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## Structure and electronic properties of graphyne polymorphs formed from 4-8 graphene

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**Abstract.** The structure and electronic characteristics of new polymorphic varieties of graphyne, obtained on the basis of the L<sub>4-8</sub> graphene layer, are investigated by the method of the density functional theory in the generalized gradient approximation. Theoretically, seven types of graphite were built:  $\alpha$ -L<sub>4-8</sub>-,  $\beta$ 1-L<sub>4-8</sub>-,  $\beta$ 2-L<sub>4-8</sub>-,  $\beta$ 2-L<sub>4-8</sub>-,  $\gamma$ 1-L<sub>4-8</sub>-,  $\gamma$ 2-L<sub>4-8</sub>-, and  $\gamma$ 3-L<sub>4-8</sub>-graphyne. However, as a result of geometric optimization, the structure of two graphyne layers ( $\gamma$ 2-L<sub>4-8</sub>- and  $\gamma$ 3-L<sub>4-8</sub>-graphyne) was transformed into a graphene structure. The sublimation energy of the remaining graphite layers is in the range from 6.63 to 6.79 eV per atom. This energy is lower than the sublimation energy of graphene layers, however, it is in the range of sublimation energies characteristic of carbon materials that are stable under normal conditions. The band gap for the graphyne layers is zero or tending to zero, therefore the properties of the layers must be metallic.

### 1. Introduction

Hybrid carbon materials consist of atoms with different hybridisation of electron orbitals. They may belong to one of four basic classes:  $sp+sp^2$ ,  $sp+sp^3$ ,  $sp^2+sp^3$  and  $sp+sp^2+sp^3$  [1]. The most interesting are the  $sp+sp^2$  carbon materials consisting of carbon atoms in two- and three-coordinated states [2-6]. Such compounds have a laminated structure (crystallographic 2D<sub>C</sub>) similar to that of graphene [2] and graphane layers [3]. The  $sp+sp^2$  material structure contains such fragments as carbyne chains with polyyne structure. This is why the  $sp+sp^2$  materials were titled “graphyne” [4]. The graphyne layers may be theoretically obtained from four basic polymorphous species of graphene [5, 6]. However, the graphyne layers obtained from L<sub>6</sub>- and L<sub>4-8</sub>-graphene are expected to be most stable structural species. In our early articles we report the calculations of layers based on L<sub>6</sub>-graphene [5] and on L<sub>3-12</sub>-graphene [6]. In work [5] we show that calculations by semiempirical quantum-mechanical methods do not give unambiguous answer about stability of graphyne layers, while the first-principle methods of the density functional theory solve such tasks quite correctly. This work presents the ab initio calculations of the structure and properties of a number of new polymorphous species of graphyne theoretically simulatable from L<sub>4-8</sub>-graphene.



## 2. Methods

New series of graphyne species may be theoretically obtained from  $L_{4-8}$ -graphene by substituting C-C bonds between  $sp^2$  hybridized atoms with carbyne chains. To obtain  $\alpha$ -polymorphs, carbyne chains should be substituted for all the bonds,  $\beta$ -polymorphs — two bonds of three,  $\gamma$ -structures — one bond. In substituting, fragments of carbyne chain with minimal sizes (only a pair of atoms) were used. As a result, seven basic structural species of graphyne layers were obtained based on  $L_{4-8}$ -graphene. The geometrically optimized structure of laminated compounds was found by the Density Functional Theory (DFT) method [12] in the Generalized Gradient Approximations (GGA) [13] (method DFT-GGA), and also electronic properties and energetic characteristics of the layers were calculated. As the design base, structural characteristics of unit cells determined at the second stage of calculations were used. The geometrical optimization and calculation of the band diagram of the compounds under study were carried out by using program code Quantum ESPRESSO [14]. To estimate the electron density of states for each phase, the  $12 \times 12 \times 12$  set of k-points was used. The wave functions were expanded in the truncated basis set of plane waves. To restrict the basis function set size,  $E_{\text{cutoff}}$  was assumed to be 1 keV. For the geometrically optimized layers, the total specific energy per atom ( $E_{\text{total}}$ ) was also calculated, as well as the band diagram.

