

Carbyne as a cluster nanoallotropic form of carbon

*N.I.Slipchenko, V.G.Udovitsky**

Kharkiv National University of Radio Electronics,
14 Lenin Ave., 61000 Kharkiv, Ukraine

*Scientific Center of Physical Technologies MESYS and National Academy of Sciences of Ukraine, 6 Svobody Sq., Box 4499, 61022 Kharkiv, Ukraine

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Since the discovery of fullerene, carbon-based nanostructures have become one of the hottest research topics in science. Carbon allotropes based on sp^3 -hybridized carbon (diamond) and sp^2 -hybridized carbon (graphite, graphene, fullerenes, nanotubes) have well-established properties, many of which are technologically relevant. But carbyne — the third allotropic form of carbon, based on the sp -hybridization of its atoms, despite of the fact that it was opened 50 years ago, still remains one of the most controversial allotropic forms of carbon. In this critical review the wide spectrum of the information concerning synthesis, investigation of properties and application of carbyne and carbyne-based nanostructures is presented. Necessity of consideration carbyne as cluster nanomaterial with special characteristics is proved.

После открытия фуллеренов углеродные наноструктуры стали одной из самых актуальных тем научных исследований. Свойства аллотропных модификаций углерода, основанных на sp^3 - (алмаз) и sp^2 -гибридизации его атомов (графит, графен, фуллерены, нанотрубки), достаточно хорошо изучены и многие из них реализованы на практике. Но карбин — третья аллотропная форма углерода, имеющая sp -гибридизацию его атомов, несмотря на то, что он был открыт более 50 лет назад, до сих пор остается одной из самых противоречивых и дискуссионных аллотропных форм углерода. В данном критическом обзоре представлен широкий спектр информации, касающейся получения, исследования свойств и применения карбина и наноструктур на его основе. Обосновывается необходимость рассмотрения карбина как кластерного наноматериала с особыми свойствами.

1. Introduction

Since the discovery of fullerenes in 1985 investigations of carbon and various carbon-based materials is one of the most actual directions in fundamental and applied science. In recent years among a great family of different carbon materials research of carbon-based nanostructures, namely, nanographites, nanodiamonds, fullerenes, nanofibers, carbon nanotubes, graphenes and others named allotropic forms or simply carbon nanoforms have aroused considerable interest. This is attributable to their unique physico-chemical properties and their appli-

cations in various fields of science and engineering both already realized, and potentially possible. At the same time the scientific discussion concerning carbon allotropy is not terminated. And if there are no significant contradictions in understanding of two allotropic modifications of carbon, namely, graphite and diamond known to a man since ancient times, the same cannot be said about its third allotropic modification — carbyne.

Carbyne, which was synthesized artificially more than 50 years ago, still remains one of the least clear and contradictory allotropes of carbon. There are vastly different

opinions as to its existence as independent allotropic modification of carbon — from recognition to complete negation. Let us cite some judgments on it of experts, complete authorities in the field of carbon materials published at different time. "Over many years diamond and graphite were the objects of the sophisticated treatment and hence they are studied and characterized comprehensively. But unambiguous and rigorous evidences of carbyne individuality and its structure have not been yet received, unfortunately. But there is a great number of publications devoted to carbyne, there are critical reviews of the accumulated experimental data, new approaches to synthesis and methods for analysis of carbon linear forms. Interest in them has quickened appreciably within recent years. Based on all this one might expect that carbyne existence will be soon found imperatively." This quotation is taken from the work [1] published in 2003. But 7 year later, in 2010, Harold Croto — one of the Nobel prize laureates in chemistry awarded to him in 1996 for discovery of fullerenes stated his explicit belief that "... existence of carbyne is a myth based on poor science and, if not, accepting of desirable for the reality" [2].

Nobody has not yet succeeded in synthesizing carbyne crystals of macroscopic dimensions and at present solution of this problem seems hardly probable or impossible in general. All experimental results in carbyne being published till now are associated with synthesis and investigation of its nanoclusters, nanowires and nanofilms, i.e. nanostructures with 0D, 1D and 2D dimensionality which can be used according to different functions. So, if carbyne is considered not as an ordinary allotropic form of carbon, comparing it to graphite and diamond, but as a cluster material, i.e. its special nanoallotropic form, then consensus can be reached between contradictory points of view about its existence. Taking into account this circumstance and mentioned above discrepancy of opinions about carbyne, the aim of this paper consists in making critical analytical overview of the available information relating to the history of discovery and study of the structure and different properties as well as fields of application of carbyne. Such information of the review will be useful to experts who are interested in carbon materials and those who want to understand the existing contradictions of different points of view to car-

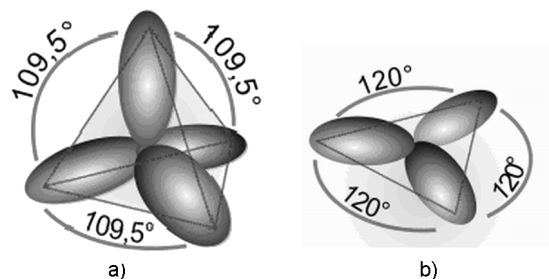


Fig. 1. Scheme of sp^3 (a) and sp^2 -hybridized (b) orbitals of the carbon atoms.

byne as one of the allotropic modifications of carbon.

