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Review paper

C_{60} – AN ASTROPHYSICAL PROBLEM TRANSFERRED INTO SOLID STATE PHYSICS

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SUMMARY: This is an introductory review of a new research area, the study of carbon clusters, whose rapid developement in the last few years has been caused by motivations from astrophysics and solid-state physics.

1. INTRODUCTION

The purpose of this paper is to present an introductory review of a new research area , the study of carbon clusters, and in particular C_{60}. At first sight, it may seem that such a subject has absolutely no relation at all with astrophysics. However, the rapid developement of the field in the last few years was actually motivated by a long-standing astrophysical problem:the interpretation of the origin of the diffuse interstellar absorption lines (DIL) (Kroto et. al., 1985, 1987).

The study of carbon clusters can be introduced by posing the following "simple" question: What is the biggest number of carbon atoms that can form a molecule? Starting from general chemical considerations, one could be tempted to quote a small number like 2 or 4. It has been observed, nearly 50 years ago, that clusters of up to 15 carbon atoms can exist (Hahn , Strassman, Mattauch et. al., 1942; Mattauch , Ewald, Hahn et. al., 1943). Work performed in the last few years has shown that this number can be as large as 60 (Kroto, Heath, O'Brien et. al., 1985), and the largest clusters synthetized so far contain 266 carbon atoms (Parker , Wurz, Chatterjee et. al., 1991).

The relevance of carbon clusters to the solution of the DIL problem is not, at present, definitely established (Krätschmer, Fostiropoulos and Huffman, 1990; Huffman, 1991). It has however been shown that these materials are extremely interesting in solid-state physics:some of their compounds are superconducting, with the critical temperatures of the order of 30 - 40 K (for example, Rosseinsky, Ramirez, Glarum et. al., 1991; Tanigaki, Eddesen, Saito et. al., 1991).

Carbon clusters are today objects of a worldwide research effort. A recent bibliography of papers on C_{60} published between 1984 and March 1992 has a length of 55 pages, while a list of research groups active in the field has another 10 pages (Smaley, 1992).

This paper has two more sections. The next one is devoted to a discussion of the possible role of carbon clusters in the solution of the DIL problem, while the final section is concerned with studies of carbon clusters and their compounds in solid-state physics.

2. INTERSTELLAR SPECTROSCOPY

First observations indicating that the reddening of starlight is due to absorption and scattering on small interstellar grains were made around 1930. A detailed recent review of the problem is given by Bussoletti and Colangeli (1990).

The analysis of spectra of interstellar materials has led to important insights in a wide range of astrophysical problems. A strong boost to the developement of the field was given by the detection of interstellar NH_3 and H_2O (Cheung, Rank, Avery et al., 1968; 1969). These and later detections of interstellar molecules have led to much effort aimed at understanding the processes of their formation. It is now generally accepted that the presence of most of the observed molecular species can be accounted for by sequences of bimolecular ion-molecule reactions, combined with reactions on the surfaces of interstellar grains (Turner, 1989). Although the presence of many molecules has been confirmed in interstellar space (i. e., the carriers of a large number of spectral lines have been determined) there remained a group of lines for which no particular carrier could be identified. Some of them were observed even before the recognition of their interstellar nature. For example, in the spectral region 440 nm $\leq \lambda \leq$ 685 nm, there exists a group of 39 diffuse absorption lines (DIL), which are known to be of interstellar origin (Herbig, 1975), but whose carriers have not yet been discovered (Wu, 1972; Herbig, 1975; Huffman, 1977; 1991; Leger and Puget, 1984; Allamandola, Tielens and Barker, 1985). The discovery in interstellar space of carbon chain molecules (cyanopolyynes) of the general form HC_nN, with $3 \leq n \leq 11$ (for example, Bell et. al., 1982) caused much speculation.

Namely, it was hardly concievable that carbon chains with as much as 11 C atoms can be synthetized by the ion-molecule reactions, which provided a satisfactory explanation for the presence and abundances of the simpler molecules. It was also discovered that polyynes and small carbon clusters (C_3) were present in circumstellar shells around carbon stars, such as IRC +10°216 (Turner, 1989).

