Physics–Uspekhi **37** (9) 927–929 (1994)

PACS numbers: 01.10Fv, 21.60.G, 36.40, 82.30.N

New directions in the study of fullerenes (International Conference on Fullerenes, San Francisco, May 1994)

The important international conference ''Fullerenes: physics, chemistry, and new directions'' was held in San Francisco in May 1994 as part of the 185th meeting of the American Electrochemical Society (AES). Its theme was the recently discovered allotropic modification of carbon in which the carbon molecules (fullerenes) have a spherical or spheroidal structure comprising a surface covered with regular hexagons and pentagons with carbon atoms at their corners. The very unusual physicochemical, optical, electrical, and mechanical properties of fullerenes in the gaseous and the condensed state have made this topic one of the most rapidly developing areas of modern science. Fullerene molecules are highly electronegative, being able to attract up to six free electrons. This makes them strong oxidising agents, able to form many new chemical compounds with new and interesting properties. The compounds of fullerenes, whose composition includes six-membered rings of carbon atoms with single and double bonds, can be treated as three-dimensional analogues of aromatic compounds. Fullerene crystals are semiconductors with a forbidden gap 1–2 eV wide, and they show photoconductivity under irradiation with visible light. The energy which holds the fullerene molecules together in the crystals is much lower than the energy of the carbon–carbon bond in the individual molecules. This makes the formation of different crystal structures possible in the solid fullerenes, and transitions between these structures have been observed under laboratory conditions. The intercalation of alkali metal atoms converts these crystals into a state having metallic conductivity, which becomes superconducting when the material is cooled to 19–33 K.

I shall assess the value of this conference by examining some of the basic trends underlying the development of the studies of fullerenes and of their derivatives. I should first of all point out the progress made in the study of the structure of the fullerene molecules, due mainly to the use of more suitable scientific apparatus. Thus, the use of the field-ion microscope (of which the most modern version has recently been developed in Japan) allows the structure of fullerene molecules of a given type to be directly 'seen'. Methods such as Auger spectroscopy and high-resolution electron spectroscopy permit the structure of chemical compounds containing fullerenes to be reliably established. Another important trend in the development of this field of study was the interest shown by most workers in progressing rapidly from the study of the individual characteristics of unusual materials such as the fullerenes to the preparation and characterisation of macroscopic objects composed of molecules of the fullerenes and of their derivatives. This progression was made possible by the advances made in the technology of the preparation, separation, and purification of fullerenes and of compounds based on them. It is thought that this approach will lead most rapidly to the achievement of interesting new results in this field of science.

This conference was the sixth in the series of fullerene conferences held under the aegis of the AES during the last few years. It was distinguished by the width of its scope and the painstaking detail of its organisation. It attracted about 250 contributions (including review papers and original reports) from dozens of laboratories active in the development and the study of fullerenes and their derivatives. The large size of the AES meeting allowed a sub-stantial number of delegates (about 30) from Russia and other countries of the former USSR to contribute to the fullerene conference, thanks to generous financial support from the Soros fund.

This conference marks a significant stage in the development of studies and techniques relating to fullerenes and their derivatives. The most striking conclusion from the conference was the continuing interest in this topic shown by the large industrial companies and by the business community in the USA and in other leading countries of the West. It appears that one of the factors mainly responsible for directly stimulating this interest was the report (first heard at this conference) of a large-scale commercial application of fullerenes in electronics. According to this report, made by the multinational Mitsubishi industrial corporation, fullerenes are used as the basic material for the production of accumulator cells. These cells, whose operation depends on the hydrogen addition reaction, are in many ways similar to the widely used metal-hydride nickel accumulators, but it was pointed out that fullerene accumulators can add on about five times more hydrogen than those based on nickel. Furthermore fullerene batteries are more efficient than batteries based on lithium, they are lighter, and they present a lower ecological and sanitary hazard. It is proposed to use fullerene accumulators as power sources in personal computers and hearing aids. Other possible commercial applications of fullerenes were widely discussed at the conference: in particular, the prodution of dyes for copying machines, photodetectors for optoelectronic apparatus, diamond and diamond-like films, medicinal preparations, superconducting materials, etc.

