SOLID C_{60}

The discovery of a method for producing the soccer-ball-shaped buckminsterfullerene molecule in abundance led also to the discovery of a totally new form of crystalline carbon.

Donald R. Huffman

The first crystals of solid C_{60}/C_{70}, grown from a benzene solution. The larger crystals in this transmission micrograph are about 20 microns across. Three crystalline forms—plates, rods and stars—can be seen; pure C_{60} forms needles. (Photograph by Wolfgang Krätschmer.) **Figure 1**

On 18 May 1990 my longtime friend and colleague Wolfgang Krätschmer called from the Max Planck Institute for Nuclear Physics in Heidelberg with a startling suggestion. The elusive molecule C_{60}, which we had slowly come to realize was abundantly present in the carbonaceous smoke we had been making since 1983, was readily soluble in benzene, he told me. This would provide a simple technique for separating the molecule from the ordinary graphite that made up over 90% of the soot we had been producing.

Within minutes I was able to verify the solubility. Then came the ultimate "Eureka" experience in my life as a solid-state physicist. With graduate student Lowell Lamb, I allowed a small drop of the red benzene solution to dry on a slide. Under the microscope beautiful little hexagonal platelets of apparently pure carbon were revealed—a brand new form of solid carbon. It was just what Krätschmer and his graduate student Konstantinos Fostiropoulos had experienced. So far as we know, the four of us were the first human beings ever to see this new form of crystalline carbon, which is shown in figure 1 just as we viewed it in the microscope. (Figure 2 shows the crystal structure of solid C_{60}.) Our new technology soon made available for the first time copious supplies of the fascinating molecule C_{60}.

Intense interest in the C_{60} molecule had begun in 1985 with the discovery that 60-atom carbon clusters were unusually dominant in the mass spectra of laser-vaporized graphite. The experiment was done by Richard Smalley's group at Rice University in collaboration with Harry Kroto of the University of Sussex, England. They found that by adjusting the timing of the laser pulses and the pressure of the helium atmosphere they could produce a dominance of the C_{60} molecule.[1] Even-numbered carbon

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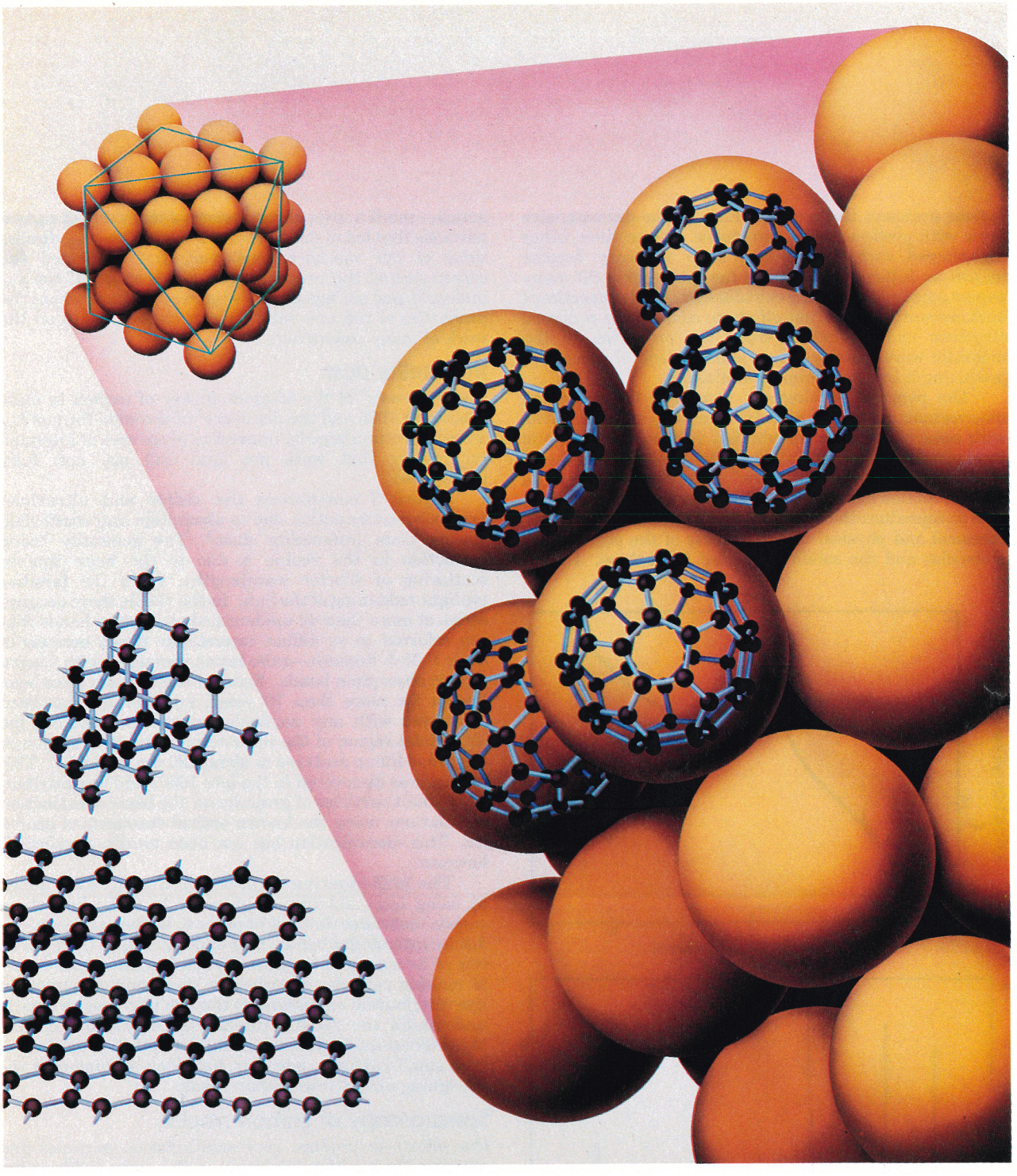


