Sorption of hydrocarbons and hydrocarbon derivatives with crystalline fullerite

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To explore the possibility of creation of a safe keeping system for combustible gases and liquids, the research of sorption of hydrocarbons and hydrocarbon derivatives with crystalline fullerite $Ñ_{60}$ is carried out. The sorption dynamics analysis shows that the system in standard conditions reaches the ultimate sorption in 7 days.

Using neutron and X-ray diffraction the structure of the compound of fullerenes and hydrocarbons with hydrocarbon chloric derivatives was studied. Also the infusion superstructure formation was determined. The possible form of these superstructures was analyzed within the limits of concentration waves theory. Examining the neutron diffraction picture of compounds, which contain heptane (C_7H_{16}), octane (C_8H_{18}) and carbon tetrachloride ($ÑCl_4$), we can see additional (with respect to pure fullerene) peaks, which can be marked using the same face-centered cubic lattice as pure fullerite has. The analysis indicated that this picture is typical for tetrahedral superstructures with wave vector ê = 2πb* and with $À_2Õ$ or $À_4Õ_3$ composition.

Using the thermogravimetry method the dependence of desorption temperature on the composition of the compound being absorbed, including (CH_2Cl_2) - ($ÑÍ\ Ñ1_3$) - ($ÑCl_4$) was received. Thermal stability of $Ñ_{60} \cdot ÑÍ_{4-n}Cl_n$ compounds goes up together with chlorine atom quantity increase in the chlorine-replaced methane molecule. Extrapolating the received dependence we can expect the desorption temperature of the potential compound with $ÑH_4$ to be close to 50°Ñ.

For the compound containing $Ñ_{60}$ and unsaturated halogen derivative – tetrachloroethylene C_2Cl_4 comparative analysis with the framework of concentration waves theory indicated that tetrachloroethylene compound represents another type of infusion superstructure as compared to the $Ñ_{60} \cdot CCl_4$, which was obtained earlier. Additional superstructure peaks take place at the neutron diffraction picture. They correspond to the star of wave vector ê=2πb* and to octahedral superstructure of $À_4Õ$ type, meanwhile CCl_4 compound corresponds to tetrahedral superstructure of $À_2Õ$ type. Precise derivative-graphical measurements confirm mole ratio fullerite/absorbate, which is 1/1 and it conforms to face-centered cubic lattice cavity occupation with $Ñ_{60}$.

Vacancies in graphene: a prospect for graphene-based spintronics

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Recently, much attention has been drawn to the studies of graphene. This material with its unique electronic properties offers, among other things, a prospect of 'atomic litography' for future molecular electronics devices. Here, we report quantum chemical studies of graphene sheets with vacancies forming a two-dimensional periodic lattice. If the vacancies are located close enough to each other, the localized wavefunctions of defect states overlap, giving rise to a high-energy band. We show that if one of the periods of the lattice is large so that the interaction between the vacancies along the corresponding direction is absent, a localized conducting channel may form along the other direction. Furthermore, the density of states in this band is spin-dependent: for one spin polarization, there exists a band gap, while for the other, an intense peak arises at the Fermi level, making such a track of vacancies effectively act as a spin-filtering waveguide.

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Rationalizing fullerene halogenation: the "LIFE" algorithm

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The widely studied reactions of halogenation of fullerenes generally provide thermodynamically preferable products. Nevertheless, even for these reactions addition pathways and mechanisms have not yet been sufficiently investigated and possible kinetic factors have not been really ruled out. One can anticipate that such factors should be of much greater relevance in many other processes of sequential addition to fullerenes. Therefore, development of methods for prediction of both thermodynamically and kinetically governed products of sequential addition to the fullerene systems with their multitude of available sites is of considerable importance. Fullerene halides, a well explored class of fullerene derivatives, can serve as a good test kit for calibration of such methods before applying them to different classes of fullerene derivatives.

