

Mechanisms of the carbon crystallization from liquid and vapour

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There had been considered liquid carbon obtaining conditions including superfine films and carbon vapour with the parameters exceeding the triple point ones. Various forms of the carbon structure crystallization from the phases obtained are also discussed.

The forms of the Stranskoy-Krastanov insular crystal growing mechanism at the crystallization from the liquid phase are analyzed based upon the limiting wetting angle measurements on the liquid carbon-graphite-vapour interface line, showing a low lyophilicity of the basic graphite bound towards its own melt. The consideration of the growing mechanism according to the scheme vapour-liquid-crystal showed the presence of the liquid on the growing stage what does not take at the vapour-crystal growing. As a result, the former mechanism leads to the formation of atomic smooth terraces and the latter occurs with the screw dislocations and final formation of the rough surface (in an atomic scale). The Raman spectra of superfine films are comparable with those of graphene with the number of layers from 1 to 6.

There had been discussed opportunities to find the surface energy of the interphase boundary by studying vicinal growing of the elementary graphite stages (with the thickness of one elementary cell parameter), perspectives of growing and a structure of nanocrystal edges with the high aspect ratio of the vapour-liquid-crystal mechanism.

Size effects in X-ray absorption and inner-shell photoemission from molecules encapsulated in fullerene

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Size dependent properties of matter, in particular, nano-scaled particles and clusters are suitably investigated by inner-shell excitations [1]. Photoemission from composite systems such as $A@C_{60}$, where A is an endohedral atom or molecule confined in a fullerene shell C_{60} , has recently attracted high attention [2].

In the present work the influence from the fullerene shell on spectral dependence of X-ray absorption and inner-shell photoemission from endohedral molecule SF_6 encapsulated in a fullerene is investigated. The special emphasis is put on the lineshape of the molecular $2t_{2g}$ shape resonance near S 2p ionization threshold. Dependence of the lineshape on the size of fullerene shells C_{60} , C_{240} and C_{540} is examined. The quasi-atomic and double barrier optical potential approaches [1] are applied to study the size dependent properties. The internal and external potential barriers describe respectively scattering of S 1s- and 2p-photoelectrons on octahedron of fluorine atoms and carbon atoms in $SF_6@C_{60(240,540)}$.

The performed calculations predict appearance of new window-like resonance features caused by interference of photoelectron waves scattered from the double barrier optical potential. The “windows” are assigned with resonance tunneling of the photoelectron through the composite system $SF_6@C_{60(240,540)}$. Strong distortion of the $2t_{2g}$ shape resonance near the “window” and substantial role of nuclear motions in the composite systems is revealed and discussed in more detail.

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Electronic structure of fluorinated single-walled carbon nanotubes studied by X-ray absorption and photoelectron spectroscopy

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In this work, the high-resolution near edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron (XPS) spectroscopies are used to elucidate the nature of chemical bonding between carbon and fluorine atoms on the surface and inside fluorinated single-walled carbon nanotubes (SWCNTs).

SWCNTs were synthesized by an electro-arc method using nickel-yttrium catalyst. The purified nanotubes had a narrow diameter distribution with an average value of ~ 1.5 nm. High-purity SWCNTs (~ 98 wt.%) are obtained in the form of paper (SWCNT paper). The direct fluorination was carried out at a temperature 222°C for 5 hours. The fluorinated SWCNTs had ~ 35 wt.% fluorine (SWCNTs+F35%). Measurements were performed at the Russian-German beamline at the BESSY II (Berlin, Germany). NEXAFS spectra of all samples were recorded at the C 1s and F 1s absorption edges in the total electron yield mode with photon energy resolution of 75 and 150 meV, respectively. The XPS spectra were recorded with the exciting photon energies of 385-1030 eV with the total energy resolution of 200 meV using Phoibos 150 analyzer.

C 1s NEXAFS spectra of F-SWCNTs show drastic changes in a spectral shape as compared to those of pristine SWCNTs. New absorption structures are similar for all the samples and reflect unoccupied electron states which are formed owing to a C-F bonding in F-SWCNTs. From a detailed analysis of C 1s and F 1s absorption spectra it was found that these F-SWCNTs are characterized by a nondestructive side-wall covalent attachment of the fluorine atoms and a formation of $\sigma(\text{C } 2p_z - \text{F } 2p)$ bonds.

Surface-sensitive XPS measurements showed that the carbon atoms at the surface of the F-SWCNT are characterized at least by two different chemical states. Based on a comparison between corresponding chemical shifts for C 1s core-level signals, it is believed that these carbon states are associated with different fluorine-carbon phases C_2F and C_4F which can be formed on carbon nanotube surfaces.

Electronic structure of CuHal@SWCNTs (Hal=I, Cl, Br) studied by X-ray absorption and photoelectron spectroscopy

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Encapsulated single-walled carbon nanotubes (SWCNTs) with inner channels filled by different compounds present the new class of composite materials. Such CNTs are of a big interest because of an opportunity to form 1D nanocrystals as well as quantum nanowires with new physical and chemical properties inside the tubes. Electronic properties of modified CNTs determine substantially the field of their application. The present study is aimed to characterize the possible chemical interaction between CuHal (Hal=I, Cl, Br) and SWCNTs in CuHal@SWCNTs and electronic structure of the latter.