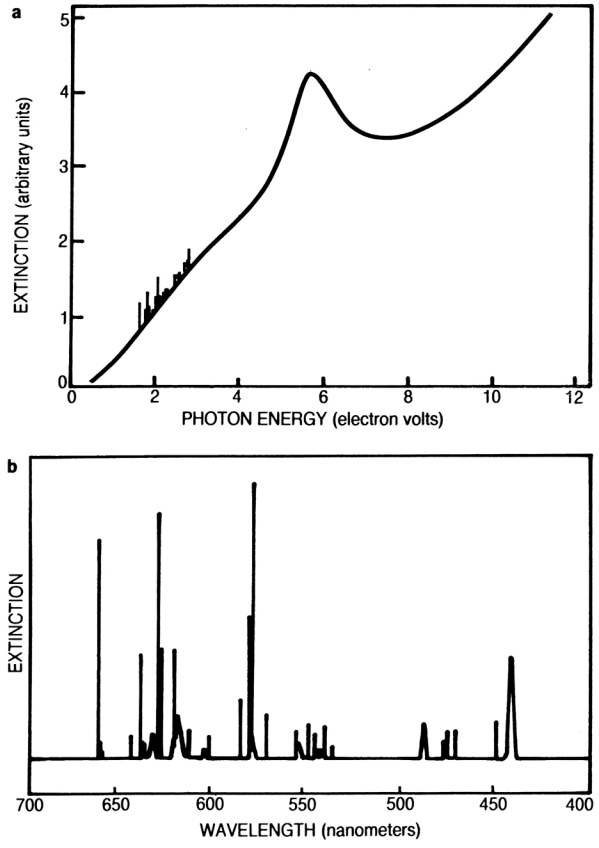
The three forms of solid carbon. The corner cut from the C_{60} crystal cube reveals a (111) crystal plane where molecules stack in hexagonal arrays, as seen in figure 6. The structures of diamond and graphite are shown at the middle and bottom left. (Drawing © Henry Hill Jr, used by permission.) **Figure 2**

clusters of greater than 40 atoms had been observed in a similar way at Exxon Laboratories,[2] but the Rice experiments showed that there was something very special about the 60-atom cluster.

The structure the Rice team proposed for the molecule was the truncated icosahedron typified by a soccer ball, with the carbon atoms at the 60 vertices of the pentagons and hexagons that make up the near-spherical surface. Later it came to light that such a structure had been proposed earlier, but no one had observed such clear and unambiguous evidence for its unique stability.[3] The molecule was named buckminsterfullerene after the

famous architect Buckminster Fuller, who did extensive work with geodesic dome structures. (Since then, other cage-shaped carbon molecules have similarly become known as fullerenes.) During the years 1985–90 many papers appeared reporting calculations of the properties of buckminsterfullerene, but efforts to confirm the proposed structure and to further study the properties of the molecule were thwarted by a general lack of success in producing it in macroscopic quantities.

The paper describing our technique for producing macroscopic quantities of crystalline C_{60} and C_{70}, along with some of the experiments that verified the new solid form of carbon, was published as the cover story in the 27 September 1990 issue of *Nature*.[4] An explosion of work on C_{60} and related molecules followed, as many workers were able to reproduce the synthesis and begin making various chemical and physical measurements of the cage-shaped molecules and the solids condensed from them. In this article I retell a little of the history of our study of carbon particles that led to the discovery of crystalline C_{60}, discuss some of our measurements that first confirmed the correctness of the proposed soccer ball shape of the C_{60} molecule, and survey some of what we now know about the properties of the new solid form of carbon, based on the work of many researchers.



