Full Symmetry of Single- and Multi-wall Nanotubes

M. Damnjanović, I. Milošević, T. Vuković and R. Sredanović
Faculty of Physics, University of Beograd, http://www.ff.bg.ac.yu
POB 368, Beograd 11001, Yugoslavia

The full symmetry groups for all single- and multi-wall carbon nanotubes are found. As for the single-wall tubes, the symmetries form nonabelian nonsymorphic line groups, enlarging the groups reported in literature. In the multi-wall case, any type of the line and the axial point groups can be obtained, depending on single-wall constituents and their relative position. Several other consequences are discussed: quantum numbers and related selection rules, electronic and phonon bands, and their degeneracy, application to tensor properties.

61.46.+w, 02.20

I. INTRODUCTION

The single-wall carbon nanotubes are quasi 1D cylindrical structures, which can be imagined as rolled up cylinders of the 2D honeycomb lattice of the single atomic layer of crystalline graphite. Frequently, several single-wall tubes are coaxially arranged, making multi-wall nanotube. Since their diameters are small (down to 0.7 nm) in comparison to lengths (up to tens of μm), the theoretical model of the extended (i.e., infinite, and hence without caps at the ends) nanotube is well justified.

The symmetry of the nanotubes is relevant both for deep insight into the physical properties (quantum numbers, selection rules, optical activity, conducting properties, etc.) and to simplify calculations. As for the single-wall tubes, symmetry studies started by the classification of the graphene tubes according to fivefold, threefold or twofold axis of the related C60 molecule, and gave just a part of their point group symmetry. The translational periodicity was discussed in context of the nanotube metallic properties. Finally, the helical and rotational symmetries were found in the screw axis was characterized in terms of tube parameters, as well as the order of the principle rotational axis.

The first goal of this paper is to complete this task, giving the full geometric symmetry of the extended single-wall nanotubes. Due to their 1D translational periodicity, the resulting groups are the line groups; it appears that only two line group families are relevant: the 5th for the chiral, and the 13th for the armchair and the zig-zag nanotubes.

The symmetry of the double- and multi-wall tubes has never been seriously studied, despite their importance for applications in nanodevices. Here, we present the exhaustive list of symmetries of such tubes. Depending on the single-wall constituents, and their relative arrangement, the resulting nanotube symmetry may be either line group or axial point group.

In section II, at first the necessary notions on the line groups are briefly summarized, and the relevant notation is introduced. Then, in subsection II A, the line groups of all the nanotubes are derived: the familiar symmetries of the original graphene lattice are transferred into the tubular geometry and those which remain symmetries of the rolled up lattice form the corresponding line group. Besides the rotational, translational and helical symmetries, the horizontal axes and (for zig-zag and armchair tubes) mirror- and glide-planes are also present. The symmetry groups of multi-wall nanotubes are studied in subsection II B. Note that among them there are also tubes being not translationally periodic.

Some of the possible applications of symmetry in the physics of nanotubes are discussed in the last section.

II. SYMMETRY OF NANOTUBES

The line groups contain all the symmetries of the systems periodical in one direction and usually are used in context of stereoregular polymers and quasi-1D subsystems of 3D crystals. It immediately follows that, being periodic along its axis, any extended single-wall nanotube has the symmetry described by one of the line groups.

All the line group transformations leave the tube axis (z-axis, by convention) invariant. Consequently, such a transformation \((P|t)\) (Koster-Seitz symbol) is some point group operation \(P\) preserving the z-axis, followed by the translation for \(t\) along the z-axis. Action on the point \(r = (x, y, z)\) gives \((P|t)r = (x', y', z')\) with

\[
x' = P_{xx}x + P_{xy}y, \quad y' = P_{yx}x + P_{yy}y, \quad z' = P_{zz}z + t.
\]
Here, $P_{ij}$ are elements of the $3 \times 3$ matrix of $P$ in the Cartesian coordinates; those coupling $z$ to the other axes vanish. Such point operations are called axial, and they form seven types of the axial point groups [1]: $C_n, S_{2n}, C_{nh}, C_{nv}, D_{n}, D_{nd}, D_{nh}$, where $n = 1, 2, \ldots$ is the order of the principle rotational axis.

There are infinitely many line groups, since there is no crystallographic restriction on the order of the principle axis, and they are classified within 13 families. Each line group is a product $L = \mathbf{Z}P$ of one axial point group $P$ and one infinite cyclic group $Z$ of generalized translations (screw-axis $T_q^n$, pure translations $T = T_0^0$, or glide plane $T_c$, generated by the transformations $(I|a)$, $(C_q^n|a)$ and $(\sigma_{a|\frac{q}{2}})$, respectively [2]). Thus, to determine the full symmetry of a nanotube, both of these factors (having only the identical transformation in common) should be found. The point factor $P$ should be distinguished from the isogonal point group $P_I$ of the line group only for the symorphic groups when $Z = T$, these groups are equal; otherwise $P_I$ is not a subgroup of $L$. Due to the convention [2] $2\pi/q$ is the minimal angle of rotation performed by the elements of the line group (if the screw axis is nontrivial it is followed by some fractional translation), as well as by its isogonal point group.

