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Chapter 2

Crystalline Fullerenes

Round Pegs in Square Holes

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The fullerenes C_{60} and C_{70} act as spherical building blocks in crystalline solids to form a variety of crystal structures. In many cases, the icosahedral molecular symmetry of C_{60} appears to play little role in determining the crystal structure. In this chapter we discuss our results on the crystallography of pure and solvated fullerenes and some general features of fullerenes as building units in crystalline solids. For pure C_{60} or C_{70}, the face-centered cubic arrangement is preferred. In solvated crystals and compounds, the packing readily adapts to form non-close-packed structures.

The existence of the molecular carbon cluster C_{60} and higher molecular weight homologues was first deduced on the basis of spectroscopic measurements in the gas phase (*1*). These studies proposed that C_{60} was a hollow molecule with the shape of a truncated icosahedron, the familiar form of the seams on a soccer ball. Because of its hollow, high-symmetry structure, C_{60} was dubbed "buckminsterfullerene"; the name "fullerene" was used to refer to the class of hollow carbon spheroids. Studies of fullerenes have been recently accelerated by the dramatic discovery by Krätschmer et al. (*2*) that bulk quantities of C_{60} and lesser quantities of larger fullerenes such as C_{70} could be generated in a carbon arc struck in a partial pressure of helium. The availability of large quantities of material quickly led to additional structural studies based on [15]C NMR (*3–7*), IR (*8*), and Raman (*9*) spectroscopy as well as crystal structure determinations of compounds containing C_{60} (*10, 11*). A complete, atomic resolution crystal structure of pure C_{60} has not yet been accomplished, but the original soccer-ball model of C_{60} is now generally accepted.

The study of C_{60} and other fullerenes has proved to be exciting from a number of viewpoints. The structure, chemistry, and physical properties of C_{60} have all yielded surprising results and unique behavior. In this chapter we concentrate on the structural aspects of solid C_{60} and C_{70} and crystalline solvates of these molecules. We discuss the growth of "single" crystals of these materials and describe the types of disorder and twinning inherent in these structures. Because of the disorder, our structural studies are necessarily more focused on a description of the unit cells and the symmetry rather than a traditional crys-

tallographic structure with atomic resolution. In addition we also will describe the relationships between pure, crystalline C_{60} and the potassium intercalated compounds K_3C_{60} (*12*) and K_6C_{60} (*13*). The alkali intercalates have recently generated a great deal of interest in fullerenes because of the occurrence of conductivity and superconductivity in these materials (*14–16*).

Powder diffraction from solid C_{60} was obtained immediately after bulk synthesis and was used in the initial identification of the 10-Å *d*-spacing expected of a close-packed array of spherical molecules (*2*). Although the unit cell of solid C_{60} is now known to be face-centered cubic (fcc) (*17*), there was some early difficulty in assigning a unit cell and indexing the powder pattern. The confusion resulted from two curious features of the diffraction from C_{60}. The first was an absence of cubic (*h*00) reflections due to zeros in the form factor of a hollow molecule. The second was the presence of a shoulder on the cubic (111) reflection that has been attributed to planar defects in the structure (*18*). The shoulder coincidentally occurs at nearly the same *d*-spacing as a hexagonal close-packing (hcp) (100) reflection, a *d*-spacing that is not allowed in fcc.

Symmetry

The beautiful icosahedral symmetry of the C_{60} molecule with its alternating five- and six-membered rings is responsible for some of the most striking features of this new form of carbon. The point symmetry of the C_{60} molecule is *m*35 (I_h), which requires only one carbon position to describe the 60 sites contained in the molecule. As a consequence, the observation of a single narrow resonance line in solid-state ^{13}C NMR spectroscopy (*3–7*) on C_{60} at ambient temperature shows that the icosahedral point symmetry is correct and also shows that the C_{60} molecules undergo rapid, isotropic rotations at room temperature. The observation of molecular rotations in solid C_{60} raises questions about the expected symmetry in crystalline C_{60}. One could argue that, because of rapid rotation, one should treat the molecules in the unit cell as featureless spheres. On the other hand, C_{60} might be expected to be fully ordered and to adopt the highest symmetry allowed under the icosahedral point group. The fully ordered model could be consistent with the NMR observations if the rotations are steplike transitions between symmetry-equivalent positions with each molecule stationary for a finite time period.

