

Structure, mechanical and filtration properties of graphyne compounds of the self-intercalated type

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ABSTRACT We performed a study of the structure and properties of hybrid carbon compounds based on graphyne layers with a self-intercalated type of crystal lattice using ab initio calculations. It is found that only compounds based on α -graphyne-1 and β 1-graphyne-2 can have an ordered crystal structure. Calculations have shown that the most stable α -type phase is tetragonal ($I/4mcm$) self-intercalated α -graphyne-1 with a density of 1.28 g/cm³, a bulk modulus of 31 GPa, a Young's modulus from 3 to 107 GPa, which is characterized by a minimum negative linear compressibility of -11.7 TPa^{-1} along the [001] axis. This makes it a promising material for use in pressure sensors. Additionally, the $I/4mcm$ phase can be used as a selective filter for hydrogen molecules, the permeability of which can be increased by uniaxial compression or stretching perpendicular to [001]. The studied nanostructured phases can be unambiguously identified from the calculated powder X-ray diffraction patterns.

KEYWORDS nanostructured materials, graphyne, mechanical characteristics, filtration properties, powder X-ray diffraction patterns, density functional theory calculations

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1. Introduction

Carbon materials constitute a distinctive class of materials due to the wide variety of physical properties, enabling their efficient application in electronics, energetics, optics, and medical science [1]. The capacity of carbon materials to manifest distinct properties while maintaining an identical chemical composition stems from the abundance of polymorphic and polytypic variants exhibited by the three main carbon allotropes: diamond, graphite, and carbyne [2–7]. In particular, the polymorphs and polytypes of diamond exhibit outstanding mechanical characteristics, which determine their applications as wear-resistant and protective coatings [8, 9], along with high thermal conductivity, which is a key property for materials used in energy conversion systems [10]. In turn, polymorphic varieties of graphene exhibit a high specific surface area and are widely used, in particular, in the production of ionistors [1]. An even greater change in the properties of carbon materials is observed when nanostructured compounds contain carbon atoms with different hybridization types [11]. Such carbon compounds are called hybrid. Hybrid phases and nanostructures can be divided into four groups, each distinguished by the hybridization (coordination) of atoms. The first group includes graphyne and carbynoid compounds consisting of sp^2 and sp hybridized atoms [12]. The second group of compounds from sp^2+sp^3 hybridized atoms is represented by experimentally observed graphite-diamond nanocomposites [13, 14], polymerized fullerenes [15, 16], as well as numerous hypothetical nanostructures and phases [17, 18]. Carbynodiamonds, carbynocubanes, and carbynoid crystals with a lonsdaleite-like structure [19] belong to the class of compounds composed of sp^3 - and sp -hybridized carbon atoms. The final group of hybrids, which consist of atoms with all three types of hybridization (coordination) in their structure, is represented by graphene layers or tetrahedral carbon frameworks, connected by carbyne chains [20, 21], as well as by polymerized carbynofullerenes [22]. The most promising group for the search for nanostructured materials with potential use as molecular filters with unique mechanical properties is the group of carbynoid hybrids (sp^2+sp), as it features a wide range of structural varieties of compounds with high porosity resulting from the presence of linear segments of sp -atoms.

Based on the classification scheme presented in [12], hybrid sp^2+sp nanostructured compounds are categorized into four structural groups, exhibiting crystallographic dimensionality from 0D to 3D (Fig. 1). The first group of quasi-zero-dimensional compounds, labeled [0D, 2-3], includes spherical-shaped molecules known as carbynofullerenes [23]. The

second group [1D, 2-3] contains graphyne nanotubes, which were first predicted theoretically [2,24] and later successfully synthesized experimentally [25]. The third group of layered [2D, 2-3] compounds is represented by graphyne layers, the study of which also followed the path from theoretical prediction [26] to successful synthesis [27] through the development of numerous methods for producing graphyne compounds with varying morphologies and degrees of structural ordering [28]. Three-dimensional phases with hinged and chiral structures belong to the fourth group of [3D, 2-3] hybrid compounds [29]. Among these structural groups, the last two are particularly notable because graphyne layers show the greatest potential as selective filters and electrodes in ion batteries [30], while three-dimensional carbynoid phases with a hinged structural type demonstrate unusual mechanical properties, namely, an increase in their linear dimensions or cross-sectional areas under hydrostatic compression [31]. The filtration applications of conventional nanostructures and carbynoid crystals are severely constrained because external mechanical stresses induce only minor changes in pore size in covalently bonded materials. The development of novel carbon materials with self-intercalated crystal lattices [32] exemplified by yne-diamonds (diamondynes) that combine covalent and van der Waals interactions [33,34], represents a viable pathway forward. Hybrid interpenetrating nanostructures featuring this mixed type of interatomic bonding could enable the development of carbon compounds that exhibit significant structural changes under external stress, thereby allowing control over the filtration properties of the porous material. Thus, the aim of the present work is to conduct an *ab initio* investigation of the structure, stability, mechanical properties, and filtration characteristics of self-intercalated hybrid compounds.

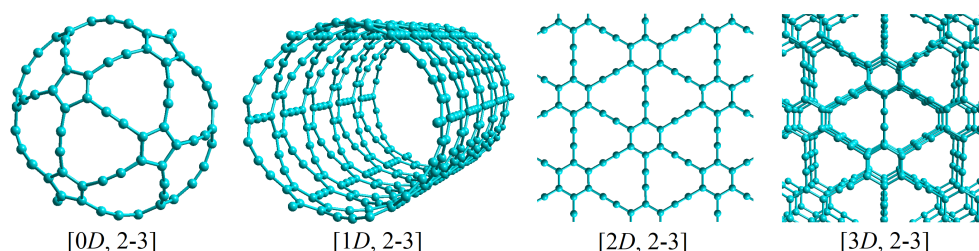


FIG. 1. Hybrid carbon nanostructures and three-dimensional phases

2. Models and computational methods

The structure of self-intercalated phases was obtained by interlocking of crystal lattices of two types of structural precursors. The first type of precursors is graphyne layers, while in addition to “graphyne-1” (G1) layers, graphyne layers with four-atom carbyne chain fragments (G2) were examined as structural precursors for self-intercalated phase formation, and their variants are shown in Fig. 2. Formation of self-intercalated phases was carried out on the basis of graphyne layers of one structural type using the method described in [35] in the range of angles from 60 to 90°. The second type of precursors are three-dimensional sp^2+sp carbon phases constructed by implantation of chain carbon units into the structure of three-dimensional graphites. Implantation of chains into the structure of three-dimensional graphites in this work was carried out by analogy with the formation of α -graphyne layers based on hexagonal graphene, therefore the compounds obtained in this way are three-dimensional hybrid phases of the α -type. In this work, three phases named *bct*-C₁₆, *sh*-C₂₄-I and *sh*-C₂₄-II (Fig. 2), were considered as precursors of the second type, which were formed on the basis of three-dimensional graphites *bct*-4, 6(3)-I-06a and *H*-6, respectively [36–38]. The choice of these phases was due to the presence of flat units with low internal stresses in their structure. The mutual penetration of three-dimensional hybrid phases was carried out in such a way that the closest distances between atoms of adjacent sublattices were maximized.