The easiest way to determine the line group $L$ of a system is to find at first the subgroup $L^{(1)}$, containing all the translations and the rotations around the principle axis (including the ones followed by fractional translations). Having the same screw axis ($T$ is a special case) as $L$, and the same order $n$ of the principle axis, this subgroup $L^{(1)} = T_q^nC_n$ is the maximal subgroup from the first line group family. Then the symmetries complementing $L^{(1)}$ to $L$ should be looked for. To complete $Z$, it should be checked if there is a vertical glide plane. Also, $C_n$ is to be complemented to $P$ by eventual additional point group generators; at most two of them are to be chosen among the mirror planes, horizontal rotational axes of order two or rotoreflection axis (refining pure rotations that are already encountered in $C_n$).

A. Single-wall nanotubes

Elementary cell of the hexagonal honeycomb lattice (Fig. 1) is formed by vectors $\vec{a}_1$ and $\vec{a}_2$ of the length $a_0 = 2.461\text{Å}$; within its area $S_g = \sqrt{3}/2a_0^2$ there are two carbon atoms at positions $(\vec{a}_1 + \vec{a}_2)/3$ and $2(\vec{a}_1 + \vec{a}_2)/3$. The single-wall nanotube $(n_1, n_2)$ is formed when the honeycomb lattice is rolled up, in such a way that the chiral vector $\vec{c} = n_1\vec{a}_1 + n_2\vec{a}_2$ becomes the circumference of the tube (its end and origin match). The tubes $(n_1, 0)$ and $(n_1, n_1)$ are called zig-zag and armchair, respectively, while the others are known as the chiral ones. The chiral angle $\theta$ becomes the circumference of the tube (its end and origin match). The tubes $(n_1, 0)$ and $(n_1, n_1)$ are called zig-zag and armchair, respectively, while the others are known as the chiral ones. The chiral angle $\theta$ becomes the circumference of the tube (its end and origin match). The tubes $(n_1, 0)$ and $(n_1, n_1)$ are called zig-zag and armchair, respectively, while the others are known as the chiral ones. The chiral angle $\theta$ becomes the circumference of the tube (its end and origin match).

**FIG. 1.** *Symmetries of the honeycomb lattice.* For the chiral $(8, 6)$, zig-zag $(6, 0)$ and armchair $(6, 6)$ tubes the chiral vectors $\vec{c}$ are depicted by the arrows. The $U$ and $U'$ axes pass through the circles (perpendicular to the honeycomb). In the zig-zag and armchair case, the bold lines $\sigma_v$ and $\sigma'_v$ represent the vertical mirror and glide planes of the lattice, being orthogonal to $\vec{c}$; the planes parallel to $\vec{c}$ are denoted as $\sigma_h$ and $\sigma'_h$; $U$ is the intersection of the mirror planes, and $U'$ of the glide planes.

There are $n = \text{GCD}(n_1, n_2)$ (the greatest common divisor) honeycomb lattice points laying on the chiral vector. The translations for $sc/n$ in the chiral direction, on the tube appear as the rotations for $2s\pi/n$ ($s = 0, 1, \ldots$) around the tube axis. Thus, the principal axis of order $n$ is a subgroup of the full symmetry of the tube $(n_1, n_2)$:

$$C_n, \quad n = \text{GCD}(n_1, n_2).$$

(2)

Obviously, $n = n_1$ for the zig-zag $(n_1, 0)$ and the armchair $(n_1, n_1)$ nanotubes.

To the primitive translation of the tube corresponds the vector $\vec{a} = a_1\vec{a}_1 + a_2\vec{a}_2$ in the honeycomb lattice, being the minimal one among the lattice vectors orthogonal onto $\vec{c}$. Therefore, $a_1$ and $a_2$ are coprimes, yielding

$$\vec{a} = -\frac{2n_2 + n_1}{nR}\vec{a}_1 + \frac{2n_1 + n_2}{nR}\vec{a}_2, \quad a = |\vec{a}| = \frac{\sqrt{3(n_1^2 + n_2^2 + n_1n_2)}}{nR}a_0,$$

(3)
with $R = 3$ if $\frac{n1-n2}{n}$ is integer and $R = 1$ otherwise. For the zigzag and the armchair tubes $a = \sqrt{3}a_0$ and $a = a_0$, respectively. The elementary cell of the tube is the cylinder of the height $a$ and area $S_t = a|c|$; it contains $\frac{S_t}{na} = 2\frac{n^2 + n1^2 + n2^2}{naR}$ elementary graphene cells. So, the translational group $T$ of the nanotube is composed of the elements $(t|a)$, $t = 0, \pm 1, \ldots$.