Extinction due to interstellar dust. **a:** The optical density over a large energy range. **b:** The diffuse interstellar bands, which appear as fine structure in **a** between about 1.6 and 2.8 eV. **Figure 3**

Interstellar dust

The discovery[1] of the 60-atom cluster of carbon in mass spectra in 1985 and the discovery[4] of the solid form of C_{60} were both stimulated by interest in properties of interstellar matter that were not (and still are not) fully understood.

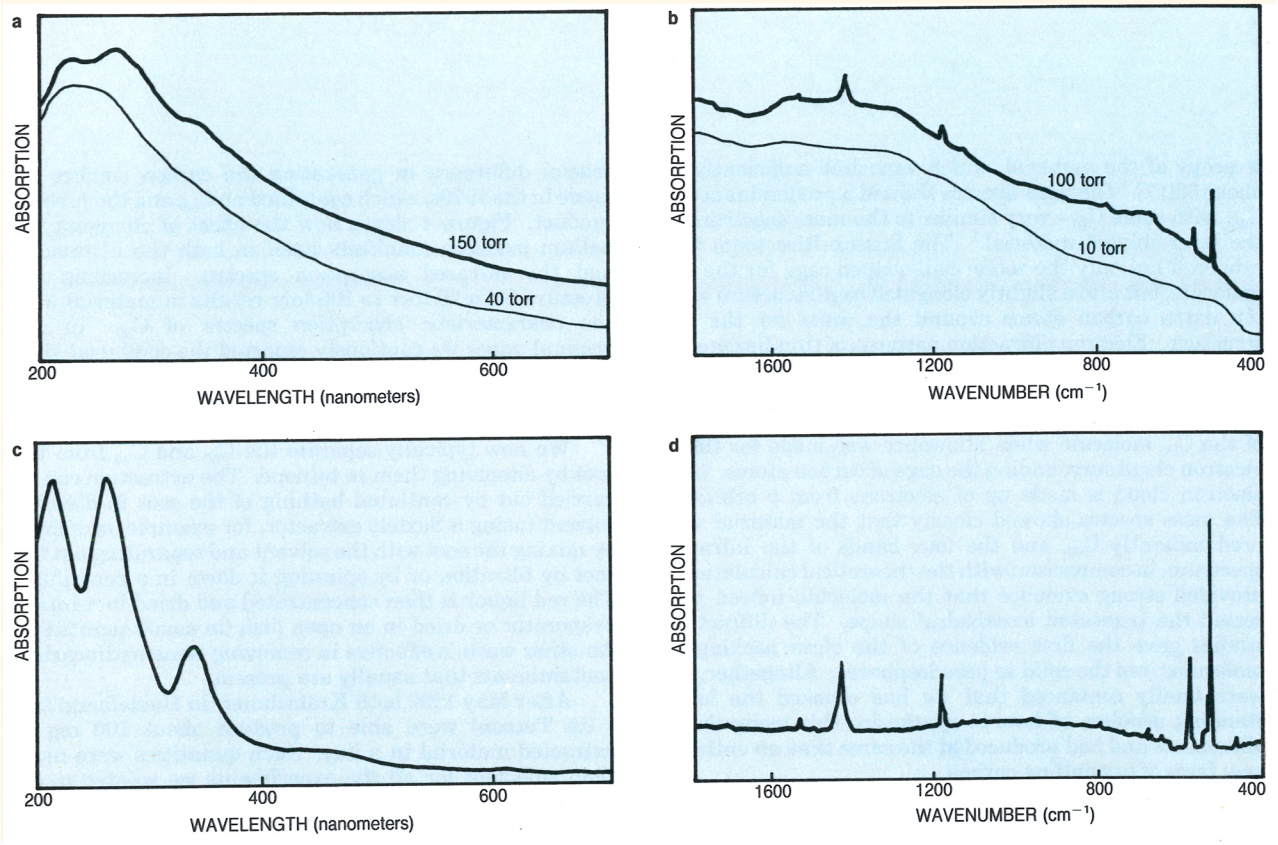
Figure 3 summarizes the visible and ultraviolet extinction (attenuation due to absorption and scattering) arising from interstellar dust.[5] The generally rising extinction in the visible is due to the more intense scattering of shorter wavelengths, as in the familiar twilight reddening of the Sun. In the visible there occurs a series of more than 40 unidentified absorption bands that are referred to as diffuse interstellar bands because of their 1–30-Å breadth—quite broad compared with typical atomic absorption bands. Some of these bands have been known for more than 70 years, but not one has been associated with any particular cause. Dominating the ultraviolet region of the interstellar extinction spectrum is a broad hump centered at about 220 nm, or 5.6 eV. This feature was discovered in the late 1960s and was attributed to small particles of graphite on the basis of extinction calculations using the known optical constants of graphite. This identification has not been totally convincing, however.

