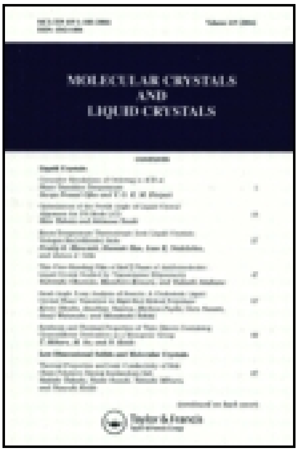

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# A New Type of Carbon: Fullerenes as Exotic Materials

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# A NEW TYPE OF CARBON: FULLERENES AS EXOTIC MATERIALS

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**Abstract** New types of carbon, $C_{60}$ and tubules, as exotic materials are presented with reference to the relevant literature. Conductivity and superconductivity found for alkali $C_{60}$ fullerides are described and discussed on a basis of crystal structure. The potential utility of the inner spaces of both $C_{60}$ and tubules is also addressed from the nano material science point of view.

## INTRODUCTION

A new type of carbon of spherical-shaped $C_{60}$ (Fig.1c)[1,2] and rod-like tubule (Fig.1d)[3,4] have generated considerable interest in fundamental aspects of science and technology. The new structures found in these materials through the $sp^3$ and $sp^2$ hybridization are expected to open a new way of nano material science, which can not be obtained from the conventional carbon materials of graphite and diamond (Fig.1a,b). From $C_{60}$ solids in combination to other elements, high conductivity and superconductivity [5] with quite high transition temperature (Tc) were reported, the latter of which is surpassed only by that of copper oxides[6-10]. Unique magnetic properties were also reported for the charge transfer complex salts of $C_{60}$ and organic donors[11]. Whereas for the tubules theoretical calculations predicted electronic properties varying from metal to semiconductor, which can be controlled by regulating the diameter and the helical arrangement of hexagons of the tubule layer[12-14]. It can be expected that these unique properties will offer the possibility to make advanced electronic devices in the future. In this paper I would like to describe general concept and ideas that can be made for these new types of carbon as exotic materials with reference to the relevant literature.

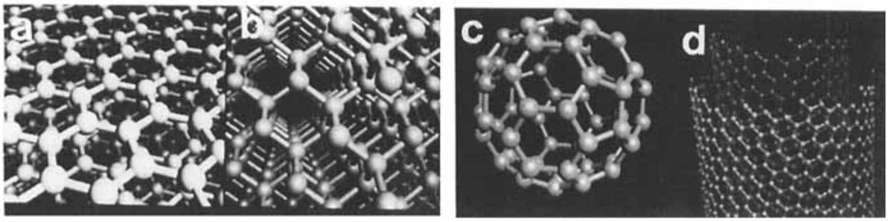

Fig.1
Four types of carbon; (a) graphite, (b) diamond, (c) $C_{60}$ and (d) tubule.

## STRUCTURE OF $C_{60}$ AND TUBULES

$C_{60}$ is a cluster-type molecule consisting of sixty carbon atoms, has a spherical shape with $I_h$ symmetry and the radius is about 0.8 nm as shown in Figs.2 and 3. From the geometrical point of view this is categorized in a closed polyhedron consisting of hexagons and pentagons. We can make various polyhedrons having closed surfaces by changing the number of hexagons with keeping the number of pentagons to be twelve according to the Euler's theorem. As a result, in principle we can expect quite many number of the $C_n$ analogues of $C_{60}$. Actually the existence of such $C_n$ compounds are experimentally confirmed (see Fig.2, here $C_{70}$ is displayed as the next major $C_n$ materials). However, the magic number of n is known to be required for the formation of such clusters, although the reason for the magic numbers still remains unclear. For instance, $C_{70}$, $C_{76}$, $C_{78}$, $C_{82}$, $C_{84}$ ... have so far been detected and isolated, but the $C_{62}$-$C_{68}$ are missing and no evidence has been reported for supporting that $C_{80}$ can be formed[15].