The encountered symmetries $T$ and $C_n$ originate from the honeycomb lattice translations: on the folded lattice the translations along the chiral vector become pure rotations, while those along $\vec{a}$ remain pure translations. These elements generate the whole nanotube from the sector of angle $2\pi/n$ of the elementary cell, with $2\frac{n^2 + n1^2 + n2^2}{na}$ elementary graphene cells. This number is always greater then 1, pointing out that not all of the honeycomb lattice translations are taken into account. The missing translations are neither parallel with nor orthogonal onto $\vec{c}$; on the rolled up sheet they are manifested as rotations (for fraction of $2\pi/n$) combined with translations (for fractions of $a$), yielding the screw axis of the nanotube. Its generator $(C_q^0 T_0 a)$ corresponds to the vector $\vec{z} = \frac{q}{n} + \frac{na}{q}$ of the honeycomb lattice, which, together with the encountered translations, generates the whole honeycomb lattice. Thus, $\vec{z}$ can be chosen to form the elementary honeycomb cell together with the minimal lattice vector $\vec{c}/n$ along the chiral direction. The honeycomb cell area $S_q$ must be the product of $|c|/n$ and the length $na/q$ of the projection of $\vec{z}$ onto $\vec{a}$: $a|c|/q = \sqrt{3}a_0^2/2$. This gives the order $q$ of the screw axis. Finally, $r$ is found from the condition that projections of $\vec{z}$ on the $\vec{a}_1$ and $\vec{a}_2$ are coprimes. This completely determines the screw axis $(Fr[x] = x - [x])$ is the fractional part of the rational number $x$, and $\varphi(m)$ is the Euler function, giving the number of coprimes less then $m$:

$$Z = T_{q}^{r}, \quad q = 2\frac{n^2 + n1^2 + n2^2}{nR}, \quad r = \frac{q}{n}\varphi\left(3 - 2\frac{n2}{n1}\right) + \frac{n1}{n\frac{n1-n2}{n}} \left(\frac{q}{n}\varphi\left(\frac{q}{n}\varphi\right) - 1\right).$$

Especially, for both the zigzag $(n, 0)$ and the armchair $(n, n)$ tubes, $q = 2n$ and $r = 1$, i.e. $Z = T_{2n}^{1}$. Note that $q$ is an even multiple of $n$. It is equal to the number of the graphene cells in the elementary cell of the tube $S_t/S_q$. Therefore, $q/n$ is the number of the graphene cells in the sector and therefore always greater then 1; this means that all the single-wall tubes have nonsymorphic symmetry groups.

To resume, the translational symmetry of the honeycomb lattice appears as the group $L^{(1)} = T_{q}^{r} C_{n}$ of symmetries of the nanotube, with $q$ and $r$ given by (4). Its elements $(C_{q}^{n} T_{0}^{0} a)$ ($t = 0, \pm 1, \ldots$, $s = 0, \ldots, n - 1$) generate the whole nanotube from any adjacent pair of the nanotube atoms. The group $L^{(1)}$ contains all the symmetries previously considered in the literature.

Note that the screw axis used here is somewhat different to the previously reported ones, due to the convention in [7]. With this convention $2\pi/q$ is the minimal rotation (followed by some fractional translation) in the group, providing that $q$ is the order of the principle axis of the isogonal point group. This explains why $q$ is equal to the number of the graphene cells contained in the elementary cell of the tube. Note that the translational period $a$ and the diameter $D$ of the tube are determined by the symmetry parameters $q$ and $n$:

$$a = \sqrt{3}a_0, \quad D = \frac{1}{\pi}\sqrt{\frac{R_{0}}{2n}}a_0.$$

Besides the translations, there are other symmetries of the honeycomb lattice: (a) perpendicular rotational axes through the centers of the hexagons (of order six), through the carbon atoms (of order three) and through the centers of the edges of the hexagons (of order two); (b) six vertical mirror planes through the centers of the hexagons formed by the atoms (through the atoms); (c) two types of vertical glide planes — connecting the midpoints of the adjacent edges, and the midpoints of the next to nearest neighboring edges of the hexagons.

