Structural varieties of carbon compounds

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Abstract. The existence of allotropic, polymorphic and polytypic structural varieties of carbon materials and nanostructures is possible. Allotropes differ by the atomic coordination in the structure. In polymorphs, the coordination is the same, but bond lengths and bond angles differ. In polytype structures, there is a different order of molecular layer packing. A theoretical analysis of the structures of polytypic varieties of carbon and their phase transformations is performed in this paper.

1. Introduction

Carbon materials can have different structures and properties [1,2]. With the same chemical composition, the material properties are determined by the structure, therefore, carbon materials can be described and classified according to their structural features [3]. To denote structural varieties, several terms are commonly used, such as allotropes, polymorphs and polytypes. A precise definition of these terms is necessary. In addition, there may exist different nanostructures, the features of which are nanoscale in one, two and three crystallographic directions [3]. All these structural varieties of carbon should be considered not isolated, but taking into account the possibility of their mutual structural transformations. Therefore, in this paper, a hierarchical classification of carbon structural varieties is considered. Also, the polytypic varieties and the possibilities of their mutual transformations are described in detail.

2. Structural classification of carbon compounds

Coordination of carbon atoms in the structure most strongly affects the properties of carbon compounds. Carbon atoms in compounds can be in 2-, 3-, and 4-coordinated states, that is, they can have a corresponding number of nearest neighbouring atoms. The coordination determines the hybridization of electron orbitals of the atom. Therefore, each coordinated state (2, 3, and 4) corresponds to the hybridized state (sp, sp^2, and sp^3). It is this feature of the structure that distinguishes various allotropic modifications of carbon. Typical allotropes are carbyne, graphite and diamond, in which the atoms are in three different coordinated states.

Each carbon atom in compounds tends to form four covalent bonds with neighbouring atoms, therefore allotropic varieties differ in the covalent bond order. In the diamond structure (4-coordinated atomic states), covalent bonds with neighbouring atoms are single, since each of them is formed by one pair of electrons. In graphene, four covalent bonds are formed with three neighbouring atoms, so one bond accounts for 1.33 electron pairs, which correspond to the bond order. In the third allotropic variety of carbon, carbyne, each atom has two neighbouring atoms, and the average bond order is two.

Based on this parameter, the remaining carbon compounds can be assigned to one of the three allotropic groups.

Another factor affecting the structure and properties of carbon compounds is their crystallographic dimension (nD_c). The number n in this parameter indicates the number of Cartesian coordinate axes along which the carbon structure has macroscopic dimensions. Therefore, compounds can have crystallographic dimension $0D_c$ (fullerenes), $1D_c$ (nanotubes), $2D_c$ (graphene layers), and $3D_c$ (3D-graphites and diamond-like phases).

Different combinations of the two parameters, nD_c and N_a, determine the individual structural groups of carbon compounds [3]. Allowing the possibility of changing the parameter N_a from 0 to 4, theoretically, the existence of twelve [nD_c, N_a] structural groups becomes possible [3]. The compounds of each structural group can be transformed into compounds of another group, changing the atomic coordination and crystallographic dimension of the compounds. These transformations can occur due to the formation of additional interatomic bonds or the breaking of existing bonds. This allows theoretically predict the structure of new carbon phases and nanostructures.

Within each structural group, variations in the compound structure are also possible. Such structural varieties should be called polymorphs. In polymorphic varieties, atoms have the same coordination, and the polymorphic structures have the same crystallographic dimension. Differences in the structures of polymorphs are due to the interatomic bond length and bond angles distortions, which can be quantitatively characterized by the parameters of *Str* and *Def*. As ideal structures in which there is no distortion (*Str* = 0 and *Def* = 0), polycumulene carbyne, hexagonal graphene and cubic diamond structures are adopted. For example, there may be four main varieties of graphene [3]. The differences in the structure of polymorphs from each other are less than the structural differences in allotropes, therefore the properties of polymorph differ less than in allotropes.

The next level of structural differences concerns the packing order of molecular layers in the structures of carbon compounds. Therefore, the existence of a variety of polytypes is possible for each polymorphic variety [4]. For example, in addition to hexagonal and rhombohedral graphites formed on the basis of graphene L_6 layers, polytypes based on other graphene polymorphs can exist [5]. In the structure of polytypes, the short-range order of the atom arrangement differs slightly. Significant differences are observed in distant coordination spheres. Therefore, the properties of polytypes differ slightly. It is necessary to carry out a theoretical analysis of the possible structure of polytypes of carbon compounds.

