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STRUCTURE AND ELECTRONIC PROPERTIES OF FLUOROGRAPHENE AND FLUOROGRAPHITE CRYSTALS

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Abstract. The paper presents the study of the structure and electronic properties of two-dimensional and three-dimensional crystals composed of monolayers of graphene polymorphs L_6, $L_{4\text{-}8}$, $L_{3\text{-}12}$, $L_{4\text{-}6\text{-}12}$, $L_{5\text{-}7}$ functionalized by fluorine atoms with various types of attachment of fluorine atoms. It reveals that the interlayer distances in the studied crystals vary within a wide range from 4,73 to 5,96 Å and volumetric densities vary from 2,43 to 3,98 g/cm^3. The value of the band gap in three-dimensional fluorographite crystals is on average 0,4 eV less than the band gap in the corresponding two-dimensional fluorographenes. The studied three-dimensional structures demonstrated a pattern: with an increase in the interlayer distance, the energy of the interlayer interaction decreases, and the volumetric density increases. The band gap of the fluorographenes and fluorographites decreases with an increase of sublimation energy. The paper establishes a correlation between the degree of C-C bond length variation of and the presence or absence of repulsive flagpole forces between the attached fluorine atoms. It proves that during functionalization, the values of the average C-C bond length increase for monolayers L_6, $L_{4\text{-}8}$, $L_{3\text{-}12}$, $L_{4\text{-}6\text{-}12}$ and $L_{5\text{-}7}$. The values of the average lengths of C-C bonds practically do not change during the formation of fluorographite from fluorographene. The variation of C-C bond lengths in fluorographites is minimal for F-L_6 T1 and equal to 0,2 %, while the maximum is observed for F-$L_{4\text{-}6\text{-}12}$ T1, which is 10,7 %.

Keywords: functionalization; fluorographite; fluorographene; polymorphism; attachment type; band gap.

Introduction

Graphite, which is a three-dimensional (3D) crystal, consists of monolayers of two-dimensional (2D) graphene bounded to each other by van der Waals forces [1]. A 3D crystal can also be constructed from monolayers of functionalized 2D graphene. Obviously, the properties of such a three-dimensional crystal will differ from the properties of 2D monolayer functionalized graphene, just as the properties of graphite differ from the properties of graphene [2–4].

In [5–12], calculations of the structure and electronic properties of fluorine-functionalized 2D and 3D crystals formed on the basis of various types of fluorographene polymorphs L_6, $L_{3\text{-}12}$, $L_{4\text{-}6\text{-}12}$, $L_{5\text{-}7}$ and $L_{4\text{-}8}$ were carried out. In order to identify new patterns, this work carries out a comparative analysis and generalization of the results obtained in these works.

Calculations and methods

In this work, computer modeling of the structure and electronic properties of two-dimensional 2D fluorographene crystals and three-dimensional 3D fluorographite crystals was carried out. Fluorographene layers were obtained by fluoridation of graphene polymorphs L_6, $L_{3\text{-}12}$, $L_{4\text{-}6\text{-}12}$, $L_{5\text{-}7}$ и $L_{4\text{-}8}$. Calculations of the structural and energy characteristics of 2D fluorographene crystals were carried out using the DFT-GGA method using the open source software package Quantum Espresso [13].

As a result of calculations, it turned out that out of a possible 17 layers of fluorographene, 15 monolayers of fluorographene F-L6, F-$L_{3\text{-}12}$, F-$L_{4\text{-}6\text{-}12}$, F-$L_{5\text{-}7}$ and F-$L_{4\text{-}8}$, shown in fig. 1, are stable. Stable layers were composed of 3D fluorographite crystals. The atom-atom potential method was used to calculate the three-dimensional structures of fluorographite. These structures were further used as the basis for calculations of the energy characteristics of the resulting fluorographites using the DFT-GGA method [13].

