Topological and quantum effects in electron transport in the metal-carbon nanocluster material

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We report results of the electron transport study in the tungsten-carbon films (TCF) in the temperature range from 4.2 to 80K for the tungsten concentration $x_W=10\div40$ at.%. The TCF are composed of tungsten nanoclusters, randomly dispersed in amorphous hydrogenated carbon matrix doped by silicon and oxygen. The deposition technology of the films is based on the combination of two methods - PCVD of the vapors of heavy silicon-organic polymer $((CH_3)_3SiO(CH_3C_6H_5SiO)_3Si(CH_3)_3)$, and DC magnetron sputtering of the tungsten target.

It is found that the conductivity of TCF $\sigma(T)$ is controlled by the classical percolation and quantum localization effects. Above the percolation threshold $x_W^c \sim 22$ at.% the system is a superconducting disordered metal, showing both an enhancement of the superconductivity and inelastic tunneling effects. The topological separation of the sample structure into finite metallic clusters surrounded by the dielectric at $x_W < x_W^c$, leads first to the onset of the asymptotic $\sigma(T) = \sigma_0 + AT^{1/2}$ specific for the quantum corrections in a weak localization regime. Further decrease of x_W shifts the system to the vicinity of the mobility edge x_W^q, which is manifested by the Altshuler-Aronov law $\sigma(T) \sim T^{1/3}$. It is worth noting that in our case the quantum effects preceded the classical percolation $x_W^q < x_W^c$, whereas the theoretical consideration suggests an opposite condition $x_W^q > x_W^c$ [1]. On the dielectric side of the metal-insulator transition, $x_W < x_W^q$, the thermal activation at the mobility edge is damped and the power law $\sigma(T) \sim T^{1.6}$ is observed. We discuss the possible reasons for the observed anomalies including clusterization of sp^2 bonds, change of the effective transport dimensionality and inelastic tunneling of the electrons between the finite conducting clusters. Support from the program of RAS "Quantum macrophysics" is acknowledged.

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Formation of M@C_{2n} (M = Gd, Ce) nanoparticles on mica surfaces

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Formation of Gd@C_{82} and Ce@C_{82} nanoparticles on clean mica surface have been studied by using atomic force microscopy (AFM). The endometallofullerenes were produced by DC electric arc discharge followed by extraction in polar solvents [1]. Nanoparticles of Gd@C_{82} and Ce@C_{82} on mica surface were formed both after thermal-vacuum deposition (10^{-7} Torr) and precipitation from N, N-dimethylformamide (DMF) solution (10^{-5} M).

On the first step regime of M@C_{2n} vacuum deposition onto the mica surface was defined. The effective thickness of deposited layers was monitored by interferential method *in situ*. Evaporation was carried out from tantalum boat (700°C) with growth-rate about 1 nm per minute. Microscopic study revealed that on initial stage of evaporation (first 10 minutes) M@C_{2n} already forms nanoparticles with mean size 10-15 nm. Afterwards single nanoparticles coalesce into aggregates with a typical dimensions 50-70 nm. On the last stage of the deposition we get continuous metallofullerenes film consisting from aggregates with a typical dimensions 50-100 nm.

Also process of M@C_{2n} nanostructures formation on the fresh mica cleavage surface poured by endometallofullerenes DMF solutions (10^{-5} M) was investigated. Microscopic study of the latest mica cleavage revealed series of atomic steps on surface 1-2 nm height. AFM scans of the mica surface, obtained after M@C_{2n} solution dry, indicated that endometallofullerenes formed chains of nanoparticles situated along atomic steps of mica. It is striking that nanoparticles formed both by vacuum deposition and by precipitation from M@C_{2n} solution have identical dimensions about 50-70 nm.

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Double photoemission from the fullerene films: angular photoelectron distributions and continuum resonant states

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The energy and the angular properties of the photoelectron emission from a monolayer fullerene film, forming a hexagonal molecular lattice on the inert substrate are investigated. We find that the angular distribution of the ionization probability experiences drastic modification with the photon energy.

This angular spectrum manifests three general features:

First, its qualitative pattern is periodically repeated together with the oscillations in the total ionization cross section (CS).