2. Condensed carbon as a polymeric material

Carbon, according to its properties, differs greatly from the elements following it in the Mendeleev's periodic system — nitrogen, oxygen and fluorine. The first and foremost surprising thing is that carbon in any of its forms under conventional condition is a solid, while nitrogen, oxygen and fluorine are gases. Melting point of nitrogen is about -210°C , and melting point of carbon in the form of graphite is about $+4000^\circ\text{C}$. D.I.Mendeleev paid attention to this fact and supposed that such difference in their properties was determined by the polymeric structure of carbon molecule, i.e. solid carbon is a polymeric substance [3]. Now the fact that the diamond crystal (of either modification — cubic or hexagonal) represents one giant spatial-laced macromolecule with sp^3 -hybridization of valence electrons (Fig. 1a) is beyond doubt. At the same time a monatomic layer in the ideal graphite also represents one polymeric but two-dimensional-laced macromolecule with sp^2 -hybridization of valence electrons (Fig. 1b).

It appeared reasonable to assume the possibility of existence of one-dimensional (chain, linear) form of carbon with sp -hybridization, which the atom of carbon reveals in many combinations with other atoms.

3. Short history of carbyne discovery

The linear form of the condensed carbon has not being discovered in a nature or synthesized artificially and remained a missing link in the carbon allotropic for a long time. In 1885 A.Bayer, the known German chemist, tried to perform synthesis of the chain carbon using derivative of acetylene

(H-C≡C-H). However Bayer's attempts to receive polyynes (compound containing no less than three insulated or conjugated C≡C bonds in the molecule) were not successful. He received very unstable hydrocarbon consisting of four molecules of acetylene joint in a chain. Instability of the lowest polyynes served Bayer as a basis for creation of the stress theory in which he made the conclusion about impossibility to obtain the chain carbon. Authority of the scientist (in 1905 he was awarded the Nobel Prize in chemistry for the works in organic dyes and hydroaromatic compounds) damped ardor of researches to the polyynes synthesis and over an extended period the works were not conducted in this direction.

In 1960 Soviet scientists V.I.Kasatochkin, A.M.Sladkov, Yu.P.Kudryavtsev and V.V.Korshak received carbyne — polyynes ($-C\equiv C-$)_n and cumulene ($=C=C=$)_n forms of carbon with linear hybridization experimentally using the method of oxidization dehydropolycondensation of acetylene and later using other methods. The polyynes and polycumulene forms are furthermore denoted, respectively, by α -form (α -carbyne) and β -form (β -carbyne). It was also determined that carbyne can be crystallized in a hexagonal system and under the pressure of 9 MPa at 1800°C a transformation of a less dense α -form into more dense β -form [4]. 11 years later the scientific discovery with the formula: "existence of a new unknown earlier phenomenon of a crystalline form of carbon — carbyne characterized by chain (linear) structure of carbon macromolecules in contrast to diamond and graphite is established experimentally" was registered in the USSR [5]. Registration of the given discovery with the priority of 1960, as it was mentioned in [4], became possible and took place only after discovery of carbyne-like materials in the nature. In 1967 it was reported about detection of the material very close to the carbyne structure in the meteorite New Urey [6]. In 1968 in a meteoritic crater Rice (Bavaria, Germany) the crystalline form of carbon of white colour called chaoite was detected [7]. Later it was revealed, that the characteristics of X-ray diffraction from chaoite also closely coincide with retrieved ones for carbyne. After finding of carbyne about two tens of other materials similar to carbyne were synthesized experimentally and found out in the nature: α - and β -carbyne, chaoite and some forms not having titles, and simply labeled by serial

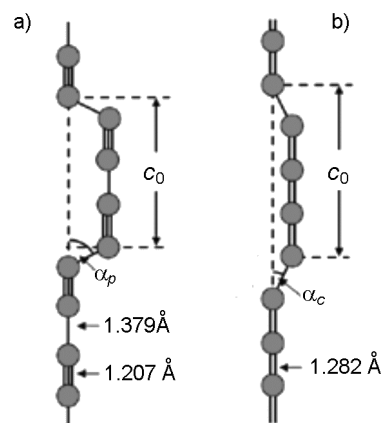


Fig. 2. Loop model of carbyne for polyynes (a) and cumulene (b) of Heimamm's et al. [14].

numbers [8]. But in all these materials except for sp -carbon atoms the presence of atoms in the conditions of sp^2 - and sp^3 -hybridization was revealed, and also atoms of other chemical elements, i.e. such materials which could not be considered as carbyne in the pure state [9].

