

**ELECTRONIC STRUCTURE AND ITINERANT MAGNETISM  
OF HYDROGENATED GRAPHENE NANOFILMS**

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**Don State Technical University, Rostov-on-Don, Russian Federation****Abstract**

The peculiarities of spin-polarized electronic structure of multilayer graphene nanofilm (4-GNL:H) within the framework of Kohn — Sham approximation were studied in the present work. The calculated band structure and spin-resolved electronic energy spectrum of the 4-GNL:H system were correlated with experimental UPS and XANES spectra of thin hydrogenated *a*-C:H films. As the band structure calculations show there is a dimensional quantization of energy spectrum in the 4-GNL:H system, and the energy gap of 0.11 eV appears in the spectrum. The self-consistent calculations also predict the existence of itinerant magnetism in the system, conditioned by hydrogen chemisorption

**Keywords**

*Graphene nanostructures, electronic structure, density functional theory, itinerant magnetism*

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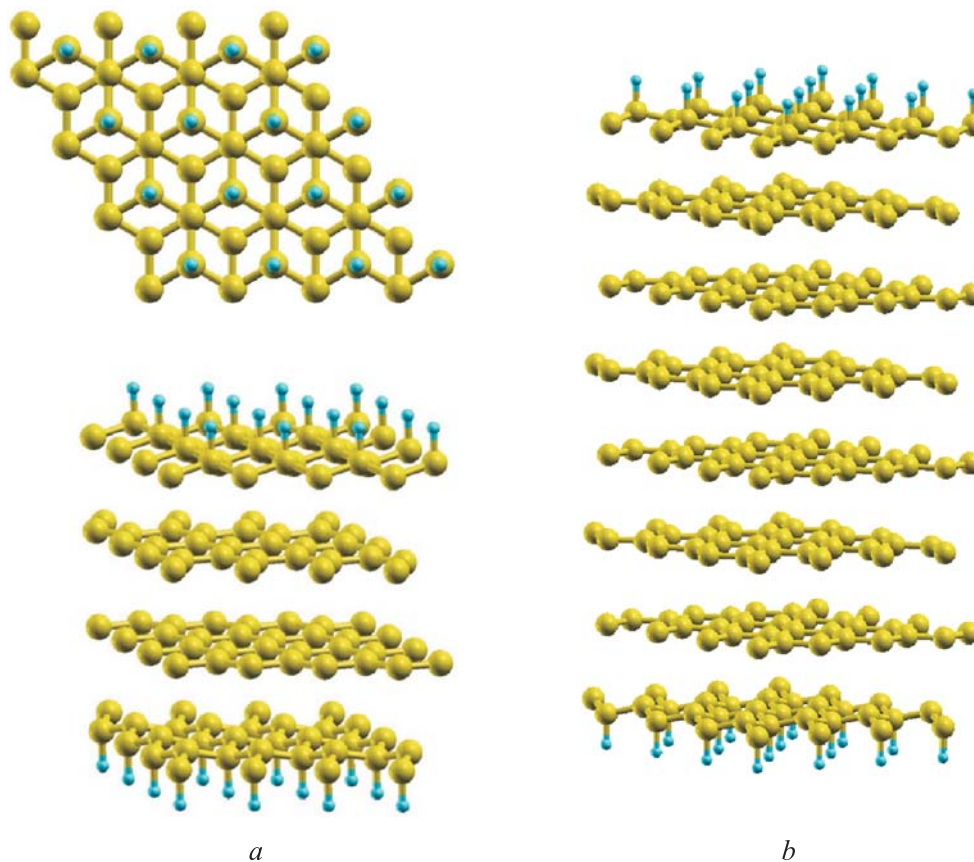
**Introduction.** In the last decade, magnetism in graphene nanostructures has been widely discussed in some papers. [1, 2]. The magnetic properties of these nanostructures are associated with noninteracting charge carriers [1], i.e., with the presence of unpaired electrons. According to the work [2], the presence of the latter leads to a weakening of the covalent bond in aromatic molecules, which is associated with an increase in the length of the C–C bond with respect to the classical  $\pi$ -electron systems. This is interpreted as a violation of spin symmetry in graphene [2]. The experimentally observed ferromagnetism of some graphene nanostructures is retained at room temperature and up to 500 K [3].