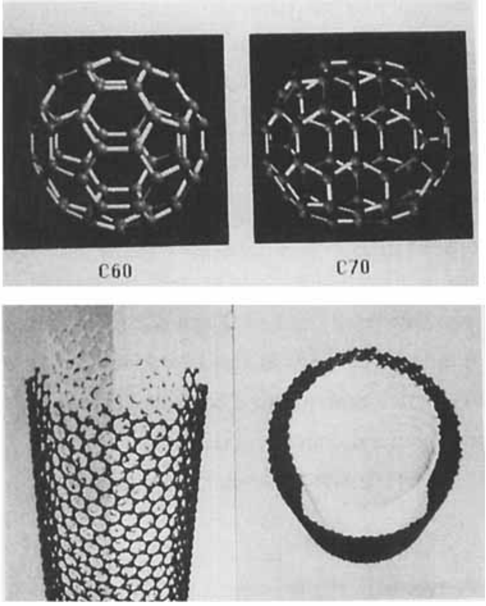

Fig.2
Structure of spherical-shaped fullerides ($C_{60}$ and $C_{70}$) and double-layered tubule.

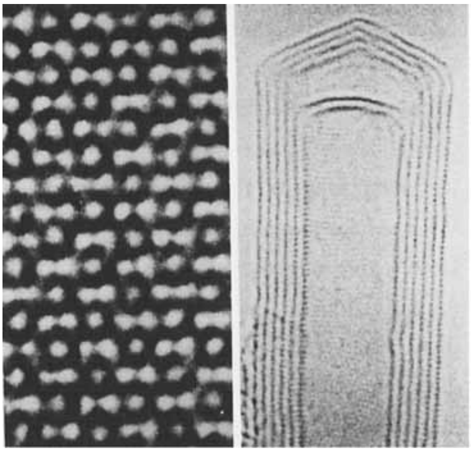

Fig.3
Images of $C_{60}$ and tubule observed by transmission electron microscope. The edge of tubules is generally closed.

Two final directions of the $C_n$ formation could be imagined, when the number of n is increased in the $C_n$ clusters described above. One is to the round shape, and the other to the rod-shape clusters. Although the final destination of the formation of such $C_n$ clusters with increasing n has not been clarified yet, rod-shaped $C_n$ materials are found in the deposits vicinity to the cathode carbon rod, while the spherical-shaped clusters are most often found in the soot produced with gas phase reactions. The tubules have hexagon in the side surface (Fig.2) and their edges are generally closed with including pentagons as shown in Fig.3. In this sense these rod-shaped tubules are also classified into $C_{60}$ family. The new types of carbon, spherical-shaped clusters like $C_{60}$ and tubules, having hexagon and pentagon networks are called fullerenes after the name of Buckminster Fuller who designed the world's largest geodesic dome[16].

## ELECTRONIC PROPERTIES OF $C_{60}$ and TUBULES

In order to have better understanding on the electronic properties of $C_{60}$ and tubules, we had better have the conceptual stand-point that $C_{60}$ is a molecular-type cluster and tubule is a crystal-type cluster. In the case of $C_{60}$, crystals are made from the $C_{60}$ units and they show various interesting solid properties. On the other hand, tubules themselves are the crystals having a regulated structure and showing unique electronic properties. As described here, although in the geometrical consideration these new types of $C_n$ materials are classified into the same family, the expected electronic properties are different.

The energy levels of $C_{60}$ are shown in Fig.4a.[17,18] As shown in this figure, the HOMO level of the $C_{60}$ molecule has degenerate five levels with $h_u$ symmetry and the LUMO level with $t_{1u}$ symmetry is triply degenerate. The five HOMO levels are completely occupied by ten electrons and $C_{60}$ has a closed-shell electronic structure. The orbitals forming these levels are $\pi$-type and the electrons delocalize over the molecule. Therefore, in principle the properties of the $C_{60}$ molecule is determined by the $\pi$-electron characters.