First, assume that C_{60} is fully ordered with the maximum possible symmetry. Icosahedral symmetry does not allow translational periodicity, a fact that provides a primary motivation for the study of quasi-crystals (*19*). An icosahedral molecule can, however, form a crystallographic lattice by loosing symmetry elements. Figure 1 summarizes the crystalline, maximal subgroups of *m*35 (*20*). The highest order maximal subgroup of the icosahedron is *m*3, a point group that retains 24 of the original 120 symmetry operations. This fact implies that in an ordered crystalline lattice, at least three carbon sites are needed to describe solid C_{60} instead of the one site needed to describe the isolated molecule. A common space group that occurs when local icosahedral symmetry is present, for example, in α-(AlMnSi) (*21*) and some virus molecules

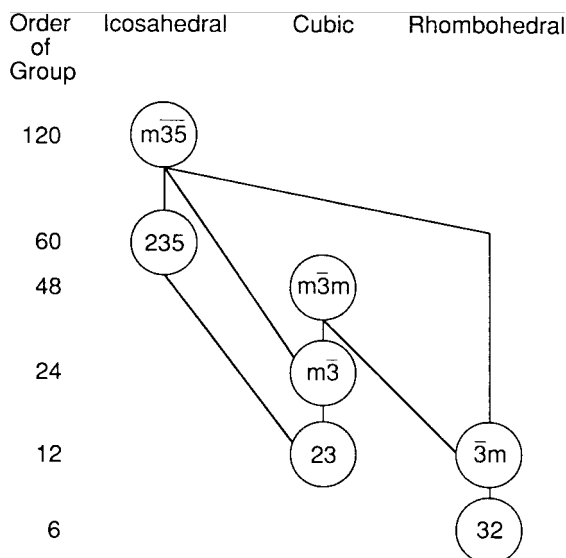| Order of Group	Icosahedral	Cubic	Rhombohedral
120	$(m\overline{3}5)$		
60	(235)		
48		$(m\overline{3}m)$	
24		$(m\overline{3})$	
12		(23)	$(\overline{3}m)$
6			(32)

Figure 1. Crystalline, maximal subgroups of the icosahedral point group $m\overline{3}5$.

(*22*), is the body-centered cubic (bcc) structure *Im*$\overline{3}$. There is, however, no requirement that the symmetry be maximized, and exceptions such as boron, which crystallizes in the lower symmetry rhombohedral space group *R*$3m$ (*23, 24*), are common. The bcc packing is plausible in that it allows planes of adjacent icosahedra to face each other, with holes at (½ ½ 0) and equivalent positions. For the truncated icosahedra, a bcc packing results in adjacent molecules having six-membered rings facing each other.

Contrary to these examples, X-ray diffraction shows that C_{60} crystallizes on an fcc rather than a bcc lattice (*17*), a result implying space group *Fm*3 rather than *Im*$\overline{3}$. From the polyhedra-packing point of view, the occurrence of fcc over bcc is surprising, despite the fact that the density of fcc is somewhat higher. In fcc the sixfold rings of the truncated icosahedra no longer face each other: The sixfold rings are oriented along [111] directions and face the empty tetrahedral sites located at (¼ ¼ ¼). These sites contain potassium in K_3C_{60} (*12*). A drawing of a C_{60} molecule oriented so that the cubic [100] axis is normal to the page is shown in Figure 2. The three carbon positions labeled C1, C2, and C3 are the positions needed to describe the molecule in *m*3. Even if the ordered description of C_{60} is correct, with molecules hopping between ordered orientations, the crystal will be prone to exhibit disorder. An example of the type of disorder one might expect is merohedral twinning (e.g., rotations by π/2 about [100]) of *Fm*3. This merohedral twinning will increase the apparent symmetry of the material to *Fm*$\overline{3}m$. The merohedral twin operation is shown in Figure 2 by the dashed lines.
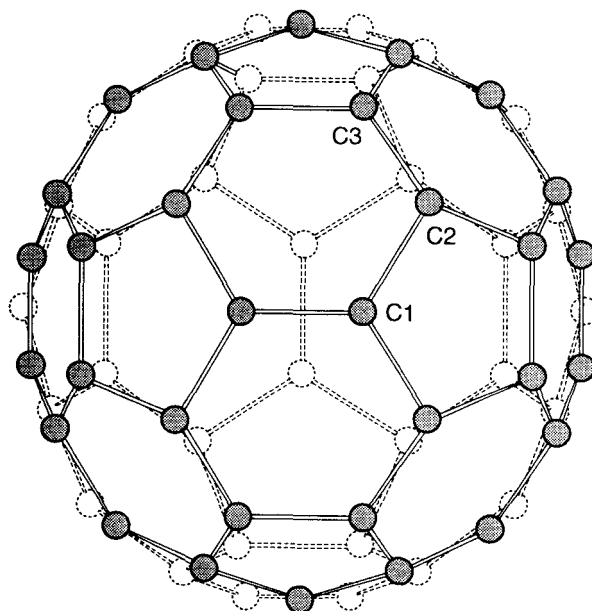
Figure 2. An idealized model of C_{60} oriented with the (h00) of the fully ordered model normal to the page. The dotted lines show the near registry of atoms that occurs upon a rotation of $\pi/2$ about (h00).

