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SOLIDS AND LIQUIDS

Structures of Diamond-like Phases

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Abstract—The diamond-like phases containing carbon atoms with the same degree of hybridization, which is close to sp^3, are classified. It is found that twenty such phases can exist, and ten of them are described for the first time. Molecular mechanics and semi-empirical quantum-mechanical methods are used to calculate the geometrically optimized structures of diamond-like phase clusters and to determine their structural parameters and properties, such as the density, the bulk modulus, and the sublimation energy. The difference between the properties of the diamond-like phases and those of diamond is found to be determined by the difference between the structures of these phases and diamond.

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1. INTRODUCTION

Diamond-like carbon phases consist of carbon atoms in which every atom forms four σ bonds with the neighboring atoms, as in the diamond structure. These phases can be divided into the following two groups: in the phases of the first group, all atoms have the same degree of hybridization (close to sp^3) and are located in crystallographically equivalent positions; in the phases of the second group, the hybridization states of atoms are also close to sp^3 but are crystallographically nonequivalent. The first-group phases are basic, and the number of these phases is limited. The second-group phases can be formed as a combination of the structures of the first-group phases, and the number of such combinations is very large and can hardly be classified. Therefore, we will restrict ourselves to considering the diamond-like phases of the first group.

The first diamond-like phase detected experimentally was hexagonal ^{2}H polytype of diamond, lonsdaleite. The unit cell of lonsdaleite belongs to the hexagonal system with parameters $a = 0.252$ nm and $c = 0.412$ nm and contains four atoms [1], and the density of this phase is 3.51 g/cm^3, which is slightly smaller than the diamond density. The space group of this phase is $P6_3/mmc$.

The second experimentally synthesized diamond-like phase is represented by polymerized cubic fullerite C_{24}. This phase was first synthesized from conventional graphite at low temperatures ($T = 77$ or 296 K) and a pressure $P > 15$ MPa [2]. The unit cell of this phase belongs to the cubic system with a lattice parameter $a = 0.5545$ nm and has 24 atoms, and the phase density is $\rho = 2.80$ g/cm^3. The authors of [3] were the first to interpret this phase as a phase consisting of structural C_{24} elements. The calculated energy gap of this phase is 1.6 eV and its bulk modulus is 196 GPa [4]. The authors of [3, 5] hypothesized the presence of other diamond-like phases based on crystal-forming C_{48} fullerenes.

A number of diamond-like phases were predicted theoretically and their structures were calculated.

The first of them, supercubane, was first studied in [6]. Its structure can be represented in the form of cross-linked carbon cages of cubane molecules [7, 8] so that cubic molecule cages are connected to each other by carbon–carbon bonds along cube diagonals.

Four diamond-like phases were theoretically studied in [9]. These phases result from the cross-linking of bundles of single-layer carbon nanotubes of the same chirality, (2,2), (3,3), and (6,0).

One of the phases is formed upon the cross-linking of (2,2) tubes and was called rectangulane [9]. The unit cell of this phase is tetragonal with lattice parameters $a = 0.4283$ nm and $c = 0.2540$ nm, contains eight carbon atoms, and has space group $I4/mmm$. The rectangulane density is 3.425 g/cm^3, which is smaller than the diamond density by 4.6%. The strength characteristics of rectangulane are of particular interest: its calculated bulk elastic modulus is 403 GPa, which is only 6.8% lower than that of diamond. It was found in later works [10, 11] that the rectangulane phase should be a semiconductor with an energy gap of 2.3–2.59 eV. The body-centered tetragonal carbon phase theoretically studied in [12, 13] and called bct C_4 is the rectangulane phase described earlier in [9]. The authors of [12, 13] found that rectangulane can be synthesized from graphite at a low temperature and a pressure more than 18.6 GPa. The authors of [14] tried to experimentally synthesize rectangulane: at a high pressure (18 GPa) and room temperature, they were able to synthesize a transparent mixed lonsdaleite–rectangulane phase (quasi-lonsdaleite), which transformed into graphite under normal conditions. The measured bulk modulus of quasi-lonsdaleite is 425 GPa.

Another phase consisting of structural units in the form of carbon nanotubes (2,2) differs from rectangulane in that these nanotubes are cross-linked by stairs. The tetragonal unit cell of this phase has parameters $a = 0.6409$ nm nd $c = 0.2549$ nm and contains 16 carbon atoms, the phase density is 3.048 g/cm^3, and the space group of this phase is $I4/mmm$ [9]. The bulk modulus of this phase was calculated to be 352 GPa. Domingos [11] found that the phase formed from polymerized nanotubes (2,2) is a semiconductor with an energy gap of 0.70 eV.

The unit cell of the phase that forms upon cross-linking of a bundle of nanotubes (3,3) belongs to the hexagonal system with parameters $a = 0.5966$ nm and $c = 0.2602$ nm and contains 12 carbon atoms, and the calculated phase density is 2.984 g/cm^3 [9]. The space group of this phase is $P6_3/mmc$, and the bulk modulus is 332 GPa.

In contrast to the previous three phases, the structure of the next phase can be formed from cross-linked bundles of the same zigzag carbon nanotubes, (2,0), (3,0), or (6,0). The hexagonal unit cell of this phase has lattice parameters $a = 0.6722$ nm and $c = 0.4213$ nm and contains 24 atoms, and the calculated density is 2.904 g/cm^3 [9]. The space group of this phase is $P6/mcc$, and the calculated bulk modulus is 326 GPa.

The polycyclopropane diamond-like carbon phase proposed in [10] can be formed from cross-linked carbon cages of cyclopropane rings. The unit cell of this phase is hexagonal and contains six carbon atoms. The elementary translation vector lengths are $a = 0.440$ nm and $c = 0.251$ nm, and the calculated phase density is 2.84 g/cm^3. The space group of the phase made of polymerized cyclopropane rings is $P6_3/mmc$. The calculation results demonstrate that this phase represents a semiconductor with an energy gap of 2.3 eV.

