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# The simplest dense carbon allotrope: Ultra-hard body-centered tetragonal C<sub>4</sub>

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## Abstract

*From crystal chemistry rationale and geometry optimization onto ground state structures with DFT-based computations, a novel ultra-hard body centered tetragonal C<sub>4</sub> (tet-C<sub>4</sub>) is proposed as the simplest dense carbon allotrope. tet-C<sub>4</sub> is identified as cohesive as diamond, and likewise built of corner sharing C<sub>4</sub> tetrahedra in all directions. Qualified as mechanically stable from the elastic constants combinations, tet-C<sub>4</sub> has Vickers hardness identical to that of both cubic and hexagonal (lonsdaleite) diamond. Dynamical stability of tet-C<sub>4</sub> derived from all positive phonon bands also allows obtaining heat capacity close to the experimental data of diamond. The electronic band structure shows insulating tet-C<sub>4</sub> with a large indirect band gap of 5 eV.*

**Keywords:** *carbon allotropes; crystal chemistry; DFT; ultra-hard materials, thermal properties, phonons.*

## Contextual introduction

It is relevant to observe interconnectedness between solid state and organic domains regarding the chemistry of carbon. Inspired from 2D 1,4-cyclohexadiene planar molecule (Fig. 1a) was enclosed in the so called 'glitter' structure with tetragonal hexacarbon  $C_6$ , thus mirroring the molecule in a crystal [1]. The structure shown in Fig. 1b consists of corner-sharing tetrahedra of  $C(sp^3)$  -white spheres- in the  $a,b$  plane, connected by  $C=C$  double bonds along  $c$ -direction. The crystal data detailed in Table 1 point to a distorted tetrahedron with angles departing from the perfect tetrahedron angle  $\angle C-C-C = 109.47^\circ$  found, for instance, in methane  $CH_4$  or diamond. Due to the two kinds of connectivity (Fig. 1b polyhedral view), the calculated mechanical properties identified  $tet-C_6$  as ultra-hard with the particularity of being metallic -whence the 'glitter' designation- while being characterized with less cohesive energy and hardness than diamond [2]. A major role in the high hardness of diamond is played by the corner sharing  $C4$  tetrahedra and the  $C(sp^3)$  hybridization characterizing the structure (Fig. 1c). Considering the tetrahedron as elementary building unit, and using above tetragonal  $C_6$ , an isolated tetrahedron 'in a box' can be identified from halving the structure (see red line crossing in Fig. 1b), letting obtain a tetrahedron within  $C_3$  stoichiometry. The structure shown in Fig. 1c obtained after geometry optimization onto the ground state with quantum mechanical calculations based on the density functional theory DFT [3] is described in the tetragonal system (cf. Table 1). However, such tetrahedron was found less cohesive, explained by the lack of 3D periodicity. Additional carbon at 0,0,0 (corner positions, Fig. 1d) let gain 3D periodicity with corner-sharing tetrahedra in all directions. The resulting  $tet-C_4$  was found as cohesive as diamond [4] and equally characterized with unique interatomic distance and angle as shown in Table 1.

Our proposition of a very simple dense carbon allotrope, i.e. with four atoms in a body-centered tetragonal unit cell ( $Z=2$ ), knowing that diamond has face-centered cubic unit cell ( $Z=4$ ), is challenging in view of the recently predicted carbon allotropes of large stoichiometries ( $C_{16}$ ,  $C_{24}$  and  $C_{36}$  [5-7]).

## Computational methodology

Based on DFT the academic Vienna Ab initio Simulation Package (VASP) [8,9] was used with the projector augmented wave (PAW) method [9,10] for the initial atomic potentials built within the gradient exchange-correlation functional (GGA) [11]. For relaxing the atoms onto ground state structure, Blöchl tetrahedron method [12] was used with Methfessel-Paxton corrections [13]. Reciprocal space Brillouin-zone (BZ) integrals were approximated with a special  $\mathbf{k}$ -points sampling [14]. Properties pertaining to the mechanical stability and hardness were derived from the sets of elastic constants. Besides, we inferred dynamic stability from the phonons computed using the harmonic approximation. The phonon band structures along the direction of the tetragonal Brillouin zone were subsequently obtained using the "Phonopy" interface code [15]. The electronic band structure was also obtained using DFT-based Augmented Spherical Wave (ASW) method [16].

