

## The Carbon Allotrope Hexagonite and Its Potential Synthesis from Cold Compression of Carbon Nanotubes

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**Abstract:** In a previous report, the approximate crystalline structure and electronic structure of a novel, hypothetical hexagonal carbon allotrope has been disclosed. Employing the approximate extended Hückel method, this C structure was determined to be a semiconducting structure. In contrast, a state-of-the-art density functional theory (DFT) optimization reveals the hexagonal structure to be metallic in band profile. It is built upon a bicyclo[2.2.2]-2,5,7-octatriene (barrelene) generating fragment molecule and is a Catalan network, with the Wells point symbol  $(6^6)_2(6^3)_3$  and the corresponding Schläfli symbol (6, 3.4). As the network is entirely composed of hexagons and, in addition, possesses hexagonal symmetry, lying in space group  $P6/mmm$  (space group #191), it has been given the name hexagonite. The present report describes a density functional theory (DFT) optimization of the lattice parameters of the parent hexagonite structure, with the result giving the optimized lattice parameters of  $a = 0.477$  nm and  $c = 0.412$  nm. A calculation is then reported of a simple diffraction pattern of hexagonite from these optimized lattice parameters, with Bragg spacings enumerated for the lattice out to fourth order. Results of a synchrotron diffraction study of carbon nanotubes which underwent cold compression in a diamond anvil cell (DAC) to 100 GPa, in which the carbon nanotubes have evidently collapsed into a hitherto unknown hexagonal C polymorph, are then compared to the calculated diffraction pattern for the DFT optimized hexagonite structure. It is seen that a close fit is obtained to the experimental data, with a standard deviation over the 5 matched reflections being given by  $\sigma_x = 0.003107$  nm/reflection.

### 1. Introduction

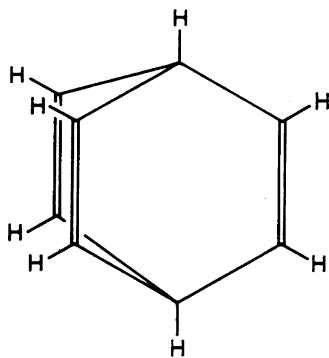
As a potential allotropic structure of C, the crystalline and electronic structure of the so-called, 3-dimensional (3D) hexagonite lattice<sup>1</sup> and some of its expanded 3D derivatives were first reported by Karfunkel et al. in 1992.<sup>2</sup> The description of the parent structure of hexagonite in their report<sup>2</sup> was substantially refined and clarified later on by Bucknum et al. in a preprint published in 2001, where an identification of the space group symmetry ( $P6/mmm$ , space group #191) and a complete set of crystallographic coordinates for the hexagonite unit cell were given.<sup>3</sup> Such a 3-dimensional (3D) hexagonite structure can be expanded into an indefinitely large number of derivative 3D structures,

by the insertion of 1,4-dimethylene-2,5-cyclohexadieneoid organic spacers into the parent hexagonite structure.<sup>2–3</sup> Expanded hexagonites include 3D crystalline materials with arbitrarily large pores directed along the crystallographic  $c$ -axis; they occur in infinite families possessing orthorhombic ( $Pmmm$ ), trigonal ( $P3m1$ ), and hexagonal ( $P6/mmm$ ) space group symmetries.<sup>2–3</sup>

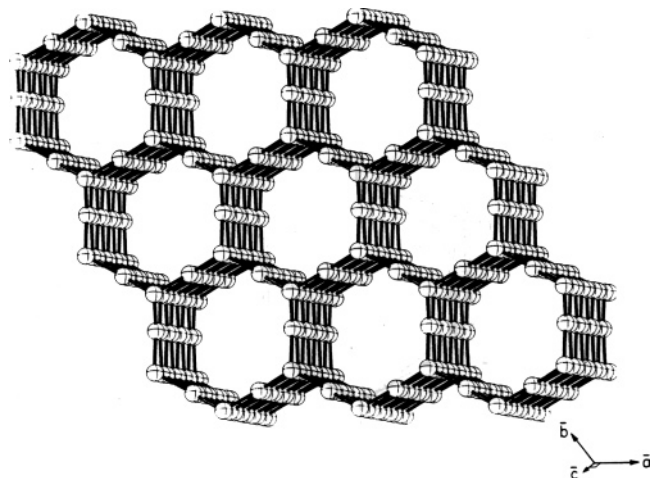
It was reported in this paper,<sup>3</sup> that hexagonite could be realized from the elaboration of a bicyclo[2.2.2]-2,5,7-octatriene (barrelene) generating fragment molecule<sup>4–6</sup> in 3D, as is shown in Figure 1.