First attempt of systematic elucidation of fullerene fluorination pathways have been reported in [1]. The present work is devoted to computational modeling of both sequential fluorination and chlorination of fullerenes. It employs a somewhat related approach (referred to as "LIFE" algorithm in analogy to the known biological model of proliferation) based on energetic criteria of selection of intermediate products. The energy calculations involve preliminary geometry optimization the AM1 level of theory with the use of the PC-GAMESS package [4] and further refinement at the DFT level of theory with the use of the PRIRODA software [2]. Testing of the "LIFE" approach has demonstrated its ability to predict all experimentally known structures. In the same time it makes possible to discover other interesting structures that may form as not yet detected admixtures or rapidly undergo further addition.

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Pathway reaction and intermediates in fullerene amination process (application in nanotechnology): an *ab initio* study

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In this research, fullerene amination process, its mechanism and pathway reaction, has been studied by quantum mechanic calculations. In initial study, we investigate several transition states i.e: $C_{60}^{+?}$, C_{60}^{++}, $C_{60}^{3+?}$, C_{60}^{2-}, $C_{60}^{??}$. All calculations carried out by ab initio study in several methods (HF/6-31G*, HF/STO-3G, B3LYP/6-31G*, MP2/6-31G*). $C_{60}^{+?}$ is the most stable structure than the others ($C_{60}^{+?} > C_{60}^{++} > C_{60}^{3+?} > C_{60}^{??} > C_{60}^{2-}$). Structures of transition states, and intermediates that in pathway reaction produced have been studied by using the same computational levels. This article contains of calculated results, diagram of energy for predict mechanism and discussion of structural parameters in reaction mechanisms in several paths for each transition states.

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Ab initio study on the structural and reactivity of cation and cation radicals of fullerene (C_{60}^{+}, C_{60}^{2+}, C_{60}^{3+})

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Fullerene (C_{60}) and its derivatives have attracted considerable interesting due to their unique molecular structure and special chemical and physical properties[1–3]. Study at Computational Chemistry level for this selected derivatives have been carried out in order to give answer to several points that experimentally are not understandable or not enough clear.

In the present work an ab intio study is presented, analyzing the properties of a series of cation and cation radicals of fullerene such as ($C_{60}^{\cdot+}$, C_{60}^{2+}, $C_{60}^{\cdot3+}$), in order to compare their reactivity and atomic charge distributions properties. The geometric of cationic and radical cationic forms of fullerene were fully optimized at HF/STO-3G level and all property calculations were performed at HF/6-31G* level of theory.

With investigation of calculation's results, resonance pass and suitable positions for addition reaction were predicated.

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Research of mechanisms of carbon nanotubes growth on alumina surface

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The aim of the work is modeling processes of nanotubes origin on oxide catalyst surface. As the catalyst γ-alumina has been was chosen as the most widespread catalyst. Acidity of the surface is caused basically by Lewis's acid centers (LAC), but namely non-completely coordinated ions of aluminium on a surface.

The calculation of adsorption energy of hydrocarbon particles (CH_3, C_2H_5, C_3H_7) on the catalyst surface has been carried out within the framework of quantum-chemical semi-empirical MNDO/PM3 and ab initio methods. As a (100) surface γ-Al_2O_3 model the molecular cluster $Al_2O_8H_7$ has been used.

The carbon particles and organic molecules settled down above (100) surface γ-Al_2O_3 in cluster middle to reduce influence of boundary conditions, then the calculation of energy adsorption has been carried out. The energy adsorption $\mathring{A}_{ads}$ has been calculated as a difference between total energies of products and reagents and results are presented in Table.

The analysis of the results has shown that particles adsorption on the active surface centre of the crystal is most energetically favorable.

Table. Energy adsorption of hydrocarbon particles on alumina surface.

