Pentaheptite Nanotubes

Ivanka Milošević[*], George Volonakis[†], Stergios Logothetidis[†], Zoran Popović[*] and Milan Damnjanović[*]

[*]*NanoLab, Faculty of Physics, University of Belgrade, Studentski trg 12, P. O. Box 368, Belgrade 11001, Serbia*
[†]*Physics Department, LTFN, Aristotle University of Thessaloniki, GR - 54124, Thessaloniki, Greece*

Abstract. Stone-Wales bond rotation converts four adjacent graphene hexagons into two pentagon-heptagone pairs. If such an algorithm is applied on all diamond shaped primitive cells of hexagons, graphene is transformed into a sheet of interlinked pentagones and heptagones. Under condition that pentagons occur only as isolated pairs 2D hexagonal and rectangular pentaheptite lattices can be obtained. We determine the symmetry of the nanotubes rolled up from these lattices along an arbitrary chiral vector and perform symmetry preserving relaxation of a large number of the simply rolled up tubular structures in order to assess stability and conducting properties of the pentaheptite nanotubes relative to the generic graphene nanotubes. Density functional tight binding calculations are performed by full-symmetry implemented *POLSym* code. Pentaheptite tubes are found to be less stable and vast majority of them to be metallic having considerably higher electronic density of states at Fermi level than their metallic conventional counterparts. We propose a pathway for synthesis of certain types of pentaheptite nanotubes directly from the conventional hexagonal nanotubes by putting them under uniaxial tension. Release of the strain goes through formation of double pentagon-heptagone pairs.

Properites of carbon nanotubes exceed those of many other materials [1]. Most of the theoretical investigations use the model of ideal, defect free carbon nanotubes, where their high symmetry [2] make the symmetry arguments extraordinary powerful. Still, carbon nanotubes may have structural defects, one of which, is a Stone-Wales bond rotation. Such a defect deform the ornament of four adjacent hexagons into pentaheptite ornament with two pentagons and two heptagons. Although it is primarily a random defect known in graphite [3], the numerical results [4–6] show the stability of the graphene allotropes, called pentaheptite, with regular tilling of pentaheptite ornaments. Here we discuss pentaheptite carbon nanotubes (57NTs), rolled up from a pentaheptite layer along an arbitrary chiral vector.

Two types of regular pentaheptite tillings of a graphene layer (Fig. 1) exist: (a) type H: hexagonal lattice with doubled graphene lattice constant (basis vectors are $\mathbf{a}_1 = 2a_0\mathbf{e}_x$ and $\mathbf{a}_2 = \mathbf{a}_0(\mathbf{e}_x + \sqrt{3}\mathbf{e}_y)$, $a_0 = 2.461\,\text{Å}$ is graphene period); (b) type R: rectangular lattice (basis vectors $\mathbf{a}_1 = \mathbf{a}_0(\mathbf{e}_x - \sqrt{3}\mathbf{e}_y)$ and $\mathbf{a}_2 = \frac{1}{2}\mathbf{a}_0(3\mathbf{e}_x + \sqrt{3}\mathbf{e}_y)$). Note that both the lattices have C_2 symmetry, but that only hexagonal pentaheptite layer has vertical mirror plane symmetry. Rolling up hexagonal or rectangular type of the pentaheptite layer along the chiral vector $\mathbf{c} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$, hexagonal or rectangular pentaheptite (n_1, n_2) nanotube is obtained (Fig. 2).

