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MAGNETISM OF GRAPHENE WITH VACANCY CLUSTERS

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Abstract. Graphene, a plane object composed of carbon atoms, is a perspective material for nanoelectronics and spintronics because of its unique electron and magnetic properties. It was found that graphene reveals spin polarization effect, i.e. its magnetic features increase when crystal defects (vacancies and clusters of vacancies) are introduced. Systematic analysis is performed by *ab initio simulation* with the use of VASP program complex in order to state spin polarization dependence of graphene on the number vacancies in a cluster and on a cluster configuration.

1. Introduction

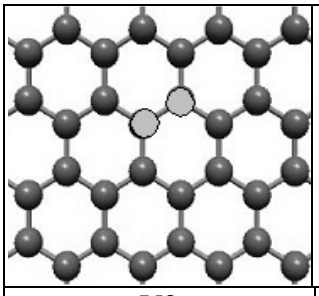
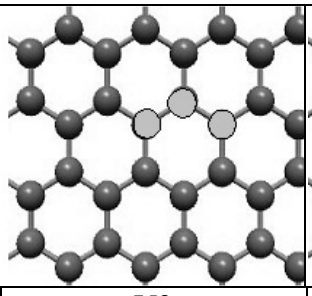
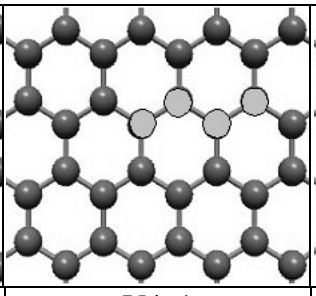
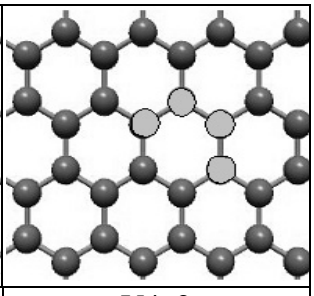
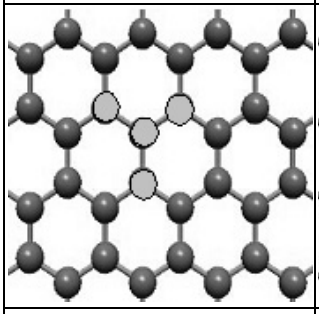
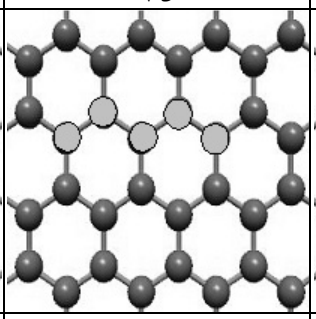
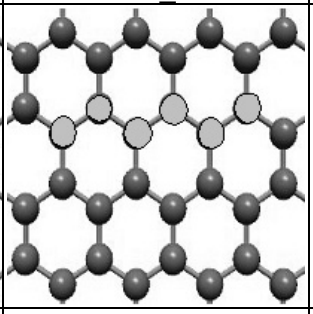
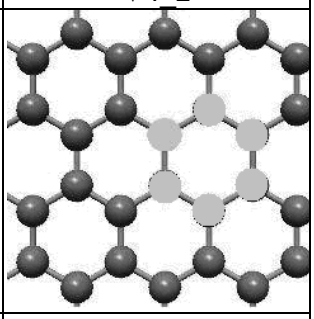
A synthesis of strictly two-dimensional crystals composed of carbon atoms (graphene) [1] is promising a wealth of new phenomena and possible applications in technology and industry [2]. The observation of anomalous transport properties, and, most exciting, the recent discovery of substantial field effect and magnetism at room temperature allows one to envisage graphene as a reasonable replacement of nanotubes in electronic applications, see, e.g. [3-5]. Most recently a novel carbon composite structure consisting of graphene multi-layers and aligned multi-walled carbon nanotubes has been discovered [6]. The new composite structure is expected to have excellent electrical and thermal properties, and therefore is likely to find many applications in electronics.

In this contribution we have studied the effect of non-magnetic impurities (vacancies) on the revealing magnetism in graphene by ab initio simulation with the use of VASP program complex [7, 8]. Different configurations of the system "Grahpene + vacancy cluster" are interesting (see Table 1). These configurations are differed by number and array of vacancies forming a cluster.

Consider briefly previous investigations. *Ab initio* VASP simulation of V1–configuration was done in [9]; the results are shown in Fig. 1. Densities of States (DOS) pictures confirm that the states "spin up" (spin↑) and "spin down" (spin↓) for V1–configuration are asymmetric near the Fermi level; this is the reason of spin state splitting and spin polarization in the "impurity" zone. A forbidden energy zone in graphene with a vacancy is absent.

