega^2 - 3\omega_1^2)\omega^2)\omega_2^4) \quad (10) \\
 & \times \left(2\cos\left(\frac{1}{2}\sqrt{3}k_y a_0\right) \left(\cos\left(\frac{3}{2}k_x a_0\right) \right. \right. \\
 & \quad \left. \left. + \cos\left(\frac{1}{2}\sqrt{3}k_y a_0\right) \right) - 1 \right) + 42\omega_0^8 + 36(\omega_1^2 - 2\omega^2 \\
 & + 6\omega_2^2)\omega_0^6 + 12(24\omega_2^4 + (-24\omega^2 + 11\omega_1^2)\omega_2^2 \\
 & + 4\omega^2(-\omega_1^2 + \omega^2))\omega_0^4 + 6(18\omega_2^4 + (22\omega_1^2 - 37\omega^2)\omega_2^2 \\
 & + 2(-10\omega_1^2 + 9\omega^2)\omega^2\omega_2^2 + 3\omega_1^2\omega^4 - 2\omega^6)\omega_0^2 \\
 & + 36(\omega_1^2 - \omega^2)\omega_2^6 + 3(-18\omega_1^2 + 13\omega^2)\omega^2\omega_2^4 \\
 & + 3(-4\omega^2 + 7\omega_1^2)\omega^4\omega_2^2 + \omega^6(\omega^2 - 2\omega_1^2) = 0.
 \end{aligned}$$

Then, we impose cyclic boundary conditions analogous to those used for a single-wall CNT.

Figures 6–8 show phonon dispersion curves of different double-wall CNTs. As in single-wall CNTs, the phonon spectrum has branches of acoustic and optical vibrations and is separated into two subbands. The spectrum of a double-wall CNT consisting of conducting single-wall CNTs likewise does not have a band gap. The dispersion curves corresponding to double-wall CNTs are seen to be “double.” As $k \rightarrow 0$, the frequency of the acoustic branch tends to zero. This vibrational mode corresponds to displacement of the double-wall CNT as a whole. However, there is another acoustic branch corresponding to longitudinal oscillations of the two CNTs forming the double-wall CNT relative to each other.

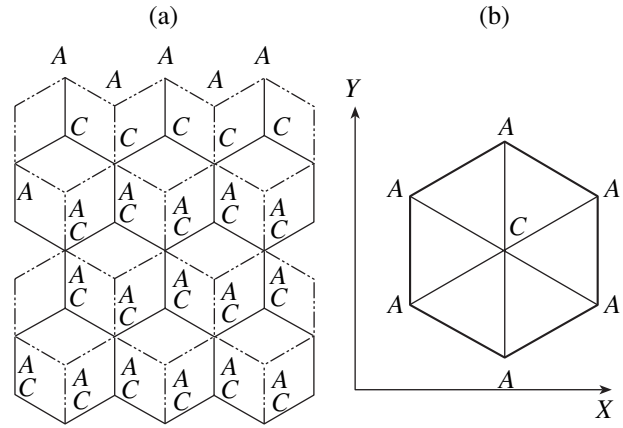


Fig. 5. Geometrical structure of the double-wall CNT model: (a) the arrangement of graphite planes with a structure of the ABAB packing type and (b) diagonal transitions between CNTs (schematic).

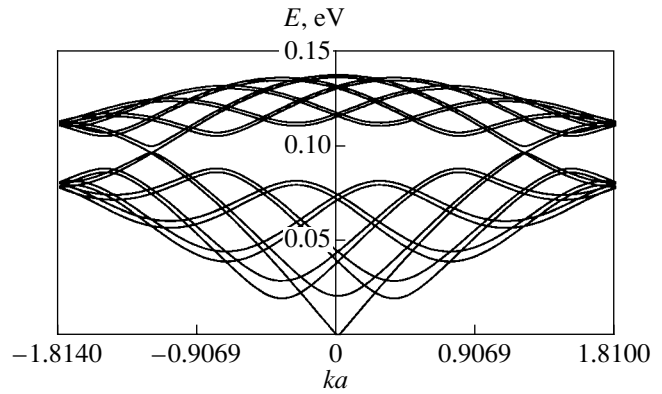


Fig. 6. Phonon spectrum of a double-wall (5, 5)@(10, 10) CNT.

