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Novel ultrahard extended hexagonal C₁₀, C₁₄ and C₁₈ allotropes with mixed sp²/sp³ hybridizations: Crystal chemistry and ab initio investigations.

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ABSTRACT

Based on 4H, 6H and 8H diamond polytypes, novel extended lattice allotropes C₁₀, C₁₄ and C₁₈ characterized by mixed sp³/sp² carbon hybridizations were devised based on crystal chemistry rationale and first principles calculations of the ground state structures and energy derived properties: mechanical, dynamic (phonons), and electronic band structure. The novel allotropes were found increasingly cohesive along the series with cohesive energy values approaching those of diamond polytypes. Regarding mechanical properties, C₁₀, C₁₄, and C₁₈ were found ultrahard with Vickers hardness slightly below that of diamond. All of them are dynamically stable with positive phonon frequencies reaching maxima higher than in diamond due to the stretching modes of C=C=C linear units. The electronic band structures expectedly reveal the insulating character of all three diamond polytypes, and conductive character for the hybrid allotropes. From the analysis of the bands crossing the Fermi level, a nesting Fermi surface was identified, allowing us to predict potential superconductive properties.

Keywords: diamond; polytypes; hardness; phonons; electron structure; hybridization; DFT

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Introduction

Diamond is mainly known in the cubic form (space group $Fd-3m$); a less common form is hexagonal one (space group $P6_3/mmc$) called lonsdaleite. Such structures are also adopted by silicon carbide SiC known to crystallize in different structures called polytypes. This appellation pertains to the stacking of layers generically named A/B/C: AB in 2H (2 layers; hexagonal system), ABC in 3C (3 layers; cubic system), ABCB in 4H (4 layers; hexagonal system), ABCACB 6H (6 layers; hexagonal system) [1]. Si and C are isoelectronic regarding the external valence shell, and diamond possesses similar polytypes such as best known 3C and 2H. The closeness of electronic structures, and despite the larger size of Si compared to C, nanostructured diamond polytypes were epitaxially grown on silicon [2]. Other diamond polytypes (4H, 8H and 9R; R for rhombohedral) were identified with calculated X-ray diffraction data published by Ownby *et al.* [3]. Later, first-principles studies of diamond polytypes were performed by Wen *et al.* [4] indicating the absence of phase transitions between them.

In 3C and 2H diamond polytypes, the carbon hybridization is purely tetrahedral sp^3 , characterizing ultrahard large band gap insulating electronic systems. The electronic structure properties can be modified by introducing trigonal $C(sp^2)$. Indeed, recent works showed that nanodiamonds with sp^2/sp^3 mixed carbon hybridization play an important role in the design of advanced electronic materials [5]. Zhai *et al.* showed progress in electrochemistry of hybrid diamond/ sp^2 -C nanostructures [6]. As for other carbon hybridizations, mixed sp^3 - sp^1 were recently identified in superhard “yne-diamond” categorized as semi-metallic [7].

In this context, a model sp^3/sp^2 C_5 was proposed as simplest hybrid form with 3 $C(sp^3)$ and 2 $C(sp^2)$ atoms per unit cell characterized by ultrahardness close to that diamond and semi-metallic electronic structure due to the presence of $C(sp^2)$ [8]. The purpose of present work was to show the effects of introducing small amounts of sp^2 carbon into 4H, 6H and 8H diamond polytypes leading to increasingly extended $C(sp^3)/C(sp^2)$ networks exhibiting smaller amounts of trigonal carbon. The investigations were based on crystal chemistry and first principles calculations within the well-established quantum mechanics framework of the density functional theory DFT [9,10].

2. Brief presentation of the computational framework

The methodology was developed in the former works (cf. [8] and therein cited papers). Summarizing the essentials, the search for the ground state structures with minimal energies was carried out with unconstrained geometry optimizations using DFT-based plane-wave Vienna Ab initio Simulation Package (VASP) [11] with energy cutoff of 500 eV. The program uses projector augmented wave (PAW) method for atomic potentials [12]. Within

DFT, the effects of exchange and correlation were treated using generalized gradient approximation (GGA) scheme [13].

The relaxation of the atoms onto ground state geometry was done applying a conjugate-gradient algorithm [14]. Blöchl tetrahedron method [15] with corrections according to Methfessel-Paxton scheme [16] were applied for geometry optimization and energy calculations respectively. A special k -point sampling [17] was used to calculate the Brillouin-zone (BZ) integrals. For better reliability, the optimization of the structural parameters was carried out along with successive self-consistent cycles with increasing Brillouin zone mesh up to $k_x = 22$, $k_y = 22$, $k_z = 4$ until the forces on atoms were less than 0.02 eV/\AA and the stress components below 0.003 eV/\AA^3 .

Investigation of the mechanical properties 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. The calculated elastic constants C_{ij} were then used to obtain the bulk (B) and the shear (G) moduli via Voigt's [18] averaging method based on a uniform strain. Besides the mechanical properties, the dynamic stability was determined from the calculated phonon spectra. They are illustrated with phonon band structures obtained using the "Phonopy" code [19]. The structure representations were obtained by the VESTA visualization software [20]. For assessing the electronic properties, the band structures were obtained by the all-electron augmented spherical wave method (ASW) [21] using the GGA functional [13] and similar Brillouin zone meshes as for VASP calculations.

3. Crystal chemistry results

The three diamond polytypes 4H (C_8), 6H (C_{12}) and 8H (C_{16}), where H stands for hexagonal (space group $P6_3/mmc$, No. 194), are shown in Fig. 1 in two representations: ball-and-stick (left) and tetrahedral stacking (right). C_8 , C_{12} and C_{16} are respectively characterized by 4 layers (ABAA'), 6 layers (ABCC'B'A'), and 8 layers (ABCBACC'A') of $C4$ tetrahedra. Such tetrahedral representations allow better illustration of the layers in primed letters A' and C' designating upside-down tetrahedra of the A and C regular layers.

Introducing trigonal sp^2 carbon was done through the occupation of $2a$ Wyckoff position with two carbon atoms at $0,0,0$ and $0,0,1/2$ in 4H and 8H polymorphs, and $2b$ Wyckoff position with two carbon atoms at $0,0,1/4$ and $0,0,-1/4$ in 6H polytype. Since these carbon atoms bring $C(sp^2)$ into the crystal structure, they are labeled 'trig' (trigonal), and C_{10} , C_{14} , C_{18} structures are labeled 'hybrid' (Table 1). The resulting structural templates as well as the pristine polytypes were submitted to full geometry relaxation leading to energy ground state structures. Fully relaxed C_{10} , C_{14} and C_{18} structures are shown in Fig. 2. In the tetrahedral representations, they are characterized by 4 layers ABAB for hybrid C_{10} , 7 layers ABB'CBB'A' for hybrid C_{14} , and

8 layers ABB'CC'DD'A' for hybrid C₁₈, respectively. However, the observed less compact stacking from spacing of the tetrahedral layers compared to pristine structures allows one to expect different physical properties such as larger compressibility as shown in next sections, on one hand, and different crystal fingerprint versus SiC (or ZnS) polytypes, on the other hand.

In Table 1a giving the resulting structural properties, the calculated values for pristine 4H and 8H polytypes (in parentheses) show good agreement with literature, thus providing reliability to the calculational framework (plane waves) and the GGA. In all polytypes there is a unique interatomic distance of ~ 1.54 Å characteristic for diamond. From the total energy, the atom averaged cohesive energy values are obtained from subtracting the atomic energy of single isolated carbon (-6.6 eV in the present work), and all polytypes possess the same magnitude of $E_{\text{coh}}/\text{atom} = -2.49$ eV also characterizing diamond.

