

Structure, Properties, and Possible Mechanisms of Formation of Diamond-Like Phases

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Abstract—An analysis was performed for relations between the structural parameters and the properties of 36 carbon diamond-like phases consisting of atoms occupying crystallographically equivalent positions. It was found that the crystal lattices of these phases were in stressed states with respect to the cubic diamond lattice. The density of diamond-like phases, their sublimation energies, bulk moduli, hardnesses, and band gaps depend on the deformation parameters Def and Str. The most stable phases must be phases with minimal parameters Def and Str and also with ring parameter Rng that is most close to the corresponding parameter of cubic diamond. The structures and energy characteristics of fullerites, nanotube bundles, and graphene layers of which diamond-like phases can be obtained as a result of polymerization at high pressures have been calculated.

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1. INTRODUCTION

The structural variety of carbon compounds is due to the possibility of locating carbon atoms in the states with various coordinations [1, 2]. In compounds with covalent type of chemical bonds, carbon atoms can be in the two-, three, and four-coordinated states. The carbon structures from four-coordinated atoms can have various crystallographic dimensions and, thus, belong to one of four structural groups: $[0D_c, 4]$, $[1D_c, 4]$, $[2D_c, 4]$, and $[3D_c, 4]$ [1, 2]. The compounds with three-dimensional crystallographic dimensionality that belong to structural group $[3D_c, 4]$ are named diamond-like phases [3]. The “diamond-like phases” name is related to their most known representative: cubic diamond. The specific features of diamond-like phases provide their high anticorrosion and mechanical characteristics, and unique optical and electronic properties [4]. This is the reason why these compounds are widely used in practice that is limited because of the complexity and high cost of the technologies of their synthesis.

The main factors that influence the process of formation of diamond and other diamond-like phases are pressure, temperature, source material, and the composition of the medium in which the synthesis occurs. The most carefully studied and developed techniques of synthesizing diamond can be classified according to the mechanisms of structure formation.

I. Formation from individual carbon atoms, nanorings, and nanochains:

(i) diamond growth from carbon of initial graphite dissolved in a metal–catalyst (or binary alloys) at high pressures and high temperatures (HPHT synthesis) [5];

(ii) chemical vapor deposition of carbon (CVD synthesis) on the surface of heated diamond seed or other phase as a result of thermal decomposition of hydrocarbons (methane, acetylene, etc) [6], carbon tetraiodide [7] or carbon oxide [8] at low pressures;

(iii) deposition of carbon on a substrate (usually silicon) from an oxygen-acetylene flame [9] and also at decomposition of a carbon-containing gas by microwave plasma [10], electrical discharge [11], or heated tungsten (or graphite) filament [12] in the presence of hydrogen;

(iv) bombardment of a substrate by carbon ionic beams (the plasma is generated using the last three methods from point (iii) (ion-beam method [13]);

(v) detonation of an explosive containing carbon with summary negative oxygen balance [14];

(vi) decomposition of graphite [15] or liquid aromatic hydrocarbons [16] as a result of high-intense pulsed laser radiation;

(vii) deposition of atomic carbon on a diamond seed as a result of thermal decomposition of CO in a water medium using catalyst in the form of a water-soluble salt that gives an alkali character to the medium [17];

(viii) growth on the surface of decomposed silicon carbide in a chlorine-containing medium at high temperatures [18];

(ix) detonation of acetylene and carbon dioxide [19];
 (x) growth of a diamond film on anode as a result of the electrolyze of organic precursors [20].

II. Formation from carbon clusters: strong shock [21] and static [22] compression of fullerenes.

III. Formation from one-dimensional carbon nanostructures:

(i) strong static compression of carbon nanotube (CNT) bundles [23];

(ii) laser ablation of multilayer CNTs [24].

IV. Formation from two-dimensional nanoprecursors:

(i) static compression of graphite without applying metals as solvent-catalysts [25] at high pressures and high temperatures (a version of the HPHT synthesis);

(ii) shock synthesis as a result of (a) compression of graphite by shock waves generated by an explosive material initiation [26], (b) action on graphite of metallic plates falling at high velocity [27], (c) power ultrasonic cavitation of graphite suspension in an organic liquid at normal conditions [28], (d) dynamic impression of a projectile with graphite into a target [29], and (e) action of ultrasonic vibrations on the graphite dispersion in liquid xenon [30];

(iii) irradiation of a carbon target (graphite) with argon ions (a version of the ion-beam method) [31].

When designing the abovementioned techniques of diamond synthesis, it was revealed that not only cubic diamond but also a number of metastable diamond-like phases could form.