The scientific content of the conference reflected fairly accurately the current trends in the studies and technological developments of fullerenes and their derivatives. Of course, the relatively small number of papers on the

Uspekhi Fizicheskikh Nauk **164** (9) 1007–1009 (1994)
Translated by J I Carasso

superconductivity and other electronic properties of solid materials based on fullerenes seemed to be inconsistent with these trends, but this can hardly be taken as evidence of a loss of interest in the high-temperature superconductivity of the fullerenes, which is still one of the most topical problems in this field. A more likely explanation is provided by the chemical emphasis of the session as a whole, and by the announcement of other fullerene conferences in 1994 (Kirchberg, Rome, Boston), which are expected to give greater emphasis to the superconductivity of materials based on fullerenes.

Many of the papers presented at this conference were aimed (to a greater or lesser extent) at the improvement of the technology of production, separation, and purification of fullerenes. The progress in this work achieved in many laboratories throughout the world has already led to a marked expansion in the production of fullerenes, and therefore also to a decrease by about an order of magnitude in the cost of the materials. In the corridors of the conference, announcements by a substantial number of firms and corporations engaged in fullerene production stressed the availability of carbon tubules and other chemical compounds based on these materials. The present cost of C_{60} (about US\$100 per gramme) makes this material accessible to laboratory studies and to developments in physics, chemical technology, optoelectronics, etc. The most widely used technology for the extraction of fullerenes from carbon black and for their subsequent purification and separation is based on the use of solvents and sorbents, which allow the selective extraction of fullerenes of a given type. This procedure, developed by Krätschmer and Huffman in 1989, is variant of liquid-phase chromatography. Its further development is associated with the preparation of the higher fullerenes in quantities sufficient for experimental studies of the physicochemical, mechanical, and optical properties of the crystals composed of molecules of the higher fullerenes of a specified type. The interest in this topic was heightened, in particular, by the prediction of high-temperature superconductivity in the solid higher fullerenes doped with alkali metal atoms. According to calculations reported at the conference the critical temperature of superconductors based on C_{84} can be as high as 100 K.

Intensive current studies of the behaviour of fullerenes in solution should lead to substantial advances in the technology of production of the higher fullerenes. This work was abundantly illustrated in the programme of the conference. Thus, several communications dealt with studies of the kinetics and thermodynamics of the soluble fullerenes. A powerful stimulus towards this work was provided by the study (during the past year) of the temperature dependence of the solubility of C_{60} in various organic solvents and in CS_2 by a group at the Stanford Research Institute. Their measurements revealed a non-monotonic dependence, with a maximum solubility at about 280 K. Many of the conference reports devoted to this theme proposed various models to account for the surprising behaviour of fullerenes in solution. The most convincing of these explanations was provided by the model proposed by workers at the Kurchatov Institute and based on the assumption of a cluster mechanism for the solubility of fullerenes. According to this suggestion, which is qualitatively consistent with many experimental findings, the fullerene molecules in solution form clusters consisting of a specific number of molecules. An increase in temperature induces the thermal decomposition of these clusters, resulting in a decreased solubility. The change in the temperature dependence of the solubility at $T \leqslant 280$ K is associated with a phase transition in the solid fullerene at $T = 260$ K, leading to the freezing out of the rotation of the fullerene molecules in the crystal and to an orientational ordering of the crystal structure. These effects produce a change in the energy parameters of the clusters in solution, and therefore also a decrease in the average number of particles in a cluster. Calculations of the temperature dependence of the solubility based on the liquid-drop model of the cluster are satisfactorily consistent with the measurements. The establishment of the cluster nature of the solubility of the fullerenes has more than an academic importance. For example, it suggests the possibility of diffusional enrichment of a solution of C_{60} with a small impurity of higher fullerenes, which are unable to form clusters because of their low concentration. For this reason the diffusion coefficient of the higher fullerenes in solution should be appreciably higher than the corresponding value for C_{60} present in solution in the form of clusters with a large number of molecules in the average cluster. This suggests an approach to the development of simple methods of enriching the solutions in the higher fullerenes, which should offer a significant increase in the effectiveness of techniques for the separation and purification of these materials.

