Conductivity of polyamids, 6, modified with fullerenes and nanoplanar carbon.

Alekseyev N.I.*, Aleshin A.N.*, Aleshin P.A.*, Charykov N.A.**, Namasbaev V.I.**, Potalitsin M.G.**, Zuev V.V.**

Ioffe Physical-Technical Institute, 194021 St.Petersburg, Russia
**ILIP Ltd, 197022 St.-Petersburg, Russia*

Polyamide,6 (kaprolon) is a polymer constructive material, used as a light weight substitution of non-ferrous metals in friction junctions. An increase in conductivity of this material, not accompanied with a loss of its mechanical characteristics, enables a substantial extension of possible applications.

The modifier, optimal from this viewpoint, is fullerene, either itself or combined with some other nanocarbon materials. The fullerene admixture of $2 \cdot 10^{-4}$ mas.% enabled the volume conductivity σ of $\sim (3 \cdot 10^{-12} - 10^{-11})$ *S/cm* and the same order of the surface conductivity at normal conditions (for pure polyamide $\sigma \sim 10^{-16}$ *S/cm* and the forbidden gap is $\sim 6 eV$).

All the samples measured within the temperature range from $300K$ to the softening point showed exponential temperature dependence of their conductivity with the weak change in the activation energy E_a. The quantity of $E_a \sim (0.8 - 1.0)$ *eV* is substantially lower than the forbidden gap of the fullerene and has a slight decrease with the fullerene concentration.

High resistance of the samples almost prohibits the measurement below $\sim 250K$. The constancy of E_a at higher temperature admits different mechanisms of conductivity to be offered, the variable range hopping between conductive metallic clusters and polaron conductivity among them. It is important that at the concentration of the fullerene molecules of $\sim 20 ppm$ the distance between them is close to the typical monomer chain length.

As the pure fullerene is an expensive modifier, the research was extended to nanoplanar carbon (multiwall graphene fragments with a typical size of $\sim 1 \mu m$). The measurements showed high conductivity of $\sim 10^{-8}$ *S/cm* at the room temperature, even if the nanoplanar carbon concentration is as low as 10^{-3} *mass*%. An amazing feature of the nanoplanar modification is exclusively slight temperature dependence of σ that enables to go down to $77K$ along the temperature axis.

The combined variants of using the fullerene and nanoplanar carbon enabled the conductivity of $\sim 10^{-6}$ to be attained.

Mechanism for carbon nanotube assembly to the bundles and calculation of existence domains for different nanotube structures on the diagram "temperature – catalytic particle diameter"

Alekseyev N.I.*, Goncharov V.D.**

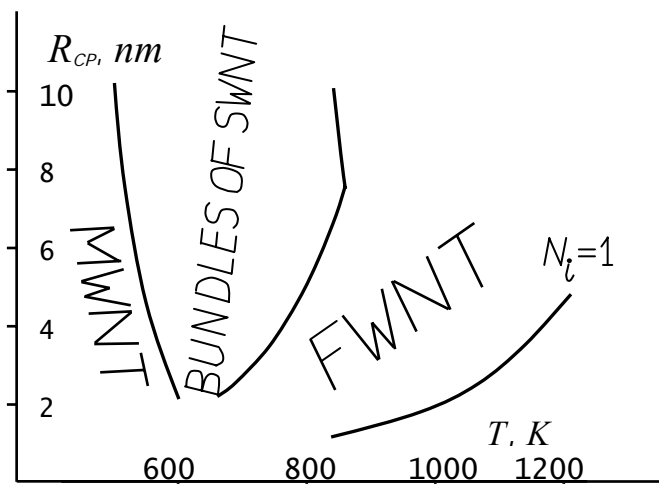** Ioffe Physical-Technical Institute, 194021 St.-Petersburg, Russia*
**Electrotechnical University (LETI), 197376, St.-Petersburg, Russia

Few walled carbon nanotubes FWCNs is a prospective carbon material with a great deal of possible applications. The optimal way for the synthesis of high quality FWCNs is a CVD technique on the surface of small size catalytic particles (CP). One of the problems on this way is the absence of algorithm for the calculation of the FWCN parameters versus the parameters of the CVD synthesis.

The said algorithm must start with the calculation of the formation of nanotube nuclei on the CP. In the model we developed since [1], such nuclei are the fragments of the fullerene-like surfaces (islets). They collectively absorb carbon from the CP to reduce its supersaturation. In the course of the calculation of the islet nucleation stage we calculated the number of the islets N_i, their typical sizes and the maximal supersaturation of the CP.

The subsequent dynamics of the islets is determined by the thermodynamical benefit of their growth in the form of nanotubes and by kinetic conditions. The calculation shows that at the moment of maximal supersaturation these conditions are valid to give the start to the growth of nanotube in the form of individual nanotubes. This growth is accompanied with the swing and the rotation of the nanotube axis with regard to the CP surface normal. If the number of nanotubes is great, the swing leads to the formation of bundles. This process determines the high temperature border between the domains of existence for the beams and individual FWNTs. A different border separates the domains of the beams of FWNTs and individual multiwall nanotubes MWNTs (Fig).

The model can be applied to the calculation of the emission electronics structures based on NTs. For example, if the structure requires that the only nanotube would form from the CPs, the conditions must be as follows. The diameter of the CP $2R_{CP}$ must not exceed ~5nm and at the same time the temperature must be higher than ~700°C. The diagram of the existence domains for the different forms of the nanotubes in the (T, R_{CP}) axis points as well to the possible domain of milder conditions.

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Sorption of metals on multiwall carbon nanotubes

Bazhenov A.V.*, Fursova T.N.*, Grazhulene S.S. Red'kin A.N., Telegin G.F.

Institute of Solid State Physics, 142462, Chernogolovka, Russia

Institute of Microelectronics Technology and High Purity Materials, 142462, Chernogolovka, Russia

Carbon nanotubes are interesting both from a fundamental point of view and as promising materials in numerous technological applications. This study concerns development of new materials that can effectively sorb metallic micro-admixtures in water solutions and be used in atomic-spectroscopy analysis of these solutions. Sorption of Ag, Cu, Pb, Cd, Fe, Mg cations on multiwall carbon nanotubes (MWNTs) produced by CVD method with Ni catalyst was experimentally investigated. We synthesized MWNTs, measure their thin-layer infra-red (IR) transmission spectra, and analyzed their sorption abilities by ordinary methods of chemistry.

We found that MWNTs sorption depends on the temperature of their synthesis T_s, which varied from 400 to 550°C. For all samples, IR spectroscopy revealed the absorption band that also existed in graphite and was explained as a result of partial breaking of the translational symmetry in crystal. This band was most intense when T_s=400°C. After a concentrated HNO_3 treatment at 90-120°C, carbonyl groups –C=O formed on MWNTs, which were active sorption centers of above-mentioned metallic cations. The concentration of carbonyl groups was maximal for MWNTs synthesized at the same T_s=400°C. These two facts revealed that T_s=400°C corresponds to the maximal concentration of defects in MWNTs. For comparison, we investigated activated charcoals, which underwent the same HNO_3 treatment and formed similar carbonyl groups.

It was the MWNTs synthesized at 400°C and treated in concentrated HNO_3 at 120°C that we found to be of maximal sorption capacity. Their sorption capacity was several times higher than the sorption capacity of activated charcoal commonly used for sorption of metals. It was also 5-10 times higher than the sorption capacity of MWNTs reported in literature.

Inelastic tunnelling of electrons in amorphous metal-carbon nanocomposites

Bozhko A.D.*, Kataeva E.A.*, Glushkov V.V.*, Ishchenko T.V.*, Shupegin M.L.[+], Demishev S.V.*

Prokhorov General Physics Institute of RAS, 119991 Moscow, Russia
[+]*Moscow Power Engineering Institute, 105835 Moscow, Russia*

The metal-carbon nanocomposites [1] are related to the class of materials perspective for the applications as functional elements in the advanced sensors, actuators, and as different types of protective coatings. For these applications the information of the mechanism of the electron transport in the materials is important. The present study is devoted to the clarification of the electron transport mechanisms in the thin (up to 1 μm) films of amorphous metal-carbon nanocomposites, containing W, Nb, and Cr as doping metals, over the temperature interval 2.5÷300K.

The amorphous hydrogenated carbon matrix of the nanocomposites, doped by silicon and oxygen, was deposited by PECVD of the polyphenylmethylsiloxane ($(CH_3)_3SiO(CH_3C_6H_5SiO)_3Si(CH_3)_3$) vapors. The metals were introduced into the growing film by the DC magnetron co-sputtering of the appropriate metal target in the form of nanoclusters with typical size ranging from 1 to 2 nm, depending on the value of metal concentration, which was varied over the range 10÷40 at.%. The concentration of silicon and oxygen in the films is close to their stoichiometric value in the initial precursor at low metal concentration.