The calculation of structural parameters and properties of crystalline phases and nanostructures was performed using the density functional theory (DFT) method implemented in the Quantum ESPRESSO software package [39]. The initial structures of the layered and three-dimensional precursors were calculated using the generalized gradient approximation (GGA) in the PBE formulation [40], using parameters from references [41,42]. Further calculations of three-dimensional phases comprising interlocked sublattices were carried out using the vdW-DF exchange-correlation functional, which correctly accounts van der Waals interactions [43]. Standard ultrasoft pseudopotential was used to account for the influence of nuclei and core electrons. For calculations in the Brillouin zone, a kinetic energy cutoff of 46 Ry was used, along with k -grids of $6 \times 6 \times 6$ or $4 \times 4 \times 4$ (if the number of atoms is at least 120). Relaxation of the structure of the phases was performed until the force acting on each atom fell below 1.5 meV/Å and the pressure fell below 0.3 kbar. As a result of the relaxation of the 2H graphite structure with this set of parameters, the calculated interplanar distances d_{002} are equal to 3.51 Å, which is less than 5 % higher than the experimentally determined value [1], suggesting that the vdW-DF method is capable of adequately calculating the structures of hybrid carbon compounds with covalent-van der Waals bonding. In addition, the calculated parameters of the crystal lattices of 3C diamond (3.582 Å) and hexagonal graphene (2.463 Å) differ by less than 0.5 % from the experimental values [1] and practically coincide with the values calculated within

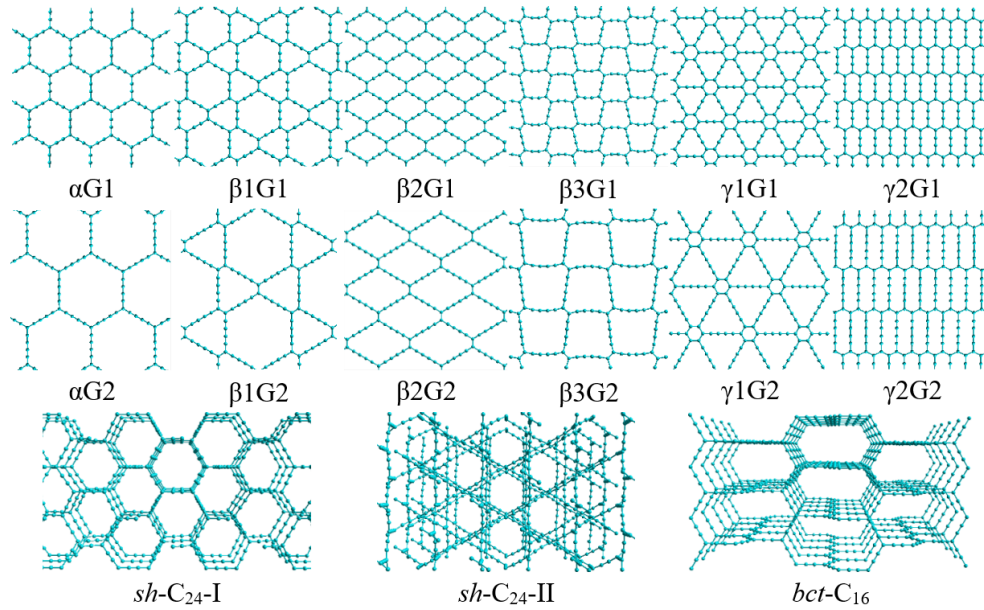


FIG. 2. Structural precursors of self-intercalated phases

the DFT-GGA method in [44]. Structural data of the most stable self-intercalated phases is provided in Supplementary materials file.

The effect of temperature on the structural stability of the three-dimensional phase with the lowest specific energy was investigated using the molecular dynamics method at temperatures up to 550 K over a period of 7 ps with a timestep of $\Delta t = 1$ fs. The calculations were performed using a doubled unit cell along with a $3 \times 3 \times 3$ k -point grid. Molecular dynamics modeling using a $1 \times 1 \times 2$ supercell was also used to investigate the motion of H_2 molecules within the crystal lattice of the most stable self-intercalated phase.

To investigate the mechanical properties of the most stable self-intercalated phase, simulations of hydrostatic compression and uniaxial mechanical stimulus along the principal crystallographic directions were performed. The bulk modulus B_0 and its derivative B'_0 were calculated using the Vinet equation [45]:

$$P = 3 \left(1 - \left(\frac{V}{V_0} \right)^{1/3} \right) B_0 \left(\exp \frac{3(B'_0 - 1)}{2} \left(1 - \left(\frac{V}{V_0} \right)^{1/3} \right) \right) \left(\frac{V_0}{V} \right)^2, \quad (1)$$

where P is the pressure; V_0 and V are the volume of the phase at zero pressure and under hydrostatic pressure P , respectively. The bulk modulus of 2H-graphite, calculated using equation (1), is 48.8 GPa, which exceeds the experimentally determined value (34 GPa [1]) by 43.5 %. The calculated value of the bulk modulus of graphite exhibits a significant discrepancy with respect to the experimental value, but demonstrates closer agreement with experimental data compared to the value of ~ 285 GPa obtained by the authors of paper [46]. For 3C diamond, the Vinet equation yields a bulk modulus of 438.4 GPa, which is in excellent agreement with the experimental value of 446.1 GPa [47].

The Young's modulus (Y) was calculated using the following formula:

$$Y = \frac{F/S}{\Delta l/l}, \quad (2)$$

where F is the tensile force magnitude; S is the cross-sectional area whose normal vector is aligned with force application direction; $\Delta l/l$ is the relative change in crystal length along the force axis. The calculated Young's modulus values for 2H-graphite under uniaxial tension along the zigzag and armchair directions demonstrate close agreement, with an average value of 0.88 TPa. This value is in good agreement with the experimental data reported in references [48, 49], which lie within the range from 0.92 to 1.1 TPa. Under uniaxial tension along the [001] direction, the calculated Young's modulus is 23.9 GPa, which is 34 % lower than the experimental value (36.5 GPa [50]), as a result of the elevated calculated value d_{002} (3.51 Å) in comparison with the experimental measurement [1].

Linear compressibility (K) can be determined as

$$K_l = -\frac{1}{l} \left(\frac{\partial l}{\partial P} \right)_T, \quad (3)$$

where l is the value of the unit cell parameter ($l = a, b, c$); T is the temperature.