SWCNTs were synthesized by an electro-arc method using nickel-yttrium catalyst. The CuHal@SWCNT nanocomposite was produced by the filling of metallic SWCNTs with inner diameter of 1.1-1.4 nm by wide-gap semiconducting CuHal nanocrystals using so-called capillary technique. Approximate loading value of CuI equals 90 wt.%, CuBr equals 50 wt.% and CuBr equals 20 wt.%. Measurements were performed at the Russian-German beamline at the BESSY II (Berlin, Germany). NEXAFS spectra of all samples were recorded at the C 1s and Cu 2p absorption edges in the total electron yield mode with photon energy resolution of 75 and 300 meV, respectively. The XPS spectra were recorded with the exciting photon energies of 385-1130 eV with the total energy resolution of 200 meV using Phoibos 150 analyzer.

The present study has shown that encapsulation of CuHal into SWCNTs is accompanied by the changes in electronic structure of CuHal because of the ones in atomic structure of CuHal in the composite and the chemical interaction between the filler and carbon nanotubes. The changes in SWNT and CuHal electronic structure appeared as a result of their interaction were analyzed.

Apparatus for investigating physical nature of nanoporous carbon structure field emission

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Cold nanoporous carbon (NPC) structures are able to emit electrons at field strength $E=1000-3000$ V/mm which is several orders of magnitude less than classical cold field emission values. Since the nature of this low-voltage emission is vague, it would be very interesting to study energy spectra of emitted electrons.

As the typical NPC emitting sample is powder stuck to a substrate surface, its surface is rather rough and the distance H between the emitter and anode can not be made too little. In case $H=1$ mm and $E=1000$ V/mm, electron energy at the anode is approximately $W=1000$ eV. If the absolute energy resolution of the spectrometer $\Delta W=0.1$ eV (which is far from the most desirable values), then the resolving power should at least be $W/\Delta W=10^4$.

One of the ways to achieve or even exceed this value is to use an energy analyser of extraordinarily high energy dispersion D . Earlier, such a device, named «Tutankhamon», was designed, made and tested experimentally [1,2], its real dispersion expressed in characteristic length units being equal to 12-13. This dispersion is approximately ten times bigger than the corresponding value of any traditional electrostatic energy analyser.

On the basis of this device, there has been elaborated an electron spectrometer, with the following main elements:

- sample holder with the heating facility up to the temperature of 500 C°;
- input lens, decelerating coefficient of which $1 < K < 10$;
- electrostatic energy analyser itself, with changeable diaphragm widths $0.1 < \Delta S < 1.0$ mm and the distance between the diaphragms of 50 mm;
- secondary-electron multiplier at the output of the analyser.

The spectrometer is placed in a stainless steel vacuum chamber with the lowest achievable residual gas pressure of 10^{-11} torr. First NPC field emission spectra have been recorded with the use of electron-counting method.

This work is supported by the RFBR, grant 08-02-01045.

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An X-ray emission spectroscopy study of the electronic structure of products of toluene diisocyanate carbonization in an Al₂O₃ matrix

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Carbonization of polymers and organic precursors in porous matrices is a common method of synthesis of a various porous carbon materials, particularly fullerenes. The peculiarity of this method is a possibility to obtain carbon nanostructures with diverse morphology and anisotropy by changing a carbonization rate, precursor concentration and adding of different catalysts. Porous carbon materials are widely used as high-performance sorption materials, catalyst carriers, membrane systems for filtration of solutions and gases etc.

In the present work fine Al₂O₃ (S_{sp}=200 m²/g) was used as a structure-forming agent for matrices obtaining. A mixture of 2,4- and 2,6- toluene diisocyanate (TDI) in the 80:20 ratio was used as carbonization precursor. Gels prepared from Al₂O₃ particles and a TDI solution in benzene were dried out at room temperature and carbonized at 750°C in argon flow.

For investigation of the electronic structure and peculiarities of chemical bonding of products of TDI carbonization in Al₂O₃ matrixes, the method of X-ray emission spectroscopy has been employed. We have obtained X-ray emission CKα- and OKα-bands reflecting energy distributions of the valence 2p-like states of carbon and oxygen, respectively. The bands were registered using an X-ray spectrometer-monochromator RSM-500 with oil-free evacuation of a spectrometer chamber. The operation conditions of the X-ray tube were the following: accelerating voltage, U_a = 5 kV; anode current, I_a = 2.5 mA. The specimens under study were rubbed into a water-cooling copper anode.

The shape of the X-ray emission CKα-band of products of TDI carbonization in an Al₂O₃ matrix resembles that of the similar band of a mixture of fullerene C₆₀ with carbon onions, and the shape of the OKα-band looks like the analogous band of γ-Al₂O₃. During registrations, the shape and intensity of the X-ray emission CKα- and OKα-bands of products of carbonization of TDI in an Al₂O₃ matrix were rather stable. This fact indicates a strong chemical bonding of the matrix with products of TDI carbonization.

