Fullerene and fullerites. New modern materials

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The discovery of a new form of pure carbon — giant molecules called fullerenes and subsequently of a new crystalline form of carbon — fullerite crystals — has been a full-scale scientific boom over the past few years. Hundreds of laboratories all over the world are being engaged in synthesizing and studying fullerenes and fullerites and their derivatives, the number of publications amounts to two thousand, and the rate and scope of researches goes on growing.

This report is not a scientific review and it is not my aim to establish scientific priorities. This is rather a scientific popular lecture that better fits in with the spirit of this session. In view of this, not to overburden my report, I shall not make individual references in the text and figures since, to be exact and consistent, the number of such references must be very large. At the end of my lecture I shall give references to several recent very good reviews devoted to individual problems of fullerene physics and chemistry. The reader will find the necessary references to originals in these reviews.

2. History

The existence of giant molecules of carbon, boron or silicon has long been hypothesized. Individual quantum chemical calculations evidenced for the possibility of stable A_{60} , A_{70} , and so on clusters. I know about the results of such calculations made and published in Moscow back in late 60s -- early 70s. Possibly, there were

other similar considerations and calculations, however, the ideas and models contained in them were hypothetical and based on general though quite sensible, from the stand point of quantum chemistry, assumptions.

It was only in 1985 that Richard Smalley's group at Rice University, Texas in collaboration with Harry Kroto at the University of Sussex, England, reported the result of their experimental studies that vapors formed upon laser vaporization of graphite contained considerable amounts of carbon clusters C_{60} , which was recognized mass-spectrometrically.

Concurrently, W.Kratschmer from the Max Planck Institute for Nuclear Physics, Heidelberg, Germany and Donald Huffman, University of Arizona, Tucson and their students L.Lamb and K.Fostiropoulos were concerned with producing «carbon smoke» by vaporizing a graphite electrode in an arc discharge in order to model the carbon state in interstellar dust. Their spectroscopic efforts have shown that «carbon smoke» contains C_{60} clusters which may well contribute to IR spectrum of interstellar dust. But they asked for more. Having collected the graphite residue resultant from spark erosion at the arc discharge, they dissolved it in benzene and, after evaporation of the solution, they got tiny crystals of C_{60} and C_{70} mixture, being first man made crystals of cited works of late has opened avenues for laboratory synthesis of macroscopic amounts of fullerenes crystals, stimulated extensive activity in this field in many laboratories all over the globe. It has opened the new era of various physical and chemical experiments with these novel materials. Today a standard technology for synthesizing fullerite crystals involves the following stages: graphite vaporization in an inert gas atmosphere, one of the arc discharge electrodes being a graphite rod, collecting the vaporization products residue from the chamber walls, dissolving this residue in an organic solvent, chromatographic column separation of solutions of various fractions from each other. The solutions are then

dried to yield microcrystalline particles (powders) of various C_N fractions and, finally, these particles are sublimed to yield C_N crystals. It appeared that in the fullerene family C_N may be very large -- more than 900, however, most stable and abundant are C_{60} and C_{70} . The molecular structure of C_{60} is shown in fig.1. This beautifully symmetric molecule belongs to the icosahedral symmetry and is formed of 12 pentagons and 20 hexagons having the same edge dimension close to that of C-C bond in graphite. So, now we know three forms of solid carbon -- diamond (fig.2), graphite (fig.3) and fullerite (fig.4). A special interest to studies of physical properties of fullerites was aroused by publication of the sensational work of the group from AT&T Bell Lab's, who reported an observation of high T_C ($\approx 10K$) superconductivity in fullerite specimens treated in potassium vapors. This phenomenon was attributed to the process of potassium atoms intercalation into the crystal lattice interstitial sites of fullerite, like it takes place with graphite. Further games with variation of the intercalant's type (of alkali metals) resulted in an increase of T_C up to 30K which, presently, is second only to T_C values of high temperature superconductors on the base of copper oxides.