This object is surrounded by dust (Morris, 1975), which orriginates in the shell, and is being ejected in the interstellar medium with the molecules. A short time after the existence of the interstellar grains was discovered, it has been shown that the physical conditions in stellar atmospheres were such that carbon particles could form and that they would be driven into the interstellar medium by radiation pressure (O'Keefe, 1939). This idea has meanwhile gained both observational and theoretical support. It is currently considered as an established fact that carbon chain molecules and carbon clusters are being ejected into the interstellar medium by stars (Kroto, Heath, O'Brien et. al., 1987; Turner, 1989) but the chemical relationship between the two species is not clear.

Modern work (Turner, 1989; Duley et. al., 1989) has shown that grains of carbon in the interstellar medium and in stellar atmospheres consist mostly of amorphous graphite. It has been proposed that carbon chains can be synthetized by reactions between carbon clusters, produced by evaporation of graphite from carbon grains and the simpler molecules present in the interstellar medium (Kroto, 1982).

The experimental confirmation of this idea came a few years later (Rohlfing, Cox and Kaldor, 1984; Heath, Zhang, O'Brien et. al., 1987) . It was shown that laser vaporisation of graphite within the throat of a pulsed nozzle generates a beam of carbon clusters C_n, with $1 < n < 190$. Only even clusters C_{2n} were formed for $20 < n < 90$, while both even and odd clusters C_n were generated for n between 1 and 30. Clusters ($n < 30$) were observed to react with H and N to form polyynes , some of which have already been detected in interstellar space (Kroto, 1988).

Large clusters were completely inert, and mass spectrometry has shown that under various clustering conditions the dominant cluster was C_{60} (Kroto, Heath, O'Brien et. al., 1985; Heath, O'Brien, Curl et. al., 1987). It was proposed that the observed behaviour of C_{60} could be the result of the stabilization by closure of a graphitic net into a hollow chicken-cage structure (Kroto, Heath, O'Brien et. al., 1985; Kroto, 1988), known in geometry as the truncated icosahedron. It is a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. A very common object of approximately this form is the football. Because of the similarity of this structure with the domes extensively constructed by the architect R. Buckminster Fuller, C_{60} and similar clusters were named the buckminsterfullerenes (fullerenes for short).

First suggestions that the fullerenes might be the carriers of the DIL were made in the discovery paper (Kroto, Heath, O'Brien et. al., 1985); they were based on the stability of the fullerenes when formed under the most violent conditions, and on the well known fact that carbon is present in the interstellar medium in the form of grains.

At the time, no optical properties of the fullerenes were known. Recent work (Krätschmer, Fostiropoulos and Huffman, 1990; Pichler, Graham, Gelsen et. al., 1991; Pichler, Friend, Romanow et. al., 1992) has allowed the recording of optical absorption spectra of solid C_{60}. A comparison of these results with the interstellar extinction curves (such as those given in Huffman, 1991) does not show any obvious similarities, apart from the UV band at 217 nm, which is close to an interstellar absorption line. On the other hand, it is known that C_{60} is related to soot (Kroto, 1988).

Experiments have shown that IR spectra of soot have 4 lines in the region expected for C_{60} (Krätschmer, Fostiropoulos and Huffman, 1990). It has also been shown that doping C_{60} with C_{70} introduces interesting changes in the spectra. For example, the optical absorption spectrum of a C_{60}/C_{70} film (Pichler, Graham, Gelsen et. al., 1991) is qualitatively similar to the interstellar extinction curve for photon energies smaller than 4 eV. This could be interpreted as meaning that carbon clusters are present in space in the form of a mixture of C_{60} and C_{70}.

When produced in laboratory (Krätschmer, Lamb, Fostiropoulos and Huffman, 1990) and dispersed in benzene, C_{60} is of wine-red colour when observed in transmitted light. This observation can, at a qualitative level, support the idea that , if it is present in space, buckminsterfullerene has some influence on the reddening of starlight; more quantitative proofs (some already exist) would be needed before one could consider this problem as being solved.