It is shown, that the conductivity *vs.* temperature dependences of the metal-carbon films possesses some common features: a) the conductivity decreases with temperature over the metal concentration range studied; b) three typical temperature intervals (appr. 10÷20K; 20÷70K, and 70÷300K) can be distinguished on the conductivity-temperature dependences; c) the conductivity depends on the temperature by the power way within each temperature interval.

The power temperature corrections to the conductivity can be discussed in terms of the inelastic tunneling of the electrons between the conducting clusters in the insulating carbon-silicon matrix along the chains of the localized states. The hopping character of the conductivity corrections is confirmed by the low values of the mobility of the electrons in the films, estimated from the first Hall effect measurements, do not exceeding the value of 0.3 cm^2/Vs. The attendant estimation of the electron concentration in the films gives 3×10^{21} cm^{-3}.

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Impact of pyrolized polyacrylonitrile structure on the process of oxidation

<u>Davletova O.A.</u>, Zaporotskova I.V.

Volgograd State University, 400062 Volgograd, Russia

Presently, research on organic semiconductors and search for new allotropic forms of carbon fullerenes have stimulated interest in the synthesis of new carbon nanocrystalline materials with modified chemical properties based on pyrolized polyacrylonitrile (PPAN), which contains a curved carbon plane. Research on elementary oxygen adsorption was carried out within the model of ion-built covalent-cyclic cluster (IB-CCC) by applying semi-empirical quantum chemical scheme MNDO.

To study the process of adsorption of atomic oxygen two-layer pyrolized poliacrilonitrile was chosen, where each layer contains 20% nitrogen atoms of the total number of atoms in one layer. The distance between the atoms in the layer is 1.4 Å, and between the layers, by analogy with graphite, it is chosen equal to 3.4 Å. We studied two variants of the layers positions relative to one another: 1) one layer is strictly above the other; 2) one layer shifted from the other by 1/2 hexagon. In the study of adsorption of atomic oxygen on one of the external surfaces of a double-PPAN (for the two proposed positions), the adsorbed atom was placed on three different atoms of the surface: 1) on a carbon atom of the carbon-atom hexagon, 2) above the carbon-atom hexagon where one carbon atom is replaced by a nitrogen atom, 3) above the nitrogen atom. The adsorption process was simulated by step-by-step movement of the adsorbed oxygen atom towards the above mentioned patterns of atoms on the surface of the layer along the perpendicular to the surface built through one of the sampled atoms.

Calculations allowed us to build a profile of the potential energy of adsorption. The analysis of the energy curves revealed that the oxygen atom is adsorbed on the surface PPAN, which is demonstrated by the existence of minimum on the energy curves. The minima illustrates the fact of chemical bond between the atom of the surface and an atom O. In order to reach the minimum, the oxygen atom must overcome a potential barrier (identifiable with the energy of activation).

Fluorination of carbon nanostructures on the base of pyrolized polyacrylonitrile

Davletova O.A., Zaporotskova I.V.

Volgograd State University, 400062 Volgograd, Russia

Polyacrylonitrile (PAN) is one of the most common and promising polymers for many applications. During the interaction of IR-radiation with the polymer the mechanism of the structure self-organization comes into effect which enables us to modify its chemical properties, accelerate chemical transformation into PAN and form nanosystems with molecular structures. As a result, the so-called pyrolized polyacrylonitrile (PPAN) is formed.

The potential of fluorine atom adsorption and the effect of the structure and chemical composition of carbon material obtained by thermal decomposition of PAN in vacuum on this process was investigated. A monolayer of polymer containing 20 % of nitrogen atoms of the total number of atoms in the structure was investigated. Adsorption of atom F on three randomly-sampled atoms of the carbon surface PPAN was studied: 1) above a carbon atom of a carbon hexagon; 2) above a carbon atom of a hexagon where there is one atom of nitrogen; 3) above a carbon atom of a hexagon where there are two atoms of nitrogen. The attack of a fluorine atom onto the polymer surface was modeled as a step-by-step movement of a F atom to a carbon atom along a perpendicular to the surface built through a random atom C. The analysis of the energy curves revealed that fluorine atoms are adsorbed on the surface of the polymer, which is supported by the presence of energy minimum on the curves which proves the fact of the formation of a chemical bond between fluorine atoms and a superficial carbon atom. Optimum distances of adsorption and corresponding adsorption energy values were computed.

The analysis of the results of optimization in geometry of the systems under study revealed that owing to the adsorption of fluorine atom on the surface of polymer the three C - C bonds of the carbon hexagon on which a fluorine atom is absorbed, appeared to be extended as compared to the initial values. It is necessary to point out that this increase in length is insignificant. Thus, it is possible to state that the adsorption of fluorine atom on a monolayer surface does not cause any significant deformation.

It has been demonstrated that fluorine atoms can be intensively adsorbed on the surface of pyrolized polyacrylonitrile.

Comparison of adsorption properties of some nanocarbon materials surfaces

<u>Davydov V.Ya.</u>, Kalashnikova E.V.

Department of Chemistry, M.V.Lomonosov Moscow State University, 119992 Moscow, Russia

Carbon adsorbents on the base of single – wall nanotubes, molecular crystal of fullerene C_{60}, graphene sheets and other carbon nanostructures are of grate interests dealing with working out of systems for storage of light hydrocarbons, hydrogen, of drug delivery systems, adsorbents for water purification and their using for separation of compounds. In all these cases the adsorption processes are the most important. So the knowledge of peculiarity of surface adsorption properties makes it possible to optimize their using in each process. The adsorption properties of carbon materials are suitable to compare with the adsorption properties of graphitized carbon black as standard with uniform surface.

The adsorption properties of thermoextended graphite, single – wall carbon nanohorns (SWNHs) and molecular crystal of fullerene C_{60} – fullerite surfaces were compared with the adsorption properties of graphitized carbon black surface.

Adsorption of nitrogen and light hydrocarbons in static conditions shows that constants of adsorption equilibrium at small coverage on graphitized carbon black surface and thermoextended graphite surfaces are similar and larger than on single – wall carbon nanohorns surface which is very much larger than the equilibrium constant on molecular crystals of fullerene C_{60} – fullerite surface.

After oxidation of single – wall carbon nanohorns and opening of nanotubes the additional nanoporosity arises and adsorption of nitrogen and light hydrocarbons increases about 2 times.

Although the aggregates of initial and oxidized single – wall carbon nanohorns can be used for the chromatographic separation of hydrocarbons and other compounds but it is difficult to use chromatography for the determination of thermodynamic characteristic of compounds adsorption on surfaces of such materials owing to kinetic difficulties of penetration of compounds in nanoporous systems.

C_{60} family and related lattices

Diudea M.V.

Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, Arany Janos Str. 11, 400028, Cluj, Romania, diudea@chem.ubbcluj.ro

The fullerene C_{60} "Buckminsterfullerene" is basically *sumanenic*, with the empty π-electron faces being only pentagonal. Four series of cages, tessellated by sumanenic circulenes $S[n]=[n:(5,6)_{n/2}]$, were generated by sequences of map operations, and their topology is described in terms of Omega, Ring, and Flower counting polynomials. Among these cages, all showing only R[5] 2-factors, those designed on the dual pair Dodecahedron/ Icosahedron (see Figure) show a unique term Omega signature, thus being classified as the C_{60} series. C_{60} itself shows the unique signature and all the members of its family show large HOMO-LUMO gap values, larger than that of the cages belonging to the other three series herein discussed. Coverings are given in terms of circulene flowers.

Map operations extended to lattice enable the design of crystal-like structures. An Euler formula extended to multi-shell polyhedra was exemplified in case of C_{60}-related radially evolved lattices. Energetics of the discussed structures are also given.
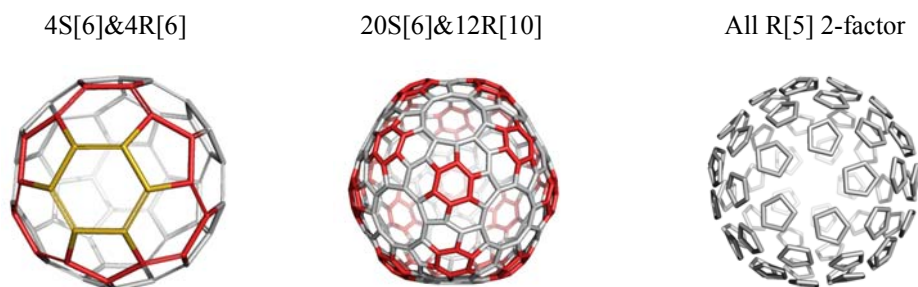
4S[6]&4R[6]   20S[6]&12R[10]   All R[5] 2-factor

Figure. Sumanenic S[6] pattern C_{60} and in 300*D/I*-5d cages; S-core in color.