Ab initio simulation of the system of 128 atoms in graphene with a monovacancy was presented in [10]. It was shown that V1–configuration was relaxed due to Jahn-Teller deformation mechanism [11]. As a result, atoms 1 and 2 (Fig. 2a) were displaced 0.14-0.17 Å from their initial position forming a pentagon structure; atom 3 has moved 0.18 Å out of the graphene plane (Fig. 2b). The charge density distribution near the vacancy indicates increasing the charge density between atoms 1 and 2 and forming a weak covalent bond. The base state is spin polarized (the magnetic moment equals 1.04 μB). It was also studied influence of the distance between vacancies on electronic characteristics. It was shown that nearby vacancies behave independently, when the distance between them equals 7 Å or more. The magnetic moment changed in a non–monotonic way depending on the distance between vacancies. In work

Table 1. Possible configurations of the "Graphene + vacancy cluster" system and their designation.

			
V2	V3	V4_1	V4_2
			
V4_3	V5	V6_1	V6_2

Here V2, V3, V4, V5 and V6 are bi–, tri–, tetra–, penta– and hepta–vacancy clusters respectively. Configuration V1 (monovacancy) is very simple and is not shown in Table 1.

[12] the results of V1–configuration simulation by density functional theory (program SIESTA) were given. It was found that the fractional magnetic moment for V1–defect existed. The magnetic moment equals 1.15 μB for the least distance between defects and 1.45-1.53 μB for greater distances.

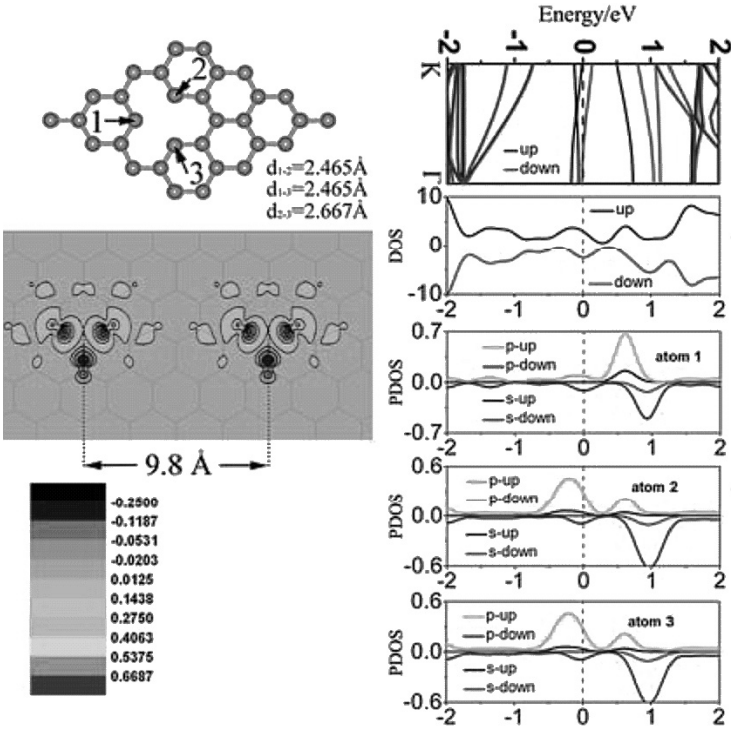


Fig. 1. Distribution of spin density, energy zones, DOS and PDOS for a V1–configuration [9].

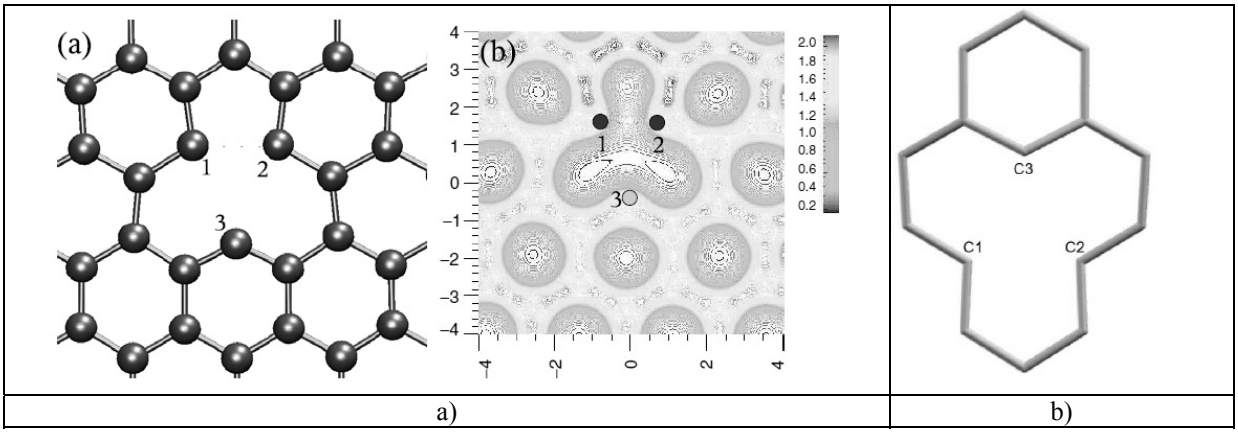


Fig. 2. Results of *ab initio* simulation for a V1–configuration [10]:
a) initial and relaxed (with image of charge density distribution in e/Å ^{3});
b) Jahn-Teller deformation.