The first diamond-like phase with a simple cubic lattice ($Pm\bar{3}m$, $a = 5.545 \text{ \AA}$) was experimentally synthesized from graphite at high pressures ($P = 15\text{--}20 \text{ GPa}$) and low temperatures ($T > -93^\circ\text{C}$) [32]. Crystals of this phase were also synthesized at $P < 1 \text{ GPa}$ and $T > 1000^\circ\text{C}$. A possible structure of this phase consisted of polymerized clusters in the form of truncated C_{24} octahedra [33].

The most extensively studied of the synthesized carbon diamond-like phases is the hexagonal $2H$ diamond polytype (lonsdaleite). Lonsdaleite was synthesized for the first time in 1967 from graphite at a pressure of 13 GPa and a temperature higher than 997°C [34]. All atoms in the lonsdaleite crystal lattice with parameters $a = 2.52 \text{ \AA}$ and $c = 4.12 \text{ \AA}$ are disposed in equivalent crystallographic states.

The synthesis of cubic carbon phase C_8 ($a = 4.279 \text{ \AA}$) was reported on in 1979, in whose structure all atomic positions were crystallographically equivalent, as a result of deposition of carbon from plasma on a single-crystal KCl surface in vacuum [35]. The C_8 phase structure is similar to the Si-III structure. This phase has the highest density (4.07 g/cm^3) among all carbon materials.

In [36], several cubic carbon phases observed in diamond-like films of the i -carbon were described; they

were synthesized by ion-beam deposition from plasma obtained during decomposition of saturated hydrocarbons (C_4H_{10} , C_2H_6 , C_3H_8 , or CH_4). The three phases had lattice parameters 3.4, 4.0, and 4.25 \AA .

Besides lonsdaleite, a number of hexagonal and rhombohedral diamond polytypes were synthesized. The first of these polytypes 6H was synthesized in the experiment with microwave plasma at low pressure in 1989 [37]; this polytype was also observed in diamond films obtained by the chemical vapor deposition method [38]. In 1996, the 4H polytype was synthesized during laser treatment of decaline [39] and polytype 15R was synthesized as a result of condensation of carbon from acetylene-oxygen flame on polycrystalline molybdenum substrates [40]. In 1998, polytype 8H was synthesized by cyclic growth-etching using an acetylene-oxygen flame, too [41]. More recently, this polytype was obtained as a result of intense (20 kW) synchrotron X-ray irradiation of graphite at normal pressure [42]. In [43], it was shown that cubic crystal can be transformed into polytypes 21R and 6H under severe load in the experiments on indentation by the Vickers method. The latter of the known polytypes, 9R, was synthesized in 2001 as a result of epitaxial growth on a Si{100} substrate irradiated by ions from a gas mixture (CH_4 or C_2H_2)/Ar/ H_2 at temperatures 600 or 700°C [44]. In [45], two face-centered cubic (fcc) phases with diamond-like structures and parameters 5.45 and 11.54 \AA were synthesized as a result of heating of carbon black to a temperature of 800°C at low pressure (10–3 Pa).

Single crystals of several diamond phases were synthesized from single-layer CNTs at 9.5 GPa and 600°C in 2002 [46]. The lattice parameter of the cubic phase was 8.8 (9.0) \AA , and three phases with hexagonal symmetry had lattice parameters $a = 2.62 \text{ \AA}$ and $c = 6.53 \text{ \AA}$, $a = 2.9 \text{ \AA}$ and $c = 5.15 \text{ \AA}$, $a = 4.9 \text{ \AA}$ and $c = 9.25 \text{ \AA}$.

In addition, two cubic diamond polymorphs were experimentally studied in 2003. One carbon phase with a simple cubic lattice (lattice parameter 5.14 \AA) was obtained from a mixture of carbon black and tetracyanoethylene during shock-wave loading [47]. Another cubic phase ($a = 14.697 \text{ \AA}$) transparent in the optical range was found in minerals of the Popigai impact crater [48].

In 2004, the high-strength hexagonal diamond-like phase ($a = 2.496 \text{ \AA}$, $c = 4.123 \text{ \AA}$) was synthesized as a result of severe ($P \approx 75 \text{ GPa}$) static compression of a bundle of disordered CNTs with diameters from 18 to 51 \AA [49]. The highly probable structure of this sp^3 phase was similar to the structures of simulated rhombic phases of P - (space group $Pmmm$) and Z -carbon (or $C_{co}\text{--}C_8$), which contain the covalent-coupled links from (2,2) nanotubes.

Cubic micro- and nanocrystals of a carbon phase with a possible diamond-like structure were synthesized by laser ablation of a carbon target in a water

solution of ethanol, acetone, and inorganic salts in 2008 [50]. The parameter of the body-centered cubic (bcc) lattice of this phase is 5.46 Å.

A nanocrystallite of the last diamond-like phase of the phases known up to now was synthesized from an onion at a pressure of 10 GPa and a temperature of 1850°C in 2014 [22]. The electron microscopy studies showed that the crystallite can have the structure of the monoclinic *M*-carbon phase that was studied theoretically [51].