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Visualisation of the cutting edge applied research in the field of fullerenes and nanotubes

Efremenkova V.M.*, Krukovskaya N.V.[+], Ustinova E.A.[+]

All-Russian Institute of Scientific and Technical Information, 125315 Moscow, Russia
[+]*Zelinsky Institute of Organic Chemistry RAS, 119991 Moscow, Russia*

We continued our scientometric studies in the field of fullerenes and nanotubes using STN International databases and AnaVist module. CAPlus (database produced by Chemical Abstracts Service) still exceeds in its publication coverage such rivals as SciSearch, INSPEC, COMPENDEX, SCOPUS and so on. The special attention was paid to the applied research, i.e. patents. Currently the total number of publication on fullerenes exceeds 40,000 patents being 15% of that number; the number of nanotube publications is about 67,000 of which patents constitute 17% according to data from CAPlus. The further analysis using AnaVist module allowed us to determine leading countries, institutions, researchers most active in the field, and to reveal the main directions of applied research.

Exponential magnetoresistance of carbon nanotube devices

Fedorov G.[1,2], Barbara Paola[2], Smirnov Dmitry[3], Jimenez David[4], Roche S.[5]

[1]Russian Research Centre "Kurchatov Institute", Russia
[2]Department of Physics, Georgetown University, Washington, DC, USA
[3]National High Magnetic Field Laboratory, Tallahassee, FL, USA
[4]Electronica, Escola Tecnica Superior d'enginyeria, UniVersitat Autonoma de Barcelona, Barcelona, Spain,
[5]Commissariat a l'energie Atomique, DSM/DRFMC/SPSMS/GT, Grenoble, France

The exceptional low-dimensionality and symmetry of carbon nanotubes (CNT) are at the origin of their spectacular physical properties governed by quantum effects. Ajiki and Ando [1] predicted that an axial magnetic field would tune the bandstructure of a CNT between a metal and a semiconductor. They predicted periodic dependence of the band gap on a magnetic flux threading the CNT crosssection with a period equal to the flux quantum. This effect arises from modulation of the Aharonov-Bohm phase of the electronic wavefunctions and peculiar topology of the graphene's Fermi surface.

Here we study magnetic field induced conversion of initially metallic carbon nanotube devices into CNT field effect transistors. Strong exponential magnetoresistance of our devices in the OFF state is observed up to room temperature. Data obtained with semiconducting CNT-based devices indicates positive exponential magnetoconductance.

By performing state of the art bandstructure calculations, that take into account high-order curvature effects, it was shown that magnetotransport of quasi-metallic CNTs is very sensitive to the CNT chirality [2]. That allows us to identify chirality of the quasi-metallic CNTs in our devices.

We also prove, both theoretically and experimentally, that the magnetic field controlled Schottky barriers significantly enhance the CNT magnetoconductance. Another important result is that band profile of the CNT can be evaluated via measurements of temperature evolution of the device magnetoresistance in the OFF state.

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Ion treatment of field emitters having fullerene coatings

Sominski G.G., Svetlov I.A., Tumareva T.A.

Saint-Petersburg State Polytechnical University, St.-Petersburg, Ruxssia

Field emitters with protective fullerene coatings were worked out and investigated by the authors [1,2]. Such emitters are prospective for electron devices operating under technical vacuum conditions. Since fullerene coatings possess high work function (more than 5 eV), it causes operating voltages increase. We found previously a possibility how to decrease the work function. It was achieved by activating the fullerene coatings by potassium ion flow [2].

Up to the moment, new data were obtained that optimize the conditions of the deposition and ion activation of the fullerene coatings. The best results on the activation were achieved upon treatment of fullerene coatings that had thickness of 2-5 monolayers and were deposited on the tungsten tip with a layer of tungsten carbide on its surface. The temperature of the tip was 500-600 K during the deposition. Optimal ions energy and dose of ions that must be fallen on the coating were accordingly 40-90 eV and $\sim 10^{15}$ ions$\cdot$cm^{-2}. As a result of such cycle of the deposition and treatment of the fullerene coating we achieved the reduction of the operating voltages. The voltages U_I corresponding to the fixed current I were reduced by a factor of 1.6-1.8. The triple repetition of this procedure (multistep treatment) allowed us to decrease U_I maximally up to 2-2,1 times.

The examination of emitters with fullerene coatings activated by potassium ion flow was performed at high emission currents. Extreme currents were determined for coatings that were formed as a result of single or triple cycles of the deposition and ion treatment. It was stated that the activation of fullerene coatings by slow ion flow (40-90 eV) decreased maximal currents in comparison with non-activated fullerene coatings. The maximal currents decrease was explained in view of the weakening of junction between the coating and the substrate after the ion treatment of the fullerene coating.

It was found a possibility to increase the maximal currents by preliminary treatment of the substrate by the flow of potassium ions with energy 1500-5000 eV. The rise of the maximal currents was reached in result of strengthening of a junction between the coating and the substrate. It was also revealed that the bombardment by such fast ions could be used for the treatment of the coating because it allowed to improve its uniformity.

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Simulation of adsorption of wet steams on a surface of non-metallic nanocrystals using cluster methods

Sajko D.S., <u>Ganzha V.V.</u>

Voronezh State Technological Academy, 394000 Voronezh, Russia

Nanoscale systems on the basis of semiconducting compounds often include thin films of corundum as a dielectric coat. During a manufacturing of such systems on a surface of these structures different gases, including wet steams, can be adsorbed.

In this work the simulation of the process of water adsorption on a surface of silicon, corundum, and apatite by cluster methods using "ab initio" and CNDO approaches are performed. Within a framework of cluster calculations the different values of the binding energy of the adsorbed molecules with a surface is obtained depending on an orientation of the surface. For finding the equilibrium bound state of water molecules on a crystal surface the Polak-Ribiere energy minimization algorithm is used. For the purposes of modeling of particular surface orientation the laminated clusters with the surfaces oriented according to the given crystal plane were created.

For checkout of the selected approach, the computer simulations were implemented. The adsorption of water molecules on (100) and (110) surfaces of silicon investigated. These results well agree with the earlier known data. Next, the simulations for corundum and apatite were applied. Because the last value agreed with the one that was obtained on a (100) surface, it allows us to make an assumption, that the results on other surfaces are reasonably justified.

For obtaining a general value of the binding energy of water molecule on a nanocrystal surface, we use the averaging of the energy value over all calculated surfaces.

Method developed in this work may be applied to the dielectric and semiconductor crystal grains.

Zone structure and chemical bonds of two-dimensional system MG/MnO(001): *Ab initio* study

Meschi B.Ch., Ryzkin A.A., <u>Ilyasov V.V.</u>[1], Nikiforov I.Ya.,
Ershov I.V., Velikochatzkii D.A.

Don State Technical University, Gagarin sq.1, 344000 Rostov-on-Don, Russia

One of the perspective directions in creation of devices for spintronics is connected with usage of carbon low-dimensional systems: graphene (MG) and carbon nanotubes (CNT's). Recently proposed method of plasma enhanced chemical vapor deposition (PECVD) [1] single layer and double layer graphene of high quality can be applied both in graphene nanoelectronics and to obtain of graphene layer on the surface of ferromagnetic materials such as dielectric oxides with low chemical activity. Such hypothetical materials based on thin ferromagnetic layer with graphite monolayer (MG), classified as two-dimensional structures 2D MG/MeO(100) (Me=3d metal) can be considered as a new direction to achieve new outstanding physico-chemical properties.

The oxide based structures because of their amazing electronic and magnetic properties always attracted the great attention. We have not come across the papers dealt with the electron structure and magnetic properties of a system alike to MG/MnO(100). Because of this it is of high interest to study the peculiarities of the band structure of such materials. In the present work the theoretical investigation of the electron structure and magnetic properties by *ab initio* calculations, which were carried out using the spin-polarized full potential method of pseudopotential with the program package Quantum Espresso. The results of the calculations showed that by the synthesis of system 2D MG/MnO(100) the reconstruction of the zone structure took place, that is responsible for the electromagnetic properties of this system. The valence band is formed mainly by 3d-electron states of Mn atom (with small admixture of O*2p*- and C*2p*-states) and is defined by hybridization of Mn*3d*-, O*2p*- and C*2p*-orbitals for both spin subsystems $N_\uparrow(E)$ и $N_\downarrow(E)$. The zone structure of MG/MnO(100) shows energy forbidden slits in electron state energy (DOS) distributions for both spin subsystems under consideration. For the system MG/MnO(100) the partial charges of valence electrons at atoms are found as well as integral spin magnetic moments at every atom. The effective charges Q_{eff} at every atom were estimated, that gave us possibility to calculate the charge transfer to bond Mn-O which were about 0.46e. Our calculations showed that in 2D MG/MnO(100) except the magnetic moment at the ion Mn^{+2} there were rather small spin magnetic moments at the atoms of carbon and oxygen. The peculiarities of interatomic interactions in the system 2D MG/MnO(100) were studied at the maps of the full electronic density (ED). The difference in the localization of ED along the bond line Mn-O determined by the interaction of magnetic atom Mn with C-atoms, that showed the formation of hybridized Mn3d- 2C2p-states of ionic bonds.

