complexes might well play a role in these well-known isotope anomalies involving carbon. Soon after the discovery of C_{60}, Heymann[95] considered the (He) complex from an astrophysical viewpoint.

Conclusions

Several astrophysical problems have been described which involve carbon chains and dust, and attention has been drawn to various chemical scenarios in the laboratory which yield very similar conditions. The cluster beam studies indicate that chains (or their monocyclic ring analogues) form first, which then evolve into fullerenes and carbon microparticles in some yet to be fully understood way. The fascinating observation of Rubin et al.[96] that C_{30} monocyclic rings dimerize spontaneously to C_{60} can be rationalized by a scheme in which a concerted series of cycloaddition steps can

result in a graphitic/fullerene network.[97] Furthermore, recent evidence suggests that fullerenes may even be the direct precursors of pure carbon microparticles accreting carbon directly from the vapor.[87] On the basis of a wealth of circumstantial evidence, we have argued that fullerene analogues must have an important role in the "galactic carbon cycle". It has been pointed out[56] that fullerene analogues do have several properties that justify their careful consideration as carriers of some ubiquitous astrophysical features and that, if they are not responsible, there is some other as yet unidentified mystery involving carbon to be unraveled.[56]

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Solid-State Chemistry of Fullerene-Based Materials

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Introduction

The availability of "large" quantities of buckminsterfullerene (C_{60}) and the related fullerenes (C_{70} etc.) has generated an explosion of research activity by synthetic and physical chemists. It is now evident that fullerene-derived *solids* are equally exciting, from both the fundamental and potential technological viewpoints, and that these solids possess many novel properties of interest to physicists and materials scientists. The 1985

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Kroto/Smalley[1] and 1990 Huffman/Krätschmer[2] discoveries have indeed provided something for everyone!

In this Account, we summarize what we have learned in the past 12 months about the pristine fullerene solids (or "fullerites") C_{60} and C_{70} and a variety of chemically-modified solids. The emphasis is on synthetic methods, structure determinations, and phase transitions. Finally we describe a new modified fullerene "C_{60} monoxide" which may lead to interesting new solid phases.

Solid C_{60} and C_{70}

The first fullerite solids were grown from benzene solution as crystals with well-developed facets and several different morphologies.[2] Because these beautiful crystals contained benzene as well as higher fullerenes,[3] and were highly faulted, the first X-ray results were misleading and led to an interpretation of a hexagonal-close-packed (hcp) structure for solid C_{60}. Subsequent work showed unambiguously that C_{60} at 300 K adopts the other close-packed structure, face-centered

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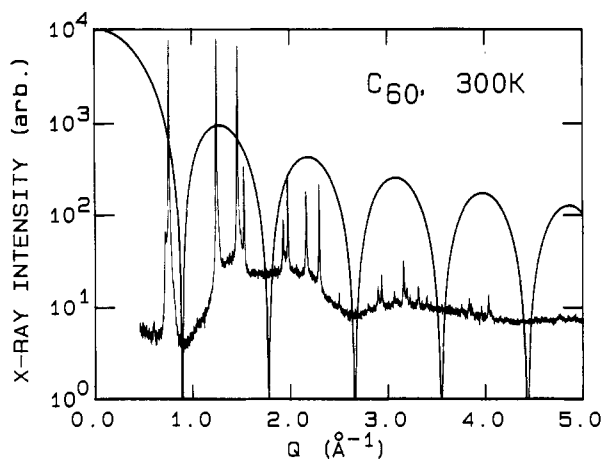
Figure 1. X-ray profile of C_{60} powder at 300 K,[5] superposed with the zero-order Bessel function $j_0(QR_0)$, $R_0 = 3.53$ Å.

cubic (fcc).[4,5] It is now generally appreciated that the observation of *intrinsic* fullerite structures requires painstaking efforts to eliminate solvent molecules, either by sublimation or by extended vacuum annealing of chromatographically-pure powder. The evolution of the C_{60} structure with temperature and hydrostatic pressure continues to attract a great deal of attention, both experimentally and theoretically.[6]