An alternative to the maximum symmetry model is to describe the C_{60} molecules as smooth, hard spheres. This description follows from the NMR results if we assume the rotations are continuous rather than steplike. The model also affords a rationalization for the selection of fcc over bcc by assuming that the structure selects the highest density available. Moreover, the symmetric shape of the C_{60} results in the absence of both a permanent dipole moment and local bond moments, a condition implying three-dimensional van der Waals bonding. A hard-sphere model does not, however, explain the selection of fcc over hexagonal close packing (hcp), a structure with an equivalent density. In other symmetric, non interacting species such as the rare gases, the crystalline structures are universally fcc (except for He, which has quantum effects).

If one assumes a theoretical model for hard-sphere interactions such as the Lennard–Jones potential, hcp stacking is preferred over fcc, a conclusion that is contrary to observation (*25*). This contradiction shows that a Lennard-Jones model will not explain the molecular coordinations of either C_{60} or solid forms of noble gases. One must necessarily invoke higher order interactions to explain the packing of C_{60} as implicitly done in the calculations of Guo et al. (*26*), who calculated that the lowest energy structure of C_{60} occurs with an orientationally distorted fcc packing. As we will discuss, hard-sphere models are useful in determining the size of unit cells in solvated

crystals, and they provide an adequate description of the room-temperature structure of C_{60}.

Sublimed Crystals

It is difficult to grow good crystals of pure C_{60} or C_{70} from solution because of the tendency of the material to form solvates or clathrates resulting from interactions with the solvent. The problems of solvation can be eliminated by using sublimation to grow crystals (*17*). When solid C_{60} is heated over a temperature gradient in an evacuated quartz tube (500 °C hot end), well-formed octahedral crystals sublime on the cool end of the tube. Powder X-ray diffraction from crushed crystals agrees with the early diffraction data (*2*). Precession X-ray photographs show full translational order and a face-centered cubic packing. Single-crystal diffractometer data are consistent with an apparent space-group symmetry *Fm*3*m* and a unit cell with $a = 14.1981(9)$ Å (25 °C, $Z = 4$. As already discussed and illustrated in Figure 1, *m*3*m* point symmetry is too high to be compatible with icosahedral symmetry. Consequently, *Fm*3*m* apparent symmetry probably results from merohedral twinning and/or disorder of *Fm*3, as illustrated in Figure 2.

A refinement based on single-crystal data and incorporating an equal and complete merohedral twinning operation proceeded as follows: Two carbon atoms put in at random positions were refined to form six-membered rings on the surface of a sphere with a 3.5-Å radius. A third carbon atom also refined to a position on the sphere around the origin, resulting in an approximate soccer-ball structure and $R = 0.10$, but with significant distortions, leading to unphysical C–C distances ranging from 1.2 to 1.7 Å. The refinement is not adequate to confirm the soccer-ball model, but it does confirm the structure of the fullerene as a hollow molecule with the carbon atoms distributed on the surface of a sphere with a 3.5-Å radius. The observed distortions are very likely to result from a combination of orientational disorder and the high thermal motion of the molecules in the solid at ambient temperatures, as indicated by NMR spectroscopy.

The lack of a well-ordered atomic structure of C_{60} at room temperature suggests that smooth hollow spheres might do equally well in refining the structure. This suggestion follows from the notion that the motion of C_{60} molecules at room temperature is isotropic. Our results as well as those of Heiney et al. (*27*) suggest that isotropic motion is the case. With hollow spheres and *Fm*3*m* symmetry, a slightly lower *R*-factor is obtained, about 8%. Practically speaking, little difference is seen in the magnitude of the errors using the ordered model and the smooth-sphere model. For calculations such as band structures, the choice of model largely depends on one's taste and the ease of application.

