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Symmetry and lattices of single-wall nanotubes

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Abstract. The full Euclidean symmetry groups for all the single-wall carbon nanotubes are non-Abelian non-symorphic line groups, enlarging the groups reported in the literature. For the chiral tubes (n_1, n_2) $(n_1 > n_2 > 0)$ the groups are $\boldsymbol{L}q_p 22 = \boldsymbol{T}_q^r \boldsymbol{D}_n$, where n is the greatest common divisor of n_1 and n_2, $q = 2(n_1^2 + n_1 n_2 + n_2^2)/n\mathcal{R}$, while the parameters r and p are expressed in the closed forms as functions of n_1 and n_2. The number $\mathcal{R}$ is three if $n_1 - n_2$ is a multiple of $3n$ and one otherwise; it divides the tubes into two bijective classes. The line group uniquely determines the tube, unless $q = 2n$ (then $r = 1$), when both the zig-zag $(n, 0)$ $(\mathcal{R} = 1)$ and the armchair (n, n) $(\mathcal{R} = 3)$ tubes are obtained, with the line group $\boldsymbol{L}(2n)_n/mcm = \boldsymbol{T}_{2n}^n \boldsymbol{D}_{nh}$ having additional mirror planes. Some physical consequences are discussed: metallic tubes, quantum numbers and related selection rules, electronic and phonon bands, and their degeneracy, and applications to tensor properties.

1. Introduction

The high symmetry of the single-wall carbon nanotubes has attracted much interest [1, 2] from the very beginning of the theoretical investigation of these systems. At first, the tubes were classified according to the principle axis of the related C_{60} molecule [3]. Then their translational periodicity was discussed [4]: due to much greater length (up to tens of μm) in comparison with diameter (down to 0.7 nm), tubes are regarded as quasi-1D crystals. Finally, the helical and rotational symmetries were found [5, 6]. In this paper we give the full Euclidean symmetry group of the infinite single-wall tubes, thus summarizing and completing these investigations.

In section 2 the necessary notions about the line groups are briefly summarized and the relevant notation is introduced. Then the line groups of all the nanotubes are derived: only the symmetries of the original 2D graphene lattice remaining the symmetries of the rolled up lattice form the corresponding line group. Besides the rotational, translational and helical symmetries, the horizontal axes and (only for zig-zag and armchair tubes) mirror and glide planes are also present. In section 3 it is shown that the symmetry group uniquely determines the tube; the exceptions are pairs of one zig-zag and one armchair tubes with the same symmetry. Some of the possible applications of the obtained results in the physics of nanotubes are discussed in the last section.

2. Symmetry of nanotubes

The line groups [7, 8] are the groups of the Euclidean symmetries of the systems translationally periodical in one direction. Besides the stereoregular polymers, typical examples are quasi-1D crystals, including the single-wall carbon nanotubes.

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Each system periodic along one axis (conveniently chosen to be the z-axis) is a regular arrangement of the monomers (elementary structural units) along the z-axis. Generally, such a regular arrangement is not achieved by pure translations, but by screw axis or glide plane, generalizing and refining the translational group. In this sense the monomer is only a part of an elementary cell. The structure of the line group of such a system reflects the structure of the system: it is factorized onto the subgroup describing the symmetry of monomer and the subgroup related to the arrangement of the monomers. Thus, each line group $\boldsymbol{L}$ is a weak-direct product $\boldsymbol{L} = \boldsymbol{Z}\boldsymbol{P}$ of a group of the generalized translations $\boldsymbol{Z}$ (arranging the monomers) and an axial point group $\boldsymbol{P}$ (symmetry of monomer). The axial point group $\boldsymbol{P}$ leaves the z-axis invariant, and it is one of the groups [9]: $\boldsymbol{C}_n, \boldsymbol{S}_{2n}, \boldsymbol{C}_{nh}, \boldsymbol{C}_{nv}, \boldsymbol{D}_n, \boldsymbol{D}_{nd}, \boldsymbol{D}_{nh}$, where $n = 1, 2, \ldots$ is the order of the principle rotational axis. The infinite cyclic group $\boldsymbol{Z}$ is either a screw axis or a glide plane group. In the latter case its generator in the Koster–Seitz notation is $(\sigma_v|\frac{a}{2})$, where a denotes the translational period of the group $\boldsymbol{L}$, while σ_v is vertical mirror plane. The generator of the screw axis group $\boldsymbol{T}_q^r(a)$ is $z = (C_q^r|\frac{n}{q}a)$, where q and r are non-negative integers such that q is multiple of n. The choice of r is not unique: to given r any multiple of $\frac{q}{n}$ may be added, with no effect on the resulting group $\boldsymbol{L}$. Two different conventions may be used to fix the value of r: (i) the minimal allowed value is used (then r is coprime with $\frac{q}{n}$); (ii) the minimal allowed value being coprime with q is considered [7]. The translational period of $\boldsymbol{L}$ contains $\frac{q}{n}$ monomers, each of them being obtained from the previous one by the rotation for $\frac{2\pi}{q}r$ followed by the fractional translation for $\frac{q}{n}a$. There are infinitely many line groups and they are classified into 13 families, differing by the factors $\boldsymbol{Z}$ and $\boldsymbol{P}$, while n enumerates the groups within the family.