Figure 1 shows a synchrotron X-ray powder profile of chromatographically-pure, solvent-free C_{60} at 300 K. All the reflections can be indexed on an fcc cell with lattice constant $a = 14.17$ Å. The first three reflections (111, 220, and 311) are observed with comparable intensities, but there is no detectable 200 intensity (expected near 0.9 Å^{-1}). This anomalous absence can be understood in terms of the X-ray form factor of orientationally-averaged C_{60} molecules. Nuclear magnetic resonance shows a high rate of rotational diffusion at room temperature.[7,8] This suggests that the ensemble-averaged charge density of each molecule is just a spherical shell whose Fourier transform is $j_0(QR_0) \equiv$ (sin QR_0)/QR_0, where R_0 is the shell radius and $Q = 4\pi(\sin\theta)/\lambda$. The smooth, oscillatory curve in Figure 1, a plot of j_0 with $R_0 = 3.53$ Å, has zeroes at values of Q corresponding to $h00$ Bragg positions with h even. A least-squares fit based on this model gives excellent agreement with the data.[5,9]

The data in Figure 1 also show an anomalous sawtooth-shaped feature straddling the 111 reflection which is not accounted for by an fcc lattice of freely-rotating molecules. Electron diffraction analysis[10] has shown that this feature arises from planar defects parallel to close-packed layers. C_{60} sublimed on holey carbon grids

crystallizes with close-packed (111) planes parallel to the surface. Rods of diffuse scattering are found parallel to the corresponding ⟨111⟩ axis. Powder averaging of these rods, coupled with the X-ray form factor of spherical shells with 3.5-Å radius, accounts for the sawtooth feature.

The fcc lattice constant of 14.17 Å implies close-packing of 10.02-Å-diameter pseudospheres, consistent with the fitted 3.53-Å radius of the C_{60} skeleton and a carbon van der Waals diameter slightly smaller than in graphite, 2.94 Å versus 3.35 Å. The notion that the intermolecular bonding is dominated by van der Waals interactions is confirmed by a measurement of the isothermal compressibility.[9] Using standard diamond anvil techniques and powder X-ray diffraction up to 1.2 GPa, we found an a-axis compressibility of $-d(\ln a)/dP = 2.3 \times 10^{-12}$ cm^2/dyn, essentially the same as the interlayer compressibility $-d(\ln c)/dP$ of graphite. Isothermal volume compressibilities $(-1/V)(dV/dP)$ are 6.9, 2.7, and 0.18 $\times 10^{-12}$ cm^2/dyn for solid C_{60}, graphite, and diamond, respectively; C_{60} is clearly the softest of the solid phases of carbon.

Upon cooling below $T_c = 255$ K, new weak reflections appear in the profile, indicating a phase transition to a simple cubic (sc) structure. Detailed measurements of the sc integrated intensity show that this transition is first order, as is also clearly observed in differential scanning calorimetry (DSC).[5] Furthermore, the lattice constant jumps by 0.044 ± 0.004 Å upon heating through T_c.[11] This is all consistent with an orientational ordering transition, as confirmed by temperature-dependent NMR.[7,8]

The low-temperature structure of C_{60} has been established by standard crystallographic techniques using both X-ray and neutron diffraction.[12-16] The refinement strategy in space group $Pa\bar{3}$ consists of aligning the molecular 3-fold axes along crystallographic ⟨111⟩ directions and then allowing each of the four molecules per fcc cube to rotate by the *same* angle $\Gamma \sim 24°$ about a different one of the four equivalent ⟨111⟩ crystal axes.[5] This locates an electron-rich short C=C bond adjacent to an electron-deficient pentagon center on the neighboring molecule,[14] strongly suggesting that weak Coulombic interactions are the driving force for the low-temperature ordering transition. This also explains why calculations and simulations based on carbon atom pair potentials fail to predict the correct ground-state structure,[17-19] whereas ad hoc modifications to the potential which include the charge localized in the covalent bonds succeed.[20,21]

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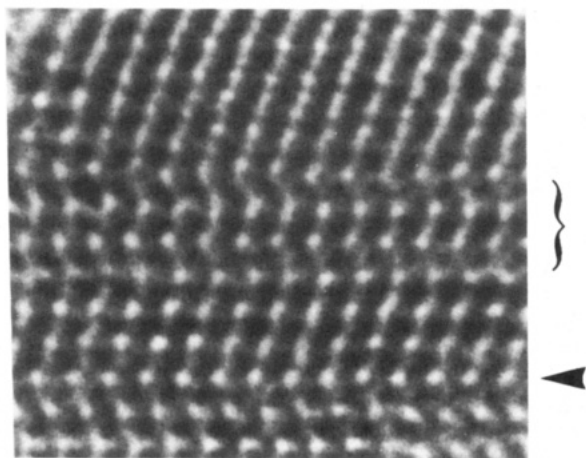(20) Sprik, M.; Cheng, A.; Klein, M. L. *J. Phys. Chem.*, submitted.