Because of the sphericity of $C_{60}$, a crystal with closed packing structure of either hexagonal closed packing (h.c.p.) or face centered cubic (f.c.c.) can be expected for the $C_{60}$ solids. In these two choices pristine $C_{60}$ is shown to be f.c.c. as is the solid crystal structure of other closed-shell elements such as Ar, Kr and Xe. The electronic states of the f.c.c. $C_{60}$ solid are also shown in Fig.4b. In solids the $h_u$ HOMO and $t_{1u}$ LUMO levels construct the bands, but this is categorized in van der Waals crystals since the molecular characteristic remains strongly. This can easily be understood considering that $C_{60}$ is a closed shell molecule with relatively large LUMO-HOMO gap. The higher edge of the valence bands consists of the $h_u$-derived levels and the lower edge of the conduction bands is made of the $t_{1u}$-derived levels. The band gap of the

$C_{60}$ solid is about 1.8 eV and is a typical semiconductor. However, it should be noted that the covalent character of the $C_{60}$ solid is relatively stronger than that of conventional van der Waals organic crystals.

In contrast to $C_{60}$, tubules themselves are crystals and band calculations have been performed by several researchers.[12-14] As shown in Fig.4c single shell tubules show variety of electronic properties depending on the diameter as well as helix determined by how a graphitic sheet rolls up to make tubules. In general the electronic properties of tubules can be related to their structures described in a fashion of $A(n_1,n_2)$, where $A(n_1,n_2)$ means the tubule made by rolling up a graphitic sheet so that the origin A(0,0) can be overlapped on the $A(n_1,n_2)$ point, as follows: (1) $n_1-2n_2=0$: metal (2) $n_1-2n_2=3m$ (m=1,2,...): narrow gap semiconductor (3) the other cases: wide gap semiconductor. As the diameter of tubules becomes larger and approaches to infinitive, these electronic properties will be the same as graphite having a semimetallic property.

The electronic properties expected between $C_{60}$ and tubules are greatly different. As for $C_{60}$ the high molecular symmetry of $C_{60}$ is responsible for the electronic properties. As described later, high conductivity as well as superconductivity with high transition temperature are observed for f.c.c. $C_{60}$ solids in combination to alkali metals. Whereas for tubules although carrier injection might be effective, the precise control of structural parameters such as diameter and helix would be much more important in order to use them as nano-electronic materials.

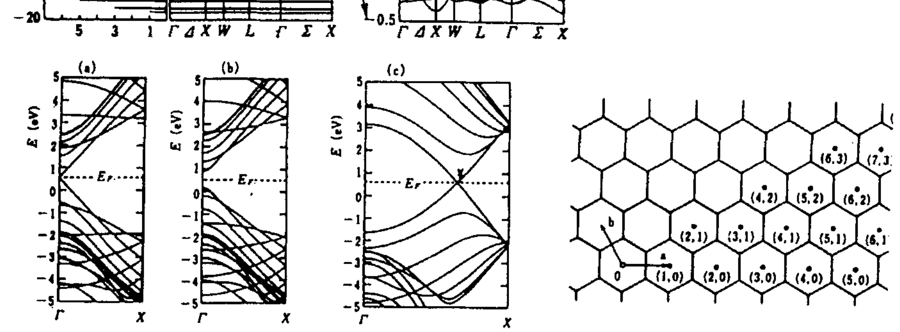

Fig.4

Band structure of $C_{60}$ solid and tubules (from Refs. 18 and 12)

## CONDUCTIVITY AND SUPERCONDUCTIVITY in $C_{60}$ FULLERIDES

As mentioned above the $C_{60}$ solid is semiconducting. There are two methods to be generally considered for carrier injection as shown in Fig.5. One is the replacement of some of $C_{60}$ by electron-rich or electron-poor molecules. This is the same technology as used in silicon. For example, B or P doping for replacing some of Si can generate P-type or N-type semiconductors, respectively. For such candidate molecules for the replacement of $C_{60}$, $BC_{59}$ and $NC_{59}$ could be considered for hole and electron injection and endohedral materials such as $La^{3+}C_{82}{}^{3-}$ could also be used. However, No such experiments have been reported to date. The other method is intercalation used for graphite. Other elements can be intercalated into the spaces of graphite layers. For example, $KC_8$ is known to be a superconducting graphite onterca;ation even though the transition temperature is quite low. In contrast to graphite having two-dimensional character, $C_{60}$ solids show three dimensional character. Instead of the interlayer spacings, the interstitial site spacings can be used for $C_{60}$. Such examples are actually reported in combination to alkali metals[6-10] and alkali-earth metals[19-21].

