

Isoglitter

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Abstract: A novel orthorhombic lattice is described that is generated upon a 1,4-cyclohexadieneoid motif, and is a model of a potential allotrope of C. The orthorhombic lattice (Ammm, space group #65) that is described, is called isoglitter as it is a structural relative of the tetragonal glitter lattice (P4₂/mmc, space group #131) first proposed in 1994 by Bucknum et al. A geometrical optimization of the isoglitter lattice, employing the Cambridge Serial Total Energy Package (CASTEP) algorithm based upon density functional theory (DFT) was performed. The present report is an account of the CASTEP optimized isoglitter crystal structure, including an idealized drawing of the unit cell, and a set of optimized crystallographic coordinates for isoglitter. Results of an electronic band structure calculation, together with a density of states (DOS) profile for the lattice based upon CASTEP, are reported as well. The unit cell of isoglitter contains 8 C atoms and has a DFT modeled density of about 3.009 g/cm³. Isoglitter is comprised entirely of planar and chair-like 6-gons, and puckered 8-gons, in its structural pattern.. The Wells point symbol for the network is cited here as (6³)(6⁵.8) and it is thus not a true graphene-diamond hybrid, where this point symbol translates to a Schlaefli symbol given as (6^{2/9}, 3^{1/2}). Based upon its connectivity, comprised of 3-connected trigonal planar vertices in a 1-to-1 stoichiometry with 4-connected tetrahedral vertices, the novel lattice is positioned midway between the graphene sheet, located at (6, 3), and the diamond lattice, located at (6, 4), in the topology mapping of structures described earlier by Wells.

1. Introduction

This communication reports the structure of a novel 3-,4-connected network. Wells has presented a systematic survey of many 3-,4-connected networks in his important monograph [1]. Those 3-,4-connected networks constituted of coordinations grouped into trigonal planar atom pairs (3-connected component), and as tetrahedral vertices (4-connected component), comprise models of C allotropes. Still, there are other possible 3-,4-connected networks, including compositions patterned on the phenacite structure-type (β -Ge₃N₄ and β -Si₃N₄) [2], which is comprised of isolated trigonal planar and tetrahedral vertices, as is shown in Figure 1. Yet another such 3-,4-connected pattern is the Waserite structure-type (Pt₃O₄) [3], which is an anionic sublattice in charge balance with alkali

metal cations, that is built from isolated square planar (Pt) and trigonal planar (O) vertices as is shown in Figure 2.

Figure 1

Figure 2

Isoglitter, as a potential structure-type of C reported in this paper, is a novel 3-,4-connected network, [1] that is built upon a 1,4-cyclohexadieneoid generating fragment. Isoglitter was first crudely described and illustrated in 1993 by Bucknum et al. in a preprint, [4] and later it has been described elsewhere, including in the Reticular Chemistry Structural Resource (RSCR) database [5]. The present report includes a description of the topology of the isoglitter structure-type, and its relationship to the glitter structure-type that has already been described previously [4, 6]. The isoglitter and glitter structure-types are thus proposed as models of possible C allotropes. A density functional theory (CASTEP-DFT) geometrical optimization of the isoglitter lattice is presented in this paper as well. [7] This geometrical optimization thus includes an identification of the symmetry space group of isoglitter, being in the orthorhombic system as Ammm (space group #65) [8]. Also, there is reported a table of optimized crystallographic coordinates for the 8 C atoms in the isoglitter crystalline pattern, and its theoretical density is reported. Finally, a band structure and DOS generated by the CASTEP program are presented for the orthorhombic isoglitter structure-type as well. The band structure reveals the hypothetical orthorhombic C lattice is metallic, with the 16th band, the highest lying π band, crossing the Fermi level along the crystallographic c -axis in the unit cell in direct space.

2. Isoglitter & Glitter

The 3-,4-connected network described in this paper, called isoglitter, is a structural relative of another C allotrope built from 1,4-cyclohexadiene units called glitter. [4, 6] Isoglitter, shown in Figures 3(a) & 3(b), is comprised of 1,4-cyclohexadiene building blocks coordinated to each other in a parallel fashion. While in contrast in the glitter

structure-type the 1,4-cyclohexadiene rings are coordinated orthogonally to each other as shown in Figures 4(a) & 4(b).