In order to determine the line group comprising all the Euclidean symmetries of the nanotube, the procedure of folding up the graphene 2D lattice is used. The symmetries of this honeycomb lattice $\mathcal{H}$ form [10] the diperiodic group $\boldsymbol{Dg}28 = \boldsymbol{D}_{6h}\boldsymbol{T}$ (with the international symbol $\frac{6}{m}\frac{2}{m}\frac{2}{m}$). The translational group $\boldsymbol{T}$ is generated by the translations for the basis vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ (with length $a_0 = 2.461$ Å). The elementary cell over these vectors contains two carbon atoms (see figure 1) at $(\boldsymbol{a}_1 + \boldsymbol{a}_2)/3$ and $2(\boldsymbol{a}_1 + \boldsymbol{a}_2)/3$. The principal axis of order six of the group $\boldsymbol{D}_{6h}$ (perpendicular to $\mathcal{H}$) passes through the origin at the centre of a hexagon. The elements of $\boldsymbol{Dg}28$ which remain the symmetries of the rolled up lattice form the tube's line group.

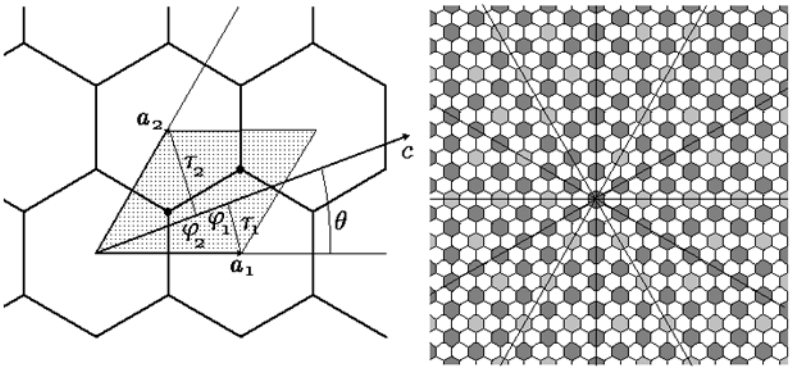

Figure 1. Honeycomb lattice. Left: projections of $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ onto the chiral vector $\boldsymbol{c}$ and the orthogonal direction are φ_i and τ_i $(i = 1, 2)$, respectively, while θ is the chiral angle. The elementary honeycomb cell is shaded. Right: the sublattice $\mathcal{H}_M$ is shaded; its subset $\mathcal{H}_3$ is shaded dark. The lines denote the mirror planes of the lattice.

At first, the translations are examined. The tube (n_1, n_2) is on $\mathcal{H}$ determined by the chiral vector $\boldsymbol{c} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2$, (with the length $c = \sqrt{n_1^2 + n_1n_2 + n_2^2}a_0$ and the chiral angle $\theta = \arctan\frac{\sqrt{3}n_2}{2n_1+n_2}$): $\mathcal{H}$ is rolled up so that $\boldsymbol{c}$ becomes the circumference of the tube. The translations of $\mathcal{H}$ along this chiral vector become the rotations around the tube axis. The minimal one among them is $\tilde{\boldsymbol{c}} = \boldsymbol{c}/n$, where n is the greatest common divisor of n_1 and n_2. Thus, the group of pure rotations of the tube is the cyclic group $\boldsymbol{C}_n$, generated by the rotation C_n for $2\pi/n$. The pure translations of the tube are the honeycomb translations in the direction orthogonal to $\boldsymbol{c}$; the minimal one is $\boldsymbol{a} = a_1\boldsymbol{a}_1 + a_2\boldsymbol{a}_2$, provided a_1 and a_2 are coprimes. Then the orthogonality condition $\boldsymbol{a}\cdot\boldsymbol{c} = 0$ is easily solved

$$\boldsymbol{a} = -\frac{n_1 + 2n_2}{n\mathcal{R}}\boldsymbol{a}_1 + \frac{2n_1 + n_2}{n\mathcal{R}}\boldsymbol{a}_2 \qquad a = |\boldsymbol{a}| = \frac{\sqrt{3(n_1^2 + n_2^2 + n_1n_2)}}{n\mathcal{R}}a_0. \tag{1}$$