Method Location	Ab initio			MNDO			PM3		
Oxides bridge	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
	-1.5			-0.6	-0.6	-	0.2	0.3	-
Octho-center	-0.9		-0.6	11.8	11.9	-	10.9	11.0	-
Tetra-center		-1.2		11.7	11.7	-	10.8	10.9	-

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On the hexagonal close packing of C_{60} buckyballs

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The monomeric fullerene C_{60} is known to exist in both the cubic (ccp) and hexagonal (hcp) close packed crystalline forms. The hcp form is metastable with respect to the ccp form. While the cubic modification has been studied extensively with both experimental and theoretical methods, the properties of the hexagonal form are yet poorly characterized. In this talk, we report on the structure simulation study of the hcp form by lattice energy minimization. The semiempirical intermolecular potential used comprises the atom-atom potential of Lennard-Jones type to respect for the van der Waals interactions of carbon atoms, while point charges q and $-2q$ placed on the single and double bonds of the molecule were intoduced to calculate electrostatic energy. This potential had been found successful in the prediction of structure parameters and the thermodynamic stability order of the known and hypothetical C_{60} packings of ccp type. The PMC program was used throughout the calculations.

The present results are in line with the evidence that the hcp packings are energetically less favorable than ccp. Moreover, we found that the structure of actually hexagonal symmetry (with the 3-fold crystallographic axis passing through the hexagonal face of the molecule, space group $P6_3/m$, $Z = 2$) occurs as a stationary point of the energy landscape rather than a minimum. When structure was allowed to go to the nearby minimum starting from the stationary-point configuration, the C_{60}-centers kept approximately their hcp positions but the molecule rotated away from triple-symmetry orientation and the lattice geometry distorted from ideally hexagonal to become monoclinic pseudo-hexagonal. The energy height of the stationary point above the minimum is only ~0.05 kcal/mol. This gap is certainly covered at nonzero temperature by an entropy contribution to the free energy stabilizing the hexagonal structure. Nevertheless, at about liquid-helium and lower temperatures the hexagonal symmetry is therefore predicted to be broken.

Note that the hexagonal structure has a shorter c-axis dimension than of monoclinic structure and can be stabilized at absolute zero by application of uniaxial stress along [001]. Intercalation of solvent molecules into the lattice voids may also stabilize the hexagonal symmetry down to absolute zero, but this critically depends on the size, shape and chemical nature of the solvent molecule which must fit accurately the size and configuration of the packing cavity.

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Potential-derived site charge models of C_{60}

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It is well recognized that the ordered low-temperature crystal structure of C_{60} can not be predicted correctly without proper account for electrostatic potential of the molecule. As a matter of fact, the atom-atom van der Waals potential of Lennard-Jones type predicts the ground-state structure of solid C_{60} to be orthorhombic, space group *Cmca*, $Z = 4$, in contradiction with cubic *Pa*3, Z=4 observed. With electrostatic energy contributions due to the point charges q and $-2q$ (q=0.25 electron) at the centers of single and double bonds, respectively, the observed cubic structure turns out to be ground-state.

Up to date, such a successful charge model, being quite empirical, was not inspected by quantum chemical methods which could provide charge distribution in the C_{60} molecule in a straightforward way. Here we report on the charge models of C_{60} based on quantum-mechanical molecular electrostatic potential (MEP). Standard SCF Hartry-Fock calculation with 6-31G(d,p) sets of basis functions have been performed with Gaussian-98 package (Frisch et al., 2002) to obtain a 3D MEP distribution. Several alternative point charge models were tried then to fit this distribution in a region surrounding the van der Waals surface of the molecule. The FitMEP program (Dzyabchenko, 2007) was used to minimize the RMS deviation of the model potential from the quantum chemical MEP by variation of both site charges and coordinates (while keeping all variables to hold the I_h symmetry of the molecule). For a few models comprising the 60, 90, 100, 120, and 180 sites the final RRMS deviations were 20, 3, 1.4, 1, 0.9 and 0.7%, respectively. Contrarily, it was quite surprising to find that the empirical bond charge model does not show any agreement with the quantum chemical MEP (RRMSD= 560% !). Attempts to improve it by adjusting charges q only with all sites fixed at the bond centers did not reduce RRMSD to lower than 50%, quite insufficient accuracy comparing to other models.