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Dependence between the frequency factor of fullerene C_{20} thermal decay and buffer gas pressure

Katin K.P., Podlivaev A.I.

Moscow Engineering Physics Institute,115409 Moscow, Russia

Lifetime of the single fullerene in the buffer gas is depended on system's temperature. This dependence is described via Arrhenius equation [1], $t=A^{-1}\exp(-E_a/kT)$, where E_a is an activation energy, A is a frequency factor, T is temperature and k is the Boltzmann's constant. In order to define parameters A and E_a, one must calculate lifetimes, which correspond to a wide range of temperatures. Due to lifetime increases with temperature reduction exponentially, to derive this time under low temperatures is problematically.

Recently was presented very efficient new algorithm for computing fullerene's C_{20} decay [2]. Usual molecular dynamics method allows to compute the fullerene during a few microseconds. Using new hybrid molecular dynamics Monte-Carlo algorithm, it stays possible to watch fullerene's live as long as one second.

The absence of new algorithm is that it converges correctly if only the buffer gas pressure is near 10^{10} Pa, and the real experimental pressure is near 10^4 Pa [3]. The problem is that the frequency factor *A* is depended on the pressure, hence, one can not derive it value using this algorithm. This is why the dependence under consideration attracts our interest.

In order to define this dependence, we have calculated lifetimes of the fullerene under exact temperature 4000K. Thermostat's influence was simulated by seldom impacts between gas molecules and carbon atoms. Potential [4], which takes into account quantum effects, was used.

We have found linear dependence between reciprocal frequency factor A^{-1} and impact's frequency with buffer gas atoms w under pressure $10\text{-}10^{11}$ Pa: $A^{-1}=aw+b$, where $a=(3.1 \pm 0.2)\cdot10^{-19}\text{sec}^2$ and $b=(3.6 \pm 0.2)\cdot10^{-18}$ sec. It means that the algorithm discussed above can be applied as extrapolational to the freuquancy factor definition under realistic pressure.

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Nanotube analysis with the desktop educational and research nanotechnological complex

Komarov I.A.

Moscow Institute of Electronic Technology (Technical University), 124498. Zelenograd, Russia

One of the main last years' trend of the world science in the sphere of nanotechnology is the developing and application of complex techniques in nanoscale object creation and visualization. The problem of nanotube integration in conventional microelectronic processes is also complex.

The main goal was to develop a method to improve nanotube integration and positioning in the task of their visualization with scanning probe microscope and routine nanoelectronic device development.

Several different ways such as nanotube deposition from the solution with an electrophoresis method, local catalyst deposition with the Kelvin probe method characterization and nanotube growth on thin film catalysts, were used to reach our aim. Such carbon nanotube features as bad adhesion to silicon dioxide substrate, substrate pollution with some impurities caused by our nanotube growth process (CVD) were revealed. Also localization of carbon nanotubes as a method to improve their visualization was studied.

A recently developed nanotechnological complex was used to implement our methods. The nanotechnological complex consists of nanotube growth system "CVDomna", scanning probe microscope, multifunctional probe system and semiconductor parameters analyzer.

It was shown that main techniques to improve nanotubes positioning are:
- Atmospheric annealing at the temperature about 450-500°C (The main goal is to remove impurities from the substrate)
- Electrophoresis as a technique to increase nanotube number on the unit of area.
- Local nanotube growth in the defined areas of the substrate as a method to improve adhesion and to remove impurities.

To improve catalyst visualization it is important to use small concentration of sol-gel catalyst. Besides it is necessary to use thermal treatment.

As a result deposition and nanotube growth methods were developed to reach our aim of nanotubes integration and positioning improvement.

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Structure of modified polysiloxan block–copolymers in neutron scattering

Voznyakovsky A.P.[3], Kudoyarova V.Kh.[1], <u>Kudoyarov M.F.</u>[1], Lebedev V.M.[2], Lebedev V.T.[2]

[1]*Ioffe Physical-Technical Institute RAS, 194021 St.-Petersburg, Russia*
[2]*Petersburg Nuclear Physics Institute RAS, 188300 Gatchina, Russia*
[3]*Lebedev Research Institute of Synthetic Rubber, 198035 St.-Petersburg, Russia*

One of the track membrane surface modification methods is covering of its surface by ultra thin polymer films. This film preserves the selective properties of track membranes, but change its surface properties. It is perspective to apply the polymer (siloxan) layer with admixture of fullerens C_{60} as these ultra thin films. The technology of preparation thin siloxan layer with different adding of fullerens has been developed.

In this investigation as extension of [1,2] we study the structure of these layers by small angle neutron scattering method [3].

The main results are in following:

1) The scattering structure lattice with range of ~5 nm, ~35 nm and ~60 nm are observed in semi diameter interval up to 70 nm;

2) The structure lattices with range of~60 nm are absent in polymer films without fullerens;

3) The structure lattices with range of~60 nm are observed only in films with fullerens, where the part of these structures are increase with fulleren concentration increasing.

It is following from these results that the main part of modificating fullerens formed well-organized cluster structures due to self-organization processes. It's needed to note that observed structures are placed in films not isolated. They can combined in more complex structures. The structures with maximum radius may consist of more small formations, observed in neutron experiment. It may be the structures containing the basic polymer systems.

It is possible to suggest, that supramolecular features of initial block–copolymers are very important in claster C_{60} formation.

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Superconductivity of fullerides $A_nHg_xC_{60}$ (A = K, Rb; n = 2, 3) synthesised from amalgams

Kulbachinskii V.A., Bulychev B.M., Lunin R.A., Kytin V.G.

Lomonosov Moscow State University, 119991 GSP-1, Leninskie gory, Moscow, Russia

The investigated fullerides $A_nHg_xC_{60}$ (A=K,Rb; n=2,3) have been synthesised by a new method using liquid alloys of metals with mercury (amalgams). The mercury which is not self-intercalated metal, may intercalate into fullerite together with self-intercalated alkaline metals. Temperature dependence of magnetic susceptibility of the fullerides was measured to get temperature T_c of superconducting transition [1].

It was found that the fulleride $K_2Hg_xC_{60}$ (where x>10) is superconductor with transition temperature T_c=20K that exceed transition temperature in K_3C_{60} (T_c=19K). According to diffractometry data the fulleride $K_2Hg_xC_{60}$ crystallizes in fcc lattice with parameter a=1.4279(3) nm. The fulleride $K_3Hg_xC_{60}$ is not superconductor and has monoclinic crystal lattice with tetragonal supercell (a=1.650 nm; b=1.080 nm; c=1.041 nm). These data shows that mercury was intercalated in fulleride lattice and even changed lattice parameters.

According to experimental data the fulleride $Rb_3Hg_xC_{60}$ is superconductor with T_c=25K and crystallizes in fcc lattice with a=1.4448(1) nm. By diffractometry data the samples with composition $Rb_2Hg_zC_{60}$ (z=6-12) or $Rb_3Hg_xC_{60}$ with x>>10 consist of two phases: $Rb_{2.92}C_{60}$ (fcc lattice) and $Rb_{0.91}C_{60}$ (orthorhombic lattice). The *fcc* phase has parameters slightly different from a=1.442 nm to a=1.446 nm depending on composition. Parametres of orthorhombic phase remain unchanged: a=0.9138 nm, b=1.0107 nm, c=1.4233 nm. The T_c for these samples varied from 19.5K to 25.5K. This value is less than T_c=28K for Rb_3C_{60}. Such relatevely low value of T_c may be because of intercalation of mercury in fulleride lattice and a deviation of a charging state of molecule C_{60} from –3. Thus, presence of mercury at initial materials considerably influences temperature of superconducting transition.

