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Structural, electronic, cohesive, and elastic properties of diamondlike allotropes of crystalline C_{40}

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The atomic models of diamondlike allotropes of crystalline C_{40} (hyperdiamond, hyperlonsdaleite and so-called autointercalated hyperdiamond) are offered and using the density-functional based tight-binding method their structural, cohesive, elastic, and electronic properties are predicted as well as their theoretical x-ray diffraction spectra are derived. Among these allotropes the autointercalated hyperdiamond C_{40} has a unique combined type of both covalent and van der Waals bonding and shows the highest density and hardness.

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Since the discovery of fullerene C_{60} (Ref. 1) and the synthesis of this molecule and some other stable fullerenes C_n $(n>60)$ in macroscopic quantities,[2,3] intensive effort has been devoted to the research of their solid derivatives. Among them to the most known systems belong the pure or doped C_{60} molecular crystals—fullerites. The lattices of these crystals are composed of the fullerenes, which have closed electronic shells and interact by means of weak van der Waals forces.[4,5]

An alternative group of fullerene-based solids is presented by crystals with strong covalent interactions between fullerenic cages. The formation of these crystals (so-called covalently bonded fullerites) is a characteristic feature[6] of small fullerenes $C_{n<60}$ with open electronic shells.[7] Among these crystals the C_{28}-based structures with diamondlike lattices, which have been called as hyperdiamonds, have attracted a significant attention. Numerous theoretical investigations on fullerene C_{28} hyperdiamonds and related systems (for example, endohedral metallofullerenes $Ti@C_{28}$, $Zn@C_{28}$, or $Na@C_{28}H_4$ as building blocks of fullerites) have been reported recently, and a set of their interesting electronic, elastic, and cohesive properties was predicted.[7–15] Moreover, the low mass density and large internal surface suggest future applications of these systems as catalysts, nanosieves, or gas storage materials.[15]

The possibility of C_{28} to form diamondlike lattices is based on the unique structural and electronic properties of C_{28} cage with tetrahedral symmetry T_d.[6,7] This open-shell molecule contains four unpaired electrons localized at four pentagon triplets in a tetrahedral arrangement. This feature makes the high reactive T_d-C_{28} fullerene similar to a sp^3-hybridized carbon "superatom," which is able to form chemical bonds by linking with other four molecules C_{28} and build diamondlike lattices.

Among other small fullerenes $(C_{n<60})$ T_d-symmetrical C_{40} cage is similar to T_d-C_{28}, because it has four unpaired electrons in an $^5A_2$ open-shell ground state. Thus, C_{40} behaves as a reactive hollow superatom with effective valence of 4.[6,7,16–18] The cage of T_d-C_{40} has 12 C_5 pentagons and 10 C_6 hexagons. There are three types of nonequivalent groups of carbon atoms: C(1), C(2), and C(3). From them four C(1) atoms are placed at the vertices of a tetrahedron, which are the triplets of C_5 pentagons, as depicted in Fig. 1. Such a structure possesses a significant potential for bonding with four atoms or molecules outside of the C_{40} cage and formation of thermodynamically stable systems (in particular, diamondlike solids), because of the presence of four dangling bonds located at its tetrahedron apices.

In this Brief Report the atomic models of three diamondlike allotropes of crystalline C_{40} are offered and their structural, cohesive, elastic, and electronic properties are predicted by means of the density-functional based tight-binding (DFTB) theory. Two of them are analogical to crystalline C_{28} allotropes[7–15]—hyperdiamond C_{40} (HD) and hyperlonsdaleite C_{40} (HL), and are classified by the space groups $Fd3m$ and $P63/mmc$, respectively. These allotropes contain voluminous cavities between covalently bonded cages C_{40}, Fig. 1. This feature is attractive for an intercalation of these materials by various atoms and molecules. Moreover, the simple estimations show that the radii of these cavities within lattices (~5.4 nm) are higher than the radii of C_{40} (~3.3 nm) forming the lattices, i.e., can be easy of access for other C_{40} fullerenes. In other words, diamondlike C_{40} phases are capable for autointercalation.