Spin polarization near vacancies for V1, V3 and V4–configurations was calculated in a tight binding approximation without atomic relaxation [13]. It was found that magnetic moment was localized near a vacancy cluster.

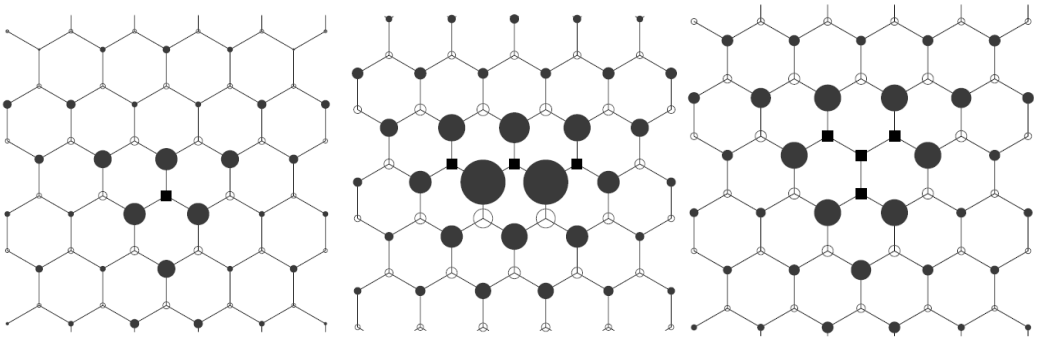


Fig. 3. Relative image of spin polarization near vacancies for V1, V3 and V4–configurations [13] .

Magnetism of big vacancy complexes was investigated [14] with the use of VASP code (Fig. 4). Ferromagnetic state was characteristic for configuration (a), but configurations (b) and (c) were antiferromagnetic. Magnetic moments were concentrated on the defect edge and faded with removing from the edge (Fig. 4d). The magnetic moment at the edge was increased with a vacancy (Fig. 4d, insertion).

Local spin polarization for planar V6_2 (a) and V4_2–configurations was investigated in [9] (Fig. 5). Calculated local magnetic moments were 5.54 and 1.97 μB respectively.

Thereby the results of studies by different methods with the use of different size crystallites without and with preliminary relaxation have shown the broad scatter of data concerning spin polarization of such system and values of magnetic moments. The main purpose of our work is to do a systematic study of magnetic properties of graphene with vacancy cluster within the framework of one and the same method with the use of one tool of the study (VASP program) to generalize the results obtained and to reveal the regularities of spin polarization in the system "Graphene + vacancy cluster".

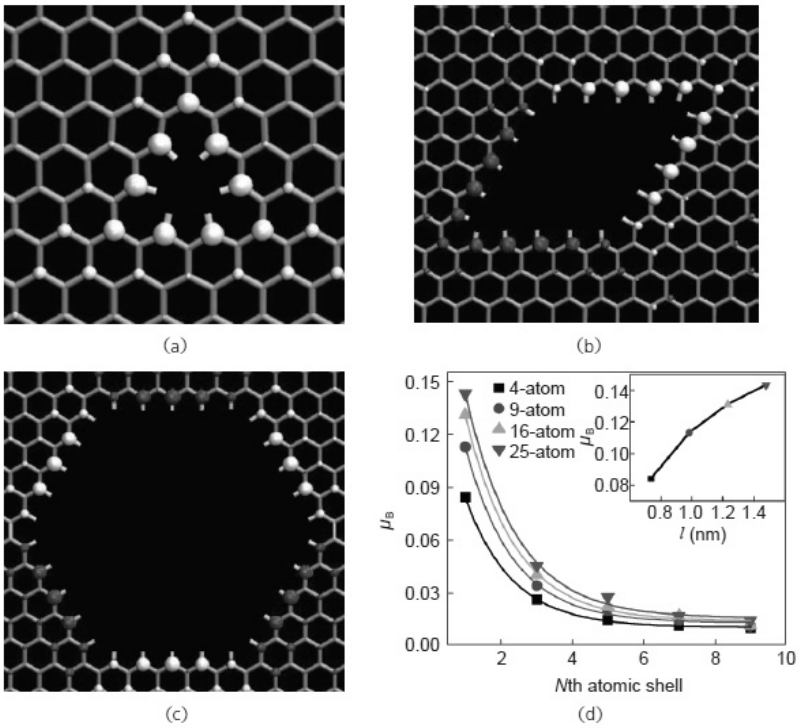


Fig. 4. Magnetic moments for big vacancy clusters in graphene [14].