Generally, symmetry of the (n_1, n_2) pentaheptite nanotube is described by a line group
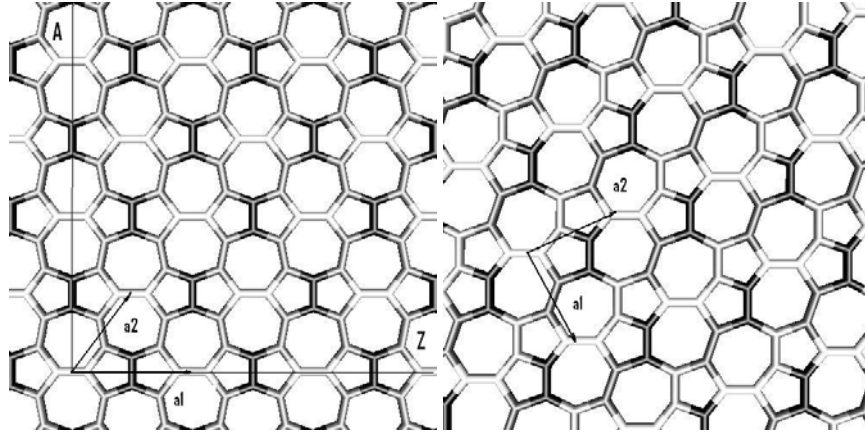
FIGURE 1. Hexagonal (left) and rectangular (right) pentaheptite carbon sheets.

of the fifth family, which is a product of screw-axis group $T_q^r(a)$, rotational group C_n, $n = \mathrm{GCD}(n_1, n_2)$, and D_1 group, generated by $(C_q^r | an/q)$ (simultaneous rotation for $2\pi r/q$ around the tube axis and translation for an/q along the same axis), C_n (rotation for $2\pi/n$ around the tube axis), and rotation for π around a horizontal axis, the so called U axis.

The group parameters q, r and n for hexagonal pentaheptite nanotubes are the same as for the conventional tubes [2], only the period a is doubled. For rectangular pentaheptite nanotubes the line group parameters are [7]:

$$q = \frac{4n_1^2 + 3n_2^2}{n\mathscr{R}}, \quad a = \frac{\sqrt{12}D\pi}{n\mathscr{R}}, \tag{1}$$

and r is more complicated function; $D = \sqrt{nq\mathscr{R}}a_0/\pi$ and $\mathscr{R} = \mathrm{GCD}(3, n_1/n)\mathrm{GCD}(4, n_2/n)$. Relative to the translational period of a generic NT, period of a corresponding R57NT quadruples, doubles or remains the same.

While all rectangular pentaheptite nanotubes are chiral, hexagonal pentaheptite nanotubes can be either chiral ($0 < |n_1| < n_2$, $0° < \theta < 90°$) or achiral (with identical left and right isomer), i.e. of the zig-zag ($n_2 = 0$, $\theta = 0°$) and of the armchair ($n_2 = -2n_1$, $\theta = 90°$) type. Apart from the fifth family line group symmetry the achiral tubes have mirror invariance and their full symmetry is thus described by the line groups belonging to the thirteenth family:

$$L^{(13)} = T_q^r(a)D_{nh}, \quad \text{achiral H57NTs;} \tag{2}$$

$$L^{(5)} = T_q^r(a)D_n, \quad \text{chiral 57NTs.} \tag{3}$$

The above described, simply rolled up pentaheptite nanotubes are used as the initial configuration for the density functional tight binding relaxation [8], in order to asses the stability and find the optimal pentaheptite tubular structures. To this end, Abud-Sartori theorem [9] is applied. It says that invariant function (e.g. total energy) has its extremes in the maximal symmetry points. Therefore, in order not to break the symmetry