Turning to hybrid C₁₀, C₁₄ and C₁₈, there is a significant change in the lattice parameters and atomic positions. The resulting large increase of the unit cell volumes is consistent with less compact crystal structures (Fig. 2). Beside interatomic C(sp³) characterizing the pristine polytypes, there is now a shorter bond $d\{\text{C}(\text{tet})\text{-C}(\text{trig})\} = 1.46$ Å due to the presence of C(sp²). The atom averaged cohesive energy of hybrid allotropes is lower, but, interestingly, there is an increase in $E_{\text{coh}}/\text{atom}$ values along the series with a closer value of hybrid C₁₈ to polytype 8H, illustrating the effect of smaller sp²/sp³ ratio. Consequently, it can be assumed that C(sp³) networks with small amount of C(sp²) in extended hybrid allotropes C₁₀, C₁₄ and C₁₈ are models capable to approach diamond nanostructures, with better results with the latter. All three allotropes' structures were deposited on CCDC (Cambridge Crystallographic Data Center) data base.

4. Charge density

Further qualitative illustration of the different types of carbon hybridization (sp³ and sp²) is obtained from the charge density projections shown by yellow volumes in Fig. 3. In C₈, C₁₂ and C₁₆ diamond polytypes (Figs. 3a, 3c, 3e, respectively), the sp³ hybridization is clearly observed as expected from the only presence of C(tet), with the yellow volumes taking the shape of a tetrahedron; and alike diamond all three polytypes are perfectly covalent.

Large changes are observed in hybrid C₁₀, C₁₄ and C₁₈ (Figs. 3b, 3d, 3f). Besides the C(tet) tetrahedral charge density, there appear continuous charge density along vertically arranged C=C=C fragments due to the inserted C(trig). In all three subfigures the charge density is no more localized as in covalent polytypes, but rather continuously distributed. Thus, we are dealing with decrease in covalence from diamond polytypes to hybrid C₁₀, C₁₄ and C₁₈. Such observation will be further illustrated with the electronic band structures.

4. Mechanical properties from elastic constants

For assessing the mechanical characteristics, calculations of elastic properties were carried out by performing finite distortions of the lattice. The elastic constants C_{ij} were then derived from the strain-stress relationship in the large-scale statistically isotropic material approximation. Subsequently, C_{ij} were used to calculate the bulk (B) and shear (G) moduli by averaging using Voigt's method [18]. The calculated sets of elastic constants are given in Table 2.

All C_{ij} values are positive, and their combinations obey rules pertaining to the mechanical stability of the chemical system: $C_{11} > C_{12}$, $C_{11}C_{33} > C_{13}^2$ and $(C_{11}+C_{12}) C_{33} > 2C_{13}^2$. The equations providing bulk B_V and shear G_V moduli are as follows for the hexagonal system:

$$B_V = 1/9 \{2(C_{11} + C_{12}) + 4C_{13} + C_{33}\}$$

$$G_V = 1/30 \{C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 6(C_{11} - C_{12})\}$$

Diamond polytypes C_8 , C_{12} and C_{16} have largest B_V and G_V , close to the accepted values for diamond ($B_V = 445$ GPa and $G_V = 550$ GPa [22]). Regarding hybrid C_{10} , C_{14} and C_{18} , large B_V and G_V are obtained, but they are smaller than those of pristine diamond polytypes. The larger moduli observed for C_{18} versus C_{10} can be attributed to the lower $C(\text{trig})/C(\text{tet})$, which leads to a mechanical behavior close to that of diamond.

Vickers hardness (H_V) of carbon allotropes was predicted using four modern theoretical models [23-26]. The thermodynamic model [23] is based on thermodynamic properties and crystal structure, empirical Mazhnik-Oganov [24] and Chen-Niu [25] models use the elastic properties, and Lyakhov-Oganov approach [26] considers topology of the crystal structure, strength of covalent bonding, degree of ionicity and directionality. The fracture toughness (K_{Ic}) was evaluated using Mazhnik-Oganov model [24]. Tables 3,4 present the hardness values calculated using all four models, as well as other mechanical properties such as bulk (B), shear (G) and Young's (E) moduli, the Poisson's ratio (ν) and fracture toughness (K_{Ic}).

Table 3 shows that X-ray density ρ systematically decreases in the $C_{18} - C_{14} - C_{10}$ row of hybrid allotropes, while pristine 4H, 6H and 8H polytypes have expected diamond density. Obviously, the introduction of additional trigonal carbon atoms leads to the formation of less dense phases. The similar trend is observed for bulk moduli of hybrid allotropes calculated in the framework of the thermodynamic model (see Table 3).

As is was shown earlier [27], in the particular case of ultrahard compounds of light elements the thermodynamic model shows surprising agreement with available experimental data. Moreover, its use is preferable in the case of dense hybrid carbon allotropes, for which Lyakhov-Oganov model usually gives underestimated hardness values whereas the empirical

models are not reliable. As it follows from Table 3, Vickers hardness of all three polytypes ($H_V = 97$ GPa) is close to that of diamond, while hardness of hybrids is expectedly lower (94 GPa for C_{18} and C_{14} , and 92 GPa for C_{10}). Other used models of hardness show similar trends between diamond polytypes and hybrids with respect to hardness, Young's modulus, Poisson's ratio and fracture toughness. Concomitantly, E , ν and K_{Ic} of all hybrids were found smaller than calculated for diamond polytypes. Thus, all phase under study have exceptional mechanical properties and can be considered as prospective ultrahard phases [29].

5. Dynamic properties from the phonons

Further confirmation of phase stability can be obtained from the phonon band structures, which are shown in Fig. 4 for 4H, 6H and 8H diamond polytypes and the novel C_{10} , C_{14} and C_{18} allotropes. along the high-symmetry lines of the hexagonal Brillouin zone provided in Fig. 4g as a guide for the eye. The vertical axis shows the frequencies given in units of terahertz (THz). Since no negative frequency magnitudes are observed, expectedly for diamond polytypes, as well as for hybrid carbon allotropes, all structures should be considered as dynamically stable. There are $3N-3$ optical modes found at higher energy than three acoustic modes that start from zero energy ($\omega = 0$) at the Γ -point, the 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). Flat bands (no band dispersion) that can be observed in hybrid carbon allotropes correspond to the aligned C-C-C fragments. The remaining bands correspond to the optical modes. They culminate at $\omega \sim 40$ THz in C_8 , C_{12} and C_{16} , the magnitude observed for diamond by Raman spectroscopy [30], and $\omega \sim 42$ THz in C_{10} , C_{14} and C_{18} with flat bands corresponding to antisymmetric C-C-C stretching as recently observed in allene (propadiene) molecule and tetragonal C_6 [31].

6. Electronic band structures and density of states

The electronic band structures shown in Fig. 5 along the high-symmetry lines of the hexagonal Brillouin zone were obtained using the ASW method [21] and calculated crystal parameters (Tables 1a,b). For diamond-like insulating C_8 , C_{12} and C_{16} , the energy levels are referred to the top of the valence band (VB), E_V . As a specific character of diamond, the band gap is indirect along k_z between Γ_{VB} and Z_{CB} with a magnitude close to 5 eV.