### *Mechanical properties*

The investigation of mechanical characteristics was based on the calculations of elastic properties by performing finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship. The mechanical properties 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 [17], based on a uniform strain. The calculated sets of elastic constants (in GPa) are:  $C_{11} = 1147$ ,  $C_{12} = 28$ ,  $C_{13} = 126$ ,  $C_{33} = 1050$ ,  $C_{44} = 461$ , and  $C_{66} = 559$ ; resulting in  $B$  and  $G$  according to Voigt for tetragonal symmetry:  $B_{Voigt}^{tetr.} = 1/9 (2C_{11} + C_{33} + 2C_{12} + 4C_{13}) = 434$  GPa, and  $G_{Voigt}^{tetr.} = 1/15 (2C_{11} + C_{12} + 2C_{33} - 2C_{13} + 6C_{44} + 3C_{66}) = 574$ . These values are very close to those of diamond (cf. Tables 1 and 2).

Vickers hardness ( $H_V$ ) was predicted using four modern theoretical models [18-21]. The thermodynamic model [18] is based on thermodynamic properties and crystal structure, while Mazhnik-Oganov [19] and Chen-Niu [20] models use the elastic properties. Lyakhov-Oganov approach [21] 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 [19].

The results are summarized in Tables 2 and 3 with relevant references to the literature data. From Table 2 the density of novel  $tet-C_4$  is found within the range for hexagonal (lonsdaleite) and cubic diamond. This also stands for Vickers hardness and bulk modulus ( $B_0$ ) calculated in the framework of the thermodynamic model of hardness. Table 3 presents the hardness calculated using all four theoretical models, and other mechanical properties such as shear modulus ( $G$ ), Young's modulus ( $E$ ), the Poisson's ratio ( $\nu$ ) and fracture toughness ( $K_{Ic}$ ). Presently proposed  $tet-C_4$  exhibits hardness and fracture toughness magnitudes very close to those of diamond (both cubic and hexagonal). It should be also noted that hardness of  $tet-C_4$  is much higher than  $H_V$ -values reported for all recently predicted carbon allotropes [5-7]. A good agreement can be noted.

### *Dynamical stability and thermal properties*

Beside structural stability criteria, the phonon band structure and density of states were calculated to infer the dynamical stability and thermal properties. Fig. 2a shows the bands of  $tet-C_4$  along the main lines of the tetragonal Brillouin zone. Along the vertical direction the frequencies are given in terahertz (THz). Since no negative frequency magnitudes are observed,  $tet-C_4$  is dynamically stable. There are  $3N = 12$  bands distributed into 3 acoustic modes and 9 optical modes. The 3 acoustic modes start 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). Then 9 bands can be counted to the highest frequency above 40 THz. The

diamond phonon band structure shown in Fig. 2b stresses furthermore the similarity with the frequency magnitude of  $\omega \sim 40$  THz also observed experimentally by Raman spectroscopy [24].

The thermodynamic properties such as entropy  $S$  and heat capacity at constant volume  $C_v$  were then calculated from the phonon frequencies using the statistical thermodynamic expressions on a high precision sampling mesh in the BZ [25]. Fig. 3 shows the temperature change of the calculated entropy and heat capacity of *tet*-C<sub>4</sub> in comparison with corresponding experimental data for diamond [26,27].

### *Electronic band structures*

Figure 4 shows the electronic band structures of *tet*-C<sub>4</sub> allotrope calculated using the all-electrons DFT-based augmented spherical method (ASW) [16] and data in Table 1. For the sake of comparison, the band structures of cubic diamond were calculated using the experimental lattice constant [3]. The energy level along the vertical line is with respect to the top of the valence band (VB),  $E_v$ . Like diamond, the band gap in *tet*-C<sub>4</sub> is indirect with a magnitude slightly larger than 5 eV. The electronic structure results illustrate further the closeness of *tet*-C<sub>4</sub> with diamond.

### *Conclusions*

From these results, the novel stable and cohesive *tet*-C<sub>4</sub> is confirmed as the simplest dense carbon allotrope very close to diamond. Such elementary configuration can also serve as a “seed” template structure to generate large cells for the search of novel ultra-hard phases [28], as well as to model physical properties of diamond modified by doping for instance [29].