Here, $\mathcal{R} = 3$ if $n_1 - n_2$ is multiple of $3n$, and $\mathcal{R} = 1$ otherwise. Knowing n and a, the screw axis generator is found as follows. Each 2D lattice translation becomes, on the tube, an element of the group $\boldsymbol{T}_q^r\boldsymbol{C}_n$. Since the honeycomb is generated by the lattice translations from its elementary cell, the tube must be generated by $\boldsymbol{T}_q^r\boldsymbol{C}_n$ from the pair of C atoms in the honeycomb elementary cell. In the tube's elementary cell there are q/n monomers, each of them containing n elementary honeycomb cells (obtained by the action of $\boldsymbol{C}_n$), and altogether there are q honeycomb cells in the tube's period. On the other hand, the area of this cylindrical surface is ca; dividing it by the area of the honeycomb elementary cell $|\boldsymbol{a}_1 \times \boldsymbol{a}_2|$, one finds:

$$q = 2\frac{n_1^2 + n_1n_2 + n_2^2}{n\mathcal{R}}. \tag{2}$$

The primitive translations $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ of the 2D lattice also generate the rolled-up lattice, i.e. the group $\boldsymbol{T}_q^r\boldsymbol{C}_n$, with elements $(C_q^{rt}C_n^s|t\frac{n}{q}a)$ $(t = 0, \pm1, \ldots; s = 0, \ldots, n-1)$. Let the element corresponding to $\boldsymbol{a}_i$ be $(C_q^{rt_i}C_n^{s_i}|t_i\frac{n}{q}a)$ $(i = 1, 2)$, i.e. rotation for the angle $\varphi_i = 2\pi(rt_i + qs_i/n)/q$ followed by the translation for $\tau_i = t_ina/q$. Then, simple geometry (see figure 1) shows

$$t_1 = -\frac{n_2}{n} \qquad t_2 = \frac{n_1}{n} \qquad s_1 = \frac{2n_1 + (1 + r\mathcal{R})n_2}{q\mathcal{R}} \qquad s_2 = \frac{(1 - r\mathcal{R})n_1 + 2n_2}{q\mathcal{R}}. \tag{3}$$

The minimal r that provides the integral solutions in s_1 and s_2 is coprime to q/n ($\varphi(m)$ is the Euler function, giving the number of coprimes not greater than m):

$$r = \frac{n_1 + 2n_2 - (\frac{n_2}{n})^{\varphi(\frac{n_2}{n})-1}q\mathcal{R}}{n_1\mathcal{R}} \quad \left(\mathrm{mod}\,\frac{q}{n}\right). \tag{4}$$

The other possible values are obtained by adding to (4) the multiples of q/n. If the value (4) and n are not coprimes, the first convention (r coprime to q) is satisfied by some of these numbers. This completes the determination of the subgroup $\boldsymbol{T}_q^r\boldsymbol{C}_n$. It belongs to the first line group family [7] with the international symbol

$$\boldsymbol{L}q_p \qquad p = n\mathcal{R}\frac{(\frac{2n_2+n_1}{n\mathcal{R}})^{\varphi(\frac{2n_1+n_2}{n\mathcal{R}})-1}q - n_2}{2n_1 + n_2} \pmod q \tag{5}$$

(p is found from (4) analogously to r, writing the general element of the line group $\boldsymbol{L}q_p$ in the form $(C_q^i|(j + \mathrm{Fr}[\frac{ip}{q}])a)$; Fr denotes the fractional part).