Figure 3(a)

Figure 3(b)

Figure 4(a)

Figure 4(b)

As can be traced from Figures 3(a) & 3(b), in the isoglitter structure-type the 3- and 4-connected constituent C atoms are linked into planar and chair-like hexagons, and into puckered octagons. The Wells point symbol [9] for isoglitter is $(6^3)(6^5.8)$, and it is thus not strictly defined as a graphene-diamond hybrid structure, but is a lattice built upon a 1,4-cyclohexadieneoid motif nonetheless. [4, 6] Earlier in 1994, Balaban et al. have described the beginnings of a new family of potential C allotropes they called the graphene-diamond hybrids [9-10]. Indeed it was thought initially by the authors of the current report, that the isoglitter lattice, being built as it is from 1,4-cyclohexadiene component substructures, would thus be the first member of an infinite series of graphene-diamond hybrid networks. In such structures all circuits are 6-gons, and within the para-(graphene-diamond) hybrid family, to which the isoglitter pattern is analogous, all planar 6-gons in these networks are parallel to each other. [9-10] However, as close inspection of Figures 3(a) & 3(b) reveal, one circuit about the symmetry equivalent tetrahedral vertices in the isoglitter pattern is in fact a puckered 8-gon. Isoglitter thus has the Wellsean Schlaefli symbol [9] of $(6^{2/9}, 3^{1/2})$. It is mapped nonetheless by its connectivity index, as exactly halfway between the locations for the graphene grid (6, 3) on the one hand, and the diamond lattice (6, 4) on the other hand, as is shown in the topology mapping of structures in Figure 5.

Figure 5

By direct comparison, in the glitter structure-type the 3- and 4-connected constituent C atoms are also linked into planar hexagons and puckered octagons. The Wells point symbol [9] for glitter is $(6^28^4)(6^28)_2$ and it is thus also not a graphene-diamond hybrid structure, but is analogous to the ortho-(graphene-diamond) hybrid family of structures. Glitter therefore possesses the Schlaefli symbol of $(7, 3^{1/3})$, and it is mapped between the location of the $(7, 3)$ series of topoisomeric networks [1], and the location for a heretofore unidentified structure-type with the topology $(8, 4)$. However, like the isoglitter lattice described above, the connectivity of glitter at $3^{1/3}$ places it between graphene at $(6, 3)$ and diamond at $(6, 4)$.

3. Density Functional Theory (DFT) Geometry Optimization of Isoglitter

Table 1 contains the density functional theory (DFT) optimized coordinates of the 8 C atoms in the isoglitter unit cell, also in Table 1 are the DFT optimized lattice parameters of isoglitter. There are 4 approximately trigonal planar C atoms in the unit cell, and 4 approximately tetrahedral C atoms in the isoglitter unit cell. The lattice parameters in the orthorhombic (Ammm, space group #65) cell are thus given as $\mathbf{a} = 2.502\text{\AA}$, $\mathbf{b} = 2.716\text{\AA}$ and $\mathbf{c} = 7.803\text{\AA}$. The crystal cell parameters and atomic positions of the 8 C atoms in the isoglitter structure-type have been optimized by using density functional theory (DFT), this optimization is based on the planewave pseudopotential technique implemented in the CASTEP package. [7, 11] The ion-electron interaction is modeled by using ultrasoft pseudopotentials. [12] The generalized gradient approximation (GGA) [13] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [14] is used. The kinetic cutoff energy for plane waves is set as 800 eV. The \mathbf{k} point separation in the Brillouin zone of the reciprocal space is 0.07 nm^{-1} , resulting in a \mathbf{k} point mesh of $5\times 6\times 2$ for isoglitter.

Table 1

From the density functional theory (DFT) lattice parameters of isoglitter in Table 1, and the drawings of isoglitter in Figures 3(a) & 3(b), one can infer that the planar

hexagons of the 1,4-cyclohexadiene substructures, from which the isoglitter lattice is generated, have a width across the π bonds of 2.502 Å, which is only slightly distorted from the dimensions of the corresponding 1,4-cyclohexadiene hydrocarbon generating fragment at 2.530 Å. [15] The **b** lattice parameter at 2.716 Å provides a measure of the stacking interaction between π bonds of the face-to-face, adjacent olefin units in the network. At this distance, the stacking interaction is minimal [16] and the network would be an insulator, were it not for the through-space interaction of p orbitals, within the symmetry adapted π crystal orbitals in its electronic structure, along the crystallographic **c**-axis. These effects can be seen in the DFT electronic band structure shown in Figure 6(a), where one sees the highest occupied π band (band #16) crossing the Fermi level from bonding states to antibonding states, that leads to a metallic status for the network, in its corresponding DOS profile accompanying the band structure in Figure 6(b).