## 3. Results and discussion

The DFT-GGA calculations gave such geometrically optimized structures as  $\alpha$ - $L_{4-8}$ ,  $\beta 1$ - $L_{4-8}$ ,  $\beta 2$ - $L_{4-8}$ ,  $\beta 3$ - $L_{4-8}$ , and  $\gamma 1$ - $L_{4-8}$ -graphyne (Fig. 1). Their difference from initial theoretically simulated structures is that the carbyne chain fragments in  $\alpha$ - $L_{4-8}$ ,  $\beta 1$ - $L_{4-8}$ ,  $\beta 2$ - $L_{4-8}$ , and  $\beta 3$ - $L_{4-8}$ -graphyne are bended. The unit cell of  $\alpha$ - $L_{4-8}$ -graphyne contains 16 atoms. There are three possible structural states of atoms in this graphyne layer. The first structural state (1) is for three-coordinated carbon atoms ( $sp^2$  hybridization). The other two states (2 and 3) are for two-coordinated carbon atoms ( $sp$  hybridization). Lengths of the fundamental translation vectors calculated by the DFT-GGA method are  $a = b = 9.726 \text{ \AA}$ . Lengths of the carbon-carbon bonds in the  $\alpha$ - $L_{4-8}$ -graphyne layer possess four different values. The bond lengths were used to calculate the orders  $\chi$  of the C-C bonds. The bond orders are not integer and range from 1.4 to 2.8. This is probably caused by  $\pi$  electron delocalization. Unit cells of the  $\alpha$ - $L_{4-8}$ ,  $\beta 1$ - $L_{4-8}$ ,  $\beta 2$ - $L_{4-8}$ ,  $\beta 3$ - $L_{4-8}$ , and  $\gamma 1$ - $L_{4-8}$  layers contain from eight to 24 atoms (Fig. 1). Table 1 presents the fundamental translation vectors calculated for them. Among the seven graphyne layers theoretically simulated on the basis of  $L_{4-8}$ -graphene, five layers ( $\alpha$ - $L_{4-8}$ ,  $\beta 1$ - $L_{4-8}$ ,  $\beta 2$ - $L_{4-8}$ ,  $\beta 3$ - $L_{4-8}$ , and  $\gamma 1$ - $L_{4-8}$ ) appeared to be stable. Two more layers,  $\gamma 2$ - $L_{4-8}$  and  $\gamma 3$ - $L_{4-8}$ , were transformed into  $L_{4-6-8}$ - and  $L_{4-8}$ -graphene in the process of geometrical optimization.

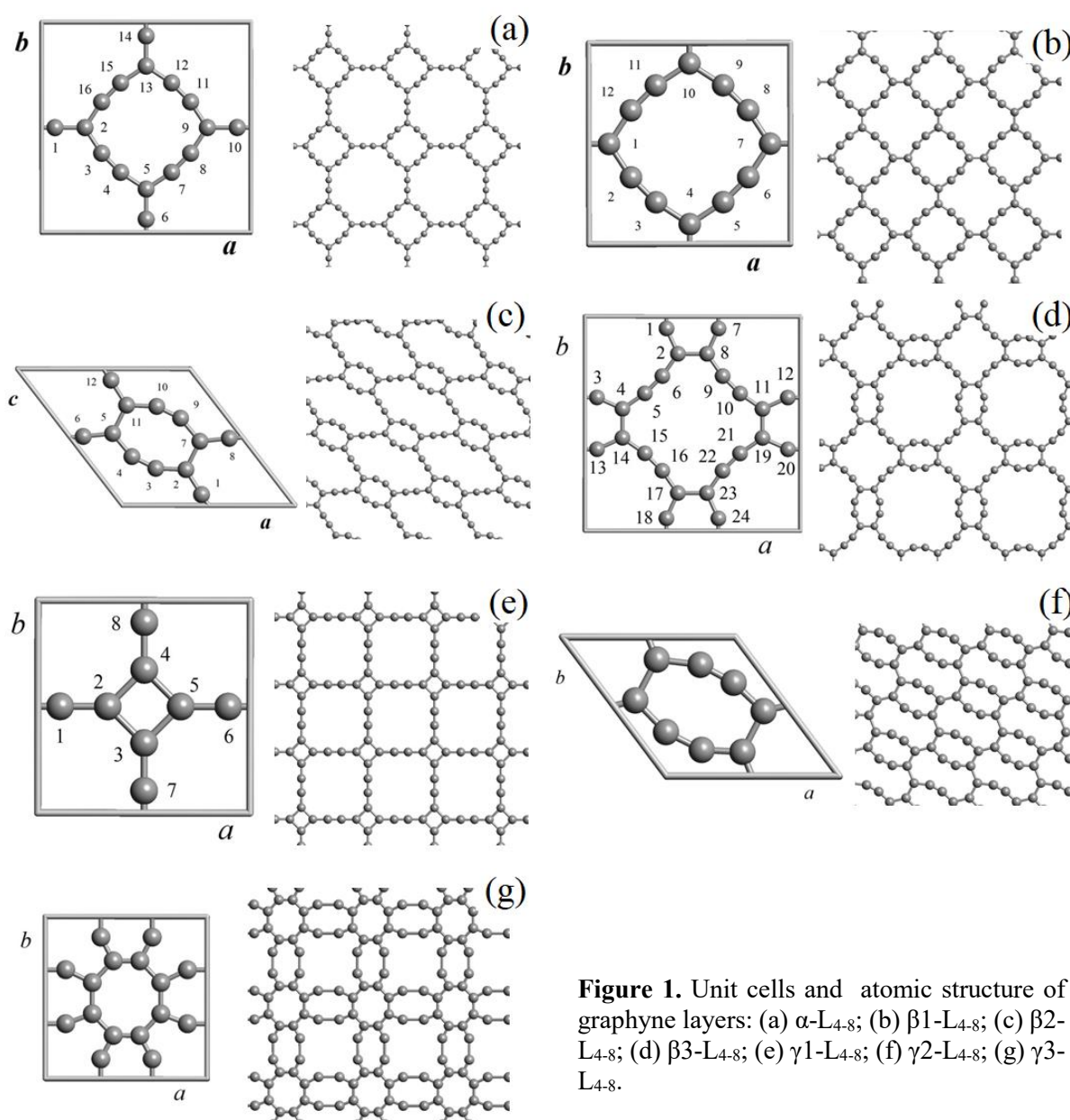
**Table 1.** The structural parameters of the graphene and graphynes of the basic polymorphs, obtained from the  $L_{4-8}$  graphene, namely: number of atoms in the unit cell (N), length of fundamental translation vectors (a, b) and angle between them ( $\gamma$ ), layer density ( $\rho$ ), total energy per atom ( $E_{\text{total}}$ ) and band gap energy ( $\Delta$ ).