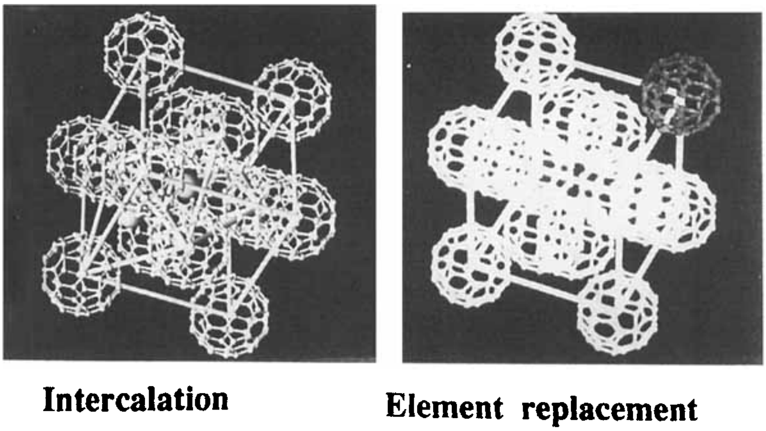

Fig.5 Two types of method for carrier injection. Intercalation is successfully used for graphite and element replacement is used for silicon.

The most attractive electrical properties have so far been found for the interactions with alkali metals. In Fig.6 the change in conductivity is shown as a function of the doping time of K. The picture in Fig.6 is one of the construction of experimental tools. The conductivity increases first with the concentration of K and decreases again. The maximum conductivity of 500 S $cm^{-1}$ is observed at x=3 for $K_xC_{60}$, and the temperature dependence of conductivity shows that $K_3C_{60}$ solid is metallic. This can be interpreted if we apply the rigid band model of $C_{60}$ solid into the intercalations. In $K_3C_{60}$ three electrons can be injected into the $t_{1u}$-derived conduction band and accordingly the band is half filled to give a metallic picture.

The carrier injection into $C_{60}$ was described above in terms of intercalation of graphite. In another word, this can also be expressed as an ionic salt. At present A and C60 are known to make various ionic solids, where A denotes the alkaline metal. This is partially because $C_{60}$ can be easily reduced into several stages of anions due to the degeneracy of the $t_{1u}$ level and has multi valences from -1- to -6. So far f.c.c. $A_1C_{60}$[22], f.c.c. $A_2C_{60}$[23], f.c.c. $A_3C_{60}$[24], body centered cubic (b.c.t.) $A_4C_{60}$[25] and body centered cubic (b.c.c.) $A_6C_{60}$[26] are reported depending on the number of A with exceptions for Na doping. In the case of K the stable phases at room temperature are $K_3C_{60}$, $K_4C_{60}$ and $K_6C_{60}$ and only $K_3C_{60}$ is metallic among these. Therefore, considering these existing crystal phases and their electronic properties the observed conductivity change can be understood, although why $A_4C_{60}$ cannot be metallic is still unclear.

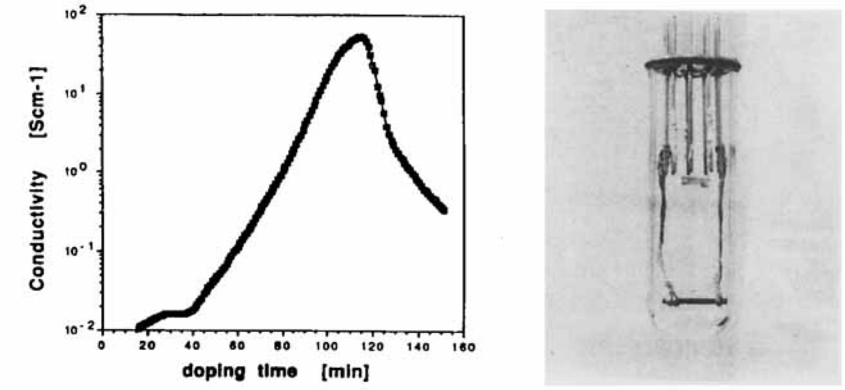

Fig.6 Conductivity of the $C_{60}$ thin film doped with K as a function of the doping time. The photograph is a set-up for experiments.