Oppositely, hybrid C_{10} , C_{14} and C_{18} behave as metals with the energy zero at the Fermi level E_F . E_F is crossed with dispersed four bands due to the 2p electrons of the trigonally coordinated carbon atoms. This feature was subsequently analyzed by calculating the four corresponding Fermi surfaces (FS) of C_{18} hybrid allotrope shown in Fig. 6a. While confirming the almost perfect two-dimensional nature of this allotrope, the Fermi surface

(especially the hexagonal ring in the center of the displayed FS) reveals a strong tendency towards nesting, which is also obvious from the metallic bands in the band structure, that cross the Fermi energy almost halfway between the Γ -point and the M-point. Hypothesizing that doubling of the in-plane cell vectors would bring the Fermi surface close to the boundaries of the hexagonal Brillouin zone and may induce a charge density wave and a concomitant lattice instability or pave the way to a superconducting phase [32,33], further calculations were done with $2 \times 2 \times 1$ cell of C_{14} allotrope presenting less atoms than C_{18} . The corresponding FS presented in Fig. 6b shows similar features of nesting as in Fig. 6a, but FS is closer to the BZ borders due to the supercell construction. The observed results stress further the hypothesis of potential superconducting behavior with 2D character generalized to all three hybrid allotropes.

7. Conclusions

The purpose of this work was to propose model carbon allotropes based on 4H, 6H and 8H diamond polytypes, modified through crystal chemistry rationale by the introduction of trigonal (sp^2) carbon, thus creating mixed $C(sp^3)/C(sp^2)$ hybridizations in C_{10} , C_{14} and C_{18} hybrid allotropes. DFT calculations allowed us to identify the hybrid forms as cohesive and stable both mechanically and dynamically, with very high hardness approaching that of diamond. The electronic band structures revealed metallic-like behavior due to the trigonal carbons with nested Fermi surfaces indicative of potential superconductivity.

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Table 1. Crystal structure parameters of hexagonal carbon polytypes and derived hybrid allotropes.

a) 4H, 6H and 8H polytypes [2] (presently calculated values are in parentheses).

$P6_3/mmc$ N°194	Polytype 4H: C_8	Polytype 6H: C_{12}	Polytype 8H: C_{16}
a , Å	2.522 (2.511)	2.522 (2.514)	2.522 (2.516)
c , Å	8.237 (8.279)	12.356 (12.394)	16.474 (16.505)
$C1(4e)$ 0 0 z	0.0938 (0.093)	0.1875 (0.187)	0.0469 (0.047)
$C2(4f)$ 1/3 2/3 z	0.1563 (0.156)	0.5208 (0.521)	0.0781 (0.0780)
$C3(4f)$ 1/3 2/3 z	–	0.6458 (0.645)	0.1719 (0.1710)
$C4(4f)$ 1/3 2/3 z	–	–	0.797 (0.797)
Volume, Å ³	45.376 (45.25)	68.064 (67.87)	90.75 (90.45)
$d_{C1(tet)-C2(tet)}$, Å	1.544	1.544	1.544
E_{total} , eV	-72.68	-109.06	-145.43
$E_{coh/atom}$, eV	-2.49	-2.49	-2.49

b) Hybrid C_8 , C_{14} and C_{16}

$P6_3/mmc$ No. 194	C_{10}	C_{14}	C_{18}
a , Å	2.496	2.500	2.502
c , Å	11.178	15.233	19.396
$C(2a)$ (trig)	0 0 0	–	0 0 0
$C(2b)$ (trig)	–	0 0 ¼	–
$C1(4e)$ 0 0 z	0.3692	0.1541	0.0753
$C2(4f)$ 1/3 2/3 z	0.1807	0.5171	0.1035
$C3(4f)$ 1/3 2/3 z	–	0.6180	0.1828
$C4(4f)$ 1/3 2/3 z	–	–	0.7903
Volume, Å ³	60.307	82.451	105.14
$d_{C1(tet)-C2(tet)}$, Å	1.545	1.544	1.536
$d_{C(tet)-C(trig)}$, Å	1.462	1.462	1.461
E_{total} , eV	-84.94	-121.45	-157.73
$E_{coh/atom}$, eV	-1.89	-2.08	-2.16

Table 2. Elastic constants C_{ij} and Voigt values of bulk (B_V) and shear (G_V) moduli of diamond polytypes and novel hybrid carbon allotropes (all values are in GPa).

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B_V	G_V
Polytype 4H: C_8	1190	105	37	1271	542	445	557
Hybrid C_{10}	922	101	39	1469	410	408	440
Polytype 6H: C_{12}	1129	160	43	1256	485	445	502
Hybrid C_{14}	972	93	69	1343	439	417	467
Polytype 8H: C_{16}	1152	99	48	1211	526	432	539
Hybrid C_{18}	1012	90	45	1325	461	412	488

Table 3 Vickers hardness (H_V) and bulk moduli (B_0) of carbon allotropes calculated in the framework of the thermodynamic model of hardness [23]

	Space group	$a=b$ (Å)	c (Å)	ρ (g/cm ³)	H_V (GPa)	B_0 (GPa)
Polytype 4H: C ₈	$P6_3/mmc$	2.5221	8.2371	3.5164	97	443
Hybrid C ₁₀	$P6_3/mmc$	2.4960	11.1775	3.3073	92	417
Polytype 6H: C ₁₂	$P6_3/mmc$	2.5221	12.3557	3.5164	97	443
Hybrid C ₁₄	$P6_3/mmc$	2.5000	15.2330	3.3867	94	427
Polytype 8H: C ₁₆	$P6_3/mmc$	2.5221	16.47429	3.5164	97	443
Hybrid C ₁₈	$P6_3/mmc$	2.5019	19.3964	3.4146	94	430
Lonsdaleite	$P6_3/mmc$	2.5221 [†]	4.1186 [‡]	3.5164	97	443
Diamond	$Fd-3m$	3.56661 [‡]		3.5169	98	445 [§]

[†] Ref. 3

[‡] Ref. 28

[§] Ref. 22

Table 4 Mechanical properties of carbon allotropes: Vickers hardness (H_V), bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν) and fracture toughness (K_{Ic}).

	H_V				B		G_V	E^{**}	ν^{**}	K_{Ic}^{\ddagger}
	T^*	LO^\dagger	MO^\ddagger	CN^\S	B_0^*	B_V				
	GPa									
Polytype 4H: C ₈	97	90	106	102	443	445	557	1179	0.058	6.5
Hybrid C ₁₀	92	79	82	74	417	408	440	971	0.103	5.4
Polytype 6H: C ₁₂	97	90	94	85	443	445	502	1094	0.090	6.2
Hybrid C ₁₄	94	72	88	80	427	417	467	1020	0.092	5.7
Polytype 8H: C ₁₆	97	90	103	100	443	432	539	1142	0.059	6.3
Hybrid C ₁₈	94	66	92	88	430	412	488	1050	0.075	5.7
Lonsdaleite	97	90	99	94	443	432	521	1115	0.070	6.2
Diamond	98	90	100	93	445 ^{††}		530 ^{††}	1138	0.074	6.4

* Thermodynamic model [23]

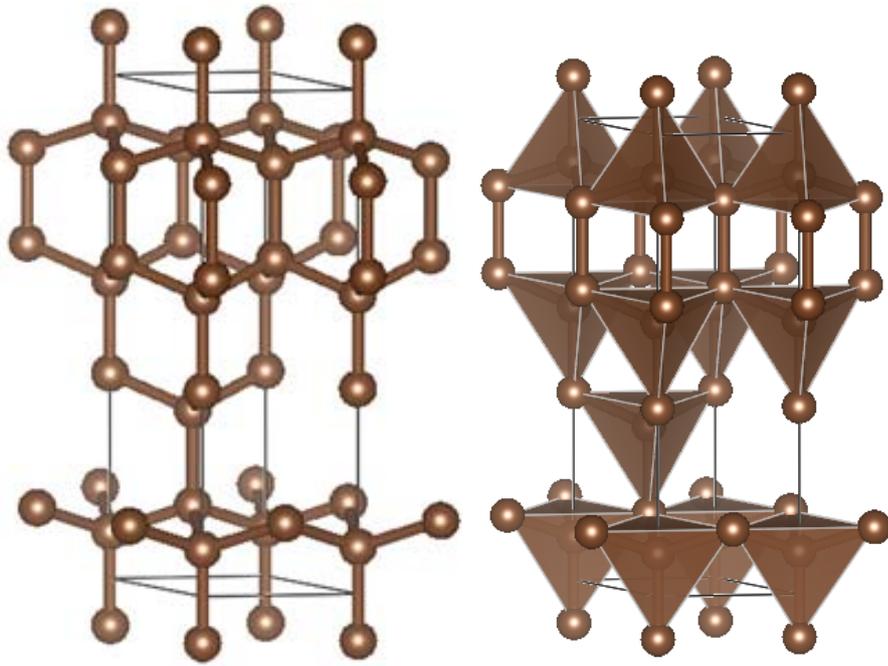
† Lyakhov-Oganov model [26]