Among the rotations, only those for $\pi$, leaving invariant the axis of $\vec{a}$, i.e. the $z$-axis of the tube, remain the symmetry of the rolled up lattice. Thus, two types of horizontal second order axes emerge as symmetries of any nanotube (Fig. 1): $U$, passing through the center of the deformed nanotube hexagons, and $U'$, passing through the midpoints of the adjacent atoms. Moreover, the first of these transformations is obtained when the second one is followed by the screw axis generator: $U = (C_{q}^{n} T_{0}^{0} a)U'$. Thus, any of them, say $U$, complements the principle tube axis $C_n$ to the dihedral point group $D_n$. This shows that at least the line group $T_{q}^{r} D_{n}$ (from the 5th family) is the symmetry group of any nanotube. Note that $U'$ just permute the two carbon atoms in the elementary honeycomb cell, meaning that all the honeycomb atoms are obtained from an arbitrary one by the translations and the rotation $U'$. Analogously, the elements of the group $T_{q}^{r} D_{n}$ generate the whole nanotube from any of its atoms. The action of the group elements on the point $r_{000} = (\rho_0, \phi_0, z_0)$ (cylindrical coordinates) gives the points

$$r_{tu} = (C_{q}^{t} T_{u}^{n} a) r_{000} = (\rho_0, (1)^n \phi_0 + 2\pi(t + s), (1)^n = 0 + \frac{n}{q} t),$$

(6) ($u = 0, 1; s = 0, \ldots, n - 1; t = 0, \pm 1, \ldots$); hereafter, the $x$-axis is assumed to coincide with the $U$-axis. Using (5), it can be shown that the coordinates of the first atom (positioned at $\frac{1}{2}(\vec{a}_1 + \vec{a}_2)$ on the honeycomb) are
The zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the chiral vector is in a perpendicular mirror plane; when the sheet is rolled up, this plane becomes the horizontal mirror plane \( \sigma \) or orthogonal onto \( \vec{c} \) (giving vertical plane). Thus, only the tubes with the chiral vectors being parallel or orthogonal to the enumerated mirror and glide planes obtain additional symmetries of these types. The zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection. Precisely, only in these cases the zig-zag and armchair tubes are immediately singled out by simple inspection.
As it has been derived in [2], the tubes $(n_1, n_2)$ and $(n'_1, n'_2)$ are invariant under the rotations around their axes for the multiples of the angles $2\pi/n$ and $2\pi/n'$ ($n = \text{GCD}(n_1, n_2)$, $n' = \text{GCD}(n'_1, n'_2)$), respectively. The tube composed of these coaxially arranged components is invariant under the rotation for $2\pi/N$, being the minimal common rotation of the components, and its multiples. Thus, the principle axis subgroup of the double-wall nanotube is $C_N$, with $N = \text{GCD}(n, n') = \text{GCD}(n_1, n_2, n'_1, n'_2)$. The horizontal second order rotational axis $U$ (and $U'$) is also symmetry of all single-wall nanotubes. Nevertheless, such an axis remains the symmetry of the composite tube only if it is common to all of the components, and then the point symmetry is $D_N$. Obviously, if a nanotube contains at least one chiral component, then $D_N$ is its maximal point symmetry. Only the tubes composed exclusively of the zig-zag and armchair single-wall components may have additional mirror and glide planes, as well as the rotoreflectational axis. Analogously to the horizontal axis, these are symmetries of the whole tube only if they are common for all of the components (the rotoreflectional axis appear only if the horizontal planes $\sigma_h$ coincides).

After the point symmetries are thereby completely determined, the more difficult study of the generalized translational factor $Z_2$ remains. At first, note that it may be completely absent. Suppose that double-wall tube has the translational period $A$. If the translational periods of its constituents are $a$ and $a'$, then $A$ is obviously the minimal distance being multiple both of $a$ and of $a'$: $A = \alpha a = \alpha' a'$, where $\alpha$ and $\alpha'$ are positive coprimes (to assure minimality). Thus, the double-wall tube is translational periodic if and only if the translational periods of its constituents are commensurate, i.e. only when $\alpha'/a$ is rational. On the contrary, if $\alpha'/a$ is an irrational number, the composed tube is not translationally periodic, and $Z_2$ is trivial (identical transformation only); the total symmetry reduces to the already found point group.

In the commensurate case it remains to examine if the translational group can be refined by a screw axis, common to all of the single-wall nanotubes. The task is to determine the screw axis generator $(C^R_Q|F)$ with maximal $Q$, appearing in both groups $L = T^a_q C_n$ and $L' = T^a'_q C_{n'}$. Thus, it is looking for the values of $Q$, $R$ and $F$ (in accordance with [2]), such that there exist integers $t$, $s$, $t'$ and $s'$ (enumerating the elements of $L$ and $L'$) satisfying

\[
(C^R_Q|F) = (C^s_{q} C^t_n | t f) = (C^s'_{q'} C^t'_{n'} | t' f') \quad \text{with} \quad F = \frac{N}{Q} A, \quad f = \frac{n}{q} a, \quad f' = \frac{n'}{q'} a' .
\]

(9)