Layer	N (atom)	a (Å)	b (Å)	$\gamma$ (°)	$\rho$ (mg m <sup>-2</sup> )	$E_{\text{total}}$ , (eV at. <sup>-1</sup> )	$\Delta$ (eV)	$E_{\text{sub}}$ (eV at. <sup>-1</sup> )	Crystal system
$L_6$ -graphene	2	2.491		120	0.74	-157.32	0	7.76	Hex
$L_{4-8}$ -graphene	4	3.429		90	0.68	-156.78	0	7.22	Tetr
$\alpha$ - $L_{4-8}$ -graphyne	16	9.726		90	0.34	-156.19	0	6.63	Tetr
$\beta 1$ - $L_{4-8}$ -graphyne	12	7.1063		90	0.47	-156.30	0	6.74	Tetr
$\beta 2$ - $L_{4-8}$ -graphyne	12	8.112	8.115	127.6	0.46	-156.25	0	6.69	Mon
$\beta 3$ - $L_{4-8}$ -graphyne	24	10.902		90	0.40	-156.23	0.06	6.67	Tetr
$\gamma 1$ - $L_{4-8}$ -graphyne	8	6.076		90	0.43	-156.35	0	6.79	Tetr

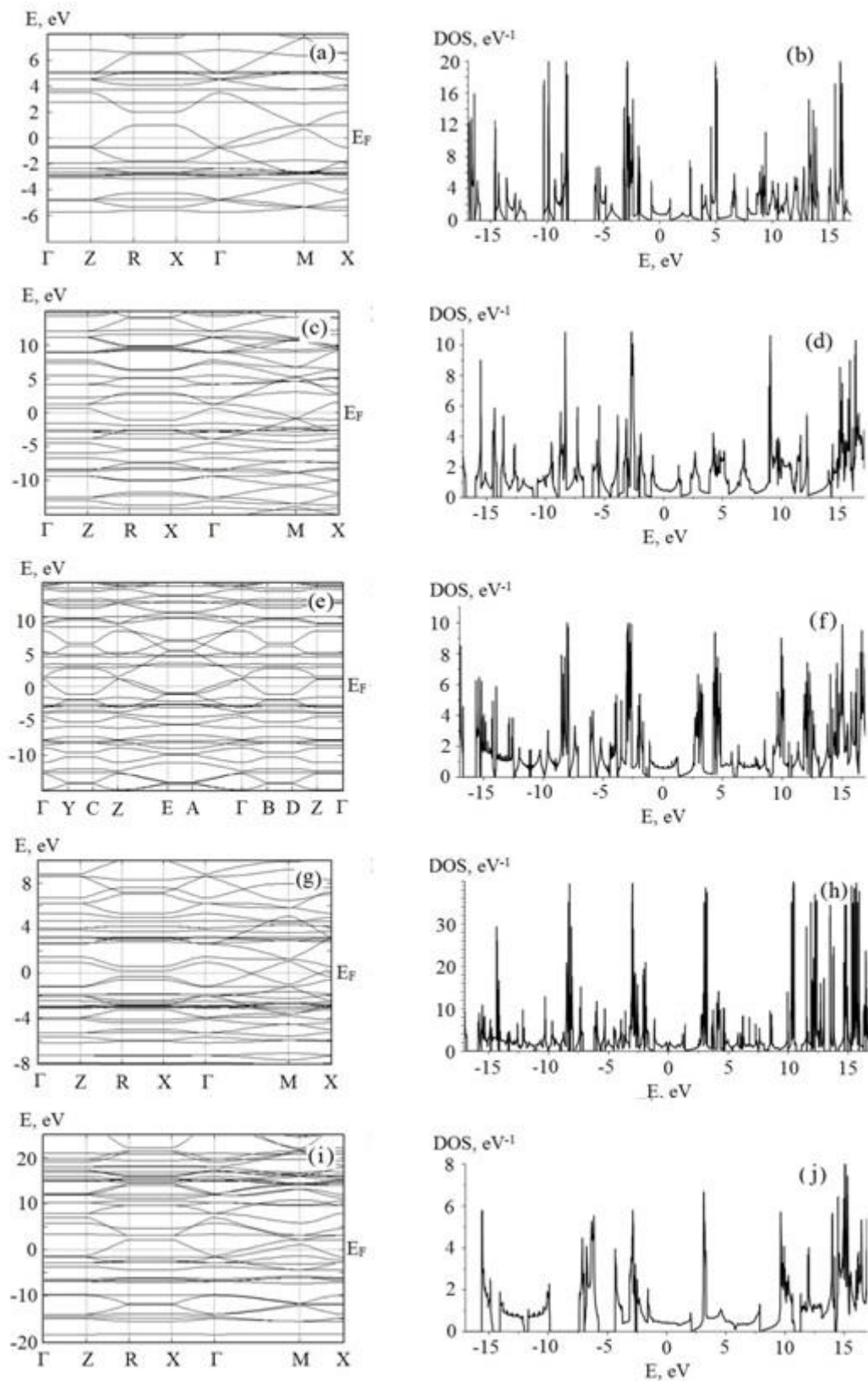
The value of total energy  $E_{\text{total}}$  per atom varies in graphyne layers from -156.19 to -156.35 eV/atom (Table 4.8). Total energies in the  $L_{4-8}$ -graphyne layers are higher than those in  $L_6$ -graphene (-157.32 eV at.<sup>-1</sup>) and  $L_{4-8}$ -graphene (-156.78 eV at.<sup>-1</sup>), and also higher than energies of graphyne layers obtained from  $L_6$ -graphene, but lower than the respective energy in experimentally synthesized fullerene  $C_{20}$ . The

minimal sublimation energy is observed in  $\alpha$ -L<sub>4-8</sub>-graphyne (6.63 eV at.<sup>-1</sup>), the maximal — in  $\gamma$ 1-L<sub>4-8</sub>-graphyne (6.79 eV at.