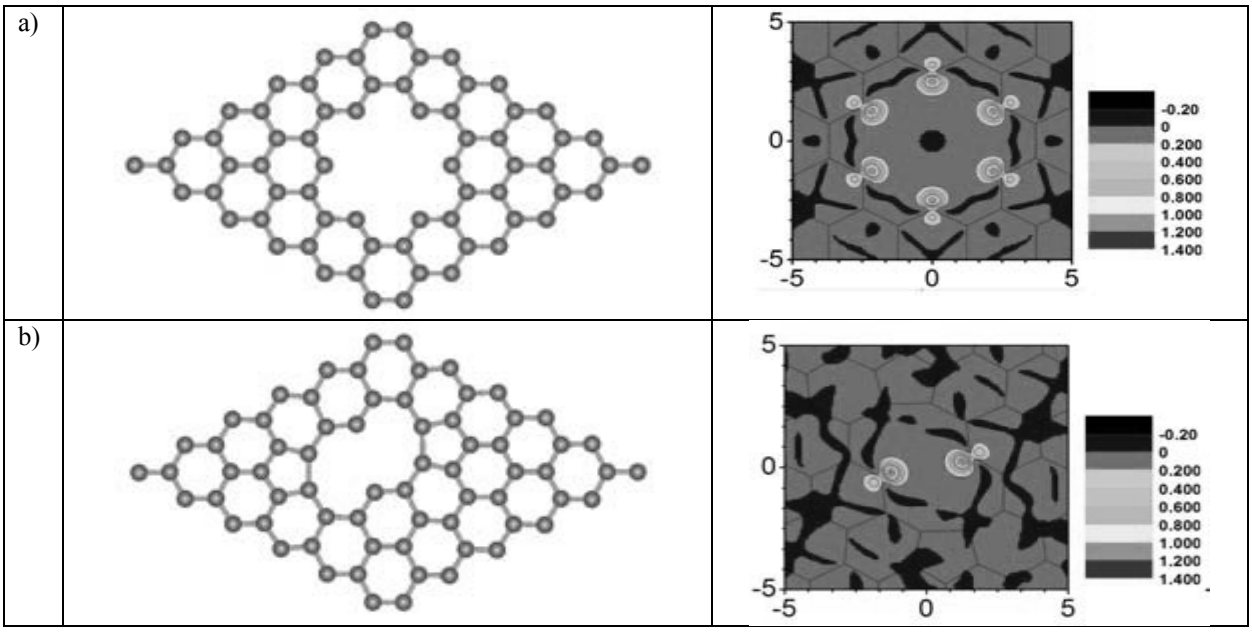


Fig. 5. V6_2 (a) and V4_2 (b) configurations after relaxation and their spin density distribution [9].

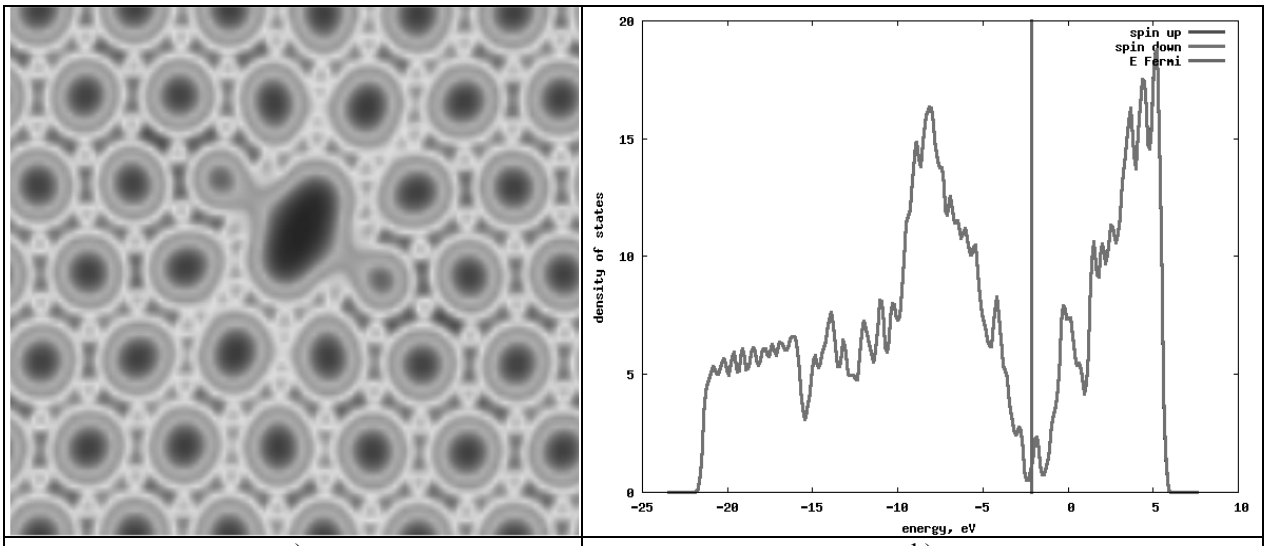
2. Methodology

Simulation including total relaxation of an investigated system was performed by using VASP (Vienna Ab-initio Simulation Package) program complex. A graphene cell of 72 carbon atoms was selected. The size of the cell was 14.76×12.78 Å. The distance between graphene planes was selected 12.8 Å in order to exclude their mutual influence. The defect density was calculated using the cell size.

