

Preservation of C hexagons in the transformation of C allotropes

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Abstract Theoretical work by Zhao et al. in (ACS Nano Lett 266(5):7226–7234, 2011) employing a novel “particle swarm methodology” has predicted the pressure-induced collapse of various, respective 1-dimensional members of the $(n, 0)$ C nanotube family, into their corresponding 3-dimensional network C patterns realized as the various C-based hexagonites. In particular, the so-called $(6, 0)$ nanotubes, in which the circumference of this nanotube type is comprised of a polyacene-like belt of six benzene-like tiles, is predicted by Zhao et al. to spontaneously collapse with extreme pressure in to the parent member of the C-based hexagonite family of lattices. This prediction is supported by an independent theoretical analysis of crystallographic data obtained in a synchrotron-nanotube experiment conducted in a diamond anvil cell in 2005 by Wang et al. Such nanotube-hexagonite phase transformations of C, are termed here as “hexagon-preserving-carbon-allotrope-transformations”, as the hexagonal C rings are preserved in the C phase transformations. By analogy, the classical phase transformation of C-based graphene to C-based diamond is described as a “hexagon-preserving-carbon-allotrope-transformation”. The details of these descriptive labels are discussed in this communication.

Keywords Crystallography · Carbon allotropy · Chemical topology · C nanotubes · High pressure · Synthesis

In 2011 Zhao et al. predicted a series of what were termed “three-dimensional nanotube polymers” using a novel so-called “particle swarm methodology” [1]. The theoretical group thus simulated the high pressure properties of groupings of various $(n, 0)$ and

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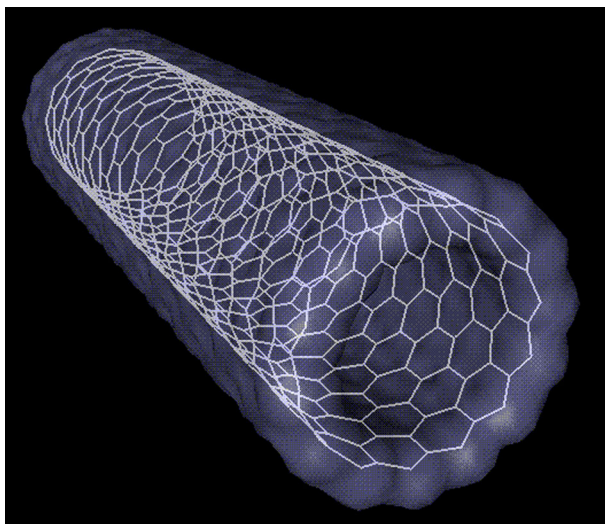


Fig. 1 A “zigzag” nanotube cylinder identified by the standard notation $(n, 0)$ where in the illustration “ n ” equals 15

(n, n) nanotubes [2], in which they discovered the spontaneous formation, at pressure, of several novel crystalline allotropes of carbon, from collapse of the corresponding nanotubes [3]. Of particular interest in the present communication is their prediction of the formation of the so-called hexagonite crystalline C allotrope and several of its expanded derivatives, [4–6] from the pressure-induced collapse of groupings of various members of the $(n, 0)$ nanotube family [3]. As each member of the $(n, 0)$ family of carbon nanotubes is comprised of all 3-connected carbon cylinders with a circumference defined by the fusing together of “ n ” benzene-like tiles, in a polyacene-like belt [2], it becomes apparent that carbon hexagons present in the component $(n, 0)$ nanotubes are preserved in the simulated high pressure phase change into the corresponding hexagonite lattices. See Fig. 1 for illustration of representative $(15, 0)$ nanotube.

In a strict structural analogy, the high pressure C phase transformation of graphite to diamond, [7, 8] involves the preservation of C hexagons in going from a 2-dimensional, all 3-connected, van der Waals layering with a Wells point symbol of 6^3 and Schläfli symbol of $(6, 3)$ [9, 10], to the densest possible sphere packing of tetrahedral C atoms as the 3-dimensional, all 4-connected, diamond lattice with a Wells point symbol of 6^6 and Schläfli symbol of $(6, 4)$ [9, 10]. The density change in such a hexagon preserving transformation of C is dramatic, as the starting graphite layered material, at a density of 2.27 g/cm^3 (see Fig. 2), collapses under extreme pressure into the corresponding 3-dimensional diamond network at a density of 3.56 g/cm^3 (see Fig. 3) [7, 8]. Thereby in comparison, the predicted transformation of $(6, 0)$ C nanotubes, with a topology of approximately 6^3 (see Fig. 1) to the corresponding hexagonite lattice with a topology of $(6^6)_2(6^3)_3$ [9, 10], as shown in Fig. 4, also involves the preservation of C hexagons in going from a van der Waals cylinder packing of $(6, 0)$ C nanotubes, that then collapses