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Single and double bonding in polymerized weakly hydrogenated fullerenes

Makarova T.L.[1,2], Kvyatkovskii O.E.[2], Zakharova I.B.[3], Buga S.G.[4], Volkov A.P.[4], Shelankov A.L.[1,2]

[1]*Umeå University, 90187 Umeå, Sweden*
[2]*Ioffe Physicotechnical Inst.,194021, St. Petersburg, Russia*
[3]*St. Petersburg State Polytechnical University, 195251 St. Petersburg, Russia*
[4]*Technological Institute for Superhard and Novel Carbon Materials, 142190, Troitsk, Russia*

We are presenting the results of our recent research into the magnetic properties of C_{60} fullerenes. We have come across a novel phenomenon: weakly hydrogenated fullerenes, prepared at predetermined synthesis conditions, form a magnetically ordered state after the laser treatment. The main points of our research are the following.

We have shown theoretically that $C_{60}H$ molecule can be prepared when the fullerenes are treated with monoatomic hydrogen. We predicted relative stability of this molecule and calculated the Raman spectra for its identification.

We used hydrogen plasma discharge to produce a film containing a certain amount of $C_{60}H$ molecules, along with inevitable amount of $C_{60}H_2$ and unreacted C_{60}.

We have shown theoretically that $C_{60}H$ molecule is paramagnetic and its spin equals nearly ½. We have predicted magnetic ordering in this phase provided the $C_{60}H$ fullerenes are polymerized.

We used different kinds of laser treatment for both polymerization and depolymerization and recorded magnetic properties simultaneously with the structural changes. The phase where fullerenes are connected with double bonds shows hysteresis loops typical for ferromagnets whereas the single bonded polymers are diamagnetic.

The essential point is to determine that the observed weak ferromagnetism is an intrinsic effect and not of some extrinsic origin. Along with thorough impurity analysis, we present a qualitative effect: The magnetic properties appear after a certain laser treatment and disappear after the laser treatment of another kind, thus laser turns magnetism on/off.

We show both experimentally and theoretically that magnetic properties are determined by the type of bonding between polymerized fullerenes. For doubly bonded odd-hydrogenated fullerenes the ground state is triplet whereas single bonded dimers are diamagnetic.

Numerical simulation of hydrocarbon cubane-based nanostructures

Maslov M.M.

Moscow Engineering Physics Institute (State University), 115409 Moscow, Russia

Highly strained cubane-based hydrocarbons attract fundamental and practical interest. They have been considered as candidates for novel high-energy materials. They can also be used as building blocks for rigid liquid-crystal compounds, in pharmaceutics, etc. Here, we report numerical calculations of the cubane C_8H_8, methylcubane C_9H_{10} and various cubane derivatives with the original developed nonorthogonal tight-binding potential [1].

We have carried out the detailed investigations of the channels and final products of cubane and methylcubane decomposition making use of the molecular dynamics simulations [2, 3]. The obtained results allow to suggest the direction of search for new ways of synthesis of cubane and methylcubane (for example, the inversion of the direction of the chemical reaction by means of the corresponding catalysts lowering the barrier of counterreaction).

Direct calculations of the cubane and methylcubane lifetimes τ at different temperatures T allowed us to find the values of the activation energy E_a and the frequency factor A in the Arrhenius equation $\tau(T) = A^{-1}\exp(E_a/k_BT)$, where k_B is the Boltzmann constant. For the cubane these values are $E_a = (1.9 \pm 0.1)$ eV and $A = 10^{16.03\pm0.36}$ s^{-1}, and for the methylcubane they are $E_a = (1.7 \pm 0.2)$ eV and $A = 10^{15.63\pm0.53}$ s^{-1}. The dependence of $\tau(T)$ is vitally needed for optimization of the synthesis conditions for these clusters and the structures derived from them.

The binding energies of the cubane-based nanostructures are 4.58; 4.89; 8.62 eV/cluster, and the intercluster bond lengths are 1.454; 1.458; 1.456 Å for linear chains, zig-zag chains, and two-dimensional networks, respectively. We find that supercubane is not a "superdense" polymorph as was expected earlier. Its density $\rho = 2.7$ g/cm^3 is less than in diamond. The intermolecular bond in the supercubane structure equals to 1.460 Å.

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Electrodynamic properties of nanocarbon-epoxy composites

Matzuy L.*, Vovchenko L.*, Prylutskyy Yu.*, Oliynyk V.*,
Launetz V.*, Eklund P.[+]

Kiev National Shevchenko University, Faculty of Physics and Radiophysics, Vladimirskaya Str. 64, 01601 Kiev, Ukraine
[+]*Pennsylvania State University, 104 Davey Laboratory, PMB 157, University Park, PA 16802-6300, USA*

We present the results of investigation of the electrical resistivity and electromagnetic radiation (EMR) shielding (frequency range of (25.5-75) GHz) of composite materials (CM) based on epoxy resin (ED20) and different forms of nanocarbon: multi-walled carbon nanotubes (MWCNT), nanographite and thermoexfoliated graphite (TEG) (content of filler was (0.5-10) wt.%).

TEG has been obtained by using more than once thermochemical treatment of initial graphite. Nanographite has been prepared by ultrasonic sonication of TEG in acetone during 40 h. The influence of structure and morphology of the nanocarbon fillers as well as their concentration on the electromagnetic shielding efficiency, namely, EMR transmission coefficient α^{tr} and dielectric coefficients ε', ε'' and $tg\delta$ were established.

It was shown that even at low TEG or MWCNT content in CM the efficiency of electromagnetic shielding is high: EMR transmission coefficient increases from 10 dB/mm for 0.5 wt.% to (20-27) dB/mm at 2.0 wt.% of nanocarbon and it is sufficiently higher in comparison with nanographite-epoxy CM. This difference can be explained by the significantly low electrical resistivity of TEG- or MWCNT-epoxy CM as compared with nanographite-epoxy CM. The real part of permittivity increases from 4.4 to 53 and from 2 to 10 with increase of nanocaron content in epoxy CM from 1 to 10 wt.% for TEG or MWCNT fillers, respectively. Also it was found that electromagnetic shielding efficiency slightly increases at increasing of EMR frequency.

Magnetic ordering in abruptly compressed FCC fullerite

Moliver S.S.

State University, 432970 Ulyanovsk, Russia

The nature of magnetic ordering in carbon materials stays an unresolved problem of experimental, theoretical, and simulation research, e.g. [1,2]. Dealing with electron structure calculations of fullerite and graphite, we verified an idea, that high-symmetry chemical bonds organization provides metallic electron configuration, where spin-triplet correlation may bring energy gain. Open-shell quantum chemistry method with the quasi-molecular model of large unit cell has given evidence for insulator-metal transition in compressed fullerite [3]. The transition is thought to be a result of an abrupt uniform compression, that is faster than atomic movements performing low-dimensional topochemical polymerization, and leads to tetrahedral (T_h) FCC-close-packed fullerite with the lattice-parameter value about 80% of pristine one. Fullerene's cage distortion in compressed FCC structure was allowed, which does not break the tetrahedral symmetry and the equivalence of the adjacent-fullerene contacts [r_5+r_5]. Self-consistent total energies of configurations t^6 (closed-shell insulator model), and t^4, t^2 (open-shell-multiplet metal model) were calculated independently.

The search of atomic displacements, bringing minimum to the ground many-electron term, in such a complicated case, as fullerite, demands to analyse the picture of chemical bonds, arising and changing during the search itself. Recent studies [2] confirm this difficulty once more. Thus, we have done a detailed examination of the previously found metal state [3]. The variable manifold was limited to the FCC parameter, 3 breathing relaxations, and 3 pentagon-distorting displacements. Everywhere t^4 configuration was a ground one, and everywhere its spin-triplet term ^3T was about 0.12÷0.15 eV lower than spin-singlet ^1T one. Therefore, if some abrupt compression of fullerite can bypass topochemical high-pressure polymerization (maybe inhomogeneously), the conducting FCC phase becomes possible as one of «3D polymer states» [2]. Spin-triplet ordering in this phase is predicted by quantum chemistry, which cannot solve, whether this ordering is ferro- or antiferromagnetic.

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Investigations of single-walled carbon nanotube formation mechanism

Nasibulin A.G.[1], Anisimov A.S.[1], Jiang H.[1], Shandakov S.D.[1], Launois P.[2], Cambedouzou J.[2], Kauppinen E.I.[1,3]

[1]*NanoMaterials Group, Center for New Materials and Laboratory of Physics, Helsinki University of Technology, Finland;*
[2]*Laboratoire de Physique des Solides, UMR CNRS 8502, Université Paris-Sud 11, 91405 Orsay, France*
3VTT Biotechnology, Finland

Many applications of carbon nanotubes (CNTs) strongly depend on the ability to synthesize coherent and defect-free nanotubes with controlled diameter, length and wall structure. The development of production methods for CNT synthesis with specific qualities requires detail understanding of the mechanisms of CNT formation.