of the folded configuration, the sp^3 model density functional tight binding calculations performed by the full symmetry implemented *POLSym* code [10], only the coordinates of the atoms generating the structure by the symmetry group and the period a of the tubes can be varied. This minimal set of atoms, *symcell*, is analogous to the translational unit cell, from which the system can be generated by translations only. In contrast to the conventional carbon nanotubes, which are completely generated from a single atom, *symcell* of pentaheptite nanotubes contains four atoms and is made out of four orbits with trivial stabilizers. It is only in the achiral hexahonal pentaheptite nanotubes that two of these atoms are interrelated by the mirror plane, reducing the *symcell* to three atoms, two of which belongs to the orbits with second order stabilizers. To summarize, only coordinates of the symcell atoms are optimized, while the other atomic positions are automatically generated by symmetry. This makes altogether thirteen parameters for the chiral pentaheptite nanotubes while for the achiral hexahonal pentaheptite nanotubes only eight independent parameters are to be varied.
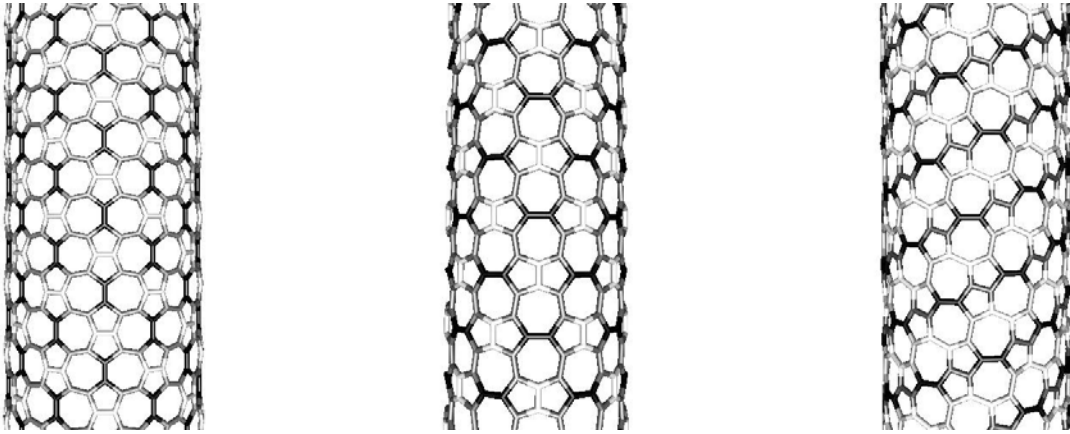

FIGURE 2.   From the left to the right: armchair (-7,14) and zig-zag (7,0) H57NTs; chiral (4,8) R57NT.

Local minimum of the total energy is found in the vicinity of the non-relaxed configuration, meaning that pentaheptite nanotubes are locally stable. However, spontaneous growth of these structures is not probable, as their total (electronic plus ionic) energy is considerably higher, for $0.2 - 1.3$ eV per carbon atom (depending on the tube) than the total energy of their generic counterparts. As the positions of the four *symcell* atoms are independent (except in a case of the achiral hexahonal pentaheptite nanotubes) variational parameters, the relaxed diameters (equal for all the atoms of the corresponding orbits) are not the same, making the tubes no more cylindrical but corrugated (i.e. cross section of the relaxed pentaheptite nanotube is not perfectly cylindrical anymore). These diameters vary up to 10 % from the average diameter.

Concerning hexahonal pentaheptite nanotubes, relative change d of the tube diameter D (with respect to the non-relaxed one given below Eq. (3)) decreases with the chiral angle. Oscillations of d visible for the tubes with the same chiral angle are obviously caused by their diameter differences, and therefore associated to curvature effects. Indeed, relaxed zig-zag tubes are significantly widened with respect to the non-relaxed ones, while the armchair ones are narrowed. However, this effect is accompanied by the simultaneous almost linear opposite change in the tube period: the zig-zag tubes are

shortened, while the armchair tubes are lengthened. These trends are regularly interpolated by other chiralities. As for the rectangular pentaheptite nanotubes, the conclusion is again that the changes of the diameter and the period have opposite signs and they are mostly chirality-dependent. Such a behavior (taking also into account change of other *symcell* atoms' coordinates) leads to the general qualitative conclusion: both heptagons and pentagons became more regular in the energetically most favorable configuration. Namely, after the Stone-Wales bond rotation nearest-neighbors' bond lengths and angles are not mutually the same, forming thus irregular pentagons and heptagons. In the stable configurations these differences lessen, and the way to get more regular ornaments depends on the tube chirality, while the curvature quantitatively modulates the changes.