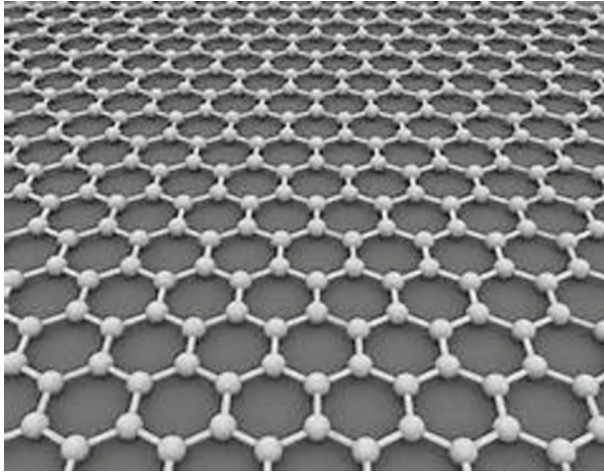
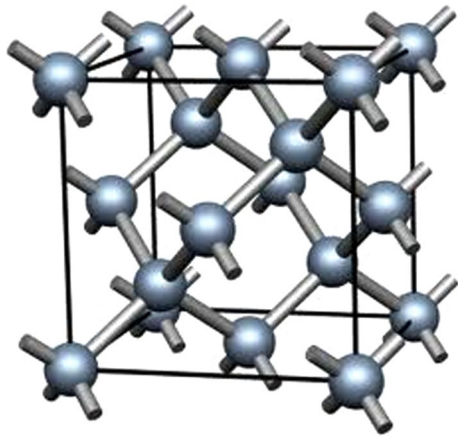


Fig. 2 The graphene plane lattice with Wells point symbol 6^3 and Schlaefli symbol (6, 3)

Fig. 3 Cubic diamond (3C) polytype with the Wells point symbol 6^6 and the Schlaefli symbol (6, 4)



into the densest possible 3-,4-connected C cylinder packing as the hexagonite lattice (see Fig. 4).

Hexagonite and its expanded derivative structural relatives, identified as “the hexagonites” in the discussion above, as well as the other discrete C allotropes including the fullerenes, nanotubes, graphene and diamond each can be characterized in a topological sense by the methodology described here [9, 10]. Thus these C patterns, as described herein, can be classified and mapped according to a chemical topology scheme introduced by the crystallographer Wells [9], and later extended by us [10]. This chemical topology scheme is based upon identifying the so-called Wells point symbol for a given structural-type, where the Wells point symbol in a generic binary stoichiometry network is given by $(A^a)_x(B^b)_y$. In this notation, the bases represent the circuitry within the structure as being in “A-gon” and “B-gon” polygonal circuits, the superscripts represent the respective connectivities of the vertices in the structure