Thus the full elaboration of the 3D hexagonite network, from the barrelene generating fragment, can be seen in Figure 2 from a perspective normal to the  $ab$ -plane of the lattice.

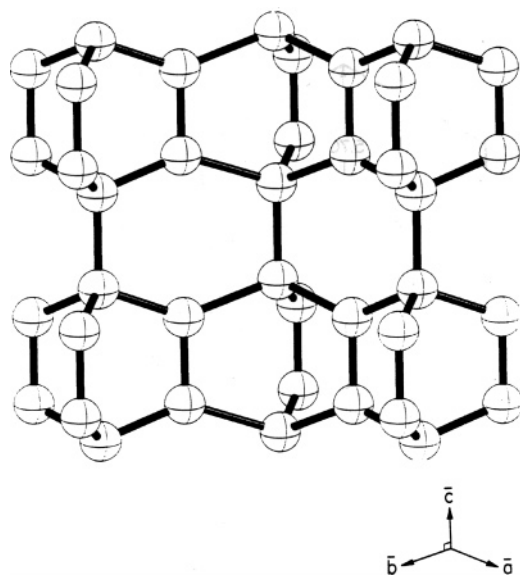
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**Figure 1.** Structure of bicyclo[2.2.2]-2,5,7-octatriene.



**Figure 2.** Extended drawing of the hexagonite lattice, viewed approximately normal to the  $ab$ -plane of the lattice.



**Figure 3.** View of the hexagonite lattice from the perspective of the crystallographic  $ab$ -plane.

Yet another perspective of this hexagonite lattice is shown in Figure 3, where there is a view of it parallel to the  $ab$ -plane.<sup>3</sup>

One can see in these various views of the hexagonite lattice, given in Figures 2 and 3, the omnipresence of 6-ness in the structure. The organic tunnels apparent in Figure 2 are indeed hexagonal macrocyclic tunnels which are further

**Table 1.** Fractional Hexagonal Crystallographic Coordinates of Hexagonite from the Original Report<sup>3</sup>

atom no.	$x/a$	$y/b$	$z/c$	$a$ (Å)	$c$ (Å)
1	2/3	1/3	0.1935	4.89	3.88
2	2/3	1/3	0.8065	4.89	3.88
3	1/3	2/3	0.1935	4.89	3.88
4	1/3	2/3	0.8065	4.89	3.88
5	1/2	1/2	0.3265	4.89	3.88
6	1/2	1/2	0.6735	4.89	3.88
7	1/12	2/3	0.3265	4.89	3.88
8	1/12	2/3	0.6735	4.89	3.88
9	5/12	5/6	0.3265	4.89	3.88
10	5/12	5/6	0.6735	4.89	3.88

built upon component hexagons. Thus in Figure 3, which is in the crystallographic  $ab$ -plane, we see illustrated the hexagon nature of these rings that are components of the larger rings directed along the  $c$ -axis and apparent in the view of Figure 2.

In the 2001 report by Bucknum et al. on hexagonite's structure,<sup>3</sup> the C—C single bonds were assumed to be 0.1500 nm, and the C=C double bonds were assumed to be 0.1350 nm, and all bond angles were assumed to be tetrahedral at 109.5°, except the trigonal C—C—C angles lying along the  $c$ -axis, which were constrained to 141°. This resulted in a crudely defined unit cell, with the lattice parameters given by  $a = b = 0.4890$  nm and  $c = 0.3880$  nm, and the set of fractional hexagonal coordinates, as listed in Table 1.