Thus, as a third crystalline C_{40} allotrope we suggest so-called autointercalated hyperdiamond (AHD), whose lattice may be described as C_{40} HD, where the cavities are com-

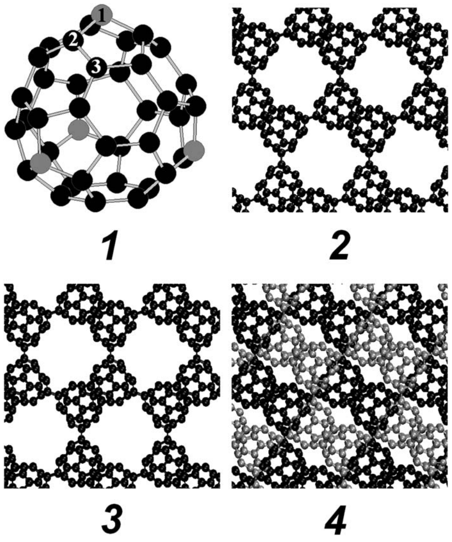

FIG. 1. Fullerene C_{40} (1) and the fragments of the optimized lattices for crystalline C_{40} allotropes: hyperdiamond (2), hyperlonsdaleite (3), and autointercalated hyperdiamond (4). For C_{40} cage three nonequivalent types of carbon atoms C(1–3) are marked.

TABLE I. Formation energies (E_{form}, in kJ/mol), lattice constants (a and c, in nm), mass density (ρ, in g/cm^3), bulk moduli (B, in GPa), and band gap (E_g, in eV) of the crystalline C_{40} allotropes according to DFTB calculations.

System	$-E_{\text{form}}$	a	c	ρ	B	E_g
HD C_{40}	427.04	1.8924		0.94	29.22	1.01
(HD C_{28})[a]	(602.80)	(1.5952)		(1.10)	(45.54)	(1.80)
HL C_{40}	422.83	1.3386	2.1860	0.78	30.25	1.01
(HL C_{28})	(598.70)	(1.1286)	(1.8429)	(1.10)	(45.90)	(1.76)
AHD C_{40}	427.59	1.8922		1.88	60.31	0.94

[a] In parentheses—the data for crystalline C_{28} allotropes as obtained at the same DFTB level. (Refs. 14 and 15).

pletely occupied with the same fullerenes C_{40}, Fig. 1. Also, the structure of C_{40} AHD can be imagined as two sublattices of C_{40} HD, which are inserted each inside other. Unit cells of HD and AHD include two and four fullerenes C_{40}, i.e., contain 80 and 160 carbon atoms, respectively.

Our calculations were performed within the DFTB,[19] which was used earlier for the simulations of diamondlike allotropes of crystalline C_{28}.[14,15] The dispersion corrected modification of DFTB with the implementation of an empirical dispersion term parametrized in the framework of the universal force field (UFF) method was used for correct description of weak van der Waals interactions.[20] This method has been found to describe the structure and energy of carbon nanostructures in good agreement with experiment and higher-level theoretical methods.

The calculated properties of the above mentioned three C_{40} allotropes: formation energies (E_{form}), lattice constants (a and c, which was kept constant and equal $\sqrt{8/3}a$ as for the ideal lonsdaleitelike lattice), mass density (ρ), and bulk moduli (B) are listed in Table I in comparison with C_{28} HA and HL as obtained at the same DFTB level.[14]