Graphene magnetism has been studied in a number of studies using the Hubbard model, the Hartree — Fock method, and the density functional theory [2, 4]. The presence of band magnetism in graphene caused by defects

formation and chemisorption was studied in the works [1, 5, 6]. In several theoretical papers, the induction of magnetism in graphene caused by interaction with a magnetic substrate has been studied [7, 8]. The existence of magnetic ordering at the edges of graphene is assumed in the works [9, 10]. Usually, the ferromagnetic properties of these structures are associated with the presence of spin asymmetry of valence electrons, which is realized by two mechanisms: 1) impurities of other elements; 2) quasi-regular defects of the carbon structure (for example, graphene nanoribbons (GNR)) [9]. The boundary geometry is responsible for the spin density asymmetry at the GNR edges, which is confirmed by the results given in the works [10, 11]. As exemplified by ZGNR/h-BN(0001) heterostructures, the spin magnetic moments (MM) of  $0,27\mu_B$ , are induced at the edges, which is more than an order of magnitude higher than that of other carbon atoms. The authors of [10, 11] attributed the nature of magnetism to the violation of the symmetry breaking of the sublattices A and B of graphene caused by the deformation of the C–C bond length at the edges of the nanoribbon. It is known [12] that the magnetic state of graphene nanoribbons is characterized by a lower energy than the nonmagnetic state. When studying the GNR band structure, there are flat bands in the vicinity of the Fermi level for both electron subsystems (spin up, spin down). The latter reveal the asymmetry of the spin density of valence electrons. The quantum confinement plays an important role in inducing the orbital MM in graphene nanostructures [9, 11].

In this paper, we studied the multilayer hydrogenated graphene films  $a$ -C:H. A nanostructure consisting of four layers of graphene is proposed, the outermost of which are hydrogenated along one of the sublattices (A or B). In this case, localized electron states appear in the electron spectrum in the vicinity of the Fermi level for both spins. The induction of MM on hydrogen and carbon atoms is observed. However, at present there is no information on the nature of the induced magnetism and the nature of the spin density asymmetry of valence electrons in graphene nanostructures. In this connection, an attempt has been made to study, from first principles, the asymmetry of the spin density of electrons and its correlation with the appearance of magnetism in graphene nanostructures using the example of multilayer graphene nanofilms (4-, 8-GNL:H), the outer ones of which are hydrogenated on one of the sublattices.

**Model and calculation methods.** As a computational model, graphene nanofilms in Bernal packing (ABAB) containing four layers are considered. The upper and lower sheets of graphene have one-sided hydrogenation of the sublattice A of graphene, and the sublattice B of graphene is not hydrogenated. A film model is also built to match the results 8-GNL:H, consisting of eight layers (Fig. 1). The thickness of 8-GNL is 25 Å, and thickness of 4-GNL is 13 Å.



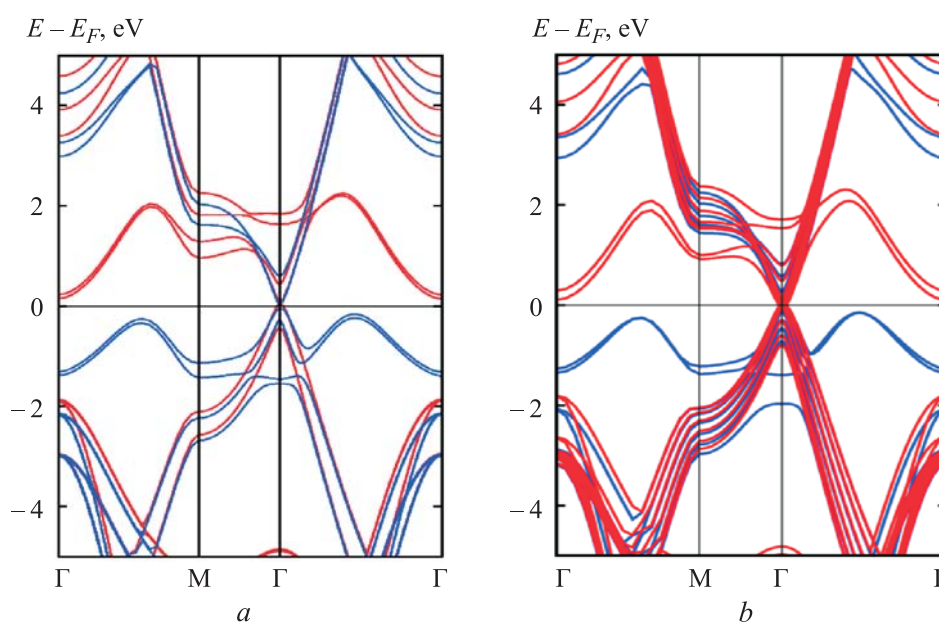
**Fig. 1.** The analytic model of graphene nanofilms 4-GNL:H (*a*) (top and side view) and nanofilms 8-GNL:H (*b*)