The 1985 experiments at Rice University were aimed at using laser ablation of graphite to make long-chain carbon molecules that might prove to be the carriers of the diffuse interstellar bands. Our experiments at the University of Arizona and the Max Planck Institute were aimed at making particles of carbon as small and as narrow in size distribution as possible so that we might more clearly understand the 220-nm interstellar extinction feature. My original interest in exploring the optical properties of very small particles, however, had been prompted by the intriguing diffuse interstellar bands.

Spectroscopy of carbon smoke

Our efforts to produce very small carbon particles and measure their extinction began in the early 1970s at the University of Arizona. Small particles in condensed smoke from vaporized graphite produced an extinction with an interesting similarity to the 220-nm interstellar feature, but some discrepancies in shape and peak wavelength remained. We made our smoke samples for those early experiments by striking an arc between graphite electrodes in a helium environment and collecting the smoke on uv-transparent substrates. More than a decade later this would prove to be the simple method for making large quantities of C_{60}, after minor changes in the production conditions.

During a sabbatical year I spent in Heidelberg in



Absorption spectra. **a,b:** Ultraviolet and infrared spectra, respectively, of graphitic soot containing C_{60} (upper curves) and graphitic soot without C_{60} (lower curves). **c,d:** Uv and ir spectra, respectively, of extracted material with no graphitic soot present. **Figure 4**

1982–83, Krätschmer and I decided to continue the graphite smoke study, because the experimental extinction still did not quite make sense. We varied parameters such as the helium gas pressure, the condition of the carbon rod tips and the current density. In the extinction spectrum of one sample we observed three small features superimposed on the usual ultraviolet extinction hump near 220 nm. The extra bumps on the hump led Krätschmer to dub this the "camel sample." Figure 4a compares this sample's ultraviolet extinction spectrum with that of "normal" graphitic smoke. Raman spectra of the camel sample also showed an extra feature not associated with any known form of carbon. Attempts to explain this strange behavior occupied us, off and on, for several years. Could this feature represent a new allotrope of carbon, long-chain molecules of carbon, quantum size effects in small particles, magic number clusters? Not likely. More probably it was just some sort of "junk" that had crept into the production process.

In 1988 Krätschmer began to use infrared spectrometry to study the unusual carbon smoke. The infrared spectra, too, showed interesting new features, which appeared to be correlated with the additional uv structure. There were, in addition to the continuum from the usual graphitic soot, four large peaks and a number of smaller ones. The number four was significant. The very high (icosahedral) symmetry of the proposed C_{60} molecule demanded that there be only four infrared active modes, an astonishingly small number for such a large molecule. Several sets of theoretical calculations (listed in reference 4) described this limitation to four active infrared bands and predicted the bands in a pattern quite similar to what we observed. Although we weren't totally convinced that we had produced C_{60}, in September 1989 we presented a paper on the subject—"Search for the uv and ir Spectra of C_{60} in Laboratory-Produced Carbon Dust"—at a conference titled "Dusty Objects in the Universe."[6] Our hesitancy arose from the proximity of two of the bands to bands known to be due to that nemesis of experimental physicists, vacuum pump fluid. The experiment that proved that the four infrared bands were not due to "junk" was done in Heidelberg: Krätschmer and Fostiropoulos produced the smoke under the same conditions, but this time used the carbon-13 isotope to make the soot. The bands shifted by the square root of the ratio of the ^{12}C to the ^{13}C mass, as expected for a *pure carbon* molecule. The result convinced us to claim "Evidence for the Presence of the C_{60} Molecule" in the title of our next paper.[7]

The stage was now set for the discovery of the extraction process and the revealing of the C_{60} crystals. Krätschmer found that C_{60} dissolves in benzene, as evidenced by the formation of a wine-red solution. This leaves the insoluble graphitic soot to be separated by centrifuging or filtering. The crystals of figure 1 gave the first glimpse of the new form of solid carbon, which we called fullerite. In all of the papers on the molecule buckminsterfullerene published following its observance in the mass spectrum, little had been said about the possibility of the solid form.