Figure 2. [110] zone axis TEM image of fcc C_{70}. Each white feature corresponds to a column of C_{70} molecules lying parallel to the electron beam. The ($\bar{1}11$) planes (or (0001) in hcp) are viewed edge-on horizontally. In the top part of the image, the stacking of close-packed layers is ABCABC (i.e., unfaulted fcc). The curly bracket indicates four close-packed layers with ABAB stacking (i.e., an hcp-type fault), and the arrow indicates an fcc twin plane ABCBA sequence. These defects occur in clusters separating large perfect fcc crystallites.

The orientational correlation time is significantly slower in the sc phase and is described as "ratcheting" between symmetrically equivalent orientations.[7,8] Furthermore, inelastic neutron scattering measurements clearly demonstrate that molecules rapidly librate about their equilibrium orientations in the sc phase.[22] Evidence for another transition at 90 K, involving a second (local) minimum in Γ, has recently been presented.[23]

Since the C_{60} lattice is rather soft, one expects an analogous molecular ordering transition at modest hydrostatic pressure. Two independent measurements[24,25] show that only ~4 kbar is required to drive T_c to 300 K. Kriza et al.[25] combined their $T_c(P)$ data and the measured latent heat to provide a Clausius–Clapeyron estimate of the fractional volume change at T_c, $\Delta V/V$ = 7.5 × 10^{-3}, in reasonable agreement with our measured value 9.3 ± 0.8 × 10^{-3}.[11]

The next-larger fullerene is C_{70}. Its elongated "rugby-ball" shape should inhibit free rotations, thus increasing T_c. C_{70} was prepared as usual except that repeated chromatography was required to reduce the C_{60} content below 1%. The as-prepared C_{70} powder was determined by X-ray and electron diffraction[26] to have a hexagonal lattice with lattice parameters a = 10.63 Å and c = 17.39 Å. The crystals, however, were unstable under the 120-keV electron beam, a phenomenon which is also observed in solvated C_{60}/C_{70} mixtures.[27] Furthermore, the FTIR spectrum revealed bands attrib-

utable to toluene (but not hexane). Evidently, solid C_{70} retains toluene more tenaciously than does C_{60}. To drive out the remaining solvent (resulting in an FTIR spectrum with no toluene lines), and to remove lattice defects, the C_{70} powder was sublimed at 810 K in a dynamically-pumped quartz tube for 12 h and then annealed at 575 K for 200 h. This procedure resulted in a primarily fcc sample, with a = 14.96 Å, but with ~11 vol % hcp phase still remaining. Bright field images from the sublimed material revealed stacking faults within the fcc crystals, similar to those observed in C_{60}.[10] The [110] zone axis image in Figure 2 shows typical defect structures.

All C_{70} samples exhibited a transition to a low-temperature phase (or mixture of phases) whose structure has not yet been determined. DSC measurements on sublimed samples showed two reproducible transitions with onsets at 276 and 337 K and heats of transition of 3.5 ± 0.5 and 2.7 ± 0.3 J/g. The combined value of 6.2 J/g is similar to the heat of the orientational transition observed in C_{60}.[5] The observations of a nearly perfect c:a ratio in the hexagonal phase and of fcc ordering naturally imply that approximately spherical objects, such as orientationally-disordered molecules, are being packed into the lattice at high temperature.

Intercalation Compounds of Solid C_{60}

Continuing rapid advances in the molecular and solid-state chemistry of C_{60} have led to the syntheses of a variety of chemically-modified phases. The discovery of van der Waals-bonded fullerene solids[2] immediately suggested to us (and others) the possibility of creating guest–host compounds, analogous to other well-known intercalation compounds,[28–30] in which the large tetrahedral and octahedral voids in the fcc lattice would play the role of van der Waals galleries in layer-type hosts, while the host structure would retain its original identity. The 3-fold-degenerate LUMO of C_{60} further suggested that optimum metallic behavior (a half-filled band) could be obtained by adding 3 electrons/molecule to the pseudo-II electronic system[31] (e.g., by inserting monovalent ions into all three void sites per C_{60}, assuming complete charge transfer). This reasoning quickly led to the discovery of the first fullerene superconductor,[32] followed in rapid succession by its identification as M_3C_{60} (M = K, Rb), as predicted,[33] and by three independent confirmations that the structure is indeed fcc with M occupying all available sites.[34–37]