Distribution of k-points 4×4×1 was selected via Monkhorst-Pack scheme. The energy cut-off condition was less than 1 meV/atom.
Densities of States (DOS) and Projected Density of States (PDOS) were calculated for series of configurations “Grahpene + vacancy cluster” with clusters consisted from 1 to 6 vacancies (see Table 1).

3. Results and discussion

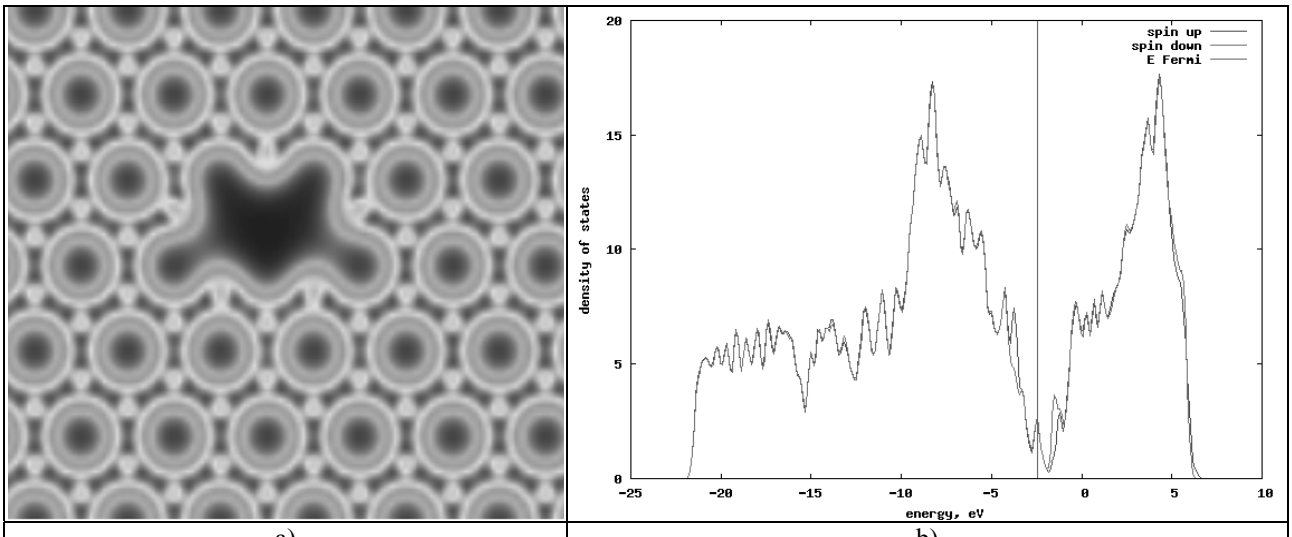
Simulation results (charge density distribution and DOS) for a V2–configuration (a bivacancy in a graphene cell) are presented in Fig. 6. As can be seen from the charge density distribution (Fig. 6a), the structure contains a defect in the form of two pentagons and one octagon. DOS dependency (Fig. 6b) indicates that electron states "spin up" and "spin down" are symmetrical, i.e. spin polarization is absent. Besides, near the Fermi level electronic states are resolved. This can indicate on the presence of additional energetic levels in the grapheme zone structure.



a) b)

Fig. 6. Charge density distribution (a) and DOS (b) for a V2–configuration.

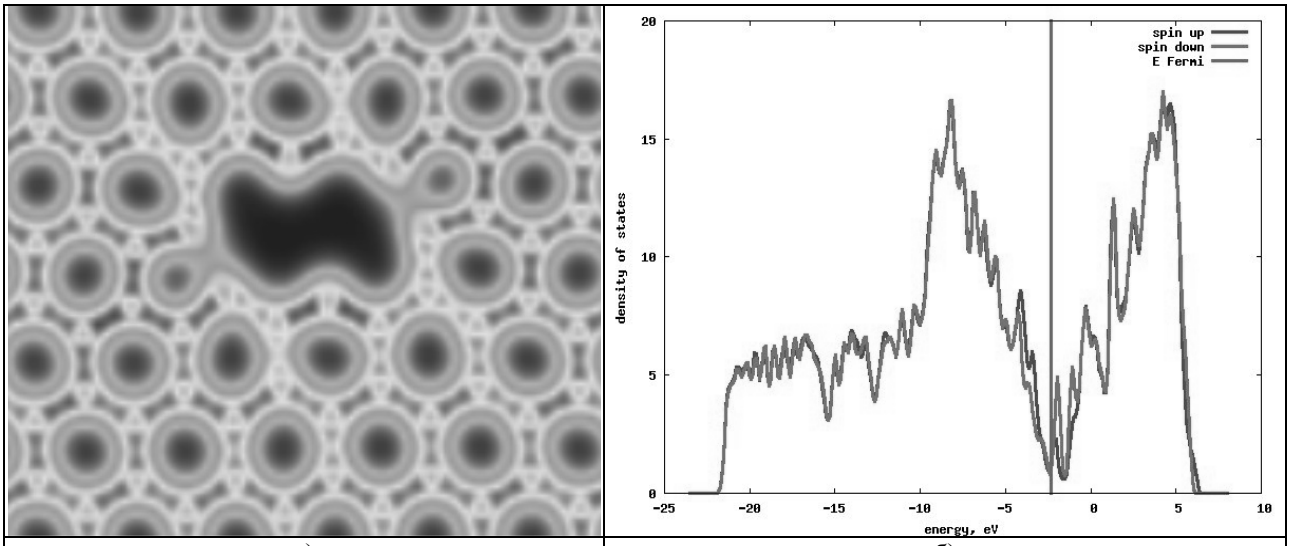
Fig. 7 illustrates the results of V3–configuration simulation. Magnetic moment for this configuration (Fig. 7b) equals 1.05 μB.