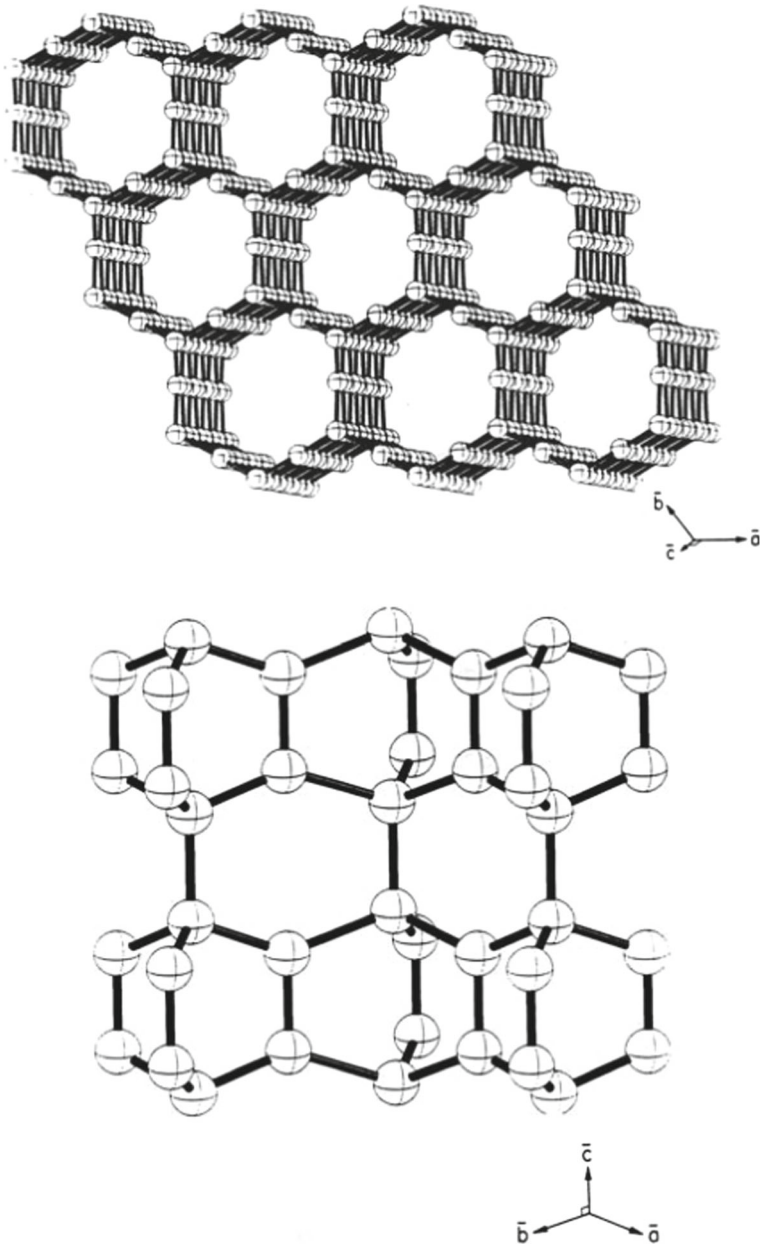


Fig. 4 Vertical and lateral views of the C-based parent “hexagonite” lattice with Wells point symbol $(6^6)_2(6^3)_3$

as “a-connected” and “b-connected”, and finally the subscripts identify the stoichiometry of the structure in terms of “x” structural components of topology “A^a”, in a ratio with “y” structural components of topology “B^b”, within the respective unit of

pattern. From analysis of this notation one can determine a weighted average polygon size in the structure, identified as “ n ” in Equation (1) below, and a weighted average connectivity in the structure, identified as “ p ” in Eq. (2).

$$n = (a \cdot A \cdot x + b \cdot B \cdot y) / (a \cdot x + b \cdot y) \quad (1)$$

$$p = (a \cdot x + b \cdot y) / (x + y) \quad (2)$$

These parameters called the polygonality “ n ” and the connectivity “ p ” are characteristic of each and every one of the polyhedra, tessellations and networks, and once identified they can be used to heuristically map the various structures in a construction briefly described here. Thus the polyhedra are characterized by a simple mathematical formula due to Euler [9, 10], shown as Equation (3) below, that forms the basis for this heuristic mapping construction. In Eq. (3) the number of vertices in the polyhedron is identified as “ V ”, and the number of edges is identified as “ E ”, and the number of faces in the polyhedron is identified as “ F ”:

$$V - E + F = 2 \quad (3)$$

And so for the various polyhedra, one can thus transform Eq. (3) into Eq. (4) shown below, by employing the alternative, though rigorous and equivalent, set of definitions of “ n ” and “ p ” for the polyhedra; given as the polygonality $n = 2E/F$, and the connectivity $p = 2E/V$ [9, 10].

$$\frac{1}{n} - \frac{1}{2} + \frac{1}{p} = \frac{1}{E} \quad (4)$$

It is thus Eq. (4), together with the analogous definitions of the weighted average polygonality “ n ”, and the weighted average connectivity “ p ”, in Eqs. (1) and (2) that can be used heuristically to create a topology mapping of all structures, as shown below in Table 1 [9, 10]. For reference, note in Table 1 that “ t ” is the tetrahedron, and “ o ” is the octahedron, and “ i ” is the icosahedron, and “ c ” is the cube, and “ d ” is the dodecahedron [6]. Note also, for reference as discussed above, in this topology map the entry (6, 3) corresponds to the graphene sheet, and the entry (6, 4) corresponds to the diamond polytypes. The Platonic polyhedra thus anchor this heuristic construction and provide the basis for the structural organization of matter.