The possibility of experimental identification of three-dimensional nanostructured carbon phases was investigated using the powder X-ray diffraction pattern simulation for characteristic chromium K_α -radiation ($\lambda_{Cr-K\alpha} = 2.2909$ Å).

3. Results and discussion

Calculations using the density functional theory method showed that the most stable are the self-intercalated (SI), phases from the α G1 and β 1G2 layers, the total energies of which are lower than the total energies of the isolated layers by 0.043 and 0.029 eV/atom, respectively. The structure of the three-dimensional self-intercalated phase 3D-SI- α G1 consists of flat α G1 layers (Fig. S1) and is characterized by a tetragonal unit cell (symmetry spacegroup $I/4mcm$) containing 32 atoms (Fig. 3a). The lattice parameters of 3D-SI- α G1 are $a = 8.460$, $c = 6.980$ Å. The density of this phase is 40.8 % lower than the calculated density of 2H-graphite and amounts to 1.28 g/cm³. The crystal structure of 3D-SI- α G1 contains three nonequivalent atomic positions (Table S1). The SI phase based on β 1G2, in which the layers are wave-like curved (Fig. S2), also has an ordered crystalline structure (Fig. 3b). The body-centered crystal lattice of the 3D-SI- β 1G2 phase belongs to the $Ibam$ space group, which features a rhombic unit cell with a basis of 120 atoms. The lattice parameters are $a = 14.33$, $b = 24.16$, $c = 7.426$ Å. The density of 3D-SI- β 1G2 is 0.93 g/cm³, which is 56.9 % lower than the calculated density of 2H-graphite. The atomic positions in the 3D-SI- β 1G2 lattice correspond to eight nonequivalent crystallographic positions (Table S2). Three-dimensional self-intercalated phases based on other structural types of graphyne layers may be unstable, since interlocking of two such layers leads to an increase in total energy of 0.12 eV/Å (for one-dimensional nanostructures).

To determine the stability of the studied SI phases based on graphyne layers, sublimation energies (E_{sub}) were calculated as the difference between the total energy of atoms in a particular phase and the energy of isolated carbon atoms. The calculated E_{sub} values for the SI phases based on α G1 and β 1G2 layers are 7.855 and 7.859 eV/atom, respectively. The E_{sub} of the self-intercalated phases based on α G1 and β 1G2 are higher than those for the graphite-like phases based on layers of the same structural types by 3 and -11 meV/atom, respectively. This indicates an increased stability of the SI phase based on α G1 with respect to the graphite-like phase from graphyne layers of the same structural type. However, in addition to phases consisting of covalently unbonded α G1 layers, three-dimensional hybrid α -type phases are likely candidates for formation during synthesis; the formation method for these phases is described in the methodology section of this work. By analogy with layered compounds, three-dimensional α -type phases should have a porous structure, which leads to the possibility of decreasing the total energy of the lattices of these phases during their mutual penetration. Therefore, in this work, the structural and energy characteristics of three new SI phases bct -C₁₆ ($P4_2/nmm$), sh -C₂₄-I ($P6_4/22$) and sh -C₂₄-II ($P6_4/22$) were also calculated, the unit cells of which are shown in Fig. 3c-e, respectively. The calculations showed that the mutual penetration of the sh -C₂₄ and bct -C₁₆ lattices in the SI- sh -C₂₄-II and SI- bct -C₁₆ structure, indeed, leads to a decrease in the total energy of these phases by 14-43 meV/atom, respectively. However, despite the presence of additional interactions between the sublattices in the three new SI phases, the sublimation energies of these phases range from 7.674 to 7.821 eV/atom, which is lower than the sublimation energy of 3D-SI- α G1. Thus, the phase of interpenetrating α G1 layers has the highest stability in comparison with the layered and covalently bonded three-dimensional (isolated and self-intercalated) α -type hybrids. It is also worth noting that the sublimation energies of the SI phases considered in this article are more than 32 meV/atom higher than the calculated value of E_{sub} of yne-diamond (daimondiyne), which is a carbon phase of the SI sublattices of δ -carbynodiamond-2.

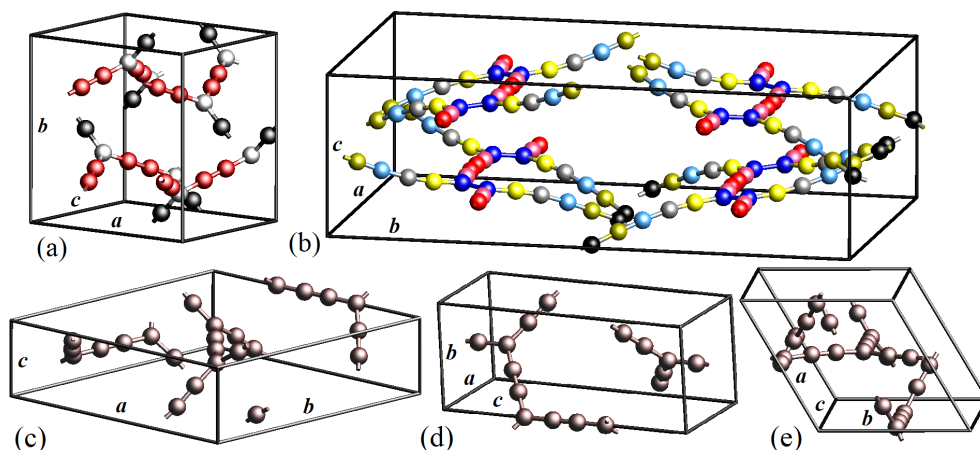


FIG. 3. Geometrically optimized structures and unit cells of 3D-SI- α G1 (a), 3D-SI- β 1G2 (b), SI- sh -C₂₄-I (c), SI- bct -C₁₆ (d), SI- sh -C₂₄-II (e) (atoms belonging to each nonequivalent position are highlighted in the same color)

To assess layer deformations in the structure of hypothetical phases, graphs of distributions of interatomic distances (Fig. 4) and angles between carbon-carbon bonds (Fig. 5) were constructed for isolated graphyne layers and their corresponding self-intercalated phases. During the structural relaxation of 3D-SI- α G1, the layers in it undergo weak deformations manifested as changes in the angles of interatomic bonds. This is evidenced by the splitting of the initial maxima

in the bond angle distribution within the isolated layer structure (Fig. 5), with minimal changing of the maxima of the interatomic distance distribution across the length range from 2.40 to 2.62 Å (Fig. 4). The interlocking of α G1 layers leads to the emergence of new peaks in the $N = f(R)$ diagram within the 3.5 – 4.0 Å range (Fig. 4), which correspond to distances between covalently unbound atoms of adjacent layers.