Note that the parameter q is the order of the principal axis of the isogonal point group [7, 8]. Only when $q = n$ do no screw axes emerge (i.e. the generalized translation group $\boldsymbol{Z}$

is pure translational). Nevertheless, according to the lemma proved in the appendix, q/n for any nanotube has the very specific form:

$$\tilde{q} = \frac{q}{n} = 2 \pmod{12}. \tag{6}$$

Obviously $\tilde{q} \geqslant 2$, and all the nanotubes have non-trivial screw axes, i.e. the corresponding line groups are non-symorphic. Moreover, $\tilde{q}$ equals two only if $\tilde{n}_1 = 1$ and $\tilde{n}_2$ being either zero (then $\mathcal{R} = 1$) or one ($\mathcal{R} = 3$), singling out the zig-zag $(n, 0)$ and the armchair (n, n) tubes, respectively. Simple inspection of the table of the line groups [7, 8] shows that for $\tilde{q} > 2$, only the horizontal axis of order two is compatible with the screw axis, while for $\tilde{q} = 2$ (then $r = 1$), mirror or glide planes may be additionally incorporated. This anticipates that the zig-zag and armchair tubes have larger symmetry groups then the chiral ones.

When the 2D translations are transferred in the tube's geometry, the remaining honeycomb symmetries can be examined. These are point group operations from $\boldsymbol{D}_{6h}$ (rotations for $\frac{2\pi}{6}i$, $i = 0, \ldots, 5$ around the vertical axis and six vertical mirror planes through the centres of the hexagons) and their combinations with 2D translations (two types of vertical glide planes—through the midpoints of the adjacent edges and through the midpoints of the next to nearest neighbour edges of the carbon hexagons, figure 1). According to the emphasized compatibility with the derived non-trivial screw axis, only the rotation for π may remain the symmetry of the rolled up lattice; indeed, this rotation gives the horizontal axis U of the tube, as it is easily seen. Additional symmetries may appear only for the zig-zag and armchair tubes. Obviously, only in these cases is there a vertical mirror plane from $\boldsymbol{D}_{6h}$ containing the chiral vector $\boldsymbol{c}$; it becomes the horizontal mirror plane σ_h of the folded lattice. Also, only in these cases is there a plane from $\boldsymbol{D}_{6h}$ that is orthogonal to the chiral vector, as well as the glide planes parallel with and orthogonal to the chiral vector. These planes become on the tube, the vertical mirror plane $\sigma_v = U\sigma_h$, the roto-reflectional plane $\sigma_h C_{2n}$ and the vertical glide plane $(C_{2n}\sigma_v|\frac{1}{2}a)$, respectively.

Thus, the derivation of the symmetry group of the single-wall tubes is accomplished. As for the chiral tubes, besides the screw axes and pure rotations, there is also the horizontal axis U, enlarging the point factor to $\boldsymbol{D}_n$. For the zig-zag and the armchair tubes only, the point factor is $\boldsymbol{D}_{nh}$, containing additional mirror planes. Altogether, the line group of the tube is:

$$\begin{aligned} \boldsymbol{L}_{\text{chiral}} &= \boldsymbol{T}_q^r \boldsymbol{D}_n = \boldsymbol{L}q_p 22 \\ \boldsymbol{L}_{\text{armchair}} &= \boldsymbol{L}_{\text{zig-zag}} = \boldsymbol{T}_{2n}^1 \boldsymbol{D}_{nh} = \boldsymbol{L}2n_n/mcm \end{aligned} \tag{7}$$

with q, r and p given by (2), (4) and (5), respectively. The isogonal point groups [8] are $\boldsymbol{D}_q$ for the chiral tubes, and $\boldsymbol{D}_{2nh}$ for the zig-zag and armchair tubes.

These results are derived for the tubes with $n_1 \geqslant n_2 \geqslant 0$, i.e. for the chiral angles $0 \leqslant \theta \leqslant \frac{\pi}{6}$. As for the tubes with $n_2 \geqslant n_1 \geqslant 0$ ($\frac{\pi}{6} \leqslant \theta \leqslant \frac{\pi}{3}$), they are obtained from the previously considered tubes as their mirror images in the plane along the armchair direction $(1, 1)$. Therefore, the line group parameters q and n are the same for the pair of the mirror reflected tubes (n_1, n_2) and (n_2, n_1), while the helical parameters r (coprime with $\tilde{q}$) and p are changed to $\tilde{q} - r$ and $q - p$, since the reflection changes the sense of the screw axis rotation. The remaining chiral vectors are obtained by the rotations for multiples of $2\pi/6$ from the encountered vectors with $0 \leqslant \theta \leqslant \pi/3$, yielding the equivalent tubes with the same line groups.