NEXAFS characterization of electronic structure for CuI@SWCNT nanocomposite

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Encapsulated single-walled carbon nanotubes (SWCNTs) with inner channels filled by different compounds present the new class of composite materials. Such CNTs are of special interest because of an opportunity to form 1D nanocrystals as well as quantum nanowires with new physical and chemical properties inside the tubes. The present study is aimed to characterize the possible chemical interaction between CuI and SWCNTs in CuI@SWCNT and electronic structure of the latter with X-ray absorption spectroscopy.

All investigations have been performed at the Russian-German beamline (RGL) [1] using experimental station Mustang for measurements of the X-ray absorption and photoemission spectra. The CuI@SWCNT nanocomposite was produced by the filling of metallic single-walled carbon nanotubes with inner diameter of 1.1-1.4 nm by wide-gap semiconducting CuI nanocrystals using so-called capillary technique [2]. Evaporated layer of CuI, powder of CuO and initial SWCNTs were used as reference samples.

NEXAFS spectra at the Cu $2p$, I $3d$ and C $1s$ edges were obtained in the total electron yield mode by detecting a sample current. Measured spectra were analyzed in the frameworks of the quasi-molecular approach [3]. The present study has shown that encapsulation of CuI into SWCNTs is accompanied by the changes in electronic structure of CuI because of the ones in atomic structure of CuI in the composite and the chemical interaction between the filler and carbon nanotubes. New details in the Cu $2p$ and C $1s$ spectra are regarded as a result of the transitions of Cu $2p_{3/2}$ and C $1s$ electrons to the same empty state of CuI@SWCNT which has hybridized Cu $3d$ -C $2p_z$ character.

This work was supported by the Russian Foundation for Basic Research (project no. 09-02-01278) and the bilateral Program "Russian-German Laboratory at BESSY".

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The nanographite 2D-structures investigation with making use of atomic-force and ion-beam methods

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From the moment of discovering in 2004 2D forms of carbon - graphene - the new perspective material has appeared. Graphene geometrical, mechanical, electric properties can be used in the different application, including electronics, sensors etc. Moreover, modification of graphite at nanometer level can lead to the new type of a material formation [1].

In this work we investigated graphite nanostructures, fabricated by four techniques: highly oriented pyrolytic graphite (HOPG) ultrasonic exfoliation, HOPG mechanical splitting, mechanical splitting with the subsequent ultrasonic exfoliation, chemical dispersion. After carrying out of splitting, the product was dissolved in 2-propanol and deposited on crystals with preliminary created gold electrodes. The measurements of received 2D-structures basic geometrical parameters have been done in atomic-force microscope (AFM). We observed the thickness of the samples fabricated by various methods vary from 2 up to 100 nanometers.

The influence of high-energy ions on graphite 2D-structures was studied using focused ionic beam module (FIB) of "NanoFab" complex (NT-MDT). FIB supplies a source of ions of gallium (Ga^+), with energy 30kV, and ultimate beam diameter about 7nm.

As a result of gallium ions beam influence with the different aperture, doze and time of influence, the part of carbon atoms evaporates from surface.

We found that changing the ion beam doze and exposure time we can control the nanographite etching depth with the step down to 1 nm. Thus this technique can be used in the nanographite thinning. We also used FIB to graphite nanoribbons of 70 nm width and 20 nm thickness. The conductance of such structures dramatically change compare to nanographite layers.

Thus, the results received in this work can be applied in nanographite 2D-structures nanoelectronics elements fabrication.

The authors would like to thank Chervonobrodov S.P. (NanCarbLab) for graphene material provision. The work was supported by the program U.M.N.I.K.

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Morphological features of carbon nanostructures synthesized by pyrolysis of benzene in the presence of sulphur

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The chemical vapour deposition (CVD) technique is one of the most promising methods used to produce carbon nanotubes (CNTs) since it provides precise process control and offers a large variety of variants of carrying out the experiments.

According to previous works, the presence of sulphur during the synthesis can influence certain morphological features of CNTs, such as leading to CNTs filled with metal [1] or junction structures [2, 3], or it can influence the number of carbon walls [3]. Nevertheless, the role played by sulphur in the production of carbon nanostructures is still not well understood.

Carbon nanostructured deposits were prepared by co-pyrolyzing benzene and ferrocene in the presence of CS₂ at the temperature of 980°C. The morphologies of the obtained structures were extensively studied by both scanning electron microscopy and transmission electron microscopy. To follow the influence of sulphur concentration on the morphology of the structures, experiments were carried out at atmospheric pressure and at reduced pressure for different concentration of CS₂.

Results concerning the morphological characteristics of the observed structures, the influence of the experimental conditions, the localisation of sulphur and the role of its concentration will be presented.