Some of the topological character of the hexagonite lattice has been described previously.<sup>3</sup> An introduction to the topological characterization of crystalline networks is given by us elsewhere.<sup>7</sup> From a perspective entirely normal to the  $ab$ -plane, as shown in Figure 2, the lattice reveals itself in this aspect to be reminiscent of the familiar hexagonal tiling of the plane, represented by the Schläfli symbol (6, 3) (or the Wells point symbol 6<sup>3</sup>) called the honeycomb tessellation. Remarkably, a view perpendicular to the  $c$ -axis, inclined by 30° from the  $a$ -axis of the unit cell, reveals yet a second perspective from which a perfect honeycomb tessellation emerges from the pattern of bonds within the hexagonite lattice. There are thus 2 views of this hexagonite pattern that reveal its high hexagonal symmetry, in space group  $P6/mmm$ , as manifested in 2 independent honeycomb motifs that are patterned in directions entirely perpendicular to each other from the perspective of the unit cell.

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,<sup>7</sup> a weighted average of the 3- and 4-connected points taken from the stoichiometry of the network, is given by  $p = 3^{2/5}$ . While the other key topological parameter, called the polygonality,<sup>7</sup> is indeed simply  $n = 6$ , as inspection of Figure 2 and 3 will reveal. One can thus represent the topology of hexagonite by the Wells point symbol (6<sup>6</sup>)<sub>2</sub>(6<sup>3</sup>)<sub>3</sub>, and this, then, has the corresponding Schläfli symbol  $(n, p) = (6, 3.4)$ .<sup>7</sup> It is a Catalan C-network that can be expanded infinitely by insertion of 1,4-dimethylene-2,5-cyclohexadieneoid organic spacers between, and within, the barrelene moieties that make

up the parent hexagonite lattice. This has been described already by Karfunkel et al. in their 1992 paper.<sup>2-3</sup>

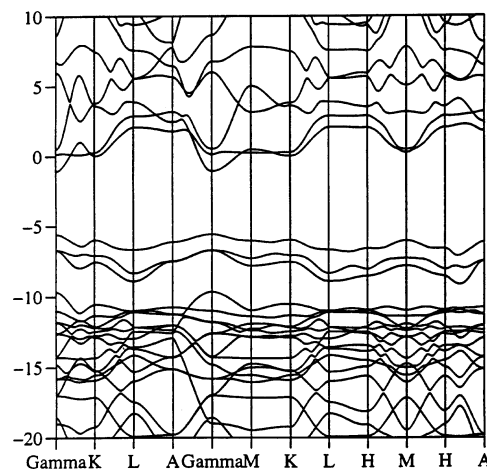
It is interesting here, in this regard, to see that hexagonite and the expanded hexagonites are represented by the collective Schläfli symbol given by  $(n, p) = (6, 3^{x/x+y})$ , where “ $x$ ” represents the number of 4-connected points in the unit of pattern (which will always be 4) and “ $x + y$ ” 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 cell in the expanded hexagonites). Hexagonite and its expanded realizations, therefore, represent a related family of Catalan 3D C-based networks that provide an interesting contrast to the Archimedean family of C-based fullerenes.<sup>8</sup> 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 number of pentagons and hexagons in the polyhedron. It should be noted in this context that a Schläfli relation exists for the polyhedra, shown as eq 1 below, that is entirely rigorous for the innumerable fullereneic structures which collectively possess the Schläfli index  $(n, p) = (5^{x/x+y}, 3)$ . In eq 1, the parameter  $E$  is the number of edges in the fullereneic polyhedron (or polyhedron),  $n$  is the weighted average polygon size over the polygons in the polyhedron (for fullereneic structures it will always be an admixture of pentagons and hexagons) and  $p$  is the weighted average connectivity over the vertices in the polyhedron (for fullereneic structures, this will always be 3). The number of edges  $E$  is related to the number of vertices,  $V$ , and the number of faces,  $F$ , by the Euler identity,<sup>7</sup> given as  $V - E + F = 2$ .