<sup>-1</sup>). The calculations of the band diagram (Fig. 2 a, c, e, g, i) and density of electronic states (Fig. 2 b, d, f, h, j) show that the electronic structure in the vicinity of the Fermi level in  $\alpha$ -L<sub>4-8</sub>-,  $\beta$ 1-L<sub>4-8</sub>-,  $\beta$ 2-L<sub>4-8</sub>-, and  $\gamma$ 1-L<sub>4-8</sub>-graphyne exhibits an overlap between the valence and conductivity bands, thus the density of electronic states is not zero at EF. This shows that those graphynes should exhibit metallic properties. In  $\beta$ 3-L<sub>4-8</sub>-graphyne the band gap 0.06 eV wide is observed near the Fermi level, which is characteristic of semiconductors. Density  $\rho$  of the L<sub>4-6</sub>-graphyne layers varies from 0.34 to 0.47 mg m<sup>-2</sup>, which is significantly lower than that of L<sub>6</sub>-graphene (0.74 mg m<sup>-2</sup>), and L<sub>4-8</sub>-graphene (0.68 mg m<sup>-2</sup>), densities  $\beta$  and  $\gamma$  being close to each other.

New graphyne polymorphs are promising materials for electronics and hydrogen energetic. The possibility to control the graphyne porous structures enables using them also as molecular sieves.



**Figure 1.** Unit cells and atomic structure of graphyne layers: (a)  $\alpha$ -L<sub>4-8</sub>; (b)  $\beta$ 1-L<sub>4-8</sub>; (c)  $\beta$ 2-L<sub>4-8</sub>; (d)  $\beta$ 3-L<sub>4-8</sub>; (e)  $\gamma$ 1-L<sub>4-8</sub>; (f)  $\gamma$ 2-L<sub>4-8</sub>; (g)  $\gamma$ 3-L<sub>4-8</sub>.



**Figure 2.** Bands structure and density of states of graphyne layers: (a, b)  $\alpha$ -L<sub>4-8</sub>; (c, d)  $\beta$ 1-L<sub>4-8</sub>; (e, f)  $\beta$ 2-L<sub>4-8</sub>; (g, h)  $\beta$ 3-L<sub>4-8</sub>; (i, j)  $\gamma$ 1-L<sub>4-8</sub>.

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