Novel Ultra-hard tetragonal Octacarbon \( C_8 \) close to Diamond from First Principles

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Abstract

Novel ultra-hard carbon allotrope is proposed with mechanical, dynamic, and thermal properties like diamond. Based on energy criteria from computations within density functional theory DFT, tetragonal \( C_8 \) stoichiometry is identified as a cohesive network of corner sharing \( C_4 \) tetrahedra illustrated by charge density projections exhibiting sp\(^3\)-like carbon hybridization. The new allotrope is mechanically (elastic constants) and dynamically (phonons) stable, exhibiting thermal properties (heat capacity \( C_v \)) in close agreement with experimental data of diamond from the literature. From the used models to evaluate Vickers hardness, a larger magnitude with respect diamond is hypothesized for the new allotrope. Electronic band structure calculations show insulating behavior with large band gap of 5 eV like diamond.

Keywords: DFT; carbon allotropes; ultra-hard, thermal properties, phonons.
1. Introduction and context

Diamond, as natural gem and man-made for applications [1] is recognized as the hardest material. However, its low thermal stability in operating conditions for tooling machinery, constitutes a major drawback that called for the search of other light elements-based compositions, mainly within the B-C-N ternary cf. [2] and therein cited works.

Focusing on diamond, the basic reason for the extreme hardness is the three-dimensional 3D arrangement of carbon (light element of the 1st period) in corner sharing \( C_4 \) tetrahedra with \( d(C-C) = 1.55 \, \text{Å} \), i.e., the sum of two \( r(C) = 0.77 \, \text{Å} \) atomic radii, producing a perfectly covalent network. Figure 1a shows the diamond cubic structure (in primitive cubic cell with \( 2 \times 4 = 8 \) atoms) with the arrangement of corner sharing \( C_4 \) tetrahedra where the angle \( \angle C-C-C = 109.47^\circ \) highlight the C sp\(^3\)-like hybridization.

In last decades large research efforts were devoted to identifying novel allotropes of carbon close to diamond using modern materials research software as CALYPSO [3] and USPEX [4]. Despite their success, thorough investigations based on energy criteria are accurately achieved thanks to calculations based on the quantum mechanics Density Functional Theory (DFT) framework. DFT was devised in two papers: in 1964 for the theoretical framework by Hohenberg and Kohn [5] and followed in 1965 by Kohn and Sham [6] who established the Kohn-Sham equations for solving the wave equation practically in calculation codes built around the DFT (cf. next section).

Such investigations, backed with liminary crystal chemistry rationale led to several works by us and others on novel carbon allotropes with different stoichiometries as hexacarbon \( C_6 \) [7] and rhombohedral \( \text{rh-C}_4 \) (or in hexagonal axes: \( \text{h-C}_{12} \)) [8]. Both the 3D carbon allotropes were indentified close to diamond in their physical (Vickers hardness \( H_V \sim 100 \, \text{GPa} \)) and dynamical (phonons, heat capacity, entropy), as well as electronic band structure properties.

Extended carbon networks [9] were investigated to address the challenging question: “is diamond the hardest material” as generally admitted? In this context, super-cubane \( C_8 \) was announced by Johnston and Hoffmann as super-dense allotrope [10]. Like in former works [2, 7, 8], the present study focuses on novel \( C_8 \) 3D allotrope based on crystal chemistry rationale with geometry optimized structures to the ground state within DFT-based calculations. The results highlight cohesive properties as well as ultra-hardness and related electronic structure properties like diamond. More specifically, the mechanical (elastic constants) and dynamical (phonons bands) stabilities of the novel octacarbon allotropes were confirmed and identified with thermal properties.
(heat capacity) alike diamond. The electronic band structures are shown to exhibit insulating behavior like diamond with large band gap of 5 eV.

2. Computational framework

For the search for the ground state structure, geometry optimizations calculations onto the ground state with minimal energies were performed using DFT-based plane-wave Vienna Ab initio Simulation Package (VASP) [11,12]. For the carbon atomic potential including valence states, the projector augmented wave (PAW) method was applied [12, 13]. Treating at the same level the exchange X and the correlation C, DFT exchange-correlation (XC) effects were accounted for using a generalized gradient approximation (GGA) [14]. The relaxation of the atoms onto ground state geometry was done applying a conjugate-gradient algorithm [15]. Blöchl tetrahedron method [16] with corrections according to Methfessel-Paxton scheme [17] was applied. A special $k$-point sampling was applied based on homogeneous distribution with rows and columns of the reciprocal lattice vectors spanning the Brillouin zone [18]. For better accuracy, the optimization of the structural parameters was carried out along with successive self-consistent cycles with increasing mesh until the forces on atoms were less than 0.02 eV/Å and the stress components below 0.003 eV/Å$^3$.