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Features of resonant F *KLL* Auger spectra from fluorinated multi-walled carbon nanotubes

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An extension of the application field for carbon nanostructures and their functionalized derivatives call for detailed knowledge of electronic structure for these new materials. The main aim of the present study was to gain a deeper insight into the nature of chemical bonding and electronic structure features for the fluorinated multi-walled carbon nanotubes, F-MWCNTs, using high-resolution F 1s absorption and resonant F *KLL* Auger electron spectra, and their analysis on a basis of the comparison with corresponding spectra of TiF₃.

All measurements have been performed at the Russian-German beamline [1]. A sample of F-MWCNTs (10 wt.% of fluorine) was prepared in air by rubbing its powder into the scratched surface of a clean stainless-steel plate. Thin (20-25 nm thick) TiF₃ layers were prepared in situ by thermal evaporation of thoroughly dehydrated TiF₃ powder from an effusion cell heated by an electron beam onto a polished stainless-steel plate. NEXAFS spectra at the F 1s edges for samples were obtained in the total electron yield mode. Photoelectron and F *KLL* Auger spectra were collected in the angle-integrated mode with the total energy resolution of 400 meV using a Phoibos 150 electron analyzer.

The most interesting effect is the change of the Auger transition energies when photon energy passing through first low-energy absorption peak: Auger-electron energy is significantly more than constant energy of normal Auger transition when the 1s electron is excited to a continuum. This finding is explained in terms of hybridized nature of free electron states near the bottom of conduction band which are responsible for the first absorption band. In this case the spatial localization of low-energy excited state provides the additional screening for initial and final states of resonant Auger-electron transition that leads to an increase in energy for spectator-Auger-electron. The conclusions on the hybridization character of low-energy free electron states agree well with results obtained previously for F-MWCNTs with x-ray absorption [2].

This work was supported by the Russian Foundation for Basic Research (project no. 09-02-01278) and the bilateral Program "Russian-German Laboratory at BESSY".

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Electrochemical behavior of carbon nanostructures at camphor and sodium cryptate adsorption

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The effect of adsorption of camphor and sodium cryptate on electrochemical behavior of carbon nanostructures has been studied by cyclic voltammetry (CV) and impedance spectroscopy. Nanopaper electrodes consisting of single-walled unitized nanotubes and columnar structures containing multi-walled nanotubes were investigated. The condensed adsorption layers (CAL) formed at electrode/solution interface by organic molecules of wireframe (diamond-like) structures are the most stable of well-known now. This fact explains choice of adsorbates. At the same time camphor is of great importance of attraction constant $a = 5-6$ characterizing lateral interaction between molecules at two-dimensional layer. The energy of two-dimensional layer averages $\sim kT \times a$ that rather exceeds value for usual surface-active substance [1,2]. The differential capacity (C) of nanopaper and columnar structures increases in aqueous solution in addition of adsorbates within all region of studied potentials 0.2-(-1.4) V (s.c.e.). The increment of C was proposed to be caused by partial disruption of bundles of nanotubes and so considerable growth of surface area accessible for electrolyte. The increase of concentration of adsorbates results in greater growth of capacity of nanopaper and columnar structures. This experimental fact was explained by considerable growth of surface area accessible for electrolyte. These bundles were formed by conglutination of single walled nanotubes during synthesis owing to Van der Waals forces. Increase in capacity of columnar electrodes was explained by splitting of carbon flakes forming these structures. In author's opinion these experimental data are the first evidence of Rebinder's effect in electrochemistry.

At the same time the presence of CAL of camphor and sodium cryptate results in remarkable decrease of spikes amplitude on CV of $\text{Fe}(\text{CN})_6^{3-/4-}$ redox reaction at nanopaper and columnar electrodes. Similarly the injection of electrons and reduction of ions of nitrate or nitrite is partly suppressed in aqueous solution over adsorbates.

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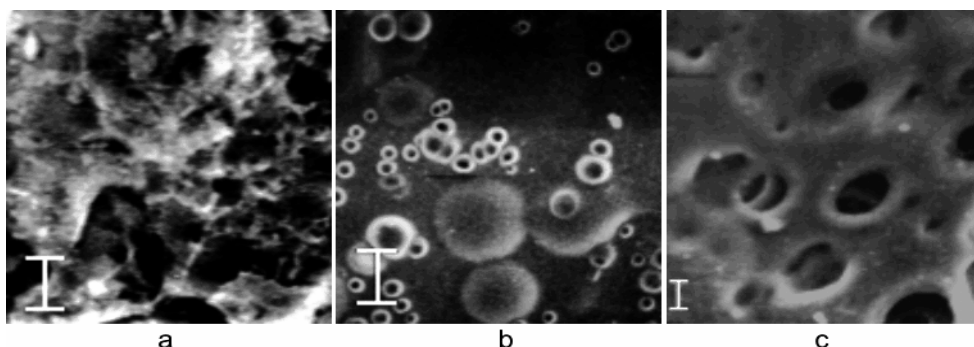
The use of cocarbonization processes for creation of the porous carbon systems