An interesting feature of the diffraction in pure C_{60} is the conspicuous absence of the (200) reflection, caused by the hollow nature of the molecule. For a spherically symmetric distribution of charge of radius r, the molecular form factor (*f*) is given by

$$f \ = \ \int \ 4\pi r^2 \ \ \sin \ \left(\frac{Qr}{Qr} \right) \mathrm{d}r$$

Assuming a shell of charge where $\rho(r) = \delta(r - R)$, then the molecular form factor is given by $f \sim \sin (QR/QR)$ where Q is the X-ray momentum transfer 4π (sin θ)/λ. Here θ is the scattering angle and λ is the X-ray wavelength. This function has zeroes at $Q = n\pi/R$, $n = 1, 2, ...$ Coincidentally, for $R = 3.55$ Å (the value obtained from single-crystal refinements), these zeros occurs almost exactly at the (h00) reflections of C_{60}. If the lattice parameter is changed slightly so that the (h00) reflections move off the zeros of the form factor, or if there is scattering from additional atoms or molecules in the unit cell other than C_{60}, the (h00) reflections will be visible. This feature makes the intensity of the (200) reflection a very sensitive probe for various effects. For example, the application of hydrostatic pressure to crystalline fcc C_{60} changes the lattice parameters and causes the (200) reflection to appear (*28*).

The presence of extra electron density in the fcc unit cell (located either inside the sphere of the C_{60} molecule or in octahedral and/or tetrahedral holes between the close-packed layers) would also result in a nonzero intensity of the (200) reflection. Because the fcc intercalated compound K_3C_{60} has two components to the scattering factor, C_{60} and K, (h00) peaks are observed (*12*). The refinement of the K_3C_{60} structure (*9*) gives the same C_{60} positions as the ordered twinned model discussed, a result suggesting that the molecules are spending finite amounts of time in symmetry positions.

In a number of situations, the motion of the C_{60} molecules is limited. One example is at low temperatures where powder X-ray diffraction and calorimetry experiments (*27*) show a phase transition at 249 K from fcc to primitive cubic in C_{60}. This feature appears to be associated with an orientational ordering of the C_{60} molecules in the cubic lattice. In the high-temperature fcc phase, all molecules are crystallographically identical, a characteristic causing all cubic reflections with $h + k + l$ = odd to be forbidden. The phase transition is characterized by the appearance of these forbidden reflections. This finding indicates that at low temperatures the molecules are no longer symmetry equivalent. ^{13}C NMR measurements show that the motional narrowing associated with tumbling of C_{60} molecules is not strongly affected at the phase transition, but the temperature dependence of the T_1 relaxation time shows a break (*29*). This result implies a change in the nature of the molecular motion at the phase transition, and the results are consistent with the model of dynamic hopping between symmetry positions in the low-temperature phase. Motion of the molecules continues until about 50 K, where the NMR line gradually broadens; such motion suggests that the transition from rotating molecules to fixed molecules occurs gradually and in an inhomogeneous manner.

A second situation in which the orientation of the C_{60} molecule appears to be fixed is in the intercalated compounds K_6C_{60} and Cs_6C_{60} (*13*). These compounds crystallize in a bcc unit cell, space group $Im\bar{3}$, the preferred crystallographic phase for packing icosahedra. The nearest-neighbor separation of

C_{60} molecules is nearly the same as in fcc, but there are 8 instead of 12 nearest neighbors. The body-centered structure allows an ordered structure with six-fold rings on adjacent molecules to face each other with four alkali atoms on each face of the cell. NMR measurements of this phase show a broadened line characteristic of a stationary C_{60} molecules.

An attempt to produce solvent-free C_{70} crystals by the same sublimation procedure described for C_{60} yielded small crystals with pentagonal faces, strongly reminiscent of pseudo-fivefold twins formed in electrodeposition of fcc Ag at high deposition rates (*30*). This result may suggest that single crystals of fcc C_{70} may be obtained by very slow sublimation. So far, the presence of extra diffraction lines in solvent-free powders of C_{60}–C_{70} mixtures, which can be indexed on an fcc cell with a larger lattice constant (a = 14.73 (2) Å, with a calculated nearest-neighbor distance of 10.415 Å), seems to support the possibility of C_{70} crystallizing on an fcc lattice. In addition, a powder obtained by subliming C_{70} yielded weak scattering that could be indexed by an fcc cubic cell. The C_{70} molecule is expected to be elongated by about 19% along one axis relative to the C_{60} molecule, and so the presence of a cubic (rather than tetrag-onal) lattice for C_{70} implies that the elongated molecule is disordered on the lattice. The observed lattice parameter is close to the value derived from the expected average dimension of the molecule.

Pentane Solvates

Slow diffusion of pentane vapor into benzene solutions of pure C_{60} or C_{70} pro-duces well-formed prismatic crystals with an unusual 10-sided columnar habit (*31*), as shown in the scanning electron microscope (SEM) photograph of Fig-ure 3. ^{1}H NMR spectroscopy of these crystals in CS_2 revealed the presence of a stoichiometric amount of *n*-pentane (with a <5 mol% impurity of benzene), an observation thus suggesting that these crystals can be formulated as fullerene • *n*-C_5H_{12} solvates. Precession X-ray photographs indicate full transla-tional order and show a pseudo-10-fold diffraction symmetry in the plane nor-mal to the columns. Diffraction in the plane containing the column axis shows ordering along the columns with a *d*-spacing of 10.08 (3) and 10.529 (6) Å for C_{60} and C_{70}, respectively. These correspond to the nearest-neighbor distances found in fcc C_{60} and C_{70} (the cubic [110] direction).