Additional to the elastic constants calculated to infer the mechanical stabilities and hardness, further calculations were carried out to verify the dynamic stability of the new carbon allotrope thanks to the phonon band structures. In the present work, the phonon modes were computed considering the harmonic approximation via finite displacements of the atoms around their equilibrium positions to obtain the forces from the summation over the different configurations. The phonon bands along the direction of the respective Brillouin zone (cubic for diamond, and tetragonal for tet.C$_8$) were subsequently obtained using "Phonopy" interface code based on Python language [19]. Thermodynamic properties such as the heat capacity $C_v$ and the entropy $S$, were finally calculated as functions of temperature to compare with experiment.

3. Results and discussions

3-1-Energy and crystal symmetry

Quite recently, we proposed a novel tetracarbon as the simplest ‘seed’ of corner sharing $C4$ tetrahedra for building large carbon edifices approaching diamond [20]. An original C$_8$ structure
was built starting from such simple unit leading to a tetragonal lattice that was fully geometry optimized to stress-free ground state. As a first assessment, energy is the prevailing criterion. The total energies: $E_{\text{total}}(\text{eV})$ and the derived atom-averaged energy $E_{\text{atom}}(\text{eV})$ are presented in Table 1 with those obtained for Diamond considered in a simple cubic cell with 8 atoms. Strikingly, tetragonal C$_8$ is found energetically very close to diamond. The densities of both systems are also very close. The crystal structures are shown in Fig. 1a and 1b showing the corner sharing tetrahedral 3D carbon networks. The angle $\angle \text{C-C-C} = 109.47^\circ$ and $d(\text{C-C}) = 1.54 \ \text{Å}$ are found in both structures thus providing signatures of purely covalent 3D carbon networks.

Table 2 details the crystal data of diamond and the new octacarbon. For diamond, a good agreement is found between calculated and literature cubic lattice constant [21]. Interestingly, while carbon is identified in a single Wyckoff position at $8a$ (0,0,0) in space group $Fd\bar{3}m$, (N° 227), tetragonal C$_8$, in space group $P\bar{4}m2$ (N° 115) shows 4 different single and double occupation carbon positions. Such a feature is relevant as template to model specific substitutions in diamond while keeping high symmetry as with B (p-doping) or N (n-doping) in view of tuning the physical properties of diamond.

3-2. Charge density 3D projections

The “electronic ↔ crystal structure” relationship is further illustrated with the charge density projections. Fig. 2 shows the charge density volumes (yellow) with perfect sp$^3$ tetrahedral shape around carbon in the tetragonal and hexagonal systems as equally within diamond. Then tetrahedral C(sp$^3$)-like carbon is the building unit.

3-3. Mechanical properties

(i) Elastic constants

The investigation of mechanical characteristics was based on the calculations of the elastic properties determined by performing finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship. Most compounds are polycrystalline, and generally considered as randomly oriented single crystalline grains. Consequently, on a large scale, such materials can be considered as statistically isotropic. They are then fully described by bulk ($B$) and shear ($G$) moduli obtained by averaging the single-crystal elastic constants. The method used here is Voigt's [22], based on a uniform strain. The calculated sets of elastic constants are given in Table 3.
All values are positive. Their combinations obeying the rules pertaining to the mechanical stability of the phase, and the equations providing the bulk $B_V$ and shear $G_V$ moduli are as follows for the tetragonal system [23]:

$$C_{ii} \ (i = 1, 3, 4, 6) > 0; \ C_{11} > C_{12}, \ C_{11} + C_{33} - 2C_{13} > 0; \text{ and } 2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0.$$  

$$B_{\text{Voigt}}^{\text{tetr}} = 1/9 (2C_{11} + C_{33} + 2C_{12} + 4C_{13}); \text{ and } G_{\text{Voigt}}^{\text{tetr}} = 1/15 (2C_{11} + C_{12} + 2C_{33} - 2C_{13} + 6C_{44} + 3C_{66}).$$

The calculated values for diamond and tetragonal C$_8$ are given in Table 3. Both exhibit large $B_V$ (> 400 GPa) and $G_V$ (> 500 GPa) magnitudes that are comparable with the accepted values for diamond: $B_V$ = 445 GPa and $G_V$ = 550 GPa [21].

Note that the bulk modulus is equal to the value obtained for tet.C$_4$ [20] but the novel tet.C$_8$ structure with the original stacking of C4 tetrahedra offers a 9 GPa larger shear modulus of 583 GPa versus $G_V$(tet.C$_4$) = 574. The consequence is that a larger hardness is expected for tet.C$_8$ as observed in next subsection.