The diamond-like phase made of polymerized carbon nanotubes (4,0) was theoretically studied in [11]. The structure of this phase consists of covalently bound nanotubes (4,0). The unit cell of the phase contains 32 atoms and belongs to the tetragonal system. The space group of the phase is $I4/mcm$, and the phase density is 3.23 g/cm^3. The calculations demonstrate that a crystal made of polymerized nanotubes (4,0) is a semiconductor with an energy gap of 3.18 eV.

Another series of the phases that can be formed from graphite, fullerene-like clusters, and nanotubes (M carbon, clathrate and tubulane phases) were studied experimentally and theoretically in [9, 12, 13, 15–20]. These phases consist of carbon or silicon atoms in states close to hybridized sp^3 states. However, atoms in these phases are located in nonequivalent crystallographic states; therefore, they are not considered in this work, in which we analyze the structures of diamond-like phases consisting of atoms in equivalent crystallographic states.

Thus, a number of diamond-like carbon phases have been experimentally synthesized and theoretically studied to date; however, the laws of formation of such phases are still poorly understood, a classification of these phases is absent, and the number of such phases and their structure are still unknown. The purpose of this work is to answer these questions.

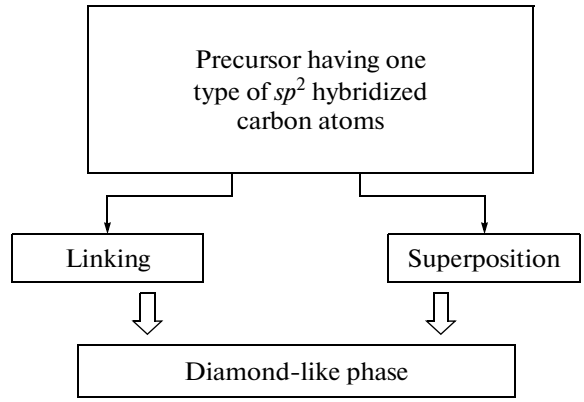

Fig. 1. Schematic diagram for model formation of diamond-like phases.

2. PROCEDURE OF MODEL FORMATION OF DIAMOND-LIKE PHASES

Carbon nanotubes (CNTs) can be formed by rolling of a graphene sheet, but this method cannot be executed experimentally. A model consideration of the CNT formation by rolling of graphene layers makes it possible to classify them. Similarly, we can propose a method for producing the first-group diamond-like phases that cannot be executed experimentally but can be used to describe their structures.

A model approach to forming diamond-like phases with the same degree of hybridization of all atoms was first suggested in [9]: the phases were formed from cross-linked bundles of single-layer CNTs of the same chirality. Our analysis demonstrates that this technique should be used to generate phases from not only CNTs but also from fullerenes and graphene layers. Phases can be formed by both cross-linking of structures and their superposition; the latter method is an obviously model method and cannot be effected experimentally.

The scheme of a model formation of diamond-like phases is shown in Fig. 1. This scheme demonstrates that the structure of any diamond-like phase can be formed by cross-linking or superposition of the sp^2 hybridized atoms making up the structures of precursors, with the atoms in the precursors being in equivalent crystallographic states.

As precursors, we can use various graphite-like structures consisting of sp^2 hybridized atoms. Such graphite-like structures can be represented by cage carbon nanostructures, namely, fullerenes (zero-dimensional) and single-layer nanotubes (one-dimensional) and layers consisting of sp^2 hybridized atoms

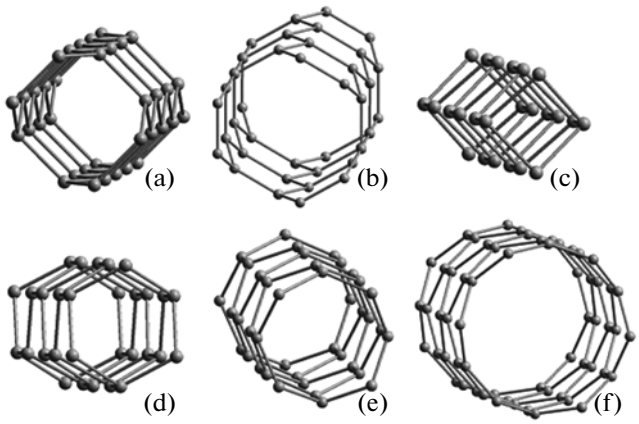

Fig. 2. Carbon nanotubes (a) (2,2), (b) (3,3), (c) (2,0), (d) (3,0), (e) (4,0), and (f) (6,0).

(two-dimensional). As the precursors, i.e., the initial structural elements, of diamond-like carbon phases, we considered the following elements: a graphene sheet, single-layer carbon nanotubes (Fig. 2), and carbon fullerene-like molecules (Fig. 3).

Apart from real graphene layers serving as precursors, we also considered three types of theoretically predicted sp^2 sheets consisting of the following regular geometric figures: (i) tetragon and octagon; (ii) triangle and dodecagon; and (iii) tetragon, hexagon, and dodecagon [21]. However, our model analysis showed that the diamond-like phases that form upon their linking can also be generated from precursors such as CNTs and some types of fullerene-like molecules. Therefore, as the two-dimensional precursors of diamond-like phases, we only considered graphene layers.