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Initial results on alkali-doped C_{60} suggested that doping can proceed beyond the $x = 3$ limit. In situ measurements of resistance versus time of exposure to metal vapor showed an initial decrease to a minimum value, later confirmed to occur at $x = 3$,[38] followed by an increase.[31] Furthermore, weight uptake and elemental analyses of C_{60} doped to saturation with K and Cs indicated a limiting composition M_6C_{60}.[39] "Intercalation" beyond $x = 3$ would require the C_{60} sublattice to adopt a symmetry different from fcc in order to provide more than three interstitial sites per molecule.

The first syntheses of metallic and superconducting M_xC_{60} were performed by vapor transport in large, dynamically-pumped volumes with no control over the stoichiometry other than in situ monitoring of the resistance.[31,32] Subsequent developments have led to four distinctly different approaches to the rational synthesis of materials with predetermined x values. Phase-pure superconductors ($x = 3$) were first obtained by reacting preweighed M and C_{60} in sealed tubes with helium.[33] We found it much more convenient to prepare initially M_6C_{60} from preweighed C_{60}, to dilute it with an equal amount of pure C_{60}, and then to anneal the mixture at 400–450 °C.[36] This dilution method eliminates the need to precisely weigh small amounts of M since the $x = 6$ phase is prepared with a large M excess. It proved invaluable in studying the binary phase diagram of Rb and C_{60}, exploiting temperature-dependent X-ray analysis of a number of samples with predetermined values of x.[37] A third method yields M_3C_{60} at modest temperatures by dissolving M and C_{60} in toluene and precipitating the product after heating at reflux in a Schlenk apparatus.[40] Finally, we are pursuing a novel and promising solid-state electrochemical method (i.e., an intercalation battery with fullerite as the working electrode[41]); advantages include precise stoichiometry control, the possibility of in situ X-ray diffraction for phase-diagram studies, and facile reactions with low vapor pressure metals.

The first direct structural evidence for intercalation into solid C_{60} came from Rietveld X-ray analysis of the saturation-doped M_6C_{60} compounds (M = K, Rb, Cs).[39] (A review giving the details of the various Rietveld refinements is in preparation.[42]) We found a non-close-packed body-centered cubic (bcc) structure for all three alkali metals, indicating that indeed a major lattice distortion accompanies doping beyond $x = 3$ (the fcc structure of M_3C_{60} had yet to be discovered). The
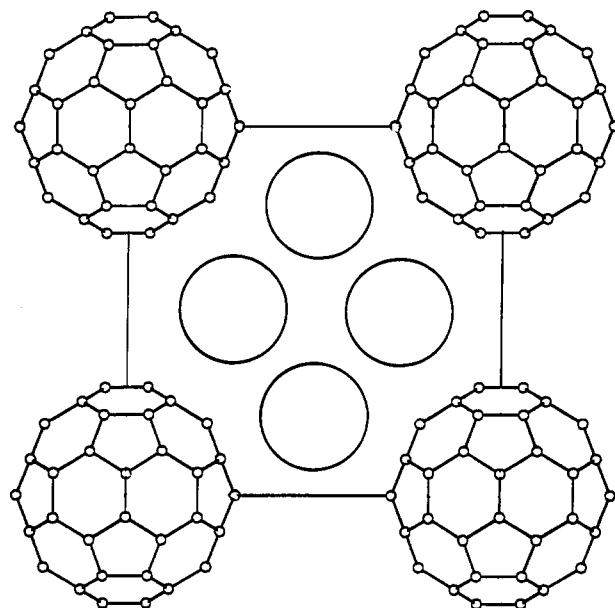