Lastly, from the optimized lattice parameters for isoglitter cited in Table 1, one can calculate a theoretical density for the orthorhombic structure-type, and compare it to the DFT optimized density of glitter, using the same CASTEP method. [17-18] With 8 C atoms in the orthorhombic cell, the density of isoglitter at 3.009 g/cm³ compares to the corresponding theoretical density of glitter at 3.080 g/cm³. Thus the DFT theoretical densities of glitter and isoglitter are almost identical, with the glitter lattice being only very slightly denser, with a density difference of less than 1%. One might expect a significant difference in these theoretical densities, and this result is interesting given that the spiroconjugation interactions known to be present in glitter [4], and its related resonance forms [17-18], should confer a superior stability to glitter over isoglitter, where in isoglitter such stabilizing resonance forms are absent. [17-18]

Figure 6(a)

Figure 6(b)

4. Conclusions

As has been described in the preceding Sections, the isoglitter lattice represents an interesting and novel crystalline C allotrope of orthorhombic symmetry (Ammm, space

group #65), that is structurally analogous to an infinite family of para-(graphite-diamond) hybrid structures. As an analogue structural pattern to these para-(graphite-diamond) hybrid structures, it is an interesting result that the C network is metallic, where the metallic status is derived from the through-space interaction of p-orbitals, within the symmetry adapted π crystal orbitals in band #16 of its electronic structure. These interacting p orbitals are present at sites of approximate C trigonal planar coordination (see Figure 3), and they lie along the crystallographic **c**-axis of the unit cell of the isoglitter material.

Figure 7 shows a graph of the relative stability of isoglitter at pressures to beyond 100 GPa, with respect to the corresponding stabilities of graphite (at the zero of the energy scale), and the glitter structural pattern, and yet another novel hypothetical allotrope of C recently proposed by Wang et al., named as w-Carbon [19]. It is clear from the calculated data in Figure 7, that isoglitter becomes a structural-type more stable than the graphite structural-type beyond approximately 100 GPa, whereas the sibling glitter C allotrope does not achieve a stability rivaling graphite across the pressure scale modeled. This result for isoglitter is intriguing from a synthetic perspective, and it thus suggests that perhaps a thermodynamic synthesis of isoglitter from graphite may be possible at synthesis pressures exceeding 100 GPa, as could be achieved in a conventional diamond anvil cell (DAC). The reader is left to speculate about the data on w-Carbon [19] in Figure 7, and to consider the tantalizing possibility of a thermodynamic synthesis of this novel structural-type from graphite at considerably lower pressures near 20 GPa.

Elasticity in the cubic diamond and tetragonal glitter C allotropes has been evaluated by Bucknum et al. previously. [20] In this analysis, Cohen's semi-empirical formula for estimating the static bulk modulus of these crystalline materials was employed. [21] From these results cubic diamond is estimated to have a static bulk modulus of about 435 GPa, while tetragonal glitter has a static bulk modulus of about 440 GPa by the same method. Because of the nearly identical DFT densities calculated for glitter and isoglitter, as reported in this paper, it is to be possible that isoglitter will have analogous elastic properties to glitter and that both structure-types, as C allotropes, would be expected to potentially surpass cubic diamond in their intrinsic strength.