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Carbon materials have the great potential for preparing of micro- and ultra-filtration membranes and sorbents for application in aggressive medium. Today porous materials from carbon are mostly prepared by the vapor activation of carbonize. The main disadvantage of this method is the problem in control of pore size and pore sizes distribution in the material. The method of cocarbonization of polymers represents the one-stage synthesis of carbon films structure with the controlled pore size distribution. We have shown by the example of polyacrylonitrile (PAN) and lignin how the carbonizing phases of these polymers interact to produce tunnel pores evenly distributed in the carbon material. This interaction in the temperature region of the maximum thermochemical activity of the polymers (250-400°C) leads to formation of the two carbonized phases which influence further structural changes of the polyaromatic carbon molecules (figure). (a) In case of the heat-treated pure



lignin powder ragged pores are well seen. (b) PAN film shows presence of the inside cavities, and the outer pores with ragged edges.. This indicates the formation of the surface solid crust and consequently to low films of PAN mechanical parameters. (c) In contrast, heat-treated film PAN-lignin with 50% content of components has uniform structure: the tunnel pores with smooth edges of 8-15 μm in diameter. Evidently, the tunnel pores are formed by the even gas evolution from even distributed lignin phase, which is less thermostable than PAN phase. At the same time, the neighborhood of PAN phase elongates the period of lignin's thermostability. In its turn, presence of lignin, telling upon cyclization, makes PAN phase more fluent. The last prevents surface crust formation, hindering the uniform thermodestruction of the intermediate. Such behavior can be used for one-stage production of highly effective carbon filtration films with controlled pores distribution.

Separating of fullerenes and their compounds in impulse inhomogeneous electric fields

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In the present study we show the possibility of separating molecules with polarizability in impulse electric fields. On the example of the electric field of the system of charged parallel wires we have estimated the angle dispersion of the fullerene molecules C_{60} , C_{70} , C_{84} using the values α of the polarization coefficients. The mathematical model of the molecules motion in the inhomogeneous impulse electric fields is presented.

We have assumed that the dominating part of the dipole interaction of the molecules with the exterior electric field is described by the potential energy $\Pi = -\alpha |E|^2$. Here $\vec{E} = -grad\Phi$ is the vector of the electric field strength. The field potential can be described as $\Phi = \Phi_0 f(\tau) \varphi(x, y, z)$, where τ is a dimensionless time parameter; x, y, z are the dimensionless coordinates; φ and f are the dimensionless structural functions expressing the field geometry and the rate of its changing in time; Φ_0 is a characteristic dimension potential value. The potential in cylindrical coordinates R, Z, θ is $\Phi = \Phi_0 [\ln(R/l) - 1] = \Phi_0 \varphi(\ln r - 1)$. For this case the Lagrangian of the molecules under consideration is

$$\sum_{i=0}^{i=n} L_i = \sum_{i=0}^{i=n} \left(\frac{\dot{r}_i^2 + r_i^2 \dot{\theta}_i^2}{2} + \frac{f^2(\tau) v}{r_i^2} \right),$$

where $v = \alpha \Phi_0^2 T^2 / ml^4$, T and l are temporal and liner scales. In case $v=1$, $T = l^2 \Phi_0^{-1} (m/\alpha)^{1/2}$. We consider the molecule motion in the fields with potential acting within a periods of time $0 < \tau < \Delta / T$ with frequency $1/10\Delta$. Here L_i is the Lagrangian of molecules motion during the action of potential pulse Φ_i with initial coordinates r_{i-1}, θ_{i-1} and energy Ξ_{i-1} . The molecular energy after n pulses transforms into

$$\Xi_n = \sum_{i=1}^{i=n} \left\{ \Xi_{n-1} + \text{Cos} \xi \left[2\varepsilon_0 \alpha \Phi_0^2 / R^3 i \Delta \right] \sqrt{2\Xi_{i-1} / m} + \left[2\varepsilon_0 \alpha \Phi_0^2 / R^3 i \Delta \right]^2 / 2m \right\},$$

where ξ is the angle between vectors of molecules velocity and vector of force F_i acting upon molecules within a period of time Δ . Thus the molecule trajectory is a curve consisting of n parts. Each part represents the motion of two types: the motion of molecules during Δ in the fields and the free linear motion during 10Δ . Taking into account the initial conditions and using the Lagrangian function, we obtain the energy integral Ξ and equation $r(\theta) = b / \left\{ \left[0,7b\theta / m + (b/r_0 - a)^{0,5} \right]^2 + a \right\}$ for the trajectory of particles, where the designations $a = r_0^2 / 2 + b$, $b = [M^2 - 2vf^2(\tau)]r_0$ are used. The obtained angle dispersions from numerical investigations and comparison them with those for static fields will be presented at the conference.

Investigation of nanocarbon films on SiC surface formed by sublimation epitaxy in vacuum

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The aim of this study was to examine the possibility of applying the technology of sublimation epitaxy of SiC in a vacuum to synthesis of nanocarbon films on the surface of silicon carbide.

The method of sublimation epitaxy has long been used to produce epitaxial silicon carbide layers with prescribed parameters. This technology is based on evaporation of a substance from the source situated in a hotter place of the reactor and its deposition onto a single-crystal substrate placed in a colder place. This study was performed using an installation for sublimation epitaxy and technological accessories employed in epitaxial processes. The only distinction was that the growth source was removed from the growth cell.