a) b)

Fig. 7. Charge density distribution (a) and DOS (b) for a V3–configuration.

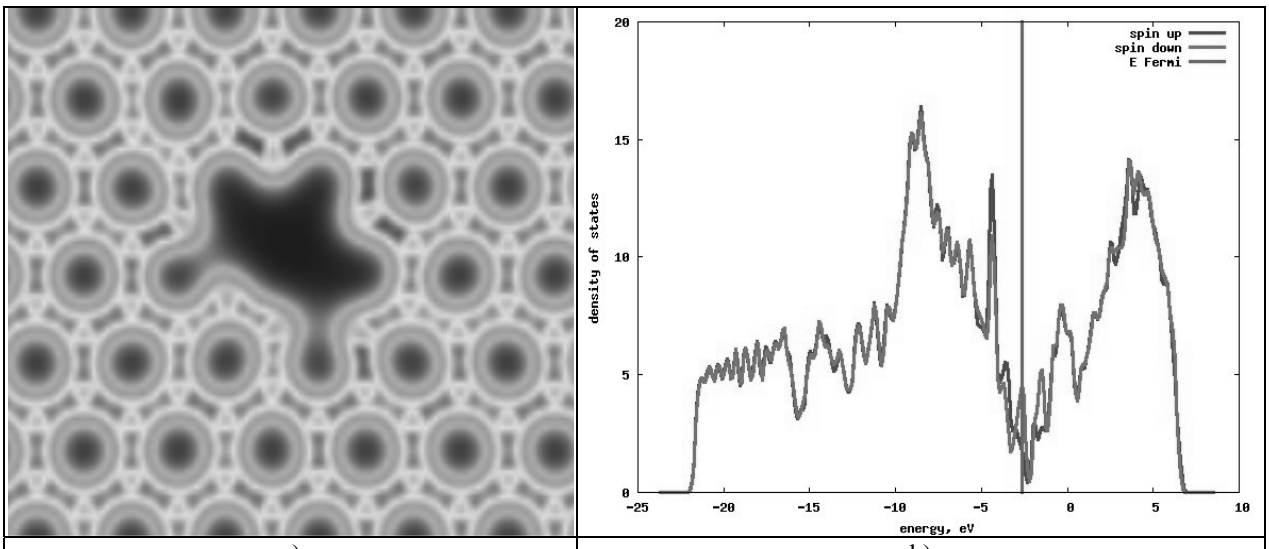
Simulation results (charge density distribution and DOS) for a V4_1–configuration (a tetra-vacancy in a graphene cell) are presented in Fig. 8. Magnetic moment of V4_1–configuration (see asymmetrical DOS for states "spin up" and "spin down" in Fig. 8b) equals 2.02 μB.



а) б)

Fig. 8. Charge density distribution (a) and DOS (b) for a V4_1–configuration.

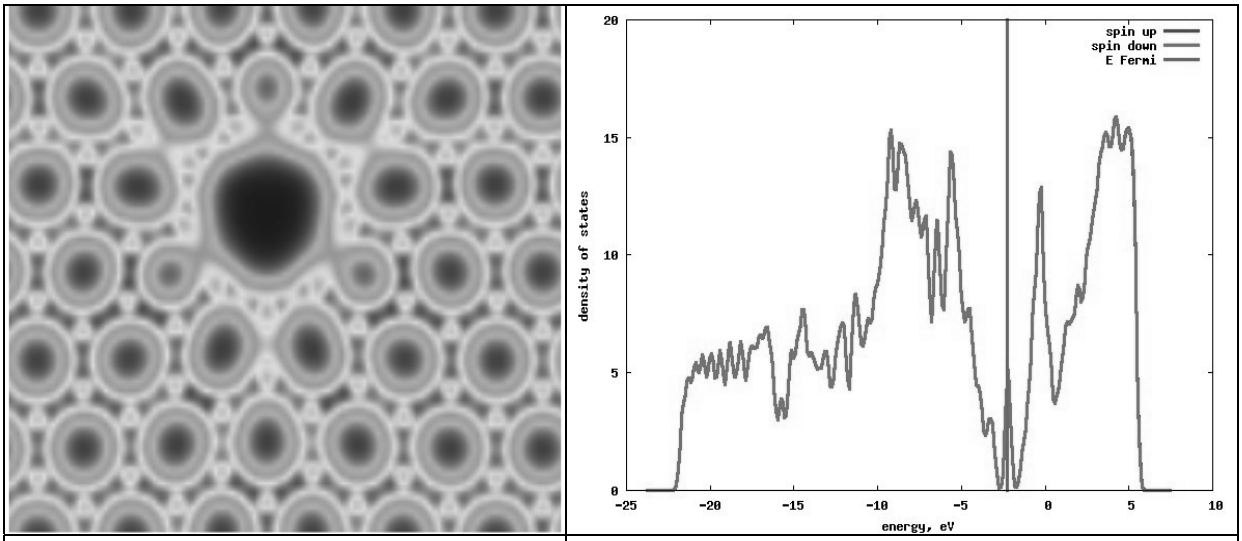
Simulation results (charge density distribution and DOS) for a V4_2–configuration are presented in Fig. 9. Magnetic moment of a V4_2–configuration (see asymmetrical DOS for states "spin up" and "spin down" in Fig. 9b) equals 1.98 μB.