Obviously, the fractional translation $F$ is multiple $F = t F^*$ of the minimal common fractional translation $F^*$, implying $A = \frac{Q}{t} F^*$. Analogously to $A$, the translation $F^*$ is found as the minimal distance being multiple both of $f$ and $f'$; thus it is given by the unique solution in the coprimes $\phi$ and $\phi'$ of the equation $F^* = \phi f = \phi' f'$. Since the translational periods of the single-wall components are multiples of their fractional translations, $A$ is multiple of $F^*$, i.e. $A = \Phi F^*$. With help of number theory, it can be shown [2] that only the tubes with the same $R$ may be commensurate; then

\[
\alpha = \phi = \sqrt{\frac{q}{n}} \sqrt{\frac{q'}{n'}} = \sqrt{\frac{q}{n} \frac{q'}{n'}}, \quad \alpha' = \phi' = \sqrt{\frac{q}{n} \frac{q'}{n'}} \quad \text{and} \quad \Phi = \sqrt{\frac{q}{n} \frac{q'}{n'}}.
\]

Thus, $Q = \Phi N/\tau$, and the minimal $\tau$ is looked for to provide the finest screw axis. The translational part of (9) immediately shows that $t = \tau \alpha$ and $t' = \tau \alpha'$. With this values substituted, the rotational part of (9) gives the equations:

\[
C^R_Q = C^{s \alpha \tau} C^t_n = C^{s' \alpha' \tau} C^{t'}_{n'}.
\]

(10)

The minimal $\tau$ for which the last equation is soluble in $s$ and $s'$ is $\tau = \Phi / \text{GCD}(\tau \alpha n', \tau' \alpha' n, \Phi)$. Finally, $Q = \text{NGCD}(\tau \alpha n', \tau' \alpha' n, \sqrt{\frac{q}{n} \frac{q'}{n'}})$, and $R$ is easily found from the first equation (9).

All these results are immediately generalized to the multi-wall tubes. Note that the generalized translations and the principle rotational axis of the multi-wall nanotube depend only on the types of their single-wall components. On the contrary, the appearance of the mirror and glide planes and the horizontal axes in the common symmetry group is additionally determined by the relative positions of these components.

It remains to give the summary of the symmetry groups of the multi-wall tubes. If at least one of the single-wall constituents is chiral, then in the commensurate case there are two possibilities: $T^a_q C_N$ corresponding to the general mutual position, and $T^R_Q D_N$ in the special mutual positions with common $U$-axis. Analogously, the tube built of the incommensurate components have the symmetry described by the point groups $C_N$ or $D_N$. If the nanotube is built of the zig-zag and armchair single-wall tubes $(n, 0)$ (or $(n, n)$), $(n', 0)$ (or $(n', n')$, . . .), the order of the principle rotational axis is $N = \text{GCD}(n, n', . . .)$. If the tube contains at least one single-wall tube of both types, no translational periodicity appears and its symmetry is described by a point group (Tab. 1). On the other hand, for the tube composed of the components of the same type (either zig-zag or armchair), the translation period is equal to that of the components. Two different situations may occur: if all the integers $n/N, n'/N$ . . . are odd (“odd” case), the translations are refined by the screw axis $T^a_{1N}$; otherwise, if at least one of these integers is even (“even” case), no screw axis emerges. The analysis of the special arrangements of the constituents with common horizontal axes, mirror or glide planes, increasing the symmetry of the total system is summarized in the table 1. Note that according to the various arrangements of
the components, any of the line and axial point groups may be the resulting symmetry for the commensurate and incommensurate components, respectively.

Here we give some realistic examples (interlayer distance $\ell$ of approximately 3.4Å, and with diameters of the single-wall components from 0.7nm to 3nm) of the double-wall nanotubes, with their symmetry groups in general positions. With the trivial isogonal point group there are the commensurate tubes (line group is $T\mathbf{C}_1$) (6,6)–(11,11), (7,7)–(12,12), (11,2)–(12,12), (22,4)–(26,11), (10,0)–(19,0), (11,0)–(20,0), (7,3)–(14,6), (21,9)–(28,12), (14,6)–(21,9), and the incommensurate pairs (the total symmetry group is trivial $\mathbf{C}_1$) (9,0)–(10,10), (15,0)–(14,14), (11,2)–(21,0), (13,4)–(14,14), (10,4)–(19,4), (6,4)–(17,1), (9,2)–(19,0), (10,0)–(17,3), (5,5)–(17,0), (6,6)–(19,0), (8,8)–(23,0), (24,9)–(35,6), (25,7)–(38,0), (27,0)–(31,8), (17,17)–(30,13), (10,0)–(11,11), (14,0)–(13,13), (17,0)–(15,15), (5,4)–(13,7), (8,6)–(21,0), (10,0)–(15,6), (16,2)–(15,15). The commensurate tubes (9,0)–(17,0), (9,6)–(15,10), (13,0)–(21,0), (5,5)–(9,9), (7,7)–(11,11), (11,0)–(19,0), have the line group $T_2\mathbf{C}_1$, while $\mathbf{C}_2$ is the symmetry of (12,8)–(18,12) and $\mathbf{C}$ (6,4)–(12,8). The incommensurate tubes with the symmetry $\mathbf{C}_2$ are: (8,8)–(22,0), (12,6)–(18,10), (8,14)–(28,0), (6,6)–(12,10), (16,0)–(14,14), (22,12)–(28,16), (16,8)–(30,0), (14,0)–(16,10), (10,8)–(16,12), (10,2)–(20,0), (26,0)–(30,8), (22,4)–(22,16), (8,2)–(18,0) and (8,8)–(16,10). Finally, the examples for the higher order principle axis are commensurate tubes (5,5)–(10,10) (with line group $T_2\mathbf{C}_2$). (8,8)–(12,12) (T$^2_2\mathbf{C}_4$). (9,0)–(18,0) (T$^3_2\mathbf{C}_9$), (12,0)–(21,0), (T$^3_3\mathbf{C}_9$), (14,0)–(22,0) (T$^1_3\mathbf{C}_2$), and incommensurate ones: (9,9)–(24,0), (18,0)–(15,15), (9,3)–(18,3), (12,9)–(27,0), (15,0)–(18,9), (24,6)–(21,21) (all with symmetry $\mathbf{C}_3$), (24,0)–(28,8), (20,12)–(32,8), (28,0)–(32,8) (C$^1_1$), (15,15)–(35,0) (C$^3_5$), (7,7)–(21,0) (C$^7_7$), (11,0)–(11,11) (C$^1_1$), (12,0)–(12,12) (C$^1_2$) and (13,0)–(13,13) (C$^1_3$).