Finally, we examined these charge models on the C_{60} crystal structure prediction problem using the PMC program for energy minimization. We found that with any of the MEP-derived models the cubic structure turned out to be metastable, ~2 kcal/mol higher in energy than the competing orthorhombic structure predicted ground-state. To conclude, the HF/6-31G MEP-derived charge models fail to predict actual stability order of C_{60} packings, in striking contrast to the empirical bond charge model. We discuss the possible reasons for such a failure and ways to fix the problem, in particular the necessity of further expansion in the gaussian basis set and consideration of polarization effects.

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Nanoactuator based on carbon nanotube:new method of control

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A set of nanoelectromechanical systems (NEMS) based on relative motion of the walls of nanotubes has been suggested recently [1-3]. Thus elaboration of methods to control the motion of nanotube walls is an actual problem of nanomechanics.

New method to control the motion of nanotube-based NEMS is proposed. It is based on the chemical adsorption of atoms and molecules on the open edges of the single-walled carbon nanotube, which results in the appearance of electric dipole moment. In this case the functionalized nanotube can be actuated by non-uniform electric field. Semi-empirical method of molecular orbitals with PM3 parametrization of Hamiltonian has been used to calculate the electric dipole moments of functionalized (5,5) nanotubes.

Possibility of the proposed method of controlling the motion of nanotube-based NEMS is shown on example of the gigahertz oscillator based on relative sliding of carbon nanotube walls. The scheme, operational principles and theory of such oscillator were considered recently [2]. The molecular dynamics simulations show that the Q factor of the gigahertz oscillator is about Q=100-1000 and the frequency increases with time [3]. Therefore to keep constant frequency of the oscillator it is necessary to compensate the energy dissipation by the external force. Here we consider the possibility to compensate the energy dissipation by applying to the movable wall a control force $F(t) = F_0 \cos wt$, where w is the desirable oscillation frequency. It is shown that the amplitude F_0 of the control force is smallest in the case of the oscillator with equal lengths of the walls and equals to $F_0 = ?F_W/32Q$, where F_W is the force retracting the inner wall into the outer one. For the considered functionalized (5,5) nanotubes the amplitude F_0 is estimated to be 0.1-1 pN. The voltage 2-10 V is sufficient to applied such force to the wall in a cylindrical or spherical capacitor. The parameters of the system and control force which allow to obtain the stationary operation with constant frequency are determined by analysis of the equation of motion.

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Ab-initio study of hydrogen chemical adsorption at surfaces of carbon nanotubes with attached platinum clusters

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In the last decade interest to the hydrogen based technology was increased extraordinary because of ecology problems and large cost of hydrocarbons. But if the task of hydrogen transformation to electrical energy is solved in many respects due to hydrogen fuel cells building, current hydrogen storage systems are inadequate to meet the needs of consumers. The main existing and proposed technologies for hydrogen storage include pressurized tanks for gaseous hydrogen and cryotanks for liquid hydrogen; hydrogen storage in various metal-based compounds, hydrogen absorption in advanced materials, including carbon nanotubes(CNT), alkali-doped CNT, graphite nanofibers, etc. Unfortunately, many existing experimental and theoretical data about H_2 adsorption in CNT and relative nanomaterials are very contradictory.

But it was surely defined that physical hydrogen adsorption at CNT surface is too weak. So in this investigation we make thorough theoretical analysis of availability of chemical hydrogen adsorption in single wall CNT ((5,5) and (8,8)), including these nanotubes containing defects (vacancies). Because of very hard dissociation of H_2 molecules at CNT surface we investigate here systems which include CNT and joined platinum cluster (plate geometry). During reversible adsorption process H_2 molecules are dissociated to H atoms at platinum plate surface easily and then they can jump and spill over CNT surface.

We made theoretical analysis of these CNT-Pt systems at different temperatures (300-900K) and pressures (0-500Bar) with help of *ab-initio* calculations (VASP 4.6 package) in the frame of the density functional formalism (DFT-GGA), plane wave basis and Vanderbult's kind pseudopotentials.