a) b)

Fig. 9. Charge density distribution (a) and DOS (b) for a V4_2–configuration.

Simulation results (charge density distribution and DOS) for a V4_3–configuration are presented in Fig. 10. Magnetic moment of a V4_3–configuration equals zero because DOS's for states "spin up" and "spin down" are symmetrical (see Fig. 10b).

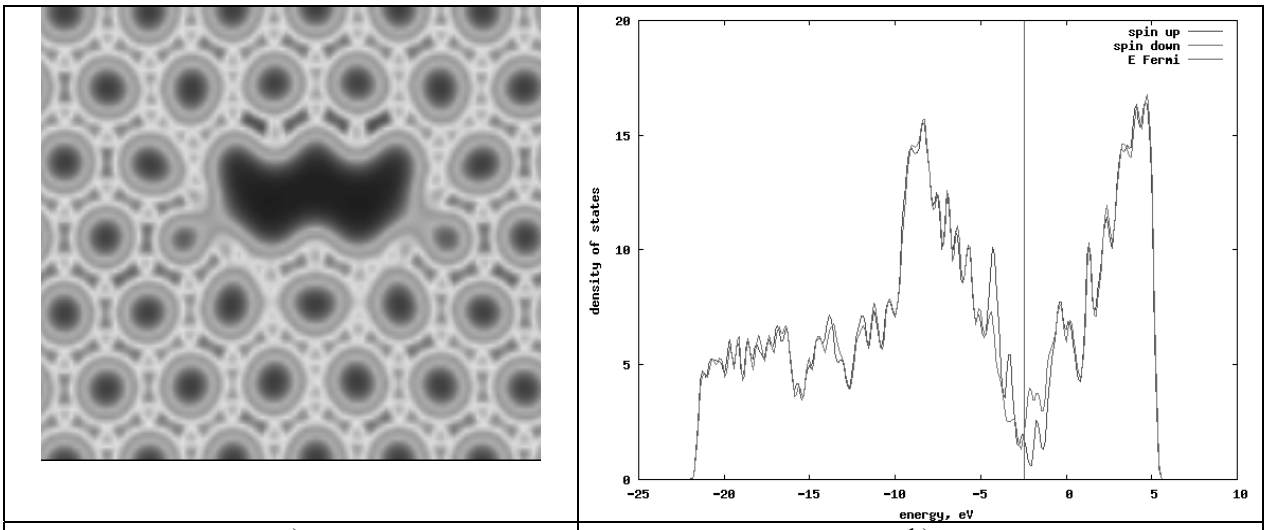


а) б)

Fig. 10. Charge density distribution (a) and DOS (b) for a V4_3–configuration.

Although the energy difference is rather small, among three tetravacancy configurations the total potential energy is the largest for a 4_3–configuration which is therefore the most stable.

Simulation results (charge density distribution and DOS) for a V5–configuration are presented in Fig. 11. Magnetic moment of a V5–configuration equals 3.28 μB.

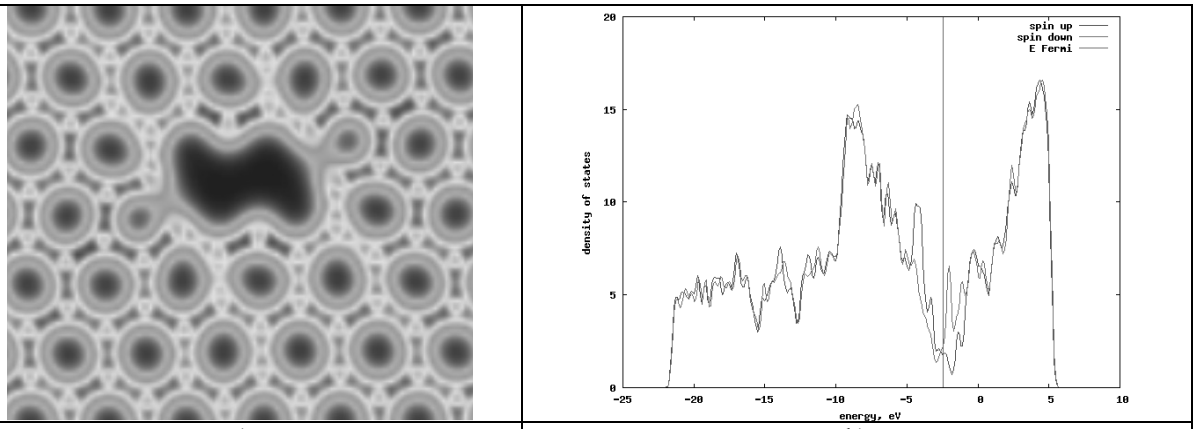


a) b)

