

# Phonon spectra of carbon nanotubes

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(Submitted 7 August 1995)

*Pis'ma Zh. Éksp. Teor. Fiz.* **62**, No. 7, 595–598 (10 October 1995)

The results of a numerical calculation of the vibrational spectra of graphite nanotubes of optimized structures are presented. This is the first time that the deformation of the wave functions of valence electrons is explicitly taken into account, on the basis of a parametric tight-binding model, in calculating the stiffness matrix of a nanotube. The results agree with the experimental data obtained by the Raman spectroscopy method. © 1995 American Institute of Physics.

In the last few years new molecular forms of carbon — graphite nanotubes (tubulenes) — discovered experimentally in 1991 (Ref. 1) have attracted the interest of many experimental and theoretical groups. Geometrically, nanotubes are cylindrical surfaces, close-packed by hexagonal carbon atomic rings. Unusual electrically conducting,<sup>2</sup> capillary,<sup>3</sup> and mechanical<sup>4</sup> properties of nanotubes have been reported in the current literature.

In the present letter we present theoretical calculations of the vibrational spectra of ideal nanotubes with optimized structure, which were carried out in the parametric, tight-binding model. This problem is of interest for several reasons. First, knowledge of the phonon modes is necessary for understanding the conducting and superconducting properties of tubulenes. Second, the computed vibrational spectra may be helpful for experimental identification of nanotubes.<sup>5</sup> In addition, we study here the so-called “problem of the transferability of the parameters” (we will use the parameters of the tight-binding method, which were adjusted in Ref. 6 to the physical properties of diamond and graphite).

Most experimental studies of the phonon spectrum of tubes are based on the method of “zone folding,” which consists of simply selecting the vibrational frequencies of a graphite plane, which correspond to definite points of the Brillouin zone.<sup>7</sup> However, as the diameter of a nanotube decreases, the error of this method increases, which can result in a substantial shift of the spectral lines. In addition, several normal modes of a tube are incorrectly interpreted when they are chosen on the basis of the spectrum of a graphite plane. Moreover, the method of empirical force constants, which was employed in Ref. 7, is of little predictive value. The empirical-potential methods employed in the literature for carbon systems<sup>8</sup> do not describe adequately two-dimensional structures with  $\pi$  bonds,<sup>9</sup> which tubulenes are. The first-principles methods are awkward and require large amounts of computer time. In view of this circumstance, our parametric tight-binding method is promising, in our view, for solving problems of this class. In contrast to Refs. 7 and 8,

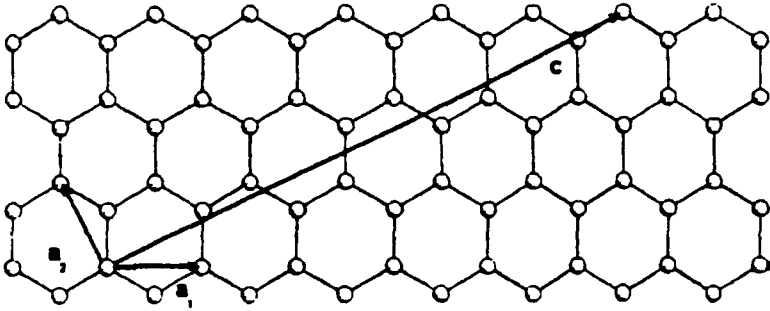


FIG. 1. Section of a graphite plane,  $\mathbf{a}_1$  and  $\mathbf{a}_2$  — primitive translation vectors;  $\mathbf{c}$  — vector determining the method of gluing of the nanotubes.

we take into account explicitly the changes introduced in the electron wave functions by displacements of the nuclei, which makes it possible to study better the electron-phonon interaction problem.

An ideal nanotube can be represented geometrically as a cylindrical surface constructed by gluing an infinite strip of an ideal graphite plane, whose width is equal to the length of the vector  $\mathbf{c}$ :

$$\mathbf{c} = i_1 \mathbf{a}_1 + i_2 \mathbf{a}_2, \quad (1)$$

where  $i_1$  and  $i_2$  are integers, and  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the basis vectors of a two-dimensional Bravais lattice (see Fig. 1). The numbers  $i_1$  and  $i_2$  determine completely the type of nanotube  $(i_1, i_2)$ , and the ratio  $i_1/i_2$  determines the spirality of the tube. When the strip is glued together, the positions of the atoms displaced from one another by the vector  $\mathbf{c}$  are equivalent. In what follows we shall assume that  $i_1 > 2i_2$ . This restriction does not lead to a loss of generality because of the symmetry of the graphite plane.

The screw-translation operators  $\mathbf{D}(\varphi, z)$ , which represent rotations by an angle  $\varphi$  around the axis of the cylinder  $\mathbf{c}$  followed by a translation  $z$  along the generatrix, form the symmetry group of an ideal nanotube. These operators are obtained from the translation vectors of the graphite plane in constructing the nanotube, and therefore they can be enumerated by the two integers  $n_1$  and  $n_2$ :

$$\mathbf{D}_{n_1 n_2} = \mathbf{D}^{n_1}(\varphi_1, z_1) \mathbf{D}^{n_2}(\varphi_2, z_2), \quad (2)$$

where the “elementary” screw translations  $\mathbf{D}(\varphi_1, z_1)$  and  $\mathbf{D}(\varphi_2, z_2)$  correspond in the graphite plane to the translations along the basis vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$ . The method of gluing the nanotubes imposes on the operators (2) the additional conditions

$$\mathbf{D}_{i_1 i_2} = \mathbf{E}, \quad (3)$$

where  $\mathbf{E}$  is the identity transformation. The symmetry group under consideration is Abelian; its irreducible representations are one-dimensional. The characters of the irreducible representations can be obtained from the following considerations. We denote the char-