‡ Mazhnik-Oganov model [24]

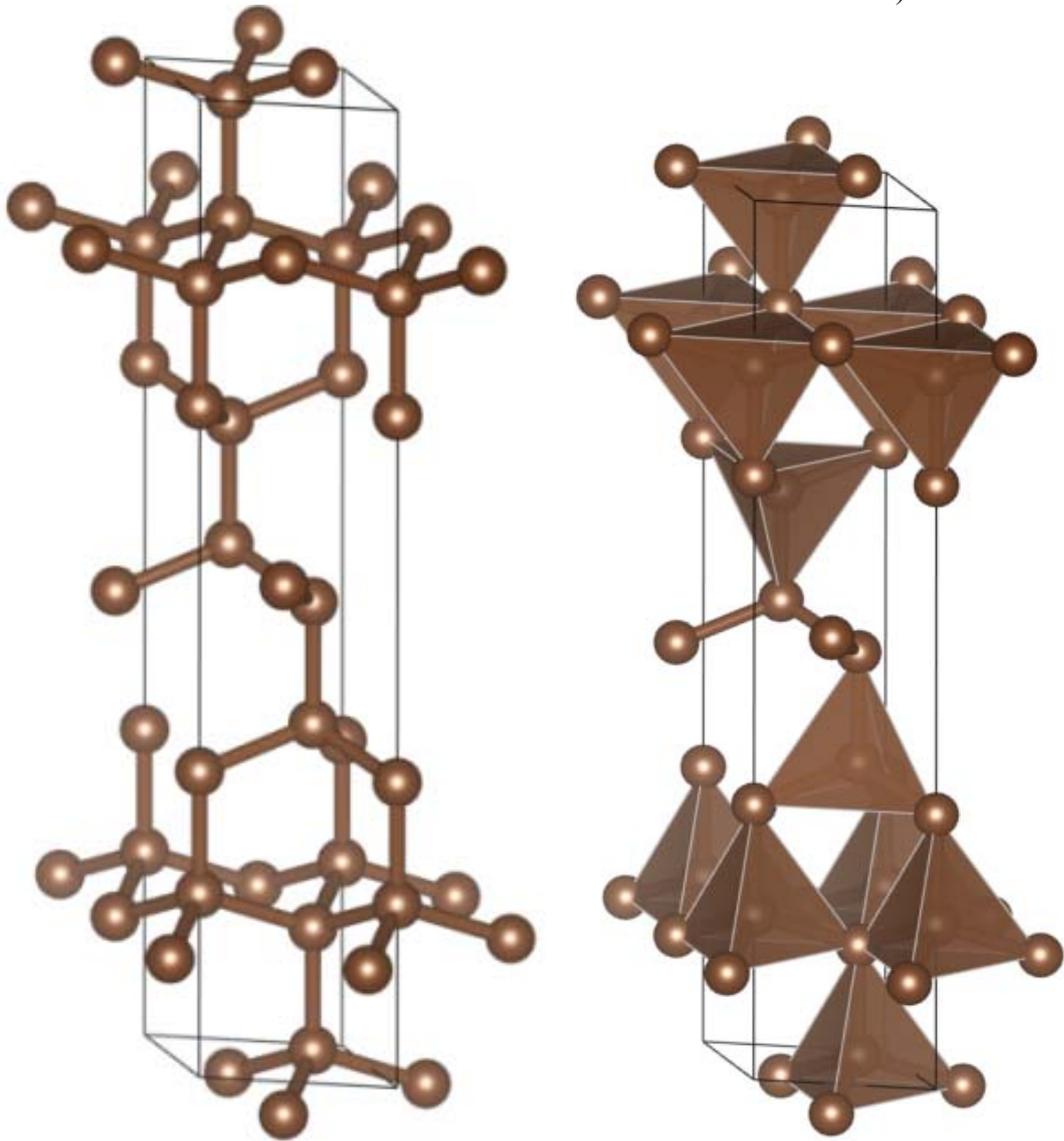
§ Chen-Niu model [25]

** E and ν values calculated using isotropic approximation

†† Ref. [22]



a)



b)