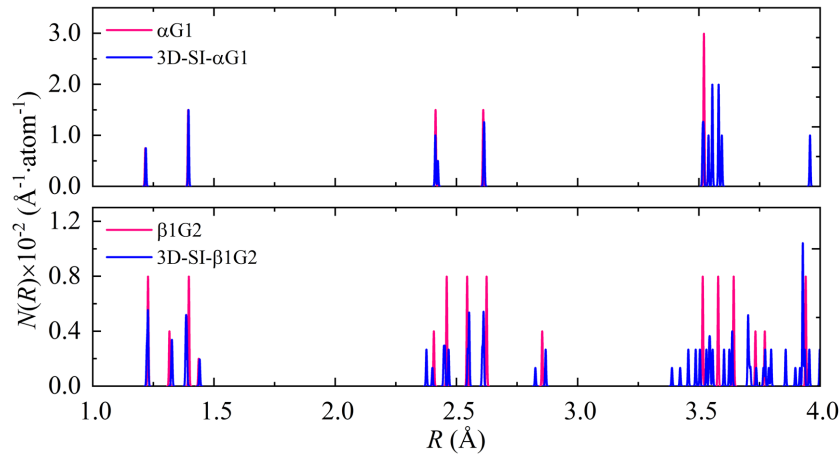


FIG. 4. Interatomic distance distribution in graphyne monolayers and 3D-SI phases

The interlocking of crystal lattices of β 1G2 layers results in their corrugated deformation, which is accompanied by multiple splitting and displacement of the maxima in the distribution of bond angles and interatomic distances within the range of 3.3 to 4.0 Å. At the same time, the distances between adjacent layers in the three-dimensional phase structure shift towards smaller values, starting from the value ≈ 3.38 Å (see Fig. 4). It should be noted that the covalent bond lengths in the structure of the both phases are close to the corresponding bond lengths in isolated layers, as can be observed in the graphs from Fig. 4 in the interatomic distance range from 1.2 to 1.6 Å.

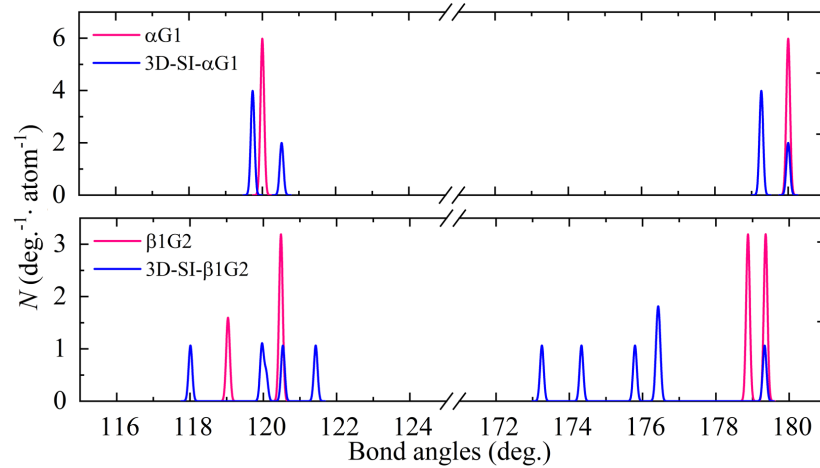


FIG. 5. Distribution of bond angles in graphyne monolayers and 3D-SI phases

Since the sublimation energy of the 3D-SI- α G1 phase is 0.784 eV/atom lower than the corresponding energy of hexagonal graphene, it is necessary to study the thermal stability of the crystal lattice of the new phase. Molecular dynamics simulations of the annealing process at 550 K for 7 ps demonstrated that the structure of the 3D-SI- α G1 phase is thermally stable, since no bond ruptures or formation of new covalent bonds within layers and between adjacent layers are observed (Fig. 6). At the same time, the structural elements of this tetragonal phase in the form of α G1 layers undergo significant deformations and bend in a wave-like manner. This particular type of deformation behavior was observed in the works [32, 35] during the calculation of the phase structure via molecular mechanics methods and simulation of its thermal annealing at 400 K.

Theoretical investigation of volumetric compression of 3D-SI- α G1 revealed that the calculated bulk modulus of this phase is lower than that of hexagonal graphite and diamond (Fig. 7a), with the B_0 value calculated by the Vinet equation being 31.0 GPa and its first pressure derivative being 2.28. During hydrostatic compression, both parameters a and b of the 3D-SI- α G1 unit cell demonstrate identical nonlinear decreases as pressure increases (Fig. 7b). This indicates

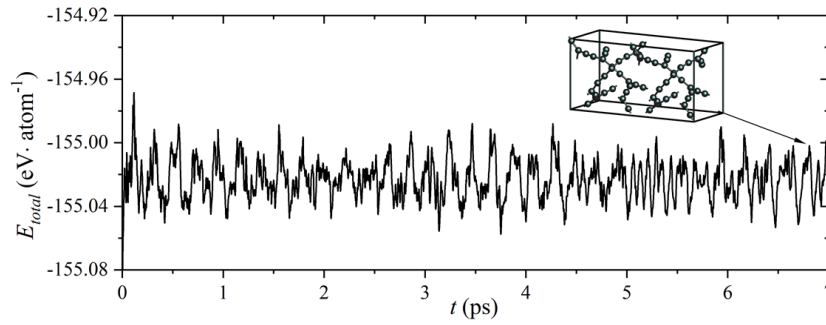


FIG. 6. Plot of the total energy versus time for 3D-SI- α G1 phase within thermal annealing simulation at 550 K

the preservation of the tetragonal symmetry of the phase and also the positive values of linear compressibilities K_a and K_b . The maximum value of linear compressibility K_a is observed in the region of $P < 2.5$ GPa and amounts to 18.2 TPa^{-1} . The unit cell parameter c of the 3D-SI- α G1 phase exhibits nonlinear increase under volumetric compression, demonstrating the presence of a rare mechanical property in the crystalline compound – negative linear compressibility K_c . The minimum value of $K_c = -11.7 \text{ TPa}^{-1}$ is observed at minimum pressure.

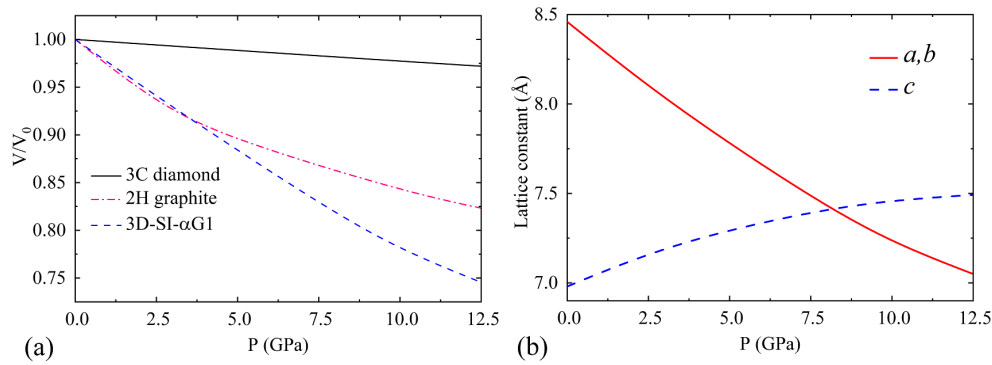


FIG. 7. Dependences of the relative volume (a) and unit cell parameters (b) versus pressure for the 3D-SI- α G1 phase under hydrostatic compression