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

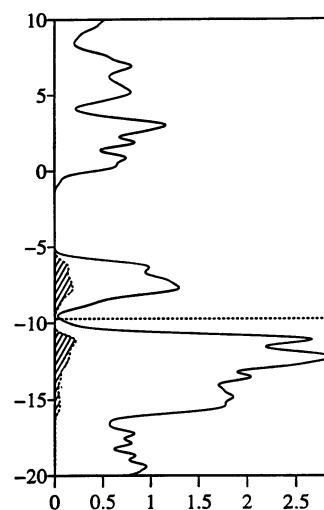
In section 2 that follows, we report on the electronic structural characteristics of the C-based hexagonite structure from the point of view of the extended Hückel molecular orbital method (EHMO), which is an approximate solid-state electronic structure algorithm based upon the tight binding methodology.<sup>9-12</sup> Next, in section 3, we report on the details of a density functional theory (DFT) geometry optimization of the parent hexagonite structure and provide a calculation of a simple diffraction pattern of hexagonite,<sup>13</sup> out to fourth order in Bragg spacings of the crystalline structure. We then compare this theoretically calculated data to experimental data, reported in 2004, for a hexagonal polymorph of carbon produced by cold compression of C nanotubes to 100 GPa pressure in a diamond anvil cell (DAC) by Wang et al.<sup>14</sup>

## 2. Electronic Structure of Hexagonite

Using the approximate electronic structure algorithm called the extended Hückel method (EHMO),<sup>9-12</sup> a calculation of the approximate band structure and density of states (DOS) of hexagonite, as an allotrope of C, were carried out.<sup>3</sup> Figure 4 shows a representation of the approximate band structure of the C-based hexagonite. Figure 5 shows the corresponding density of states (DOS); this is derived from the band structure shown in Figure 4.



**Figure 4.** Electronic band structure of the hexagonite crystal structure.



**Figure 5.** Density of states (DOS) of the hexagonite crystal structure.

Thus Figures 4 and 5 indicate that the hexagonite structure should be a C-based semiconductor,<sup>3</sup> in this approximation, where 3 unoccupied  $\pi^*$  bands are relatively low lying and separated from the  $\sigma^*$  manifold by several eV of energy.<sup>3,15</sup> One could therefore envision the doping of the pores of hexagonite with univalent alkali metals, divalent alkaline earth metals, or trivalent rare earth metals to form conducting or indeed, with the corresponding stoichiometry, insulating metal-organic composite structures, in which the metals readily ionize in the parent C-lattice and donate their valence shell electrons to the higher-lying, unoccupied  $\pi^*$  bands of the host hexagonite lattice.<sup>3</sup> The electronic features of such doped hexagonites and their potential applications in high technology remain an unexplored vista of both theory and, potentially some day, experiment.<sup>16-18</sup>

## 3. DFT Optimization of Hexagonite Structure

The C-based hexagonite structure, as described in previously in section 1, has been optimized with the DFT algorithm named CASTEP, and the details of the optimization calculations are reported herein.<sup>19</sup> The CASTEP code has been adequately described elsewhere.<sup>20</sup> The results indicate a much different optimized geometry for hexagonite than was

**Table 2.** CASTEP Optimized Fractional Hexagonal Crystallographic Coordinates and Lattice Parameters of Hexagonite

atom no.	$x/a$	$y/b$	$z/c$	$a$ (Å)	$c$ (Å)
1	2/3	1/3	0.1840	4.772	4.129
2	2/3	1/3	0.8160	4.772	4.129
3	1/3	2/3	0.1840	4.772	4.129
4	1/3	2/3	0.8160	4.772	4.129
5	1/2	1/2	0.3400	4.772	4.129
6	1/2	1/2	0.6600	4.772	4.129
7	0	1/2	0.3400	4.772	4.129
8	0	1/2	0.6600	4.772	4.129
9	1/2	0	0.3400	4.772	4.129
10	1/2	0	0.6600	4.772	4.129