Thus, by now, a great many diamond-like phases were synthesized. Since the synthesis of such phase in 1963, new diamond-like phases are discovered constantly and, it is possible, the multitude of new diamond-like phases can be synthesized in the immediate future. Because of this, a theoretical analysis of possible structures of these phases is necessary. The foundations of the theoretical technique that makes it possible to describe the structures of all possible diamond-like phases were outlined in [1–3]. Based on this technique, the structures and the properties of diamond-like phases consisting of atoms disposed in the equivalent crystallographic positions were studied theoretically in [52–54]. This work is devoted to generalized discussion of the results of those theoretical studies of the diamond-like phases simulated from graphene layers [52], nanotubes [53], 3D graphites [53], and fullerene-like clusters [54], and also to the analysis of possible methods of synthesizing these phases in the experiments.

2. TECHNIQUE

The structural parameters and the energy characteristics of the carbon compounds analyzed in this work were calculated by the density functional theory (DFT) in a generalized gradient approximation using the Quantum ESPRESSO program packet [55]; the B3LYP exchange-correlation functional was used [56]. The parameters used in these calculations were given in [52–54].

The bulk moduli of the diamond-like phases were calculated using the modified Kumar–Sharma equation of states [57]

$$E - E_0 = V_0 \left[\frac{9(B_0 + 2B_1)}{16} \left(\left(\frac{V}{V_0} \right)^{8/3} - \frac{4}{3} \left(\frac{V}{V_0} \right)^2 + \frac{1}{3} \right) - B_1 \left(\frac{9}{11} \left(\frac{V}{V_0} \right)^{11/3} - \left(\frac{V}{V_0} \right)^3 + \frac{2}{11} \right) \right],$$

where E_0 and E , V_0 and V are the total energies and the volumes of a crystal before and after deformation, respectively, B_0 and B_1 coefficients with the dimensionality of pressure. The range of varying the relative volume V/V_0 is [0.941, 1].

The Vickers hardness of the phases was determined by the method from [58]

$$H_V = \left[\prod_{\alpha=1}^n (350(N_e^\alpha)^{2/3} \exp(-1.191f_i^\alpha)/(d_\alpha)^{2.5})^{n^\alpha} \right]^{1/\sum n^\alpha},$$

where H_V has dimensionality in GPa, n is the number of various covalent bonds in the unit cell of the crystal, N_e^α is the number of valence electrons in 1 Å³, n^α is the number of the α -type bonds, d_α is the α -bond length in Å, and f_i^α is the ionic factor (for carbon materials, $f_i^\alpha = 0$).

3. RESULTS AND DISCUSSION

In [52–54], we calculated the structures and the properties of 36 diamond-like phases. The model technique of the calculations using the joining and combinations of precursors from three-coordinated atoms was described in [1, 2]. From the 36 phases, the 18 phases (*LA5*, *LA7*, *LA8*, *LA10*, *TA2*, *TA4*, *TA6*, *SA3*, *SA4*, *CA5–CA12*, and *CB*) were studied for the first time. Table 1 gives the notations of the phases according to the types of structural precursors (*L* are layers, *T* are tubes, *S* are spirals, and *C* are clusters), the notations of these phases used in [59–79], and also the

types of zeolite structures corresponding to the phases. In the phases, all atomic positions were crystallographically equivalent. The crystal lattices of the most part of the phases had zeolite analogs (Table 1). Up to now, zeolite analogs have not been found for 14 phases. It is likely that each of the diamond-like phases must have its zeolite analog and conversely. An analysis of zeolite structures from four-coordinated atoms in the equivalent positions showed that only one of zeolites known up to now had no corresponding diamond-like phase. It is the *ANA* with the ring parameter 4²6²8². The structure of the corresponding diamond-like phase was unstable, according to the DFT–GGA calculations. It should be noted that there are four phases *LA1*, *LA2*, *LA4*, and *CA4*.

An analysis of the relations between the properties and structural characteristics of the carbon diamond-like phases showed that there were clear dependences of the properties on the structural parameters. For example, the phase density decreased as the deformation parameter Def [3], characterizing the deviation of

Table 1. Alternative names of cubic diamond and diamond-like phases, similar zeolite structures, and also the works in which these phase were (*) obtained experimentally or (**) studied theoretically