By calculation of chemical potential of adsorbed and gaseous hydrogen it was shown that at all examined temperatures and pressures hydrogen is easy adsorbed chemically at Pt surface, but equilibrium hydrogen concentration at joined to Pt surface CNT is few ($<10^{-6}$). At that hydrogen atoms may be effectively adsorbed at CNT vacancies ($n_H/n_{vac.}$~0.4 at T = 450K and P = 500bar). By precise quantum mechanical calculations of frequencies of H atom jumps on CNT and PT surfaces it was established that hydrogen can be moved and stored at these surfaces at temperatures T>500K only.

Optical absorption and reflection spectra of single-walled SiC nanotubes

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Recently, several experimental groups (see, e.g., [1, 2]) have succeeded in synthesizing silicon carbide nanotubes (SiC-NTs), which are very promising materials for applications in high-temperature harsh-environment nanoelectronics, nanosensors and nanoactuators, as well as for biotechnology applications. These newly synthesized nanotubes are also interesting from a fundamental point of view as a suitable laboratory, complementary to carbon and boron nitride nanotubes, for exploring fascinating quasi-one-dimensional physics at the nanometer length scale. As a part of the systematic progress in this field, optical studies of SiC-NTs are especially important and desirable, because they can provide valuable insights into the electronic structure of these tubes and, in addition, open up a new promising field of scientific research and technological applications. In this report, the optical characteristics (absorption and reflection coefficients) of single-walled SiC-NTs are calculated for the first time using a simple **k·p** two-band model of the electronic structure of such tubes. We find that the optical absorption and reflection spectra of these tubes exhibit rich characteristic resonant structures associated with dipole-allowed direct interband electron transitions between successive mirror-pairs of van Hove singularities in the electronic density of states of the tubes. It is also shown that the optical spectra exhibit a pronounced dependence on the chirality index of the tubes, thus suggesting a way to characterize the diameter and chirality of SiC-NTs by using optical absorption and/or reflection spectroscopy.

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New rings and balls model of atomic structure of a disordered matter

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Work is devoted to algorithms of construction of close-packed atomic structures of the disordered matter. The new algorithm of construction of amorphous structure of single matter from polyhedrons which sides are correct triangles is considered. Linear search of all polyhedrons with number of vertices (atoms) n ? 14 is made. It is found that the structure of a close-packed atomic cluster in a hard spheres model is determined by a set of nine polyhedrons. Five of them named basic. They can appear independently in amorphous structure at the close-packed regions of a single matter. The rest four types of polyhedrons named as growth polyhedrons participates in formation of other atomic clusters. The operations that are necessary for construction of compound polyhedrons with greater number of vertices are also formulated. It is shown, how such polyhedrons can be taken apart onto simplexes. Such simplicial structure is a basis for representation of atomic structure of disordered material as an incommensurate system.

For all considered polyhedrons, including Bernal's polyhedrons, for equal numbers of vertices the number of edges in each of them coincides with number of edges of a tetrahedral chain.

The atomic clusters with number of bonds greater, than appropriate tetrahedral chains are found. They can arise due to relaxation of a structure of an amorphous material and lead to its hardening before the transition of this material into a solid state has been completed.

Changes of atomic structure of a liquid at laminar flow are considered.

The viscosity coefficient at laminar flow of a liquid expressed owing to quantity of the double-well atomic configurations caused by reorganization of various polyhedrons. Because of these reorganizations a diffusion of substance is occurring. The diffusion equation of laminar flow of a liquid is obtained which correspond to the mixing of substance in this process.