3. Structural analysis of polytypes

The theoretical analysis was carried out by enumeration of all possible combinations of molecular layers packing in unit cells of different sizes. As a result of the analysis of the graphite and diamond polytype structures, the possibility of the existence of isomeric varieties of polytypes was established. Polytypes with a period of recurrence $N > 5$ have a number of isomeric varieties with the same N, but have different hexagonality (H) (table 1). As a result, several polytypes with a different recurrence periods have a close or identical hexagonality [4]. Apparently, they can simultaneously form and sustainably exist at identical values of thermodynamic parameters, since their cohesion energies have close values [4]. Isomeric structures with the same period (N) can have different hexagonality. The formation of different polymorphic varieties probably can occur as a result of mutual phase transformations.

4. Modeling of polytype phase transformations

When modelling polytype phase transitions, it was assumed that they could be due to changes of graphene layers in the graphite crystals or molecular layers in diamond crystals. It was assumed that they can occur due to shifts of graphene layers in graphite crystals or molecular layers in diamond crystals. Calculations of the activation energy of the shifts were performed using the atomic-atomic potential method for graphite. The image of the area of the relative shift of graphene layers is shown in figure 1. The results of calculating the binding energy of neighbouring layers depending on the shift

are shown in figure 2. The height of the potential barrier that must be overcome in order to shift the layer from one local minimum to another is 65 μeV/atom. Therefore, in graphite nanocrystals, the ordered structure can be absent at room temperature, and the structural transformations of some polytypes into others can occur continuously.

Table 1. Structural characteristics of polytypes (N is the period of layer packing; M_N is the number of all possible combinations; L_N is the number of allowable combinations; P_N is the number of allowable combinations minus equivalent ones; F_N is the number of unique polytypes; H is the hexagonality of the polytype; W is the probability of polytype formation. Shown in the brackets are the equivalent combinations of those having smaller values of N).

N	M_N	L_N	P_N	F_N	H (%)	Layer alternation	W (%)
2	9	6	1	1	100	ABAB…	100
3	27	6	1	1	0	ABCABC…	100
4	81	18	3	1	50	ABAC…	66.67 (100)
5	243	30	5	1	40	ABABC…	100
6	729	66	11	2	66.7	ABABAC…	54.55 (66.67)
					33.3	ABACBC…	27.27 (33.33)
7	2187	126	21	3	57.1	ABABABC…	33.33
					57.1	ABABCAC…	33.33
					28.6	ABACABC…	33.33
8	6561	258	43	6	75	ABABABAC…	18.6 (20)
					75	ABABACAC…	9.3 (10)
					50	ABABACBC…	18.6 (20)
					25	ABABCABC…	18.6 (20)
					50	ABABCBAC…	18.6 (20)
					25	ABACBABC…	9.3 (10)

The activation energy of the diamond layer was calculated by the density functional theory method for the successive shift of two atoms (with numbers 4 and 5 in figure 3) in the *ab*-plane from the position ($2a/3$; $b/3$) to the position ($a/3$; $2b/3$). In diamond, the molecular layer shift energy is 2.3 eV/atom (figure 4). Such shifts of layers can cause phase transformations of the structure of any noncubic polytype into the structure of any other polytype. In addition, shear transformations can be the cause of the formation of crystals with random packing of layers [6]. Phase transitions of some polytypes into others are possible in nanodiamonds at high temperatures, whereas in macrocrystals these transitions may be absent due to the significant value of the activation energy necessary for shifts in the molecular layer.