High Tc superconductivity is also reported for the ionic solids having the stoichiometric composition of $A_3C_{60}$ in f.c.c. lattice. In this structure both crystallographic interstitial sites, one larger octahedral (O-) and two smaller tetrahedral (T-) sites per $C_{60}$, are occupied by A elements, and the alkali-metals are thought to be completely ionized. Since the f.c.c. $A_3C_{60}$ crystals differ from the other existing crystal phases from the view point of electrical properties, the detailed studies of the crystal structure of this phase is crucial. In the following the lattice parameters of $A_3C_{60}$ are simply discussed in connection to the observed superconductivity.

The lattice parameters ($a_0$) of these $A_3C_{60}$ compounds are shown in Fig.7 as a function of the total volume of $A^+$ cations in the unit cell[27]. In general $a_0$ would have a good correlation with the ionic radii of alkali-metals. Actually at first glance the lattice parameters ($a_0$) seem to vary according to the size of alkali-metal cations in a simple

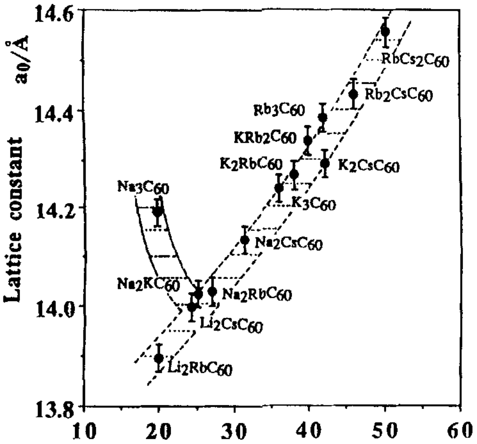

Fig.7 The relationship between $a_0$ and the total volume of the intercalated alkali cations. The f.c.c. cell is taken as an equivalent b.c.t. cell with $a_{b.c.t.}=a_{f.c.c.}/\sqrt{2}$. P shows the turning point previously supposed.

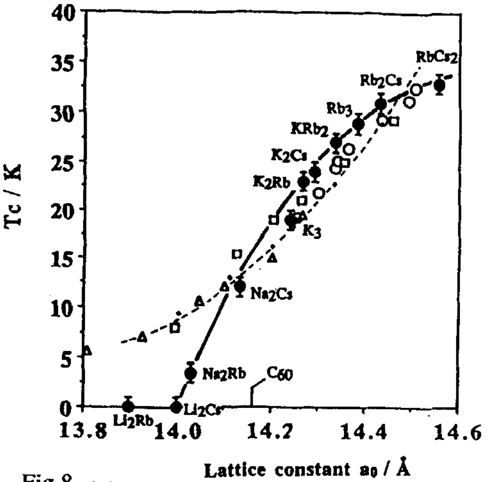

Fig.8 The relationship between Tc's and $a_0$'s for $M_3C_{60}$ (M=Li, Na, K, Rb, Cs and their binary alloys) superconductors in a wide range of $a_0$ (from Refs. 28 and 29).

manner as shown in this figure. Looking a bit closer, however, we can see a slight difference in lattice contraction in the small lattice parameter region. For instance, $Na_3C_{60}$ and $Na_2KC_{60}$ do not follow the line of the lattice parameters. The other thing to be pointed out is that $KCs_2C_{60}$ is not plotted in this figure, since the phase stability of this composition is much less than that of the other $A_3C_{60}$ fullerides. The discrepancies in lattice parameter and the instability of f.c.c. crystal phase take place in the following two cases. The former discrepancy is the case that the O-site is occupied by alkali-metals with small ionic radius compared to the site space. Owing to the mismatching between the cation size and the O-site spacing the $C_{60}^{3-}$-$A^+$ coulombic interactions would become small relatively to the central field repulsive interactions and, therefore, the lattice cannot contract to be closely packed. The latter phase instability occurs when the T-site is forced to expand by the occupation of alkali-metals with large ionic radius, where the stress in the lattice causes the f.c.c. structure to another stable crystal structure having energy minimum.