**Author Contributions:** Samir F. Matar: Structure conceptualization. Software. Computations. Vladimir L. Solozhenko: Hardness evaluation. Expertise in hard materials.

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**Data Availability Statement:** Data supporting the 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. Carbon allotropes. Distances are in Å; energies are in eV. (pw – present work)

	C <sub>6</sub> [1,2]	C <sub>3</sub> [pw]	C <sub>4</sub> [pw]	C <sub>8</sub>
Space group (No)	<i>P4<sub>2</sub>/mmc</i> (131)	<i>P-4m2</i> (115)	<i>I-4m2</i> (119)	<i>Fd-3m</i> (227)
<i>a/b/c</i>	2.59/2.59/5.97	2.52/2.52/3.42	2.53/2.53/3.57	3.565*
C1	(2 <i>f</i> ) ½, ½, ¼	(1 <i>c</i> ) ½,½,½	(2 <i>a</i> ) 0,0,0	(8 <i>a</i> ) 0,0,0
C2	(4 <i>i</i> ) ½, 0, 0.112	(2 <i>g</i> ) ½, 0, 0.263	(2 <i>d</i> ) ½,0,¼	—
d(C1-C1)	1.536	1.497	1.547	1.544
d(C1-C2)	1.338	—	—	—
∠C-C-C	106°/114°	107.28°	109.47°	109.47°
Energy	-51.82	-21.59	-36.36	-72.72
Cohesive energy/at	-2.04	-0.59	-2.49	-2.49

\* Experimental lattice constant  $a = 3.5666 \text{ \AA}$  [4]

Atomic energy. C: -6.6 eV.



Table 2 Vickers hardness ( $H_V$ ) and bulk moduli ( $B_0$ ) of carbon allotropes calculated in the framework of the thermodynamic model of hardness [18]

	Space group	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\rho$ (g/cm <sup>3</sup> )	$H_V$ (GPa)	$B_0$ (GPa)
<i>tet</i> -C <sub>4</sub>	<i>I-4m2</i>	2.5271	2.5271	3.5740	3.496	97	440
Lonsdaleite	<i>P6<sub>3</sub>/mmc</i>	2.5221 <sup>[23]</sup>	2.5221 <sup>[23]</sup>	4.1186 <sup>[23]</sup>	3.516	97	443
Diamond	<i>Fd-3m</i>	3.56661 <sup>[4]</sup>	–	–	3.517	98	445 <sup>[23]</sup>

Table 3 Mechanical properties of carbon allotropes: Vickers hardness ( $H_V$ ), bulk modulus ( $B$ ), shear modulus ( $G$ ), Young's modulus ( $E$ ), Poisson's ratio ( $\nu$ ) and fracture toughness ( $K_{Ic}$ )

	$H_V$				$B$		$G_V$	$E^{**}$	$\nu^{**}$	$K_{Ic}^{\ddagger}$
	T <sup>*</sup>	LO <sup>†</sup>	MO <sup>‡</sup>	CN <sup>§</sup>	$B_0^*$	$B_V$				
	GPa									
C <sub>4</sub> (#119)	97	89	110	111	440	434	574	1195	0.041	6.4
Lonsdaleite	97	90	99	94	443	432	521	1115	0.070	6.2
Diamond	98	90	100	93	445 <sup>††</sup>		530 <sup>[23]</sup>	1138	0.074	6.4

\* Thermodynamic model [18]

† Lyakhov-Oganov model [21]

‡ Mazhnik-Oganov model [19]

§ Chen-Niu model [22]