Whether or not C_{60} is the carrier of the DIL is, at the time of this writing (end of June 1992), a completely unsolved problem. A possibly interesting path towards the solution could be the investigation of the optical absorption spectra of mixtures of C_{60} and C_{70}. By varying the relative abundances of the two components, and eventually adding some higher order fullerenes, one could aim at extending the region of similarity of the interstellar extinction curves and the optical spectra of the fullerenes. Unfortunately, due to the well-known information exchange problems with the rest of the world, the present author is unaware as to whether there has been any work in that direction.

3. SOLID STATE PHYSICS

The quantities of C_{60} produced in early experiments were extremely small. The synthesis of larger amounts of buckminsterfullerene, of the order of 100 mg in a day, became possible only recently (Krätschmer, Lamb, Fostiropoulos and Huffman, 1990).

The input substance for this process is pure graphitic carbon soot. It is produced by evaporating graphite electrodes in a rare helium atmosphere (the partial pressure of He is only about 100 torr). The soot is then scraped from the collecting surfaces of the evaporation chamber, and then dispersed in benzene. In this way one obtains a wine-red to brown liquid, whose exact colour is concentration dependent. The liquid is then separated from the soot and slowly dried, the final result being a crystalline material of dark brown or black colour.

After purification (the method for which has also been proposed) of the material obtained in this way, mass spectrometry shows that it is a mixture of fullerenes of various order, in which the most abundant component is C_{60}.

From the moment they could be produced in "large" quantities, laboratory research on the fullerenes has developed along the following three directions:
- the possible occurence of superconductivity;
- studies of phase transitions;
- the determination of their crystal structure.

Measurements of the electrical conductivity of pure C_{60} have shown that it is an insulator (Huffman, 1991). However, when intercalated with alkali-metal atoms to form the "fullerides" (Holzer, Klein, Huang et. al., 1991), it becomes a superconductor. Experiments were done on the fullerides of the composition A_xC_{60} , where A denotes an alkali-metal atom. It was thus shown that K_3C_{60} has a critical temperature $T_c \cong 19.3$ K (Holzer, Klein, Huang et. al., 1991) , which was increased to $T_c \cong 28$ K for A = Rb (Rosseinsky, Ramirez, Glarum et. al., 1991). Further increases of the critical temperature were obtained with more complicated doping. A compound of the form Cs_2RbC_{60} has $T_c \cong 33$ K (Tanigaki, Eddesen, Saito et. al., 1991), while the compound $Rb_2Tl_{2.2}C_{60}$ has a critical temperature as high as $T_c \cong 42.5$ K (Huffman, 1991).

The superconducting energy gap was measured for some of the fullerides. For example, it has been found for Rb_3C_{60} (Zhang, Chen, Kelty et. al., 1991) that $2\Delta/k_BT_c = 5.3$. This is comparable to values found for the high-temperature copper oxide superconductors, but it is considerably higher than the material-independent weak coupling prediction of the BCS theory, which gives for the gap the value of $2\Delta/k_BT_c = 3.53$. The implication of this result is that the fullerides are first examples of three dimensional strong coupling organic conductors. Should this similarity be confirmed, it could facilitate the explanation of the mechanism of superconductivity in the fullerides. Although various proposals exist (Pickett, 1991), no definitive theoretical consensus has emerged on the topic (Pietronero, 1992).

An experimental result which could be theoretically interesting is that the fullerides of the composition A_3C_{60} are isostructural (the lattice is f. c. c) and that the critical temperature increases monotonically with the size of the unit cell. A similar behaviour has been obtained for the density of states at the Fermi level, $N(E_F)$, (Fleming, Ramirez, Rosseinsky et. al., 1991), which implies that changes in T_c can somehow be accounted for by the changes in $N(E_F)$.