In the first stage, the sample was annealed at 900°C and a residual pressure of $\sim 10^{-5}$ mm Hg for 2 h to remove from the substrate surface the "natural" silicon oxide formed if a silicon carbide substrate is exposed to air. Then, the sample temperature was raised to 1200°C and, after that, the temperature was gradually elevated to 1300-1400°C in steps of 100°C.

After each stage of annealing, the surface of the samples was examined by means of atomic-force microscopy (AFM). The structure of the carbon films obtained was studied by reflection high-energy electron diffraction (RHEED). The chemical composition of the film obtained was studied by Auger and Raman spectroscopy.

The possibility of formation of nanocarbon layers on the SiC surface by sublimation in an open system was demonstrated. This technique requires no additional etching of samples in hydrogen or a silicon vapor, which considerably simplifies the process of film deposition. The thickness of the films obtained depends on the annealing temperature of a sample. According to RHEED data, the resulting film contains 2D crystals of graphite. The data obtained suggest that the optimal temperature range for formation of graphene on the SiC surface is 1300-1400°C. The electrical parameters of the samples obtained will be presented in full volume paper.

Shock compressibility of C₇₀ fullerene via synchrotron radiation technique

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Shock compressibility of C₇₀ fullerene was measured with the use of pulsed-periodical source of synchrotron radiation of the Institute of Nuclear Physics SB RAS. The starting specimens were prepared by high (1 GPa) hydrostatic pressure treatment of powdered C₇₀ fullerene with a hexagonal close-packed structure. The powder was made by JSC "Fullerene center" (Nizhny Novgorod, Russia). The specimens had a density of 1.65 g/cc, a diameter of 15 mm and a thickness of 2.5-3.5 mm. Specimens were loaded by impacts of metal plates (with a diameter of 16 mm) accelerated by high explosives up to velocities of 1300-1800 m/s. Synchrotron radiation technique [1] was used to measure the parameters of the shock-compressed fullerite. This method of measurements is based on immediate visualization of X-T diagram of shock-wave processes by measuring a degree of attenuation of synchrotron radiation by an explored material during passage of a shock wave through this material. It was obtained that the experimental Hugoniot of C₇₀ fullerene in the explored pressure range (6.3-9.3 GPa) is allocated below the experimental Hugoniot of C₆₀ fullerene [2] on pressure - specific volume plane.

The work was supported by RFBR (project no. 07-02-00625). The authors thank O.B. Tsiok and L.G. Khvostantsev (IHPP RAS) for high hydrostatic pressure treatment of the specimens.

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Thermal behavior of C₆₀ and C₇₀ fullerenes in various environments

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The unique properties of the fullerenes have lead to intensive studies of the fullerene containing materials. The development of the techniques of their obtaining is considerably conditioned by the stability of the fullerenes' molecules and their crystalline phase – fullerites. However, the data of their thermal stability available in the literature are quite contradictory and ambiguous both for pure C₆₀, C₇₀ and their mixture.

The thermal stability studies of the fullerenes/fullerites were carried out using the powders of C₆₀ (99.5%) and C₇₀ (>98%) previously tableted under P=800 MPa and then the tablets were annealed over the temperature range from 500 to 1050°C during 30 minutes both in CO (closed graphite crucibles) and in vacuum (quartz ampoules, P ~ 10 Torr).

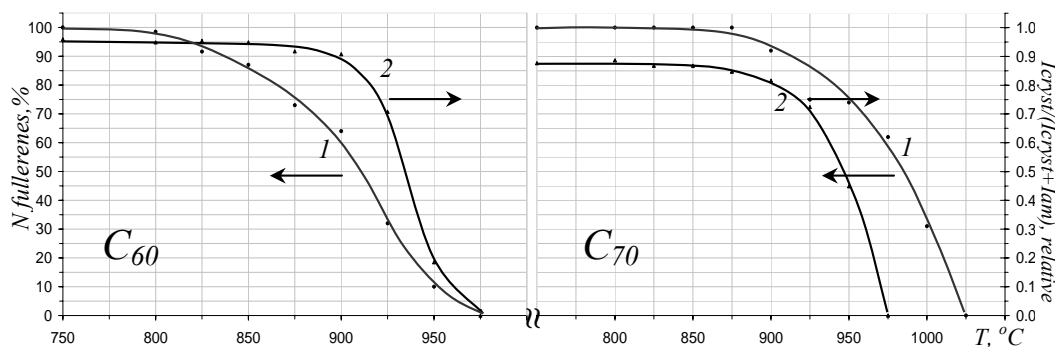


Fig. Thermal stability of fullerenes (1)/fullerites (2) C₆₀ and C₇₀

It has been established by the methods of X-ray diffraction and UV-vis spectroscopy that thermal stability of both the fullerene and fullerite C₇₀ is higher than that of C₆₀ (Fig.). It has also been shown that the thermal behavior of the fullerenes/fullerites is significantly affected by heating environment and by the presence of solvent residues. The thermal stability of the fullerenes by CO heating is considerably higher than that in the vacuum. It has been established that recrystallization from the toluene solution of C₆₀ and C₇₀ results in a substantial decrease of their stability after annealing in CO. The recrystallization of C₇₀ from the gaseous phase (sublimation), which involves removal of both the oxygen residues and the trace of the solvent, leads to a considerably increase of their thermal stability.