(ii) **Hardness**

Vickers hardness ($H_V$) was predicted using four pertinent theoretical models of hardness [24-27]. The thermodynamic model [24] is based on thermodynamic properties and crystal structure, while Mazhnik-Oganov [25] and Chen-Niu [26] models use the elastic properties. Lyakhov-Oganov approach [27] considers topology of the crystal structure, strength of covalent bonding, degree of ionicity and directionality. The fracture toughness ($K_{IC}$) was evaluated within the Mazhnik-Oganov model [25].

The results are summarized in Table 4 presenting Vickers hardness calculated using the different theoretical models and other mechanical properties such as shear modulus ($G$), Young's modulus ($E$), the Poisson's ratio ($\nu$) and fracture toughness ($K_{IC}$). Interestingly the hardness of the tet.C$_8$ shows larger magnitude than diamond with two models: Mazhnik-Oganov [25] model and Chen at al. model [26] but not with the thermodynamic model [24] where $H_V$, is found equal to the value admitted for diamond. However, concomitantly with Mazhnik-Oganov model, the fracture toughness: $K_{IC}$(tet.C$_8$) = 6.7 MPa·m$^{1/2}$ is found larger than calculated for diamond with $K_{IC} = 6.4$ MPa·m$^{1/2}$.

Consequently, the novel octacarbon allotrope can be considered as prospective ultra-hard material, at least as well as diamond.
3-4. *Dynamical stabilities from the phonons.*

Beside structural stability criteria observed for the new carbon allotrope from the positive magnitudes of the elastic constants and their combinations, the phonon modes were subsequently computed. Phonons are quanta of vibrations; their energy is quantized through the Planck constant ‘h’ used in its reduced form \( \hbar = h/2\pi \) giving with the wave number \( \omega \) the energy: \( E = \hbar \omega \).

Besides the novel allotrope the phonon band structures were obtained for diamond for the sake of comparison. Fig. 3 shows the phonon bands. Along the horizontal direction, the bands run along the main lines of the respective Brillouin zone (reciprocal k-space), i.e., cubic (Fig. 3a) and tetragonal (Fig. 3b). The vertical direction shows the frequencies given in units of terahertz (THz). Since no negative frequency magnitudes are observed, expectedly for diamond, but also for tetragonal C₈, the structure can be considered as dynamically stable. There are 3N-3 optical modes at higher energy than three acoustic modes starting from zero energy \( (\omega = 0) \) at the \( \Gamma \) point, center of the Brillouin Zone, up to a few Terahertz. They correspond to the lattice rigid translation modes of the crystal (two transverse and one longitudinal). The remaining bands are 21 but the higher the symmetry, the degeneracy is observed with bands found at a given frequency, and a reduction in the number of dispersion curves is observed as obvious from the comparison of diamond few bands and the larger number of bands for the two octacarbon polymorphs. In the three panels the energy range is the same for all three phases, i.e. from 0 to 40 THz, stressing furthermore their similar behaviors, especially with the magnitude observed for diamond by Raman spectroscopy: \( \omega \sim 40 \) THz [28].

3-5. *Thermal properties.*

Following the phonon band structures, the thermal properties such as the entropy and the heat capacity \( C_v \) were calculated using the statistical thermodynamic expressions from the phonon frequencies on a high precision sampling mesh in the BZ (cf. the textbook by Dove on ‘Lattice Dynamics’ [26]). As shown in Fig. 4, tetragonal C₈ and Diamond present similar curves for the temperature change of the entropy and heat capacity at constant volume. The black curve stands for the temperature change of Helmholtz free energy: \( F = U - TS \) where \( U \) stands for the internal energy and \( S \) for entropy. For the two carbon allotropes, the free energy decreases with temperature as expected from the equation above because \( S \) increases with \( T \) almost linearly as it can be seen in both panels. The entropy \( S \) and the heat capacity are close to zero up to 100 K. Above 100 K, \( S \) increases continuously and almost linearly up to the highest temperatures. For \( C_v \), a validation of the calculation results was found from experimental data on diamond up to high temperatures obtained by Victor
back in 1962 [27]. The discrete experimental points obtained from 300K up to 1000K by steps of 100K are plotted as blue diamond symbols on the calculated curve (green). They are found exactly on the calculated diamond curve (Fig. 4a), and only slightly below the calculated $C_V$ curve in $tet.C_8$ (Fig. 4a), thus providing an additional proof for the closeness of the new carbon allotrope to diamond.

### 3.6 Electronic band structures.

Fig. 5 shows the electronic band structures obtained using the all-electrons DFT-based augmented spherical method (ASW) [28]. For the sake of comparison, the band structure of diamond is exhibited. The bands develop along the main directions of the cubic (diamond) and tetragonal ($tet.C_8$) Brillouin zones,

The energy level along the vertical line is with respect to the top of the valence band (VB), $E_V$. As a specific character of diamond (Fig. 5a), the band gap is indirect (see green arrow) with a magnitude slightly larger than 5 eV, whereas at the center of the Brillouin zone the energy gap is larger, as observed in the literature [29]. This feature also characterizes the tetragonal allotrope exhibiting indirect band gap between $\Gamma_{VB}$ and $Z_{CB}$, i.e., along $k_z$.