Phase	Alternative notation	Zeolite structure	References
LA1	Diamond, cubic diamond, polytype 3C	—	[5]*
LA2	Hexagonal diamond [34], lonsdaleite [59], diamond 2H polytype	—	[34, 59]*
LA3	8-tetra(2,2)tubulane [60], bct C ₄ [61], graphane-A3 [3], 3D (2,2)-II [62]	BCT [63]	[60]**
LA4	High-dense phases C ₈ [35], bc8 [64], graphane-A4 [65]	—	[35]*, [64]**
LA5	Graphane-A5 [65], Y-carbon [66]	ZIF-4 [67]	[65, 66, 68]**
LA6	8-tetra(3,3)tubulane [60], phase <i>Imma</i> [69], graphane-A6 [65]	ABW [63]	[60]**
LA7	Graphane-A7 [65]	—	[65, 68]**
LA8	Graphane-A8 [65]	GIS [63]	[65, 68]**
LA9	rh6-II [70]	—	[65, 71]**
LA10	—	MON [63]	[71]**
TA1	16-tetra(2,2)tubulane [60], tubulane-A1 [3], 3D (2,2)-I [62]	ATN [63]	[60]**
TA2	12-hexa(3,3)tubulane [60], tubulane-A2 [3], 3D (3,3)-III [62]	CAN [63]	[60]**
TA3	Tubulane-A3 [3]	DFT [63]	[3]**
TA4	Tubulane-A4 [3]	—	[3]**
TA5	Dimer(4,0) <i>I4/mcm</i> [72], tubulane-A5 [3]	—	[72]**
TA6	Tubulane-A6 [3], (4,0)-I [62]	—	[3]**
TA7	24-hexa(2,0)tubulane [60], tubulane-A7 [3], 3D (6,0)-III [62]	AFI [63]	[60]**
TA8	36-hexa(3,3)tubulane [60], 3D (3,3)-II [62]	ATO [63]	[60]**
TB	hcp C ₃ [61], tubulane-B [3]	NPO [63]	[61]**
SA1	C-CFS [73]	—	[73]**
SA2	hP3 [74]	—	[74]**
SA3	—	—	[53, 75]**
SA4	—	—	[53, 75]**
CA1	Tetrahedral diamond [76], fullerane-A1 [3], T-carbon [77]	—	[3, 76, 77]**
CA2	Fullerane-A2 [3]	—	[3]**
CA3	Supercubane [76], fullerane-A3 [3]	ACO [63]	[3, 76]**
CA4	SC fullerite C ₂₄ [33], fullerane-A4 [3]	LTA [63]	[32]*, [33]**
CA5	Fullerane-A5 [3]	MER [63]	[3]**
CA6	bcc C ₆ [78], fullerane-A6 [3]	SOD [63]	[78]**
CA7	Fullerane-A7 [3]	RHO [63]	[3]**
CA8	Fullerane-A8 [3]	KFI [63]	[3]**
CA9	Fullerane-A9 [65]	FAU [63]	[65, 68]**
CA10	—	CHA [63]	[68]**
CA11	—	GME [63]	[68]**
CA12	—	RWY [63]	[71]**
CB	Fullerane-B [3], fcc-C ₁₂ [79]	—	[3]**

angles between bonds in a specific phase from the diamond angle 109.47° (Fig. 1), increased. The range of varying the densities was from 1.210 g/cm³ (CA12) to 3.554 g/cm³ (SA2) [52–54], and the range of varying

the deformation parameter was from 0° (LA1) to 254.2° (CA1). In addition, there was a correlation between the phase density and the value of ring parameter Rng [52–54]: the phases with the ring

parameters which minimally differed from the diamond parameter 6^6 had the maximum densities.

One more significant property of the diamond-like phases that characterizes their stability is the difference with respect to the total energy of the diamond energy (ΔE_{diam}). The difference ΔE_{diam} also can be interpreted as the difference sublimation energy. The values of ΔE_{diam} for the diamond-like phases were in the range from 0.03 (*LA2*) to 1.51 eV/atom (*CA12*) [52–54]. No clear dependence of ΔE_{diam} on one of the deformation parameters (Def or Str [52]) was observed (Figs. 2a and 2b). However, there is a correlation of ΔE_{diam} simultaneously with two parameters Def and Str that is expressed in a cup-shaped energy surface in the space of three variables (Fig. 2c). The value of ΔE_{diam} was linearly dependent on a parameter that was a combination of Def and Str (Fig. 2d). These correlations between ΔE_{diam} and the deformation parameters are explained by the fact that Def and Str complement one another, and each significantly influences the total energy.

The mechanical properties of carbon phases with diamond-like structures were characterized by the calculated values of bulk modulus B_0 and the Vickers hardness H_V . The bulk moduli of the group of *L* phases were calculated in this work, and the moduli of *T*, *S*, and *C* phases were calculated in [53, 54]. The values of B_0 varied from 141.2 (*CA12*) to 458.1 GPa (*LA9*). There is a clear relation between the bulk modulus and the density: B_0 is proportional to the density (Fig. 3a). The maximum deviations from the linear dependence correspond to the phases with high parameter Str and a quite high density with respect to those of diamond (*LA1*). Since there is correlation between the density and Def (Fig. 1), the analogous near-linear dependence $B_0 = f(\text{Def})$ can be built.