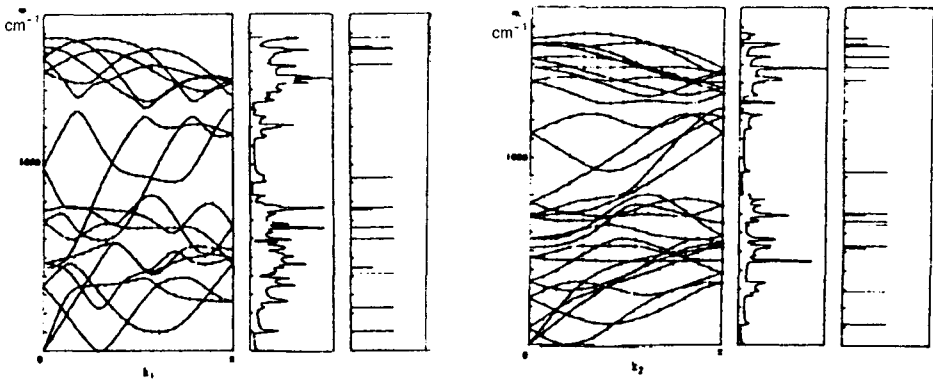


FIG. 2. Phonon spectra of the nanotubes. The phonon dispersion curves are shown on the left-hand side; the dashes mark the frequencies corresponding to clusters of finite length. The phonon density of states in relative units is shown at the center. The optically active modes are shown on the right-hand side, the short segments correspond to one-dimensional irreducible representations of the symmetry group of a nanotube, and the long segments correspond to two-dimensional representations; a — nanotube (7.3), b — nanotube (5.0).

acters of the operators  $\mathbf{D}(\varphi_1, z_1)$  and  $\mathbf{D}(\varphi_2 z_2)$  as  $\exp(ik_1)$  and  $\exp(ik_2)$ . An arbitrary screw-translation operator  $\mathbf{D}_{n_1 n_2}$  will then assume the form  $\exp[i(k_1 n_1 + k_2 n_2)]$ . It follows from the condition (3) that

$$\exp[i(k_1 i_1 + k_2 i_2)] = 1 \quad \text{or} \quad k_1 i_1 + k_2 i_2 = 2\pi n, \quad (4)$$

where  $n$  is an arbitrary integer. Therefore, all irreducible representations of the group of screw translations of an ideal graphite nanotube can be enumerated by one continuous number and one discrete number, and either  $k_1$  or  $k_2$  can be regarded as continuous. The case  $i_2=0$  is an exception. This case determines nanotubes which are called “zigzag” nanotubes in the literature. The symmetry analysis of nanotubes performed above makes it possible to classify their vibrational spectra.

The vibrational spectra of the nanotubes were numerically calculated for finite tube fragments, which were preoptimized with respect to the total energy, with periodic boundary conditions, corresponding to the action of screw-translation operators, along the atomic screw lines. The total energy of a tube was calculated in the tight-binding model with parameters which were adjusted in Ref. 6 to the physical characteristics of diamond and graphite. The formulas for calculating the dynamical matrix in the tight-binding model are given in Ref. 10, where the vibrational spectrum of a carbon fullerene cluster was studied.

We calculated numerically the vibrational spectra of graphite nanotubes with different radii and spiralities. Figure 2 shows, as an example, the numerical data on the calculation of the dispersion curves and the phonon density of states in the nanotubes (7.3) and (5.0). The figure also shows the frequencies of the optically active modes determined from the symmetry analysis of the nanotubes. The continuous number  $k_1$  for the tube (7.3) and the number  $k_2$  for the tube (5.0) is plotted along the horizontal axis on the phonon dispersion curves (see Fig. 2). The dashes in the phonon spectra in Fig. 2

correspond to the vibrational frequencies of 30-Å and 50-Å-long tube fragments; the solid curves were constructed from the dispersion relations for an infinite nanotube but using the dynamical matrix for a particular finite fragment. A comparative analysis of the vibrational spectra of tube fragments of different lengths showed that the error in Fig. 2 does not exceed 0.5%.

The experimental data on the Raman spectra of tubulene-containing materials with large-radius tubes (radii of the order of hundreds of angstroms) indicate the presence of a peak near  $1581\text{ cm}^{-1}$  and a weak peak near  $1350\text{ cm}^{-1}$  (Refs. 11–13). Our numerical results for tubes with smaller radii (of the order of several angstroms; see Fig. 2) qualitatively agree with these data, but the numerical results do not agree completely with the experimental data on the basis of the approximation employed, since a characteristic feature of the tight-binding model is that the maximum vibrational frequency is overestimated, as was indicated in Ref. 9.

Investigation of the optically active modes of the vibrations of nanotubes of different structures revealed the following tendencies. As the tube radius increases, the frequencies in the upper part of the spectrum increase and the frequencies in the lower part of the spectrum decrease. As the tube radius increases, the lines corresponding to the high frequencies cluster in the region  $1650\text{--}1700\text{ cm}^{-1}$ , which corresponds to the Raman frequency of an isolated graphite plane, calculated on the basis of our tight-binding model. The frequencies of several phonon modes (including the “breather” mode) do not depend on the spirality of the nanotubes; the frequencies of the other phonon modes exhibit the same tendencies with increasing spirality as observed with increasing tube radius.

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Translated by M. E. Alferieff