**TABLE I. Symmetry of the multi-wall zig-zag and armchair tubes.** For the periodic tubes, the line groups (and families) and the isogonal groups are in the "odd" columns if all the ratios $n/N$, $n'/N$, ... are odd, and in the "even" columns otherwise. The point groups of the tubes with both zig-zag and armchair components is in the last column. In the first column the relative positions of the component tubes are characterized by the coinciding symmetry elements (beside the common principle axis in the general position). Here, $(U,U')$ denotes the horizontal axis, which is $U$-axis in some of the constituents, and $U'$-axis in the remaining ones (to exclude the additional mirror or glide planes). Also, $(\sigma_h, \sigma_v')$ is the plane being $\sigma_h$ in some of constituents (with even $n$, necessarily), and $\sigma_v'$ in the remaining tubes; in the incommensurate case, the same groups are obtained when $\sigma_v'$ planes are in common.

| Relative position | "Odd" | "Even" | "Odd" | "Even" | Point group |
|------------------|--------|--------|--------|--------|-------------|
| General          | $T^2_{2N}C_N$ | (1)    | $T\mathbf{C}_N$ | (1)    | $C_{2N}$    |
| $\sigma_h$       | $T^2_{2N}C_{Nh}$ | (4)    | $T\mathbf{C}_{Nh}$ | (3)    | $C_{2N}h$   |
| $\sigma_v$       | $T^2_{2N}C_{Nv}$ | (8)    | $T\mathbf{C}_{Nv}$ | (6)    | $C_{2N}v$   |
| $\sigma_v'$      | $T^2_{2N}C_{Nv}$ | (8)    | $T\mathbf{C}_{Nv}$ | (6)    | $C_{2N}v$   |
| $(U,U')$          | $T^2_{2N}D_N$ | (5)    | $T\mathbf{D}_N$ | (5)    | $D_{2N}$    |
| $\sigma_h, \sigma_v$ | $T^2_{2N}D_{Nh}$ | (13)   | $T\mathbf{D}_{Nh}$ | (11)   | $D_{2N}h$   |
| $\sigma_h, \sigma_v'$ | $T^2_{2N}D_{Nv}$ | (13)   | $T\mathbf{D}_{Nv}$ | (12)   | $D_{2N}v$   |
| $(\sigma_h, \sigma_v') | $T^2_{2N}C_{Nh}$ | (4)    | $T\mathbf{S}_{Nh}$ | (2)    | $C_{2N}N$   |
| $(\sigma_h, \sigma_v'), \sigma_v$ | $T^2_{2N}D_{Nh}$ | (13)   | $T\mathbf{D}_{Nh}$ | (9)    | $D_{2N}h$   |
| $(\sigma_h, \sigma_v'), \sigma_v'$ | $T^2_{2N}D_{Nv}$ | (13)   | $T\mathbf{S}_{Nv}$ | (10)   | $D_{2N}v$   |
III. CONCLUDING REMARKS