The problem of the crystal structure of buckminsterfullerene and its changes under the influence of various external parameters (i. e., the structural phase transitions) has been attacked by various experimental methods. The structure of the C_{60} cluster proposed in the discovery paper (Kroto et. al., 1985) implies the existence of two different bond-lengths between carbon atoms. This has recently been confirmed by NMR measurements (Yannoni, Bernier, Bethune et. al., 1991). C atoms placed on any given pentagon are separated by (1.45 ± .015) Å, while the corresponding number for those on a hexagon is (1.40 ± .015) Å. The moment of inertia of a C_{60} molecule, approximated as a three-dimensional free rotor, is $I = 1.0\ 10^{-43}$ kg m^2 (Lu, Li and Martin, 1992). At room temperature C_{60} molecules are placed at f. c. c. lattice sites in solid C_{60} (Stephens , Mihaly, Lee, 1991). Recent powder neutron diffraction experiments (David, Ibberson, Dennis et. al., 1992 a, b) have shown that solid C_{60} is of cubic structure in the temperature range between 5 K and 320 K. The material undergoes a first-order phase transition at $T_c \cong 260$ K, and a continious phase transition has been detected at 90 K. In the high temperature region, that is for $T > 260$ K, the lattice of solid C_{60} is f. c. c, but the individual C_{60} molecules are orientatonally disordered, undergoing continious reorientation. High-pressure experiments ($P < 5$ kbar) have shown that the high temperature transition is pressure dependent, with $dT_c/dP = 11.7$ K/kbar (Kriza, Ameline, Jérome et. al., 1991). A small structural anomaly has been detected at 155 K. Below 260 K the mechanism of molecular reorientation changes; it is modelled as reorientation about a single axis, and the lattice is simple cubic.

These data have been successfully described (Lu, Li and Martin, 1992) by a model representing the interaction between carbon atoms on different C_{60} molecules as a combination of van der Waals and Coulomb interactions, and then minimizing the total energy.

High-pressure, low temperature experiments have also been done (Kriza, Ameline, Jérome et. al., 1991; Nunez-Regueiro , Monceau, Rassat et. al., 1991). They indicate the existence of two phase transitions, at 3 kbar and 150 - 200 kbar. It is interesting to note that these values of transition pressure can be predicted within the classical theory of dense matter proposed by P. Savić and R. Kašanin (Čelebonović, 1992 a). The volume compressibility of solid C_{60} has been measured (Fischer, Heiney, McGhie et. al., 1991). Its value, $-\partial \ln V/\partial \ln P = (7 \pm 1)\ 10^{-12}$ cm^2/dyn, makes C_{60} the softest known solid composed only of carbon; this value is consistent with the previously mentioned idea of van der Waals + Coulomb intermolecular bonding.

Finally, a few words about the packing of individual molecules of buckminsterfullerene in crystalline C_{60}. A crystal consisting of a mixture of C_{60} and C_{70} in the proportion 90 : 10 was recently studied by transmission electron microscopy (Wang and Buseck, 1991). The immages obtained showed projections of hollow C_{60} molecules in close-packed configurations. On some of the immages the existence of domain-like structure was detected; namely, regions containing fullerenes both smaller and larger than C_{60} were detected. By measuring the diameters of the immages, fullerenes as small as C_{32} and as large as C_{130} were detected. It is not clear whether the larger fullerenes were formed as a consequence of radiation dammage in the electron microscope, or due to some spontantenous reaction.

4. CONCLUSION

This paper had the aim of introducing the field of carbon cluster research to a previously uninterested reader. Due to the complexity of the field and the rapidity of its developement, no attempt of completeness was made; for instance, we have not entered into details concerning optical studies of the fullerenes, although these could have usefull consequences in astrophysics. Results acquired so far in superconductivity of the fullerenes could have applications in two different areas: astrophysics (because conductivity is related to optical parameters of a system) and solid-state physics (it seems that by carefully complicating the doping the critical temperature rises).

A general conclusion is that carbon cluster research is a rapidely developing field on the border of astrophysics and solidstate physics. It is hoped that this paper will arise sufficient interest of at least some readers so as to initiate them to begin scanning the literature and attempting to do some research on their own.

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C_{60} – АСТРОФИЗИЧКИ ПРОБЛЕМ ПРЕНЕТ У ФИЗИКУ ЧВРСТОГ СТАЊА

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Прегледни чланак

У овом чланку дат је увод у проблематику истраживања јата (тзв. кластера) атома угљеника. Мотиви за експлозиван развој истраживања у овом домену су двоструки: потичу из астрофизике (проблем дифузних апсорпционих линија међузвезданог порекла) и физике чврстог стања (једињења угљеникових кластера са алкалним елементима су суперпроводна). У раду су приказани одабрани постигнути резултати а указано је и на неке отворене проблеме и могуће путеве њиховог решавања.