The work was supported by the fundamental research program of Presidium of the Russian Academy of Sciences “Physical-chemical features of nanocarbon structures and metal-carbon nanocomposite obtained by mechanosynthesis”.

Emission spectroscopy as the main control method for carbon nanoparticles synthesis

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In 1990, as soon as the article of W. Kraetschmer et al. was published, the interest to graphite electrode arc had appeared again. The carbon-helium plasma, i.e. the plasma of “fullerene arc”, was investigated, and also the spectral characteristics of noble gas glow discharge containing gaseous fullerene at low pressure were investigated [1, 2]. There are no references in literature about spectral characteristics of atmospheric pressure plasma, where the processes of fullerene, nanotube and metal-carbon nanocluster formation occurs. The difficulty of these investigations is the necessity to filter radiation of high-temperature area of plasma for registration only the temperature area of these nanostructures formation, 2500-3500K. The setup was produced for these investigations, where the arc was constructively isolated from fullerene formation area [3]. Unlike the radiation of low-pressure fullerene arc plasma, in the carbon-helium flow we observed the absence of CN and other molecular bands. Visible range was filled by wide lines corresponding to carbon clusters radiation. Also in the spectrum the lines corresponding C₂ cluster were found. The radiation of metal-contained fullerene plasma had more complicated spectrum because of presence of metal cluster lines. As the result of the investigations the ability was appeared first to compare experimental distribution of carbon clusters in fullerene arc of atmospheric pressure with theoretical one.

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Study of the orthorhombic polymeric phase of C₆₀ under high-pressure using X-ray synchrotron radiation

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Recently, we have evidenced and reported a new structural transition mechanism (at ca 0.5 GPa) involving the long time (typically 50-150 hrs) action of pressure using a laboratory XRD apparatus, during the course of which the 1D-O polymer phase is converted into a new polymeric phase of lower crystal symmetry [1]. Unfortunately, because of the low resolution and the small number of available Bragg peaks, it was not possible to refine our model against the thus obtained experimental data, and further higher resolution synchrotron radiation experiments were needed.

The latter were recently carried out at the ESRF/ SNBL BM01A beamline under high pressure using much shorter exposition times (typically 10 min). In contrast to the first laboratory experiment, and for reasons which are still eluding us, no photo-induced transition to a lower symmetry state was observed this time up to 6 GPa. The obtained powder diffractograms are all consistent with an orthorhombic cell. A Birch-Murnaghan equation of state is fitted to the resulting pressure-volume data for the O phase.

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Change of C₆₀ fullerites properties under irradiation with electrons and ions

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Interaction of charged particles with fullerites C₆₀ is of technological (due to appearing of extraordinary mechanical properties, structural stability) as well as fundamental interest.

In order to investigate the influence of electron and ion beams induced changes on the structure and hybridization which cause changes in physical properties we have performed this study of C₆₀ fullerites (films of C₆₀, d=2000 nm on Si (100) substrate) as a function of the fluence of 1,8 MeV electron and 140 keV Fe⁺ irradiation with different doses. Using X-ray's diffraction we have investigated structural changes, using Raman spectroscopy – vibrational properties of irradiated fullerites, with help of photoluminescence and spectral ellipsometry we have studied electron structure.

Irradiation of fullerites structure with highenergetic electrons leads to polymerisation of molecules that is confirmed by appearance of new structural reflections in diffraction pattern, complicated transformation of electron structure and splitting of vibrational modes in the Raman spectra.

Results showed that with increasing of Fe⁺ ion influence formation of defects leads to destruction of fullerene molecules. On the first stages of irradiation is observed increase of lattice parameters because of filling of interstitials with knocked atoms of carbon and with Fe atoms. Further, when dose achieves 10¹⁴ ions/cm² is observed broadening of photoluminescence peaks, disappearing of most vibrational modes.

X-ray spectral investigation of electronic structure peculiarities in carbon onions, nanotubes and fullerenes

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Expansion of nanotechnology applications requires thorough investigations of new carbon nanomaterials unique properties that are mostly determined by the electronic structure. Therefore the energy distribution of Cp -electrons in carbon onions, nanotubes and fullerenes has been investigated by means of the ultrasoft X-ray spectroscopy method. The CK_{δ} -emission bands have been obtained with apparatus distortions 0,2 eV. Specially made trap prevented additional underlying of the CK_{δ} -bands from hydrocarbons vapors.