3. Uniqueness and lattice geometry

The set of the generators of the derived line groups contains, besides U and, in the zig-zag and armchair cases, σ_h, two generators of the group $\boldsymbol{L}q_p = \boldsymbol{T}_q^r \boldsymbol{C}_n$. There are two natural choices

of them: the factorized form emphasizes the pair $z = (C_q^r|\frac{n}{q}a)$ and C_n, while the international notation is based on the generators $(I|a)$ and $h = (C_q|\frac{p}{q}a)$. Since (as has been pointed out) $\boldsymbol{T}_q^r\boldsymbol{C}_n$ corresponds to the group $\boldsymbol{T}$ of $\mathcal{H}$, the latter must be generated by the pair of the vectors corresponding to the generators of the former one. Easy calculation with the help of (3) and (1) shows that the corresponding vectors are $\boldsymbol{z} = -\frac{(1-r\mathcal{R})n_1+2n_2}{q\mathcal{R}}\boldsymbol{a}_1 + \frac{2n_1+(1+r\mathcal{R})n_2}{q\mathcal{R}}\boldsymbol{a}_2$, $\tilde{\boldsymbol{c}}$ (the first choice), $\boldsymbol{a}$ and $\boldsymbol{h} = \frac{(\mathcal{R}-p)n_1+2n_2}{q\mathcal{R}}\boldsymbol{a}_1 + \frac{2n_1+(\mathcal{R}+p)n_2}{q\mathcal{R}}\boldsymbol{a}_2$ (the second choice). The coordinates of all these generators must be coprimes, to ensure that the obtained cell is elementary (the parameters r and p can be also found from this requirement).

Note that all the involved quantities can be separated into two classes: those independent of n (e.g. $\boldsymbol{a}$, r, $\mathcal{R}$, $\boldsymbol{z}$, $\boldsymbol{h}$), and those proportional to n (e.g. $\boldsymbol{c}$, n, q, p). The latter ones can be divided by n, yielding additional quantities independent of n (like $\tilde{q}$, $\tilde{\boldsymbol{c}} = \tilde{n}_1\boldsymbol{a}_1+\tilde{n}_2\boldsymbol{a}_2$, $\tilde{p}$). If $\tilde{\mathcal{H}}$ denotes the subset of the honeycomb lattice $\mathcal{H}$ with coprime coordinates, then to each vector $\boldsymbol{c}$ from $\mathcal{H}$ corresponds a unique 'projection' $\tilde{\boldsymbol{c}}$ from $\tilde{\mathcal{H}}$ (this map is obviously idempotent). All the collinear vectors in $\mathcal{H}$ have the same projection. The vectors corresponding to the generators of the line groups are from $\tilde{\mathcal{H}}$; being independent on n, the same vectors $\boldsymbol{z}$, $\tilde{\boldsymbol{c}}$, $\boldsymbol{a}$ and $\boldsymbol{h}$ characterize all the nanotubes with the collinear chiral vectors. These chiral vectors differ by lengths $c = n\tilde{c}$. Since n becomes the order of the generator C_n of the line group, the corresponding line groups are different: their generators differ despite having the same representative vectors on $\mathcal{H}$. This means that the line group parameters r (given by (4)) and $\boldsymbol{a}$ are constant along the same chiral direction, while q is determined by the value $\tilde{q}$ corresponding to the projection $\tilde{\boldsymbol{c}}$ of this direction onto $\tilde{\mathcal{H}}$, and to all other collinear lattice vectors (i.e. $n\tilde{\boldsymbol{c}}$) corresponds $q = n\tilde{q}$.

The lattice $\mathcal{H}$ is a disjoint union of the subsets $\mathcal{H}_1$ and $\mathcal{H}_3$, containing the chiral vectors with $\mathcal{R} = 1$ and $\mathcal{R} = 3$, respectively (the vector 0 is in $\mathcal{H}_3$). The first subset generates (by the integer linear combinations) the whole lattice $\mathcal{H}$, while $\mathcal{H}_3$ generates the sublattice $\mathcal{H}_M$ of $\mathcal{H}$, containing all the vectors (n_1, n_2) such that $n_1 - n_2$ is multiple of three. Its complement $\mathcal{H}_S = \mathcal{H} \setminus \mathcal{H}_M$ is a subset in $\mathcal{H}_1$ (the tubes with the chiral vectors from $\mathcal{H}_M$ are metallic, and the other ones are semiconducting). Projections of $\mathcal{H}_3$ to $\tilde{\mathcal{H}}$ give the subset $\tilde{\mathcal{H}}_3 = \tilde{\mathcal{H}} \cap \mathcal{H}_3 = \tilde{\mathcal{H}} \cap \mathcal{H}_M$, with the coprime pairs $(\tilde{n}_1, \tilde{n}_2)$ such that $\tilde{n}_1 - \tilde{n}_2$ is multiple of three ($n_1 - n_2 = 3k$ means $\mathcal{R} = 3$ on $\tilde{\mathcal{H}}$), while $\mathcal{H}_1$ is projected onto the remaining part $\tilde{\mathcal{H}}_1 = \tilde{\mathcal{H}} \cap \mathcal{H}_1 = \tilde{\mathcal{H}} \cap \mathcal{H}_S$.

