Structure and electronic properties of 5-7 graphene

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Abstract. The electronic properties and the geometrically optimized structure of the 5-7 graphene layer were calculated by the methods of the density functional theory in the generalized gradient approximations. The L₅-₇ graphene should have metallic properties, since the density of its electronic states at the Fermi level is different from zero. The sublimation energy is 7.49 eV, which is less than the sublimation energy for the hexagonal graphene layer, but higher than the sublimation energy of such basic polymorphous varieties of graphene as L₄-₈, L₃-₁₂, and L₄-₆-₁₂.

1. Introduction
Polymorphic varieties of graphene differ from hexagonal graphene in that the three-coordinated (sp² hybridized) atoms that make up the graphene layers are located not at the vertices of hexagons, but at the vertices of the polygons having a different number of sides [1,2]. In the structure of the basic polymorphous varieties of graphene, all the atoms are in equivalent structural positions. There can be only four main polymorphs of graphene: L₆, L₄-₈, L₃-₁₂, L₄-₆-₁₂ [2,3]. Existence of an unlimited variety of polymorphic variations of graphene where the atoms are located in more than one structural position is possible [4]. Interest in polymorphous varieties of graphene was caused by the fact that some of them should have semiconductor properties, rather than metallic properties. Formally, graphene polymorphs can be considered as monolayers consisting of topological defects 4, 5, 7, 8, and so on, which replace the hexagons of the usual graphene layer [5]. The stability of defects and the layers consisting of them increase as the difference between the number of sides in the defect and the number of sides in the hexagon diminishes. Therefore, the most stable defects should combine 5-7 topological defects and graphene layers constructed from such defects. In this paper, the structure and electronic properties of one of the structural varieties of the L₅-₇ graphene are studied.

2. The methods of model calculations
Calculations of the geometrically optimized crystal structure, the density of electronic states, and the band structure of the L₅-₇ graphene were performed by the methods of the density functional theory (DFT) [6] in generalized gradient approximations, (GGA) [7]. Calculations of the electronic properties and geometrically optimized structure were performed using the Quantum ESPRESSO software package [8]. An oblique unit cell of a minimal area containing 8 atoms and a rectangular expanded unit cell containing 16 atoms were observed in the calculations (figure 1). The volume distribution of
the electron density was calculated for three-dimensional unit cells corresponding to the stacks of graphene layers with an interlayer distance of 10 Å. This distance ensured the absence of influence of adjacent layers on each other, therefore the calculated structure of the layers and their properties corresponded to the values characteristic for isolated layers. Densities of electronic states were calculated using a set of k-points: $12 \times 12 \times 12$. The wave functions were decomposed along a truncated basis set of plane waves, and the dimension of the set of basic functions was limited to the value $E_{\text{cutoff}} = 1$ keV.

Figure 1. Geometrically optimized structure of the 5-7 graphene layer: (a) crystal lattice; (b) oblique unit cell; (c) rectangular unit cell.

3. Results and discussion
As a result of the calculations, a geometrically optimized structure of the 5-7 graphene layer was found (figure 1a). The choice of various unit cells did not affect the values of the structural parameters. In $L_{5.7}$ graphene there are three structural positions corresponding to atoms number 4, 5 and 7, designated in a rectangular unit cell or atoms number 2, 3 and 1 in an oblique unit cell (figure 1b, 1c). This is one of the main differences between the $L_{5.7}$ graphene and the graphene layers of the main polymorphic varieties $L_{6}$, $L_{4.8}$, $L_{3.12}$ and $L_{4.6.12}$ where all the atoms are in the same structural positions [1-3]. Therefore, 5-7 graphene layer has five different lengths of interatomic bonds ($r_{ij}$) and seven different angles between bonds ($\phi_{ijk}$) characterizing three structural positions of atoms. The calculated values of these structural parameters are given in table 1.

| $r_{ij}$ (Å) | $\phi_{ijk}$ (°) |
|--------------|------------------|
| $r_{4.7}$   | 1.492            | $\phi_{4.7}$ | 130.44 |
| $r_{4.5}$   | 1.413            | $\phi_{4.5}$ | 122.50 |
| $r_{5.10}$  | 1.399            | $\phi_{5.7}$ | 107.06 |
| $r_{2.4}$   | 1.406            | $\phi_{4.5.10}$ | 110.32 |
| $r_{15.16}$ | 1.426            | $\phi_{4.5.6}$ | 139.36 |
|             |                  | $\phi_{13.15.16}$ | 127.35 |