As the precursors of diamond-like phases made of single-layer CNTs, we used the following six nanotubes: (2,2), (3,3), (2,0), (3,0), (4,0), and (6,0) (see Fig. 2). This limited number of nanotubes is related to the following: when CNTs with large indices are cross-linked or superposed, some carbon atoms remain sp^2 hybridized, which results in hybrid sp^3–sp^2 rather than diamond-like structures; when chiral tubes with small indices (e.g., (2,1), (3,1)) are cross-linked, diamond-like phases consisting of sp^3 atoms in different hybridized states, which are not considered in this work, form.

The third possible sp^2 precursor of a diamond-like phase can be represented by a series of cage carbon nanostructures, namely, fullerene-like molecules C_4, C_6, C_8, C_{16}, C_{24}, and C_{48} (Fig. 3). A small number of fullerenes in this series is related to the fact that only hybrid sp^3–sp^2 phases can be obtained by cross-linking or superposition of fullerenes containing a large number of atoms, as in the case of large-diameter CNTs. The second limiting factor (which eliminates many fullerene-like molecules with less than 48 atoms), is the requirement that carbon atoms must be in equivalent states. Therefore, the molecules that do not meet this requirement do not enter into this series. The third limitation decreasing the number of precursor molecules is the necessity of forming periodic crystalline structures from precursor molecules. Periodic structures can be constructed from molecules that only have a two-, three-, four-, six-, or eightfold symmetry axis. Among the fullerene-like precursor molecules noted above, only the C_{12} molecule is absent; it is not eliminated according to these three criteria. This molecule does not enter in the series, since the diamond-like phase that results from the cross-linking of such molecules can also be formed by cross-linking of cage C_{48} molecules.

The first mechanism of generating diamond-like phases is the cross-linking of sp^2 hybridized nanostructures. One operation leads to the formation of carbon–carbon bonds between precursor atoms. Examples of diamond-like phase formation by the cross-linking of fullerene-like molecules and CNTs are given in Figs. 4 and 5, respectively. The cross-linking mechanism is not only a model mechanism: it occurs experimentally during polymerization.

The second mechanism of model formation of diamond-like phases consists in the superposition of the

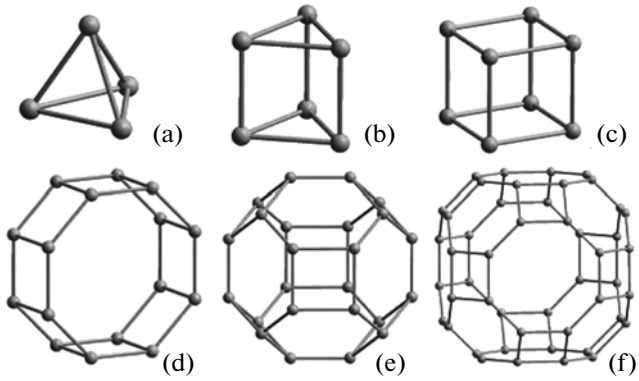

Fig. 3. Carbon cages of fullerene-like molecules: (a) C_4, (b) C_6, (c) C_8, (d) C_{16}, (e) C_{24}, and (f) C_{48}.

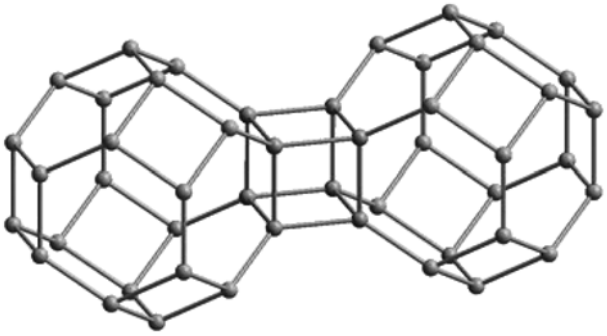

Fig. 4. Model formation of the structure of fullerane A4 by linking of the square faces of C_{24} fullerenes.

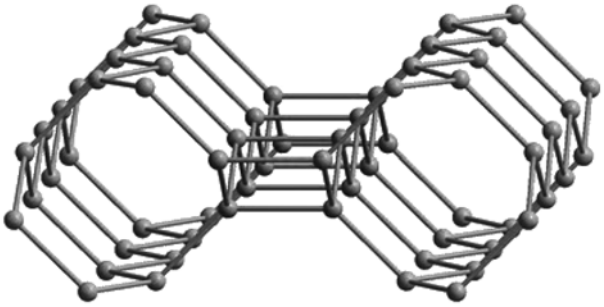

Fig. 5. Fragment of the structure of tubulane A1 that demonstrates linking of two nanotubes (2,2).

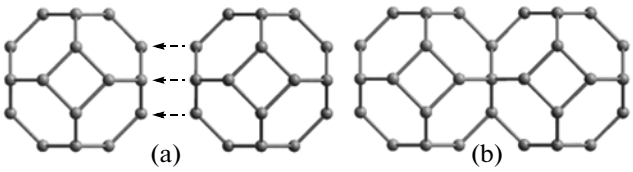

Fig. 6. Mechanism of forming the structure of fullerane A6 by the superposition of C_{24} fullerenes: (a) approaching of the square faces of the fullerenes and (b) superposition of the fullerene walls.

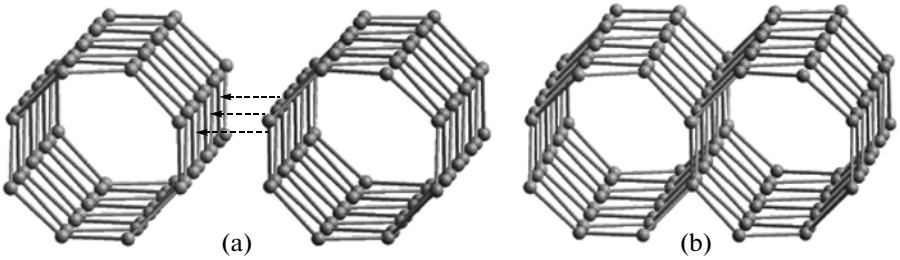

Fig. 7. Mechanism for the formation of tubulane A6 based on the superposition of zigzag nanotubes (4,0): (a) approaching of nanotubes and (b) superposition of the CNT walls.

