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Dependence of Energy Distribution of Valence Electrons of Carbon Nanomaterials in Different Atomic-Structural States on Their Sizes

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Ultra-soft x-ray emission spectroscopy was applied to study the electronic structure of a number of carbon nanomaterials. The energy distribution of valence electrons was investigated in fullerenes, onions and multi-walled nanotubes obtained using catalysts and without them. It was found that the width of the CKα-bands somewhat increases in the following sequence C60-C70-onions-nanotubes. Narrowing the spectra was revealed when decreasing sizes of nanomaterials of the same kind. It was established that shapes of the CKα-bands in C60, C70, onions, nanotubes are different due to changing the degree of πpz- and σsp2+ πpz-overlapping.

Key words: fullerene, carbon onion, nanotube, electronic structure, x-ray emission spectrum, valence band, hybridization

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Existence of carbon in different structural states, namely in a form of fullerenes, onions and nanotubes have been attracted significant attention to investigations of their atomic-structural characteristics, properties and peculiarities of the electronic structure. In the last few years, a large number of theoretical [1-5] and experimental [6-10] studies have been carried out on the electronic structure of individual nanomaterials. However, the energy resolution achieved in [7-10] by other authors did not make it possible to reveal a number of features in the spectra which could be detected by us. Moreover, the integrated study of the electronic structure of carbon nanosized materials in different atomic-structural states has not been realized yet.

Differences of the atomic structure in different modifications of carbon have to affect the electronic structure peculiarities of the nanomaterials under investigation. So, it is of interest to study the dependence of the peculiarities of the energy distribution of the valence *p*-electrons in fullerenes (C_{60}, C_{70}), onions and multi-walled nanotubes (MWNT) on the atomic structure. At the same time, it is well known [11-15] that the peculiarities of the electronic structure of these materials are affected by the dispersion of crystal materials up to nanosizes. The energy redistribution of the valence electronic states in these specimens is a result of the great contribution of surface atoms with broken bonds into the interatomic interaction. In contrast to crystalline nanopowders, ideal fullerenes do not posses broken bonds and in ideal onions and carbon nanotubes they exist only on the ends of the onions/nanotubes and the contribution of the broken bonds into the total value of bonds is insignificant in the above materials. Therefore, it is necessary to elucidate, whether effects of narrowing and changes of the shape of the CKα bands under decreasing sizes of carbon materials become apparent and in what way.

With this purpose the CK_α-emission bands of the above nanomaterials have been investigated since these bands reflect the energy distribution of the C*p*-electrons, which make the main contribution into the interatomic interaction in these modifications of carbon.

C_{60} studied in the present paper was obtained by "MER Corporation" with high purity (99,9 %). Carbon onions were synthesized by the detonation from nanodiamonds, which were annealed in a high vacuum 10^{-5} Pa, in a way similar to [16] at 1500 ºC for 10 min. Catalytic nanotubes with average diameter 20 nm was obtained by Pryluckij E.V. in the low-temperature process of the carbon single-oxide conversion at the presence of Co (11%) and Fe (30 %) catalysts. Nanotubes with diameters 4 and 140 nm were produced by "MER Corporation" in arc-discharge.

The CK_α-spectra of the carbon nanomaterials investigated were obtained by means of the ultrasoft X-ray emission spectroscopy using a spectrometer PCM-500. The spectrometer energy resolution in the range corresponding to the energy of the TiL_l-band was found to be about 0,2 eV. The operation conditions of the electron tube were: accelerating voltage, U_a=5 kV; anode current, I_a=2,5 mA (I_a=0,5 mA when fullerenes were investigated). To prevent superimposition of the CK_α-band of hydrocarbons vapors the trap freezing these vapors out was used.

In order to establish the reasons of changes of the electronic structure in the sequence C_{60}-C_{70}-onions-nanotubes, the CK_α-emission bands of these nanomaterials were compared (Fig. 1). The CK_α-spectra presented in Fig. 1 have been normalized so that intensities of their main peaks "*c*" are equal.