assumed to pertain in the initial report by Bucknum et al. of the structure.<sup>3</sup> The C–C single bonds in the structure are found to be fairly closely related to each other with a uniform length of about 0.1521 nm. The C=C double bonds in hexagonite are 0.1326 nm in length. The C=C–C trigonal angles are about 115°, while the C–C–C trigonal angles are 130°, and the tetrahedral angles within the cage of the barrelene substructures are 103°, while outside this cage the tetrahedral angles are 115°. Finally, and most importantly, the lattice parameters optimized for the hexagonite structure by CASTEP are given as  $a = 0.4772$  nm and  $c = 0.4129$  nm. Therefore, the optimized coordinates of the 10 C atoms in the hexagonite unit cell are given in Table 2. The density<sup>21</sup> of hexagonite is calculated to be 2.449 g/cm<sup>3</sup>; it lies between the density of the 3-connected carbon form, graphite, at 2.27 g/cm<sup>3</sup>, and the density of the 4-connected carbon form, diamond, at 3.56 g/cm<sup>3</sup>, but is closer to graphite's density than to diamond's density.

From the CASTEP optimized lattice parameters we can calculate a simple diffraction pattern for the C-based hexagonite structure,<sup>13</sup> and such a powder pattern is shown with Bragg spacings enumerated out to fourth order for the lattice in Table 3. For comparison in Table 3, we report a set of 5 Bragg reflections recorded from a sample of C nanotubes which have been cold compressed in a diamond anvil cell and have transformed into what is believed to be a novel hexagonal polymorph of C, which nonetheless possesses an unknown structure.<sup>14</sup> This latter C polymorph is able to be quenched at room pressure, as well. The Bragg spacings in this cold-compressed sample of C nanotubes were monitored using the specialized technique of energy-dispersive-X-ray-diffraction (EDXRD) on a specially constructed high-pressure DAC synchrotron beamline at the Cornell High Energy Synchrotron Source (CHESS) in Ithaca, NY.<sup>14</sup>

One can see in Table 3 that the 5 reflections in the EDXRD data set of the C nanotube sample, as cold-compressed in the DAC to over 100 GPa, readily match the set of Bragg spacings calculated theoretically from the optimized set of lattice parameters provided for the hexagonite lattice from the CASTEP algorithm.<sup>19,20</sup> The average deviation over the 5 reflections in the experimental data set matched to the calculated Bragg spacings of the optimized hexagonite structure is given by  $\Delta x = 0.003040$  nm/reflection, while the standard deviation over the 5 matched reflections in the

**Table 3.** Observed Diffraction Data of Proposed Hexagonal C Polymorph Compared to Calculated Hexagonite Pattern from CASTEP Optimization

calculated hexagonite reflections $a = 0.4772$ nm, $c = 0.4129$ nm		C polymorph reflections <sup>a</sup>	absolute deviation per reflection <sup>b</sup>
(hkl)	$d$ -spacing, nm	$d$ spacing, nm	$\Delta d$ -spacing, nm
100	0.4133		
001	0.4129		
110	0.2386		
101	0.2921		
111	0.2066	0.2155	0.0089
200	0.2066	0.2155	0.0089
002	0.2065	0.2053	0.0012
102	0.1847		
120	0.1562		
201	0.1848		
211	0.1461	0.1495	0.0034
221	0.1146	0.1161	0.0015
212	0.1246	0.1248	0.0002
222	0.1033		
300	0.1378		
003	0.1376		
103	0.1306		
130	0.1146	0.1161	0.0015
301	0.1307		
311	0.1104		
331	0.07810		
313	0.08808		
333	0.06886		
203	0.1146	0.1161	0.0015
302	0.1146	0.1161	0.0015
320	0.09481		
223	0.09015		
232	0.08616		
332	0.07422		
323	0.07808		
321	0.09241		
312	0.1002		
213	0.1033		
104	0.1002		
401	0.1002		

<sup>a</sup> Wang, Z.; Zhao, Y.; Tait, K.; Liao, X.; Schiferl, D.; Zha, C.; Downs, R. T.; Qian, J.; Zhu, Y.; Shen, T. *Proc. Natl. Acad. Sci. (PNAS)* **2004**, *101* (38), 13699–13702. <sup>b</sup> Average deviation over the 5 reflections compared is 0.003040 nm/reflection.