In this paper we carried out investigations of single-walled carbon nanotube (SWCNT) growth in a laminar flow aerosol (floating catalyst) reactor [1, 2]. The SWCNTs were synthesized by the carbon monoxide disproportionation reaction on Fe catalyst particles formed by ferrocene vapor decomposition. On the basis of *in situ* sampling of the product collected at different locations in the reactor, catalyst particle crystallinity, the kinetic process of the SWCNT growth and reasons for the SWCNT growth termination were studied. Catalyst particles captured before SWCNT nucleation as well as inactive particles were determined to have the cementite (Fe_3C) phase, while particles with pure γ- and α-Fe phases were found to be embedded in the SCWNTs. The growth rate in the temperature range of 804 to 915°C varied from 0.67 to 2.7 μm/s. The growth rate constant can be described by an Arrhenius dependence of $k = k_o \exp\left(-E_a/RT\right)$ with an activation energy of $E_a = 1.39$ eV. CNT growth termination was explained by phase transition from α-Fe to γ-Fe phase in the catalyst particles. A high temperature gradient during the SWCNT growth was found to not have any effect on the diameter and as a result on the chirality of the SWCNTs.

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Capillary introduction of elementary fluorine and oxygen into single-walled carbon nanotube: semi-empirical research

<u>Prokofyeva E.V.</u>, Zaporotskova I.V.

Volgograd State University, 400062 Volgograd, Russia

Saturation of the internal cavity in single-walled carbon nanotubes with various chemical elements is promising for creating new composites with unique and valuable properties. Therefore, research of these filled composite nanotubulenes, including gas-fased ones, is rather urgent. As experiments have demonstrated open-bordered nanotubes possess capillary properties [1].

Molecular clusters of carbon nanotubes of (n, n) and $(n, 0)$ types ($n = 6, 8$) have been considered. Fluorine F and oxygen O atoms were introduced into the cavity of the tubes through its open border. The experiment was conducted by applying the quantum-chemical semi-empirical calculation schemes MNDO and MNDO/PM3.

The introduction of atoms F and O into the tubulene cavity was simulated by their step-by-step movement towards the nanotube along its main longitudinal axis and permeation into its cavity through the border. The surface profiles of potential energy have been calculated. The analysis of the results has revealed that the permeation of an oxygen atom into the tubulene $(6, 0)$ does not occur, and intensive capillary suction takes place in tube $(6,6)$, with the formed compound being stable. The atom F does not permeate tubulene $(6, 0)$, and it permutes into the cavity of $(6, 6)$ uninhibitedly. The introduction of atoms O and F into $(8, 0)$ tubes is possible, but the systems formed are metastable, the process of capillary introduction of these atoms into tubes $(8, 8)$ is uninhibited, intensive and stable. The length of the nanotube has no impact on the permeation process.

Stabilization iron nanoparticles for magnetic fluids

Rodin V.M.*, Emelianov G.A.*, Vozniakovskii A.P.*,
Udin V.E.[+]

FSUE S.V. Lebedev Rubber Research Institute, 198035 St.-Petersburg, Russia
[+]*Institute of MacromolecularCompounds RAS, 199004 St.-Petersburg, Russia*

Magnetic fluids are used in various technologies. Stability of dispertions of ferromagnetic nanoparticles in fluids can be advanced while using surfactants. Surfactants generate protective shell and prevent coalescence of particles. We have developed and tested the method for stabilization Fe nanoparticles by fluoro-organic radicals (R_f). The principal idea consists in stabilization of metal nanoparticles by means of formation of stable Fe-S-R_f bond system. Consequently, monomolecular fluoro-organic layer is formed on iron's surface. It generates additional interface interaction between iron nanoparticles with polymer matrix and promotes uniform distribution. It is shown that sinters are destroing in process of stabilization. Magnetic fluids on basis of low-molecular silicone and modified iron nanoparticles show high viscosity increment in magnetic field. It is noted that nature of R_f occurs an influence on fluid rheology.

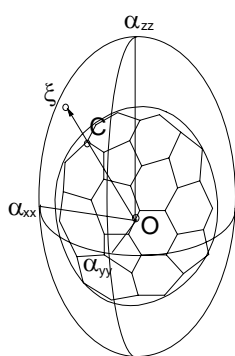# Fullerenes reactivity in terms of local curvature and polarizability

Sabirov D.Sh.[*+], Bulgakov R.G.[*], Khursan S.L.[+‡]

[*]*Institute of Petrochemistry and Catalysis RAS, Ufa, Russia*
[+]*Bashkir State University, Ufa, Russia*
[‡] *Institute of Organic Chemistry, USC RAS, Ufa, Russia*

Reactivity of C_{20}, C_{36}, C_{76} and other fullerenes discovered recently in contrast to well-studied C_{60} and C_{70} has been poorly understood due to their low availability. So, theoretical methods of studying the reactivity become expedient. Earlier different indices have been used to estimate fullerenes reactivity. Those limited predictive possibility makes working out of new theoretical methods expedient.

In the present study indices of local curvature k and polarizability-in-direction ξ have been used to measure reactivity of fullerenes in the different reactions of addition:

$$k = 2\sin \theta / a, \qquad\qquad \xi = f(\psi, \varphi),$$

where a – average internuclear distance between reaction site of the fullerene molecule and its neighboring atoms, θ – pyramidalization angle, ψ and φ – directive angles when molecule of a fullerene and ellipsoid of its polarizability are described jointly in the polar coordinates. So, fullerene molecule is approximated with ellipsoid circumscribed around fullerene skeleton in the case of calculation of k values and with ellipsoid of polarizability in the case of calculation of ξ. Geometries of reactants, tensors of polarizability and heats of reactions have been calculated by PBE/3z method.

Heat effects of addition of various reactants (*e.g.*, O_3, H•, F•, CH_2N_2) to fullerenes are in linear dependence on k values. The increase of local curvature nearby reaction center leads to increase of heat effect of addition. Values k are suitable for general correlation which allows to describe fullerene molecules of different structure in common. Fullerenes reactivity in terms of ξ indices are in accordance with curvature estimations. The increase of polarizability-in-direction indices of reaction center is accompanying with the increase of heat effect of addition. Use of criterion $\xi > \alpha_{av}$ (average polarizability) for 6.6 bonds of higher fullerenes allows to elect the most reactive bonds toward various reactants. Those bonds are located in on tops of fullerene molecules. Performed theoretical estimations are in accordance with experimental data. Curvature and polarizability approaches to estimation of fullerenes reactivity extrapolated to some fullerene derivatives also show good agreement with experimental data.

Broken spin-symmetry HF and DFT approaches. A comparative analysis for nanocarbons

Sheka E.F.

Peoples' Friendship University of the Russian Federation, 117923 Moscow, Russia

The quantum-chemical approach generalization for systems with weakly interacting electrons ultimately requires taking into account the electrons correlation and passing to computational schemes that involve full configurational interaction (CI). However, the traditional complete-active-space-self-consistent-field (CASSCF) methods that deal correctly with two electron systems of diradicals and some dinuclear magnetic complexes, cannot handle systems with a large number of the electrons due to a huge number of configurations generated in the active space of the system so that for m singly occupied orbitals on each of n identical centers 2^{mn} Slater determinants should be formed by assigning spins up or down to each of the nm orbitals [1]. It has been accepted until recently, that CASSCF type approaches are non-feasible for many-odd electron systems such as fullerenes, CNTs, and graphene. Thus, addressing single-determinant approaches appeared to be the only alternative.

The open-shell unrestricted broken spin-symmetry (UBS) approach suggested by Noodleman [2] is well elaborated for both wave-function and electron-density QCh methodologies, based on unrestricted single-determinant Hartree-Fock scheme [3] (UBD HF) and the Kohn-Sham single Slater determinant procedure DFT (UBS DFT) [4]. The UBS approach main problem concerns spin-contamination of the calculation results. The interpretation of UBS results in view of their relevance to physical and chemical reality consists in mapping between the eigenvalues and eigenfunctions of exact and model spin Hamiltonians. While the implementation of UBS HF approach, both *ab initio* and semiempirical, is quite standard and the wished mapping is quite straightforward, this is not the case of the UBS DFT due to the problem with total spin. As known, DFT cannot be directly applied to calculation of the spin and space multiplet structure and a number of special procedures, that all are beyond the pure DFT scope [7], are suggested to overcome the difficulty. The procedures differ by computation schemes as well as by obtained results so that UBS DFT is theory-level-dependent [5, 6].

The paper presents a comparative analysis of the UBS HF and UBS DFT calculations results related to fullerenes, carbon nanotubes, and graphene. A comparison of the results to findings obtained with the application of many-body CI schemes [7, 8] highlights the UBS HF high ability to quantitatively describe practically important consequences of weak interaction between odd electrons of the studied nanocarbons.