Simulation of stretching of 3D-SI- α G1 along the [001] direction revealed that the Young's modulus of this phase in the elastic deformation region is 106.6 GPa. This value is less than 11 % lower than the calculated values for the [100] crystallographic direction of the graphite-like phase composed of α G1 layers [51], and is 4.4 times higher than the calculated Young's modulus value for 2H graphite under stretching in the [001] direction. The Poisson's ratios associated with 3D-SI- α G1 stretching along the [001] direction, calculated relative to the [100] and [010] directions, are equal to 0.89. During the uniaxial stretching of the 3D-SI- α G1 phase in the elastic deformation region along the [001] direction, an increase in its density by 2.5 % is observed. This result is consistent with the negative linear compressibility K_c and is typical for materials exhibiting this property [31]. Under uniaxial stretching up to relative elongation $\varepsilon = 0.022$ along the [100] and [010] directions, the 3D-SI- α G1 hybrid phase deforms according to Hooke's law, when the Young's modulus reaches the value of 3.1 GPa. The Poisson's ratios during stretching of 3D-SI- α G1 along the [100] direction range from 0.01 (μ_c^a) to 0.98 (μ_a^b). These values are close to the Poisson's ratio values of thin anisotropic rods of single-crystal graphite, calculated based on experimentally determined elastic constants [52]. In uniaxial compression, the functional dependencies of the unit cell parameters a and c on pressure can be adequately approximated by third- and second-order polynomials, respectively, as follows:

$$a = -1.117 \cdot 10^{-3} \cdot P^3 + 3.154 \cdot 10^{-2} \cdot P^2 - 3.333 \cdot 10^{-1} \cdot P + 8.464,$$

$$c = -8.874 \cdot 10^{-5} \cdot P^2 - 5.749 \cdot 10^{-3} \cdot P + 6.979,$$

where $[a] = [c] = \text{\AA}$; $[P] = \text{GPa}$.

The tetragonal phase composed of self-intercalated layers of α G1 has extended pores in the form of channels along the c -axis in its structure (see Fig. 3a), which are presumably capable of serving as accumulation sites or diffusion pathways for small molecules or metal ions. In the tetragonal unit cell there are four pores with a radius of 3.15 $\text{\AA}$ at the following positions: (0, 0, 0), (0.5, 0.5, 0), (0, 0, 0.5), (0.5, 0.5, 0.5). Therefore, the maximum possible filling of the lattice with hydrogen cannot exceed 25 atomic percent (2.1 mass percent). Density functional theory calculations have shown that when an H_2 molecule moves along the center of the 3D-SI- α G1 channel in the [001] direction, the system's energy changes sinusoidally (Fig. 8a). A unit cell with a doubled c parameter contains four positions of the H_2 molecule with

minimal energy, corresponding to the pore positions. Shortest transition between minimal energy positions requiring an energy of 0.080 eV. This value is close to the energy barrier height for hydrogen molecule diffusion (0.05 eV) through the largest rings in the γ 1G2 layer [53]. Direct investigation of H_2 molecule trajectories in a 3D-SI- α G1 supercell using molecular dynamics simulations has shown that the hydrogen molecule is capable of moving along the channel at temperatures above room temperature. The trajectory of the molecule's motion represents an irregularly shaped spiral (Fig. 8b). This makes diffusion of molecules containing atoms of elements from the second period and higher practically impossible. The hydrogen permeability of the 3D-SI- α G1-based material can be controlled via uniaxial compression, which should lead to a decrease in pore diameters. In particular, at pressure of ~ 8 kbar (P_{22} component), the structure of the phase undergoes a 13.9 % compression along the a axis and this deformation results in a substantial decrease (53 %) in the ΔE value (0.037 eV). The dependence of the energy barrier height ΔE on the value of a/a_0 under uniaxial compression of 3D-SI- α G1 along the [100] direction is a fourth-order polynomial:

$$\Delta E = -572.0 \cdot x^4 + 2117 \cdot x^3 - 2935 \cdot x^2 + 1807 \cdot x - 416.9,$$

where $x = a/a_0$. Calculations of the diffusion energy barrier for a larger molecule, such as methane, have shown that the value of this barrier (0.20 eV) is 2.5 times higher than ΔE for a hydrogen molecule (Fig. 8a).

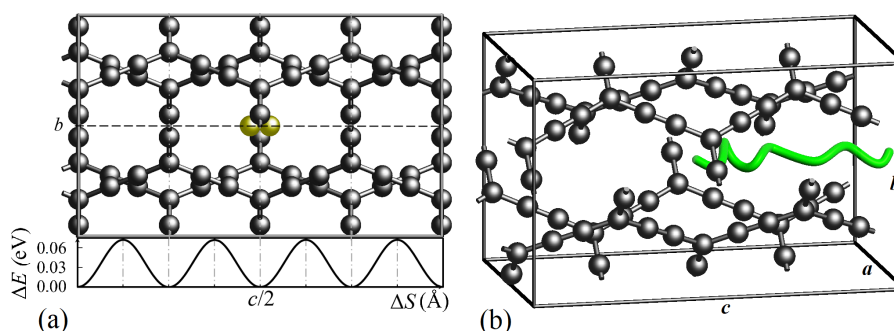


FIG. 8. (a) Dependence of the potential energy of the H_2 molecule versus its position along the channel axis in the crystal lattice of the 3D-SI- α G1 phase (the value of the c parameter of the supercell is 13.96 Å). (b) Standard trajectory of H_2 molecule movement within the structure of the 3D-SI- α G1 phase at $T > 400$ K (the diffusion path of the molecule is marked in green)

The possibility of identifying new three-dimensional phases was investigated through the analysis of simulated powder X-ray diffraction patterns (Fig. 9), for which structural parameters were obtained from ab initio calculations. The X-ray patterns were calculated for the weighted average of the chromium K_α -series radiation, as for characteristic radiation with a shorter wavelength, the maxima of phases with large crystal lattice parameters shift to the region of small diffraction angles, which leads to difficulties in detecting such materials. The calculated diffraction angles of the most intense maxima of the layer phase from γ 1G1 deviate from the experimentally observed values [27] by only 0.2° . In the case of hexagonal graphite, the calculated value of the diffraction angle characteristic of coherent scattering of radiation on the (002) crystal faces differs from the experimental value [54] by only 1.7° . The most intense maximum for 3D-SI- α G1 corresponds to the (110) crystal face with diffraction angle of $2\theta = 22.1^\circ$. The presence of this maximum is not sufficient for unambiguous identification of 3D-SI- α G1, since the maxima of phases α G1 and γ 1G1 layered phases with AB stacking deviate from the position of this maximum by less than 0.1° . However, the 3D-SI- α G1 phase can be identified by maxima for the (200), (211), and (220) crystal faces, which correspond to diffraction angles of 31.4 , 40.3 , 45.0° and do not overlap with maxima of other phases with relative intensity exceeding 5 %. The most intense maximum of 3D-SI- β 1G2 corresponds to the diffraction angle of 10.9° , which differs from the angle of the most intense maximum of the graphite-like phase composed of β 1G2 layers by less than 0.5 %, therefore these phases are indistinguishable in the region of small diffraction angles. The identification of 3D-SI- β 1G2 can be performed based on the (110) diffraction maximum, which has the second highest intensity at a diffraction angle of 18.6° , as this maximum does not overlap with the high-intensity maxima of 2H-graphite, layered graphynes, and 3D-SI- α G1.