4. Carbyne structure

All long-standing history of investigation into carbyne structure and its other properties down to the present time is disputable. It contains contradictory judgements of the contributors, among which there is even a full denying carbyne as an independent allotropic modification of carbon grounded only on the sp -hybridization of its atoms [2, 10–12]. The first model of carbyne structure, offered by the authors of its discovery, guessed, that the carbon chains have the strictly linear form and are arranged in parallel with each other forming a lattice of a hexagonal type. Later this model was improved and for the best conformity to the data of X-ray diffraction a little bit other arrangement of linear carbon circuits in a unit cell was offered [13]. But this model also didn't give a good conformity between theoretical and experimental data and R.Heimann has offered a "loop" model for better correspondence with experimental data [8, 14]. According to this model the carbyne chains are perceived not to be linear, and contain fractures (loops), as it is shown in a Fig. 2.

It is supposed that such chains with loops-fractures are placed in space in such a way that they also form a lattice of a hexagonal type (Fig. 3) [11].

Mathematical calculations show that the loop length, i.e. c_0 parameter can be ex-

pressed through the fractures angles of the chain in polyynes α_p and cumulene α_c , and also through a number of atoms in the chain fracture n and a length of single, double and triple bonds between atoms of carbon (C-C, C=C, C≡C) in the following way [14]:

$$c_0(\text{polyynes}) = \\ = \frac{n}{2}r(\text{C} \equiv \text{C}) + \left(\frac{n}{2} - 1 + \cos\alpha_p\right)r(\text{C} - \text{C}),$$

$$c_0(\text{cumulene}) = \\ = (n - 1)r(\text{C} = \text{C}) + \cos\alpha_c r(\text{C} - \text{C}).$$

Parameters n , α_p , α_c are variable in the given model; this makes it possible to carry out fitting for reaching better correspondence between theoretical calculations and experimental data of diffraction. Now when analyzing the peculiarities of the carbyne structure based on the loop model the ideas are also suggested that in such a structure the carbon atoms can form a covalent bond not only with atoms of this chain but with the carbon atoms from the closely located neighboring chains [15]. It was hypothesized [16] that the carbyne structure can be considered as an intermediate between the graphite and diamond structures. Such a structure in authors' opinion can be obtained if graphite is subjected to a strong compression along the axis c . One more structure model suggests that the linear sp -sections in carbynoids alternate with the carbon atoms in sp^2 - and sp^3 -states. In this case sp^2 - and sp^3 -atoms bend chains, and the bonds remaining free can be used for formation of interchain bonds or for binding of impurity atoms [9, 17, 18].

A short overview of the offered carbyne structure models has shown that there is no general agreement as to the given problem, and three dimensional structure of the ideal carbyne remains the subject of the continuing discussions. In the last few years interest to computer modeling increased and investigations into computer modeling of a possible three dimensional carbyne structure were started [15, 17–19].

5. Diagram of the carbon phase state and discussion about the carbyne place on it

Plotting the carbon phase diagram in the possible bigger range of values for pressure and temperature represents considerable sci-

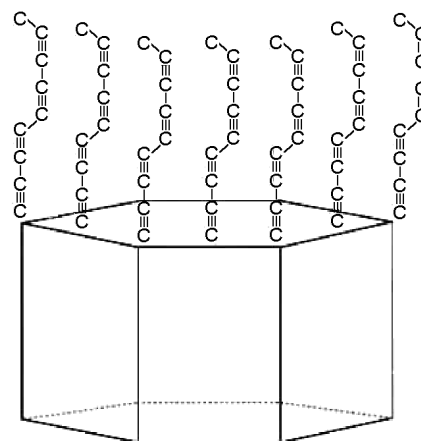


Fig. 3. Carbyne hexagonal lattice model formed by the chains with loops [11].

entific interest for studying the properties of carbon in different aggregate forms and understanding of patterns of formation and interconversions of its different allotropic modifications. Moreover, the phase diagram of carbon represents also a considerable practical interest, as it allows forecasting capabilities of creation and properties of different carbon materials. First of all, the phase diagram of carbon is interested earlier (and continuous to be interested now) for the scientists involved in the studying of the problem of diamonds synthesis. The curve of graphite — diamond equilibrium and condition of each of these phases equilibrium represent a special interest for such purposes. One of the first phase diagrams of carbon in a broad band of pressures and temperatures has been created by F. Bandy and his employees [20]. Later, in the process of appearance of new experimental data, it was repeatedly updated and supplemented by him. One of the last versions of the diagram plotted by this author on the data for 1994, which even now are frequently used and cited in the literature, is shown in Fig. 4 [21].

It should be noted, that, despite of a great number of carried out researches into thermal properties of carbon, its phase diagram still contains much "blank spaces" and inconsistency between results obtained by different authors. It is stipulated by considerable experimental difficulties, because the miscellaneous phases of carbon become stable at extreme temperatures and pressure. The researches in the field of high temperatures and pressures are hampered not only by complexity of their reaching, but also methodically exact measurement with a