The line group parameter q determines the length c of the chiral vector as $c = \sqrt{\frac{qn\mathcal{R}}{2}}a_0$. Consequently, on each of the subsets $\tilde{\mathcal{H}}_1$ and $\tilde{\mathcal{H}}_3$ the chiral vectors of the tubes with the same $q = \tilde{q}$ are on the same circle with the radius c. Analogously, the length of the vector $\boldsymbol{z}$ is determined by $\tilde{q}$ and r as

$$z^2 = (z_1^2 + z_1z_2 + z_2^2)a_0^2 = \frac{3 + r^2\mathcal{R}^2}{2\tilde{q}\mathcal{R}}a_0^2. \tag{8}$$

Thus, all the tubes with same r and $\tilde{q}$ have the vectors $\boldsymbol{z}$ on the same circle with radius z. The angle χ between the vectors $\boldsymbol{c}$ and $\boldsymbol{z}$ is given by $\tan\chi = \sqrt{3}/r\mathcal{R}$, revealing that the parameter r determines the angle of the helix generated by the helical group $\boldsymbol{T}_q^r$.

Theorem 1. *The line group parameters* $\{q, r, n\}$ *uniquely characterize the non-equivalent tubes, except that to* $\{2n, 1, n\}$ *correspond two tubes: the zig-zag tube* $(n, 0)$ *and the armchair one* (n, n).

Proof. Since r is independent of n, and q is proportional to n, it is sufficient to prove the theorem for the parameters $\{\tilde{q}, r, 1\}$ of the line groups corresponding to $\tilde{\mathcal{H}}$. At first, we prove that these parameters can be the same for two tubes with the chiral vectors $\tilde{\boldsymbol{c}}$ and $\tilde{\boldsymbol{c}}'$ both from the same subset $\tilde{\mathcal{H}}_1$ or $\tilde{\mathcal{H}}_3$ if and only if they are equivalent. Indeed, since $\tilde{c} = \tilde{c}'$ and $z = z'$,

while $\chi = \chi'$, there is a rotation for angle $\theta - \theta'$ mapping the lattice basis $\{\tilde{\boldsymbol{c}}, \boldsymbol{z}\}$ into the basis $\{\tilde{\boldsymbol{c}}', \boldsymbol{z}'\}$. But, connecting two bases of $\mathcal{H}$, this rotation is a symmetry of the honeycomb lattice: $\theta - \theta'$ is multiple of $\frac{\pi}{3}$, and the tubes are equivalent. It remains to compare the tubes from $\tilde{\mathcal{H}}_1$ and $\tilde{\mathcal{H}}_3$. Since z^2 is a positive integer (in the units of a_0^2), (8) requires $r^2\mathcal{R}^2 + 3 = 2\alpha_{\mathcal{R}}\mathcal{R}\tilde{q}$ with $\alpha_{\mathcal{R}}$ being a positive integer. For the subsets $\tilde{\mathcal{H}}_1$ and $\tilde{\mathcal{H}}_3$, this gives $r^2 + 3 = 2\alpha_1\tilde{q}$ and $3r^2 + 1 = 2\alpha_3\tilde{q}$. It follows that $(3\alpha_1 - \alpha_3)\tilde{q} = 4$, with the unique solution $\tilde{q} = 2$, $\alpha_1 = \alpha_3 = 1$ and $r = 1$. □

From (1) follows $a_2 - a_1 = -3(\tilde{n}_1 + \tilde{n}_2)/\mathcal{R}$, and this is multiple of three if and only if $\mathcal{R} = 1$. Thus, $\boldsymbol{a}$ and $\boldsymbol{c}$ are always from the different subsets $\mathcal{H}_{\mathcal{R}}$. Moreover, if $\boldsymbol{c}$ (together with $\tilde{\boldsymbol{c}}$) is from $\mathcal{H}_3$, then $\boldsymbol{z}$ must be from $\mathcal{H}_1$, since otherwise $\tilde{\boldsymbol{c}}$ and $\boldsymbol{z}$ would not generate $\boldsymbol{T}$. On the other hand, if $\boldsymbol{c}$ is from $\mathcal{H}_1$, then the coordinates of $\boldsymbol{z}$ satisfy $(z_1 - z_2)\tilde{q} = (\tilde{n}_1 - \tilde{n}_2)r - 3(\tilde{n}_1 + \tilde{n}_2)$. It has been emphasized that instead of r, the values $r_\alpha = r + \alpha\tilde{q}$ ($\alpha = 0, \ldots, n-1$) can be used. Among them, at least one is a multiple of three, giving the equivalent generator $\boldsymbol{z}_\alpha$ from $\mathcal{H}_3$ (since by (6) $\tilde{q}$ is not divisible by three). To resume, the basis $\{\boldsymbol{z}, \tilde{\boldsymbol{c}}\}$ generating the tubes line group can be always chosen such that its vectors belong to different subsets $\mathcal{H}_{\mathcal{R}}$.