Next, when the photoelectron is temporarily captured within the molecular cage, the symmetry of the angular emission pattern is mainly determined by the symmetry of the single molecule. Contrary, for the photoelectron state mainly located outside the C_{60} (where the total CS shows local minima) the angular dependence of the emission reproduces the symmetry of the lattice.

In the vicinity of the CS minima there exists narrow photon energy interval ~ 0.1 eV where the preferred directions of emission are suddenly changed.

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Copolymers of ethylene and perfluorovinyl ethers with perfluorometoxypropenyl radicals as a base of film-forming materials with a wide range of application

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The requirement of security of ecological safety and reduction in power consumption at industrial process of separation of mixtures lend impetus to development of traditional technologies.

At present time, practically all polymers, which are available in the volumes, sufficient for practical use has been tested as film-forming fluoropolymers. Nevertheless, a synthesis problem of new types of polymers possessing, in comparison with known ones, improved parameters remains actual.

Film-forming fluoropolymers with high resistance to corrosive media up to high temperatures are promising candidates for protective coatings.

One has a particular interest in polymers, containing $\tilde{N}F_3OCF_2CF_2CF_2$. Perfluorometoxypropyl radical possess unique thermodynamic properties and can be purposefully obtained.

Therefore, it was noted that presence of methylene and perfluorinated parts in the main chain leads to formation of nanoclusters of methylene units.

It has been surveyed possible ways of using such polyfluorinated copolymers as a protective surface and selectively permeable membranes.

Hence, it has been examined interaction of copolymer composition of ethylene and perfluoroalkylvinyl ether with low-molecular compounds, possible components of environment. Some dates, possessing science and practical interest were obtained. Method of synthesis, determination of structure and some properties of perfluoroalkylvinyl ether and copolymer are reported.

Features of physics-chemical interaction with low-molecular compounds are established.

We plan to improve method of synthesis this copolymer for the purpose of standardization of products' main parameters. Moreover we will elaborate conditions of monomer's synthesis which will be acceptable for pilot industry. Furthermore on basis of this polymer and nanocarbons we plan to create composite material.

High emission current from nanocarbon composite materials

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It is known[1] that a single tip in a field (not explosive) emission allows to yield current density practically equal to electron stream towards the solid-vacuum boundary [1]. According to the measurements of electrical conductance [2], individual CNT is capable to sustain the current amounting to 2 mA. This value corresponds to current densities 10^7-10^8 A/cm^2. Experimentally observed ultimate field emission current from individual CNT amounts to ~100 μÀ [3].

Taking into account the moderate emission current (~10 μÀ) from individual tip, the great number of potential emitters from CNT must allow to get total emission current up to 100 A from 1 cm^2 area. By present time there is a series of the experimental works in which the current density level close to the theoretical value is reported. For example, in [4] the current density up to 1 A/cm^2 for 16 emitters with area 0.5×0.5 mm^2 each is shown. The density of vertically standing CNT was 10^6cm^{-2}. Peak values of the current of 30 mA at modulation frequency of 1.5 GHz and 29 MV/m field intensity were achieved.

In this connection, the decrease in measured currents for larger emitter areas (up to 1 cm^2) seems to be unexpected. The record figures reached for emission are presented in [5]. For real emitters with total area about 1 cm^2 these values are less than 1 mA.

In our work we explore field emission properties of a new class of the emitters formed by coating the CNT-polymer composite film onto the flat metal substrate. At present we succeeded to obtain 125 mA of emission current at 7 kV voltage potential for interelectrode gap of 0.5 mm (14 V/μm) for the field emitter diameter of 1 cm. The stable values of emission current of 10-15 mA at field intensity amplitude 7-8 V/μm have been obtained at the half-period sine voltage of 50 Hz.

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Molecular orbital calculations of C_{20}@(8,8)

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The possibility of encapsulation of small fullerenes inside nanotubes was considered recently [1]. It was shown that the armchair (8,8) nanotube is the smallest carbon nanotube which can encapsulate fullerene C_{20} [1]. We use the semiempirical PM3 molecular orbital method with periodic boundary conditions along the nanotube axis [2] to study the structure and properties of the system C_{20}@(8,8). The method was used previously to study the fullerene C_{20} [3] and to calculate the Kekule structure of the ground state of the $(5, 5)$ nanotube [4].