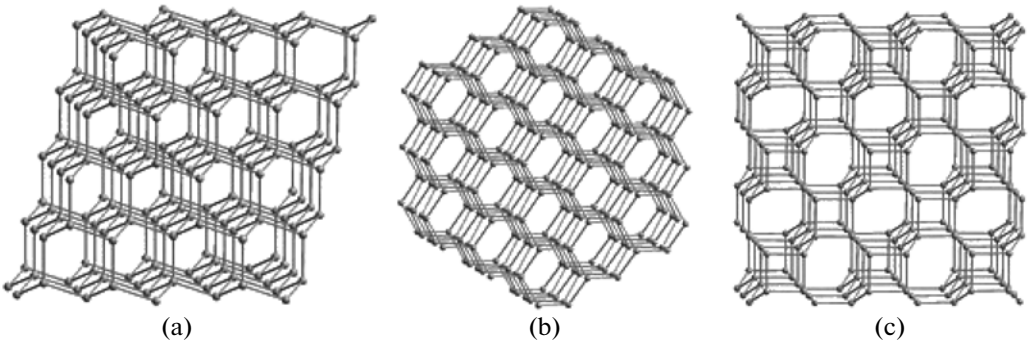

Fig. 8. Fragments of the structures of graphanes (a) A1, (b) A2, and (c) A3.

atoms of their sp^2 precursors: the same faces of precursor nanoparticles are superposed, atoms in one of the coinciding faces are removed, and the broken bonds are joined. Figure 6 and 7 show examples of forming diamond-like phases from fullerenes precursors and CNTs, respectively.

3. RESULTS AND DISCUSSION

An analysis of the scheme of diamond-like phase formation indicates that all diamond-like phases can be divided into the following three structural families: (1) graphanes are formed from graphene shets; (2) tubulanes, from nanotubes (tubulenes); and (3) fulleranes, from fullerene-like molecules. All families of diamond-like phases are called from the names of precursor structures by changing suffix "en" into suffix "an," which is used for alkanes in which every carbon atom form four σ bonds with the neighboring atoms.

Moreover, we introduced symbols in the names of phases indicating the method of their production: A stands for cross-linking and B is superposition. Different phases from the same family produced by the same method were indicated by different numbers.

As a result of a theoretical analysis, we found twenty diamond-like phases (Table 1): three of them are graphanes (Fig. 8), eight of them are tubulanes

Table 1. Structural characteristics of diamond-like phases calculated by molecular mechanics method MM+ (in parentheses, we give the values calculated by semi-empirical quantum-mechanical method PM3 if they differ from those calculated by the MM+ method)

Phase	Precursor	Bond angles, deg					
		β_{12}	β_{13}	β_{14}	β_{23}	β_{24}	β_{34}
Graphane A1	Graphene sheet	109.47					
Graphane A2	Graphene sheet	109.71 (109.78)			109.23 (109.16)		
Graphane A3	Graphene sheet	114.14 (111.41)	112.61 (113.48)				90.00
Tubulane A1	CNT (2,2)	112.73 (113.61)		135.00	113.74 (110.99)	90.00	
Tubulane A2	CNT (3,3)	117.33 (118.07)		120.00	115.97 (114.18)	90.00	
Tubulane A3	CNT (2,0)	90.00	110.23 (111.44)		131.56 (131.16)		83.13 (82.32)
Tubulane A4	CNT (3,0)	117.75 (115.51)	101.13 (104.05)	140.03 (141.41)	116.06 (113.44)	90.00	
Tubulane A5	CNT (4,0)	117.20 (115.92)	111.19 (113.37)	128.97 (129.49)	116.29 (114.56)	90.00	
Tubulane A6	CNT (4,0)	111.71 (111.35)	118.77 (119.72)		110.95 (109.87)		82.66 (83.37)
Tubulane A7	CNT (6,0)	112.34 (111.63)	126.98 (128.54)	107.12 (108.48)	111.90 (110.67)	111.13 (109.28)	82.27 (83.31)
Tubulane B	CNT (3,3)	117.19 (115.20)	116.83 (117.65)				60.00
Fullerane A1	C_4	144.74			60.00		
Fullerane A2	C_6	129.45 (132.60)		132.80 (128.30)	60.00	90.00	
Fullerane A3	C_8	125.26			90.00		
Fullerane A4	C_8	135.00	120.00		90.00		
Fullerane A5	C_{16}	128.30 (126.61)	90.00	135.00	118.79 (122.50)	90.00	
Fullerane A6	C_{24}	90.00	120.00				90.00
Fullerane A7	C_{48}	120.00	135.00	90.00		135.00	90.00
Fullerane A8	C_{48}	120.00	135.00	91.10 (91.72)	90.00	88.90 (88.28)	125.26
Fullerane B	C_{48}	90.00	135.00		120.00		60.00