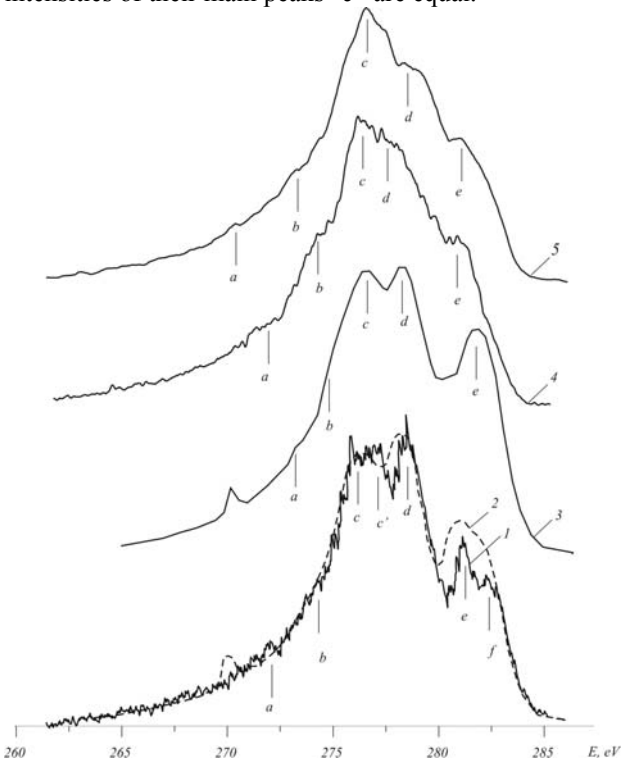

Fig. 1. The X-ray emission bands of fullerene C_{60}, obtained by us (1), fullerene C_{60} [9] (2), fullerene C_{70} [9] (3), onion (4), multi-walled nanotubes (5).

As can be seen from Fig. 1, the low-energy parts of the spectra of the nanomaterials investigated have a very similar shape, and only the "*b"* feature of the onions CK_α-band is noticeably greater resolved in comparison with that of other nanomaterials under investigation. It is evidence of the fact that the energy distribution of the *p*-electronic states involving into the sp^2-hybrid bonds, which are reflected in the low-energy parts of the CK_α of the materials studied, are similar. At the same time changes of shapes of the X-ray emission bands were found in the energy region 275÷277 eV due to increasing relative intensity of the "*c"* maximum and decreasing relative intensity of the "*d*" peak when going from fullerenes to onions and nanotubes. The minimum of the CK_α band dividing the "*c*" and "*d*" peaks is the deepest in the C_{60} spectrum and the shallowest in the nanotubes' CK_α. The deepest minimum is observed in the bands of fullerenes C_{60} since there are bonds with two different lengths (0,144 nm between two pentagons and 0,139 nm between the pentagons and hexagons) in the C_{60} molecule surface [17]. As a result, the overlapping degree of the Cp_z-orbitals with the sp^2-states in C_{60} atoms on distances 0,139 nm inside the molecules differs from that in atoms on the distances 0,144 nm. Therefore, the $\sigma+\pi_5$ and $\sigma+\pi_6$ mixed sub-bands reflected in the "*c*" and "*d"* maxima in C_{60} are separated.

The C_{60} CK_α-emission bands obtained by us with apparatus distortions $\Delta E<0{,}2$ eV are very similar to those measured in [9] with $\Delta E=0{,}4$ eV (Fig. 1, curves 1 and 2). In spite of the smaller resolution of the elements of the fine structure of the spectra [9], these electronic structure peculiarities reflect the energy states of the C*p*-electrons in fullerenes quite well. In order to ascertain the differences of the energy distribution of the C*p*-states in C_{60} and C_{70}, it is necessary to analyze the CK_α-emission bands obtained in [9] under equal experimental conditions.

From comparison of C_{60} bands it is clear that the relative intensity of the "*d"* peak and its separation from the "*c"* peak decrease obviously due to the decreasing density of the mixed σ+π-binding states and broadening region of their distribution when going to fullerene C_{70} (Fig. 1, curve 3). It is a consequence of the decreasing degree of the Cp_z- and sp^2-orbitals overlapping inside the C_{70} molecules as compared with that in C_{60} and the presence of four σ-bonds, which are longer, then those in C_{60}. A quite strong division of the top of the CK_α-emission band into two peaks is still observed in the spectrum of C_{70} since two groups of bonds (0,137÷0,141 nm and 0,146÷0,147 nm) can be conditionally marked out among eight interatomic distances.