As hexagonite is a 3-,4-connected network, it contains an admixture of 3-connected and 4-connected vertices in the unit cell. The overall connectivity of the lattice, p , is taken as a weighted average of the 3- and 4-connected points as obtained from the stoichiometry of the network. It is thus given by the decimal, or fractional, number $p = 3.4$., as identified above. While the other key topological parameter in this analysis, called the polygonality, is indeed identified as simply the integer $n = 6$, as inspection of Fig. 4 will reveal, as discussed above. One can thus represent the topology of hexagonite by the Wells point symbol $(6^6)_2(6^3)_3$ and this, then, has the corresponding Schläfli symbol $(n, p) = (6, 3.4)$, as described earlier. It is a Catalan C-network, that can be expanded infinitely by insertion of 1,4-dimethylene-2,5-cyclohexadieneoid organic

Table 1 Chemical topology mapping of the structure of matter according to coordinate pairs (n, p) identified for each pattern

p	3	4	5	6	7	8	...
n							
3	†	o	i	(3,6)	(3,7)	(3,8)	
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)	
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)	
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)	
7	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)	
8	(8,3)	(8,4)	(8,5)	(8,6)	(8,7)	(8,8)	
:							
:							
:							

spacers between the barrelene moieties that make up the parent hexagonite lattice. This has been described already by Karfunkel et al. in their 1992 paper [4–6].

It is interesting here to see that hexagonite, and the expanded hexagonites, are represented by the collective Schläfli symbol given by $(n, p) = (6, 3^{x/x+y})$, where “x” represents the number of 4-connected points in the unit of pattern, and “x + y” represents the sum of the numbers of 3- and 4-connected points in the unit of pattern, which will increase in increments, as the 1,4-dimethylene-2,5-cyclohexadieneoid organic spacers are added to the unit of pattern in the expanded hexagonites. Thus one sees that the C-based hexagonites will possess discrete connectivities, p, that range from 3.0 (in the graphene limit) to 3.4 (in the hexagonite limit). Hexagonite, and its expanded derivatives, therefore represent a related family of Catalan 3D C-based networks that provide an interesting contrast to the Archimedean family of C-based fullerenes [6]. In contrast to the Catalan hexagonites, the fullerenes collectively have the Schläfli index $(n, p) = (5^{x/x+y}, 3)$, where “x” is the number of hexagons in the polyhedron, and “x + y” is the sum of the numbers of pentagons and hexagons in the polyhedron [6]. The Schläfli relation, shown as Eq. (4) above, applies to all of the innumerable polyhedra, including the many fullerenes described by the Schläfli notation in this discussion. Note that the parameter “E” in Eq. (4) refers to the number of edges in the respective polyhedra with Schläfli symbol (n, p). The number of edges “E” is thus related to the number of vertices, “V”, and the number of faces, “F”, by the Euler identity, given in Eq. (3).

One could thus picture the corresponding (n, 0) nanotube powder, packed into the open gasket of a diamond anvil cell (DAC), at an ambient density of about 1.75 g/cm^3 . If one then supposes that the individual nanotubes, in the disordered powder, spontaneously become ordered with the onset of extreme pressure, and become aligned with their cylinder axes normal to the pressure axis of the DAC, they then would form a van der Waals cylinder packing of nanotubes structurally comprised of component C hexagons. Pressure could then be further applied to the organized powder, and the (n, 0) nanotube assembly of individual, parallel C cylinders would then eventually make physical contact with each other, and this would then comprise a closest cylinder packing of nanotubes, but not the densest possible cylinder packing of C.

Evidently, at a pressure of about 1 Mbar [3], the densest possible (6, 0) nanotube cylinder packing of component C hexagons, collapses into the densest possible hexagon-preserving C cylinder packing, as the hexagonite lattice is created in the form of nanocrystals with a crystalline density of approximately 2.45 g/cm^3 , see Fig. 4 [6]. Therefore, the pressure-induced phase transformation of powdered (6, 0) nanotubes to nanocrystalline hexagonite, in one particular instance of the predictions of Zhao et al. of the synthesis of the C-based hexagonites [1], is supported by the corresponding theoretical analysis of Bucknum et al. [6]. This structural phase transformation of 1-dimensional C nanotubes, to the corresponding 3-dimensional hexagonite C lattices, in each and every case described by Zhao et al for the various (n, 0) nanotubes, preserves the C hexagons through the transformation to the denser 3-dimensional lattice structure. Such structural C phase transformations are identified here as “hexagon-preserving-C-allotrope-phase-transformations” and it can be observed, as described above, that such structural transformations are entirely analogous to the transformation of graphite into diamond [7,8], as C hexagons in this classical pressure-induced structural phase transformation, are preserved in each respective end-member, in the course of the transition to the denser structure of diamond.

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