The carbon allotrope glitter as n-diamond and i-carbon nanocrystals

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In the carbon science literature, there have been various reports over the previous few decades of potentially novel crystalline forms of carbon emerging as kinetically stabilized, nanometer scale fragments recovered from the explosive remnants of heated, shock compressed graphite and other precursors of C by rapid cooling. Two nanometer-sized and crystalline forms of C that are particularly prominent in these studies are the so-called n-diamond and i-carbon forms. [1-8] Figure 1 below, thus shows a high resolution electron micrograph (HREM) of a representative nanocrystalline C droplet of n-diamond synthesized by such shock methods, where the indexation of the lattice image is to a diamond model. [1-8]

In previous work by us [9], we have shown that the commonly observed diffraction patterns of these carbon nanocrystals recorded by several research groups around the world, are consistent with the calculated diffraction pattern of a novel form of carbon we have proposed called glitter. As shown in Figure 2, glitter is a tetragonal allotrope of carbon [10] in space group P4$_2$/mmc (#131), with a calculated density of about 3.08 g/cm^3, and the density functional theory (DFT-CASTEP) [11] optimized lattice parameters given as **a** = 0.2560 nm and **c** = 0.5925 nm. Figure 3 shows an extended structural drawing of the glitter allotrope of carbon.

In addition to the diffraction evidence for n-diamond and i-carbon having the glitter structure, the calculated band structure of glitter (DFT-

CASTEP) [9] shows it to be metallic, like the observed electrical characteristics of these carbon forms. In this Letter, we report on a comparison of the diffraction pattern observed for nanocrystalline n-diamond and i-carbon forms by these investigative teams, with the calculated diffraction pattern of glitter based upon lattice parameters optimized using the DFT-CASTEP method [11]. The close fit of the latter dataset to that observed for n-diamond and i-carbon, as reported herein, suggests that indeed i-carbon may be of the same structure as n-diamond, and that they both may have the tetragonal glitter structure.

Table 1 reports the theoretical diffraction pattern for the glitter allotrope of carbon [12], using the DFT optimized lattice parameters described above, as shown in columns 1 & 2 [11]. The Bragg spacings for glitter were calculated with the standard crystallographic formula for the tetragonal crystal system, as reported by Warren et al. and shown in Equation (1). [12] In column 3 of the table is reported the combined diffraction pattern for the n-diamond C form, labeled as (n) [5], and the i-carbon C form, labeled as (i) [1]. Column 4 reports the absolute deviation (Δd) between the observations and the theoretical diffraction data for the glitter model, and the percentage absolute deviation ($\Delta d/d$ (x) 100) can be derived from this data. Table 2 reports the DFT optimized geometry of the glitter model.

$$1/d_{hkl}^2 = ((h^2 + k^2)/\mathbf{a}^2) + l^2/\mathbf{c}^2 \tag{1}$$

There are 10 diffraction observations for n-diamond [5], and 9 diffraction observations for i-carbon [1], in the reported datasets. There are thus 2 outliers that have been omitted from the comparison shown in Table

1, with the n-diamond dataset having an outlier at 0.2060 nm [5] (ascribed to the cubic diamond (111) reflection), and the i-carbon dataset having an outlier at 0.2120 nm (also ascribed to the cubic diamond (111) reflection). Analysis over the other 17 observations in the combined n-diamond [5] and i-carbon [1] datasets, shows that the DFT optimized glitter model fits these 17 observations with an average percentage deviation (%d) of 1.41% (98.59% agreement between the model and the n-diamond and i-carbon experimental dataset).

It is believed that the uncertainties associated with recording electron diffraction data from carbon nanocrystals, in the work on n-diamond [5] and i-carbon [1] described here, is within a 2% uncertainty, and we believe here that the glitter model [10] is thus a reasonable explanation for the numerous observations of kinetically stabilized C forms reported in the literature as n-diamond and i-carbon. [1-8]

References

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[11] CASTEP (Cambridge Serial Total Energy Package) was created and developed by Professor M.C. Payne and others in the 1980's. It is a computational procedure based upon the density functional theory (DFT). Professor M.C. Payne and his colleagues are located in the Theoretical Condensed Matter group in the Cavendish laboratory at Cambridge University. Dr. Chris J. Pickard kindly performed and provided the calculations on the glitter structure to the authors. The details of the CASTEP program are described in *Rev. Mod. Phys.*, **64**, 1045, (1992). For the present implementation of CASTEP, used to optimize the structural

parameters of glitter, ultrasoft pseudopotentials were employed, the basis set had an energy cutoff of 400 eV and k-point sampling was done with a 10x10x4 mesh.