Although the 10-sided morphology and diffraction symmetry are remin-iscent of features found in decagonal quasicrystalline materials (*32, 33*), the dif-fraction patterns can be completely indexed on the basis of a primitive mono-clinic, non-close-packed unit cell together with a twinning operation. Any twinned close-packed structure is ruled out by the presence of a diffraction peak with a *d*-spacing of 15.8 Å for C_{60} (16.4 Å for C_{70}). In a close-packed structure with equivalent nearest-neighbor planes, the lowest order *d*-spacing [e.g., the cubic (111)] would be about 8 Å. A unit cell that is consistent with the diffraction data can be formed by shearing every second fcc (001) plane of the unsolvated cell in a [110] direction, as shown in Figure 4. This shearing
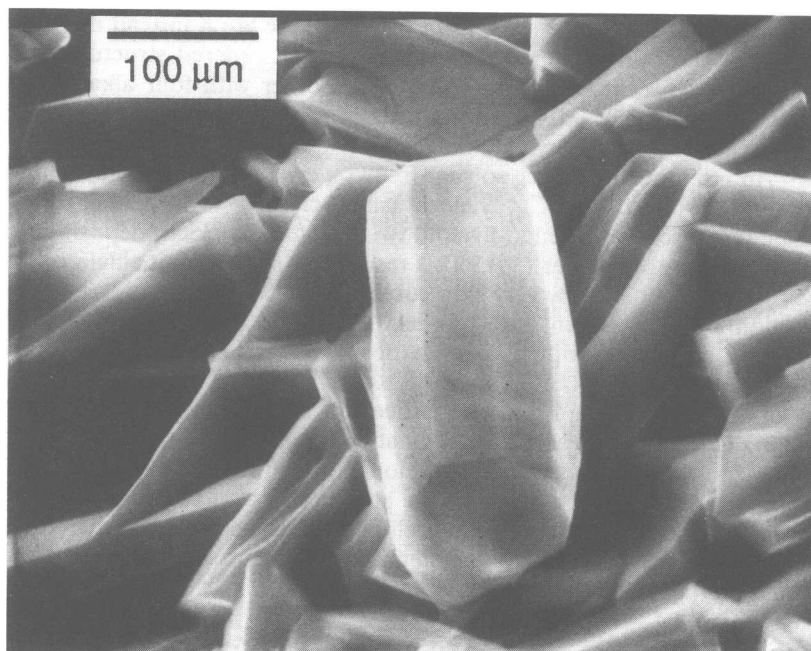
Figure 3. An SEM photograph of a pentane-solvated crystal of C_{60}. The wavy lines in the photograph are artifacts due to charging of the sample.
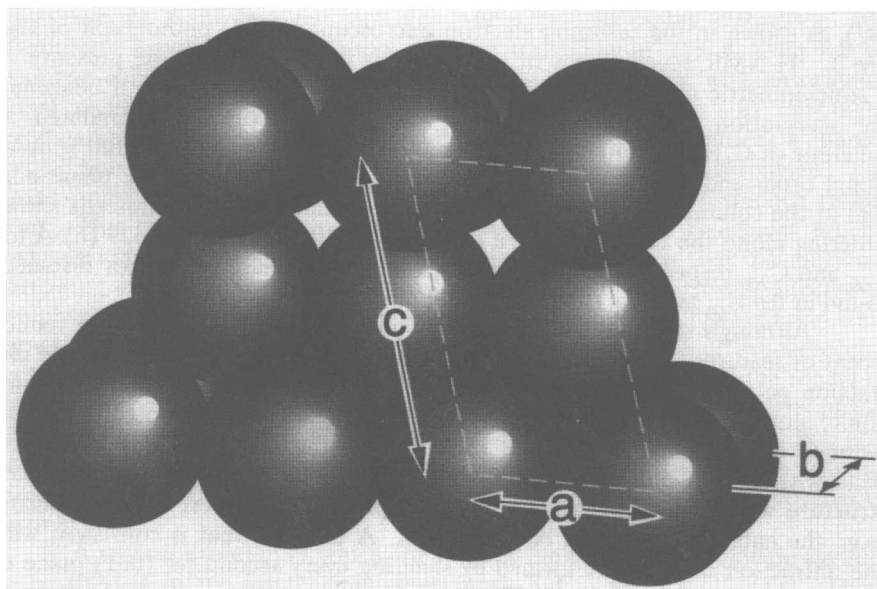

Figure 4. A unit cell that is consistent with the diffraction from pentane-solvated C_{60} and C_{70}. The cell can be formed by shearing an fcc cell along a cubic [110] direction.