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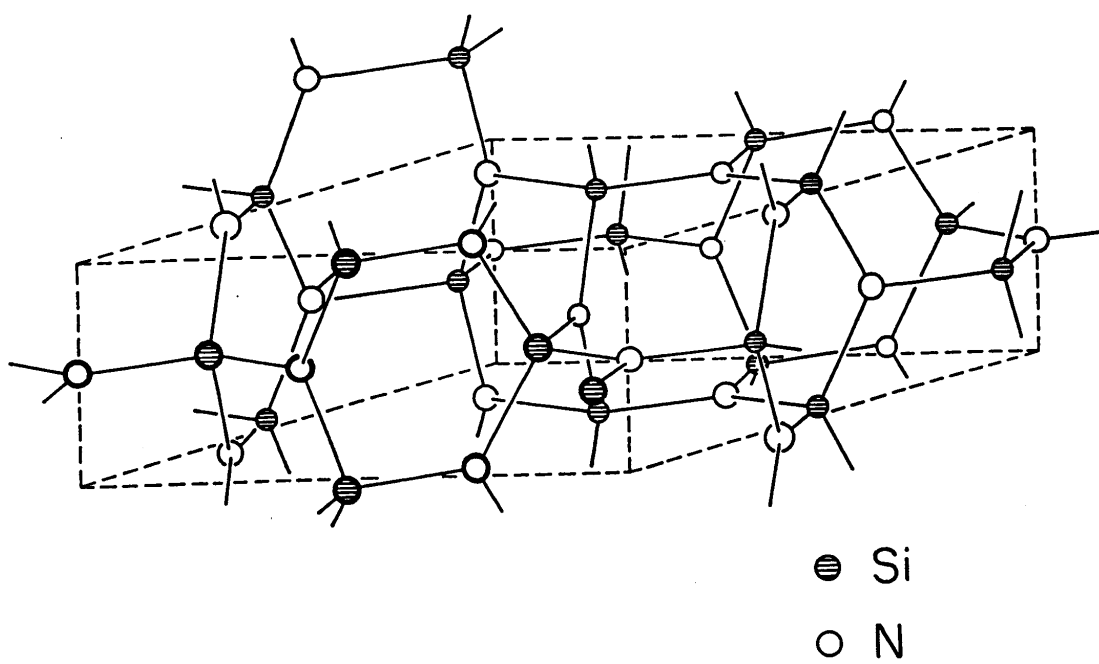


Figure 1: Unit of pattern of hexagonal phenacite structure-type as a β - Si_3N_4 lattice in space group $P6_3/mc$

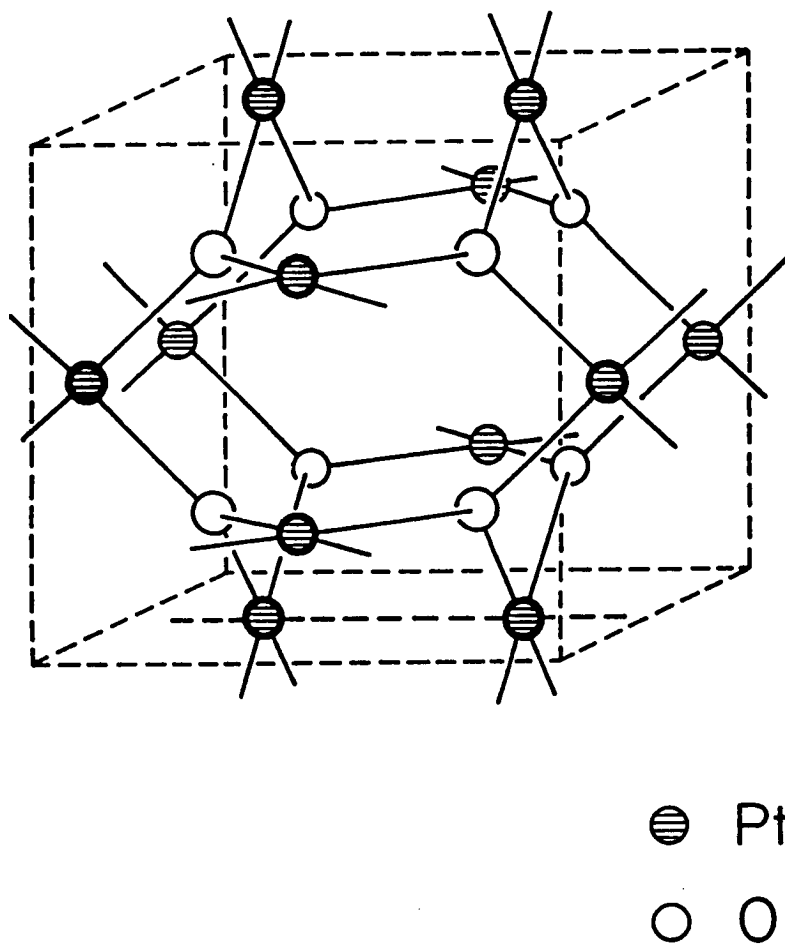


Figure 2: Unit of pattern of cubic Waserite structural type
in space group $Pm-3n$