Since we were probably the first people ever to possess this new form of solid carbon, we realized that every experiment we did on it would be a first. We did mass spec-

troscopy of the material, which vaporized sufficiently at about 350 °C. The mass spectra showed a predominance of C_{60}, with some C_{70}—very similar to the mass spectrum of the laser-ablated material.[1] The Sussex–Rice team had proposed not only the soccer-ball-shaped cage for the C_{60} molecule, but also a slightly elongated cage structure with ten extra carbon atoms around the waist for the C_{70} structure. Electron diffraction patterns of thin hexagonal platelets showed a high degree of crystalline order, and x-ray diffraction powder patterns showed a nearest-neighbor spacing of about 10 Å, consistent with the expected size of the C_{60} molecule when allowance was made for the π electron cloud surrounding the cage of carbon atoms. (A π electron cloud is made up of electrons from p orbitals.) The mass spectra showed clearly that the material was predominantly C_{60}, and the four bands of the infrared spectrum, in comparison with the theoretical calculations, provided strong evidence that the molecule indeed possessed the truncated icosahedral shape. The diffraction studies gave the first evidence of the close packing of molecules into the solid as pseudospheres. Altogether, we were finally convinced that we had cracked the long-standing problem of how to synthesize this molecule in abundance and had produced at the same time an entirely new form of crystalline carbon.

Production method

Figure 5 shows the steps in the synthesis and extraction of solid C_{60}. Rods of spectrographic-grade graphite are butted together, and a high current, on the order of 100 amps, is passed through the rods. Both ac and dc currents have been successful. In our original production method, we narrowed the tips to about 1 mm, but we now commonly use rods about 6 mm in diameter. Carbon vaporizes in the vicinity of the contact, producing a carbon plasma that condenses into a graphitic soot. This soot collects on the surfaces provided or on the walls of the chamber. The helium gas pressure proved to be the crucial difference in generating the carbon smokes we made in the 1970s, which contained no C_{60}, and the present product. Figure 4 shows how the effect of changing the helium pressure manifests itself in both the ultraviolet and the infrared absorption spectra. Increasing the pressure from 20 torr to 100 torr results in material with the characteristic absorption spectra of C_{60}. In our original paper we cautiously reported the combined yield of C_{60} and C_{70} as "a few percent." The yield later proved to be more like 8%, typically, and now groups are reporting yields that exceed 40% in some cases.

We now typically separate the C_{60} and C_{70} from the soot by dissolving them in toluene. The extraction can be carried out by continual bathing of the soot in distilled solvent (using a Soxlett extractor, for example) or simply by mixing the soot with the solvent and separating out the soot by filtration or by spinning it down in a centrifuge. The red liquor is then concentrated and dried in a rotary evaporator or dried in an open dish (in small quantities). An ether wash is effective in removing some hydrocarbon contaminants that usually are present.

After May 1990 both Krätschmer (in Heidelberg) and I (in Tucson) were able to produce about 100 mg of extracted material in a day. Such quantities were more than sufficient for all the experiments we wanted to do. As soon as the process was made public the demand for larger quantities arose. A number of groups including our own reported scaling up the production to more than a gram a day using various forms of chambers, ranging from an aluminum beer keg to ultrahigh-vacuum components and glass bell jars. It has been a source of considerable pleasure for us to have published a technique for producing a new solid material and to find that researchers everywhere have been able to quickly reproduce the synthesis so successfully.

In a short while several groups reported success in separating the C_{60} and C_{70} by liquid chromatography. The color of the pure C_{60} solution turned out to be magenta, while that of the pure C_{70} solution was orange. The three strong peaks in the ultraviolet were attributable to C_{60}. More recently, larger fullerenes such as C_{76}, C_{78} and C_{84} have proved to be abundant enough to be isolated in milligram quantities.