It has been clarified so far that only f.c.c. $A_3C_{60}$ is metallic and superconducts under certain temperatures. The superconductivity can be checked by either transport or diamagnetic susceptibility measurements. However, so far, the preparation of high quality single crystal or thin films of f.c.c. $A_3C_{60}$ containing binary alkali-metals is still not well established. Therefore, the magnetic diamagnetic shielding measurements are generally employed for studying the $T_c$'s using polycrystalline powder samples. The $T_c$ of the prepared samples can be evaluated from the on-set temperature of the shielding curves.

The $T_c$ values of these compounds are plotted as a function of lattice parameter in Fig.8.[28-30] In this figure the data of high pressure experiments and the expectation from the simple BCS theory are also shown. There are two important aspects that should be noted. One is that the actual Tc decreases very far from both the pressure data and the simple BCS expectation in small lattice parameters. The other is that $T_c$ increase seems to be saturating in the large lattice parameter region. These are very important and should be understood for explaining what controls Tc in these new superconductors family. So far the highest Tc among these superconductors family is 33 K for $RbCs_2C_{60}$.[9]

## IMPORTANCE OF INNER SPACE

Another concern that we should point out for these new carbon materials is the inner space insides the cages. $C_{60}$ has an open spherical space of about 8 Å inside the hollow. Tubules also have a cylindrical shaped space inside. These nano-cavities will offer many possibilities in nano science to us.

If other electron-donating elements comared to $C_{60}$ can be introduced into the hollow as shown in Fig.9a, the molecules negatively charged outside and positively charged inside would be obtained. This could look like atomic elements whose size is extremely large[31]. New crystals might be achieved from these quasi-atomic elements. On the other hand, the tubules have a quite narrow and long space inside the inmost tubule of multi-layered tubules as shown in Fig.9b. This inner space could accommodate variety of materials from inorganic to organic compounds. Nowadays quantum confinements are of large interests, however experimental examinations related to these phenomena are generally difficult and such studies are limited mainly to theoretical considerations. The encapsulation in tubules might open a way to nano science for studying the influence of such confinements on electrical and optical properties of materials.

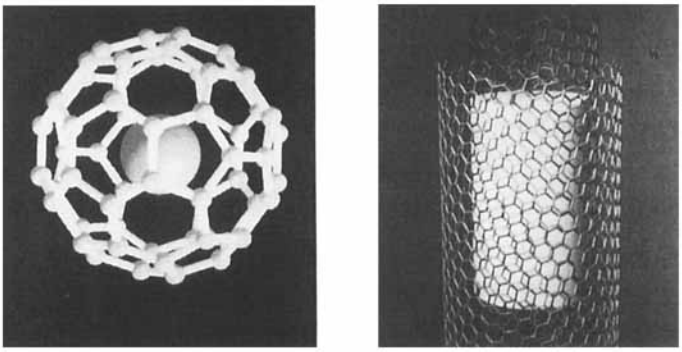

Fig.9 Graphics of $C_{60}$ and tubule encapsulating other elements.

A lot of experimental data show that some of elements such as Sc, Y, and La can actually be introduced into the hollow of the $C_{82}$ molecule, but so far no success has been reported for $C_{60}$. Depending on the size of the elements relative to the inner-space of $C_{82}$, $Sc_n@C_{82}$ (n=1-3), $Y_n@C_{82}$ (n=1,2) and $La@C_{82}$ are spectroscopically found, where @ denotes the endohedral state. These are now being isolated for the final structural confirmation. Similar endohedral modifications on the tubules have recently been also reported.[35] As can be seen in Fig.10a lead oxides can successfully be introduced into the inmost tubule after breaking up the edge of tubules. Furthermore the way of opening the edge of tubules using oxidation is possible[36], and therefore we have possibilities of confining a variety of materials in the nano cavity world. Another remark to be mentioned with regard to the inner space of fullerenes is the encapsulation of inorganic crystals in the large size $C_n$ fullerenes usually with n=1000. Using the encapsulating large $C_n$ fullerenes the air-sensitive substances could be protected. Such example is reported for large fullerenes encapsulating $LaC_2$.[37,38] A lot of examples are reported regarding such encapsulations to date. These might also open a way to medical applications. The substances to be sensitive to oxygen or other outer environment can be protected by encapsulation and be released in the special position of body.