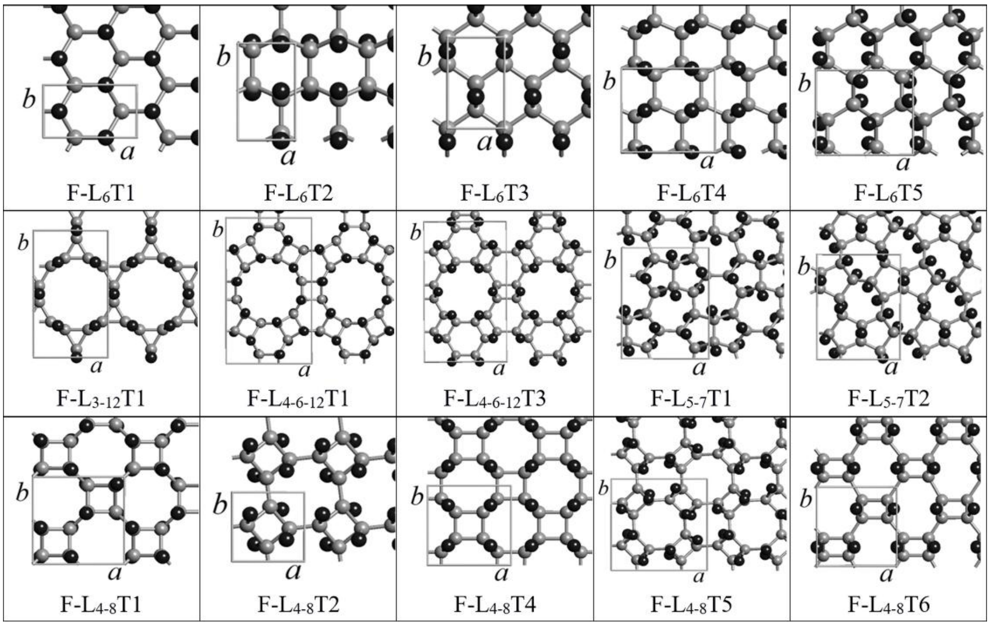

Fig. 1. Fluorographene monolayers used for building 3D-fluorographite crystals: F-L6, F-L3-12, F-L4-6-12, F-L5-7 и F-L4-8

Results and discussions

Table 1 shows the structural parameters: d_L – interlayer distance, S – length of the shear vector and ρ – bulk density; and energy characteristics of the resulting 2D fluorographene crystals and 3D fluorographite crystals: E_{VdW} – energy of van der Waals bonds between layers; E_{sub2D} and E_{sub3D} are the sublimation energy of fluorographenes and fluorographites, respectively; E_{g2D} and E_{g3D} are the band gaps of fluorographenes and fluorographites, respectively.

Table 1

Interlayer distance d_L, shear vector length S, bulk density ρ, Van der Waals energy E_{VdW}, sublimation energy of fluorographenes E_{sub2D} and fluorographites E_{sub3D}, band gap of fluorographenes E_{g2D} and fluorographites E_{g3D}

Crystal	S, Å	d_L, Å	ρ, g/cm^3	$E_{VdW}\cdot 10^2$, eV	E_{sub2D}, eV	E_{sub3D}, eV	E_{g2D}, eV	E_{g3D}, eV
F-L_6T1	0,00	5,39	3,26	3,04	14,32	14,37	3,321	2,727
F-L_6T2	1,09	4,73	3,98	4,81	14,19	13,94	3,390	3,114
F-L_6T3	1,52	5,75	3,26	2,93	14,31	14,33	3,557	3,108
F-L_6T4	1,68	5,60	3,30	3,19	14,08	14,19	4,195	3,666
F-L_6T5	1,06	5,46	3,23	3,02	14,20	14,22	3,044	2,505
F-L_{3-12}T1	1,47	5,76	2,43	1,85	13,77	13,83	3,43	3,032
F-L_{4-6-12}T1	0,05	5,49	2,59	2,38	13,84	13,89	3,193	2,827
F-L_{4-6-12}T3	3,46	5,77	2,64	2,37	13,80	13,83	4,150	3,682
F-L_{5-7}T1	3,71	5,50	3,21	2,90	13,85	13,90	4,09	3,663
F-L_{5-7}T2	3,36	5,57	3,39	3,13	14,17	14,24	3,32	3,126
F-L_{4-8}T1	2,78	5,46	2,91	2,65	13,98	14,04	3,211	2,781
F-L_{4-8}T2	0,00	5,18	2,97	3,08	13,36	13,44	4,958	4,599
F-L_{4-8}T4	1,74	5,55	3,12	3,11	14,05	14,12	3,946	3,413
F-L_{4-8}T5	3,14	5,96	2,75	2,23	13,56	13,60	4,686	4,322
F-L_{4-8}T6	1,74	5,57	3,09	3,13	14,01	14,08	4,877	4,257