One of the possible methods for the synthesis of self-intercalated-type crystals is chemical carbonization of polymers, which can lead to the removal of non-carbon atoms and the partial formation of triple carbon-carbon bonds [55]. Another potential method of synthesis involves the polymerization of molecular precursors (monomers) with structural elements of graphyne layers [56] on a substrate with rectangular or trapezoidal protrusions. In this case, it is possible to form a three-dimensional self-intercalated phase through mutual penetration of graphyne layers into each other at the edges of the substrate material protrusions. The porosity of the forming hybrid phase should be determined by the distance between the protrusions. The synthesis of self-intercalated graphyne phases from molecular precursors can probably also be realized by their polymerization to form thin films on flat substrates in the presence of metal atoms. It is assumed that metal atoms can stabilize the structure of the films by preventing the binding of carbyne chains at low temperatures, in analogy with the mechanism of stabilization of the structure of carbynoid molecular crystals stable up to $\sim 130^\circ\text{C}$ [19]. For example,

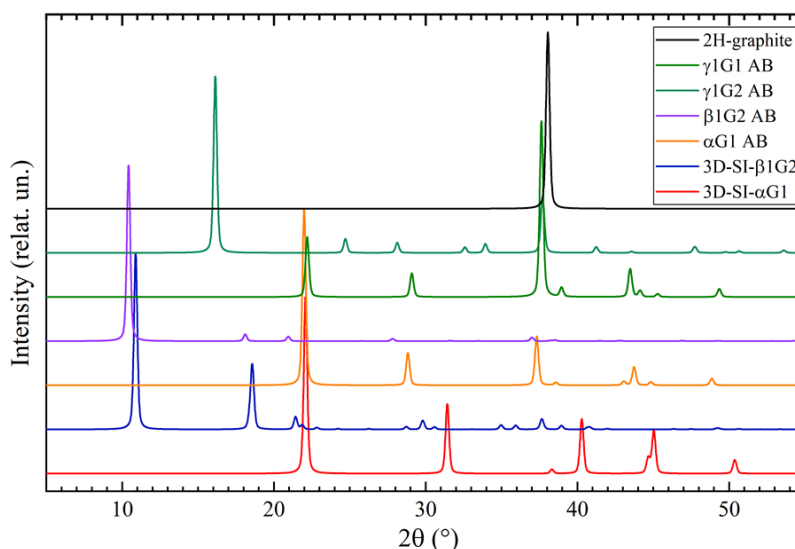


FIG. 9. Calculated powder X-ray diffraction patterns of graphite and graphyne phases

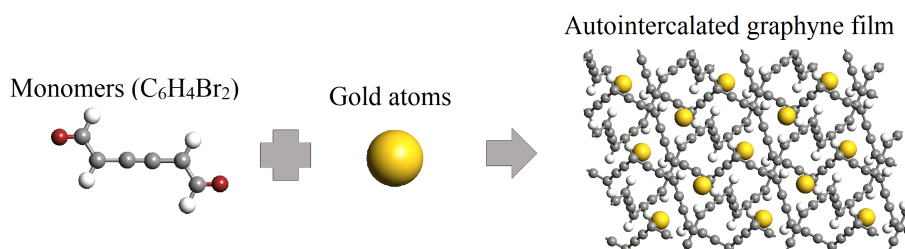


FIG. 10. Scheme of the formation of a thin 3D-SI- α G1 film from monomers (H atoms are shown in white, C atoms are shown in gray, Br atoms are shown in red, and Au atoms are shown in gold)

Fig. 10 shows a scheme of the formation of a 3D-SI- α G1-type film from $C_6H_4Br_2$ molecules in the presence of stabilizing Au atoms film structure at the initial stage of growth.

4. Conclusions

In this paper, the results of quantum-mechanical modeling of the structure and properties of graphyne compounds with covalent-van der Waals type of interatomic bonds of various crystallographic dimensions, which can be treated as self-intercalated, are presented. Ab initio calculations have shown that the most stable of the quasi-one-dimensional self-intercalated compounds are nanostructures based on α -graphyne-1 and β 1-graphyne-2. It was found that a hybrid phase of interlocking α -graphyne-1 layers, designated 3D-SI- α G1, should be more stable than the layered phase of α -graphyne-1 and has the highest probability of formation among self-intercalated phases based on α -type hybrid precursors. According to calculations, 3D-SI- α G1 has a tetragonal crystal lattice ($I/4mcm$) formed by α -graphyne-1 layers, the shape of which is close to the shape of flat isolated layers. The three-dimensional self-intercalated phase of β 1-graphyne-2 layers, designated as 3D-SI- β 1G2, according to calculations, should be more stable than an isolated β 1-graphyne-2 monolayer, but less stable than a graphite-like phase with AB packing of layers of the same structural type. The 3D-SI- β 1G2 phase is characterized by orthorhombic symmetry ($Ibam$) and consists of wave-curved layers. The densities of 3D-SI phases based on graphyne layers range from 41 to 57 % of the graphite density. The tetragonal phase should be the most stable, as its structure does not break down at least up to 550 K, which is close to the temperature limit of γ 1-graphyne-1 [27].

Modeling of volumetric compression for the tetragonal phase 3D-SI- α G1 has demonstrated that the material has an elastic modulus value of 31.0 GPa. Furthermore, this phase should exhibit negative linear compressibility along the c axis, with the minimum value (-11.7 TPa^{-1}) observed at low pressures. Under uniaxial strains up to 19 %, the structure of 3D-SI- α G1 remains stable, with Young's moduli of this phase ranging from 3.1 to 106.6 GPa. A material based on the 3D-SI- α G1 phase can be used as a selective filter in hydrogen energetics, since the energy barrier to hydrogen penetration through pores is more than 2.5 times lower than the corresponding value for larger molecules. One of the unique features of this compound is that the energy barrier for hydrogen diffusion can be significantly reduced by 53 % over increasing the external stress applied perpendicular to the [001] axis to a relatively low value of ~ 8 kbar.