Table I. Lattice Parameters for Pentane-Solvated C$_{60}$ and C$_{70}$

| Lattice | C$_{60}$ Primitive Monoclinic | | C$_{70}$ Primitive Monoclinic | | A-Centered Orthorhombic | |
	Obs.	Calc.	Obs.	Calc.	C$_{60}$ Obs.	C$_{70}$ Obs.
a	10.14 (3)	10.08	10.618 (6)	10.53	10.071	10.529
b	10.08 (3)	10.08	10.529 (6)	10.53	10.138	10.618
c	16.50 (5)	16.642	17.33 (1)	17.38	31.447	33.019
β	107.73 (3)	107.63	107.70 (3)	107.63	90	90

NOTE: Values of *a*, *b*, and *c* are given in angstroms, and β values are given in degrees. The numbers in parentheses are the standard error of the mean.

produces a primitive monoclinic cell with parameters of $a = b = D$, $c = 1.651D$, $\beta = 107.63°$ (with D the diameter of the fullerene contact sphere, e.g., 10.04 Å for C$_{60}$). (Further cell reduction of the model gives an A-centered orthorhombic cell, but we will continue to refer to the primitive monoclinic cell as it is more descriptive of the twinning operations.) The model parameters are remarkably close to the observed lattice parameters as obtained from twinned crystals on a four-circle diffractometer and summarized in Table I. The shearing of the fcc packing creates holes in the twinned structure that likely accommodate solvent. As there is one hole per two fullerene molecules in the unit cell, each hole should contain two pentane molecules to conform to the stoichiometry as determined by solution NMR spectroscopy.

The observed twinning and crystal morphology can be simulated by using the monoclinic unit cell just outlined. Twin domains can be obtained by first rotating the unit cell 180° around the *a*-axis, followed by a rotation around the *b*-axis of $180° - 2\beta* = 35.26°$, as illustrated in Figure 5. Successive pie-shaped domains obtained by this twinning operation can form a shape with nearly regular 10-fold morphology, as shown in Figure 6. The twinning rotates the cell by an irrational fraction, so the model predicts that twinned crystals should have a break or crack in their structure of $360° - 352.65° = 7.35°$. Measurements of the ω angles of reflections of different twin domains on a four-circle diffractometer indeed reveal such a deviation from perfect 10-fold symmetry, with an experimental gap-size of 5°.

The fact that the observed unit cell and twinning operation in these solvates can be simulated so well with a hard-sphere model indicates that the near 10-fold symmetry of the crystals is probably unrelated to the icosahedral molecular symmetry of C$_{60}$. It is also remarkable that C$_{70}$ crystallizes in exactly the same way as C$_{60}$, exhibiting an isotropic increase in the lattice parameters (4.7%, 4.5%, and 5.0% in *a*, *b*, and *c*, respectively). The observation of an isotropic increase of lattice parameters suggests that (at least at room temperature) the nonspherical C$_{70}$ molecule packs with random orientations, without alignment of the elongated axis of the C$_{70}$ molecule in the crystal. As discussed, the random nature of C$_{70}$ packing is also observed in unsolvated material.