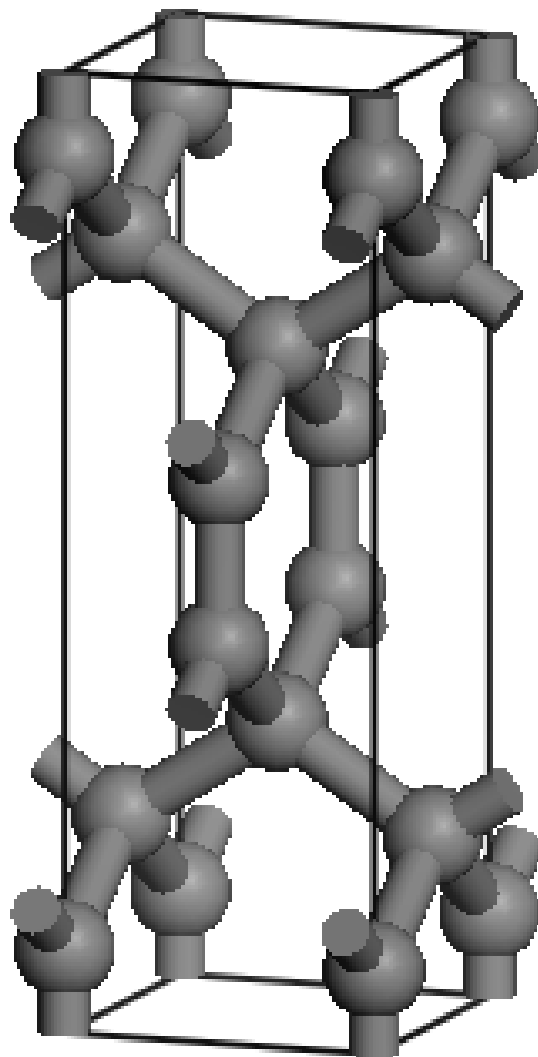


Figure 3(a): Primitive cell (unit of pattern) of orthorhombic isoglitter C allotrope in space group Ammm

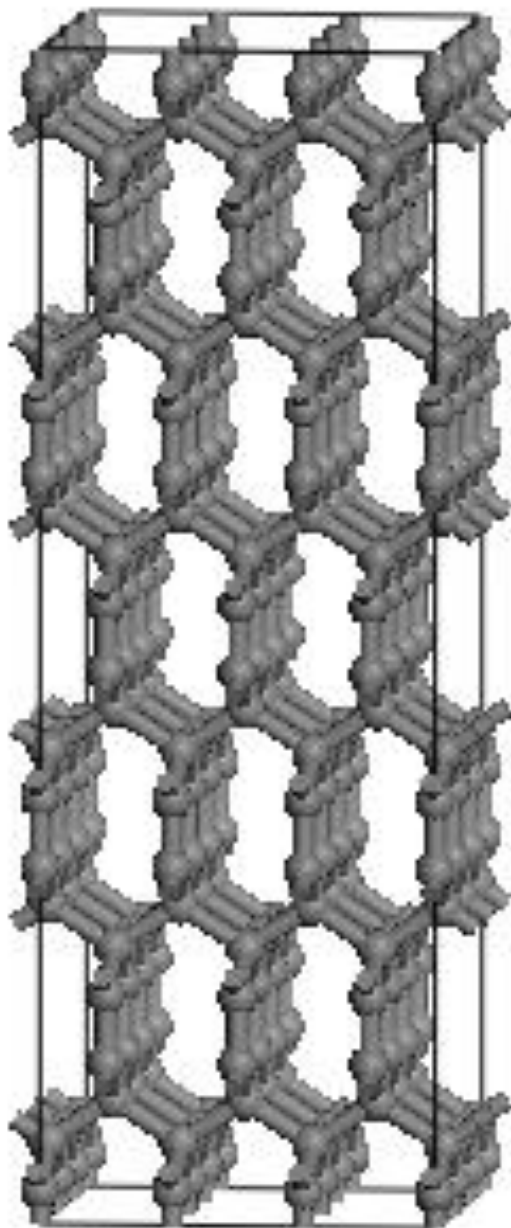


Figure 3(b): Extended view of isoglitter lattice (Ammm)
as a 3x3x3 section of the structure