\*\*  $E$  and  $\nu$  values calculated using isotropic approximation

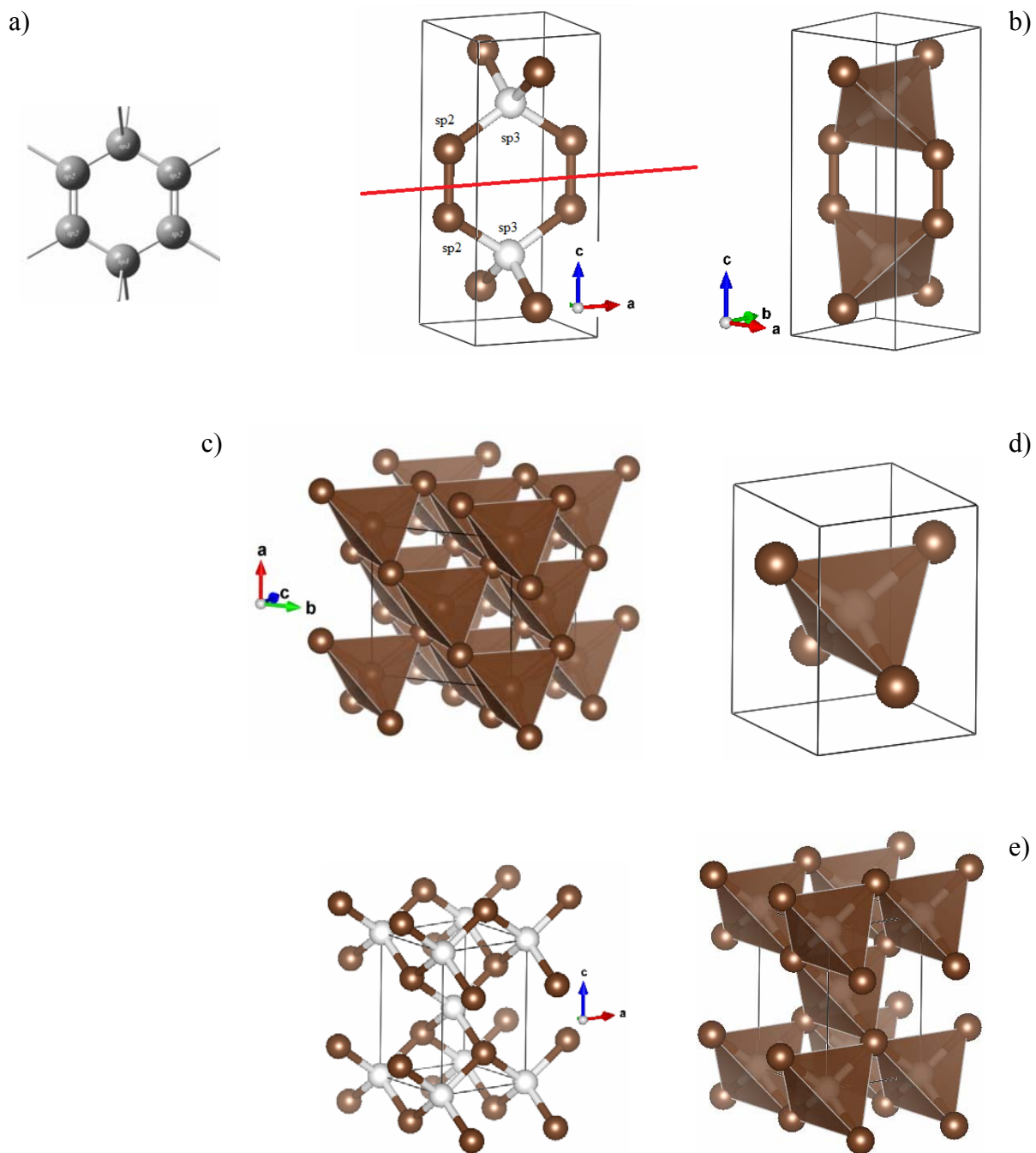


Fig. 1. a) 1,4 cyclohexadiene; b) tetragonal 'glitter' C<sub>6</sub> built of sp<sup>3</sup> C atoms (white spheres) connected with sp<sup>2</sup> C atoms; c) cubic diamond; d) isolated carbon tetrahedron structure; e) novel tetragonal C<sub>4</sub> with corner sharing tetrahedra.