The formation of solvates–clathrates by the fullerenes is by no means limited to pentane as included solvent. In various crystallization attempts
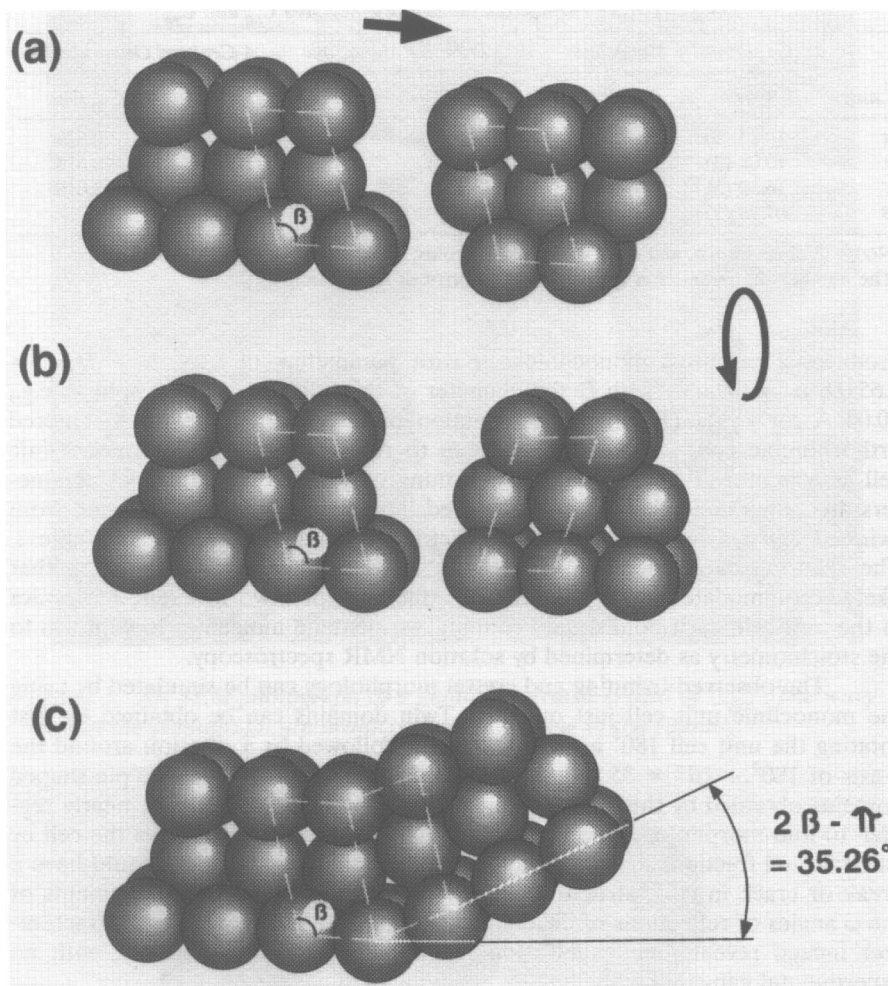
Figure 5. Model for the twinning observed in crystals of pentane-solvated C_{60} or C_{70}.

(including crystallizations from CS_2–pentane mixtures and even from pure benzene), we have observed crystals with a linear ordering of the fullerene molecules similar to that along the *a* axis in the pentane solvates. However, in most of these cases the diffraction patterns of the crystals in the perpendicular direction show strong azimuthal smearing of the reflections. This smearing may suggest that the monoclinic, sheared fcc structure is not unique to the pentane solvates, but that only in the pentane solvates does one have alignment of the tunnels to give full three-dimensional translational order.
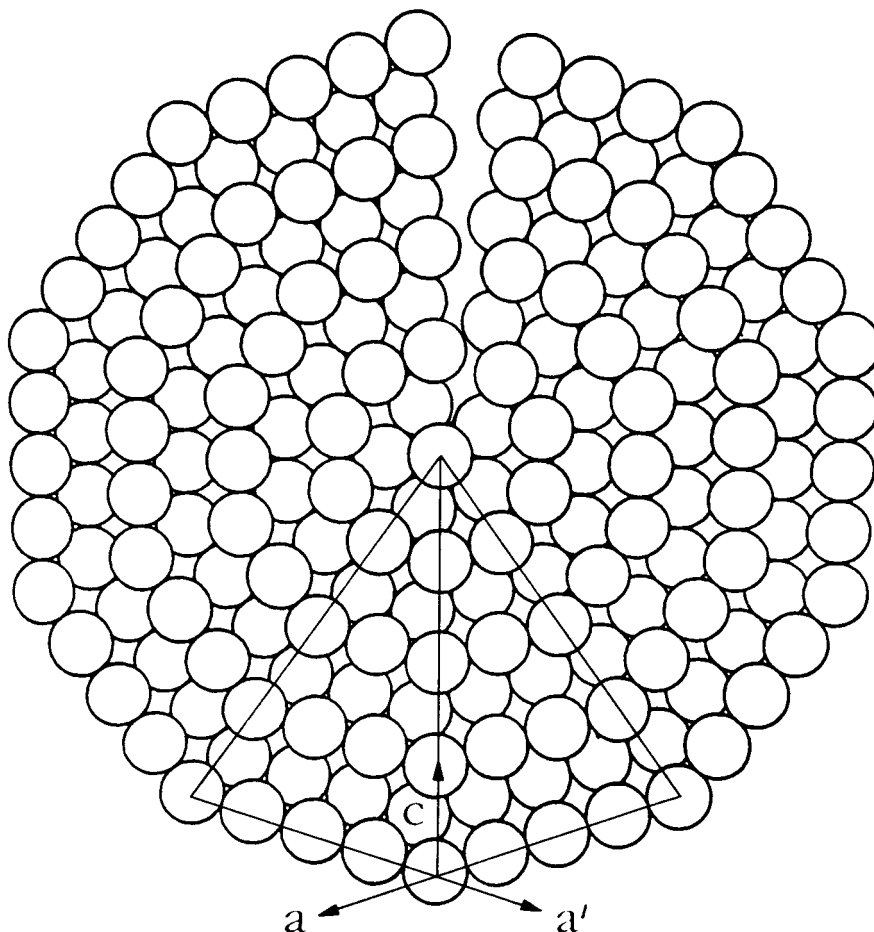
Figure 6. A collection of twins (obtained by the operation shown in Figure 5) illustrating the formation of a 10-sided crystal.