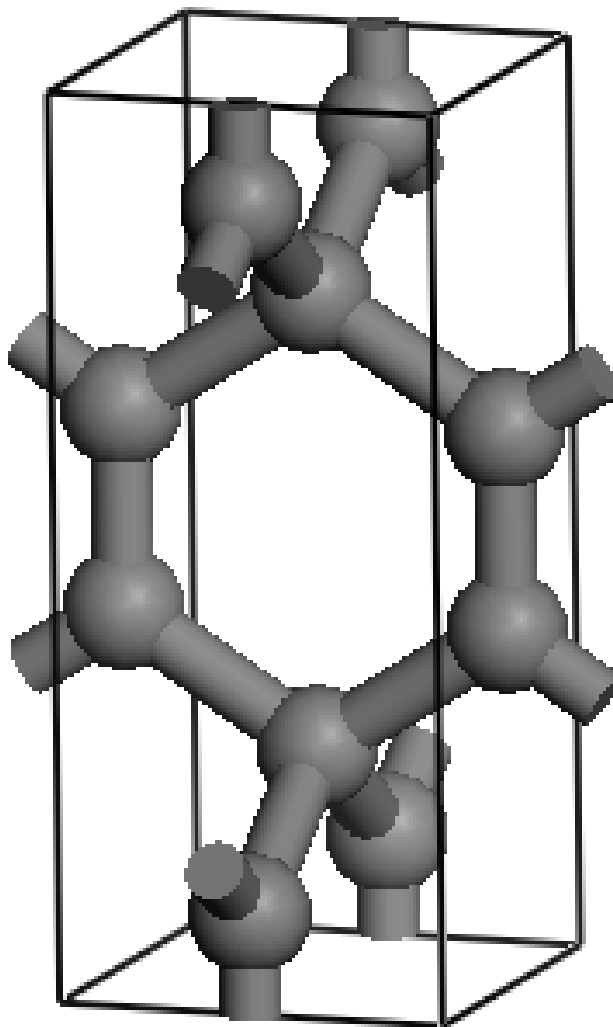


Figure 4(a): Primitive cell (unit of pattern) of tetragonal glitter
C allotrope in space group $P4_2/mmc$