To estimate the relative stability of C_{40} allotropes, their Gibbs free energies ($G=\Delta H+P\cdot V-T\cdot S$) should be calculated. Since our band structure calculations are performed at zero temperature and zero pressure, G becomes equal to the enthalpy of formation, ΔH, which can be estimated from the total energies of C_{40} allotropes and its constituents—free fullerenes C_{40}. The formation energies (E_{form}) of C_{40} allotropes with respect to the "free" fullerenes C_{40} are defined as $E_{\text{form}}=\{E_{\text{tot}}(C_{40}^{\text{cryst}})-NE_{\text{tot}}(C_{40}^{\text{free}})\}/N$, where E_{tot} are the total energies of a unit cell of C_{40} allotropes and free fullerene C_{40} at their optimized geometries. In this way, negative value E_{form} indicates that it is energetically favorable for given reagents to mix and form the stable crystals, and *vice versa*. The results (Table I) show that E_{form} for all crystalline C_{40} phases are negative, i.e., their formation is favorable. Among them the high-dense allotrope AHD is the most stable. However, the difference in the formation energies between AHD and HD is small: $\Delta E_{\text{form}}\sim 0.55$ kJ/mol of C_{40} molecules. It can be explained considering the nature of interaction between C_{40} cages in these crystals. In C_{40} HD and HL, like in their topological analog—C_{28} HD and HL—the neighboring cages form the covalentlike C(1)–C(1) bonds. For autointercalated hyperdiamond C_{40} a rough estimation gives that the distance between two C_{40} cages belonging to different diamondlike sublattices is equal to 0.4 nm. This value is comparable with van der Waals gap, i.e., with the interlayer distance in graphite (or interlayer distance in coaxial multiwalled nanotubes or multishell fullerenes), when between two graphene layers appears van der Waals bonding.[1–4] Thus, besides strong covalent C(1)–C(1) bonds AHD phase is characterized by weak van der Waals interaction between the fullerenes of different sublattices.

Therefore, C_{40} AHD may be considered as a type of fullerite, where the nature of interaction between molecules combines both types of bonding, which are presented in molecular crystals ($C_{n\geqslant 60}$-based fullerites) and in alternative group of $C_{n<60}$-based covalently bonded fullerites.

Let us discuss the predicted properties of C_{40} allotropes. Bulk moduli B of C_{40} HD and HL became smaller than for topologically identical C_{28} HD and HL, and are twice less than B for C_{40} AHD. This is a consequence of the much lower density of chemical bonds in C_{40} HD and HL compared with C_{28} HD and HL and C_{40} AHD. Note that the bulk moduli of both isostructural C_{40} and C_{28} allotropes HD and HL are smaller than the bulk modulus of C_{40} AHD. This sequence correlates with change of their mass density ρ, see Table I.

The calculated band structures of the crystalline C_{40} allotropes are shown in Fig. 2, and their total and partial densities of states (DOSs) are in Fig. 3. All crystals C_{40} are semiconducting materials with very similar band gaps of about 1.0 eV, see Table I. Besides, crystalline C_{40} HD and HL with higher amount of sp^2 hybridization of atoms and larger part of π component in the bonding have smaller gaps (about 0.75 eV less) than their crystalline C_{28} analog. This result agrees well with the known tendency[14] of fullerite gap reduction by decrease of the content of sp^3 covalent bonds between C_n molecules and the growth of a system of benzene rings.

The occupied bands in the range from −9 to −2 eV consist of the C $2s$ and C $2p$ states responsible for σ and π bonds within and σ bonds between the C_{40} cages. The shape of DOS for C_{40} fullerites is characterized by numerous well-defined peaks below Fermi level, which are associated with π bonds of network of aromatic hexagons within C_{40} cages. The distributions of the C 2 s and C $2p$ densities of states (Fig. 3) confirm predominantly covalent bonding character in C_{40} allotropes. The difference in the shape of DOS between various solid C_{40} allotropes does not have a pronounced character because of weak van der Waals interaction between the walls of C_{40} cages, which is not able to perturb the electronic structure considerably.