The conference showed a special interest in the problems of the application of fullerenes in medicine and pharmacology. One of the main difficulties facing the successful solution of these problems is the preparation of water-soluble, nontoxic compounds of fullerenes which can be introduced into human organisms and be carried by the blood to the organ requiring therapeutic treatment. One of the first compounds of this type was synthesised from diphenethylamino succinate, and is widely used in medico-biological experiments with fullerenes.

Among other directions in the study of fullerenes and their derivatives the conference found the endohedral complexes based on fullerenes specially stimulating. This class of compounds consists of fullerene molecules with one or more atoms of an element other than carbon located within the molecule. Arguments on the possible existence of these compounds have now subsided, and information on their physicochemical properties is continually growing. The conference was greatly impressed by the presentation at one of the sessions of a periodic table with the atoms known to form endohedral complexes shown cross-hatched: about one-third of the table was cross-hatched. The possibility of preparing endohedral complexes on the basis of fullerene molecules greatly widens the scope of studies and of applications of fullerenes. Thus, the idea of producing anticancer preparations on the basis of water-soluble endohedral fullerene compounds with radioactive isotopes intercalated within the fullerene structure is being actively examined. By introducing such a drug into a tissue it should be possible to interact selectively with the cells affected by the tumour and prevent their further multiplication. Fairly reliable methods of preparing, separating, and identifying endo-hedral compounds are now available, but the problem of preparing and studying these compounds in the condensed state remains on the agenda. To solve this problem we need to increase the operational yield of the apparatus used for the synthesis of endohedral compounds by one or two orders of magnitude in order to make available gramme quantities of the compound.

Studies of the preparation, characterisation, and application of carbon tubules border on the work on fullerenes and their derivatives. These structures, formed (like the fullerenes) during the thermal evaporation of graphite, consist of elongated cylindrical surfaces defined by regular hexagons with carbon atoms at the corners. The diameter of the tubules is of the same order as that of the fullerene molecule, or slightly higher, and their length can exceed their diameter by a factor of ten. Like the fullerenes, tubules can be filled by atoms of various elements, and this gives them a new set of physicochemical properties. The conference discussed the formation from the tubules of macroscopic objects like plaits consisting of many tens of tubules, of planar ordered structures of the thin film type, etc. It is interesting to note that unlike the crystalline fullerenes, which are semiconductors, the structures produced by the tubules can have a metallic conduction. It should also be noted that the electrical properties of films based on carbon tubules are strongly dependent on the substrate material. In addition to the fullerenes and the carbon tubules, closed spheroidal structures based on graphite layers have attracted detailed studies. These structures, which have been named ‘onions’, can have different sizes and shapes, and appear to be relatively stable formations.

An analysis of the results of this conference suggests that the interest of the scientific community in new developments in the field of fullerenes and their derivatives has not abated, and continues to increase. The fullerenes, discovered during purely physical studies of carbon clusters, are formed during the thermal evaporation of graphite. They have now become worthy of study by chemists, materials scientists, and energy specialists as well as by physicists. The result of all this work has been not only new knowledge, but also new materials and new technologies, capable of changing the face of our civilisation. We believe that recent developments in the field of the fullerenes and their derivatives will prove to be an instructive example of the influence of fundamental studies on applied developments and on new technologies. We have already witnessed this influence: for example, when the discovery of semiconductors and the subsequent studies of their properties led to the creation of information technologies without which contemporary society would be inconceivable. The possibility that developments in the field of fullerenes may also lead to fundamentally important changes on a global scale cannot be excluded.

A V Eletskii