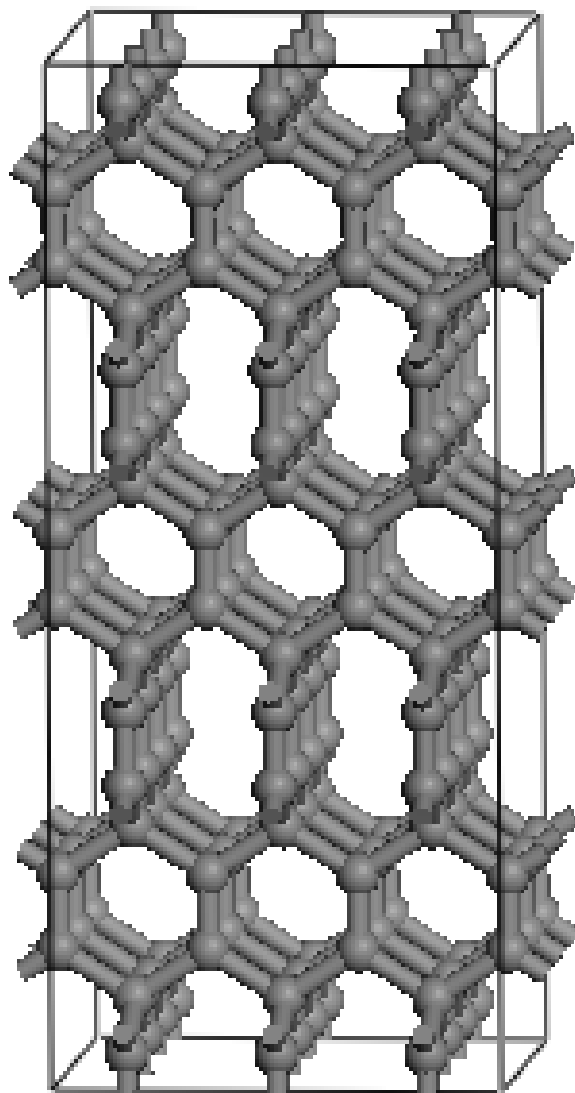


Figure 4(b): Extended view of glitter lattice ($P4_2/mmc$)
as a 3x3x3 section of the structure

| $n \backslash p$ | 3 | 4 | 5 | 6 | 7 | 8 | ... |
|------------------|-------|-------|-------|-------|-------|-------|-----|
| 3 | t | 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) | |
| ⋮ | | | | | | | |

Figure 5: Chemical topology mapping of polyhedra, tessellations and networks in a Schlaefli space