[12] B.E. Warren, (1990) *X-ray Diffraction*, 1st edition, Dover Publications, Inc., Mineola, NY, : 21-22. The formula used to calculate Bragg spacings in the tetragonal crystal system of glitter, is given in the book by B.E. Warren in the following format: $1/d_{hkl}^2 = ((h^2 + k^2)/\mathbf{a}^2) + l^2/\mathbf{c}^2$

Table 1: Observed diffraction data of i-carbon (i) and n-diamond (n) compared to theoretical diffraction data of P4$_2$/mmc tetragonal glitter

calculated glitter reflections a = 0.2560 nm, c = 0.5925 nm		experimental reflections*	absolute deviation per reflection
(hkl)	d-spacing, nm	d-spacing, nm	Δd-spacing, nm
100	0.2560	0.25500 (i)	0.0010
110	0.1810	0.17800 (n)	0.0030
110	0.1810	0.18200 (i)	0.0010
200	0.1280	0.13000 (i)	0.0020
201	0.1251	0.12600 (n)	0.0009
220	0.09060	0.09060 (i)	0.0000
220	0.09060	0.08980 (n)	0.0008
211	0.1124	0.11000 (i)	0.0024
212	0.1068	0.10400 (n)	0.0028
103	0.1564	0.15100 (i)	0.0054
130	0.08095	0.07960 (n)	0.0013
301	0.08446	0.08350 (i)	0.0009
203	0.1074	0.10700 (n)	0.0004
302	0.08200	0.08180 (n)	0.0002
320	0.07100	0.07260 (n)	0.0016
232	0.06905	0.06830 (n)	0.0007
002	0.29630	0.30400 (i)	0.0077

*(i) K. Yamada and A.B. Sawaoka, *Carbon*, **32(4)**, 665, (1994) & (n) H. Hirai and K. Kondo, Science, **253**, 772 (1991).

Table 2: DFT-CASTEP Crystallographic Coordinates of the Glitter Unit Cell

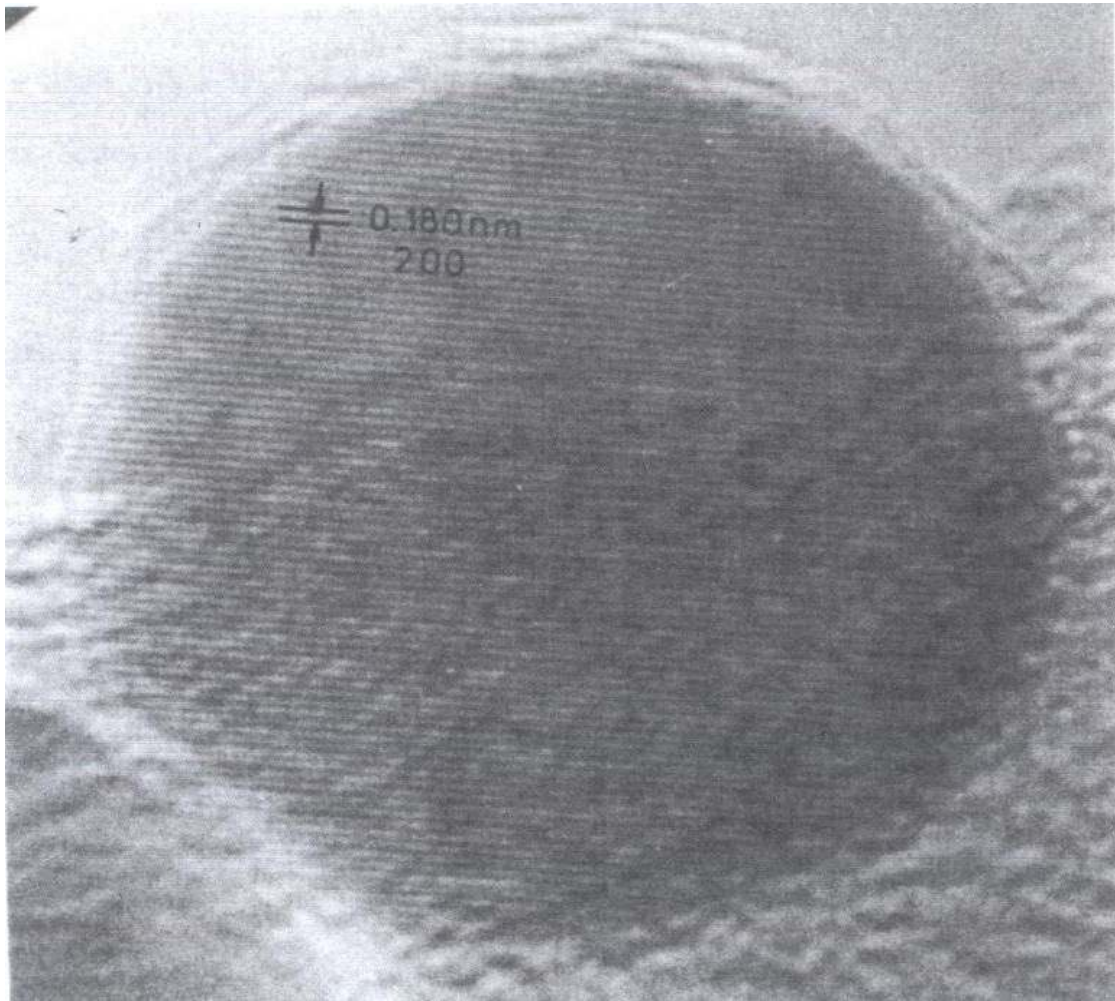| Atom#	x	y	z	**a**	**c**
1	0	0	0	2.564Å	5.928Å
2	1.2820	0	0.8168	"	"
3	1.2820	0	2.1468	"	"
4	0	0	2.9640	"	"
5	0	1.2820	3.7808	"	"
6	0	1.2820	5.1108	"	"