experimental data set is given by  $\sigma_x = 0.003107$  nm/reflection. Clearly all the data, over the 5 matched reflections in the experimental data set, have deviations that fit to within less than  $3\sigma_x = 0.009321$  nm of the standard deviation of the data set, as is reflected in Table 3. In a parallel comparison of the experimental data set given here of the hexagonal C polymorph, with the commonly observed Bragg reflections from cubic diamond, it is important to point out that only the cubic diamond reflections (111), with a Bragg spacing of 0.2060 nm, and (220), with a Bragg spacing of 0.1261 nm, matched to the experimental set of reflections for the hexagonal C polymorph.<sup>22</sup>

A caution should be made here with regard to the size of the data set, with only 5 reflections to fit; clearly the model proposed here of the hexagonite lattice as an explanation of the experimentally derived EDXRD synchrotron data set for



a proposed hexagonal polymorph of C is not constrained as much by observation as one would like it to be. With only 5 observations to work with, such a fit between experimental and theoretical diffraction data is little more than an educated guess.

Still, the authors of the report<sup>14</sup> state that their fit to the data can be interpreted (from the reflections that they have indexed to the data set of 5 Bragg spacings from a hexagonal model with lattice parameters  $a = 0.249$  nm and  $c = 0.412$  nm) from rules of systematic absences among the hexagonal space groups to a structure that lies in the hexagonal space group  $P6m2$  (#190).<sup>14</sup> We offer here in response to this point that the hexagonite lattice lies in the very closely related hexagonal symmetry space group  $P6/mmm$  (#191). It would therefore appear that the 2 sets of data, while only consisting of 5 matches, are closely connected together by considerations of the potential symmetry of the unknown C phase. These considerations thus include such a proposed model as the hexagonite lattice.

#### 4. Discussion of Densities of Carbon Phases

One area of disagreement in the current comparison of theoretical and experimental data is in the density reported by Wang et al.<sup>14,21</sup> in their compression study of the C nanotubes and that reported for the candidate hexagonite structure from first principles theory. Experimentally, the density<sup>14</sup> of the hexagonal C polymorph of an unknown structure is given as  $3.6 \pm 0.2$  g/cm<sup>3</sup>; while the theoretically calculated value for the density of hexagonite<sup>21</sup> is some 32% lower than this experimental value, at 2.449 g/cm<sup>3</sup>, it is thus important here to note that the density of the starting nanotube powder material in this compression synthesis can be estimated to be lower than the known density of fullerite at 1.75 g/cm<sup>3</sup>.

Wang et al. proposed that the C material of unknown structure should have a density in excess of the density of diamond, at 3.56 g/cm<sup>3</sup>, based upon thermodynamic arguments. They reasoned that a polymorph of C would have collapsed to a denser structure than diamond given the high pressures involved in the study to well over 100 GPa.<sup>14</sup> It is believed by the authors of the present study, however, that the inhomogeneous nature of the C material produced in the synchrotron study,<sup>14</sup> in which amorphous C was present in the quenched DAC sample, along with the novel crystalline phase, suggests that possibly kinetically stabilized products, such as the low-density C material hexagonite,<sup>21,23</sup> may have been formed. The current study does not rule out such a kinetically favored crystalline C product from forming at such high pressures exceeding 100 GPa.<sup>23</sup> Indeed it is physically reasonable to expect that the starting nanotube powder material, at a density of less than that of fullerite at 1.75 g/cm<sup>3</sup>, could quite possibly have collapsed to the hexagonite lattice at a density of 2.449 g/cm<sup>3</sup>, in their study, if such a lattice was thermodynamically a stable phase up to 100 GPa, otherwise.