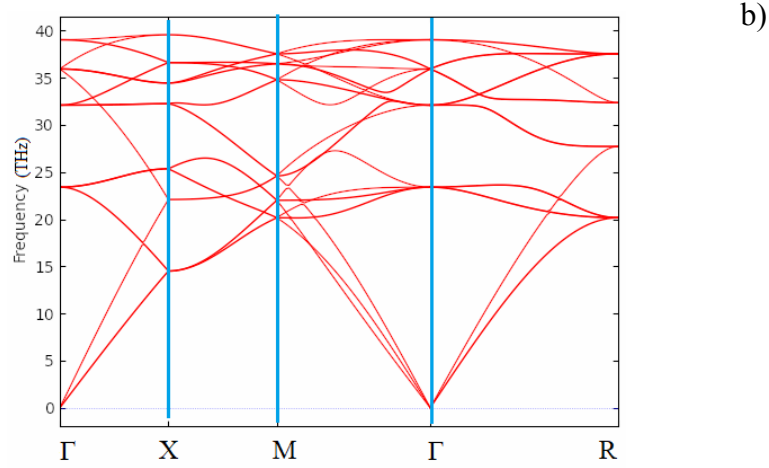
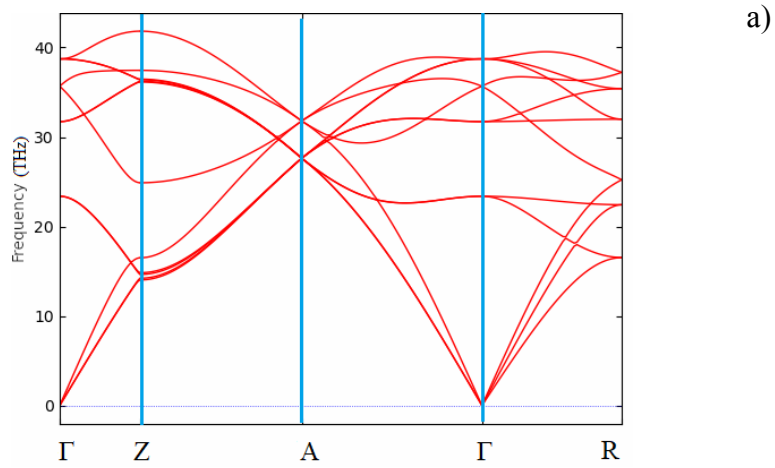


Fig. 2. Phonon band structure along main lines of the tetragonal (a) and cubic (b) Brillouin zones: a) *tet-C<sub>4</sub>*, b) cubic *C<sub>8</sub>* (diamond).

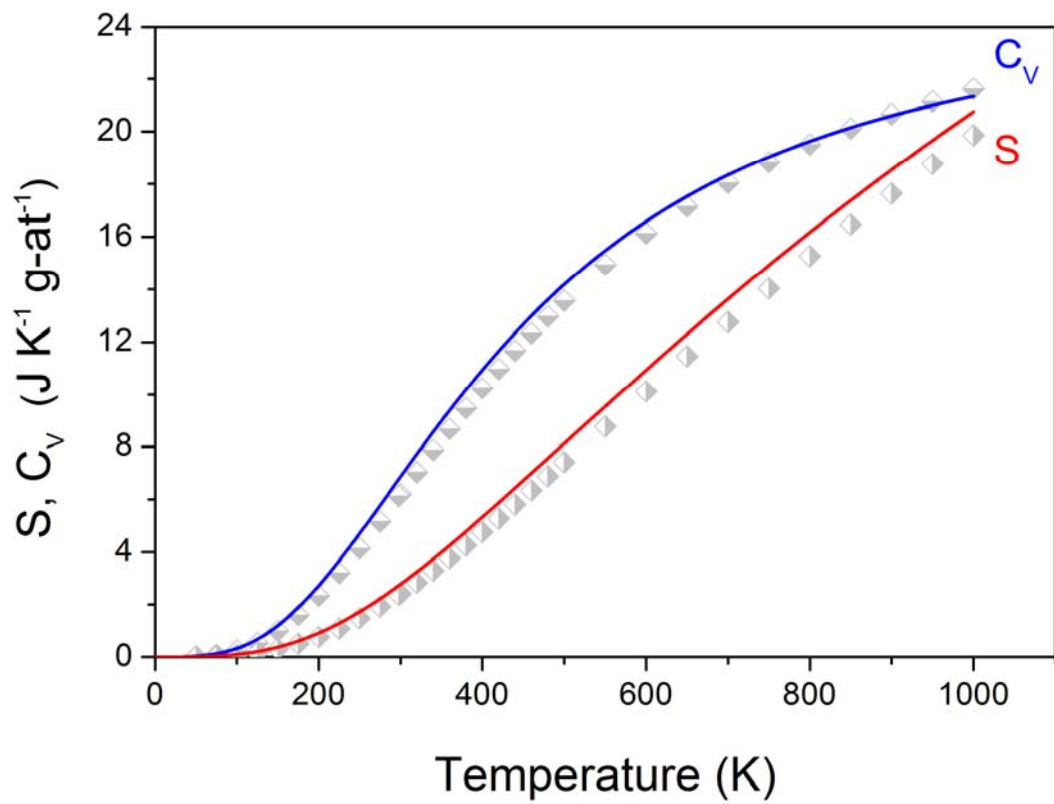


Fig. 3. Entropy and specific heat at constant volume of tetragonal C<sub>4</sub> as functions of temperature. Experimental data for diamond [26,27] are shown as gray symbols.