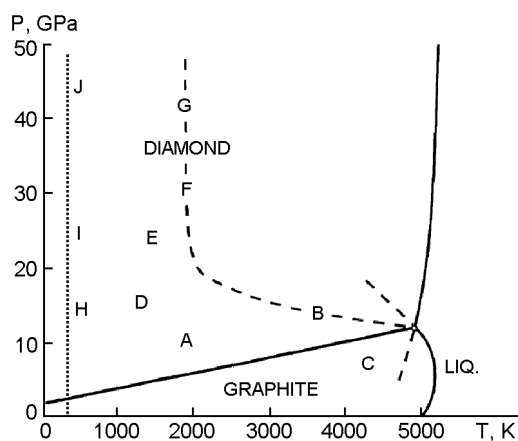


Fig. 4. P, T — phase diagram of carbon: solid lines represent equilibrium phase boundaries; A — a segment of commercial synthesis of diamond from graphite using catalysts; B — P/T threshold of very fast solid-solid transformation (less than 1 ms) of graphite to diamond; C — P/T threshold of very fast transformation of diamond to graphite; D — a segment of a hexagonal diamond; E — the upper ends of shock compression that convert particles of hexagonal graphite to particles of hexagonal diamond; F — the upper ends of shock compression that convert hexagonal graphite to cubic diamond; B, F, G — threshold of P/T cycles that convert either type of graphite or hexagonal diamond into cubic-type diamond; H, I, J — a path along which a single crystal hexagonal-type graphite compressed in the c -direction at room temperature reversibly loses some graphite characteristics and acquires properties of diamond-like polytype [21].

minimum error, that is necessary for comparison of the results of different researches. In such a situation the role of theoretical calculations and physical simulation, and comparison between the obtained results and experimental data increases [22–24].

As of carbyne, the problem where on the phase diagram is a segment of its existence is also debatable. Until recently the problem of carbyne existence on the phase diagram of carbon found the reflection in existence of two alternative phase diagrams of carbon [25]. According to first of them [26, 27] in temperature range 2600–3800 K there are steady phases of carbyne. At full conversion of graphite into carbyne the carbyne triple point a solid-liquid-vapor is implemented, its pressure and temperature are, respectively, equal to: $P = 2 \cdot 10^4$ Pa, $T = 3800$ K. According to the second phase diagram [21]

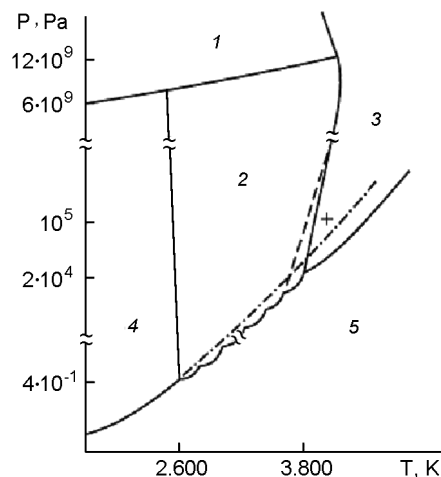


Fig. 5. The part of the phase diagram of carbon, in which there is a carbyne segment: 1 — diamond, 2 — carbyne, 3 — liquid, 4 — graphite, 5 — vapor.

there is only graphite triple point with parameters: $P \sim 10^7$ Pa, $T \sim 5000$ K. The existence of the carbyne segment in this diagram is questioning. One of the most important motives for discussion about the phase diagram of carbon is the necessity of legible understanding of behavior and prediction of melting point of carbon construction materials, first of all of graphite at its heating to high temperatures. The generalization of numerous experimental works results in a conclusion that graphite as a construction material, depending on heating velocity, will behave variously. At fast heating, for example, with a pulsed laser beam, in experiments it was obtained the melting point $T_{melt.} \sim 5000$ K, and at sluggish heating in fixed experiments $T_{melt.}$ of graphite turns out to be approximately 1000 K (or even more) less. It is quite correctly explained by fact that at sluggish heating the graphite-carbyne solid phase transition is possible in graphite [28]. For the first time such suggestion was proposed by A.G.Whittaker [26, 27] and he marked the carbyne segment on the phase diagram. Fig. 5 shows this phase diagram supplemented by value a triple point (+) obtained in [29].

Until the present time the solid state graphite — carbyne transition was observed by different authors in many experiments and consequently does not provoke the special objections against the possibility for existence of the mentioned above two alternative phase diagrams — with carbyne segment and without it [21, 25–27]. The apparent inconsistency in existence of dif-

ferent phase diagrams of carbon is eliminated in the event that for the description of all possible thermodynamic states passing by carbon at its heating, not only pressure and temperature (P , T), but also the third variable — dT/dt (heating rate U_h) are used. In such a case the phase diagrams, close to the fixed diagrams with the carbyne triple point (carbyne-liquid-vapor) are implemented at $U_h \leq 10$ K/c. At $10 \text{ K/c} \leq U_h \leq 10^8$ K/c the non-steady phase diagrams are implemented. In the process of increase in U_h the expansion of carbyne segment is narrowing and temperature and pressure in the triple points of graphite-carbyne-vapor and carbyne-liquid-vapor are increasing. At $U_h \geq 10^8$ K/c the phase diagram without the carbyne segment is implemented [28, 30].