It was reported in their study<sup>14</sup> that the hexagonal C polymorph produced under pressure partially indented the diamond anvils in the high-pressure cell used. It was conjectured by Wang et al. that the hexagonal, crystalline C

phase, which was quenched from high pressure, was a superhard phase of C. They estimated a bulk modulus of at least 447 GPa for the C form in the study. In this instance, it is worth pointing out that a semiempirical estimate<sup>24,25</sup> of the bulk modulus of hexagonite, despite its low density of 2.449 g/cm<sup>3</sup>, puts it at a value of  $B_0 = 445$  GPa. This comes from a semiempirical formula for bulk modulus in materials, developed by Cohen et al.,<sup>24,25</sup> and is

$$B_0 = \frac{1972 - 220I \langle N_c \rangle}{\langle d \rangle^{3.5} 4} \quad (2)$$

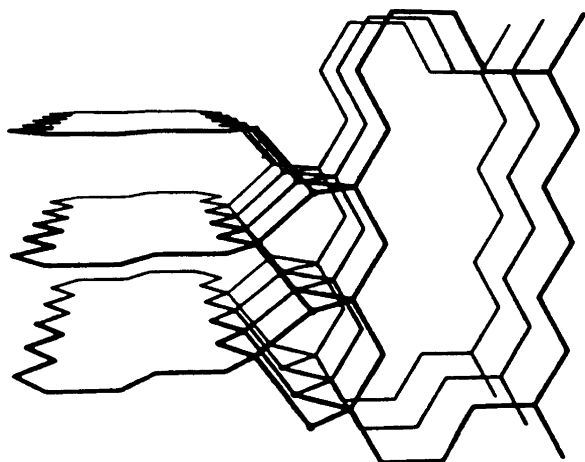
Here in formula 2, the parameter  $I$  represents the degree of ionicity of the bonding in the unit cell of a given material. For the C form of hexagonite this parameter is just 0, because the hexagonite structure is assumed to be a C polymorph in this instance. The parameter  $N_c$  is the averaged coordination number in the unit cell; this is just the connectivity in the lattice,  $p$ , which has a value of 3.4 for hexagonite, as was discussed above. Finally, the parameter  $d$  is the weighted average bond distance in the unit cell. The C–C single bonds have a length of 0.1521 nm, while the C=C double bonds are 0.1326 nm in length, in the CASTEP hexagonite optimization. They average out to a distance of about 0.1460 nm over the unit cell. These unit cell parameters thus lead to a semiempirical estimation of  $B_0$  for hexagonite that is listed above. One can see that the bulk moduli from experiment and from theory are in good agreement with each other.

#### 5. Conclusions

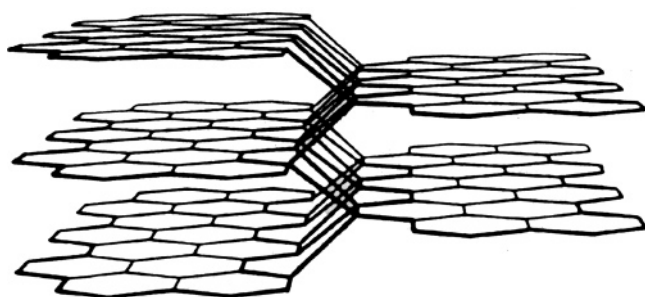
In this communication, a geometry optimization of the novel, hypothetical form of C called hexagonite<sup>2,3</sup> has been performed using a state-of-the-art DFT-based program called CASTEP.<sup>20</sup> The lattice parameters for the hexagonal unit cell are given as  $a = 0.4772$  nm and  $c = 0.4129$  nm. The density of the C polymorph has been optimized to be 2.449 g/cm<sup>3</sup>. The coordinates for the 10 C atoms in the hexagonite unit cell are thus listed in Tables 1 and 2.<sup>3</sup>

From the optimized lattice parameters of hexagonite, a simple diffraction pattern has been calculated<sup>13</sup> of the Bragg spacings in the crystalline material out to fourth order. From this optimized diffraction pattern, a comparison has been carried out over a set of 5 Bragg reflections obtained from an experimental study in which C nanotubes have been cold compressed in a diamond anvil cell (DAC), on a specially designed high-pressure beam line.<sup>14</sup> Comparison of the 2 data sets yields a close fit over the 5 experimentally determined X-ray reflections, with an average deviation given by  $\Delta x = 0.003040$  nm/reflection and a standard deviation of  $\sigma_x = 0.003107$  nm/reflection. It therefore appears possible that the cold compressed nanotubes in the high pressure study have collapsed under compressive forces into the hexagonite structure, which was first proposed as a likely structure for C to adopt by Karfunkel et al.<sup>2</sup> in 1992 and Bucknum et al.<sup>3</sup> in 2001.