The average interlayer distance by types d_L = 5,4 Å in fluorographites F-L_6T1 – F-L_6T5, as it turned out, practically coincides with the distance d_L = 5,3 Å obtained in an experiment of X-ray diffraction analysis [14] on a fluorographite sample, synthesized in the Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences in Novosibirsk according to the method described in [15]. From table 1 it can be seen that the difference between the minimum d_L = 4,73 Å in F-L_6T2 and the maximum d_L = 5,96 Å in F-L_{4-8}T5 values of the interlayer distance is quite significant – 1,23 Å (40 %).

The difference between the minimum and maximum values of bulk density is also quite significant: 1,55 g/cm^3 (50 %). From fig. 2 it can be seen that there is a one-to-one correspondence between the interlayer distance d_L and the bulk density ρ – the larger d_L, the smaller ρ.

The interlayer bond energy E_{VdW} is maximum in fluorographite F-L_6T2 ($E_{VdW} = 4{,}81\cdot 10^{-2}$ eV) and is more than 2,6 times higher than the minimum value E_{VdW} in fluorograpite F-L_{3-12}T1 ($E_{VdW} = 1{,}85\cdot 10^{-2}$ eV).

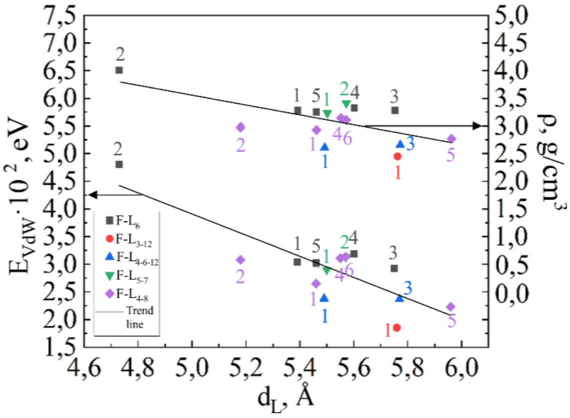

Fig. 2. The graph of interlayer distance ***dL*** versus bulk density ***ρ*** and Van der Waals energy ***EVdW***

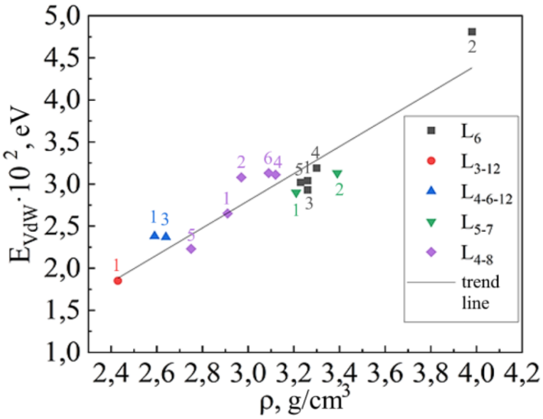

Fig. 3. The interlayer bond energy ***EVdW*** versus bulk density ***ρ***

There is a connection between the van der Waals energy E_{VdW} and the interlayer distance d_L, as can be seen from fig. 2 – the greater E_{VdW}, the smaller d_L. According to fig. 3, there is also a connection between the Van der Waals energy E_{VdW} and the density ρ, namely, the higher the Van der Waals energy, the higher the bulk density.

The sublimation energy of 3D fluorographite crystals, with the exception of F-L6T2 fluorographite, is slightly (0,5 %) higher than the sublimation energy of 2D fluorographene crystals. Fluorographene and fluorographite F-L_6T1 have the highest sublimation energy, and fluorographene and fluorographite F-$L_{4\text{-}8}$T2 have the lowest.