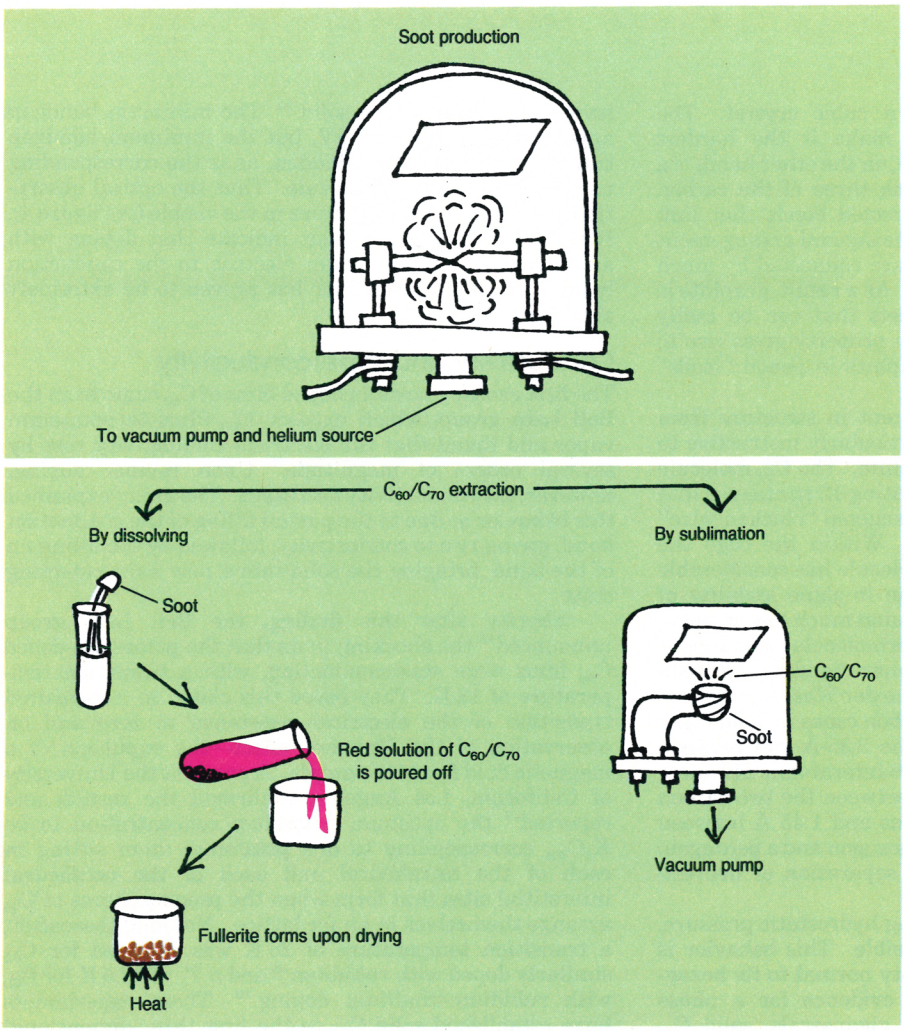
As soon as C_{60} became available in solid form—as small single crystals, as microcrystalline powder and as thin films—many of its physical properties were measured. The state of knowledge of this solid went from essentially zero in May 1990 to the rather remarkable understanding of the physical properties we have today. The table at the left, compiled from a variety of sources, summarizes some of the known physical properties of solid C_{60}. At this time there are no comprehensive reviews of solid C_{60}. However, the annotated bibliography put together by Smalley contains references to the works from which the entries in the table were taken.[8]

Properties of solid C_{60}

Density	1.7 g/cm^3
Crystal structure	Facc-centered cubic
Nearest-neighbor distance	10.04 Å
Cage diameter	7.1 Å
Lattice constant	14.198 Å
Index of refraction	2.2 at 630 nm wavelength
Infrared-active modes	1429, 1183, 577, 528 cm^{-1}
Bulk modulus	18 gigapascals
Ionization potential	7.6 eV
Cohesive energy	
per C_{60} molecule	1.5 eV
per atom	7.4 eV
Electrical conductivity	Nonconductor
Electron bandgap	1.5 eV
Effective mass of conduction band electron	1.3 m_e
Superconducting T_c	
K_3C_{60}	19 K
Rb_3C_{60}	29 K
Cs_2RbC_{60}	33 K
$Rb_{2.7}Tl_{2.2}C_{60}$	42.5 K

Crystal structure

Both electron diffraction of individual crystals like those in figure 1 and x-ray powder diffraction showed a high degree of crystalline order suggestive of a close packing of the molecular pseudospheres into hexagonal patterns. The 60-atom cages have a 7.1-Å diameter and a nearest-neighbor spacing of 10 Å. Scanning tunneling microscope images clearly show the hexagonal arrays of closely



Scheme for producing solid C_{60} and C_{70}. **Figure 5**

packed balls and reveal frequent faults in the lattice (figure 6).

Because the carbon is assembled into such large spheres, the spacing between molecules in the lattice is also rather large, giving rise to the possibility of both inadvertent and deliberate interstitial doping. This characteristic makes it difficult to grow single crystals from solution without incorporating solvent molecules into the lattice. However, workers at AT&T Bell Laboratories have managed to grow solvent-free single crystals from the vapor phase using purified C_{60} material. The crystals have a face-centered-cubic structure with a spacing between centers of 10.04 Å. This crystal structure gives solid C_{60} a density of about 1.7 g/cm^3, making it considerably lighter than graphite (2.3 g/cm^3) or diamond (3.5 g/cm^3).

Solid-state nuclear magnetic resonance measurements show that the C_{60} molecules actually rotate in their lattice positions at room temperature, giving rise to a single nmr line.[9] Only as the temperature is decreased is the rotation sufficiently hindered to allow the substructure in a broadened line to be seen. Such rotation was a major problem in efforts to confirm the exact positions of atoms in the C_{60} molecule. A group at the University of California, Berkeley, overcame this difficulty by managing to attach a tether to the molecule in the form of osmium tetraoxide and then growing crystals of the constrained molecule.[10] Their x-ray diffraction results accurately verified the predicted atomic positions in the (slightly modified) C_{60} molecule.