The calculated Vickers hardness H_V that characterizes the resistance of a crystal to plastic deformation under local force action was 90.0 GPa for cubic diamond, which agrees well with the experimental value (96 GPa) [80]. The diamond-like phases have H_V from 49.4 (*CA12*) to 90.0 GPa (for phases *LA1* and *LA2*). The phases with highest densities had the maximum hardness. A dependence $H_V \sim \text{Def}$ took place between the hardness and deformation parameters Def (Fig. 3b).

The band gap width (E_g) of the diamond-like phases was found as the difference of the energies of electrons in the conduction band bottom and the valence band top, based on the densities of states [52–54]. The band gap widths of carbon diamond-like phases took values from 0.82 (*LA9*) to 5.44 eV (*LA1*). Twelve phases with the band gap widths $0.82 < E_g < 3$ eV must have semiconducting properties, while the other 24 phases were wide-band-gap semiconductors ($E_g > 3$ eV). It was found that there was a correlation between the band gap width E_g and the difference total energy

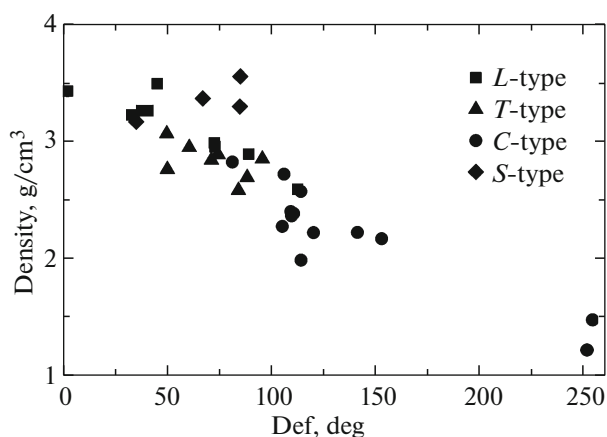


Fig. 1. Densities versus deformation parameter Def for diamond-like phases.

ΔE_{diam} (Fig. 4). A relative wide scatter of points in Fig. 4 shows that E_g is dependent on not only the total energy of the system, but also the crystal symmetry, the interatomic bond lengths and the angles between these bonds. Thus, the electronic properties of the carbon diamond-like phases can be changed due to internal stresses in the structure. In addition, the band gap width can be changed as a result of doping with alkali-metal atoms into the largest pores of the crystal lattice.

The thermal stability of any carbon phase must be determined by the stability of its most stressed structural link. The structural chains of the diamond-like phases are carbon skeletons of saturated hydrocarbons (cycloalkanes) and small clusters on their basis. The quantitative characteristic of the stability of structural links is ring parameter Rng [52–54]. At normal pressure, cubic diamond consisting only of six-membered rings ($\text{Rng} = 6^6$) is the most stable polymorph of four coordinated atoms, since it transforms to graphite only at temperatures higher than 1200°C [4]. Since the structures of most of the diamond-like phases contain carbon rings from three and four links, the upper boundary of the thermal stability of these phases will be determined by the stability of cyclopropane, cyclobutane, and tetraasterane and is approximately 450–500°C. The stability of other links in the form of clusters and ladder molecules at normal conditions was discussed in [53, 54]. All the diamond-like phases studied in this work can be stable at room temperature, since not only the structural units described above but also molecules of saturated hydrocarbons with more stressed carbon skeletons called propellanes are stable at normal conditions.

At low pressures, graphite is the most stable carbon polymorph, while cubic diamond is metastable [4, 81]. Therefore, all the diamond-like phases studied in this work will be metastable at the atmospheric pressure, which significantly decreases the probability of their