All the geometrical symmetries of the nanotubes are found. In addition to the rotations, translations and screw-axes, observed previously, the single-wall tubes always possess horizontal rotational axes; the zig-zag and armchair tubes have mirror and glide planes in addition. Thus, the full symmetry group is \( T_\nu D_n \) for single-wall chiral tubes and \( T_\nu^2 D_{n,h} \) for zig-zag and armchair ones. The parameters \( q \) and \( r \) of the helical group are found in the simple and closed form. Since \( 2\pi/q \) is the angle of the minimal rotation (combined with fractional translation) performed by the symmetry group, the order of the principle axis of the isogonal group is \( q \) and it is always even. Moreover, \( 2q \) is the number of the carbon atoms in the elementary translational cell of the tube. Let us only mention here that the different tubes cannot have the same symmetry parameters \( q, r, n \) and \( a \). This profound property means that the line group is sufficient to reconstruct the tube (as it is demonstrated by (8)), i.e. that the symmetry completely determines the geometry and all consequent characteristics of nanotube. The symmetries of the multi-wall tubes are quite diverse: depending on types of the single-wall components and their arrangements, all the line and axial-point groups emerge: armchair and zig-zag tubes can be combined to make a prototype for any line or axial symmetry group. This immediately shows that the properties of the nanotubes may vary greatly, depending not only on the single-wall constituents, but also on their mutual positions.

There are many physical properties based on symmetry, and the presented classification of the nanotubes according to their symmetry can be widely exploited. The most familiar consequence of symmetry, the special forms of the tensors related to the characteristics of the system, depends on the isogonal group.

Further, the symmetry can be used to find good quantum numbers. To begin with the single-wall nanotubes. The translational periodicity is reflected in the conserved quasi-momentum \( k \), taking the values from the 1D Brillouine zone \((-\pi, \pi]\), or its irreducible domain \([0, \pi]\). Also, the \( z \)-component of the quasi-angular momentum \( m \) is the quantum number caused by the symmetry of the principle rotational axis; it takes on the integer values from the interval \((-\frac{\pi}{2}, \frac{\pi}{2}]\), and characterizes the nanotube quantum states. The parity with respect to reversal of the \( z \)-axis, induced by the horizontal rotational axis \( U \), is the last quantum number common to all the single-wall tubes. The even and the odd states with respect to this parity are conventionally denoted by \(+\) and \(-\). For the zig-zag and the armchair tubes there is additional vertical mirror plane parity, introducing the quantum numbers \( A \) and \( B \), to distinguish between the even and the odd states (the parity with respect to the horizontal mirror plane is dependent on the above discussed \( U \) and \( \sigma_v \) parities, \( \pm \) and \( A/B \)). Concerning the multi-wall tubes, \( m \) is quantum number again. Again, \( z \)-reversal and vertical mirror parities may appear, depending on the concrete symmetry of the nanotube. Nevertheless, the tubes with incommensurate components are not periodic, and in such cases the quasi-momentum \( k \) is not an appropriate quantum number; it may be interesting experimental question whether the approach of modulated systems can be applied to restore this quantity. The simple criterion of commensurability of the single-wall tubes is derived: they have same \( R \) and \( \sqrt{\frac{2\pi}{mq}} \) is an integer. The involved symmetry parameters \( q \) and \( n \) are discrete, allowing exact experimental check of commensurability.

The enumerated quantum numbers may be used to discuss and predict many characteristics of the nanotubes, but the most sophisticated approach to classification and properties of different quantum states is based on the irreducible representations of the corresponding line and point groups. Let us remind that these representations are labeled by the derived quantum numbers. The most exhaustive possible information on selection rules, comprising the conservation of quantum numbers, for the processes in the nanotubes has become available after the full line (or point) group symmetry has been established.

The dimension of an irreducible representation equals degeneracy of the corresponding energy level. For the periodic tubes, the degeneracy of the energy bands is at most fourfold; nevertheless, if the time reversal symmetry of the (spin-independent) Hamiltonian is encountered, the maximal degeneracy is eight-fold. Further, the possible degeneracies are only two-, four- and eight-fold. As for the multi-wall nanotubes with incommensurate components, the dimensions of the irreducible representations of the axial point groups are one, two and (if the time reversal symmetry is included) four, showing the possible degeneracies of the energy levels. Note that the maximal of the enumerated degeneracies (eight- and four-fold) is not possible for the tubes containing at least one chiral single-wall component. Moreover, the degeneracy of the multi-wall tube in the general position of its component is at most two-fold, which is caused by the time reversal symmetry exclusively.