Phase	Precursor	Lengths of C–C bonds, Å			
		L_1	L_2	L_3	L_4
Graphane A1	Graphene sheet	1.543 (1.546)			
Graphane A2	Graphene sheet	1.538 (1.522)	1.540 (1.548)		
Graphane A3	Graphene sheet	1.548 (1.522)		1.562 (1.567)	
Tubulane A1	CNT (2,2)	1.508 (1.492)	1.561 (1.564)		1.539 (1.572)
Tubulane A2	CNT (3,3)	1.524 (1.486)	1.548 (1.545)		1.570 (1.606)
Tubulane A3	CNT (2,0)	1.576 (1.586)	1.519 (1.502)	1.551 (1.562)	
Tubulane A4	CNT (3,0)	1.504 (1.483)	1.558 (1.566)	1.594 (1.606)	1.542 (1.554)
Tubulane A5	CNT (4,0)	1.506 (1.485)	1.552 (1.554)	1.554 (1.561)	1.549 (1.583)
Tubulane A6	CNT (4,0)	1.520 (1.487)	1.551 (1.541)	1.572 (1.593)	
Tubulane A7	CNT (6,0)	1.523 (1.489)	1.551 (1.536)	1.552 (1.555)	1.605 (1.662)
Tubulane B	CNT (3,3)	1.495 (1.498)		1.478 (1.515)	
Fullerane A1	C_4	1.408 (1.406)	1.442 (1.494)		
Fullerane A2	C_6	1.440 (1.441)	1.479 (1.543)		1.499 (1.573)
Fullerane A3	C_8	1.510 (1.446)	1.568 (1.570)		
Fullerane A4	C_8	1.498 (1.456)	1.546 (1.557)	1.565 (1.591)	
Fullerane A5	C_{16}	1.517 (1.505)	1.535 (1.511)	1.573 (1.589)	1.549 (1.579)
Fullerane A6	C_{24}	1.562 (1.560)			
Fullerane A7	C_{48}	1.511 (1.501)		1.540 (1.566)	
Fullerane A8	C_{48}	1.550 (1.505)	1.611 (1.600)	1.561 (1.497)	1.592 (1.583)
Fullerane B	C_{48}	1.450 (1.499)	1.495 (1.540)	1.450 (1.492)	

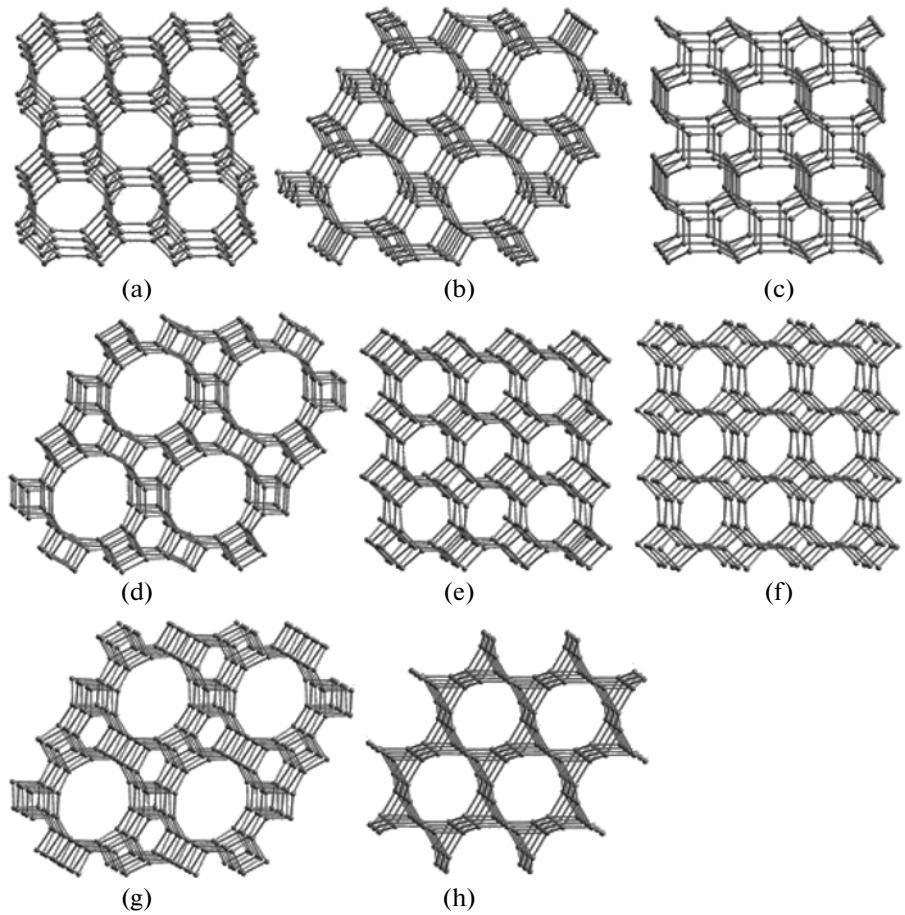

Fig. 9. Fragments of the crystal structures of tubulane phases (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, (f) A6, (g) A7, and (h) B.

(Fig. 9), and nine of them are fulleranes (Fig. 10). The graphane phases can only have type A; that is, they can only be produced upon cross-linking of graphene layers. Graphane B phases are absent. From all tubulane and fullerane phases, only two phases, namely, tubulane B and fullerane B are formed by superposition, and the other 15 phases belong to A phases formed by cross-linking. Fullerene-like molecule C_4 is the minimum structural element in the precursors of diamond-like phases (Fig. 3a), and their maximum element is represented by a graphene sheet.

The designations of diamond-like phases according to the developed classification scheme correspond to the following names of the well-known phases: graphane A1 corresponds to diamond; graphane A2, to lonsdaleite; graphane A3, rectangulane; fullerane A3, supercubane.

A comparative analysis of the structures of all diamond-like phases consisting of sp^3 hybridized carbon atoms shows that they differ only in the states of atoms. The difference in the states is determined by the relative orientation of the carbon–carbon σ bonds formed by every atom. The structural states of atoms (relative orientation of their bonds) is most correctly described by six angles β_{ij} ($i \neq j$; $i, j = 1, 2, 3, 4$, where i and j are bond numbers) between each pair of four bonds (Fig. 11). Bond lengths L_i represent another group of parameters that characterize the structural state of an atom; these quantities are likely to be functions of three angles adjacent to each bond.