Figure 1: High Resolution Electron Micrograph (HREM) of 25 nm droplet of nanocrystalline n-diamond
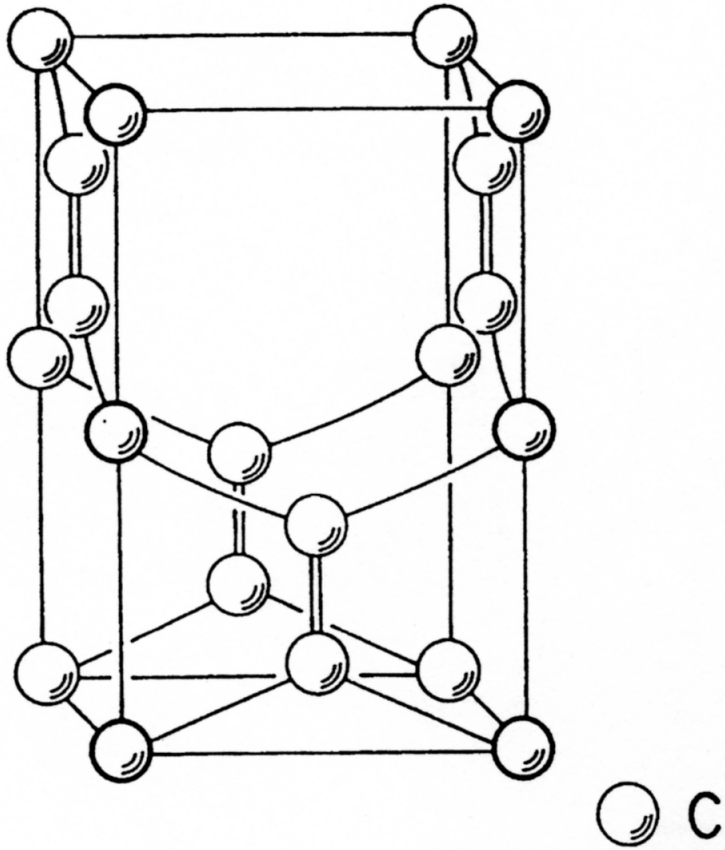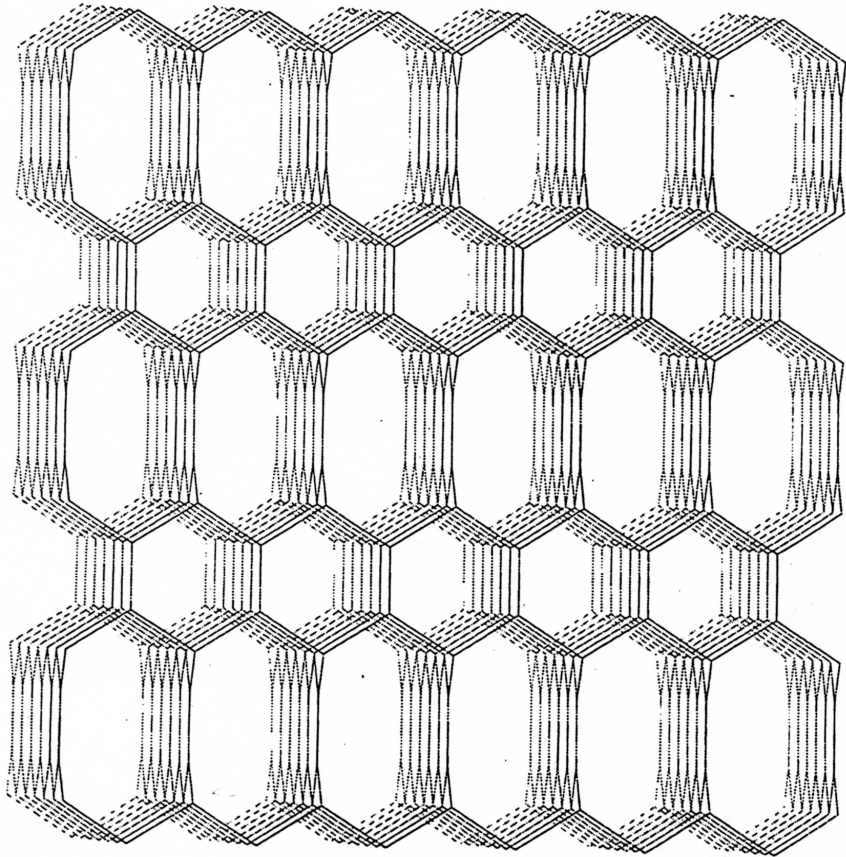
Figure 2: The unit of pattern of glitter

Figure 3: An extended view of glitter