On the internal field with non-uniform potential, excited by thermal fluctuations of molecules C_{60} in crystal

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In the review [1] a number of models of the movement of the charged particles in the field with the non-uniform potential in a crystal is considered. A.I. Akhiezer also questioned on propagation of the conclusions, made for crystals, on solid matters with structure containing symmetry of the fifth order. The geometrical analysis of the thermal fluctuations of molecules C_{60} in the model of the face-centered cubic crystal [2] has allowed to describe the method of the combinatorial transformation crystallographic arrangement of molecules C_{60} in the first coordination sphere in the arrangement of molecules C_{60} with symmetry of the fifth order. At this transformation of the trajectory of movement of molecules C_{60}, which make the first coordination sphere with elements of symmetry of the fifth order, are located so, that they create conditions for spontaneous excitation of local electromagnetic fields. The set of so formed local fields in the first coordination spheres of molecules C_{60} of a crystal is sufficient for creation in the whole crystal of a field of non-uniform potential.

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Endofullerenes C_{60} with different metal atoms

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Endohedral fullerenes M@C_{60} are of great interest from the point of both experimental and theoretical studies of new type of chemical species. Their formation occurs due to the geometrical confinement of atoms inside the closed carbon cage C_{60}. A question on chemical bonding of an endoatom with carbon *a priori* is open since the simple geometrical reasons provide the possibility of these systems due to the confinement. However, bare metal atoms as well non-metal elements in atomic form usually are strongly reactive, and the M-C bond formation is very probable. Non-metal atoms (e.g. N, P) can produce the endohedral structures M@C_{60} with negligible effect upon the carbon cage, while the active metals interact much stronger with C_{60} [1-3]. The localization of endoatoms within the cage and resulting symmetry of the structures also depend dramatically on the nature of endoatoms. In spite of many theoretical and experimental works on endofullerenes there is no systematic analysis of the endoatom nature effects to be possible to predict properties of any M@C_{60}. In the present work, we calculate a series of M@C_{60} models with metal atoms corresponding to both known realistic endofullerenes (alkali, rare earth elements) and to the hypothetical ones to date (Ag, Cu, Au, etc) assuming arbitrary symmetry. DFT and SCF Hartree-Fock methods with ECP and all-electronic basis sets were used.

The calculations demonstrate the three principal factors to be of importance for interpretation of the endofullerenes: (i) ionization potentials of metal atoms that are decreasing from Au to alkali metals and result in the corresponding effects of charge transfer between metal and carbon; (ii) atomic (ionic) radii for the metals providing geometrical ability of atom localization changes with respect to the center; (iii) the contribution of different atomic orbitals into the metal-C_{60} bonding: *ns* for typical active metals mixed with *np* for heavy ones and *ns* and *(n-1)d* for transition metals. There are anomalous values of effective charge in the case of Ag and Li due to different reasons: *d*-orbitals, and very small atomic radius, respectively. Thus, the present research allows to suppose qualitatively the features of many endofullerenes without direct calculations and measurements.

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Electronic structure and chemical bonding of nano-size diamond-like structures

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The wide application of nano-structured materials in various areas of engineering has caused significant interest of the researchers to study of a nature of formation of unique properties of marked materials. To the most perspective directions of research it is necessary to relate study of electronic structure and chemical bonding of such materials. The special interest is represented by porous crystal materials, the electronic structure of which is investigated unsufficiently for the most complete understanding of mechanisms of formation of their properties. The application of zoned methods of account to porous objects causes basic difficulties.

In the given work for account of density of electronic states (DOS) of materials with distributed nanopores an opportunity of approach of local coherent potential within the framework of the multiple scattering theory are submitted [1]. By us as model is used cluster with 235 atoms, at centre of which is placed pore with radius 0.3 nm, by analogy to work [1]. The lack of atoms of sublattices of atoms-components can be accompanied by reorganization of a lattice from absent bonding and to result in reduction of parameter of a crystal lattice. In the given model the pores borrow 20% of volumes of the whole crystal.

On an example cubic BN is shown, that presence of nanopores in a crystal results in downturn of potential on atoms B and N. The local DOS on atoms-components are calculated in view of concentration of atoms of a grade A (or B) on each coordination sphere similarly to work [2]. The reorganization of a energy spectrum of a valence band in system BN-pore rather BN is connected to carry a charge in low-energy area at atoms B (0.65 e) and N (0.11 e), with than reduction of intensity of maxima on a curve TDOS is connected. The downturn of density of condition with energy 0.70 Ry can be caused by reorganization of sp^3-configurations B and N in sp^2-configuration. The similar transformation of electronic configurations took place in porous SiC [3]. The condition with energy 0.46 Ry appear steadiest and corresponds, on our sight, sp^3-configuration, for which is characteristic a orientation of the covalent binding between atoms B and N.