Also, the lattice dynamics can be studied. As it has been mentioned above, the whole single-wall tube can be obtained from its arbitrary atom by the action of the elements of its symmetry group \( \{8\} \); in group theoretical language, this means that the whole nanotube is a single orbit of this group, and this is the orbit \( a_1 \) for the chiral, \( b_1 \) for the zig-zag, and \( d_1 \) for the armchair tube. Thus, the normal modes (phonons), are already classified. The dynamical representation of the chiral tube is decomposed onto the following irreducible components (the summation over \( k \) is over the interval \((0, \pi]\); in the primed sum \( m \) takes integer values from \((0, \frac{2}{\pi}]\), otherwise from \((-\frac{\pi}{2}, \frac{\pi}{2}]\); the
It can be seen that all of the 6n vibrational bands are double degenerate, as it has been anticipated. As for the zig-zag and armchair tubes the corresponding decompositions are (summation in $m$ is over integers from $(0, n)$, and in the primed sums from $(0, \frac{n}{2})$):

\[ D_{\text{chiral}}^{\text{dyn}} = 3(oA_o^+ + oA_o^- + \pi A_o^+ + \pi A_o^- + oA_{n/2}^+ + \pi A_{n/2}^-) + 6 \sum_{m}^{'}(\pi E_m + oE_m) + 6 \sum_{k,m} E_m. \]

Analogous data can be directly found for each nanotube. This classification can be used to simplify calculation of the vibrational bands, the obtained bands are automatically labelled by the symmetry based quantum numbers, meaning that Raman and IC spectra can be directly extracted by the selection rules. Note in this context, that the Jahn-Teller theorem is proved both for the point and for the line groups.

Božović (OXXEL GmbH, Bremen) and dr G. Biczó (Central Research Institute for Chemistry, Budapest), who paid our attention to this subject. Also, we thank to dr R. Kostić (Institute of Physics, Beograd) for some remarks.

---

* E-mail: yqoq@afrodita.rcub.bg.ac.yu
1. S. Iijima, Nature, 354, 56 (1991).
2. M. S. Dresselhaus, Carbon Nanotubes, APS Tutorial, 1998.
3. M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, San Diego, 1998.
4. M. S. Dresselhaus, G. Dresselhaus and R. Saito, Phys. Rev. B 45 6234 (1992).
5. N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. 68, 1579 (1992).
6. C. T. White, D. H. Robertson and J. W. Mintmire, Phys. Rev. B 47 5485 (1993).
7. R. A. Jishi, L. Venkataraman, M. S. Dresselhaus and G. Dresselhaus, Phys. Rev. B, 16 11176 (1995).
8. I. Milošević, R. Zivanović and M. Damnjanović, Polymer, 38 4445 (1997).
9. M. Damnjanović and M. Vuječić, Phys. Rev, B 25, 6987 (1982).
10. I. Milošević, A. Damnjanović and M. Damnjanović, ch. XIV in Quantum Mechanical Simulation Methods for Studying Biological Systems, eds. D. Bicout and M. Field, Springer-Verlag, Berlin, 1996.
11. Elliot J P and Dawber P G 1979 Symmetry in Physics (London: Macmillan)
12. The standard notation is used: $\sigma_v$ is vertical mirror plane, $I$ is $3 \times 3$ identity matrix, while $a$ denotes the translational period. Also, $C_{\mu}^r$ is the rotation for $2\pi r/q$ around z-axis, where $0 \leq r < q/n$ and $q/n$ are coprime integers. Instead of this helical group $Z^*$ generated by $(C_{\mu}^r | \frac{n}{r} a)$, the groups generated by $(C_{\mu}^r | \frac{n}{r} a)$, with $r_i = r + i \frac{n}{r}$, $i = 1, \ldots, n - 1$, give the same full symmetry group $Z^*$. Among these $r_i$ there is at least one being coprime with $q$; with this $r_i$, it is obvious that the set $(C_{\mu}^r | t \frac{n}{r} a)$ contains the rotations for all the multiples of $2\pi/q$ (followed by some translations).
13. M. Damnjanović, T. Vuković and I. Milošević, Preprint FPBU 5/98.
14. Y. Saito, T. Yoshikawa, S. Bandow, M. Tomita and T. Hayashi, Phys. Rev. B 48, 1907 (1993).
15. S. L. Altmann, Band Theory of Solids. An introduction from the Point of View of Symmetry (Clarendon Press, Oxford, 1991).
16. I. Božović, M. Vuječić and F. Herbut, J. Phys. A 11, 2133 (1978); I. Božović, M. Vuječić, J. Phys. A 14, 777 (1981).
17 I. Milošević and M. Damnjanović, Phys. Rev., B 47 7805 (1993).
18 I. Božović, N. Božović and M. Damnjanović, J. Phys. A 18 (1985) 923.
19 M. Damnjanović, I. Milošević, M. Vujičić, Phys. Rev. B 39 (1989) 4610; M. Damnjanović, I. Milošević, Phys. Rev. B 43 (1991) 13482.
20 Since the whole zig-zag and armchair nanotube is produced by action of the subgroup $T_2nD_n$ on an arbitrary atom, each atom is invariant under one (nontrivial) transformation of the full symmetry group (the stabilizers of the atoms are nontrivial).
   For example, the starting atom is invariant under the point group $C_{1v}$ in the zig-zag, and under $C_{1h}$ in the armchair tube.
21 A. Charlier, E. Mc Rae, M. F. Charlier, A. Spire and S. Forster, Phys. Rev. B 57 (1998) 6689.