The above presented results demonstrate the similarity in the electronic structure and stability of C_{40} allotropes proposed. To clarify the possibility of an experimental identification of these allotropes, which could be synthesized, for example, by deposition of C_{40} fullerenes on some surfaces, we have simulated their theoretical x-ray diffration (XRD) patterns using the optimized geometries. Assuming the polycrystallinity of a material, the average scattering power I, in electron units, is given by the Debye formula

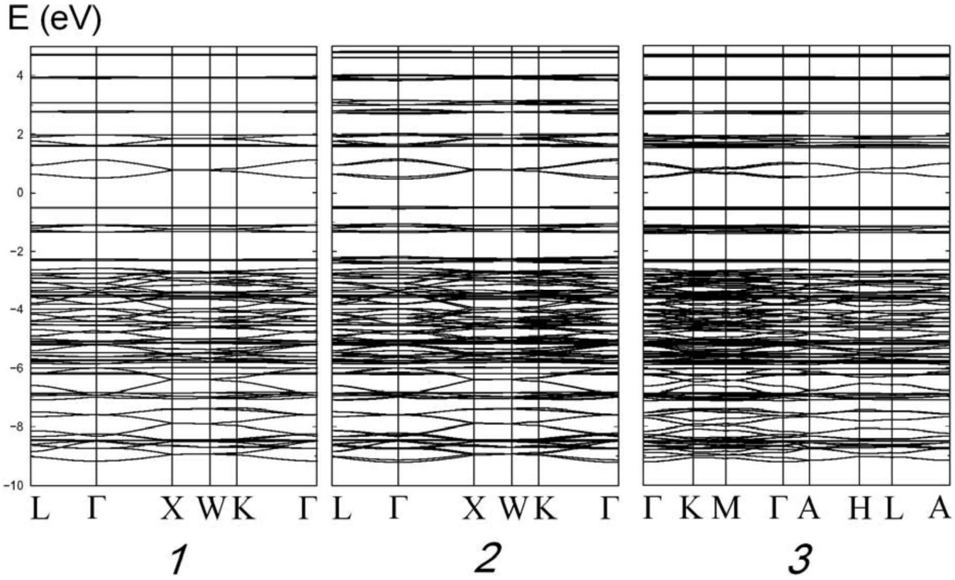

FIG. 2. Band structures for crystalline C_{40} allotropes: hyperdiamond (1), autointercalated hyperdiamond (2), and hyperlonsdaleite (3). The energy is given relative to the Fermi energy $E_F = 0$ eV.

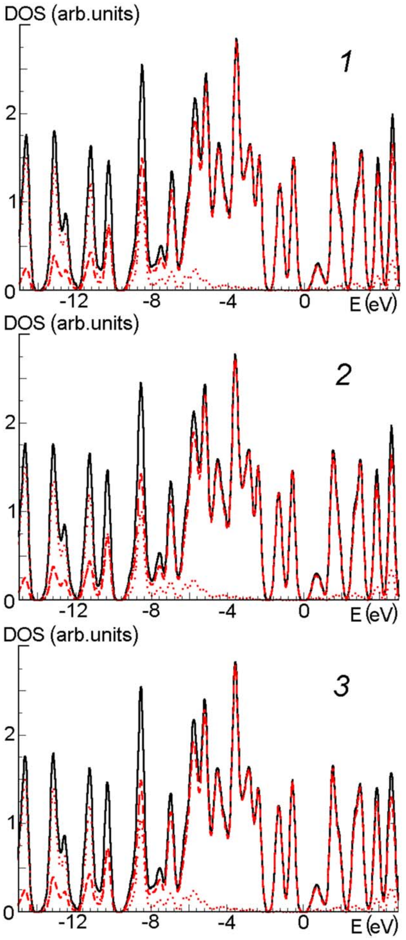

FIG. 3. (Color online) Calculated total (black) and partial (red) C 2s and C 2p densities of states (solid, dotted, and dashed lines, respectively) of the crystalline C_{40} allotropes: hyperdiamond (1), hyperlonsdaleite (2), and autointercalated hyperdiamond (3). The energy is given relative to the Fermi energy $E_F = 0$ eV.