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Mass transfer in the metal-fullerene structures

Shpilevsky E.M.

Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, Minsk, ul. P. Brovki, 15, Belarus

Nanostructured materials are characterized by significantly developed and extended grain boundaries. Surface layer contains approximately 50% atoms if the width of grain boundary is δ=0.5-1.5 nm and an average grain size is d = 10-20 nm. Interface contains from 50 to 10% of substance in nanostructured materials with the grain size from 10 to 100 nm. Mass transfer in such structures has a number of peculiarities.

Solution of diffusion task for nanostructured films revealed a possibility of Kirkendall size effect, i.e. shift of original boundary for materials of different degree of dispersion (even if they have equal diffusivity coefficient values).

Surface migration of atoms and molecules is influenced by the surface energy gradient. In some particular cases we managed to divide diffusion and force (drift) constituents of mass transfer.

In nanostructures phase formation can occur, and these phases are not common for the systems of massive state. Metastable phases in ultradisperse structures were observed in number of systems before [1]. Formation of phases $Cu_{60}C_{60}$, Sn_xC_{60}, $Ti_xO_yC_{60}$ in thin film structures was established by us though these metals do not interact with corpuscular carbon.

In metal-fullerite structures joint (cluster) migration mechanism can occur. Volume of C_{60} molecule is 14-16 times more than that of metal atom. Metal clusters can be placed in fullerite vacancies, in addition octahedron and tetrahedron pores dimensions in fullerite lattice are comparable to the metal atoms diameter, that is why metal atoms can be placed in these pores without deformation of original matrix C_{60}.

Mechanical strains that occur in thin metal-fullerenes films reinforce diffusion in process both of producing films and of annealing. Gap strains will most contribute to inner strains values at the interface of metal and fullerene, while metal lattice will stretch out and that of fullerites will shrink. Concentration strains connected with alien atoms are the critical parameters in monolayer films.

Anomalously high diffusivity coefficients of different impurities in crystals C_{60} are caused by large intermolecular space in these crystals that allows easy modification of fullerites properties by doping them by metal atoms.

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Field emitters on the base of nanocarbon composite materials

Sominski G.G.[1], Tumareva T.A. [1], Sezonov V.E.[1], Gordeev S.K.[2], Korchagina S.B.[2], Sakseev D.A.[3]

[1]*Saint-Petersburg State Polytechnical University, St.-Petersburg, Russia*
[2]*Central Research Institute of Materials, Russia*
[3]*Ioffe Physical-Technical Institute RAS, St.-Petersburg, Russia*

Composite materials may be interesting as promising sources of the field emission because they make possible the joining of small-structured materials having different nature. The aim of the present work is to define the influence of the close vicinity of materials that have the distinctive work function $e\varphi$ on the field emission. In view of this, a composite consisting of lanthanum hexaboride ($e\varphi \approx 2.8$ eV) granules in pyrographite ($e\varphi \approx 4.8$ eV) matrix was investigated. LaB_6 granules had an irregular form with typical dimensions that were not more than 40 μm. Pyrocarbon layers, which had thickness not exceeding over 100 nm, enveloped and connected these granules to each other. Analysis that was performed by means of Scanning electron microscope JEOL FESEM revealed an existence of the unordered nano- and microcluster structure that was distributed almost uniformly on the sample surface.

A field near the cathode surface was created by the positive voltage U on a transparent (~75%) grid. The distance d between the cathode and the grid was 2.5 mm. Electrons emitted from the cathode and passed through the grid bombarded a screen-anode and formed on it the picture that showed distribution of the electron flow from the cathode surface. The durable (~10 hours) "formation" of the cathode was made at the initial stage of experiments. That formation included heating of the cathode up to ~500-700°C and the current extraction at the voltages $U \leq 10$ kV. As a result, the cathode operation was stabilized and the field emission fluctuations were diminished. The field emission reached 50-70 μA at the anomalously small fields $E=U/d\sim 4\cdot 10^4$ V/cm. The measured emission could not be explained at such fields even taking into account the field enhancement near the surface protrusions. In this connection, it is necessary to search another reasons for such emission currents.

Abnormally low threshold of semiconductors field emission was explained [1] by the strong field origin at the deep traps and various defects near the surface of these materials. But the investigated composite cathodes were made from the materials with good conductivity. In view of this, besides mentioned above mechanism (and probably, in the main), the emission was secured by those parts of the cathode surface where electron could exit in vacuum from contacts between pyrocarbon and LaB_6. The fields of the contact region could be estimated as $\Delta U/\Delta l$, where $\Delta U \approx 2$ V is the contact potential difference that is equal to work function difference of pyrographyte and LaB_6, and Δl is the distance between these material boundaries near the surface. At $\Delta l \leq 1$ nm, the fields of such spots may be $\geq 2\cdot 10^7$ V/cm that is enough for obtaining measured currents.

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Expansion of graphite oxide lattice due to high pressure induced water insertion

Talyzin A.V.[1], Solozhenko V.L.[2], Kurakevych O.O.[2], Szabo T.[3], Dékány I.[3], Kurnosov A., Dmitriev V.[5]

[1]*Department of Physics, Umee University, SE-901 87 Umee, Sweden*
[2]*LPMTM-CNRS, Universitŭ Paris-Nord 93430 Villetaneuse, France*
[3]*Department of Colloid Chemistry and Nanostructured Materials,University of Szeged H-6720 Szeged, Hungary*
[4]*Bayerisches Geoinstitut, Universitòt Bayreuth D-95440 Bayreuth, Germany*
[5]*SNBL, European Synchrotron Radiation Facility, 38043 Grenoble, France*

Expansion of structure upon compression is a rare phenomenon that has been observed in composite systems due to incorporation of liquid pressure transmitting media into nanopores. A new type of anomalous pressure dependence of the unit cell volume is found for graphite oxide. The interlayer spacing of graphite oxide pressurized in the presence of water continuously increases by an extraordinary ~28-30% with a sharp maximum at ~ 1.3-1.5 GPa [1]. The increase of unit sell volume upon pressure increase is explained by incorporation of water into the interlayer space of the graphite oxide structure. The change from "negative" to positive compressibility at ~1.4-1.5 GPa coincides with the solidification of liquid water into ice VI. At the same moment, the buckled graphene layers are stretched and slightly expanded laterally. The maximum of interlayer spacing was also observed during decompression at the point of ice melting.

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Scientometric indicators for evaluating the carbon nanotechnology development

Terekhov A.I.

Central Economics and Mathematics Institute RAS, Moscow, Russia

Nanomaterials are the weighty part of nanotechnology (NT) and carbon nanomaterials are so important for it, as silicon is for electronics. In E. Osawa opinion, if fullerenes could not be discovered in 1985 and carbon nanotubes (CNT`s) in 1991, coming of NT could be postponed for a few decays. The impact of these discoveries was so big that fullerenes and nanotubes continue to occupy high positions in international research arena. The discovery of graphene in 2004 made the positions even more strong.

Search and practical use of the new forms of carbon are one of the milestones in the history of NT development in Russia. Home scientists have a number of achievements on this way, but only the access to the world information resource (SCISEARCH, SCOPUS, US PTO and WIPO databases, etc) and forming the national databases (e.g. databases of VINITI, RFBR, ROSPATENT) allow to assess their efforts and research output on the systematic basis. SCI database is the number one for scientometric analyses. Preliminary analysis of statistics, extracted from it, revealed some trends, in particular:

■ shift of the world research community interests from fullerenes to CNT`s since 2001, accompanied by rearrangements in the group of leading countries. Swift progress made by Chinese scientists in this field;

■ sharp increasing the world summary flow of publications on graphene, attracting significant attention among NT researchers by its unique mechanical, electrical and optical properties;

■ Russia keeps the fourth place on the publishing activity in the field of fullerenes, but has gone down on the tenth place in the field of nanotubes by 2005 and further still lower. Nevertheless Russian papers on nanotubes are cited in average more frequently than ones in such disciplines as physics and chemistry. Our scientists are coauthors of high cited papers on fullerenes, CNT`s, and graphene.

In-depth analysis with RFBR, USA NSF and patent databases enabled: i) to analyze and compare the structure of the project research on nanomaterials, granted by RFBR and USA NSF; ii) to provide some characteristics of infrastructure ensuring the basic research in the field of carbon nanomaterials in Russia (institutions, research community, etc); iii) to count and analyze the patent statistics as more indicative of commercialization potential; iv) to identify connections of input financial indicators with output scientometric ones.

Solar fullerenes and carbon nanotubes

Udovyk O.O.

Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Krzhizhanovsky St., 03142 Kyiv, Ukraine

Fullerenes and carbon nanotubes have become a major field in condensed matter physics and chemistry. However, the large-scale production of these materials with high yield and selectivity is still a crucial problem. Conventional methods for the synthesis of fullerenes, such as electric arc discharge and laser ablation, fail when the process is being scaled up to higher power levels.

The solar vaporization process seems to be more promising using the solar reactor, in which a graphite rod contained under vacuum pressure behind a hemispherical quartz window is directly irradiated with peak solar concentration ratios exceeding 7000 suns and the vaporized carbon (at temperatures above 3300K) is swept out by Ar, quenched, and collected in a filter bag. The key parameters characterizing this process are the carbon soot mass flow rate and the desired product yield. The former is a function of the target temperature, whereas the latter is a function of specific reactor variables such as fluid flow patterns, residence times, and concentration of the carbon vapor in the carrier gas, target temperature, and temperature distribution in the cooling zone.

Catalytic filamentous carbon (CFC) can be produced by the solar thermal decomposition of hydrocarbons in the presence of small metal catalyst particles. Solar furnace experiments confirmed that nanotubes can be obtained using Co/MgO catalyst for CO and CH_4H_2 and those nanofibers can be obtained on Ni/Al_2O_3 catalyst for CO, CH_4, CH_4H_2, and C_4H_{10}. A solar chemical reactor, used for such experimental runs, consists of a quartz tube containing a fluidized bed of catalyst and Al_2O_3 grains. A secondary reflector, composed of a two-dimensional CPC coupled to an involute, provides uniform irradiation on the tubular reactor. CFC formed typically has the following properties: surface area 100 to $170 m^2/g$, pore volume 0.4 to 0.8 cm^3/g, micropore volume 0.004 to 0.008 cm^3/g, and average pore diameter 10 to 40 nm.

New data on compressibility of molecular fullerites C_{60} and C_{70}

Yagafarov O.F., Gromnitskaya E.L., Lyapin A.G., Brazhkin V.V., Kondrin M.V., Bogdan A.V.

Institute for High Pressure Physics RAS, 142190 Troitsk, Russia

Physical properties of the most stable quasi-spherical fullerites C_{60} and C_{70} are the subjects of much study. However there is no yet the complete view on behavior of their elastic properties under pressure: the data on elastic properties under pressure is scanty or contradictory. Here we present improved ultrasonic study of elastic moduli of polycrystalline fullerites C_{60} and C_{70} in the temperature range 77–340 K at pressures up to 2.5 GPa. Elastic properties of C_{60} and C_{70} at normal conditions were accurately measured using an ultrasonic piezometer [1]. The ultrasonic wave travel time and sample length in isothermal experiments were measured on compression and in isobaric experiments on heating (≈1 K/min). The anomalies in dependencies of elastic characteristics were identified as phase transition points.

Analysis of values of bulk and share moduli, theirs derivatives and their relation reveals in C_{60} significant increase of the non-central forces negative contribution to the shear modulus under pressure. This negative non-central contribution is associated with mutual intramolecular deformations due to molecular interactions as non-point objects.

The independent measurements of the density allowed the comparison of adiabatic and isothermal moduli. Bulk modulus can be calculated using two different methods: by differentiating equation of state (isothermal B_T), and using sonic wave velocities and density (adiabatic B_S). For fcc phase of C_{60} the B_S and B_T values are in accordance with each other, and both moduli have a high pressure derivative (~20). Comparison of B_S and B_T for sc and glassy phases of C_{60} gives outstanding results. Behaviour of B_S and B_T dependencies under pressure differ appreciably, although the difference calculated from the empirical intermolecular central potential is less than 1 % [2]. Dependence $B_T(p)$ is in good agreement with data of previous studies [3,4], while pressure derivative B_S corresponds to the calculation based on the empirical potential [2]. The nature of this difference is discussed and molecular deformations considered as the possible reason for such behaviour of bulk moduli dependencies.

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Magnetization training effect in fullerene-containing single molecular magnet

Zagainova V.S.[1], Makarova T.L.[1,2], Spitsina N.G.[3], Yagubskii E.B.[3]

[1]Umea University, Department of Experimental Physics, 90187 Umeå, Sweden
[2] Ioffe PTI RAS, 194021 St. Petersburg, Russia
[3]Institute of Problems of Chemical Physics RAS, 142432 Chernogolovka, Moscow Region, Russia

The family of manganese-based single molecular magnets (SMMs) is the best known and characterized by the highest blocking temperatures. For this reason, the development of new Mn_{12}-based magnets, i. e. chemical design and synthesis, and experimental studies of the received samples, is necessary for drawing regularities and better understanding of SMM phenomenon.

The preparation and physical characterization are reported for the $Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4$ where $R = C_6H_5$ ($Mn_{12}Bz$); C_6F_5 ($Mn_{12}F_5$), and 1:1 complexes $Mn_{12}F5C_{60}$ (**1**). $Mn_{12}BzC_{60}$ (**2**). We present a comparison of magnetic properties of $Mn_{12}Bz$, $Mn_{12}F_5$ and their molecular complexes containing $[C_{60}]$ fullerene. Our results confirm the idea that the ligand structure significantly influences the magnetic behaviour of Mn_{12}-based SSMs.

DC magnetic measurements were performed at a Quantum Design SQUID magnetometer (MPMS-XL-1) on microcrystalline powder samples. The dc magnetic susceptibility (χ_M) data were collected in the 1.76-300K range in a 0.01 T magnetic field. Complexation with fullerenes significantly reduces magnetization values for both (**1**) and (**2**) complexes. However, fullerenes cause qualitative changes in the QMT dynamics. While in $Mn_{12}Bz$ the QTs are absent and $Mn_{12}F_5$ demonstrates one QT at 8000 Oe, both (**1**) and (**2**) complexes "restore" the QTs at "classical" positions at 4000 and 8000 Oe. Addition C_{60} to $Mn_{12}F_5$ increases the squarness of the hysteresis, i.e. one observes the soft ferromagnet → hard ferromagnet transition. Apparently, the fullerenes provide an exchange pathway for the Mn interaction in (**1**).

Even more dramatic changes are observed for the (**2**). The M(H) curve for the $Mn_{12}BzC_{60}$ sample does not return to the initial point after the cycle of 1T → - 1T → 1T measurements. Magnetization progressively increases after each cycle of such measurements. Both (**1**) and (**2**) demonstrate magnetic memory effect: after storage in 1T field for several hours the M(H) curve reaches its maximum amplitude becoming asymmetric about zero, and doesn't relax after repeated 1T → - 1T → 1T cycle, but gradually regains symmetry.

C$_{60}$CdS thin film as a bulk heterojunction

Zakharova I.B.[*], Suprun E.I.[*], Makarova T.L.[+,‡]

[*]*State Polytechnic University, 195251 St.-Petersburg, Russia*
[+]*Ioffe Physico-Technical Institute, 194021 St.-Petersburg, Russia*
[‡]*Umeå University, 90187 Umeå, Sweden*

Organic-semiconductor fullerene based complexes are of great interest as a material for photovoltaic devices. Donor-acceptor complexes in comparison with inorganic semiconductors have a higher internal quantum yield. An interpenetrating network of donor and acceptor materials is a bulk heterojunction and can be used to increase the efficiency of converting solar energy in the photocell. In this research, C$_{60}$CdS thin films have been obtained and studied for the first time. We have developed the vacuum deposition technique for producing C$_{60}$CdS thin films in quasiequlibrium conditions. Absorption in the visible and UV range, photoluminescence, Raman spectra of the films have been studied. To determine the structure and spatial charge distribution in the films we used AFM method in an electric field. It was shown that the films have polycrystalline structure with grain size about 100 nm where crystallites are electrically inhomogeneous in 10-20 nm region near grain boundaries. This charge inhomogeneity may be related either to the charge transfer between the components of the system or to the presence of two phases with different work function. Raman spectroscopy of the C$_{60}$CdS films revealed the appearance of A$_g$(2)-derived modes of C$_{60}$ (1469 см$^{-1}$) situated 12 -23 cm^{-1} lower in energy. The softening of the pentagonal pinch mode reflects the charge transfer processes and depends on the technological regimes, i.e. on film structure and composition. IR spectroscopy revealed an additional absorption peak near the absorption edge of C$_{60}$. This observation is typical for intercalated fullerene systems. Luminescence spectra demonstrate quenching of the CdS-related peaks and simultaneous increase of the C$_{60}$-related peaks. Experimental demonstration of the charge transfer processes between C$_{60}$ and CdS molecules and the formation of donor-acceptor molecular heterojunctions indicates the suitability of using C$_{60}$CdS composite films and hybrid structures as novel photovoltaic material.