Figure 3. Schematic of the cube face normal to z of the bcc cell of M_6C_{60}, M = K, Rb, or Cs. The lattice constants are 11.39, 11.54, and 11.79 Å, respectively. Large circles represent Cs^+ in scale with the cube edge. Small circles are C atoms, not to scale. An equivalent C_{60} molecule is centered at $(^1/_2, {}^1/_2, {}^1/_2)$ (not shown). M coordinates (clockwise from top) are (0.5, 0.72, 0), and (0.78, 0.5, 0), (0.5, 0.28, 0), and (0.22, 0.5, 0) with respect to an origin at the bottom left corner. Faces normal to x or y may be visualized by rotating the diagram ±90°, a consequence of molecular orientation with 2-fold axes along cube edges.[39]

bcc structure is shown schematically in Figure 3. Twelve M atoms/cell can be visualized as four-atom diamond-shaped motifs centered on $(^1/_2, {}^1/_2, 0)$ and equivalent positions. Each C_{60} is surrounded by 24 M atoms, and each M is in a distorted tetrahedral environment of four C_{60} molecules. The shortest distances between C_{60} centers are 9.79 and 10.21 Å for K and Cs, respectively. These bracket the 10.02-Å value in the undoped fcc phase. The near-neighbor C–Cs distances lie in the range 3.38–3.70 Å, compatible with the 3.2-Å sum of van der Waals C and ionic Cs radii. All the Cs–Cs near-neighbor distances are 4.19 Å, considerably greater than the ionic diameter 3.34 Å.

In addition to the stoichiometric fcc phase ($x = 3$, superconducting), a stoichiometric body-centered-tetragonal (bct) phase observed at $x = 4$,[35,37,43] and the bcc ($x = 6$) phases, direct evidence for a dilute fcc doped phase, $0 < x \leq 1$, and for a substoichiometric bcc phase, $x \sim 5$, was obtained. In contrast, $x = 3$ and $x = 4$ appear to be line phases with very small solubility of Rb vacancies and interstitials at 300 K. This was deduced as follows. A sample with $x = 2.9$ was observed to consist of two fcc phases with slightly different lattice constants. The majority phase relative intensities were characteristic of Rb_3C_{60} ($a = 14.42$ Å), while the minority fcc phase gave $a = 14.24$ Å and an intensity pattern consistent with a dilute fcc doped phase (estimated $x \leq 1$) rather than with pure C_{60}. (^{13}C NMR shows phase separation in samples with global $x = 1.5$ and 2.0,[44] consistent with the present results.) Results

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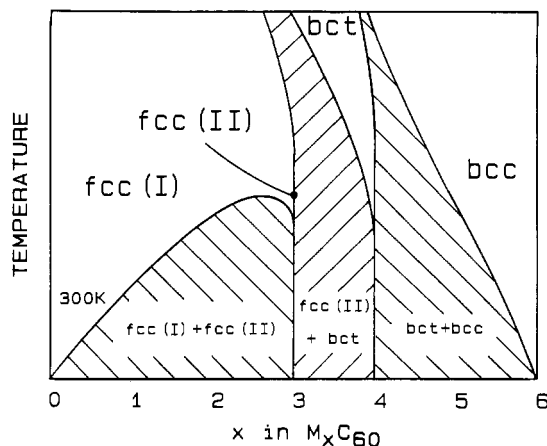116 *Acc. Chem. Res., Vol. 25, No. 3, 1992*

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Figure 4. Provisional schematic phase diagram for the alkali-metal–solid C_{60} system. Shaded regions denote two-phase coexistence. The temperature scale is indicated approximately by the 300 K label in the lower left corner.[37]
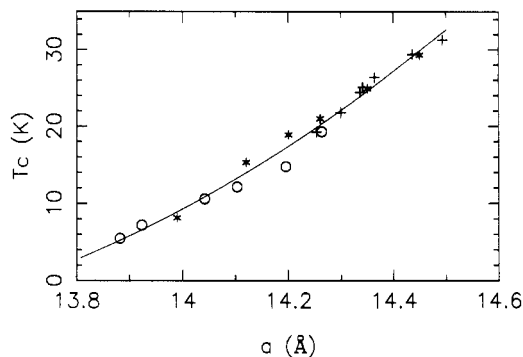

Figure 5. Superconducting transition temperature versus lattice parameter. $a(P)$ X-ray data converted to $T_c(a)$ using the raw $T_c(P)$ data of Sparn:[49] (O) K_3C_{60}; (*) Rb_3C_{60}; + symbols are the directly-measured points from a number of $M_{3-x}M'_xC_{60}$ compounds at 300 K, 1 bar.[48] The solid curve is a quadratic fit.[50]

from a sample with $x = 3.3$ confirmed that the miscibility gap between fcc ($x = 3$) and bct ($x = 4$) extends all the way to the melting point, as required by the different symmetries. Finally, a sample with nominal Rb concentration $x = 5$ showed essentially phase-pure bcc but with $a = 11.47$ Å, significantly smaller than the 11.54 Å characteristic of the saturation $x = 6$ phase. This demonstrates that the bcc structure is not a line compound at 300 K. Also, the bct $\rightarrow$ bcc transition with increasing x must be first order by symmetry, and therefore the bct/bcc miscibility gap must extend up to the melting point.