A mechanism for the formation of thin films based on 3D-SI- α G1 is proposed, resulting from the polymerization of $C_6H_4Br_2$ monomers in the presence of gold atoms. Since the studied nanostructured phases can be considered as a set of interlocked graphyne layers with the structure similar to isolated layers, the most accurate identification of hybrid self-intercalated phases is possible using X-ray diffraction analysis and high-resolution electron microscopy.

References

- [1] Pierson H.O. *Handbook of Carbon, Graphite, Diamond, and Fullerenes: Properties, Processing, and Application*. Noyes, Park Ridge, New Jersey, 1993, 402 p.
- [2] Belenkov E.A., Greshnyakov V.A. Classification of structural modifications of carbon. *Physics of the Solid State*, 2013, **55**, P. 1754–1764.
- [3] Belenkov E.A., Greshnyakov V.A. Diamond-like phases obtained from nanotubes and three-dimensional graphites. *Physics of the Solid State*, 2015, **57**, P. 1253–1263.
- [4] Urade A.R., Lahiri I., Suresh K.S. Graphene properties, synthesis and applications: A review. *JOM*, 2022, **75** (3), P. 614–630.
- [5] Choudhary M., Sharma A., Raj S.A., Sultan M.T.H., Hui D., Shah U.M. Contemporary review on carbon nanotube (CNT) composites and their impact on multifarious applications. *Nanotechnology Reviews*, 2022, **11** (1), P. 2632–2660.
- [6] Greshnyakov V.A., Pavlik V.V., Belenkov M.E., Kulakova E.A. Carbon clathrates C_{24} , C_{28} and CA6: Structure formation and properties. *Letters on Materials*, 2026, **16** (1), P. 23–29.
- [7] Zheng W., Liu Qi-J., Liu Z.-T., Zhang Z.-Q. First-principles calculations of structural, electronic and elastic properties of carbon allotropes. *Materials Science in Semiconductor Processing*, 2022, **146**, 106692.
- [8] Brazhkin V.V. Ultrahard nanomaterials: myths and reality. *Uspekhi Fizicheskikh Nauk*, 2020, **190** (6), P. 561–584.
- [9] Baimova J.A. An overview of mechanical properties of diamond-like phases under tension. *Nanomaterials*, 2024, **14** (2), 129.
- [10] Guo L., Liu Y., Chen Z., Hongao Y., Donadio D., Cao B. Generative deep learning for predicting ultrahigh lattice thermal conductivity materials. *NPJ Computational Materials*, 2025, **11**, 97.
- [11] Zhang Y., Pan F., Ni K., Zhu Y. 3D carbon crystals: theoretical prediction and experimental preparation. *National Science Review*, 2025, **12** (5), nwaf125.
- [12] Ouyang T., Cui C., Shi X., Li J., Zhang C., Tang C., Zhong J. Systematic enumeration of low energy graphyne allotropes based on coordination-constrained searching strategy. *Physica Status Solidi (RPL) – Rapid Research Letters*, 2020, **14** (12), 2000437.
- [13] Luo K., Liu B., Hu W., et al. Coherent interfaces govern direct transformation from graphite to diamond. *Nature*, 2022, **607**, P. 486–491.
- [14] Li B., Luo K., Ge Y., Zhang Y., Tong K., Liu B., Yang G., Zhao Z., Xu B., Tian Y. Superior toughness and hardness in graphite–diamond hybrid induced by coherent interfaces. *Carbon*, 2023, **203**, P. 357–362.
- [15] Yamanaka S., Kini N. S., Kubo A., Jida S., Kuramoto H. Topochemical 3D Polymerization of C_{60} under High Pressure at Elevated Temperatures. *Journal of American Chemical Society*, 2008, **130**, P. 4303–4309.
- [16] Laranjeira J., Marques L., Melle-Franco M., Strutynski K., Barroso M. Clathrate structure of polymerized fullerite C_{60} . *Carbon*, 2022, **194**, P. 297–302.
- [17] Liu J.Q., Gao Q., Hu Z.P. HSH-carbon: A novel sp^2 - sp^3 carbon allotrope with an ultrawide energy gap. *Frontier of Physics*, 2022, **17**, 63505.
- [18] Wang C.T., Bu K. Superpentagraphene C_{34} : A two-dimensional network structure of C_{20} fullerene. *Materials Today Physics*, 2024, **43**, 101401.
- [19] Lou W., Windl W. First principles study of the structure and stability of carbynes. *Carbon*, 2009, **47**, P. 367–383.
- [20] Liu L., Hu M., Liu C., et al. 3D hybrid carbon composed of multigraphene bridged by carbon chains. *AIP Advances*, 2018, **8**, 015019.
- [21] Zhang W., Chai C., Fan Q., et al. A novel two-dimensional sp^2 - sp^3 hybridized carbon nanostructure with a negative in-plane Poisson ratio and high electron mobility. *Computational Material Science*, 2020, **185**, 109904.
- [22] Podlivaev A.I., Openov L.A. C- C_{20} carbyne-carbinofullerene chains. *Physics of the Solid State*, 2019, **61** (12), 680.
- [23] Enyashin A.N., Sofronov A.A., Makurin Y.N., et al. Structural and electronic properties of new α -graphyne-based carbon fullerenes. *Journal of Molecular Structure: THEOCHEM*, 2004, **684**, P. 29–33.
- [24] Coluci V.R., Braga S.F., Legoas S.B., et al. Families of carbon nanotubes: Graphyne-based nanotubes. *Physical Review B*, 2003, **68**, 035430.
- [25] Li G., Li Y., Qian X., et al. Construction of tubular molecule aggregations of graphdiyne for highly efficient field emission. *The Journal of Physical Chemistry C*, 2011, **115**, P. 2611–2615.
- [26] Baughman R.H., Eckhardt H., Kertesz M. Structure-property predictions for new planar forms of carbon: Layered phases containing sp^2 and sp atoms. *The Journal of Chemistry Physics*, 1987, **87**, 6687.
- [27] Desyatkin V.G., Martin W.B., Aliev A.E., Chapman N.E., Fonseca A.F., Galvão D.S., Miller E.R., Stone K.H., Wang Z., Zakhidov D., Limpoco F.T., Almahdali S.R., Parker S.M., Baughman R.H., Rodionov V.O. Scalable Synthesis and Characterization of Multilayer γ -Graphyne, New Carbon Crystals with a Small Direct Band Gap. *Journal of the American Chemical Society*, 2022, **144** (39), P. 17999–18008.
- [28] Gao X., Liu H., Wang D., et al. Graphdiyne: synthesis, properties, and applications. *Chemical Society Reviews*, 2019, **48** (3), P. 908–936.
- [29] Wang J.T., Chen C., Li H.D., et al. Three-Dimensional Carbon Allotropes Comprising Phenyl Rings and Acetylenic Chains in $sp+sp^2$ Hybrid Networks. *Scientific Reports*, 2016, **6**, 24665.
- [30] Abdi G., Alizadeh A., Crochala W., et al. Developments in Synthesis and Potential Electronic and Magnetic Applications of Pristine and Doped Graphynes. *Nanomaterials*, 2021, **11**, 2268.
- [31] Baughman R.H., Stafstrom S., Cui C., et al. Materials with Negative Compressibilities in One or More Dimensions. *Science*, 1998, **279** (5356), P. 1522–1524.
- [32] Greshnyakov V.A., Pavlik V.V. New nanostructured carbon compounds based on graphyne layers. *Chelyabinsk Physical and Mathematical Journal*, 2025, **10** (1), P. 147–157.
- [33] Enyashin A.N., Ivanovskii A.L. Structural, electronic, and elastic properties of Y-diamonds and their BN analogues. *Diamond and Related Materials*, 2013, **38**, P. 93–100.
- [34] Bastos C.M.O., Santos E.J.A., Alves R.A.F., et al. Entangled Interlocked Diamond-like (Diamondynes) Lattices. *American Chemical Society Omega*, 2025, **10**, P. 46065–46070.
- [35] Greshnyakov V.A., Pavlik V.V. Calculations of the structure and properties of autointercalated graphyne layers. *Letters on Materials*, 2023, **13** (4), P. 323–328.
- [36] Hoffman R., Hughbanks T., Kertesz M., Bird P.H. A Hypothetical Metallic Allotrope of Carbon. *Journal of the American Chemical Society*, 1983, **105**, P. 4831–4832.
- [37] Tamor M.A., Hass K.C. Hypothetical superhard carbon metal. *Journal of Materials Research*, 1990, **5** (11), P. 2273–2276.
- [38] Winkler B., Pickard C.J., Milman V., Thimm G. Systematic prediction of crystal structures. *Chemical Physics Letters*, 2001, **337**, P. 36–42.