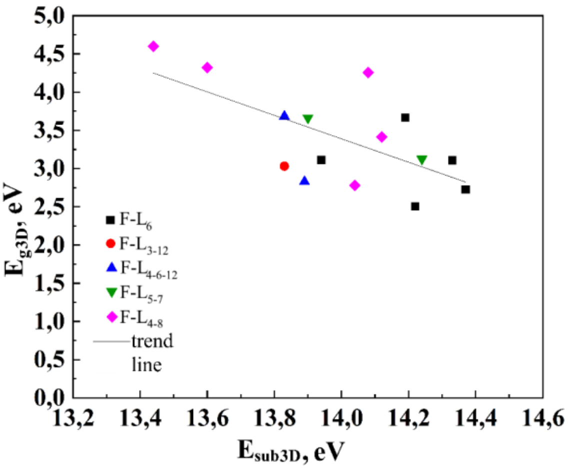

Fig. 4. The band gap ***Eg3D*** versus sublimation energy Esub3D in fluorographites

In fluorographites F-L_6T1 and F-$L_{4\text{-}8}$T2 there is no layer shift, that is, $S = 0$ (layer packing type AA), and in other fluorographites S is not equal to zero (layer packing type AB) and varies within a fairly wide range (from 0 to 3,71 Å). Note, that despite the same type of layer packing – type AA (no shear), fluorographites F-L_6T1 and F-$L_{4\text{-}8}$T2 are very different from each other in sublimation energies: for F-L_6T1 E_{sub} = 14,37 eV, while for F-$L_{4\text{-}8}$T2 E_{sub} = 13,44 eV.

It is interesting to note that, contrary to expectation, we did not find a link between the interlayer distance d_L and the shift S.

According to [16], in pure (non-functionalized) graphite the interlayer distance in AA type packaging is greater than in graphite in AB type packaging. In the functionalized materials studied in this work – fluorographites – no similar correlation between the distance d_L and the type of packaging was found.

The band gap of the studied fluorographites E_{g3D} varies widely from 2,51 eV (F-L_6T5) to 4,60 eV (F-$L_{4\text{-}8}$T2). It is on average 0,4 eV less than the band gap in fluorographene monolayers E_{g2D}.

Fig. 4 shows the dependence of the band gap E_{g3D} on the sublimation energy E_{sub3D} in fluorographites. It can be seen that the band gap decreases with the increase in sublimation energy. A similar dependence is observed in fluorographenes.

Based on the band gap, the fluorographenes and fluorographites we are studying should be classified as semiconductors or dielectrics.

Table 2 shows the average lengths of C-C bonds in the carbon frameworks of pure polymorphs of layered (2D) (graphenes) and three-dimensional (3D) (graphites) structures and fluorine-functionalized polymorphs of fluorographene (2D) and fluorographite (3D) and their relative changes: d_{C0} is the average length of the C-C bond in the functionalized material (flurographene or fluorographite),

$\delta = \dfrac{d_C - d_{C0}}{d_{C0}} \cdot 100\%$ is the relative increase in the length of the C-C bond as a result of functionalization, $\Delta = \dfrac{d_{C\max} - d_{C\min}}{d_C} \cdot 100\,\%$ – spread – the relative difference between the maximum $d_{C\max}$ and minimum $d_{C\min}$ length of the C-C bond in the carbon framework.