Calculations of the atomic and electronic structure were performed with the Kohn — Sham approximation using pseudopotentials and decomposition of crystalline orbitals in a plane wave basis. The essence of the method is to build effective atomic potentials for the system under study, taking into account the interaction of the ionic core with valence electrons for which the crystal orbitals do not contain knots and can easily be represented in the plane wave basis. Then the Kohn — Sham equations are solved self-consistently using the generalized gradient approximation for the exchange-correlation interaction [13, 14]. As a result of the calculation, the electron density distribution in the system under study is found. A software package *QUANTUM ESPRESSO* [15] was used as a tool for numerical simulation, which has established itself as a reliable open-source computing system with a large set of exchange-correlation functionals. In this work, we used the exchange-correlation functional with the correction to take into account the dispersion interaction in the form PBE-D2 [10]. The cut-off energy of 340 eV was used. To integrate the flat Brillouin zone, we used a

grid of 96 points in the irreducible part. To construct the band structure along the directions of high symmetry, the energy eigenvalues were calculated for 200 points in the Brillouin zone. The convergence of the total energy of the cell was provided to  $10^{-4}$  eV / cell. Calculations of the band spectrum and the partial density of electronic states are performed in a spin-unrestricted version.

**Electronic structure.** After performing the structural relaxation procedure, the vertical distance between the first and second (third and fourth) sheets of graphene was  $d_{12} = 3,13$  Å, and between the inner sheets on average was  $d = 3,2$  Å. We note that the hydrogenation of the outer sheets of graphene is accompanied by deformation of the C–C bonds of 2,8 %. The latter leads to a violation in them of the symmetry of the sublattices A and B of graphene, and also to the stratification in the direction (0001) by  $\Delta = 0,34$  Å. C–H length  $d_{C-H} = 1,16$  Å.

The band structure of graphene nanofilms for electronic subsystems with spin up and spin down is shown in Fig. 2. The Dirac cone in the 4-GNL: H system is shifted by  $\Delta E_F = \pm 110$  meV relative to the Fermi level, the electronic subsystem with spin-up is experiencing a downward shift, and the subsystem with spin-down is experiencing shifting upward. The energy gap is more than 110 meV for both electronic subsystems. In the 8-GNL:H nanofilm, the situation in the vicinity of the Fermi level changes. For both spin subsystems, the



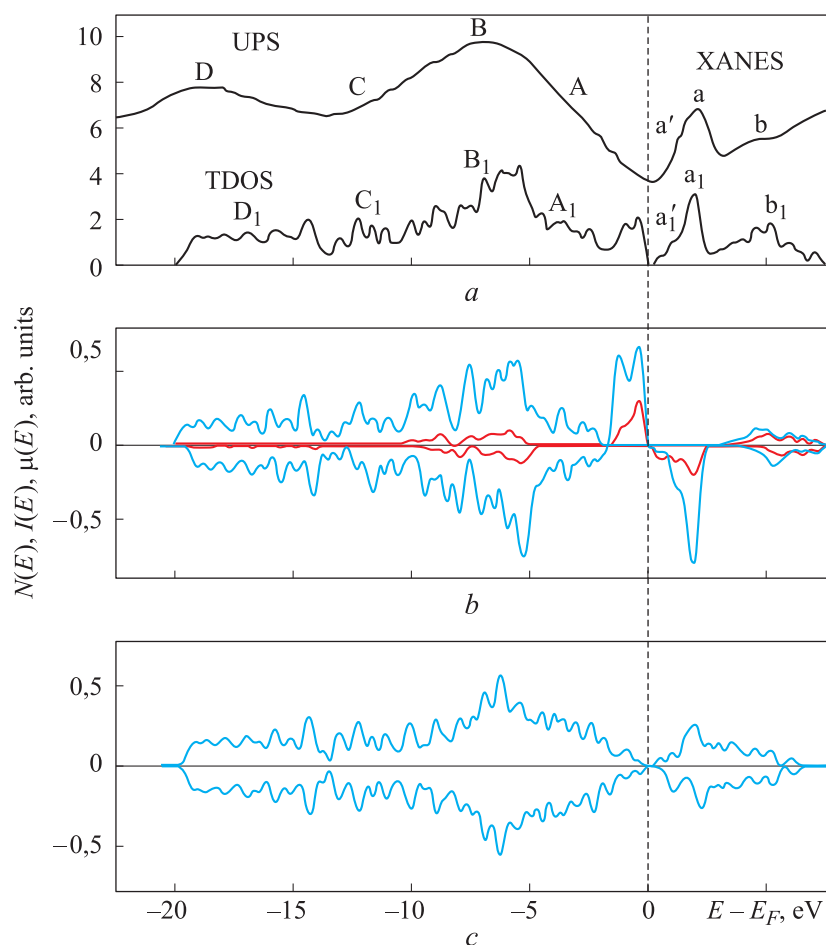
**Fig. 2.** Calculated band structure 4-GNL:H (a) and 8-GNL:H (b) for both spins (blue and red curves match spin up and spin down)