The lengths of the bonds and the angles between them differ from the values characteristic for hexagonal graphene. This indicates a deformation of the $L_{5.7}$ structure compared to the $L_{6}$ structure. The calculation of the total energy per atom showed that for 5-7 graphene, this value is -157.05 eV/atom. The sublimation energy, which was found as the difference between the energy of an atom in a graphene layer and the energy of an isolated carbon atom, was 7.49 eV/atom. This value is less than the sublimation energy of hexagonal graphene (7.78 eV/atom), but higher than the sublimation energy...
of all other major polymorphic graphene varieties described in [3]. This indicates a lower stability of the L_{5,7} graphene compared to hexagonal graphene and a higher stability of the structure of the L_{5,7} graphene compared to other polymorphous graphene varieties.

The values of the unit cell parameters for the rectangular cell are \( a = 7.511 \, \text{Å}, b = 5.893 \, \text{Å} \), and for oblique cells \( a = b = 4.804 \, \text{Å} \). The number of atoms in a rectangular unit cell is 16, the number of atoms in an oblique unit cell is 8. The values of the coordinates of atoms in the unit cells are given in fractions of the vectors of elementary translations and are shown in table 2.

| \( N_e \) | \( x \) (a) | \( y \) (b) | \( N_e \) | \( x \) (a) | \( y \) (b) |
|---------|--------|--------|---------|--------|--------|
| Oblique unit cell of the L_{5,7} graphene |
| 1       | 0.046  | 0.060  | 9       | 0.612  | 0.336  |
| 2       | 0.112  | 0.285  | 10      | 0.547  | 0.560  |
| 3       | 0.112  | 0.836  | 11      | 0.612  | 0.785  |
| 4       | 0.295  | 0.336  | 12      | 0.860  | 0.060  |
| 5       | 0.360  | 0.560  | 13      | 0.795  | 0.285  |
| 6       | 0.295  | 0.785  | 14      | 0.795  | 0.836  |
| 7       | 0.453  | 0.181  | 15      | 0.954  | 0.439  |
| 8       | 0.453  | 0.940  | 16      | 0.954  | 0.681  |
| Rectangular unit cell of the L_{5,7} graphene |
| 1       | 0.121  | 0.121  | 5       | 0.879  | 0.879  |
| 2       | 0.116  | 0.434  | 6       | 0.884  | 0.566  |
| 3       | 0.407  | 0.593  | 7       | 0.593  | 0.407  |
| 4       | 0.566  | 0.884  | 8       | 0.434  | 0.116  |

The results of calculations of the band structure and density of electronic states of the L_{5,7} graphene are shown in figures 2 and 3, respectively. The choice of the unit cell did not have a significant effect on the results - the dependence of the density of electronic states on energy is practically identical for orthorhombic and monoclinic unit cells. This indicates the correctness of the results obtained. It can be seen from the graphs that, at the Fermi energy level, the density of electronic states is different from zero - there is no band gap and, therefore, the 5-7 graphene layer should have metallic properties. The density of electronic states at the level of the Fermi energy in the L_{5,7} graphene turned out to be non-zero, so that there is a significant overlap of the valence and conduction bands, and not only their tangency in hexagonal graphene.

![Figure 2](image_url)

**Figure 2.** Band structure of the L_{5,7} graphene layer: (a) orthorhombic unit cell (b) monoclinic unit cell.
4. Conclusions

Thus, as a result of calculations of the structure and electronic properties of the new polymorphic variety of 5-7 graphene, it was established that the sublimation energy of this structure turned out to be lower than that of hexagonal L₆ graphene, but higher than the sublimation energy of all other major polymorphic varieties of graphene. This indicates a high degree of stability of this structural variety and the possibility of its experimental synthesis. 5-7 graphene does not have a band gap at the Fermi energy level and must have metallic properties.

References

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Figure 3. Density of electronic states of the L₅₋₇ graphene: (a) orthorhombic unit cell (b) monoclinic unit cell.