Fig. 11. Charge density distribution (a) and DOS (b) for a V5 configuration.

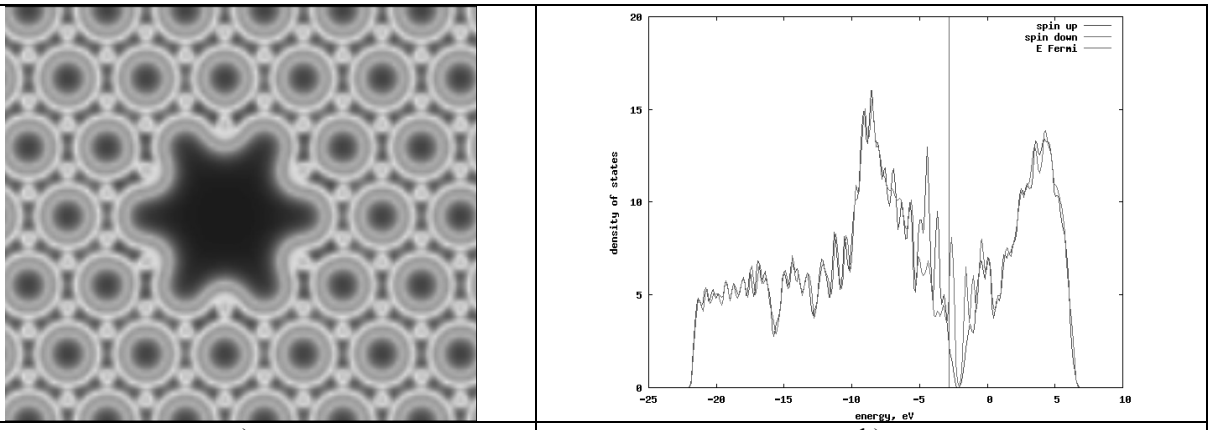
Simulation results (charge density distribution and DOS) for a V6_1–configuration (6 vacancies as a fragment of vacancy dislocation in graphene) are presented in Fig. 12. Magnetic moment of a V6_1–configuration equals 4.50 μB (see asymmetrical features of DOS's for states "spin up" and "spin down" in Fig. 12b).

Simulation results (charge density distribution and DOS) for a V6_2–configuration (6 vacancies form a ring) are presented in Fig. 13. Magnetic moment of a V6_2–configuration equals 5.49 μB.



a) b)

Fig. 12. Charge density distribution (a) and DOS (b) for a V6_1–configuration.



a) b)

Fig. 13. Charge density distribution (a) and DOS (b) for a V6_2–configuration.

A V6_2–configuration is more preferable energetically than a V6_1–configuration.

Table 2. Magnetic properties of graphene with a vacancy cluster.

Graphene + vacancy cluster – system	Number of vacancies in the cluster	Manifestation of the magnetic polarization, Yes(+)/No(–)	Calculated magnetic moment, μB
V1	1	+	0.51 [1]; 1.04 [2]; 1.15 [3]; 1.45-1.53 [4]
V2	2	–	0
V3	3	+	1.05
V4_1	4	+	2.02
V4_2	4	+	1.98; 1.97 [9]
V4_3	4	–	0
V5	5	+	3.28
V6_1	6	+	4.50; 4.45 [9]
V6_2	6	+	5.49; 5.54 [9]

Legend:
[1] Calculation without taking into account Jahn-Teller deformation [9]
[2] Jahn-Teller deformation was taken into account [10]
[3] For distances less than 7 Å between two nearby vacancies [13]
[4] For distances more than 7 Å between two nearby vacancies [13]

4. Conclusions

Systematic investigation of magnetic properties of graphene with vacancy cluster was carried out. Results of ab initio simulation presented are made within the framework of one and the same method with use of one tool for the study (VASP program). The main purpose of the work was generalization of the influence of vacancy number and configuration of the vacancy cluster in order to reveal the regularities of spin polarization in the system "Graphene + vacancy cluster". Spin polarization in the system "Graphene + vacancy cluster" was confirmed. Monotonic increasing of the magnetic moment in the investigated system "Graphene + vacancy cluster" was stated with the exclusion of V2 and V4_3–configurations. Magnetic moment is located near a vacancy cluster. Satisfactory agreement with corresponding results of other works was obtained.

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