5. Conclusions

Thus, the structural classification of carbon compounds is described. Structural varieties of carbon compounds can be divided into allotropes, polymorphs and polytypes. The structures of allotropes differ from each other in the number of atoms in the first coordination sphere. In polymorphs, the first coordination number is the same, but the bond lengths and bond angles are different. Polytype structures differ only in the packing order of the molecular layers. In addition, a theoretical analysis of the structure of carbon polytypic varieties was carried out, and the phase transformations of graphite and diamond polytypes were calculated.
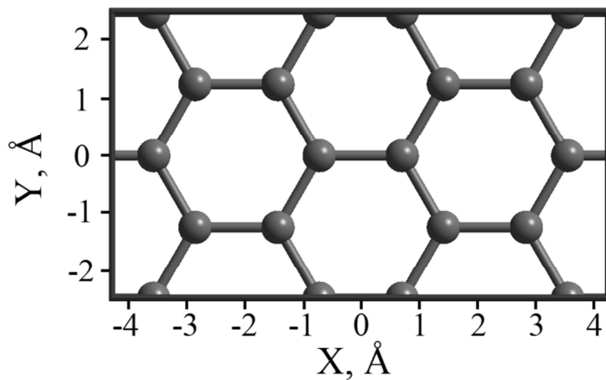
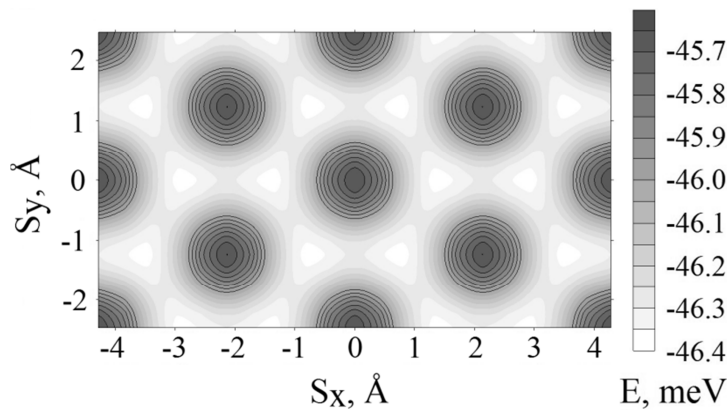**Figure 1.** Graphene layer fragment within which relative shifts of adjacent layers were performed.

Figure 2. Dependence of the van der Waals energy (E) on the graphene layer shifts along the X and Y axes.
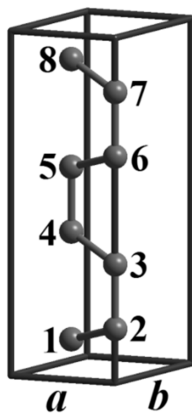

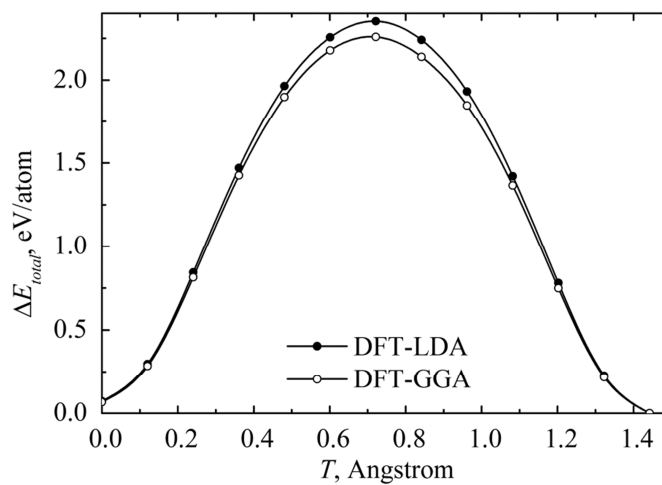**Figure 3.** Hexagonal diamond unit cell.

Figure 4. Dependences of the difference total energy on the shear vector modulus for the shifted molecular layer in 2H diamond.

References
[1]   Pierson H O 1993 *Handbook of Carbon, Graphite, Diamond, and Fullerenes: Properties, Processing and Applications* (Park Ridge: Noyes) p 43
[2]   Lisovenko D S, Baimova Yu A, Rysaeva L Kh, Gorodtsov V A and Dmitriev S V 2017 *Phys. Solid State* **59** 820
[3]   Belenkov E A and Greshnyakov V A 2013 *Phys. Solid State* **55** 1754
[4]   Belenkov E A and Greshnyakov V A 2017 *Phys. Solid State* **59** 1926
[5]   Enyashin A N and Ivanovskii A L 2011 *Phys. Status Solidi B* **248** 1879
[6]   Greshnyakov V A and Belenkov E A 2017 *J. Exp. Theor. Phys.* **124** 265