Thus from consideration of above mentioned results follows, that the considered model of nanjpores in crystals with structure of diamond does not contradict published experimental dat& about peculiarities of an electronic spectrum of real nano-structured materials.

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Electronic structure and stability of diamond nanoparticles and «3d-metal-nanodiamond» solutions

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The necessity of search of new materials for modern engineering makes active development of crystal physics on study of mutual influence of electronic subsystems, especially at presence in an oriented lattice of defects of casual replacement. In particular, at replacement infringement of symmetry of a crystal concerning the inversion can be observed, that in many cases results in occurrence of new properties.

One of the important problems of technological use of nano-size diamonds is his temperature instability at 900-1000 degrees Celsius, that «diamond-graphite» is displayed in phase transformation [1]. Usually the surface of nano-particles of diamond is impregnated by transitive 3d-metals, that raises temperature stability of such system. Despite progress in technological use of the given reception, the nature of this phenomenon up to the end is not investigated. In the present work influence of electronic subsystem Ni, diamond used for modifying, on his energy structure and chemical bonding was studied. For account total and local density of electronic condition C and Ni in system the «diamond-Ni» is used a method of local coherent potential within the framework of the multiple scattering theory in a combination to model of a virtual crystal, described earlier [2]. Are designed total and partial local densities of electronic state of carbon and Ni in system «diamond – Ni».

The analysis of results has allowed to find out some laws, in particular, the influence of a subsystem Ni to an electronic energy spectrum of diamond was displayed in increase of electronic states, as at a ceiling of a zone, that will be coordinated with representations of the authors of work [3], and in area XANES. Marked peculiarities of an electronic energy spectrum should result in change physical properties of nano-structured materials on the basis of system «diamond – Ni».

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Electronic and magnetic properties of MnO clusters inside nanotube

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In the present work electronic structure and Mn*K*-spectra of absorption in clusters MnO, placed in one of channels of matrix MCM-41 [1] are theoretically investigated. In the given aspect it is necessary to take into account two circumstances. First is, that the interaction between the 2p-hole in the core level and 3d-electrons is essential [2], therefore the *K*- spectra of absorption are defined by local electronic structure and give the information about the degree of symmetry of ions Mn in the particular cluster. Secondly the sizes of clusters and their positions inside the channels and the interaction with the matrix-carrier are of high importance for our understanding the appropriate formation of properties of nanocomposites. Consequently as a model object the small cluster of MnO isolated or localized inside a channel of the matrix-carrier. At the first stage the position of the cluster near the wall of the nanotube is theoretically investigated. The study was carried out for clusters of different size composed of 27 or 81 atoms of the cubic lattice. For the theoretical investigation of the electronic structure the objects and their Mn K-absorption edges the code FEEF8 [3] was used. The coordinates of atoms of the fragment of the nanotube were found with the program TubeGen 3.3 J.T.Frey and D.J. Doren. The distance to the wall of the nanotube was varied in the range 2.257? -2.657? with the step 0.2?