Crystallization of C_{60} from a CS_2–hexane mixture produced crystals that again indicate linear ordering of fullerene spheroids in one direction, but with full three-dimensional translational order and sixfold symmetry in the orthogonal direction. ^{1}H NMR measurements indicate that these are crystals of a stoichiometric hexane solvate $C_{60} \cdot C_6H_{14}$. The X-ray diffraction pattern can be indexed on a primitive hexagonal cell with lattice parameters $a = 33.651$ (4) Å and $c = 10.177$ (2) Å. These cell parameters are identical to those reported by Hawkins et al. (*34*) for crystals grown from pure hexane. Hawkins et al. assumed their crystal contained no solvent and attempted a structure determination with 13 C_{60} molecules in the cell on the basis of their density measurements. Our NMR data indicate that a better description may be obtained with

12 C_{60} • C_6H_4 formula units per unit cell. In the diffraction data, the primitive cell is only weakly populated with six peaks at the cubic (111) d-spacing quite prominent. This weak population suggests that, like the case of pentane incorporation, the hexane solvate might be described by a modification of the fcc cell to accommodate hexane. However, unlike the pentane solvate, the twinning operations are true symmetry operations, resulting in a new unit cell.

Undoubtably other solvates of C_{60} and other fullerenes can be prepared. A solvate of C_{60} with cyclohexane has been reported (*35*) with a 24-Å fcc cell, but a complete structure of this solvate has not been described. Additionally, we have observed that pentane diffusion into CS_2 solutions of the fullerenes produces crystals of both C_{60} and C_{70} with the incorporation of CS_2 as indicated by SEM/EDAX (energy-dispersive X-ray analysis). Unlike pentane-benzene, the CS_2 solvates have different morphologies for C_{60} (flattened needles) and C_{70} crystals (stubby prisms). However, both of these crystal types suffer from extensive translational disorder and are prone to severe cracking, perhaps from loss of incorporated CS_2.

Summary

Despite early difficulties in synthesizing large quantities of fullerenes, these molecules have proved to be remarkably robust with surprising and unusual physical properties. At this stage, most work has focused on C_{60} because it is available in the largest quantities. C_{70} is less well studied, and higher molecular weight fullerenes have thus far received much less attention.

Both C_{60} and C_{70} crystallize in a variety of habits and form a number of solvates, salts, and compounds. Although one can make polycrystalline, unsolvated powder by carefully drying solutions of C_{60} or C_{70}, it is very difficult to grow unsolvated single crystals from solutions. Large "single" crystals of C_{60} can be obtained by sublimation. The crystals have a well-defined morphology but a large degree of orientational disorder, both static and dynamic. The disorder has made a traditional crystal structure of C_{60} at room temperature difficult. Both an ordered model where C_{60} molecules hop between symmetry positions and an orientationally disordered model where molecules are represented by spheres give similar refinement errors. True ordered structures of C_{60} have been obtained by stopping the molecular rotation by forming compounds (*10, 11*) or alkali intercalates (*12, 13*).

Well-formed, highly ordered, solvated crystals of C_{60} and C_{70} can be obtained by solution growth (*31, 34*). For crystals grown from pentane or hexane, solution NMR spectroscopy indicates that stoichiometric amounts of solvent are incorporated into the structure. For pentane, a twinned crystal with pseudo-10-fold symmetry can be indexed with a unit cell derived by shearing an fcc cell along [110]. The result is tunnels in the structure that can contain solvent molecules. Despite the 10-fold nature of the morphology and the diffraction, pentane-solvated fullerenes are not related to decagonal quasicrystals, but instead can be fully indexed with a primitive monoclinic, twinned cell. The

structure of the hexane solvate is presently unsolved. The dimensions of the unit cell and the lack of dense diffraction spots suggest that the unit cell could be derived from a modification of the fcc cubic cell as in the pentane solvate.

Pure C_{70} and solvates of C_{70} crystallize on the same lattice as C_{60} under the same conditions at ambient temperatures. The elongated C_{70} molecules apparently have random orientations in the lattice so that C_{70} effectively packs as as spherical unit.

Acknowledgments

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