It should be pointed out that the general idea of the molecular structure of fullerenes, similar to that of aromatic materials, has suggested that fullerenes and fullerites should be inert, chemically inactive materials. This, however, is not the case. It has been demonstrated that fullerenes can participate in numerous chemical reactions with the formation of various chemical derivatives of fullerenes. This gave birth to a new broad field of organic chemistry which, undoubtedly, is very promising. ,

So, two approaches and, correspondingly, two different scientific fields can be distinguished in the fullerene and fullerite science:

first approach is to regard fullerites as stable formations that let atoms of

small radius — mainly alkali atoms — intercalate into their interstitial positions. In this case the chemical bonds remain intact in fullerene molecules. An investigation of the physical properties of such alkali-doped compounds may be called the fullerene physics of today;

second approach concentrates on possible chemical reactions involving breakdown of bonds inside the fullerene molecules and formation of derivatives. This province is the fullerene chemistry.

Let us discuss these approaches at greater length and consider the principle results obtained.

3. Fullerite physics

An important division of this science is structural analysis of fullerite crystals. It has necessitated the development of special structural methods related to so-called Rietveld refinement. This method, used in powder diffractometry, is based on the acceptance, from rational considerations, of apriori structural model and its subsequent correction so that the positions of all the diffraction lines were coincident with those derived from model calculations. To define reliably structures of various phases of pure and intercalated fullerenes this method is combined with a method of integral intensity measurements of different X-ray diffraction lines, with Laue methods to study single crystals, with neutron diffraction and electron diffraction methods.

1) Pure fullerite C_{60}

At room temperature a pure C_{60} has a crystalline FCC structure (fig.4), but herewith the molecules are orientationally disordered due to their rapid quasi averaged spinning. In the X-ray time scale all the four molecules of the cubic cell are structurally equivalent. The lattice parameter $a=14,16E$ comprises the value of the van der Waals molecular diameter $D = 10E$. At cooling below $T_m = 249 - 260$ K the

phase transition to a simple cubic lattice (SC) is observed. This transition was documented by different structural methods — powder, on single crystals (X-ray), and, also, neutron and electron diffractions. Differential scanning calorimeter method confirms that the phase transition is a first order. Temperature dependence of C_{60} molecules spinning characteristics was studied in detail using the NMR on ^{13}C isotope. It was shown that above 140K there was one more phase transition, leading to narrowing of NMR lines (fig.5).

Effect of pressure. As the hydrostatic pressure is increased, the self-absorption edge moves to the red spectrum side and the absorption edge shape changes (fig.6). The compressibility modulus of C_{60} was defined from the displacement of the X-ray diffraction lines position under pressure.

2. Intercalated fullerenes

As it has been mentioned, an interest to these materials was essentially stimulated by observation of high- T_c superconductivity in C specimens annealed in alkali-metal vapors (fig.7). Diffraction and morphology studies of C_{60} specimens aged at elevated temperatures in alkali-metal vapors have shown that such treatment gives rise to different phases in the system A_xC_{60} where A (Na, K, Pb, Cs).

The following isolated phases have been documented:

A_2C_{60} — insulating ,

A_3C_{60} — conducting ,

A_4C_{60} — insulating ,

A_6C_{60} — insulating ,

Structural fragments of these phases are shown in fig.8 where large balls stand for fullerene C_{60} molecule and small ones for alkali-metal atoms. Fig.9 depicts schematically phase diagrams for C_{60} doped with various alkali metals. All the diagrams are seen to be of the same type, they exhibit clearly stoichiometric phases,

and the intermediate compositions correspond to two-phase mixtures.