More recent structural studies using high-resolution synchrotron-x-ray powder diffraction have revealed a first-order phase transition to a structure consisting of a simple cubic lattice with a four-molecule basis.[11] The orientational disorder present at room temperature gives way to orientational ordering of molecules as the temperature is lowered through 249 K. Even in this phase the molecules ratchet between symmetry-equivalent positions. At much lower temperatures, the rotational motion is frozen.

Diamond, graphite and solid C_{60}

The picture of solid C_{60} that emerges from these findings is one in which groups of 60 carbon atoms are bound tightly into almost spherical, soccer-ball-shaped buckminsterfullerene molecules, and these molecules are arranged in a crystal lattice that is a close-packed array of the rotating spheres. It is thus a molecular crystal of pure carbon, completely unlike the other crystalline forms of carbon—diamond and graphite.

Figure 2 shows the contrasting atomic arrangements in these three forms of carbon. Diamond is a tetrahedral coordination of carbon atoms in which each atom is connected to its four nearest neighbors by equivalent,

highly directed bonds, forming a cubic crystal. The resulting mechanical properties make it the hardest known natural material. Graphite, on the other hand, is a highly anisotropic crystal in which three of the carbon valence electrons form highly directed bonds that link each atom to three neighbors in a hexagonal arrangement within a plane. Adjacent planes are connected by much weaker van der Waals attractions. As a result, graphite is characterized by very strong sheets that can be easily separated from one another. This property gives rise to the widespread application of graphite in pencil "leads" and dry lubricant.

While solid C_{60} is quite different in structure from either of the other forms, it is particularly instructive to compare and contrast it with graphite. The C_{60} molecule achieves its curvature by incorporating 12 pentagons into its cage, thereby distorting the hexagonal "chicken wire" plane of graphite into a sphere. Within the cage the bonding is very strong, and the molecule has considerable structural stability, similar to the in-plane stability of graphite. The C_{60} molecules are bound much less strongly into the crystal lattice. The intermolecular bonding is analogous to the weak interplanar bonding between graphite layers and is also due to van der Waals attraction. The distance between adjacent carbon cages in solid C_{60} is about 2.9 Å, as compared with the 3.35-Å gap between atomic planes in graphite. The two interatomic distances within a C_{60} molecule are 1.40 Å between the two carbon atoms shared by adjacent hexagons and 1.45 Å between the two carbon atoms shared by a hexagon and a pentagon. These values bracket the 1.42-Å separation of nearest-neighbor atoms in graphite.

Under application of increasing hydrostatic pressure, solid C_{60} is at first quite compressible. This behavior is similar to graphite's compressibility normal to its hexagonal layers. While there is no evidence for a phase transition up to pressures of 20 gigapascals, solid C_{60} becomes much stiffer (less compressible) as its carbon cages come into contact with one another.[12] At very high pressures it may even become as incompressible as diamond.

Electronic structure

Optical absorption measurements on the first thin films of C_{60} (see figure 4), along with simple electrical resistance measurements, indicated that the solid is a nonconductor. In early photoemission measurements the energy spectrum of electrons emitted when the sample is excited by high-energy photons was found to be quite similar for C_{60} molecules in the gas phase and C_{60} prepared as a thin film.[13] The similarity of the gas-phase and solid-phase data indicated that the electronic structure of the molecule is retained, to a large extent, as the solid forms from the molecules. The important first ionization potential, which had been the subject of several calculations, was measured to be 7.6 eV. Detailed photoemission measurements by a group at the University of Minnesota using variable-frequency synchrotron light have provided details of both the occupied and unoccupied electron bands.[14] Even the early molecular orbital calculations for the free molecule show rather good agreement with the electronic structure determined by these photoemission experiments.

Band structure calculations for solid C_{60} indicate a close correspondence between energy levels in the free molecule and in the solid, although some broadening of the levels does occur in the solid.[15] The minimum bandgap appears to be about 1.5 eV, but the minimum bandgap transition is optically forbidden, as is the corresponding transition in the free molecule. Thus the optical absorption shows only weak structure in the visible (see figure 4). Both theory and experiment indicate that doping with alkali metals contributes an electron to the conduction band. This doping behavior has proven to be extremely significant.