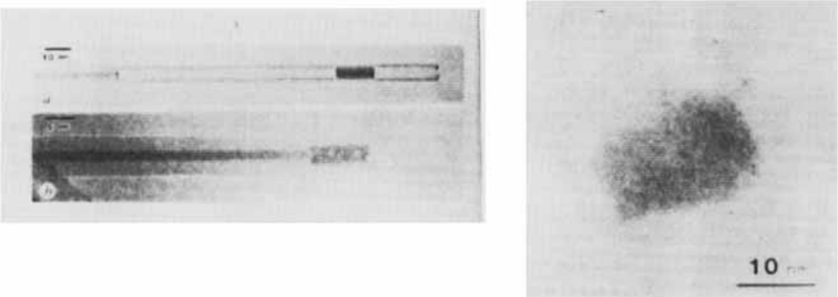

Fig.10 Electron microscope images of metal encapsulating tubules and a large fullerene containing metal carbide (from Refs. 35 and 38).

## CONCLUDING REMARKS

At present two new types of carbon are added to the conventional carbon materials of graphite and diamond. As described here the new forms of carbon show very interesting variety of properties. A new stage of material science including applications are starting using fullerenes as exotic materials.

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## REFERENCES

1. Kroto H. W., Heath J. R., O'Brien C., Curl R. F. and Smalley R. E., Nature, 318, 162 (1985).
2. Krätschmer W., Lamb L. D., Fostiropoulos K and Huffman D. R., Nature 347, 354 (1990).
3. Iijima S., Nature 354, 56 (1991).
4. Ebbesen, T. W. and Ajyan P. M., Nature, 358, 220 (1992).
5. Haddon R. C., Hebard A. F., Rosseinsky M. J., Murphy D. W., Duclos S. J., Lyons K. B., Miller B., Rosamilia J. M, Fleming R. M., Kortan A. R., Glarum S. H., Makhija A. V., Muller A. J., Elick R. H., Zahurak S. M., Tycko R., Dabbagh G. and Thiel F. A., Nature, 350, 320 (1991),
6. Hebard A. F., Rosseinsky M. J., Haddon R. C., Murphy D. W., Glarum S. H., Palstra T. T. M., Ramirez A. P. and Kortan A. R., Nature, 350, 600 (1991)
7. Holczer K., Klein O., Huang S.-M., Kaner R. B., Fu K.-J., Whetten R. L. and Diederich F., Science, 252, 1154 (1991)
8. Rosseinsky M. J., Ramirez A. P., Glarum S. H., Murphy D. W., Haddon R. C., Hebard A. F., Plastra T. T. M., Kortan A. R., Zahurak S. M. and Makhija A. V., Phys. Rev. Lett., 66, 2830 (1991)
9. Tanigaki K., Ebbsen T. W., Saito S., Mizuki J., Tsai J. S., Kubo Y. and Kuroshima S., Nature, 352, 222 (1991)
10. Murphy D. W., Rosseinsky M. J., Fleming R. M., Tycko R., Ramirez A. P., Haddon R. C., Siegrist T., Dabbagh G., Tully J. C. and Walstedt R. E., J. Phys. Chem., Solids, 53, 1321 (1992)
11. Allemand P.-M., Chemani K. C., Koch A., Wudl F., Holczer K, Donovan S., Grüner G and Thompson J. D, Science 253, 301 (1991).
12. Hamada N., Sawada S. and Oshiyama A., Phys. Rev. Lett., 68, 1579 (1992).
13. Mintmire J. W., Dunlop B. I. and White C. T. Phys. Rev. Lett, 68, 631 (1992).
14. Tanaka K., Okawara K., Okada M and Yamabe T., Chem. Phys. Lett., 191, 469 (1992).
15. Wakabayashi T. and Achiba Y., Chem. Phys. Lett, 190, 465 (1992).