- [39] Giannozzi P., Andreussi O., Brumme T., Bunau O., Buongiorno Nardelli M., Calandra M., Car R., Cavazzoni C., Ceresoli D., Cococcioni M., Colonna N., Carnimeo I., Dal Corso A., de Gironcoli S., Delugas P., DiStasio Jr. R.A., Ferretti A., Floris A., Fratesi G., Fugallo G., Gebauer R., Gerstmann U., Giustino F., Gorni T., Jia J., Kawamura M., Ko H.-Y., Kokalj A., Kucukbenli E., Lazzeri M., Marsili M., Marzari N., Mauri F., Nguyen N.L., Nguyen H.-V., Otero-de-la-Roza A., Paulatto L., Ponce S., Rocca D., Sabatini R., Santra B., Schlipf M., Seitsonen A.P., Smogunov A., Timrov I., Thonhauser T., Umari P., Vast N., Wu X., Baroni S. Advanced capabilities for materials modelling with Quantum ESPRESSO. *Journal of Physics: Condensed Matter*, 2017, **29** (46), 465901.
- [40] Perdew J.P., Burke K., Ernzerhof M. Generalized Gradient approximation made simple. *Physical Review Letters*, 1996, **77** (18), P. 3865–3868.
- [41] Belenkov E.A., Greshnyakov V.A., Mavrinskii V.V. Ab initio calculations of layered compounds consisting of sp^3 or $sp+sp^2$ hybridized carbon atoms. *Nanosystems: Physics, Chemistry, Mathematics*, 2021, **12** (6), P. 672–679.
- [42] Greshnyakov V.A., Belenkov E.A. Structure, Electronic Properties, and Stability of Carbon Double Layers Composed of Atoms in the sp^3 -Hybridized State. *Journal of Experimental and Theoretical Physics*, 2021, **133** (6), P. 744–753.
- [43] Thonhauser T., Zuluaga S., Arter C.A., et al. Spin Signature of Nonlocal Correlation Binding in Metal-Organic Frameworks. *Physical Review Letters*, 2015, **115**, 136402.
- [44] Belenkov E.A., Greshnyakov V.A. Modeling of phase transitions of graphites to diamond-like phases. *Physics of the Solid State*, 2018, **60** (7), P. 1294–1302.
- [45] Vinet P., Ferrente J., Smith J.R., et al. A Universal Equation of State for Solids. *Journal of Physics C: Solid State Physics*, 1986, **19** (20), L467.
- [46] Wang J.T., Chen C., Kawazoe Y. New Carbon Allotropes with Helical Chains of Complementary Chirality Connected by Ethene-type π -Conjugation. *Scientific Reports*, 2013, **3**, 3077.
- [47] Occelli F., Loubeyre P., LeToullec R. Properties of diamond under hydrostatic pressures up to 140 GPa. *Nature Materials*, 2003, **2**, P. 151–154.
- [48] Poot M., Herre S. J. Nanomechanical Properties of Few-Layer Graphene Membranes. *Applied Physics Letters*, 2008, **92**, 063111.
- [49] Bosak A., Krisch M., Mohr M., Maultzsch J., Thomsen C. Elasticity of single-crystalline graphite: Inelastic x-ray scattering study. *Physical Review B*, 2007, **75**, 153408.
- [50] Kelly B.T. *Physics of graphite*. Applied Science Publishers, 1981, 477 p.
- [51] Zhang Y.Y., Pei Q.X., Wang C.M. Mechanical properties of graphynes under tension: A molecular dynamics study. *Applied Physics Letters*, 2012, **101**, 081909.
- [52] Gorodtsov V.A., Lisovenko D.S. Carbon and non-carbon layered nanowhiskers. *Engineering Physics*, 2009, **4**, P. 36–38 (in Russian).
- [53] Zhang H., Zhao X., Zhang M., et al. Three-dimensional diffusion of molecular hydrogen in graphdiyne: a first-principles study. *Journal of Physics D: Applied Physics*, 2013, **46**, 495307.
- [54] Howe J.Y., Rawn C.J., Jones L.E., et al. Improved crystallographic data for graphite. *Powder Diffraction*, 2003, **18** (2), P. 150–154.
- [55] Zhivulin V.E., Pesin L.A., Belenkov E.A., Greshnyakov V.A., Zlobina N., Brzhezinskaya M. Ageing of chemically modified poly(vinylidene fluoride) film: Evolution of triple carbon-carbon bonds infrared absorption. *Polymer Degradation and Stability*, 2020, **172**, 109059.
- [56] Kilde M.D., Murray A.H., Andersen C.L., Strom F.E., Schmidt K., Kadziola A., Mikkelsen K.V., Hampel F., Hammerich O., Tykwinski R.R., Nielsen M.B. Synthesis of radiaannulene oligomers to model the elusive carbon allotrope 6,6,12-graphyne. *Nature Communications*, 2019, **10**, 3714.

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