These and other results are summarized in the schematic phase diagram shown in Figure 4, depicting the coexistence features of temperature- and x-dependent structures.[37] The composition axis is dominated at low temperature by regions of two-phase coexistence. The first such region, $0 < x < 3$, is analogous to Safran's model for layer intercalates[46] since the end points are isostructural (i.e., the superlattice symmetry is independent of x). Further work is necessary to determine if the structure exemplified by the minority fcc constituent is such an ordered stoichiometric phase at some T. A better analogy for the second two coexistence regions, $3 < x < 4$ and $4 < x < 6$ at $T = 0$, is potassium-doped polyacetylene, in which the two-dimensional superlattice symmetry changes discontinuously with chemical potential.[45]

Efforts to understand the physical properties of M_xC_{60} have naturally focused on the superconducting $x = 3$ phases.[47] A monotonic increase of superconducting transition temperature T_c with alkali size was deduced from an empirical linear correlation between T_c and lattice constant (a) at constant pressure,[48] suggesting (in the context of weak-coupling BCS theory) that T_c depends only on the overlap between near-neighbor C_{60} molecules and not explicitly on the nature of the intercalate.[48,49] We tested this correlation over a larger range of a by measuring the pressure depen-

dence of a for K_3C_{60} and Rb_3C_{60} and then scaling by measured $T_c(P)$[49] to obtain T_c versus a.[50] The *overall* behavior (Figure 5) is still generally consistent with a universal phenomenon which depends only on intermolecular separation, but not surprisingly the correlation is no longer linear over the larger range of parameters. More importantly, the fact that data for different M (including some pseudobinaries) all lie on the same curve allows us to rule out electron pairing mediated by phonons involving the alkali ions.[51]

It is now well established that the insulator–metal transition in alkali-doped C_{60} is due to electron transfer from guest to host.[52] The fact that M_xC_{60} is a molecular metal for some range of x is explained by the large electron affinity of C_{60} and its low reduction potential. Analogous acceptor salts, resulting for example from oxidative intercalation by halogens, would appear to be ruled out by the large C_{60} *molecular* ionization potential[53] and by the absence of reversible oxidation steps in solution electrochemistry,[54] although the electrostatic penalty per molecule could be partially offset by the Madelung energy of a resulting ionic lattice. A (subsequently withdrawn) announcement of superconductivity above 57 K in iodine-doped C_{60} suggested that acceptor intercalation might be possible. However, Ohno et al. recently presented photoemission evidence that only small amounts of iodine are taken up by solid C_{60}, resulting in a nonmetallic product which is not a definite compound.[55] Using different reaction conditions, namely, vapor-phase reaction of iodine with pure C_{60} at 250 °C for several days in evacuated Pyrex tubes, we readily obtained a highly crystalline phase of ideal stoichiometry $C_{60}I_4$.[56] The 300 K resistivity exceeds 10^9 Ω-cm, the color is indistinguishable from that of C_{60}, and superconductivity was not observed above 4 K.

X-ray diffraction revealed a single, highly crystalline new pattern independent of the starting mixture; thermogravimetric analysis gave a C_{60}:I ratio of 3.7 ±