### 4. Conclusions

In this work a novel ultra-hard carbon allotrope, $tet.C_8$ was proposed with electronic, mechanical, dynamic, and thermal properties close to diamond. The hardness assessment provides Vickers hardness seemingly larger than diamond.

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**Data Availability Statement**: Data supporting reported results including CIF files can be made available on demand.

**Conflicts of Interest**: The authors declare no conflict of interest.
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Table 1. Total and atom averaged energies of diamond and the novel octacarbon allotrope

| Space group N° | $E_{\text{total}}$ eV | $E/\text{at.}$ eV | V Å$^3$ | $\rho$ g/cm$^3$ |
|----------------|----------------------|-----------------|--------|----------------|
| $C_8$ diam. ($Fd\bar{3}m$, #227) | -72.75 | -9.095 | 45.20 | 3.529 |
| $C_8$ tet. ($P\bar{4}m2$, #115) | -72.76 | -9.095 | 45.21 | 3.529 |

Table 2. Crystal parameters from DFT calculations

a) Diamond (Fig. 1a).

Space group $Fd\bar{3}m$, (N° 227). $a = 3.5623$ Å (3.5666 Å[21]). Atm. position: C at 8a 0,0,0

b) Tetragonal $C_8$, space group $P\bar{4}m2$ (N° 115). (Fig. 1b).

$a = b = 2.5190$ Å; $c = 7.1244$ Å. (Z=2)

| Atom | Wyckoff | x | y | z |
|------|---------|---|---|---|
| C1   | 1a      | 0.0 | 0.0 | 0.0 |
| C2   | 1d      | 0.0 | 0.0 | ½ |
| C3   | 2f      | ½  | ½  | ¼ |
| C4   | 2g      | ½  | 0.0 | 1/8 |
| C5   | 2g      | ½  | 0.0 | 5/8 |
Table 3 Elastic constants $C_{ij}$ and Voigt values of bulk ($B_V$) and shear ($G_V$) moduli of new carbon allotropes (all values are in GPa).

|       | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ | $H_V$ | $B_V$ | $G_V$ |
|-------|----------|----------|----------|----------|----------|----------|-------|-------|-------|
| $C_8$ ($Fd\overline{3}m$) | 1051     | 125      | 560      | 103      | 443      | 560      |       |       |       |
| $C_8$ ($P\overline{4}m2$) | 1171     | 29       | 134      | 1068     | 466      | 570      | 113   | 445   | 583   |

Table 4 Mechanical properties of tet.C8 and Diamond: Vickers hardness ($H_V$), bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$), Poisson’s ratio ($\nu$) and fracture toughness ($K_{IC}$).

|       | $H_V$ | $B$ | $G$ | $E^{**}$ | $\nu^{**}$ | $K_{IC}$ |
|-------|-------|-----|-----|---------|-------------|----------|
|       | T*   | LO† | MO‡ | CN§     | $B_V$       | $B_V$    |
|       | GPa  |     |     |         |             |          |        |
| $C_8$ (#115) | 98   | —   | 112 | 111     | 445         | 445      | 583    | 1217  | 0.044 | 6.7   |
| Diam. (#227) | 98   | 90  | 100 | 93      | 445‡‡       | 560‡‡    | 1138   | 0.074 | 6.4   |

* Thermodynamic model [24]
† Lyakhov-Oganov model [25]
‡ Mazhnik-Oganov model [27]
§ Chen-Niu model [26]
** $E$ and $\nu$ values calculated using isotropic approximation
‡‡ Calculated in present work (Table 3)
‡‡ Ref. 28
Figure 1. Sketches of the crystal structures highlighting corner-sharing tetrahedral arrangement: a) Diamond in simple cubic representation C\textsubscript{8}, b) Tetragonal C\textsubscript{8}. 
Figure 2. Charge density yellow volumes showing tetrahedra shapes around carbon in a) Diamond in simple cubic representation C₈, and b) Tetragonal C₈
Figure 3. Phonons band structures. a) Diamond in simple cubic representation $C_8$, b) Tetragonal $C_8$
Figure 4. Thermodynamic properties from entropy and heat capacity $C_V$ in a) Diamond, and b) Tetragonal $C_8$. 

Diamond SG#227
- Helmholtz free energy
- Entropy
- Heat capacity $C_V$
- Experimental $C_V$

tet.C8 SG#115
- Helmholtz free energy
- Entropy
- Heat capacity $C_V$
- Experimental diamond $C_V$
Figure 5. Electronic band structures. a) Diamond in FCC setting, and b) Tetragonal C₈