The relative intensity and resolution of the «*d*» peak in the onions spectrum decrease in comparison with those in C_{60} and C_{70} spectra. But nature of these changes is different from that in fullerenes. Distances between two atoms of carbon in each layer of onions are equal but the surfaces forming onions have different diameters, which decrease when deepening into the particles. The overlapping degree of the πp_z-states and the sp^2-hybride orbitals inside the spherical atomic surfaces increases owing to the increasing curvature of particles surfaces when approaching the onions core. Since onions particles are formed by 3-15 concentric shells, the overlapping degrees of the π and σ-orbitals change uninterruptedly. The division of the top of the onions bands is smaller then that in fullerenes C_{60} and C_{70}.

The relative intensity of the «*d*» peak almost does not change but the minimum dividing features "*d*" and "*c*" becomes shallower when going from onions to nanotubes (Fig. 1, curves 4 and 5). It is conditioned by the addition of the contributions of the states, which are involved in the π-bonds along the nanotubes axes, in the mixed π+σ-states in the radial planes and in different layers of nanotubes, to the energy redistribution.

Quite noticeable changes are observed in the region of high energies corresponding to the pure π-states when going from fullerene C_{60} to nanotubes (Fig. 1). Particularly, intensity of this π-sub-band in the CK_α of C_{70} increases (but in the onions and nanotubes CK_α it does not) in comparison with that of C_{60}. Besides, the above π-sub-band is divided into two peaks «*e*» and «*f*» only in the C_{60} CK_α-spectrum. It is conditioned on the fact that in the C_{60} spectrum the «*e*» feature reflects the π_4-sub-band appeared owing to overlapping of the p_z-obitals above the surface of fullerenes atoms on the distances of about 0,139 nm. The «*f*» feature reflects the π_5–sub-band due to overlapping of the p_z-obitals in carbon atoms on the distances of about 0,144 nm. The «*e*» and «*f*» features reflect the electronic states

involving into the π-bonds over the molecules surface. Separation of these peculiarities was not observed in the spectra of C_{70}. It is concerned with the fact that the energies of electronic states involved into these π-bonds between the C_{70} atoms on five distances (which are different but have the nearly equal values) differ slightly and the energy regions corresponding to these electronic states overlap.

It makes the rising of intensity of the «*e*» maximum in the C_{70} CK_α. A decrease of intensity of the π–sub-band and its separation from the main maximum occur when going to the onions CK_α. It is obliged to the fact that the degrees of the π-overlapping of the p_z-orbitals are similar in each sphere in onion since distances between two neighboring atoms binding by the sp^2-hybride σ-bonds in onions are equal in contrast to those in fullerene. But a curvature of the spherical atomic surfaces increases when deepening into onion. As a result the degree of the π-overlapping over the spherical surface decreases and the overlapping of the p_z-orbitals with the sp^2-states inside the spheres increases. In a consequence of such continuous changing of the π-overlapping of these states over and inside the surfaces of onions layers the corresponding energy regions overlap. As a result the separation of the π-sub-band from the main maximum decreases.

In the spectra of nanotubes intensity of the «*e*» feature reflected the πp_z-states and separation of «*e*» peak from the main maximum are the same as those in onions. It concerned obviously with the fact that the π-overlapping in the radial plain over the surface of nanotube is smaller then that inside MWNT. The π-overlapping will be changed quasicontinuously when increasing the curvature of nanotubes walls from the outer to the inner one. Therefore, it is similar to the change of the curvature of the onions layers. It obviously leads to resemblance of the shapes of the «*e*» features in onions and nanotubes. The Cp_z-orbitals overlapping degrees above the surfaces and inside the nanotubes along their axes are identical. Degrees of these overlapping are different from that in radial planes. Therefore, states involved in these overlapping will be concentrated in the energy intervals, which are intermediate between those corresponding to the overlapping in the radial planes above and inside nanotubes. It leads to the decreasing separation of the «*e*» feature from the main maximum.

Quite noticeable differences were revealed when comparing the full width at half-maximum (FWHM) of the spectra of the nanomaterials under investigation. In the sequence C_{60}-C_{70}-onion-nanotubes the emission bands are noticeably broadened owing to the increasing contribution of the σ-states into the sp^2-interaction as a consequence of the overlapping of the Cp_z-orbitals with the tangentially directing orbitals when decreasing the surface curvature of the nanocarbon materials.

From the above analysis it is clear that differences in degrees of the π-overlapping of the Cp_z-orbitals with sp^2-hybryd bonds inside and over the curved atomic surfaces with hybrid bonds and the contribution of the mixed σ+π-binding states inside fullerenes, onions and nanotubes decrease in the sequence C_{60}-C_{70}-onion-nanotubes.