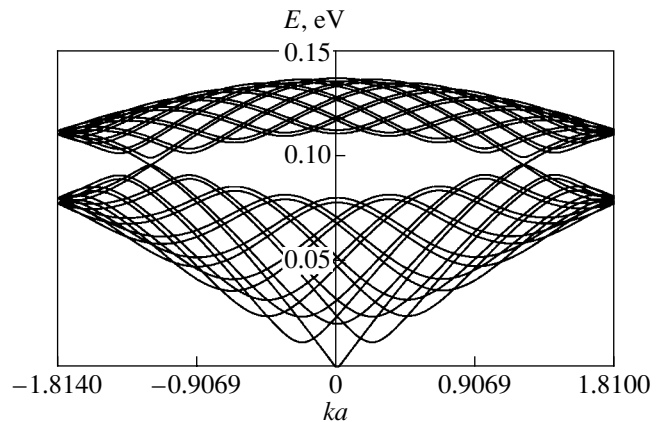


Fig. 7. Phonon spectrum of a double-wall (8, 8)@(13, 13) CNT.

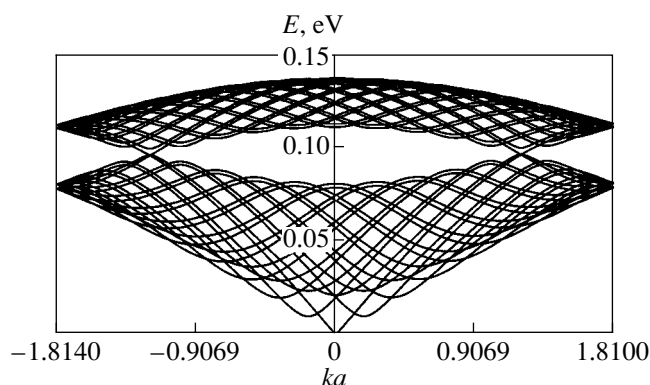


Fig. 8. Phonon spectrum of a double-wall (10, 10)@(15, 15) CNT.

4. CONCLUSIONS

Let us state the main results and conclusions.

(i) We have studied the phonon spectra of single-wall and double-wall carbon nanotubes (CNTs) using a periodic cluster model. On the whole, the calculated phonon spectra of single-wall CNTs agree with the data available in the literature. The phonon spectra of semiconducting CNTs have a gap between the acoustic and optical bands, in contrast to the spectra of conducting CNTs. Furthermore, in zigzag CNTs, there are phonon modes corresponding to standing waves, in which the atoms vibrate in antiphase and the energy is not transferred.

(ii) The dispersion curves of double-wall CNTs have been found to be double. Such doublet phonon modes distinguish double-wall tube structures from other objects. This feature can be used for experimental identification of double objects.

(iii) With regard to electron–phonon interaction, the above feature of the double-wall CNT phonon spectrum can have an effect on the character of conduction. This is a subject for further study.

ACKNOWLEDGMENTS

The authors thank M.B. Belonenko (Volgograd State University of Architecture and Civil Engineering)

for helpful discussions of the results of the present study and valuable advice.

This study was supported by the Russian Foundation for Basic Research, project no. 04-03-96501.

REFERENCES

1. P. Harris, *Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century* (Cambridge University Press, Cambridge, 1999; Tekhnosfera, Moscow, 2003).
2. S. Reich, C. Thomsen, and J. Maultzsch, *Carbon Nanotubes: Basic Concepts and Physical Properties* (Wiley, Berlin, 2003).
3. M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996).
4. R. A. Jishi, M. S. Dresselhaus, and G. Dresselhaus, *Phys. Rev. B: Condens. Matter* **47**, 16671 (1993).
5. R. A. Jishi, L. Venkataraman, M. S. Dresselhaus, and G. Dresselhaus, *Chem. Phys. Lett.* **209**, 77 (1993).
6. R. A. Jishi, D. Inomata, K. Nakao, M. S. Dresselhaus, and G. Dresselhaus, *J. Phys. Soc. Jpn.* **63**, 2252 (1994).
7. P. C. Eklund, J. M. Holden, and R. A. Jishi, *Carbon* **33**, 959 (1995).
8. R. A. Évarestov and V. A. Smirnov, *Group Theory Methods in Solid-State Quantum Chemistry* (Leningrad State University, Leningrad, 1987) [in Russian].
9. A. B. Bolotin and N. F. Stepanov, *Group Theory and Its Applications to Molecular Quantum Mechanics* (UAB “Elcom,” Vilnius, 1999) [in Russian].
10. G. S. Ivanchenko and N. G. Lebedev, in *Proceedings of the Sixth All-Russian Youth Conference on Physics of Semiconductors and Semiconductor Optoelectronics and Nanoelectronics, St. Petersburg, Russia, 2004* (Petersburg, 2004), p. 81 [in Russian].
11. R. Saito, M. S. Dresselhaus, and G. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1999).
12. G. S. Ivanchenko and N. G. Lebedev, in *Abstracts of the Seventh Biennial International Workshop “Fullerenes and Atomic Clusters,” St. Petersburg, Russia, 2005* (Ioffe Physicotechnical Institute, St. Petersburg, 2005), p. 281 [in Russian].

Translated by I. Zvyagin