Vast majority of the pentaheptite nanotubes are metallic [5, 6]. Band gaps observed in the hexagonal pentaheptite nanotubes are lower than 1.5 eV, while in a case of the rectangular pentaheptite nanotubes it is not greater than 0.7 eV. As a rule (with only few exceptions), if generic carbon nanotube is semi-conducting, band gaps of its semi-conducting pentaheptite counterparts are much lower. However, there also exist few semi-conducting pentaheptite nanotubes which generic carbon nanotubes are metallic (i.e. of the armchair type).
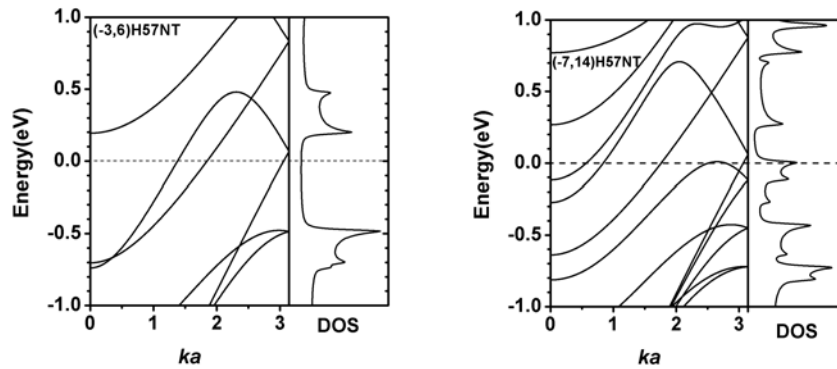
FIGURE 3. Electronic band structure and density of states in the Fermi level region of the hexagonal pentaheptite nanotubes (-3,6) and (-7,14). Their generic graphitic nanotubes are of the armchair type: (6,6) and (14,14), respectively.

Most of the pentaheptite nanotubes have larger electronic density of states (DOS) at the Fermi level than their graphitic armchair counterparts. This is due to the band topology of pentaheptite nanotubes which is characterized by several sub-bands crossings at the Fermi level, Fig. 3. However, this is not the rule: some of the pentaheptite nanotubes although generated from conventional (n,n) tubes turn out to be either narrow or moderate band gap semiconductors. Calculations of the electronic band structure of the defective (n,n) tubes [11] showed that DOS at the Fermi level increases with the concentration of bond rotation defects. Our calculations reveal however that direct extrapolation of the results obtained for the defective nanotubes is not plausible.

It is shown that there are two types of pentaheptite carbon nanotubes: hexagonal and rectangular. Full symmetry group is found for each of them. It is a line group well parameterized by the chiral indices. Further, it is shown that the pentaheptite tubular structures

can be generated from four atoms by applying all symmetry transformations (except for armchair and zig-zag hexagonal tubes where three atoms suffice). The symmetry based results extensively facilitated DFTB calculations, including relaxation as the first step in establishing local stability. It is found that the relaxed configurations are corrugated, and mostly conducting.

Difference in total energy between pentaheptite nanotubes and their conventional counterparts is found to be rather small. Therefore, it is conceivable to induce the transitions between the allotropes by the external influence. As a rule, we found that the total energy of the deformed generic carbon nanotubes (so that their diameter and period match the corresponding parameters of the relaxed pentaheptite nanotubes) is even larger than the total energy of the pentaheptite nanotubes, i.e. in such a way deformed conventional nanotubes are unstable. As a typical example we consider hexagonal pentaheptite (4,0) nanotube, with total energy greater than that of its generic (8,0) counterpart for 0.5 %. Still, it is for 2 % less than the energy of conventional (8,0) nanotube with the diameter enlarged and the period (and z-coordinate of the single *symcell* atom) diminished for 14 %, to match the parameters of hexagonal pentaheptite nanotube (4,0). Thus the specific types of the external mechanical influence [12] may induce transition from graphitic nanotube to its pentaheptite allotrope. However, this may drastically change the conducting properties of carbon nanotube: while (8,0) is semi-conducting, the deformed structure has even the larger gap ($\sim 2.2\,\text{eV}$), while hexagonal pentaheptite nanotube (4,0) is metallic. Such a result, revealing a sort of induced semiconductor-meatl phase transition, might be applied to construct carbon nantotube based electromechanical switch.

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