6. Development of methods of carbyne synthesis on the basis of modern technologies

The development and research of different chemical and physical methods of carbyne and carbyne containing structures synthesis, for example, thin films, composites etc. is now proceeded. Alongside with elaborated earlier methods of chemical synthesis of carbyne by realization of different reactions of liquid and gaseous reactants, methods of electrochemical synthesis and synthesis in a flame of combustion of different hydrocarbon and other carbon-containing compound are also developed. Among the physical methods of synthesis, which now are frequently mentioned in the publications associated with laboratory synthesis of carbynes, it should be noted the following:

- Synthesis in plasma of an arc discharge between graphite electrodes located in the gas or liquid environment;
- Synthesis at laser ablation of graphite;
- Synthesis at magnetron and ion-beam sputtering of carbon targets etc.

It is possible to acquaint in more detail with different methods of carbyne and carbyne containing materials synthesis in the monographs and reviews [8, 9, 11, 31–33], and also in the numerous original articles indicated in the references of these works. But despite of a great number of executed experimental synthesis of carbyne nobody has yet succeeded in receiving its pure crystals of the macroscopic sizes or pure powder till now. Only carbyne containing mixtures with different quantity of impurities and cross-links between the chains were always received [12]. Therefore commercial produc-

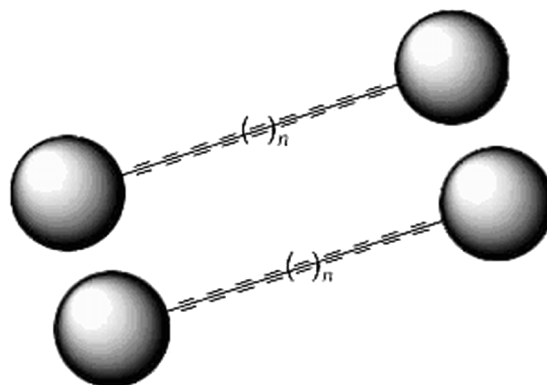


Fig. 6. Model demonstrating stabilization of carbyne chains.

tion and sales of the certificated material is also absent, and the researches are carried out only using the samples obtained under laboratory conditions. Moreover, the works on chemical synthesis of solid phase structures consisting only of carbon linear chains are explosion-dangerous owing to a high reactivity of such chains and tendency to formation of cross-links between them with exothermic effect [2, 34]. Therefore, according to the settled now opinion a pure carbyne as the third allotropic form of carbon, in contrast to graphite and diamond, can exist only in the form of nano structures (particles, films, clusters etc.) or incorporations in matrixes of any other materials. In [35], for example, it is said, that the carbyne crystals, synthesized and detected in the nature, do not exceed 100 nm in size.

7. Methods of carbyne chains stabilization

Different methods of long carbyne chains stabilization are now developed taking into account the surveyed above problems of instability and poor reproducibility arising at their synthesis. One of such methods consists in fastening (vaccination) of different molecules or functional groups on each of end of the chain [11, 36], which should perform some role of an anchor stabilizing a chain, as it is shown in a Fig. 6 [36].

In this case the maximum long linear carbon chains, which has been synthesized and stabilized using a vaccination of endgroups, contain no more than 44 atoms of carbon [37, 38]. An alternative method, which is theoretically modeled now and is already implemented in experiment, is the synthesis of carbyne chains inside carbon nanotubes [39–41]. Fig. 7a shows the atomic model of a carbyne chain placed inside the central tube of the four-layer carb-

on nanotube and Fig. 7b shows transmission electron microscopy image of a high resolution [40], supporting the opinion of the authors about the presence of the carbon chain (C-chain), about 20 nm in length (such a chain should contain more than 100 atoms of carbon), in a right-hand part of the innermost tube of the multilayer carbon nanotube.

The presence of carbon chains inside the multilayer CNT, obtained by an arc method in [40], besides the electron microscopy images is also confirmed instrumentally by the Raman spectroscopy. The $sp-sp^2$ hybrid systems (Cn@SWNT), consisting of the aligned single-wall CNT containing inside the linear carbon circuits (Cn) obtained using PECVD method are considered in [41]. Confirmation of the presence of linear carbon chains inside single-wall CNT in such hybrid system is also the presence of a strong band in range of wave numbers $\sim 1760-1860\text{ cm}^{-1}$ of its Raman spectrum. It is also noted, that the conduction electrons in such hybrid system behave similarly to a Tomonaga-Luttinger liquid. In [42] it was reported that Ag nanoparticles, their average size being equal to 20–40 nm, forming water-colloidal solution are used for stabilization of linearly-bound carbon chains. Such solution was mixed with a solution containing polyene chains and then put on a substrate. After evaporation of a solvent the cluster system containing silver nanoparticles and carbon chains was formed. The system was stable enough in time. Other methods for stabilization of the chains of linearly-bound carbon atoms are also being developed.