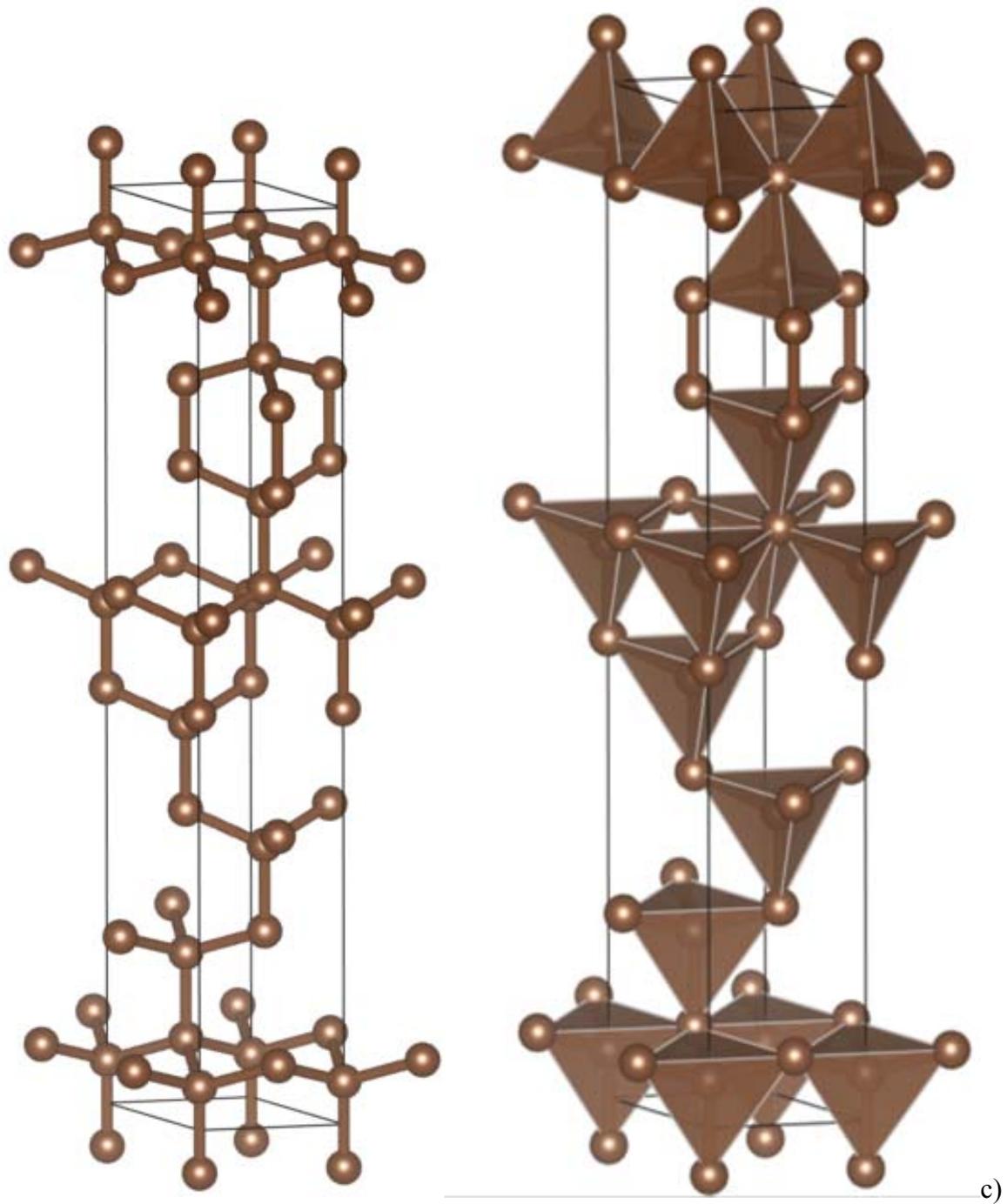
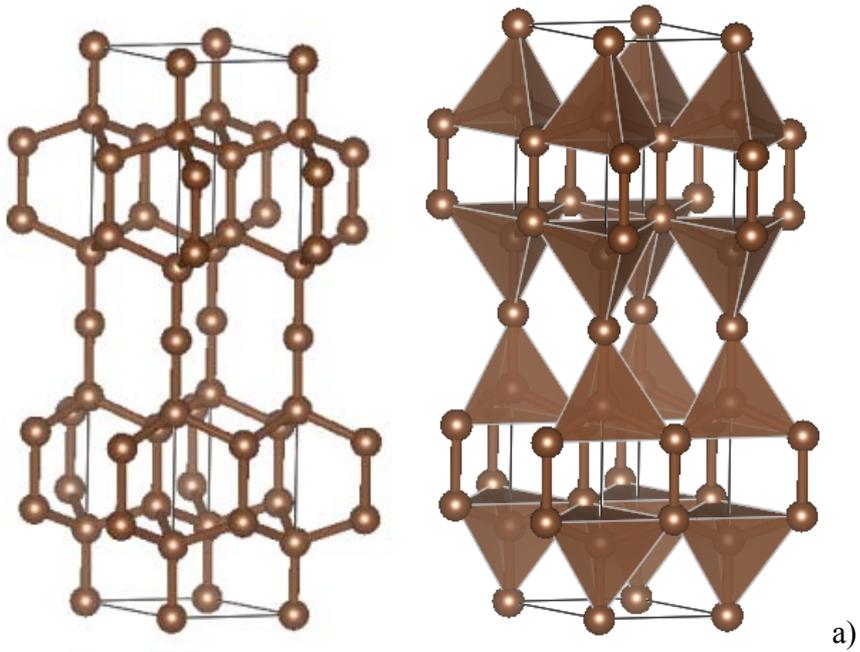
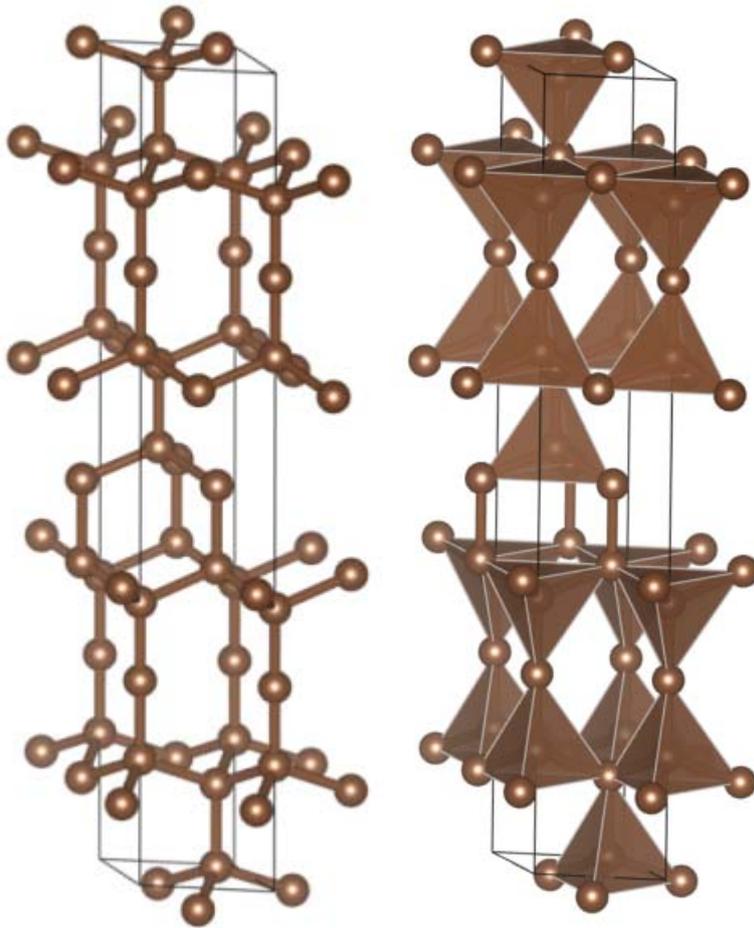


Figure 1. Sketches of hexagonal diamond polytypes (left) and their polyhedral representation (right): a) 4H (C₈), b) 6H (C₁₂) and c) 8H (C₁₆).



a)



b)