Of course this is a low-temperature part of the diagram of state. The questions of how these phases decompose or melt at elevated temperatures as well as the questions concerned with the value of their mutual solubility are to be quantitatively specified. It has to be noted, too, that ternary combinations of the type $A_x A'_{3-x} C_{60}$ (A and A' are different alkali metals) have already been synthesized. In order to specify the regions of existence of such phases one has to construct ternary diagrams of state. For some of them the phase structures have been already defined and it has been shown how A and A' atoms get distributed in octahedral and tetrahedral interstitial positions. It is precisely for the double intercalant $Rb_2Cs C_{60}$ that a maximal $T_c = 31.3K$ is observed.

The calculation of the sizes of octahedral and tetrahedral interstitial sites and their comparison with alkali metals atomic radii-in order to construct models of their rational arrangement -- are based on the structural models in which, usually, the van der Waals radius is taken to be

$$R_w = 5.01 \text{ \AA}$$

These calculations have already been performed both for real and hypothetical structures (BBC, BCT). Along with calculations of the exact position of diffraction lines (Rietveld refinement) this necessitated a great body of computation and creation of special computer programs (EASY/PULVERIX, NRCVAX) and others. The obtained results are rather promising, they suggest that the quantitative theory of formation of principal physical properties of intercalated fullerenes may be created earlier than it can be done for other multicomponent systems.

Conductivity and superconductivity of alkali metals fullerenes

$(A_x C_{60})$ were studied most comprehensively for the system $K_x C_{60}$ where, precisely, superconductivity had been discovered, and then the phase $K_3 C_{60}$ was

identified as superconducting.

Later in a series A_xC_{60} other superconducting phases were found and, particularly, the triple ones of the type $A_xA'_{3-x}C_{60}$ having $T_c > 30K$, which, presently, is exceeded only by compounds on the base of copper oxides. As it has been shown in fig. 7, T_c varies from 10K for Na_2CsC_{60} to 31K for Rb_2CsC_{60} . It turned out that the T_c value depends explicitly on the lattice parameter of intercalated fullerites, i.e. on the atomic volume of cations penetrated into the fullerite lattice (fig.10). The T_c value is seen to increase as the parameter a is increased. Importantly, that a change in a can be attained both by variation of cations combination and by superposition of an external hydrostatic pressure. As this takes place, all the points fit well into the general regularity (fig.10).

These results were the base for important experiments when along with alkali metals ammonium ions were used as intercalating ions, which readily led to additional increase of T_c (fig.11).

The structure of the obtained phase and the arrangement of ions in interstitial sites were defined by X-raying (fig.12).

Further understanding of the character of particular phases in the system A_xC_{60} is corroborated by the calculations of the band electronic structure of these phases. The calculations were based on the Extended H 5t 1kel Theory (EAT). The results are shown in fig.13.

The calculations show that the Fermi level of the superconducting phase A_3C_{60} locates near the maximum of the density of states of the conduction band, as it ought to be in accord with classic superconductivity theory. Investigations of variations of the Raman spectrum of C_{60} , as an alkali metal was being intercalated, proved very useful.

Fig.14 illustrates schematically individual Raman spectrum regions with

indications of what vibrational types are responsible for a particular spectrum region.

Observations of the K_3C_{60} superconducting phase formation have shown that the high-frequency spectrum region changes during this event. Then as the potassium content increases and the K_6C_{60} phase forms the spectrum changes again (fig.15). These data suggest the conclusion that the occurrence of superconductivity in the K_xC_{60} system is related to the electron-phonon interaction in vibrations of the $Ag(2)$.

Significant role of the electron-phonon interactions in the process of current-carrier coupling in the K_3C_{60} system is also supported by the presence of isotopic effect for T_c observable in K_3C_{60} at substitution of ^{12}K by ^{13}K isotope (fig.16).

These data bear witness for the fact that electron-phonon interactions play a significant role in the mechanism of the occurrence of high-temperature superconductivity of intercalated fullerenes. They also raise hope for consistent construction of quantitative physical theory of this phenomenon [1,3].