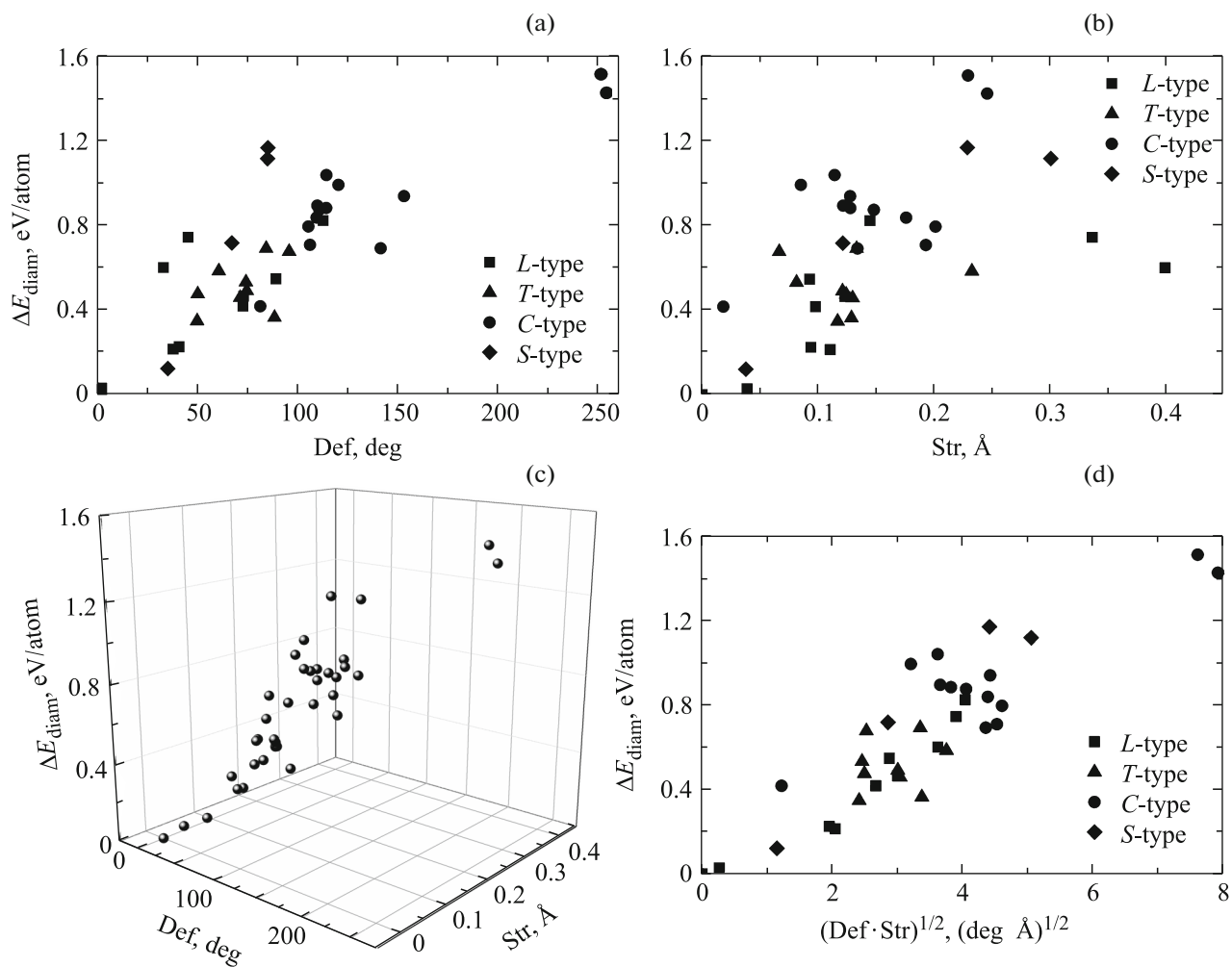


Fig. 2. Dependences of the difference total energies of diamond-like phases on deformation parameters (a) Def, (b) Str, (c) Def and Str, and (d) their combination.

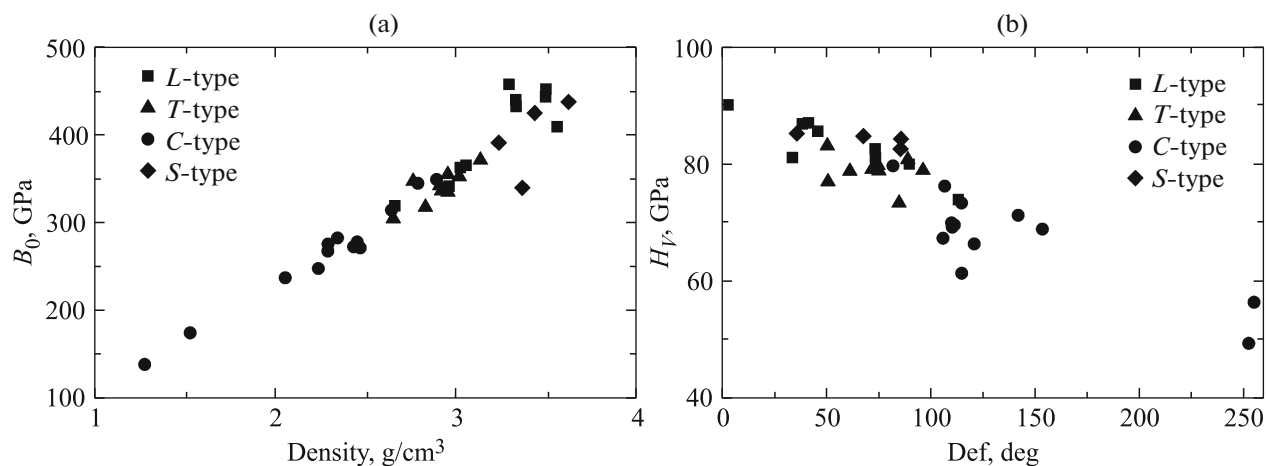


Fig. 3. Dependences of (a) bulk modulus B_0 on the density and (b) hardness H_V on deformation parameters Def for diamond-like phases.