Table 2

Average length of C-C-bond d_{C0} and d_C, the relative increase of the length of the C-C-bond as a result of the functionalization δ, the spread of the lengths of C-C-bonds in the carbon frame Δ

Monolayer notation	Pure polymorphs (graphenes and graphites)		Functionalized polymorphs (fluorographenes and fluorographites)					
	2D, 3D		2D			3D		
	d_{C0}, Å	Δ, %	d_C, Å	δ, %	Δ, %	d_C, Å	δ, %	Δ, %
L_6T1	1,43	0,2	1,57	9,8	0,1	1,57	9,8	0,2
L_6T2			1,60	11,9	5,3	1,61	12,6	5,4
L_6T3			1,58	10,5	1,1	1,58	10,5	1,8
L_6T4			1,59	11,2	5,1	1,59	11,2	6,0
L_6T5			1,59	11,2	1,9	1,59	11,2	3,1
$L_{3\text{-}12}$T1	1,41	6,3	1,54	9,2	3,3	1,54	9,2	3,6
$L_{4\text{-}6\text{-}12}$T1	1,45	7,6	1,59	9,7	10,3	1,59	9,7	10,7
$L_{4\text{-}6\text{-}12}$T3			1,61	11,0	1,5	1,61	11,0	1,9
$L_{5\text{-}7}$T1	1,41	8,9	1,57	11,3	4,4	1,56	10,3	8,8
$L_{5\text{-}7}$T2			1,57	11,3	8,4	1,60	13,5	9,4
$L_{4\text{-}8}$T1	1,44	6,3	1,57	9,0	6,8	1,57	9,0	6,7
$L_{4\text{-}8}$T2			1,58	9,7	4,2	1,58	9,7	4,2
$L_{4\text{-}8}$T4			1,58	9,7	4,9	1,58	9,7	4,9
$L_{4\text{-}8}$T5			1,60	11,1	2,3	1,60	11,1	2,3
$L_{4\text{-}8}$T6			1,58	9,7	3,8	1,58	9,7	3,8

A sufficiently large value of δ, indicating a significant increase in the average length of the C-C bond d_C, indicates a deterioration in the structural properties of the studied graphenes and graphites during their functionalization.

In functionalized materials, during the transition from layered structures to three-dimensional ones, the values of d_C and δ practically do not change, which indicates that the strength properties of layered and three-dimensional structures remain unchanged. In functionalized materials, the difference in the lengths of C-C bonds in the carbon frame Δ during the transition from 2D to 3D crystals also practically does not change.

Noteworthy is the fact that there is a wide variety of C-C bond lengths in the carbon framework: from 0,2 % in F-L_6T1 to 10,7 % in F-$L_{4\text{-}6\text{-}12}$T1 in 3D-crystals. The reason for this is the following. In layers of both 2D fluorographenes and 3D fluorographites, fluorine atoms attached to neighboring carbon atoms in the C-C chain on one side of the layer (fig. 5, *a*) are close to each other and are repelled by flagpole forces [17, 18]. Let's call this option of attaching fluorine atoms to the carbon frame option *a*. Due to the repulsion of fluorine atoms, stretching occurs – elongation of the corresponding C-C bond. In another case, fluorine atoms attached to neighboring carbon atoms in the C-C chain on different sides of the layer (fig. 5, *b*) are far from each other and significant flagpole forces do not arise between them. Let's call this option for addition of fluorine atoms option *b*.

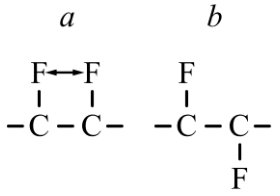

Fig. 5. Options for attaching fluorine atoms to the carbon frame: *a* – option *a*, *b* – option *b*

In the FL_6T1 layer, fluorine atoms are attached according to option *b*, so the C-C bonds in it are not stretched. Ultimately, it turns out that in the FL_6T1 layer, just as in the original L_6 graphene, all C-C bonds have the same length, and the degree of spread in the lengths of C-C bonds Δ up to a calculation error (0,2 %) is equal to zero.

In the FL_6T2 layer, unlike the FL_6T1 layer, there is not one, but two groups of fluorine atoms: one group is attached according to option *a*, the other according to option *b*, so that some C-C bonds are stretched, while others are not. Therefore, this layer has a large degree of spread of the lengths of C-C bonds: Δ = 5,3 %.

In the $FL_{4\text{-}6\text{-}12}T3$ layer there are two groups of C-C bonds: in one, short C-C bonds inside hexagonal cycles are stretched due to flagpole forces, in the other, long C-C bonds inside quadrangular cycles are not stretched. As a result, in the $FL_{4\text{-}6\text{-}12}T3$ layer, the scatter in the lengths of C-C bonds turns out to be quite small (Δ = 1,5 %) and less than in the original non-functionalized graphene $L_{4\text{-}6\text{-}12}$, where Δ = 7,6 %.