The geometrical optimization of the structures of all diamond-like phases was performed by molecular mechanics method MM+ [22] and semi-empirical quantum-mechanical method PM3 (parametric method number 3) [23, 24]. The semi-empirical PM3 method uses the LCAO (linear combination of atomic orbitals) modification of the MO (molecular orbital) method. To find the eigenfunctions (MO) and eigenvalues (MO energies) of a Hamiltonian, we solved the Hartree–Fock–Roothan equation by neglecting the diatomic differential overlap. We used a change of 0.002 kcal/(Å mol) in the energy gradient as the criterion of completing the geometrical optimization of a structure in calculations.

Bond angles β_{ij} were measured for all diamond-like phases in the fragments of geometrically optimized structures. The numerical values of the angles are given in Table 1. A comparative analysis of angles β_{ij} of

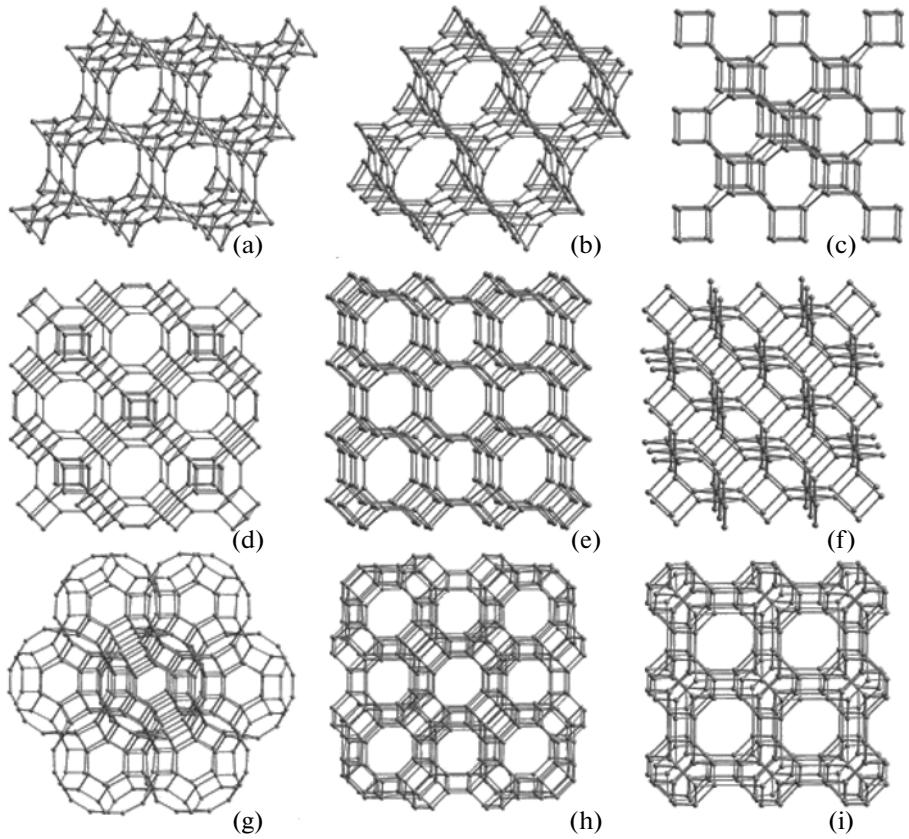

Fig. 10. Fragments of the structures of fulleranes (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, (f) A6, (g) A7, (h) A8, and (i) B.

all phases demonstrates that they fall in the range from 60.00° to 144.74°. The bond angles in all diamond-like phases apart from diamond are lower or higher than 109.47°. The number of angles β_{ij} lower than 109.47° was found to vary in the phases from one to three, and the number of angles β_{ij} higher than 109.47° varies from three to five. Angles β_{ij} were determined in structures geometrically optimized by different methods; therefore, the numerical values of the angles are not always identical. The maximum discrepancy between the values of β_{ij} calculated by the MM+ and PM3 methods was 4.5° for fullerane A2.

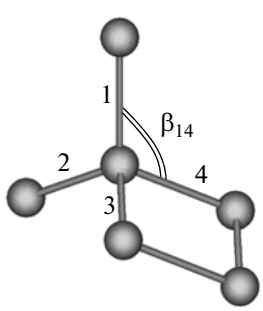

Fig. 11. Example of the numbering of bonds and the determination of angle β_{14} (graphane A3).

The bond angles calculated in the diamond-like phases vary from 1.408 to 1.611 Å for the MM+ method and from 1.406 to 1.662 Å for the PM3 method (Table 1). All four σ bonds are the same only in diamond and fullerane A6; two types of bonds are detected in six phases; three different bonds are present in seven phases; and five phases are characterized by four types of σ bonds. The bond lengths calculated by the MM+ and PM3 methods are strongly different: the minimum difference between the σ bond lengths is 0.002 Å for tubulane A5, and the maximum difference is 0.074 Å for fullerance A2.