8. The main properties and application of carbyne and carbyne containing materials

Let's dwell on the properties and already known and potential applications of carbyne and materials based on. Thus it is necessary to take into account the fact that now, as mentioned above, there are no well reproducible methods and techniques for obtaining carbyne samples identical enough in a structure and properties. Therefore the results, received by the different authors, describing carbyne properties can not be compared among themselves quantitatively with a high correctness and it is possible to compare them only qualitatively. For example, chaoite, found in the nature, has white color (sometimes with a grey shade) [7] and it is frequently named as a white carbon. The main properties of carbyne synthesized

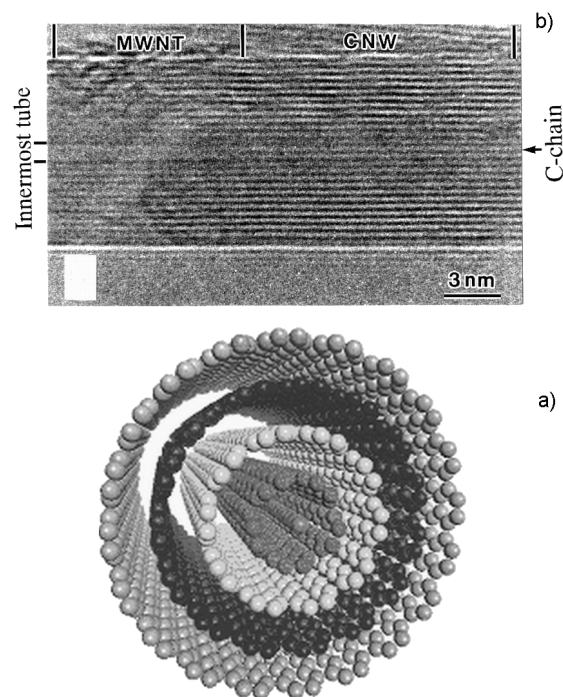


Fig. 7. Atomic model of a carbon chain inside the four-layer CNT (a) and transmission electron microscopy image of a high-resolution fragment of multilayer CNT containing in the internal tube a carbon chain (b) [40].

by the authors of the discovery [5] were as follows [4]. Outwardly it represented a microcrystalline powder of a black color with a density of $\sim 1.9-2\text{ g/cm}^3$. It was a semiconductor of n -type, its band gap was $\sim 1-2\text{ eV}$ and photoconductivity was considerable, which was not lost up to the temperature of 500°C . This gave the possibility to use it for creation of photoresistors and different photoelectric devices. Heat capacity of all carbyne samples being studied was significantly higher than that of graphite, for example, at the temperature of 80 K — it was more than by a factor of 1.5. Thus on increase of the heat capacity a series appears: diamond-graphite-carbyne. The studied samples of carbyne demonstrated inertness to different oxidizers, except for ozone. With chlorine the reaction took place at temperatures above 800°C . Carbyne showed chemical inertness approaching to diamond at boiling in a mixture of nitrogen and sulphuric acids (1:1) [4]. But these and a number of other results obtained earlier about thermal and chemical stability of carbyne and materials on its basis weakly conform with the recently obtained results concerning stability of carbyne-like structures included in the structure of cluster carbon materials.

Nanostructure carbon films prepared in a high vacuum has been *in situ* and *ex situ* studied in the works [43, 44]. The films represented matrixes of sp^2 -carbon with inclusions of sp -carbon clusters, in which polyynes and polycumulene chains were present. Stability of the films content in a high vacuum, and also at effect on them of gaseous hydrogen, helium and nitrogen was detected by Raman spectroscopy method. The effect of dry air resulted in destructions of a sp -fraction, as a result an essential decrease in intensity of an appropriate band ($\sim 2100\text{ cm}^{-1}$) at invariable D and G bands in Raman spectra was observed. The one of these spectra is shown in Fig. 8 [43].

From the given figure it is apparent that the band $\sim 2100\text{ cm}^{-1}$ is strongly asymmetrical and its fitting by Gaussian functions gives two separate bands appropriate to cumulene and polyyne. The authors of the work [44] also studied stability of the films composition at their heating in the range from the room temperature up to 200°C and have found out, that the samples heating, even a little bit above that of the room temperature, resulted in destruction of carbyne fraction in the films. It was reported in [45] that thermal destruction of carbynoide structures, obtained through dehydrochlorination of polyvinylchloride, started only at heating above 220°C , this is indicative of higher thermal stability of the researched structures, than it was informed in [44].

Carbyne and a number of materials based on it basis have the properties rather valuable for their biomedical application. These are such properties, as absence of toxicity, high biological compatibility, and chemical stability to biological liquids, high thromboresistance and also antibacterial and antifungal action. Such valuable properties make it possible to use carbyne-based coatings, for example, for creation of synthetic prostheses of blood vessels or various types of implants, which are used in orthopedy, urology, stomatology etc. [46–48].