$$I(s) = \sum_i \sum_j f_i f_j \frac{\sin(s r_{ij})}{s r_{ij}},$$

where r_{ij} is the distance between ith and jth atoms and f_i and f_j are the atomic scattering factors of the ith and jth atoms. s is the x-ray scattering vector and is equal to $s = 4\pi \sin \theta / \lambda$, 2θ is diffraction angle, and λ is x-ray wavelength (in our calculations 1.542 Å like for nickel filtered Cu $K\alpha$ radia-

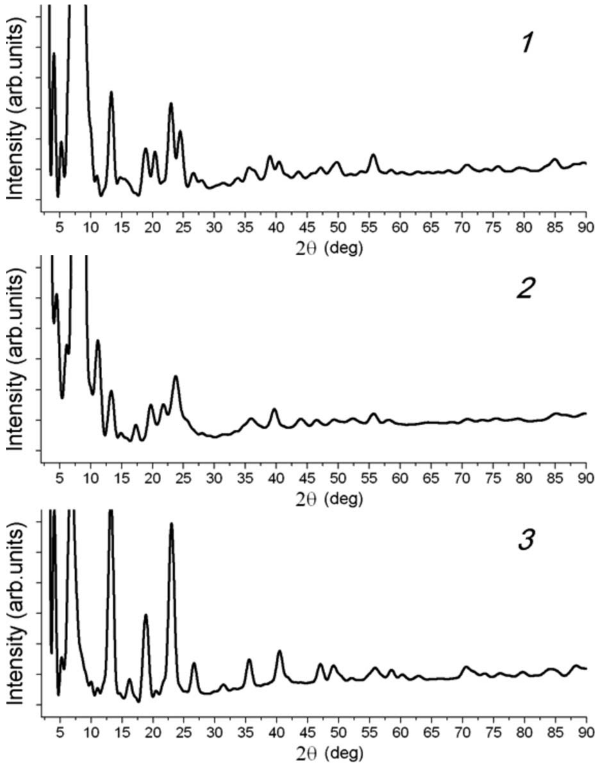

FIG. 4. Theoretical XRD spectra of the crystalline C_{40} allotropes: hyperdiamond (1), hyperlonsdaleite (2), and autointercalated hyperdiamond (3).

tion). The values of the atomic scattering factors were taken from Ref. 21.

Comparing theoretical XRD spectra (Fig. 4) one can see a characteristic feature of XRD for C_{40} AHD: distinct peak at 23.5°, which is similar to (002) peak for graphite and caused by the presence of C_6 hexagons, which belong to the fullerenes of different sublattices and are situated parallel. In XRD spectra of C_{40} HD and HL this pattern is not so much distinct and is separated into a few reflexes.

In conclusion, the atomic models of diamondlike crystalline allotropes composed of C_{40} fullerenes as building blocks (hyperdiamond, hyperlonsdaleite, and so-called autointercalated hyperdiamond) were constructed and their structural, elastic, cohesive, and electronic properties were predicted by means of the DFTB method. We have shown that all these C_{40} allotropes will be energetically stable systems and are semiconducting. However, their mechanical characteristics differ considerable. Namely, the bulk modulus for the most stable allotrope with higher mass density—C_{40} autointercalated hyperdiamond—is twice larger than bulk moduli for C_{40} hyperdiamond and hyperlonsdaleite.

Besides, special interest represents the bonding between C_{40} molecules inside this allotrope, which has twofold character (covalent and van der Waals), i.e., combines the types of the interactions presented in two main groups of the known fullerites C_n: in molecular crystals ($C_{n\geqslant 60}$-based fullerites) and in alternative group of $C_{n<60}$-based covalently bonded fullerites. We believe that this finding may stimulate future search for C_n assembled materials with such unconventional "mixed" bonding mechanism.

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