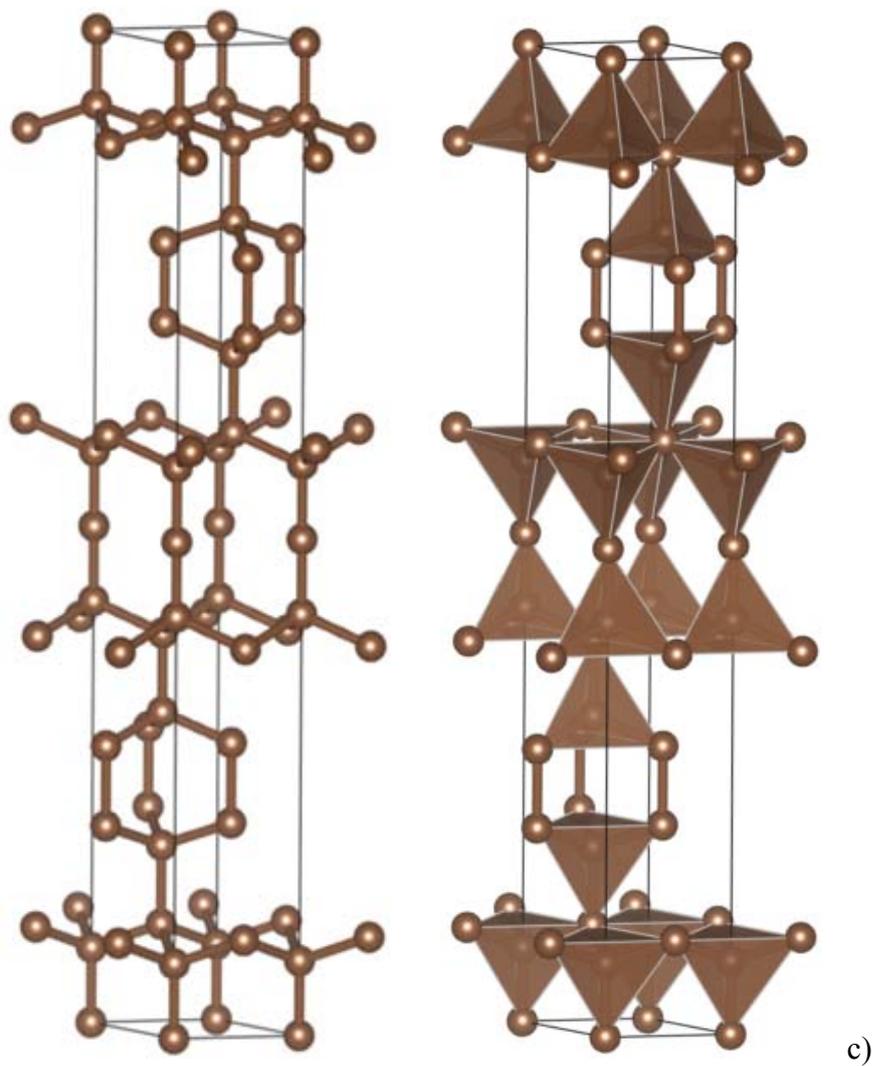
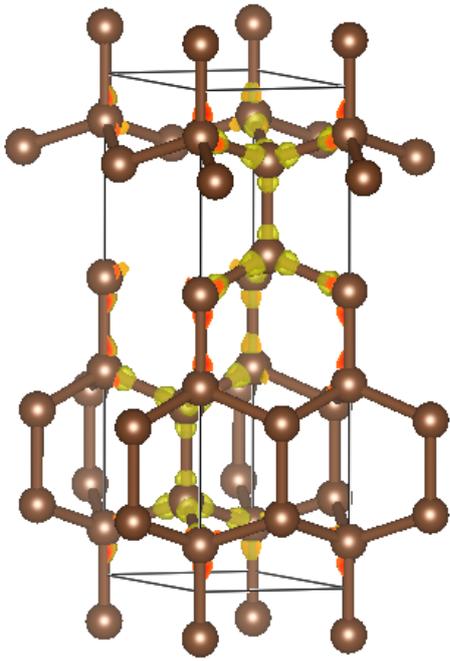
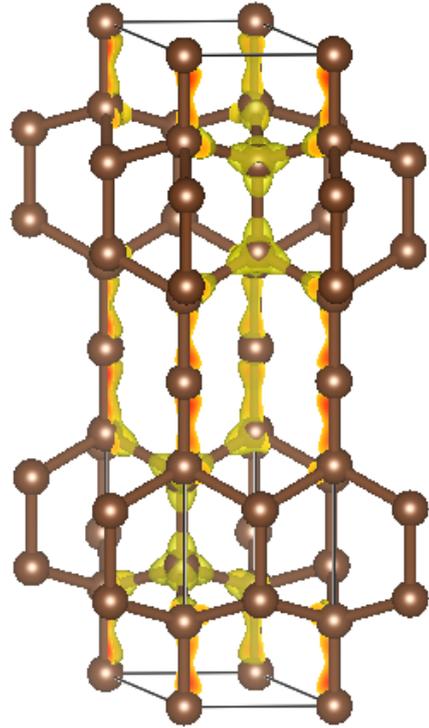


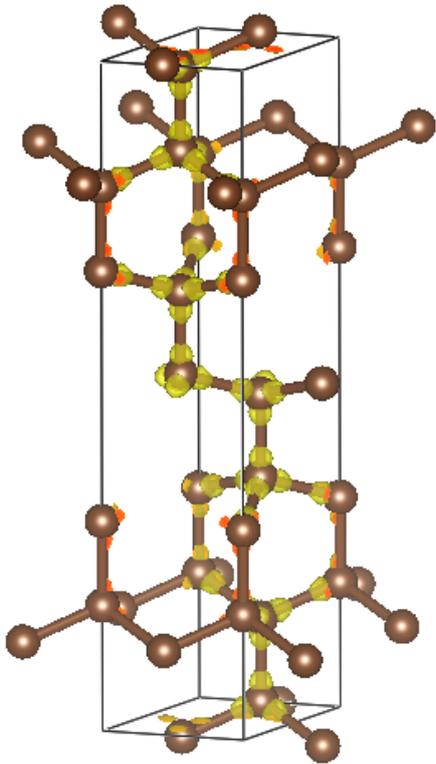
Figure 2. Sketches of hybrid carbon allotropes (left) and their polyhedral representation (right): a) C₁₀, b) C₁₄ and c) C₁₈.



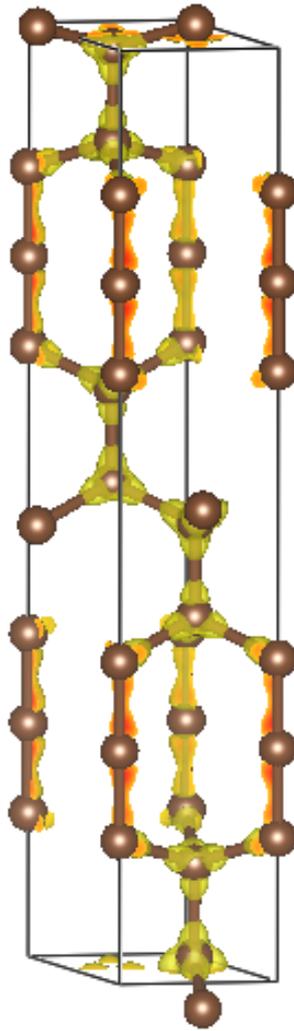
a)



b)



c)



d)