Some specific symmetry properties of the metallic tubes can be derived. Since $\mathcal{H}_M$ is a sublattice in $\mathcal{H}$, with the elementary cell containing three cells of $\mathcal{H}$, the metallic tubes can be studied also with help of this lattice. The translational group $\boldsymbol{T}_M$ of $\mathcal{H}_M$ is an index-three subgroup of $\boldsymbol{T}$, resulting on the tube in the index-three subgroup of (5). There are two possibilities for $\boldsymbol{c}$: either it is from $\mathcal{H}_3$ (as well as $\tilde{\boldsymbol{c}}$) or from $\mathcal{H}_1$. In the first case, $\boldsymbol{a}$ is in $\tilde{\mathcal{H}}_1$, i.e. in $\mathcal{H}_S$, as well as $\boldsymbol{z}$. Thus, these vectors should be substituted by $3\boldsymbol{a}$ and $3\boldsymbol{z}$ to obtain the $\mathcal{H}_M$ lattice vectors, with $3\boldsymbol{z}$ and $\tilde{\boldsymbol{c}}$ generating $\boldsymbol{T}_M$. On the tube, these correspond to $(C_q^r|\frac{n}{q}a)^3$ and C_n, generating the line group $\boldsymbol{T}_q^{3r}(3a)\boldsymbol{C}_n$. If $\boldsymbol{c} \in \mathcal{H}_1 \cap \mathcal{H}_M$, then n is divisible by three, then $\boldsymbol{a}$ and (suitably chosen) $\boldsymbol{z}$ are in $\mathcal{H}_3$, but $\tilde{\boldsymbol{c}}$ is not, and $3\tilde{\boldsymbol{c}}$ must be chosen as the generator of the $\mathcal{H}_M$. On the tube $\boldsymbol{z}$ and $\tilde{\boldsymbol{c}}$ correspond to $(C_q^r|\frac{n}{q}a)$ and $C_{n/3}$, generating the line group $\boldsymbol{T}_{q/3}^{r/3}(a)\boldsymbol{C}_{n/3}$. Thus, a metallic tube is a quasi-1D crystal composed of three subcrystals obtained by the action of the found groups on the pair of the neighbouring C atoms: each subsystem contains every third monomer of the original tube if $\mathcal{R} = 3$, and one third of each original monomer if $\mathcal{R} = 1$.

4. Concluding remarks

The full symmetry group of the single-wall carbon nanotubes are $\boldsymbol{L}q_p 22 = \boldsymbol{T}_q^r\boldsymbol{D}_n$ for the chiral tubes and $\boldsymbol{L}2n_n/mcm = \boldsymbol{T}_{2n}^1\boldsymbol{D}_{nh}$ for the zig-zag $(n, 0)$ and the armchair (n, n) ones. These groups of the geometrical symmetries contain horizontal rotational axes and, in the cases of the zig-zag and armchair tubes, mirror and glide planes, in addition to the previously reported rotations, translations and screw axes. The parameters q and r (and p) of the helical group are found in the simple and closed form. The principal axis of the isogonal point group of the tube is of the order $q = 2n \pmod{12n}$, halving the number of the carbon atoms in the translational period of the tube.

The different tubes have different symmetry groups. Especially, knowing the symmetry parameters q, r and n, the corresponding nanotube can be identified, with the exception of the pairs $(n, 0)$ and (n, n), having the same groups, but still different translational periods. The symmetry parameters q, r and n are discrete, thus allowing, at least in principle, exact experimental determination, being sufficient to identify the tube. Moreover, single-wall carbon tubes are single orbit systems, i.e. the whole tube is generated by the line group action on the single C atom. This means that the symmetry completely determines the geometry of the

tube and all consequent physical characteristics. For the chiral tubes the stabilizer is trivial, i.e. when the initial C atom is fixed, each other atom uniquely determines the element of the line group mapping it to the initial one (the orbit a_1 in the notation of [7]). The zig-zag and armchair tubes are produced by the action of the subgroup $\boldsymbol{T}^1_{2n}\boldsymbol{D}_n$ on an arbitrary atom, and the stabilizers of the atoms contain two elements (the orbits are b_1 for the zig-zag, and d_1 for the armchair tubes).