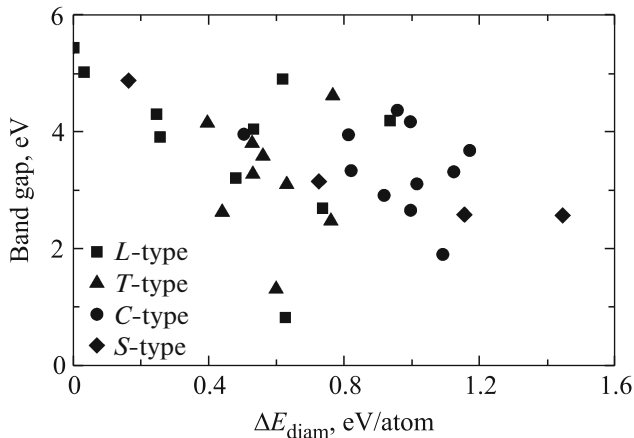


Fig. 4. Dependence of the band gap width of diamond-like phases on the difference total energy ΔE_{diam} .

synthesizing during polymerization of graphene fragments or by chemical vapor deposition. It is possible that carbon phases with a diamond-like structure can be synthesized in these conditions by selecting a medium composition, catalysts, and substrates. However, even in this case, the phases consisting of the most stable six-member carbon rings, i.e., cubic diamond [4, 6–13, 37, 38, 40, 41], diamond polytypes [4, 37, 38, 40, 41], and C_8 [35], will form predominantly.

One of the methods of solving the problem of synthesizing other diamond-like phases can be a strong static compression of precursors from three-coordinated atoms (graphite, nanotubes and other) in the temperature range to 500°C, since graphite (and other sp^2 compounds) is metastable at high pressures [81]. The static compression is more preferable to the shock compression, since, during the shock compression, the initial material is subjected to adiabatic compression, which increases the temperature of the system [4]; as a result, it can become higher than the limiting temperature of the stability of most of the diamond-like phases. The probability of the phase transition of a precursor to a diamond-like phase will be high when the specific total energies of the initial and final phases will be the same [82]. The theoretical calculations performed in [51, 66, 74, 83] showed that phase $LA3$ (bct C_4) and other diamond-like phases with several atomic Wicoff positions can be synthesized as a result of a cold compression of graphite versions in the pressure range from 5 to 27.3 GPa. However, at these pressures, transparent metastable phases, not diamond or diamond-like phases, were observed; the metastable phases inversely transformed to graphite [81, 84]. Our calculations showed that the pressures of the phase transition of graphite to phase $LA3$ were substantially higher: 60 GPa in the calculations in the local density approximation (LDA) and 74–76 GPa when using the DFT–GGA method. Therefore, most of diamond-

like phases for which graphite is a precursor can be synthesized at a pressure significantly higher than 27 GPa. At ultra-high pressures ($P > 0.5$ TPa), only two diamond-like phases $LA2$ [85] and $LA4$ [64] can be more stable than diamond. To obtain other diamond-like phases with relatively low sublimation energies and densities, more stressed sp^2 precursors with the carbon skeleton structure similar to the structure of chains of corresponding phases must be needed. Table 2 lists these precursors found as a result of the theoretical analysis and the DFT–GGA calculations. It seems likely that the structures of the diamond-like phases can be obtained as a result of polymerization of sp^2 nanostructures (stacks of graphene layers, nanotube bundles, and fullerene condensates) at relatively low pressures and temperatures. Table 2 gives only the diamond-like phases for which the sublimation energies were lower than corresponding energies of precursor condensates by the value that was not larger than 0.4 eV/atom. The fulfillment of this condition must provide the stability of the phases at normal conditions.

The crystal structures of the seven L phases can be formed from three versions of graphene layers: L_6 , L_{4-8} , or L_{4-6-12} . The probability of obtaining three L phases ($LA4$, $LA8$, and $LA9$) from the precursors considered in Table 2 is minimal, since the difference of the total energies of these phases and corresponding initial structures was higher than 0.4 eV/atom. The structure of the group of the T phases were synthesized during polymerization of polymorphous versions of graphene layers or nanotubes with the minimum chirality indices. A major portion of the C phases forms as a result of joining of clusters, and some C phase form as a result of joining polymorphs of graphenes L_{4-8} or L_{4-6-12} . It is likely that phases $CA1$, $CA12$, and CB do not form as a result of linking of the cluster precursors during compression, since fullerene-like clusters $C_4[3^3]$ and $C_{12}[3^6]$ were unstable according to the DFT calculations. The structure of phase $CA9$ can form on the basis of the C_{24} fullerite with nondense fcc diamond-type lattice. Four S phases can only be synthesized from 3D graphites, a combination of sp^2 precursors, or structural links with low crystallographic dimensionality consisting of three- and four-coordinated atoms.