We have found that the structure of the empty (8,8) nanotube in the ground state is the Kekule structure with tripling of the translational period and two essentially different bonds. The bond lengths difference is 0.002 nm. In the ground state of the system C_{20}@(8,8) the angle between nanotube axis and threefold symmetry axis of the fullerene C_{20} is 2.3 degrees and the binding energy of the fullerene C_{20} in the (8,8) nanotube is $U = 0.97$ eV. The consistent value of the interaction energy is obtained with the help of semiempirical potential for analogous systems [1]. The calculated value of energy U is close to the experimental value of the graphite interlayer interaction energy 35 ± 10 meV/atom [5]. Thus we reveal the Van der Waals interaction between the nanotube and the fullerene which causes only negligible distortions of both nanotube and fullerene structures. The calculated eigenfrequency of small vibrations of the fullerene C_{20} along the nanotube axis in the ground state of the system is 120 GHz.

The barriers for motion and rotations of C_{20} and corresponding frequencies of small vibrations are calculated. These barriers are used to estimate the diffusion coefficients for sliding of C_{20} along nanotube axis and the temperature of orientational melting of the system C_{20}@(8,8).

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$\tilde{N}_{60}$ fullerenes as $\mathbf{h}^6$-ligands in transition metals $\boldsymbol{\pi}$-complexes

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The fulerene derivities contaning the metal atoms bonded to the fullerene cage by the bonds of η^2-type were known comparatively long, however the formation of the η^n-complexes (n>2) was of certain difficults.

In this work we discuss the problem of existence of the complexes of the C_{60} fullerenes and their derivatives with the transition metal atoms interacting with a carbon atoms of η^6-π-type.

The calculations of the fullerene C_{60} derivatives $\tilde{N}_{60}R_6$ (R=−, H, F, Cl, Br, CN) where groups R were in the so-called α-positions with respect to the hexagon face were carried out by the DFT-PBE approach. Further the modeling of molecular and electronic structure of the complexes of these molecules with moieties $Cr(C_6H_6)$, $Cr(CO)_3$, MoC_6H_6 è $Mo(CO)_3$ was carried out. Moreover the "dimer" systems $C_{60}R_6$–M–R_6C_{60}, (M=Cr, Mo, R=−, H, F) also were considered.

It was found that addition of six groups R to the carbon atoms disposed in the α-positions with respect to the one of the C_{60} fullerene hexagons promoted the formation of stable complexes. It was shown that similar complexes of "bare" C_{60} can also exist, although their stabilities are far less.

Trapping centers of free charge carriers in the fullerene C_{60} based molecular crystals

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Previously it was reported that original photoelectric properties of fullerene C_{60} complexes with organometallic donors are caused by their unique crystalline structure [1]. It is well known, that optical and electrical properties of semiconductors depend on the defective structure and the local levels in the band-gap, as a consequence. Howere, the information about transpotr properties of given fullerene based compounds is completely absent.

The aim of the work was revealing and detail research of local levels in the band-gap of fullerene C_{60} molecular complexes with copper (II) diethyldithiocarbamate ($\{Cu(Et_2dtc)_2\}_2*C_{60}$) and coordination dimers formed by cadmium/mercury di(n-propyl)dithiocarbamate and the ligand dimethylpiperazine ($[\{(Cd/Hg)(n\text{-}Pr_2dtc)_2\}_2*DMP]*(C_{60})_5*(C_6H_5Cl)_2$) affecting their transport properties.

Thermostimulated currents (TSC) measurements revealed in all materials traps located below the LUMO level of fullerene on 0.43 eV. It allows to suppose that trapping centers are caused by one type of defects. Most probably they are solution molecules disordered in the hollows of the crystal lattice. At the same time the form of TSC spectra indicates various modes of thermostimulated conductivity (monomolecular, bimolecular or mixed with different overtrapping degree) associated with unequal concentrations relations of charge carriers on the shallow and deep trapping centers.

Experementaly obtained parametres eneble to plot thermostimulated current curves analytically calculated within the limits of TSC theory to confirm proposed suppositions.

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