forbidden gap is absent, and the Dirac cone remains unbiased. Thus, the appearance of a gap in a thinner 4-GNL:H nanofilm can be associated with the size quantization of the energy spectrum. It should be noted that in the band spectrum of the 4-, 8-GNL:H systems there are, so-called defect bands located in the range of energy values  $-2-0$  eV and  $0-2$  eV, moreover, these bands are completely spin-polarized, that is, the filled states correspond only to one orientation of the spins (spin up) and the unfilled defective states to the opposite direction (spin down). The appearance of defect bands is associated with the chemisorption of hydrogen on one of the sublattices, as a result of which the charge distribution of  $\pi$ -electrons and the spectrum of carbon  $2p_z$ -orbitals change.

To compare the obtained calculated results with the experiment, we selected the X-ray photoelectron and absorption spectra of hydrogenated carbon films obtained by decomposition of ethylene in a DC glow discharge [17, 18]. As a result of annealing at a temperature of 500 °C the initially amorphous structure of these carbon films gradually changes to graphite-like, and the concentration of hydrogen in them is significantly reduced. Local electron density of states for the first two graphene monolayers, total density of states (TDOS) of the system 4-GNL:H, as well as the TDOS mapping for the system 4-GNL:H with the ultraviolet photoelectron spectrum of the top of the valence band (UPS) [17] and the near region of the K-absorption edge of amorphous hydrogenated carbon films of type *a*-C:H are presented in Fig. 3 [18].

The combination of electron energy spectra (TDOS) for a 4-GNL:H graphene nanostructure with the UPS and XANES spectra was performed at peaks with energies of  $-7.0$  and  $1.8$  eV. The structure of the valence band of the 4-GNL:H system contains two broad bands B and D and satisfactorily reflects the van Hove features in the ultraviolet photoelectron spectrum of *a*-C:H hydrogenated carbon [17].

The calculated electron energy spectrum (TDOS and PDOS) allows determining the A and C bands that are not observed on the experimental spectrum due to insufficient resolution, which is 1.2 eV [17]. The widths of the marked bands A, B, C, and D were 2.4, 6.7, 2.6, and 6.5 eV, respectively. The top of the valence band (band B) is mainly formed by  $2p$  states and small contributions of  $2s$  states of carbon and hydrogen atoms. Along with the good agreement between the features (A, B, C, D, a', a, b) of experimental UPS [17] and XANES [18] spectra in *a*-C:H films and the calculated spectrum (TDOS curve) of carbon in 4-GNL, there is a difference around the Fermi level. Thus, in the calculated spectrum on the TDOS and PDOS curves (first layer), there is a doublet of the density of occupied electron states with energies of  $-0.9$  and



**Fig. 3.** Total DOS 4-GNL (a) per supercell, local partial 2*p*-DOS of carbon (blue lines) and 2*s*-DOS hydrogen (red lines) of the first layer (b) and carbon of the second layer (c) for both spins (UPS [17] and XANES spectra [18] of the amorphous hydrogenated carbon films a-C:H)

-0.4 eV, which is not observed in the UPS spectrum [17]. This doublet on the PDOS curve is formed mainly by the C2*p* and H2*s* states of the electronic subsystem with a spin-up sublattice A of graphene in the first layer (Fig. 3, b). In particular, the sublattice A of graphene interacts with hydrogen. The contribution of C2*p* electrons prevails over the contribution of H2*s*-electrons in a ratio of 2.5:1. In addition, there is a mixing of these electronic states, which indicates their hybridization. According to the authors of the work, the reorganization of the electronic structure of carbon atoms of the graphene sublattice interacting with hydrogen atoms is responsible for the appearance of this doublet.