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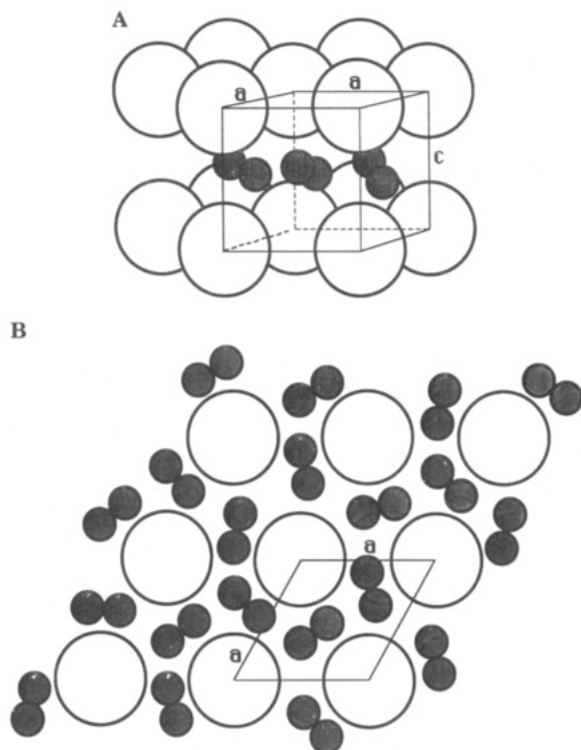
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Figure 6. Schematic structure of $C_{60}I_4$ derived from Rietveld X-ray analysis.[56] (A) 3-D perspective with $R \simeq 3.5$ Å C_{60} skeletons and $r \simeq 1$ Å van der Waals iodines scaled to the $\simeq 10$-Å lattice constants. Note the similarity to the structure of stage-1 layer intercalates. (B) Basal plane projection using the same scaling. There is no long-range order in the occupancy of iodine sites.[56]

0.7. The composite structure of C_{60} and I_2 sublattices, shown schematically in Figure 6A, recalls the stage-1 graphite intercalation compounds:[28] an eclipsed sequence of close-packed C_{60} layers is interleaved with iodine guest layers which reside in the van der Waals galleries. The refined iodine coordinates and fractional occupancies of inequivalent sites give reasonable I–I distances with no long-range order on the I sublattice. The shortest I–I distance is 2.53 Å, close to the 2.72-Å intramolecular distance in elemental I_2.[57] There are two such I_2 molecules per unit cell, nearly centered on trigonal-prismatic sites with their axes canted $\simeq 11°$ out of the midplane. Intermolecular distances are 3.78 and 5.02 Å, which compare favorably to the corresponding intra- and interlayer molecular separations 3.50, 3.97, and 4.27 Å in solid I_2.[57] The refinement points strongly to molecular (neutral) I_2 as the predominant intercalated species.

We conclude, in agreement with Ohno et al.,[55] that solid C_{60} is oxidized very little if at all by exposure to iodine vapor. On the other hand, the observation of a definite, possibly nonstoichiometric, highly crystalline compound containing substantial iodine is no doubt attributable to our reaction conditions, in which the compound is allowed to equilibrate with the 3–4-atm saturation vapor pressure of the intercalate. Oxidative intercalation of C_{60} remains an open question. For the moment, formation of the new compound $C_{60}I_4$ appears to be more nearly analogous to the uptake of neutral water by clay minerals than to the formation of the ionic salts typified by graphite compounds and the

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alkali-intercalated fullerites.

Exohedral Solids

A. Halogenated Fullerenes. Exohedral solids derive from fullerenes with foreign atoms or molecules covalently bonded on the outside of the carbon cage. Solution-grown single crystals of exohedral organometallic clusters have been exploited to establish the truncated icosahedral structure of the C_{60} molecule.[58,59] The first exohedral cluster was $C_{60}H_{36}$,[60] but neither a solid-state nor molecular structure was reported. With sufficiently vigorous reagents it is possible to obtain exohedral solids *directly* from solid C_{60} and C_{70} (i.e., to chemically modify the fullerene *and* produce a new lattice at the same time).

In the case of fluorine, covalent attachment occurs readily in the solid state.[61] Mass spectrometry reveals broad distributions of F per fullerene, peaked near 36 and 44 for C_{60} and C_{70}, respectively; IR confirms the presence of covalent C–F bonds. We have, however, been unable to reproduce the results presented in a later report in which complete fluorination to $C_{60}F_{60}$ was claimed.[62] The fluorinated solids, white to yellow in color and stable in air, are crystalline, with the same fcc symmetry at 300 K, but with smaller coherence lengths than the starting material. The fcc lattice constants are 17.0 and 17.6 Å for samples of average composition $C_{60}F_{36}$ and $C_{70}F_{44}$, as compared to 14.17 and 14.96 Å for pure C_{60} and C_{70}. This scaling, and the persistent absence of a 200 reflection, are consistent with close-packing of pseudospheres which are larger in radius than the parent fullerene by essentially a C–F bond length. The apparent lattice disorder, greater in $C_{70}F_{44}$ than in $C_{60}F_{36}$, is most likely due to a broad distribution of effective radii associated with the nonspecificity of the fluorination process. Interestingly, preliminary contact angle measurements on thin films suggest that fluorinated fullerenes may be useful as lubricants.