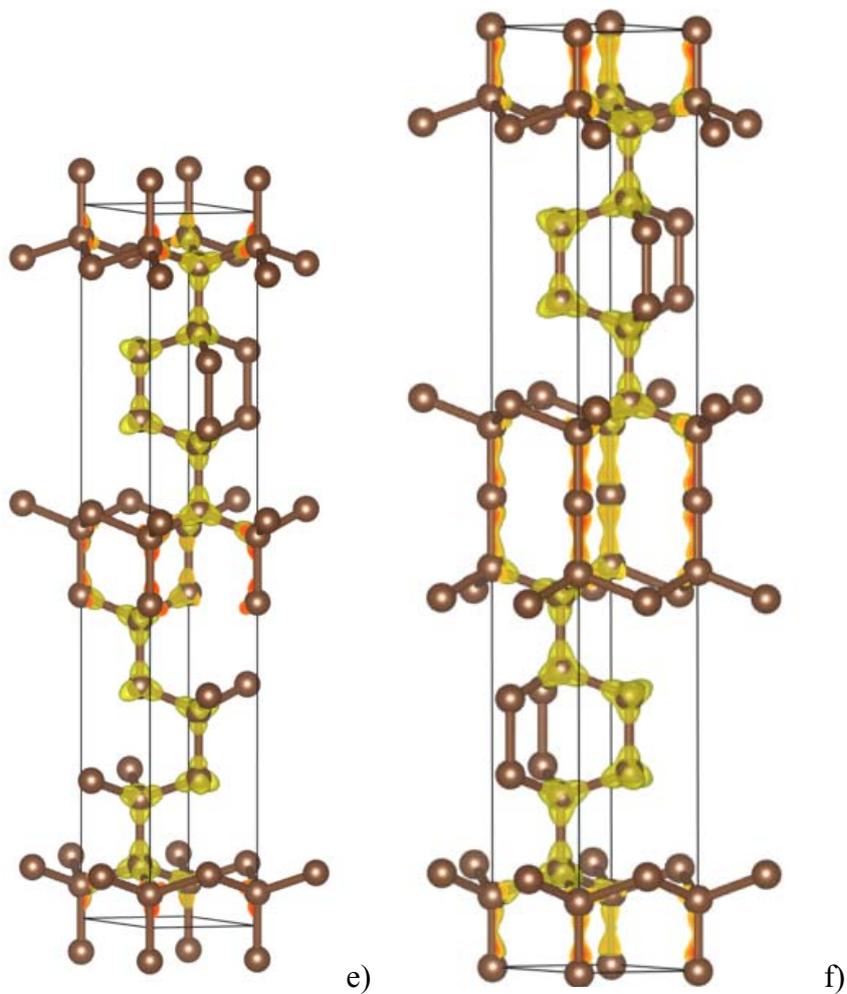
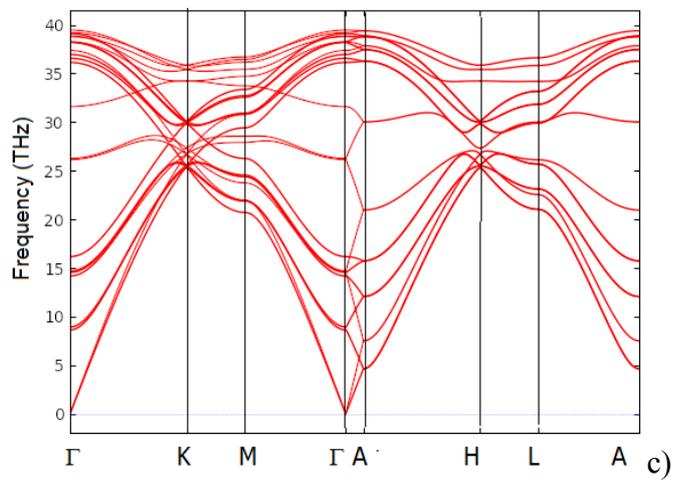
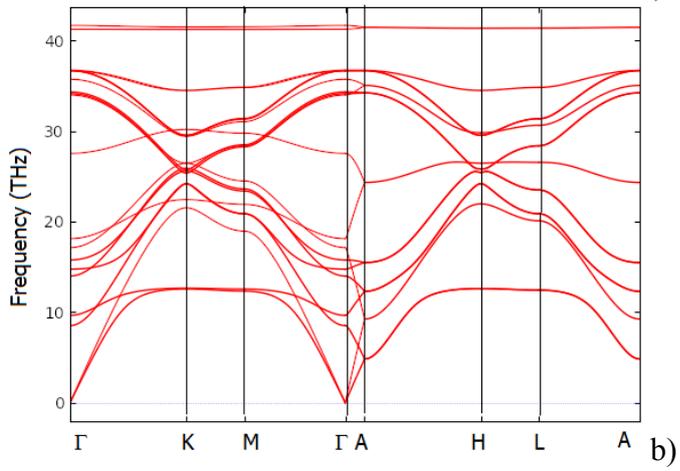
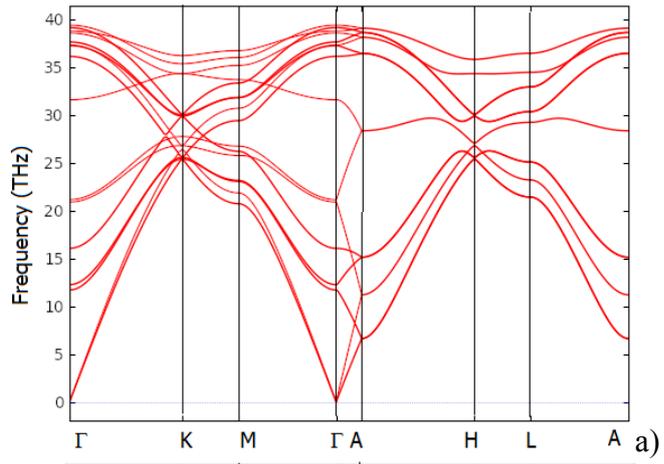
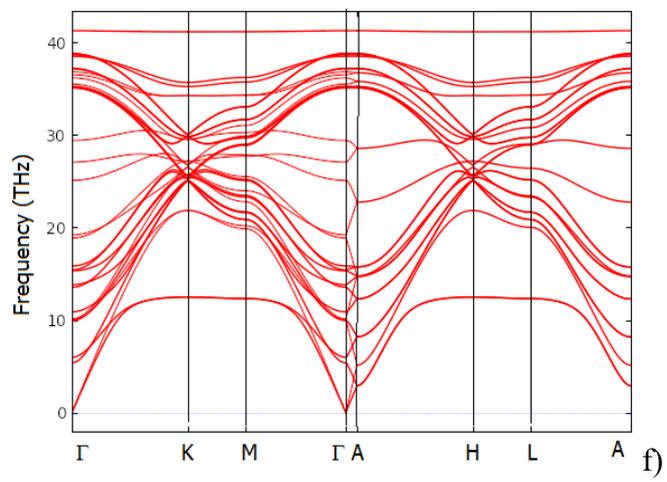
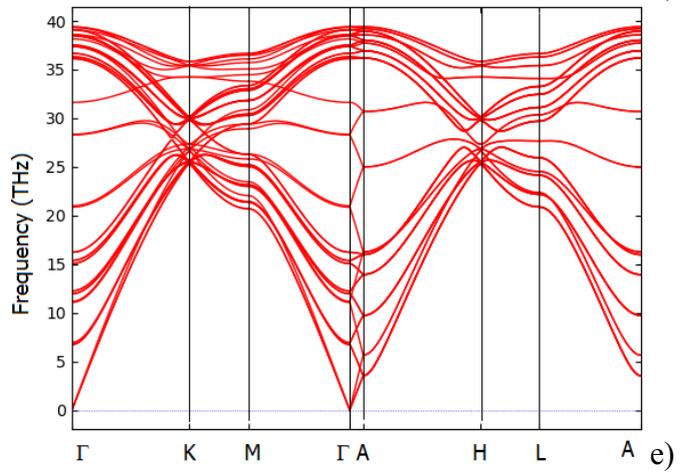
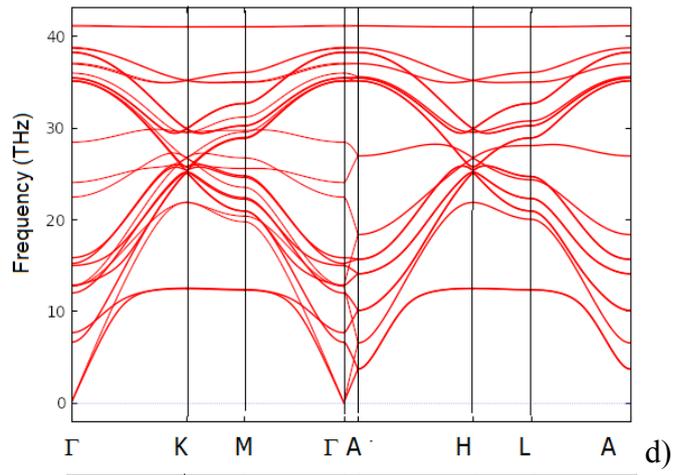
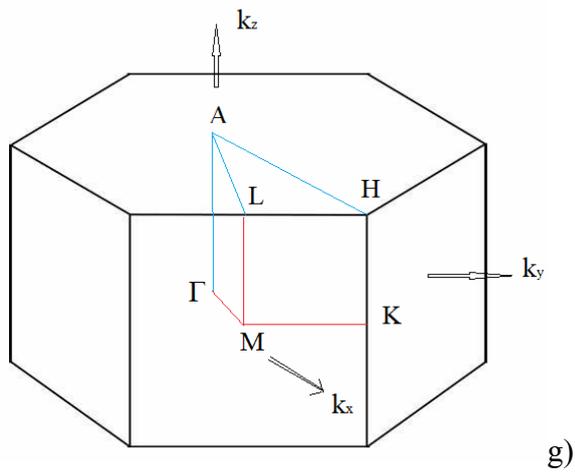


Figure 3. Charge density projections (yellow volumes) of diamond polytypes 4H (C_8), 6H (C_{12}) and 8H (C_{16}), and novel hybrid carbon allotropes: a) 4H, b) C_{10} , c) 6H, d) C_{14} , e) 8H, and f) C_{18} .







g)

Figure 4. Phonons band structures along major directions of the hexagonal Brillouin zone shown in last panel: a) 4H polytype, b) hybrid C_{10} , c) 6H polytype, d) hybrid C_{14} , e) 8H polytype, f) hybrid C_{18} , g) hexagonal Brillouin zone.