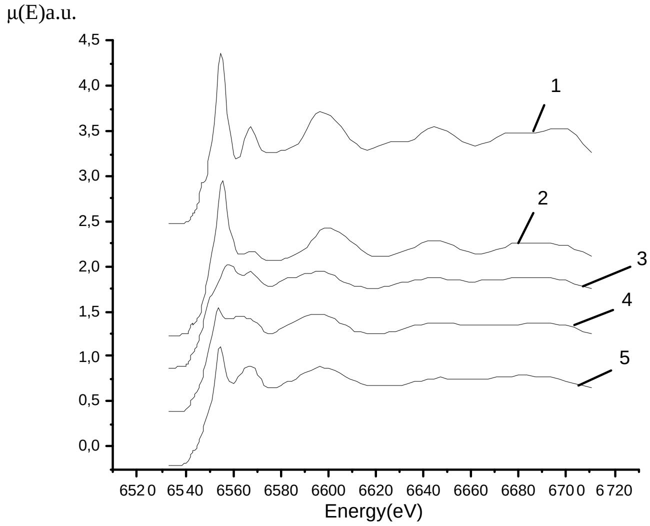

Fig.1. Theoretical Mn*K*-absorption: for isolated clusters (1,2) and MnO clusters inside nanotube (3-5)

By comparison the degree of coincidence of the positions of peaks of Mn K-absorption spectra of the modeling object with one of the isolated cluster with 81 atoms (the curve 1 in the Figure) and the isolated cluster with 27 atoms (the curve 2) the optimization of the length of chemical bonding of the nearest Mn atom to the wall of the nanotube of the cluster with 27 atoms (the curves 3 and 4) was carried out. For the bond length 2.257? (curve 5) the best accordance for the first three peaks of Mn *K*-absorption edge to the model object (curve 1) is observed, that corresponds, as we suppose, to the optimal position of the cluster in the nanocomposite.

At the second stage the electron structure of the electrons in the conduction band well as the form of XANES and the contributions of the electrons of “different symmetry” to Mn *K*-absorption are discussed. These results were used to explain the experimental magnetic properties of the MnO in some composites.

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Density functional and semiempirical studies of fullerene C_{60} derivatives with silicon-containing and alkyl groups

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In recent years considerable research interest has been focused on silicon-containing fullerene derivatives since they can serve as a basis of advanced materials for nano-electronics. We have already reported synthesis of new silylated fullerene compounds R_nC_{60} (R=$SiMe_3$, $SiCl_3$, n = 4, 6, 8, 10, 12) [1]. In the present work we carried out the DFT (B3LYP/3-21G) and semiempirical (AM1) calculations to investigate the electronic structures of these and related fullerene systems. The molecular geometries were optimized for the neutral, cationic and anionic species with the SiH_3, $SiCl_3$, $SiMe_3$, CH_3, CH_2Ph and CMe_3 groups. The molecules bearing two and four CH_3, SiH_3 and $SiMe_3$ substituents were investigated by both the DFT and AM1 methods. For the other systems only semiempirical calculations were performed. The most stable isomers were found for the molecules containing bulky $SiMe_3$ and CMe_3 fragments. To analyze the role of the substituent nature the other groups were placed to the same positions. The ionization potentials (IPs), electron affinities (EAs) and average R-C_{60} bond dissociation energies (BDEs) were estimated.

For pristine C_{60}, the DFT IP and EA values (7.7 and 2.4 eV, respectively) agree very well with the experimental ones (7.4 and 2.6 eV, respectively). The introduction of the substituents considered decreases IP substantially, the $SiMe_3$ group having the strongest influence (IP = 6.7 eV for $(SiMe_3)_2C_{60}$). The changes in EA are not so large. The semiempirical calculations overestimate both the IP and EA values (8.4 and 4.1 eV, respectively for C_{60}). However, the trends in the substituent influence found by the DFT and AM1 methods are similar.

The average DFT BDEs for the neutral derivatives containing two CH_3, SiH_3 and $SiMe_3$ groups are 51.7, 41.3 and 45.5 kcal/mol, respectively. The C_{60}-CH_3 bond appears to be, therefore, about half as strong as the Ph-CH_3 bond. Interestingly, an introduction of two additional CH_3 or SiH_3 groups in the *para* positions of the neighboring 6-member rings of R_2C_{60} leads to a ~ 1.5 kcal/mol increase in average BDEs. A similar stabilization effect was found by the AM1 calculations for the neutral R_4C_{60} and R_8C_{60} molecules (R = $SiMe_3$, $SiCl_3$). The data obtained are of help in studying the reactivity of functionalized fullerenes.

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