There are many physical properties based on symmetry, and the presented classification of the nanotubes according to their symmetry can be widely exploited. At first, the symmetry determines the conserved 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 [11] $[0, \pi]$. Also, the z-component of the quasi-angular momentum m is the quantum number caused by the symmetry of the isogonal rotations; it takes on the integer values from the interval $(-\frac{q}{2}, \frac{q}{2}]$, and characterizes the nanotube energy bands. These quantum numbers are usually used (e.g. [2]). Alternatively, the helical quasi-momentum $\tilde{\kappa} \in [0, \pi]$ can be considered; it not only incorporates the quasi-momentum, but also a part of the angular momentum. The remaining quasi-angular momentum is then given by the quantum number $\tilde{m}$ taking the integer values from $(-\frac{n}{2}, \frac{n}{2}]$ ($\tilde{k}$ and $\tilde{m}$ are used in [5]). The next quantum number is the parity with respect to the reversal of the z-axis, induced by the horizontal rotational axis U. Finally, only for the zig-zag and the armchair tubes, is there additional vertical mirror plane parity. The quantum numbers are closely related to the representations of the line groups, and classify the irreducible ones (see [12] for the representations related to k and m, and [7] for $\tilde{k}$ and $\tilde{m}$). Thus, it is easy to make the assignation of the energy bands (electronic, phononic etc) by the quantum numbers, immediately giving their degeneracy and the selection rules [13, 7]. In this context, let us only mention here that the zero gap of the metallic tubes (within the tight binding approximation [2, 5]) for the tubes with the chiral vectors from $\mathcal{H}_M$ appears since the contributions to the electronic band energy of the mentioned three identical subcrystals cancel for some bands.

Many other physical applications of the line group symmetry are already considered, and may now be directly applied: the results on the specific forms of the tensorial characteristics of the tubes [14] (determined by the isogonal groups), vibronic coupling [7], phase transitions, invariant potentials [15] and x-ray form factors [16] are available. Finally, let us emphasize that, since the tubes are single-orbit systems, the quantum states of the (quasi)particles related to different physical processes transforms according to the ground representation [9] of the symmetry group. This simplest induced representation enables one to apply the most powerful modified group projector technique [17], and its computer implementations in the physics of nanotubes [8].

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Appendix. Orders of isogonal rotations

As shown in the main text, the order of the principal axis of the isogonal group is $q = n\tilde{q}$. It appears that the integer $\tilde{q}$ may take quite specific values.

Lemma 1. *For any pair of integers n_1 and n_2 with the greatest common divisor n, there exist*

non-negative integer k, satisfying:

$$\tilde{q} = 2\frac{n_1^2 + n_1 n_2 + n_2^2}{n^2 \mathcal{R}} = 12k + 2 \qquad \textit{with} \quad \mathcal{R} = \begin{cases} 3 & \textit{if} \quad n_1 - n_2 = 0 \pmod{3n} \\ 1 & \textit{otherwise.} \end{cases}$$

Proof. Using coprimes $\tilde{n}_1$ and $\tilde{n_2}$, with the difference $\Delta = \tilde{n}_1 - \tilde{n}_2$, one easily finds $\tilde{q} = 2(\tilde{n}_1^2 + \tilde{n}_1\tilde{n}_2 + \tilde{n}_2^2)/\mathcal{R} = 2(3\tilde{n}_1^2 + 3\Delta\tilde{n}_2 + \Delta^2)/\mathcal{R}$. All possible cases are examined: if $\mathcal{R} = 3$, then $\Delta = 3d$ and while $\tilde{n}_2 = 3m \pm 1$, excluding the case when simultaneously m and d are odd and even (then $\tilde{n}_1$ and $\tilde{n}_2$ are both even, and not coprimes); if $\mathcal{R} = 1$, then $\Delta = 3d \pm 1$, excluding $\tilde{n}_2$ even while d is odd. It is easily checked that $\tilde{q} - 2$ is multiple of 12. □

Consequently, $\tilde{q}$ is not divisible by three, but it is always even and greater than one.

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