There are great potentials in application of separately taken carbyne chains in nanoelectronics, in particular, to realization of the carbon electronics concept offering creation of all units of electronic circuits only on the basis of carbon materials. Theoretical investigations show, that the linear carbon chains consisting only of sp -hybridized carbon atoms, should have perfect conductivity, i.e. they should have properties of quantum molecular conductors with 1D-

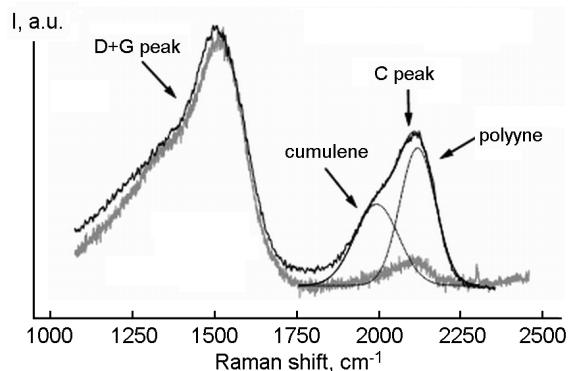


Fig. 8. Fragment of Raman spectra, taken *in situ* (upper) and *ex situ* (lower).

dimensionality [49, 50]. More sophisticated quantum structure with still weakly studied properties, which can find broad application in nanoelectronics, is also a unit carbon chain surrounded by a single- or multi-walled carbon nanotube [39–41], together with every possible other structures containing carbon chains and CNT. Thus, it was revealed, that the carbon chains located in the structures with CNT, have rather high thermal stability. In [51] the clusters of double-walled CNT were subjected to an annealing in the graphite furnace at temperature 1500°C in argon environment. Such heat treatment has resulted in formation of carbon chains in the space between outside walls of adjacent tubes. It was substantiated by a high-resolution electron microscopy and occurrence of new band samples at 1855 cm^{-1} in the Raman spectrum which was referred to oscillatory modes of again formed carbon chains. Otherwise Raman spectrum did not undergo changes. Then the obtained samples with carbon chains were subjected to a heat treatment in the oxygen-containing environment. The new band remained strong enough after the heat treatment at 400°C , it considerably weakened after the heat treatment at 500°C and after the heat treatment at 600°C faded absolutely. In [52] there was developed an original technology of obtaining nanostructures representing CNT, inside which there are two other CNTs, bridged among themselves by the chain of carbon atoms (Fig. 9).

The authors mark a sufficiently high stability of such a nanostructure, which did not fail under the action of an electron beam within 30 seconds. By the results of molecular-dynamic modeling they conclude, that such nanostructure, which can find application in nanoelectronics, can be stable up to the temperature of 1000 K. However,

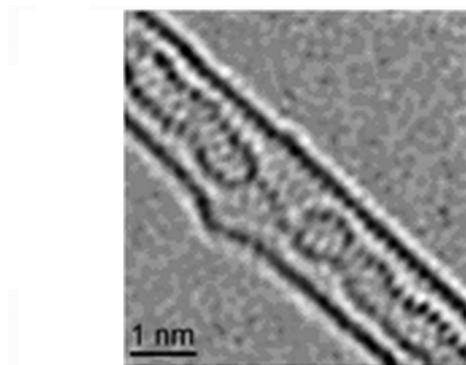


Fig. 9. TEM-image of nanostructure containing two CNTs that are inside other CNTs and which are interconnected by a carbon chain [52].

this conclusion has not been yet confirmed experimentally.

Owing to the unique electronic structure of carbyne and different structures based on it have a non-linear optical sensitivity and hyperpolarizability [53], that is valuable when developing different electrooptical systems. The feasibility of obtaining a ferromagnetic state is also demonstrated [54], the probability of existence of superconductivity in carbyne-like structures is also supposed [8, 55]. Moreover, the materials based on carbyne have also demonstrated interesting magneto-resistance and thermoelectric properties, which can find practical use [56].

Carbyne as a nanocluster material

In recent years clusters and cluster materials attract the increasing attention of experts of different profile, because in comparison with conventional materials having homogeneous structure and composition, clusters have special electrical, optical, magnetic, mechanical etc. properties [57–60]. A number of the theoretical and experimental works published recently testifies validity of carbyne-containing materials consideration as cluster materials with different degree of ordering. An estimation of the quantitative contents of carbyne chains in the nanocluster material is given in some of them. The Raman spectroscopy is one of the basic methods for determination a type of carbon atoms hybridization in a sample [61]. It was established in [62], that in amorphous diamond-like films of carbon, obtained by laser ablation of graphite, the concentration of sp -, sp^2 - and sp^3 -hybridized carbon makes $\approx 6\%$, $\approx 43\%$ and $\approx 51\%$, respectively. And in [63] it was established by

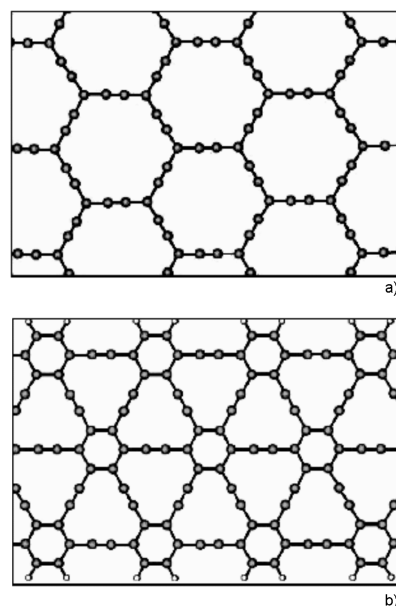


Fig. 10. Two of the offered structures of graphyne layers: a — α -graphyne, b — β graphyne.

a NEXAFS-method (NEXAFS-Near Edge X-ray Absorption Fine Structure) that *in situ* studied cluster carbon films obtained by condensation of carbon nanoparticles formed by laser ablation of graphite in He environment, the contents of sp - and sp^2 -carbon equal, respectively, 10 % and 25 %. Thus, later in one of recent works [64] it was reported, that the atoms of carbon are mainly in a sp -hybridization in nanoparticles at once after their formation (up to the moment of condensation on the substrate). Then, with the increase in a life time of such nanoparticles a signal appears, testifying occurrence of a sp^2 -hybridization of the carbon atoms in their spectra.