As a result, the C–H interactions are lost, firstly, the symmetry of the sublattices (A and B) of graphene, as indicated by the deformation of the C–C

bond length by 2.8 %; secondly, the symmetry of the spin density of the valence states of C2p electrons (see Fig. 3, b). No similar doublet is observed on the 2pDOS curve of the second graphene layer. For a spin-down electron subsystem, localized free electron states are observed at an energy of 1.8 eV. This peak is formed by unoccupied C2p and H2s states of the electronic subsystem with spin down of the first layer (see Fig. 3, b). In this case, the contributions of C2p and H2s electrons are determined by the ratio 3:1.

**Itinerant magnetism.** The model of the 4-GNL:H system is constructed so that one of the graphene sublattices is bonded with hydrogen. As the calculation in the paramagnetic state shows, the 4-GNL:H system is characterized by a half-filled band of defective states that crosses the Fermi level, and a peak of the density of electronic states is noted at the Fermi level. According to the Stoner model, ferromagnetic ordering may occur in such a system, which lowers the total energy of the system due to the exchange interaction. In addition, according to the second Lieb theorem in the Hubbard model, in the case of a bipartite lattice that graphene has, any violation in the balance of electrons belonging to different sublattices should lead to the ground state of the system with a resulting spin number of 1/2 [19]. In the case of the 4-GNL:H system, electrons belonging to the same graphene sublattice participate in the formation of the  $sp^3$  chemical bond. Thus, the exposure of ferromagnetic properties in this system is explained in the framework of the Stoner model of band magnetism. Simulation of the thermal distribution of electrons using Fermi — Dirac statistics also showed that band magnetism in the 4-GNL:H system can exist at relatively high temperatures (over 300 K). The occupation of atomic orbitals was analyzed and the effective charges and local magnetic moments at the 4-GNL:H atoms were calculated (Table).

**Magnetic moments and effective charges on carbon and hydrogen atoms in a 4-GNL:H graphene nanostructure**

Layer number	Layer atoms	Magnet moment $\mu_B$	Effective charge $e$
–	H	0.23	0.1
1A	C	–0.1	–0.1
1B		0.84	0.1
2		0	0
3		0	0
4B		0.84	0.1
4A		–0.1	–0.1
–	H	0.23	0.1

Analysis of the data in the table makes it possible to note the existence of charge transfer from hydrogen atoms to carbon atoms of graphene sublattice A in the first and fourth layers. As a result, a negative charge of  $-0,1e$  is accumulated on carbon atoms interacting with hydrogen. On the carbon atoms of the sublattice B of graphene a positive charge of  $0,1e$  occurs. The carbon atoms of the sublattice A of graphene are induced by MM  $-0,1\mu_B$  spin down. As expected, the maximum MM is induced on the carbon atoms forming the sublattice B of graphene, and is  $0,84\mu_B$ .

**Conclusion.** A model of 4-GNL:H graphene nanofilms is proposed and the features of their atomic and electronic structures are studied on the basis of the pseudopotential method in the framework of the density functional theory. Calculations showed that the proposed nanofilms have interesting electronic properties. In particular, the presence of energy gap with a width of more than 0.1 eV in the electron energy spectrum is shown. Moreover, due to the chemisorption of hydrogen on the surface of 4-GNL:H nanofilms, band ferromagnetism can occur, which exists up to room temperature values. These properties of the 4-GNL:H system, along with the asymmetry of the directions of shifts of the Dirac cone for electronic subsystems with spin up and down, allow to assume the promise of the proposed nanofilms in spintronics devices.

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	<p>В Издательстве МГТУ им. Н.Э. Баумана вышло в свет учебное пособие автора</p> <p><b>И.Ю. Савельевой, И.В. Станкевича</b></p> <p><b>«Математическое моделирование процессов теплопроводности методом конечных элементов»</b></p> <p>Приведены формулировки стационарных и нестационарных задач теплопроводности. Рассмотрены основные особенности построения численного решения этих задач в рамках конечно-элементной технологии.</p> <p>Для студентов 3-го и 4-го курсов факультета «Фундаментальные науки» МГТУ им. Н.Э. Баумана, изучающих дисциплины «Уравнения математической физики», «Методы вычислений», «Математическое моделирование», «Прикладные пакеты инженерного анализа», «Математические модели механики сплошной среды» и выполняющих соответствующие курсовые работы. Может быть полезно студентам старших курсов других факультетов, изучающим численные методы решения краевых и начально-краевых задач.</p> <p><b>По вопросам приобретения обращайтесь:</b> 105005, Москва, 2-я Бауманская ул., д. 5, стр. 1 +7 (499) 263-60-45 press@bmstu.ru <a href="http://baumanpress.ru">http://baumanpress.ru</a></p>
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