16]. "Fullerenes–Synthesis, Properties and Chemistry of Large Carbon Clusters", ACS Symposium Series 481 (American Chemical Society, Washington D. C.), Hammond G. S. and Kuck V. J. eds., 1992.
17. Haddon R. C., Acc. Chem. Res. 25, 127 (1992).
18. Saito S. and Oshiyama A. Phys. Rev. Lett, 66, 2637 (1991).
19. Kortan A. R., Kophylov N., Glarum S., Gyorgy E. M., Ramirez A. P., Fleming R. M., Thiel F. A. and Haddon R. C., Nature, 355, 529 (1992)
20. Kortan A. R., Kophylov N., Glarum S., Gyorgy E. M., Ramirez A. P., Fleming R. M., Zhou O., Thiel F. A., Trevor P. L. and Haddon R. C., Nature, 360, 566 (1992)
21. Kortan R, private communication.
22. Zhu Q., Zhou O., Bykovetz N., Fischer J. E., McGhie A. R., Ramanow W., Lin C. L., Strongin R. M., Cichy M. A and Smith III A. B., Phys. Rev. B., in press.
23. Rosseinsky M. J., Murphy D. W., Fleming R. M., Tycko R., Ramirez A. P., Siegrist T., Dabbagh G. and Barrett S. E., Nature, 356 416 (1992)
24. Stephens P. W., Mihaly L., Lee P. L., Whetten R. L., Huaang S.-M., Kaner R. and Deideerich F., Natture, 351, 632 (1991)
25. Fleming R. M., Rosseinsky M. J., Ramirez A. P., Murphy D. W., Tully J. C., Haddon R. C., Siegrist T., Tycko R., Glarum S. H., Marsh P., Dabbagh G., Zahurak S. M., Makhija A. V. and Hampton C., Nature, 352, 701 (1991)
26. Zhu Q., Cox D. E., Fischer J. E., Kniaz K., McGhie A. R. and Zhou O., Nature 355, 712 (1992).
27. Tanigaki K., Hirosawa I., Mizuki J. and Ebbesen T. W., Chem. Phys. Lett, 213, 395 (1993).
28. Tanigaki K. Hirosawa I., Ebbesen T. W. and Mizuki J., J. Phys. Chem. Solids, in press.
29. Tanigaki K., Hirosawa I., Ebbesen T. W., Mizuki J., Shimakawa Y., Kubo Y., Tsai J. S. and Kuroshima S., Nature, 356, 419 (1992)
30. Tanigaki K, Ebbesen T. W., Tsai J.-S., Hirosawa I., and Mizuki J., Euro. Phys. Lett., 23, 57 (1993).
31. Oshiyama A. Saito S., Condensed Matter Physics, in press.
32. Chai Y., Guo T., Jin C., Haufler R. E., Chibante L. P. F., Fure J., Wang L., Alford J. M. and Smalley R. E., J. Phys. Chem., 95, 7564 (1991).
33. Shinohara H. Sato H., Ohkohchi M., Ando Y., Kodama T., Shida T., Kato T and Saito Y., Nature 357, 52 (1992).
34. Xie Q., J. Am. Chem. Soc., 114, 3978 (1992).
35. Ajayan P. M. and Iijima S., Nature 361, 333 (1993).
36. Ajayan P. M., Ebbesen T. W. Ichihashi T., Iijima S., Tanigaki K. and Hiura H., Nature 362, 522 (1993).
37. Ruoff R. S. Lorents D. C., Chan B, Malhotra R. and Subramoney S., Science, 259, 346 (1993).
38. Tomita M., Saito Y. and Hayashi T., Jpn. J. Appl. Phys. 32, L280 (1993).