Thus differences between the widths of the CK_α-bands of different kinds of the carbon nanomaterials can be revealed due to the changing degrees of the π-overlapping of the Cp_z-orbitals one with another and with sp^2-hybride states.

Comparison of the CK_α-emission bands (normalized so that intensities of their main peaks «*c*» are equal) of a number of carbon nanomaterials (fullerenes C_{60} and C_{70}, graphite and onions, nanotubes with diameters 4 and 140 nm, highly- and low-imperfect nanotubes) is presented on Fig 2. The peculiarities depending on the change of sizes of these nanomaterials are revealed in every pair. As have been stated above the change of widths of the CK_α- and others emission bands was observed in a number of crystalline materials [11-15] owing to a contribution of the surface atoms with broken bonds (which number is commensurable with a quantity of volume atoms) into the interatomic interaction when dispersing materials.

However, the sp^2-hybride states in fullerenes are involved into the closed σ-bonds and the number of the broken bonds in nanotubes is small. Therefore, it is important to compare the CK_α-emission bands of materials of the same kind but with different sizes to elucidate the reasons of the CK_α-bands broadening when going from the smaller to larger objects.

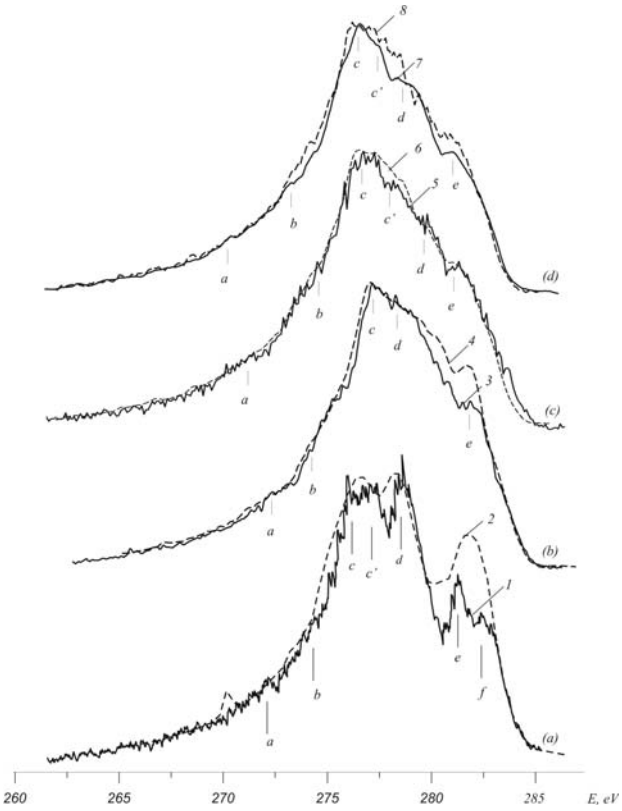

Fig. 2. The CK_α-emission bands of C_{60} (1), C_{70} [9] (2), onions (3) and thermally exfoliated graphite (4), nanotubes with diameter 4 nm (5), nanotubes with diameter 140 nm (6), catalytic nanotubes with diameter 20 nm (7), catalytic nanotubes with diameter 70 nm (8).

It is necessary to compare the CK_α-bands of C_{60} and C_{70} obtained under equal conditions [9] to elucidate the dependencies of the C*p*-electrons energy distribution on the fullerenes sizes. From Fig. 2 *a* (curves 1 and 2) it is clear that the C_{70} spectrum is somewhat wider (by 0,2-0,5 eV) then that of C_{60} due to a shift of the long-wave contour of the C_{70} CK_α relative to that of C_{60}, whereas the high-energy parts of the contours of the «*e*» maxima completely coincide. It is determined by the fact that the surface curvature decreases and the torsion angles between the vertexes of hexagons and planes of a spatial figure corresponded to a geometric shape of fullerene increase when going from C_{60} to C_{70}. It leads to decreasing the overlapping of the sp^2- and Cp_z-orbitals inside the molecules and increasing the overlapping of p_x- and p_y-orbitals, which are tangential to the molecules surface. It is followed by the additional splitting of these p_x- і p_y- states. The contribution of the sp^2-states involved into bonds with different lengths (particularly l=0,137 nm, that somewhat shorter then that in C_{60}) increases in this energy interval in C_{70}. It is reflected in the broadening of the C_{70} central CK_α-band in comparison with that of C_{60}.