In the $FL_{4\text{-}6\text{-}12}T3$ layer there are more C-C bonds stretched due to flagpole forces than in the $FL_{4\text{-}6\text{-}12}T1$ layer. Therefore, the average length of C-C bonds in the $FL_{4\text{-}6\text{-}12}T3$ layer, where d_C = 1,61 Å, is greater than in the $FL_{4\text{-}6\text{-}12}T1$ layer, where d_C = 1,59 Å.

Conclusions

Computer modeling of the structure and electronic properties of two-dimensional and three-dimensional crystals fluorographenes and fluorographites was carried out. Fluorographenes – fluorine-functionalized graphene polymorphs $F\text{-}L_6$, $F\text{-}L_{3\text{-}12}$, $F\text{-}L_{4\text{-}6\text{-}12}$, $F\text{-}L_{5\text{-}7}$ and $F\text{-}L_{4\text{-}8}$, of various types of attachment. Fluorographites consisted of parallel stacked monolayers of fluorographene polymorphs. It was found that in the resulting structures, interlayer distances and bulk densities vary widely from layer to layer. Bulk density, interlayer distance and interlayer van der Waals energy show linear correlation with one another, in which: the greater the interlayer distance, the lower the bulk density and interlayer interaction energy, and the greater the interlayer interaction energy, the greater the bulk density. The sublimation energy of 3D fluorographite crystals is practically not different from the sublimation energy of 2D fluorographene monolayers. The band gap in fluorographite crystals is on average 0,4 eV less than the band gap in fluorographene monolayers. Based on the band gap, the studied fluorographites can be classified as semiconductors or dielectrics. It was found that the band gap in both fluorographenes and fluorographites decreases with increase of sublimation energy. The relation between the degree of spread of the lengths of C-C bonds, the order of fluorine atom arrangement on sides of the carbon layer framework, and the presence or absence of repulsive flagpole forces has been established.

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СТРУКТУРА И ЭЛЕКТРОННЫЕ СВОЙСТВА ФТОРОГРАФЕНОВЫХ И ФТОРОГРАФИТОВЫХ КРИСТАЛЛОВ

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Аннотация. Проведено исследование структуры и электронных свойств двумерных (2D) (фторографенов) и трехмерных (3D) (фторографитов) кристаллов, составленных из функционализированных фтором монослоев полиморфов графена L_6, L_{3-12}, L_{4-6-12}, L_{5-7} и L_{4-8} с различным типом присоединения атомов фтора. Установлено, что в исследуемых 3D-кристаллах изменяются в широких пределах межслоевые расстояния: 4,73 ÷ 5,96 Å и объемные плотности: 2,43 ÷ 3,98 г/см^3. Значение ширины запрещенной зоны во фторографитах в среднем на 0,4 эВ меньше ширины запрещенной зоны в соответствующих фторографенах. Во фторографитах обнаружена закономерность: с увеличением межслоевого расстояния энергия межслоевого взаимодействия уменьшается, а объемная плотность увеличивается. Обнаружено, что ширина запрещенной зоны как во фторографенах, так и фторографитах уменьшается при увеличении энергии сублимации. Установлена связь между степенью разброса длин С-С-связей и наличием или отсутствием расталкивающих flagpole-сил между присоединяемыми атомами фтора. Наблюдается, что при функционализации значения средней длины С-С связи увеличиваются для монослоев L_6, L_{3-12}, L_{4-6-12}, L_{5-7} и L_{4-8}. Значения средних длин С-С связей при формировании фторографита из фторографена практически не изменяются. Разброс длин С-С связей варьируется от 0,2 % в F-L_6T1 до 10,7 % в F-L_{4-6-12}T1 для фторографитов.

Ключевые слова: функционализация; фторографит; фторографен; полиморфизм кристаллов; тип присоединения; ширина запрещенной зоны.

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