Another structural characteristic of diamond-like phases (*R*) symbolically describes the structure of the rings consisting of the minimum number of covalent bonds and including one atom. The number of such different rings passing through one atom in diamond-like phases is always six, since such a ring should always have two bonds adjacent to a certain atom and every atom has four bonds. Therefore, the number of various combinations of bond pairs is six. Figure 11 shows the fragment of the structure of graphane A3 that contains a four-member cyclobutane ring formed upon the closure of three and four bonds. In diamond-like phases, cyclobutane and cyclohexane rings are most often present (they were detected in 16 phases);

Table 2. Structural parameters and properties of diamond-like phases calculated by semi-empirical quantum-mechanical method PM3 (in parentheses, we give the values calculated by molecular mechanics method MM+). C is the cubic crystallographic system, T is the tetragonal crystallographic system, and H is the hexagonal crystallographic system

Phase	Structural parameters					
	R (rings of sp^3 atom)	D, grad	Unit cell parameters			
			system	a, Å	c, Å	N_C, atoms
Graphane A1	6^6	0.00 (0.00)	C	3.57 (3.56)	–	8
Graphane A2	6^6	1.86 (1.44)	H	2.52 (2.51)	4.15 (4.12)	4
Graphane A3	$4^1 6^5$	37.45 (36.68)	T	4.35 (4.31)	2.52 (2.60)	8
Tubulane A1	$4^2 6^3 8^1$	74.28 (75.33)	T	6.46 (6.40)	2.58 (2.61)	16
Tubulane A2	$4^2 6^4$	71.38 (71.78)	H	6.03 (6.04)	2.59 (2.63)	12
Tubulane A3	$4^2 6^2 8^2$	93.94 (91.52)	T	3.56 (3.58)	4.31 (4.23)	8
Tubulane A4	$4^2 6^3 8^1$	86.31 (92.90)	H	6.84 (6.76)	4.41 (4.52)	24
Tubulane A5	$4^2 6^3 8^1$	74.70 (74.67)	T	6.92 (6.84)	4.41 (4.48)	32
Tubulane A6	$4^1 6^5$	49.28 (50.61)	T	7.01 (6.98)	4.17 (4.23)	32
Tubulane A7	$4^1 6^5$	49.77 (54.19)	H	6.86 (6.81)	4.17 (4.26)	24
Tubulane B	$3^1 6^5$	87.91 (86.63)	H	4.42 (4.31)	2.53 (2.55)	6
Fullerane A1	$3^3 12^3$	254.21 (254.21)	C	7.47 (7.33)	–	32
Fullerane A2	$3^1 4^2 8^3$	153.79 (150.37)	H	5.04 (4.79)	4.94 (4.95)	12
Fullerane A3	$4^3 8^3$	105.79 (105.79)	C	4.81 (4.88)	–	16
Fullerane A4	$4^3 6^2 8^1$	105.00 (105.00)	C	5.87 (5.88)	–	24
Fullerane A5	$4^3 8^3$	114.11 (112.08)	T	7.05 (7.13)	4.80 (4.63)	32
Fullerane A6	$4^2 6^4$	81.06 (81.06)	C	4.41 (4.45)	–	12
Fullerane A7	$4^3 6^1 8^2$	120.00 (120.00)	C	7.38 (7.35)	–	48
Fullerane A8	$4^3 6^1 8^2$	110.26 (109.53)	C	8.97 (9.18)	–	96
Fullerane B	$3^1 4^1 6^2 8^2$	141.06 (141.06)	C	9.40 (9.12)	–	96

Phase	Properties of phases			
	density ρ, g/cm^3	packing coefficient f	bulk modulus K, GPa	sublimation energy E_{sub}, kcal/mol
Graphane A1	3.50 (3.53)	0.34 (0.34)	483	167.2
Graphane A2	3.49 (3.55)	0.34 (0.34)	474	166.3
Graphane A3	3.36 (3.30)	0.32 (0.33)	427	163.7
Tubulane A1	2.97 (2.98)	0.29 (0.29)	393	159.9
Tubulane A2	2.93 (2.89)	0.28 (0.28)	333	158.9
Tubulane A3	2.92 (2.95)	0.29 (0.29)	329	160.0
Tubulane A4	2.58 (2.68)	0.26 (0.26)	331	159.4
Tubulane A5	3.03 (3.05)	0.29 (0.29)	390	160.0
Tubulane A6	3.12 (3.10)	0.31 (0.31)	418	162.0
Tubulane A7	2.82 (2.80)	0.28 (0.28)	354	161.0
Tubulane B	2.79 (2.92)	0.25 (0.25)	–	157.6
Fullerane A1	1.53 (1.62)	0.13 (0.13)	–	133.4
Fullerane A2	2.20 (2.43)	0.21 (0.20)	–	145.7
Fullerane A3	2.87 (2.75)	0.27 (0.27)	342	154.3
Fullerane A4	2.37 (2.36)	0.23 (0.23)	249	153.7
Fullerane A5	2.68 (2.72)	0.26 (0.26)	–	157.0
Fullerane A6	2.79 (2.77)	0.28 (0.28)	323	161.8
Fullerane A7	2.38 (2.41)	0.23 (0.22)	207	158.9
Fullerane A8	2.66 (2.47)	0.26 (0.26)	–	155.0
Fullerane B	2.31 (2.53)	0.21 (0.21)	–	154.9

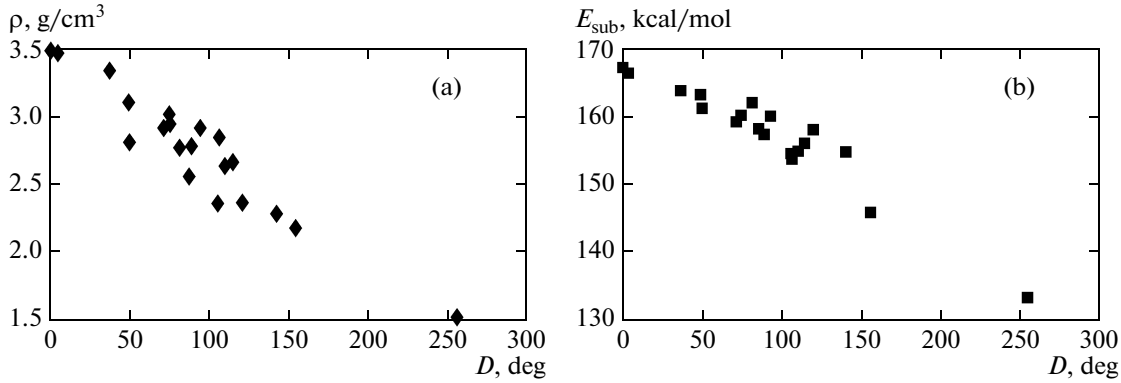

Fig. 12. Dependences of (a) density ρ and (b) sublimation energy E_{sub} of a diamond-like phase on deformation parameter D calculated by the PM3 method.

cyclooctane rings are found in 11 phases; cyclopropane rings are detected in four phases, and cyclododecane rings are found in one phase (Table 2).