Comparison of the CK_α-emission bands of thermally exfoliated graphite and onions (Fig. 2 *b*), where distances between the graphene layers are almost equal, showed that the width of the main maximum in onions is much less then that in thermally exfoliated graphite. This narrowing of the spectrum when going from graphite to onions is observed not only in the region, where the σ+π- and the π-bindnig states are concentrated, but also in the low-energy part, where the sp^2-hybride states involved in the σ-bonds are located. It is a result of the considerable contribution of the C*p*-states (dehybridized due to breaking of the bonds on edges of graphene fragments) to the energy distribution. It is confirmed by the data of the high-resolution electron microscopy (Fig. 3), which show that onion layers are torn.

Comparison of the spectra of nanotubes with diameters 4 and 140 nm (Fig. 2 *c*) obtained without catalysts revealed the broadening of the CK_α-emission bands only in the energy region $h\upsilon$=277,5÷279 eV. It can be caused by the decreasing curvature of MWNT when increasing diameters with decreasing the overlapping degree of the p_z-orbitals and σ-states inside nanotubes. These changes are due to the increasing of the «*d*» feature intensity when going from nanotubes with diameter 4 nm to those with diameter 140 nm. It is owing to the CK_α-band width increasing.

Comparison of the spectra of the catalytic MWNT with diameters 70 and 20 nm (Fig. 2 *d*) (thin MWNT with diameter 20 nm contain many defects after purifying from 11 % Co catalyst) showed that the width of the CK_α of thick nanotubes at $I>1/2I_{max}$ (where I is spectra intensity) was greater then that in the spectrum of thin imperfect nanotubes. Difference between stated widths is greater then that in the spectra of MWNT obtained without catalysts. It is due to the additional contribution of broken bonds in thin catalytic nanotubes, which appeared when purifying nanotubes from catalysts, into the narrowing of the CK_α of thin nanotubes.

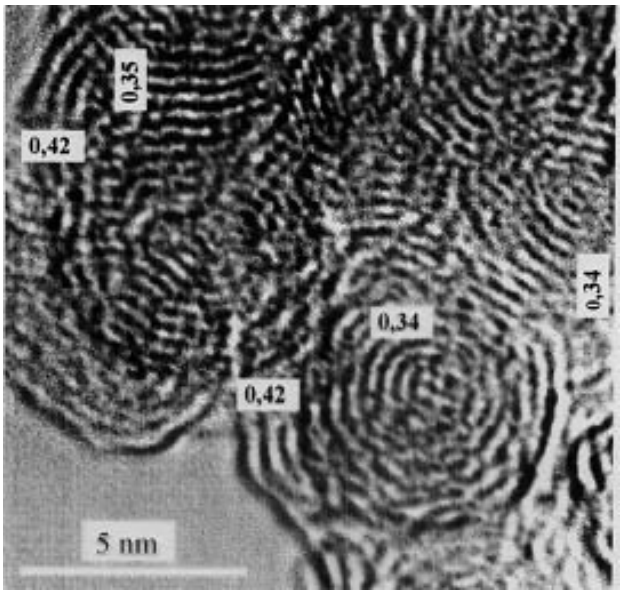

Fig. 3. Onion particles images obtained by means of the high-resolution electron microscopy.

Thus, comparison of the narrowing of the CK_α-bands of nanomaterials of different kinds showed that in the sequence C_{60}-C_{70}-onions-nanotubes these narrowings increase especially with (besides changing of π-overlapping) the increasing number of the broken bonds in these nanomaterials due to the presence of edges, ends and vacancies, which quantity in onions and nanotubes is greater then in fullerenes.

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Залежність енергетичного спектра валентних електронів нановуглецю в різних атомних станах від їх розміру

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Методом ультрам‘якої рентгенівської емісійної спектроскопії вивчено електронну структуру ряду вуглецевих наноматеріалів. Досліджено енергетичний розподіл валентних електронів в фулеренах, оніонах і багатостінних вуглецевих нанотрубках, одержаних з використанням каталізаторів і без їх участі. Виявлено зростання ширини CKα-смуг в послідовності C60-C70-оніони-нанотрубки. Виявлено звуження спектрів при зменшенні розмірів наноматеріалів одного виду. Встановлено, що форми CKα-смуг в C60, C70, оніонах і нанотрубках різні завдяки зміні ступенів πpz- та σsp2+ πpz-перекриттів.