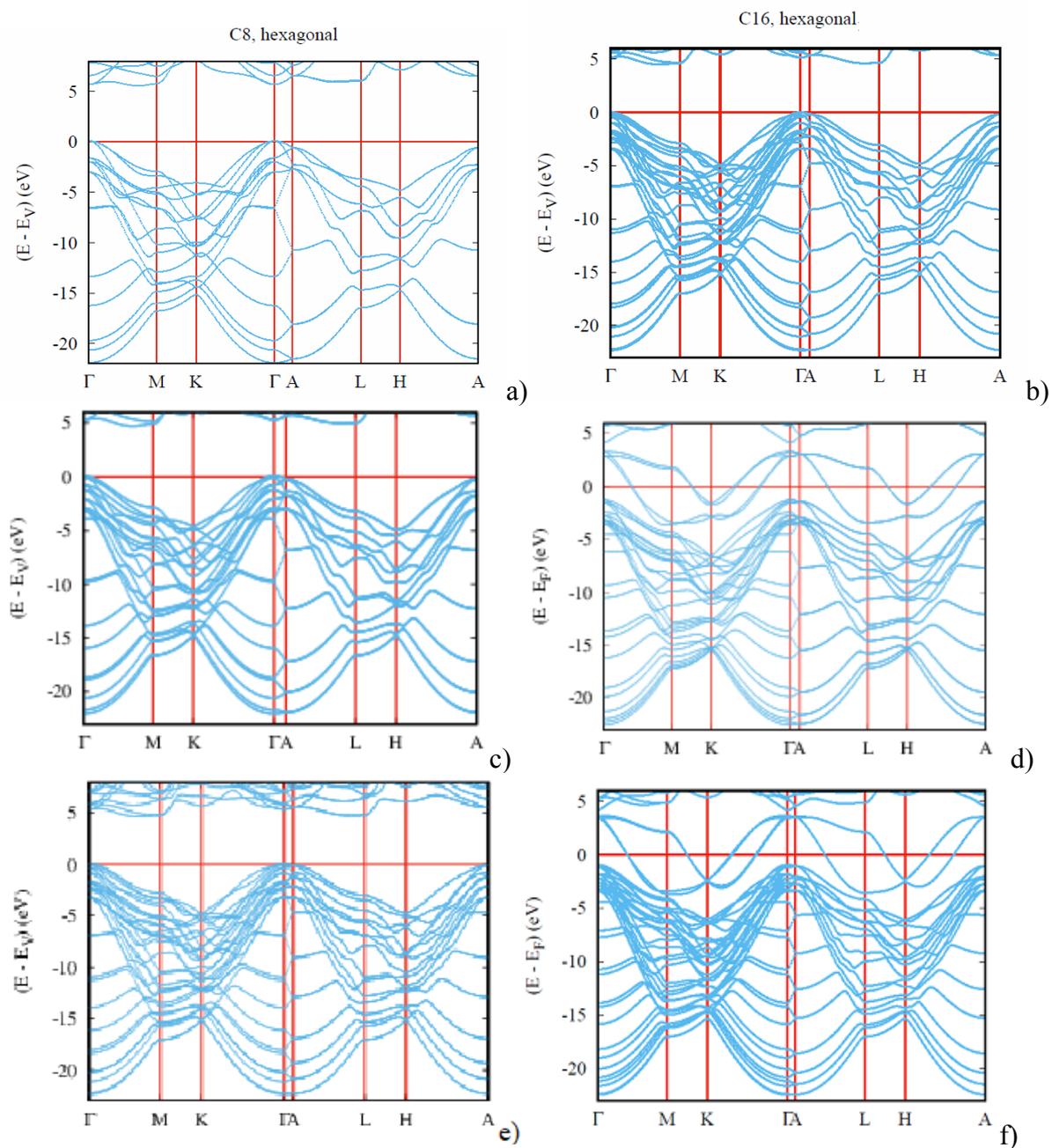


Figure 5. Electronic band structures along major directions of the hexagonal Brillouin zone. a) 4H polytype, b) Hybrid C₁₀, c) 6H polytype, d) Hybrid C₁₄, e) 8H polytype, f) Hybrid C₁₈.

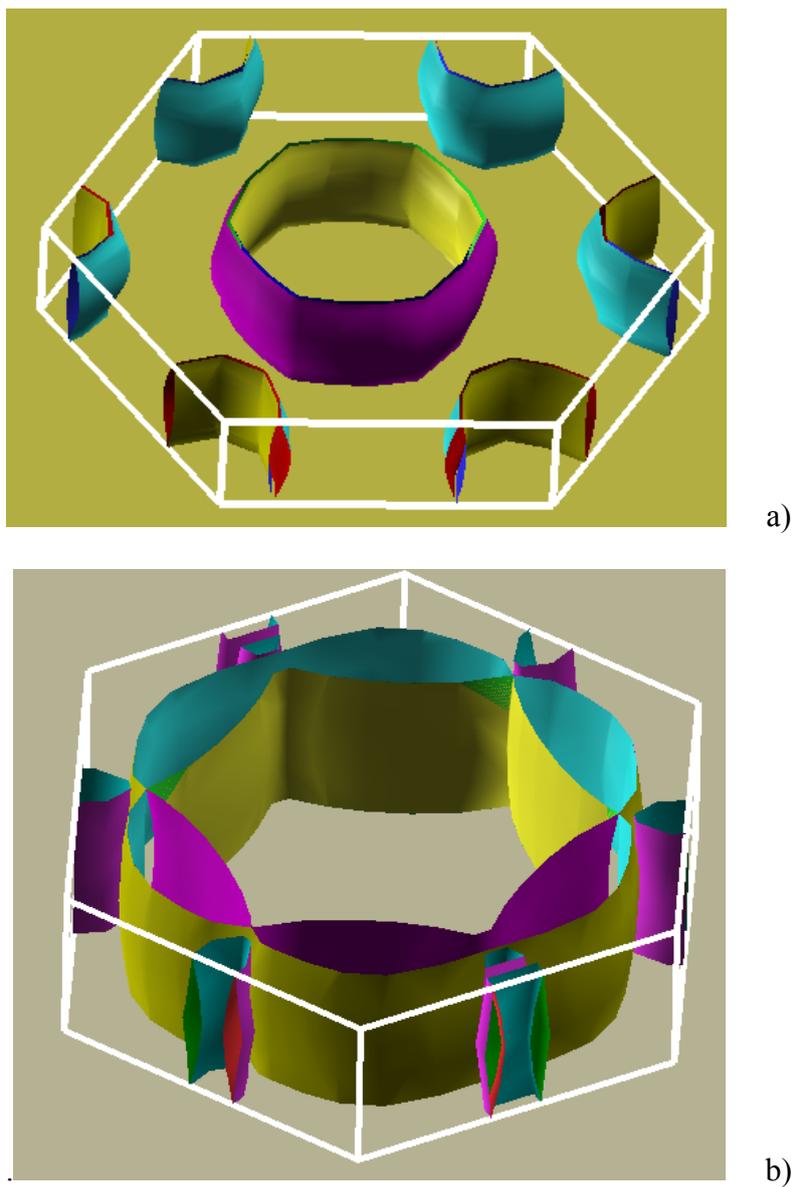


Figure 6. Fermi surface corresponding to the bands crossing E_F of hybrid C_{18} allotrope (a) and Fermi surface for $2 \times 2 \times 1$ supercell of hybrid C_{14} allotrope (b)