To characterize the deformation of the structures of diamond-like phases, we introduced parameter D, which is the sum of the moduli of the differences between angles β_{ij} and diamond angle $\beta_{diamond}$ = 109.47°,

$$D = \sum_{i=1}^{3}\sum_{j>i}^{4}|\beta_{ij} - \beta_{diamond}|.$$

A comparative analysis of the deformation parameters of various diamond-like phases demonstrates that, for both optimization methods (MM+, PM3), the values of D fall in the range from 0° to 254.21° (Table 2). The deformation parameters are minimal for graphanes (lower than 37.45°), range from 50.33° to 93.94° for tubulane phases, and are maximal for fulleranes (81.06°–254.21°). Parameter D correlates with the number of rings consisting of less than six links: the deformation parameter increases with decreasing number of links in rings or increasing the number of such rings.

The unit cells of the diamond-like phases belong to the following crystallographic systems (Table 2): seven phases belong to the cubic system, seven phases belong to the tetragonal system, and six phases belong to the hexagonal system.

The densities of the diamond-like phases calculated by the MM+ method fall in the range from 1.62 g/cm^3 for fullerane A1 to 3.55 g/cm^3 for graphane A2, and those calculated by the PM3 method range from 1.53 g/cm^3 for fullerane A1 to 3.50 g/cm^3 for graphane A1 (see Table 2). The maximum discrepancy between the densities calculated by the MM+ and PM3 methods is 9.5% for fullerane A2, and the minimum discrepancy is 0.4% for tubulane A5. When comparing the data in Table 2, we found that the density of the diamond-like phase is proportional to deformation parameter D (Fig. 12a), and this dependence is interpolated best of all by the function

$$\rho = A_1 + B_1 D,$$

where A_1 = 3.5 ± 0.1 g/cm^3 and B_1 = (–8 ± 2) × 10^{-3} g/(cm^3 deg). Packing coefficient f a diamond-like phase (Table 2) ranges from 0.13 (fullerane A1) to 0.34 (diamond).

Bulk elastic moduli K of diamond-like phases at 298 K were calculated by the semi-empirical quantum-mechanical PM3 method with the procedure proposed in [25]. The bulk modulus of diamond $K_{diamond}$ calculated by the PM3 method (483 GPa) agrees well with the experimentally measured modulus (442 GPa) [26], which proves the correctness of the calculated bulk moduli of the diamond-like phases presented in Table 2. The cubic (graphane A1) and hexagonal (graphane A2) diamonds have the maximum bulk moduli, 483 and 474 GPa, respectively. Fullerane A7 has the minimum bulk elastic modulus (207 GPa), which is smaller than $K_{diamond}$ by 57%. The following two phases among the diamond-like phases have the maximum bulk moduli: graphane A3 (427 GPa) and tubulane A6 (418 GPa). These values are smaller than $K_{diamond}$ by 12 and 13%, respectively. The diamond-like phases having graphene sheets as precursors have larger bulk moduli as compared to the phases containing links of nanotubes or fullerene-like units. Deformation parameter D is found to be directly proportional to bulk modulus K: $D \propto K$.

The sublimation (atomization) energies of diamond-like phases were calculated by the PM3 method (see Table 2). The small difference between the energy calculated for diamond (E_{sub} = 167.2 kcal/mol) and the corresponding experimental energy (170 kcal/mol [27]) indicates the correctness of the sublimation energies calculated for the diamond-like phases. The sublimation energies presented in Table 2 range from 133.4 kcal/mol for fullerane A1 to 167.2 kcal/mol for graphane A1. Diamond-like phases with high densities and bulk moduli have the maximum sublimation

energies. The dependence of the sublimation energy of a diamond-like phase on the deformation parameter (Fig. 12b) is well approximated by the function

$$E_{\text{sub}} = A_2 + B_2 D,$$

where $A_2 = 169 \pm 3$ kcal/mol and $B_2 = (-12 \pm 2) \times 10^{-2}$ kcal/(mol deg).

4. CONCLUSIONS

We suggested a classification scheme for the diamond-like phases consisting of carbon atoms in equivalent crystallographic states. We found that twenty such phases can exist. We were the first to describe ten of them. We used molecular mechanics method MM+ and semi-empirical quantum-mechanical method PM3 to calculate the geometrically optimized structures of diamond-like phase clusters and to determine their structural parameters and properties, such as the density, the bulk modulus, and the sublimation energy.

The sublimation energies of all diamond-like phases are lower than that of diamond, which points to their lower thermodynamic stability. This means that such phases cannot be synthesized under thermodynamically equilibrium conditions. Graphane phases are thought to be synthesized from graphite under shock loading. Tubulane phases can be formed by the compression of bundles made of CNTs of the same chirality in the direction normal to the nanotube axis. Fullerane phases can be formed upon three-dimensional compression of fullerites. The necessity of searching for the methods of experimental synthesis of diamond-like phases is related to the fact that they can be used as structural and abrasive materials and as a molecular sieve due to their high strength and low density.

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