Similar solid-state and solution reactions with Cl_2 and Br_2 have been reported to afford complex mixtures of $C_{60}X_n$.[63,64] Importantly, the parent C_{60} molecule can be regenerated in 50–80% yield via a variety of chemical, thermal, and electrochemical methods. These results lead to the conclusion that the integrity of the fullerene framework is largely maintained under the reported halogenation conditions.

B. C_{60} Oxide: The First Fullerene Epoxide. Ultraviolet irradiation of C_{60} in benzene saturated with oxygen produces a new monofunctional fullerene $C_{60}O$ as the sole isolable product in 7% yield.[65] A signifi-

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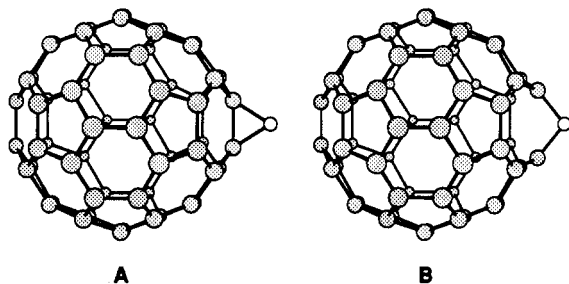
Figure 7. Epoxide and annulene models for $C_{60}O$. Only the former is consistent with NMR data.

cantly higher isolated yield (17%) was observed upon the addition of benzil.[66] The Exxon group observed the same oxide as a minor component of the fullerene mixture generated via resistive heating of carbon rods. Extensive oxidation and fragmentation of C_{60} are also induced by UV irradiation in hexane[67,68] or by heating in the presence of oxygen.[69]

The NMR, FTIR, and UV–vis spectra of $C_{60}O$ suggest that this new fullerene retains the essential electronic and structural character of C_{60}. The epoxide structure (Figure 7A), of C_{2v} symmetry, would derive from oxidation of one of the 30 equivalent double bonds in C_{60}. Alternatively, the oxoannulene (Figure 7B), analogous to the structure proposed for $C_{70}O$,[70] could arise via valence isomerization of the epoxide. The preponderance of evidence, however, favors the epoxide structure. Preliminary X-ray diffraction results suggest a crystal structure not unlike that of pure C_{60}, with an orientational ordering transition below room temperature. Attempts to establish the molecular structure by single-crystal X-ray diffraction are in progress.

Endohedral Cluster Solids

A search for endohedral cluster solids, constructed from non-carbon atoms encapsulated by fullerenes, has been triggered by the recent confirmation (using two different syntheses) of endohedral molecules typified by $(La@C_{82})$.[72,73] A lattice of such molecules would be

expected to exhibit properties of both the pristine and alkali-intercalated structures: unusual dynamics and phase transitions associated with close-packed pseudospheres, possibly interesting electronic and magnetic properties associated with delocalized or unpaired M valence electrons, etc. One can even speculate about the possibilities afforded by intercalation into an endohedral cluster lattice. Progress along these lines is presently blocked by the difficulty in separating and isolating $(M@C_n)$ molecules.

Concluding Remarks

It seems inevitable that new surprises in the molecular and solid-state chemistry of fullerenes and fullerites will continue to be discovered. While the study of alkali-metal intercalation compounds is already in a mature phase, ternary compounds which show intriguing property enhancements relative to binaries are only poorly characterized at present.[71] In addition to metallic and superconducting behavior, it appears likely that interesting magnetic properties may also be achievable with chemically-modified fullerites.[74] Recent discoveries suggest that fullerites may even be precursors to useful forms of diamond.[75,76]

In order to consolidate the spectacular advances of the last 12 months, more attention needs to be paid to detailed materials characterization, defect structures, purification, and processing. A serious effort to optimize thin film morphology seems warranted both for fundamental studies of doped phase properties and for eventual applications.[38] It seems quite unlikely that materials quoted as "pure C_{60}" contain nothing but C_{60}; HPLC analysis can rule out higher fullerenes, but other species may still be present, as suggested by substantial residues after thermogravimetric analysis in inert gas flows.[77,78]

We and others owe a large debt to Kroto, Smalley, Huffman, and Krätschmer for discovering fullerenes and fullerites.

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