Conductivity and superconductivity

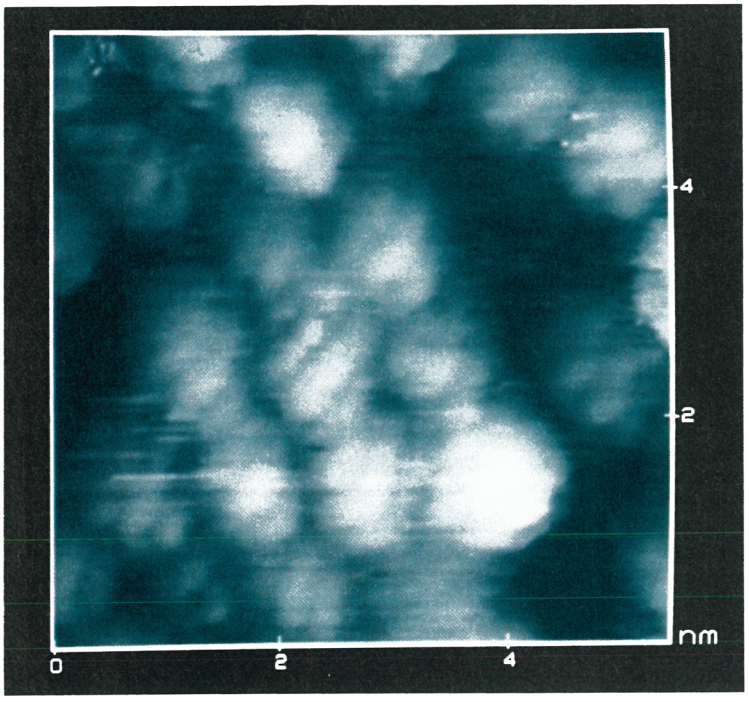
The first exciting news on doped films of C_{60} came from the Bell Labs group, which exposed C_{60} films to potassium vapor and found that the electrical conductivity rose by several orders of magnitude. Upon further doping, however, the conductivity decreased. The group explained this behavior as due to the partial filling of the conduction band, giving rise to conductivity, followed by the filling up of the band, bringing the solid into a new nonconducting state.

Shortly after this finding, the Bell Labs group announced[16] the shocking news that the potassium-doped C_{60} films were superconducting, with a transition temperature of 18 K. They based this claim on a measured transition of the electrical resistance to zero and on observation of the Meissner effect—the expulsion of a magnetic field from the sample. A group at the University of California, Los Angeles, confirmed the results and reported[17] the optimum potassium concentration to be K_3C_{60}, corresponding to one potassium atom sitting in each of the tetrahedral and each of the octahedral interstitial sites that form when the pseudospheres of C_{60} arrange themselves in an fcc lattice. Not long thereafter, a transition temperature of 28 K was reported for C_{60} similarly doped with rubidium[18] and a T_c of 42.5 K for C_{60} with rubidium–thallium doping.[19] These experiments have established solid C_{60} as the first three-dimensional organic superconductor.

In addition to the potential practical usefulness of such superconductors and the possible further increase of T_c in the future, the mechanism of the superconductivity of the fullerite superconductors is stimulating considerable interest. A recently completed experiment on the pressure dependence of the transition temperature may shed light on the mechanism.[20] The experiment found a strong decrease in T_c as pressure increases. A simple model to explain this assumes the transition temperature is determined primarily by the density of electron states at the Fermi level. Since the conduction band derived from the lowest unoccupied molecular orbitals is narrow, there is a rather high density of states. Under pressure, the molecules move closer together, increasing the width of the conduction band and decreasing the density of states, leading to a decrease in T_c. The higher T_c for rubidium doping is similarly explained as resulting from a slight expansion of the lattice due to the larger size of the impurity, with an attendant decrease in conduction band width. It appears the fun has only just begun for both experimenters and theorists in the superconductor ball game.

C_{60} in the interstellar medium?

During the years 1985–90, when C_{60} was not available for general experimentation, there was considerable speculation about buckminsterfullerene's being the source of various mysteries in interstellar spectroscopy.



C_{60} molecules in a lattice plane. This scanning tunneling microscope image shows the hexagonal packing of the C_{60} spheres. (Micrograph by Dror Sarid, University of Arizona.) **Figure 6**

As soon as Krätschmer and I became convinced that we were observing the four infrared-active bands of C_{60}, it was clear that these bands did not fit any observed astronomical features. Nor did the visible and ultraviolet spectra of solid films of fullerenes or of separated C_{60} and C_{70} solutions have any obvious resemblance to the 220-nm band or the diffuse interstellar bands. Although interstellar C_{60} might be ionized, first measurements of the spectra of the ions have not shown any obvious match with interstellar bands. Even if C_{60} is ionized or is modified by, say, proton attachment, it seems likely that the infrared vibrational bands will not be greatly shifted. Therefore astronomical observations in the vicinity of the four infrared-active bands may continue to be one of the best means for detecting C_{60} in its various possible modifications.

The mystery of the diffuse interstellar bands—the problem that helped motivate both the discovery[1] of the C_{60} molecule in mass spectra and the discovery[4] of the solid form of C_{60}—remains unsolved. In presenting our story to audiences ranging from public school classes to scientists at symposiums on C_{60}, I have often claimed one of its morals to be, "Everything has not yet been discovered." The mystery of the diffuse interstellar bands continues to proclaim this fact.

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