It should be noted that the structures of diamond-like phases can be obtained not only from precursors consisting of only carbon atoms, but also during polymerization of organic molecules with carbon skeletons similar to the structural chains of the desired phases. However, it is difficult to obtain macroscopic crystalline structure using such a synthesis method.

Table 2. Crystal lattice parameters (a , b , c , Z) and sublimation energies E_{sub} of the structural precursors from three-coordinated atoms for corresponding diamond-like phases (types of lattices: SH is simple hexagonal, ST and BCT are simple and body-centered tetragonal, respectively; BCO is base-centered orthorhombic, R is rhombohedral, and M is monoclinic lattices)

Structural link	Type of lattice	a , Å	b , Å	c , Å	Z , atom	E_{sub} , eV/atom	Diamond-like phase
Graphene L_6	SH	2.488	2.488	7.241	4	7.92	–
The same	R	2.488	2.488	11.16	6	7.92	$LA1$
"	BCO	4.308	2.488	7.361	8	7.92	$LA1, LA2$
"	SH	2.488	2.488	3.854	2	7.91	$LA2, LA3, LA5$
Graphene L_{4-8}	BCT	3.469	3.469	7.245	8	7.36	$LA3, LA5, LA7, TA3$
The same	BCT	3.469	3.469	13.97	16	7.36	$LA10$
"	ST	3.469	3.469	3.687	4	7.36	$LA3, LA6, LA7, TA1, TA3, TA5, TA6, CA3, CA5$
Graphene L_{4-6-12}	BCO	11.80	6.812	6.453	48	7.22	–
The same	R	6.811	6.811	9.674	36	7.22	$CA6, CA10$
"	SH	6.812	6.812	3.728	12	7.22	$TA2, TA4, TA7, TA8, CA11$
Graphene L_{3-12}	SH	5.256	5.256	6.586	12	6.80	–
The same	SH	5.256	5.256	3.307	6	6.79	$TB, CA2$
CNT(3,0)	SH	6.425	6.425	4.242	12	6.66	$LA2$
CNT(4,0)	M	7.469	7.469	4.252	16	7.11	–
The same	ST	7.296	7.296	4.252	16	7.11	$TA5, TA6$
CNT(6,0)	SH	9.483	9.483	4.294	24	7.51	$TA7$
CNT(2,2)	M	6.609	6.609	5.228	16	6.76	–
The same	ST	6.395	6.395	5.217	16	6.76	$LA3, TA1$
CNT(3,3)	SH	9.026	9.026	2.475	12	7.38	$TA2, TA8$
$C_8 [4^3]$	FCC	8.250	8.250	8.250	32	5.21	–
The same	BCC	7.003	7.003	7.003	16	5.20	$CA3, CA4$
$C_{24} [4^1 6^2]$	FCC	11.70	11.70	11.70	96	6.71	$CA6$
The same	BCC	8.087	8.087	8.087	48	6.73	–
"	SC	7.205	7.205	7.205	24	6.72	$CA4$
$C_{48} [4^1 6^1 8^1]$	FCC	13.00	13.00	13.00	192	7.02	$CA4$
The same	BCC	10.51	10.51	10.51	96	7.00	$CA8$
"	SC	8.754	8.754	8.754	48	7.00	$CA7$

4. CONCLUSIONS

Thus, the analysis of the structural data for the 36 carbon diamond-like phases consisting of four-coordinated atoms in crystallographically equivalent positions showed that the crystal lattices of these phases are in stressed states as compared to the cubic diamond lattice. The degree of stresses of the phases is characterized by deformation parameters Def and Str and ring parameter Rng. The properties of diamond-like phases such as the density, the sublimation energy, the bulk modulus, the hardness, and the band gap width are dependent on the deformation parameters. The phases with minimal parameters Def and Str and the ring parameter closest to Rng (6^6) of cubic diamond are most stable at normal conditions.

Of the 36 carbon phases studied in this works, only four phases were synthesized up to now. It is likely other phases can be obtained as a result of polymerization of nanostructured precursors consisting of three-coordinated atoms at high pressures. The precursors can be graphene layers, CNTs, and fullerene-like clusters. The diamond-like phases contain layered, tubular, or cluster structural fragments; because of this, a number of nanostructures which have yet not been synthesized are likely can be obtained during a partial destruction of the phases that is accompanied by the transition of atoms from the four- to three-coordinated states. Among such nanostructures are, e.g., polymorphic versions of graphene L_{4-8} , L_{4-6-12} , or L_{3-12} .

The laws similar to those found for carbon diamond-like phases likely must be valid also for other compound with a predominantly covalent type of the chemical bond and diamond-like structures: crystal silicon [73, 86], silicon carbide [87], boron nitride [88], boron carbide [89], etc.

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