4. Fullerene chemistry

Investigation of chemical reactions which involve fullerenes and of the properties of these reactions products is a vast and rapidly developing field of today's organic chemistry. Since this audience consists mainly of physicists, it would serve no purpose to go into the heart of the chemical problems, I shall, therefore, only briefly list them. The people interested in these questions I can refer to the excellent review by Roger Taylor and David R. Walton published in Nature in the summer of 1993 [2].

Roughly speaking, all fullerene compounds can be classed into three categories:

1. Intercalated compounds wherein fullerene molecules in the crystal lattice

sites retain their integrity and identity whereas foreign atoms occupy interstitial positions in the lattice.

2. Endohedral clusters obtainable upon capturing of a non-carbon atom inside a fullerene molecule (encapsulation). In this case the fullerene molecule also retains its structure.

3. Exohedral solids formed from fullerenes to which foreign atoms or molecules are covalently bonded on the outside of the carbon cage.

We have already discussed the first type compounds. I can only add that intercalating atoms may be not only alkali-metal atoms (cations), but, also, e.g. iodine atoms which, in these processes, probably manifest themselves as anions. The $C_{60}J_4$ phase was found in the $C_{60}J_x$ system, its structure was examined by x-raying and characterized. Another interesting C_{60} — derivative intercalated compound is tetrakis — dimethylaminoethylene (TDAE) of the formula $C_2N_4(CH_3)_8$. Despite a large number of different atoms in the molecule all of them have a comparatively small atomic radius and molecules as a whole can locate in the interstitial sites of the C_{60} structure. This compound, is specifically, a ferromagnetic, having the Curie temperature of about 16K, which, so far is the highest among organic ferromagnetic. Seemingly, a partial charge transfer from intercalant's molecules (or atoms) to fullerene's molecules is of importance for structure stabilization in all intercalated compounds.

As for endohedral cluster solids, then we know, so far, the La (a) C_{60} compound, where the symbol (a) implies that La atoms are inside the cage. There were other attempts to synthesize endohedral cluster solids with other rare-earth atoms inside the cage, however, low quality of specimens and inadequacy of experimental material do not make it possible to draw final conclusion about the crystalline structure of these compounds.

An investigation of the chemical reactions leading to the formation of the third type compounds i.e. exohedral ones as well as of the structure of these compounds is, precisely, the province of the fullerene chemistry comprising the main ideas and approaches of organic chemistry. The key moment in the understanding of the fullerene molecule behavior in various chemical reactions is that the occurrence of the double bond in pentagonal ring must be excluded. There is only one way of packing pentagons and hexagons so that a stable isomer could be formed. Some versions are illustrated in fig.17. As contrasted from aromatic molecules, fullerenes do not possess atoms of hydrogen or other added groups, — therefore, they are not capable of substitution reaction. Substitution reactions can take place only with derivatives, especially those formed by addition. The electronic structure of fullerenes molecules suggests that they ought to have an increased electron attracting. This governs their chemical behavior, for example, they readily react with nucleophiles.

At a slow crystallization from benzene C_{60} fullerene molecules yield solvates, $(C_6H_6)_4C_{60}$ in which spinning of the molecules is so slow that it is possible, using x-ray diffraction method, to define the structure of the single crystals.

The same results are obtained at crystallization from cyclohexane. There are some other complexes from which co-crystallization with benzene occurs. All these materials obtained at co-crystallization exhibit so-called host-guest structures, an example of which with ferrocene is shown in fig.18. Here is much in common with intercalated compounds when structural stabilization occurs due weak interaction related to charge transfer.

Analogous structures are obtained at the interaction with sulphur ($C_{60}S_{16}$ and $C_{70}S_{48}$). These are formed of S_8 rings.

As for remaining typical chemical reactions of fullerenes, known by the present time, I shall restrict myself to their brief listing.

Anion formation and oxidizing processes

These processes are of clear electrochemical nature. In process is rather typical for organic chemistry and it is being intensively studied using platinum as catalyst. The interaction of C_{60} with t-butyl-lithium belongs to the same class of reactions. Details of such reactions are rather complicated.