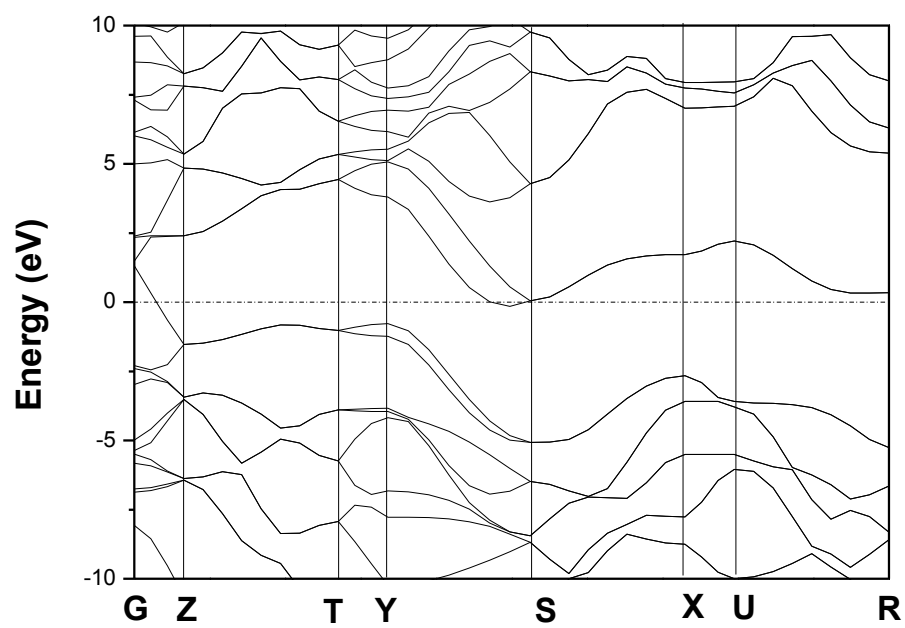


Figure 6(a): Electronic band structure of isoglitter C allotrope

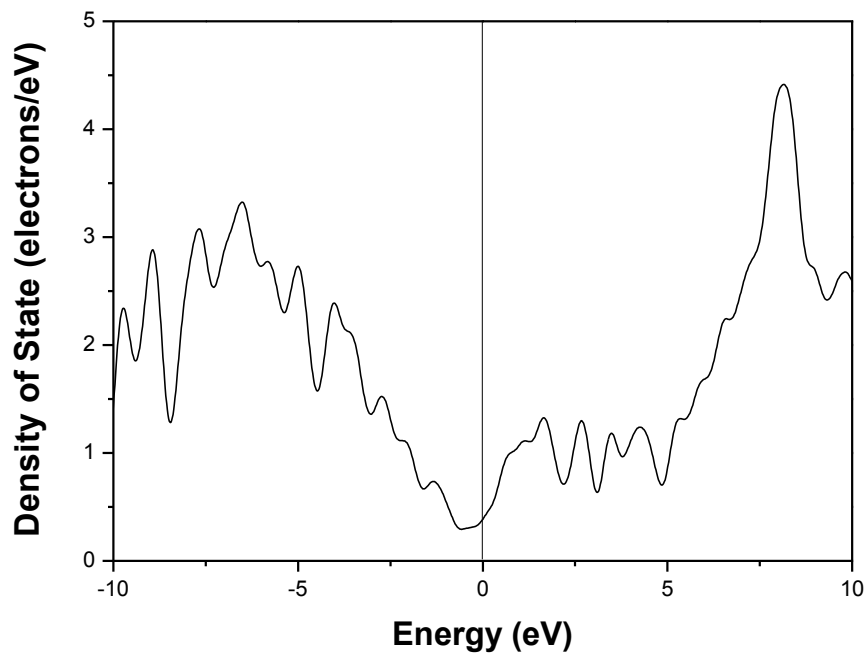


Figure 6(b): Density of states (DOS) profile of the isoglitter C allotrope

Table 1: Fractional orthorhombic crystallographic coordinates of the C isoglitter unit cell, with optimized lattice parameters **a**, **b** and **c** in Å units

| Atom# | x/ a | y/ b | z/ c | a | b | c |
|-------|-------------|-------------|-------------|---------------------|----------|----------|
| 1 | 0 | 0 | 0.08585 | 2.502, 2.716, 7.803 | | |
| 2 | 0 | 1/2 | 0.1891 | " | | |
| 3 | 1/2 | 1/2 | 0.3108 | " | | |
| 4 | 1/2 | 0 | 0.4141 | " | | |
| 5 | 1/2 | 0 | 0.5858 | " | | |
| 6 | 1/2 | 1/2 | 0.6891 | " | | |
| 7 | 0 | 1/2 | 0.8108 | " | | |
| 8 | 0 | 0 | 0.9141 | " | | |

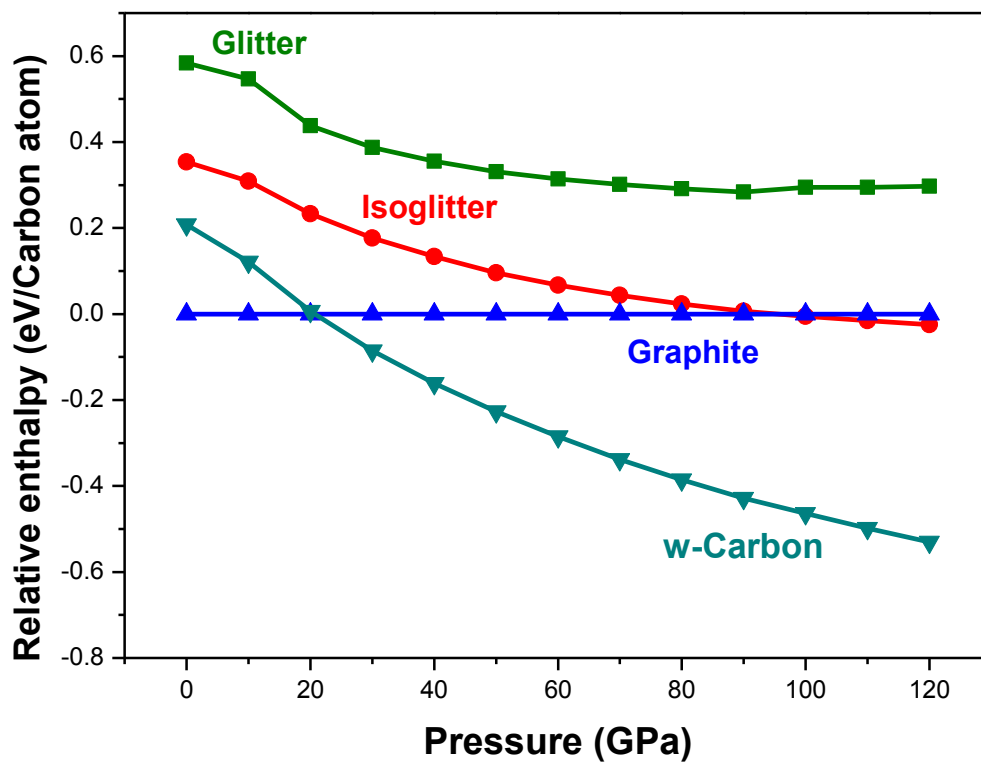


Figure 7: Relative stability scale of isoglitter, glitter, w-Carbon and graphite Carbon allotropes with pressure