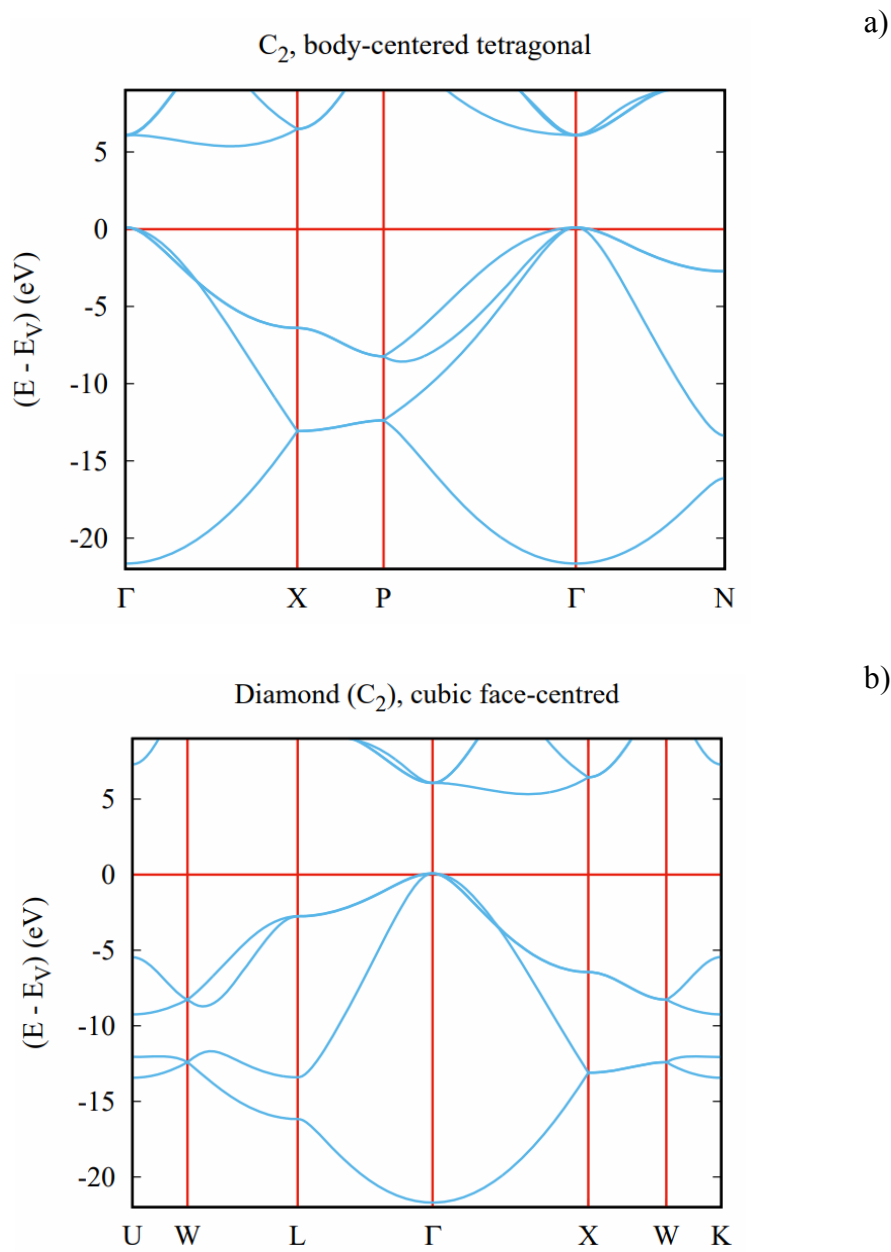


Fig. 4. Electronic band structure of a) tetragonal  $C_4$  in body center setting, and b) cubic diamond in face centered setting.