It should be emphasized here that the parent structure, called hexagonite, that represents the first member of a possibly infinite family of related Catalan C polymorphs has



**Figure 6.** Structure of a variety of the “ortho-” graphite-diamond hybrids.



**Figure 7.** Structure of a variety of the “para-” graphite-diamond hybrids.

possibly been synthesized in the experimental study cited here by Wang et al.<sup>14</sup> This infinite family of 3D network C structures, that are collectively described as Catalan networks, represent an interesting contrast to the infinity of Archimedean fullerene structures first identified in 1985 by Kroto et al.<sup>26</sup> Collectively, the hexagonites and the fullerenes, being semiregular structures, can be contrasted, on one hand, with the graphite and diamond polytypes, which are regular (Platonic) structures of C, given by the Wells point symbols  $6^3$  and  $6^6$ , respectively.<sup>7</sup> Speculatively, on the other hand, these semiregular structures can be contrasted, as well, with the Wellsean (or topologically irregular) tetragonal glitter network, which has been previously optimized and shown to have a stability close to that of hexagonite<sup>22,23</sup> and with the Wells point symbol given by<sup>27,28</sup>  $(6^28^4)(6^28)_2$  and other such irregular networks enumerated by Merz et al.,<sup>29</sup> A. F. Wells,<sup>30,31</sup> and others<sup>27–29</sup> and the references therein. And finally, of course, the hexagonites can be speculatively compared directly to the infinite family of graphite-diamond hybrids proposed in 1993 by Balaban et al.<sup>32</sup> which share the same Catalan Wells point symbol given by  $(n, p) = (6, 3^{x/x+y})$ , as described above. A couple of varieties of the graphite-diamond hybrids are shown in Figures 6 and 7.<sup>32</sup> It is important to note that the graphite-diamond hybrids collectively circumscribe several infinities of potential C structures, all of which possess orthorhombic symmetry, and which, to date, have not been structurally optimized in any of their various forms.

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## References

- (1) The C structure described in this communication, and elsewhere, with the name hexagonite is not to be confused with the inorganic mineral structure of the same name. The authors felt it appropriate to name the C structure, described herein, as hexagonite because of the special circumstance of its hexagonal symmetry space group ( $P6/mmm$ , #191), combined with its further 6-ness, as distinguished by its topological polygonality, given by  $n = 6$ , in which all of the smallest circuits in the corresponding network are hexagons.
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- (15) The CASTEP-DFT method calculates the band structure of hexagonite to be metallic, in contrast to the result from the approximate EHMO method, which calculates the hexagonite structure to have a semiconducting band profile. It is believed by the authors of the present study that the EHMO calculations of semiconducting hexagonite are potentially closer to a true reflection of the electronic structure of this material than that provided by the DFT results, based upon the fact that hexagonite can be viewed as a layering of delocalized  $\pi$  bonding ( $sp^2$ ) sandwiched between insulating layers of C  $\sigma$  bonding ( $sp^3$ ) and thus cannot realistically be represented as a 3D metallic structure.
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- (19) CASTEP (Cambridge Serial Total Energy Package) is a plane wave pseudopotential code, based upon density functional theory (DFT), that was used to optimize the hexagonite structure in the present report. Therefore, for the present implementation of CASTEP, used to optimize the structural parameters of hexagonite, the local density approximation (LDA) was used, ultrasoft pseudopotentials were employed, the basis set had an energy cutoff of 400 eV, and k-point sampling was done with a  $10 \times 10 \times 4$  mesh. The ultrasoft pseudopotentials used in the calculation are due to Vanderbilt (Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B* **1990**, *41* (Rapid Communications), 7892–7895.) The Brillouin zone was sampled at a density of  $0.004 \text{ nm}^{-1}$ .
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