It has been revealed that the p -band in CK_{δ} of fullerene C_{60} splits due to the different degrees of the p -overlapping over the C_{60} surface of p_z -orbitals in atoms at distances of 0,139 and 0,144 nm. In contrast to fullerenes degrees of such a p -overlapping of p_z -orbitals in onions are equal since distances between atoms in each sphere are the same. However, curvature of spherical atomic surfaces increases when deepening into the onion particle. So the p -overlapping degree of p_z -orbitals decreases over the particle's surface and increases within the particle.

The p -overlapping of p_z -orbitals within the spherical atomic surfaces in onion is noticeably smaller than that in fullerene but it increases when deepening into the onion particle. Therefore the mixed $p+y$ -subbands can appear within the onion particle due to the overlapping of the pp_z -states and sp^2 -hybride orbitals. Occurrence of the $p+y$ -binding states is possible due to the fact that the diamond core of onion is covered by graphene sp^2 -atomic layers. These layers prevent from growth of flat 001 graphene layers after sp^3 -hybrid bonds breaking.

It was shown that in nanotubes emission bands as compared with onions additional differences in degrees of p -overlapping in radial direction and along the nanotubes axis appear. This overlapping is greater in radial planes within nanotubes. ppp -states with smaller energy involved in such a p -overlapping admix to $pp\sigma$ -states. Degrees of ppp -overlapping along the nanotubes axes are equal but smaller than that in radial direction within nanotubes.

Study of C₆₀ peapods after high-pressure- high- temperature treatment

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The application of high pressure to C₆₀ peapods at moderated temperatures generally leads to formation of polymeric chains of C₆₀ molecules with 2+2 cycloaddition bonds inside the pods (one-dimensional crystal). However, the influence of higher temperatures at high pressure and is still unknown.

The present work is devoted to study of products formed from C₆₀ peapods after treatment at 8 GPa as function of temperature up to 1200°C by SEM, TEM, XRD and Raman techniques. It was confirmed that at temperatures up to 600°C, the C₆₀ molecules polymerised in forming the known 1D polymeric crystal with C₆₀-C₆₀ distance of 9 E. Note that at room pressure this distance was about 9.8 E. We found also that at 1000°, the peapods begin to transformed into different products including nanodiamonds particles, amorphous carbon and graphitic ribbons. At 1200°C , only well formed graphite was found.

Diffusion characteristics of water in the vicinity of single-nano buckydiamond as revealed by quasielastic neutron scattering

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The stability of an aqueous dispersion system should depend on the structural-dynamic characteristics of the carbon nanoparticles (CNP) hydration shell that, in turn, are connected with the properties of its own hydrogen-bonds network and the pattern of “carbon - water” interaction. The study of hydration effects, i.e. the influence of dissolved particles on the microdynamics of surrounding water molecules, is the main goal of experiments by inelastic neutron scattering on the water dispersions of CNPs.

Only the quasi-elastic region of neutron scattering (QENS) showed the most noticeable difference between the single-nano buckydiamond (SNBD)¹ colloid and bulk water (BW).

The diffusion characteristics of stable aqueous dispersion of SNBD (concentration 80 mg/ml, average particle size 8 nm)¹ and bulk water (BW) as the reference system were investigated by QENS².

Dispersion water was considered as a binary system consisting of BW and hydration water (HW) incorporated in the nearest surrounding of SNBD.

The relative fraction of HW was estimated about 3%, and this quantity corresponds to 2–3 layers of water molecules adjacent to SNBD. The diffusion characteristics of HW demonstrate the remarkable deterioration of molecular mobility compared to BW due to slowing down the rotational mobility and increasing the residence lifetime of molecules. The quantity of HW per 1 g of ND is estimated as ~ 0.2 g HW/1 g SNBD.

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Application of the x-ray photoelectron spectroscopy method for studying the variation of the magnetic moment of the 3d-metal atoms in nanoforms

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At present, unique physical properties of nanoparticles are the subject of intensive studies. Magnetic properties occupy a special place among them since the differences between a bulk material and a nanomaterial are revealed most clearly in them. X-ray photoelectron spectra give the information about local characteristics of the substance structure in contrast to conventional methods which give the integrated information about a studied sample. A method of the x-ray photoelectron spectroscopy has been developed for the determination of the atomic magnetic moment of 3d metals, which is important for structurally non-uniform clusters and nano-objects in which metal atoms with different nearest surroundings can differ in the magnitude of the atomic magnetic moment.

The interpretation of the 3s-spectra of transition metals within the framework of the one-electron theory describes the $3s^{-1}$ multiplet in 3d metals as two energetically well-separated groups of components. Based on the investigation of the 3d-metal reference systems, the parameters of the x-ray photoelectron spectra correlating with the magnetic moment of the metal atom have been determined, and the model has been offered for the atomic magnetic moment determination with respect to the intensities and the distance between the maxima of the multiplet splitting in the 3s-spectra of metals, and the valence bands shape. Using the model, the variation of the metal atomic magnetic moments and the structure are first explained in $\text{Fe}_{50}\text{Co}_{50}$, invar alloys, liquid metals and carbon-metal nanostructures. The investigations of the carbon-metal nanostructures show increasing atomic magnetic moment on Co and Ni atoms compared to pure metals and the appearance of the atomic magnetic moment on Cu atom.