It is known, that action of high-pressure and temperature on carbyne-containing carbon materials results in alteration of a quantitative ratio of phases with a different hybridization of carbon atoms [65]. Using the mentioned method the authors of [66–68] received cluster carbon materials with the different contents of sp -, sp^2 - and sp^3 -phases in them. Then, studying temperature dependence of specific electrical resistance of samples at constant and alternating current of different frequency and interpreting conductivity in the framework of the theory of jump-conductivity, it was found, that the increase in part of sp^2 -bond in carbyne samples causes transition from one dimensional to two dimensional, and then to three-dimensional conductivity. Investigation into

the features of cluster carbon material conductance gives the possibility to estimate approximately size of the clusters in it. It is reported in [66], that physical properties of the synthesized carbyne-containing solid-state samples can be described in the framework of the model of nanocluster material with typical dimensions of carbyne clusters 1–10 nm.

The materials considered above on the basis of carbyne as a matter of fact represent cluster materials being a mixture of non carbon phases and sp -, sp^2 -, sp^3 -carbon phases with different spatial distribution and quantitative ratio between them, which can change in time or at variation of thermodynamic conditions. Thus it is supposed, that inside the cluster the atoms of carbon have the same hybridization and only on the boundary of clusters, where their interconnection takes place, the mixed hybridization of carbon atoms is possible. It is really existing materials. Different problems touching hypothetical new carbon structures, consisting of hybrid carbon phases are also considered in the scientific literature now. One of such structures, where the presence of considerable quantity of carbyne chains and distant order in their arrangement is supposed, has been named graphyne [69, 70]. In the graphyne layers sp^2 -hybridized atoms of carbon are joined by polyyne carbyne chains of different length, i.e. they represent a hybrid ($sp + sp^2$) carbon phase. Two of the offered graphyne structures are shown in Fig. 10. Depending on the length of sp chains they distinguish accordingly graphyne, graphyne — 2, graphyne — 3, graphyne — 4, ..., graphyne — n , where n is a quantity of pairs of atoms in the chain.

Different exotic graphyne structure of carbon, for example, nanoribbons [71], nanotubes [72], as well as the structures based on the hybrid $sp + sp^3$ -carbon phase etc. are researched theoretically and considered in the literature. Many times carbon surprised the researchers by its wonderful properties. Time will probably show the real existence of the mentioned above hypothetical carbon phases based on the strictly ordered arrangement of carbyne chains.

10. Conclusions

The analysis of the given above information on carbyne structure and properties, which in many cases has a contradictory nature, gives the basis for following conclusions. Carbyne as an independent allotropic form of carbon which based on sp -hybridiza-

tions of its atoms, can be stable or quasi stable to exist only as nanostructures (clusters), i.e. it is not usual, in the accepted understanding, allotropic form of carbon, as graphite and diamond, but nanoallotropic form of carbon. Therefore, there is a reason to consider carbyne-containing materials as cluster nanomaterials, representing a matrix of various types of carbon or other materials including nanosized clusters of sp -hybridized carbon. At such approach the mentioned above doubts and inconsistencies in views on a capability of existence of carbyne as independent allotropic form of carbon fade and according to our opinion there are all grounds to assert, that carbyne exists as the third allotropic form of carbon, but it has its own peculiarities. This confirms once more the diversity of carbon in the nature recognized by all.

At the first stages of development of materials production technology and study of their properties the principle "contents – property" was used for a long time, then it became clear, that more exact and productive is the principle "contents – structure – property". The present stage of development of materials technology, in particular, of nanomaterials dictates the necessity of transition to the principle "contents-dimension-structure-property". And in the situation with the carbyne application of such principle allowed us to interpret correctly all features of its physicochemical properties.

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Карбін як кластерна наноалотропна форма вуглецю

М.І.Сліпченко, В.Г.Удовицький

Після відкриття фулеренів вуглецеві наноструктури стали однією з найбільш актуальних тем наукових досліджень. Властивості алотропних модифікацій вуглецю, що базуються на sp^3 - (алмаз) та sp^2 -гібридизації його атомів (графіт, графен, фулерени, нанотрубки), досить добре вивчено і багато з них практично реалізовано. Але карбін — третя алотропна форма вуглецю, що має sp -гібридизацію його атомів, не дивлячись на те, що його було відкрито більш як 50 років тому, до цього часу залишається однією з найбільш суперечливих та дискусійних алотропних форм вуглецю. У цьому критичному огляді представлено широкий спектр інформації, що стосується отримання, дослідження властивостей і застосування карбіну та наноструктур на його основі. Обґрунтовується необхідність розгляду карбіну як кластерного наноматеріалу з особливими властивостями.