Addition reactions

These reactions can be categorized into three groups:

- 1) Cycloadditions ,
- 2) Additions involving bridging ,
- 3) Additions of separate groups ,

Category 2 comprises reactions with the formation of epoxides from isolated C_{60} . These are oxygen bridges.

Addition of methylene to C_{60} and C_{70} goes via the formation of carbon bridged. There are recent reports on synthesis of methanofullerenes. In reactions with metals than as aromatics. Among reactions of addition of individual groups one may distinguish addition of halogens and hydrogen. Only 24 groups can be added to C_{60} so that two of them were not neighbours (fig.19).

Specific structure of $C_{60}Br_6$ is shown in fig.20.

Polymerization

Polymers comprising C_{60} may be confined to three types: two of them are the pearl necklace type, fig.21, the third type is pendant chain, fig.21. One may assume that their two- and three — dimensional versions may be described as a polymer network or lattice. Probably, the third type having a direct bond between the cages

forms at polymerization of C_{60} under the ultra-violet irradiation in the absence of oxygen. In conclusion of this section I give the general scheme of all chemical reaction involving fullerenes (fig.22).

Conclusion

It is clear that besides a great scientific interest investigations of fullerenes promise considerable practical implementation.

In addition to what has been already mentioned, they can be used in solid state quantum electronics, optics and in production of electric batteries.

Many opportunities for chemical technology and chemical analytical methods are in sight.

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Fig.1. Fullerene C_{60} molecule.

Fig.2. Diamond crystal structure.

Fig.3. Graphite crystal structure.

Fig.4. Fullerite C_{60} crystal structure .

Fig.5. ^{13}C NMR spectra of solid C_{60} at indicated temperatures
(a-g) h-tetramethylsilane.

Fig.6. Absorption edge spectra of C_{60} crystal at $T = 300\text{K}$ and pressure up to 20 GPa curves 1-6 correspond to pressure 0, 0.9, 3.1, 9.5, 14, 20. GPa respectively.

Fig.7. Shielding measurement for $\Lambda_x \Lambda_{x-3} C_{60}$ (normalized).

Fig.8. Schematic structures of C_{60} and $A_x C_{60}$. C_{60} — large spheres, A — small spheres

Fig.9. Proposed phase diagram for $A_x C_{60}$

Fig.10. Relationship of the superconducting T_c to the unit cell size of A_3C_{60} .

■ A_3C_{60} — normal pressure
 ■ and Δ — data from K_3C_{60} and Rb_3C_{60} under pressure

Fig.11. Normalized d.c. magnetic susceptibilities of Na_2CsC_{60} and $(NH_3)_4Na_2CsC_{60}$ measured in a field 2,5 Oe.

Fig.12. A model of $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$ with ordered $\text{Na}(\text{NH}_3)_4$ tetrahedra the C, Na, Cs, N and H atoms are represented by grey, red green, bene and white spheres respectively

Fig.13. Energy band structure of the metallic K_3C_{60} compound

Fig.14. Various vibrations in the A_3C_{60} compounds can contribute to electron-phonon coupling and may be important for superconductivity.

Fig.15. Raman spectra evidence for charge transfer from potassium atoms to the C_{60} molecules.

Fig.16. Isotopical effect. Magnetization transition in isotopically pure $K_3^{13}C_{60}$ occurs at the temperature 0,4K lower than in $K_3^{12}C_{60}$.

Fig.17. Possible disposition of two pentagonal rings adjacent to a hexagonal ring. Disposition *b* and *c* introduce instability.

Fig.18. Host-guest structure of C₆₀ (ferrocene)₂.

Fig.19. Schlegel diagram showing the 24 non adjacent sites in C₆₀.

Fig.20. Structure of $C_{60}Br_6$.

Fig.21. «Pearl necklace» and «pendant chain» polymers that in principle can be made of fullerenes.

Fig.22. Some general reactions known to occur with C_{60} fullerenes.