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DIFFRACTION SYMMETRY IN CRYSTALLINE, CLOSE-PACKED C_{60}

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ABSTRACT

We have grown crystals of the carbon structure C_{60} by sublimation. In contrast to solution-grown crystals, the sublimed crystals have long range order with no evidence of solvent inclusions. Sublimed C_{60} forms three dimensional, faceted crystals with a close-packed, face-centered cubic unit cell. We have refined a crystal structure using the "soccer ball" model of the C_{60} molecule. The results indicate that the C_{60} molecule has the expected spherical shape, however the data are not sufficiently accurate to unambiguously determine atomic positions.

INTRODUCTION

Recent results reporting the observation of the carbon structure, C_{60}, first as a molecular species[1] and later as a bulk solid[2,3] have sparked considerable interest in the physical properties of this new material. The C_{60} molecule is proposed to have atoms distributed on the surface of a sphere with alternating five and six member rings as in the pattern of seams on a soccer ball.[4,5] Since bonds to carbon are satisfied and there is no permanent dipole in the molecule, one can think of the solid C_{60} as an assemblage of weakly interacting spheres with only van der Waals bonding between spheres. X-ray powder diffraction and transmission electron microscopy (TEM) have shown that C_{60} spheres crystallize with a close-packed structure and nearest neighbor distances of 10.05 Å.[2] The spherical geometry of the C_{60} molecule (and its icosohedral shape) has led to speculation that disorder is intrinsic to solid C_{60}. This concept is supported by solid state ^{13}C nuclear magnetic resonance (NMR) experiments where at room temperature a single, narrow line indicates that the C_{60} molecules are not stationary, but are tumbling isotropically about fixed points in the lattice with a tumbling frequency greater than 10^5/sec.[6] The NMR experiments reported thus far do not describe details of the rotation, e.g. a "ratcheting" between symmetry positions or random, continuous motion may occur. In principal, a ratcheting motion would allow for a conventional determination of the complete crystal structure by diffraction, although the atomic positions might be expected to have large thermal parameters.[7]

EXPERIMENTAL

The preparation of bulk quantities of C_{60} and C_{70} was facilitated by the discovery that both species are present in the soot resulting from striking a carbon arc in low pressure He gas (~ 100 torr).[2] The C_{60} and C_{70} molecules appear to be chemically stable and they are soluble in aromatic solvents, e.g. benzene and toluene, as well as CS_2. The solubility of C_{60}/C_{70} allows one to extract a mixture of the two species from the raw soot by use of a Soxhlet apparatus in boiling toluene. We prepared an extract as described above, and then further purified the extracted mixture by passing the material through an alumina chromatography column with a hexane eluent.

The interaction of C_{60} and C_{70} with the solvent is complex and is not well understood. From mass spectrometry and powder x-ray diffraction, it is clear that the solvent either binds with the solid material or it is interspersed in voids in the solid. Crystals can easily be grown from solution, but they are often solvated and usually do not have close-packed structure seen in powder diffraction. Solution grown C_{60} crystals have been reported with C_{70} co-crystallization,[8] with a non close-packed hexagonal unit cell,[9] and with a monoclinic unit cell.[10]

The crystals used in this study were sublimed from a collection of needle-shaped C_{60} crystals that had previously been crystallized from benzene. The crystals were placed in a quartz tube and pumped dynamically to 10^{-6} torr while the temperature was ramped to 500 °C overnight. Transport of a substantial fraction of material to the room temperature section of the tube was observed without crystal growth. The tube was then sealed under vacuum and placed in a furnace with the hot end of the tube at 500 C. C_{60} crystals grew on the cooler portion of the tube near the furnace entrance in less than thirty minutes.

The crystals obtained by sublimation are of extraordinary quality as compared with our solution grown crystals. The crystals are three dimensional, with well-formed facets and sizes ranging up to 400 μm diameter. From single crystal data the unit cell was determined to be face-centered cubic (fcc), with a lattice parameter of 14.1981(9) Å. (The earlier report[2] of a hexagonal close-paced (hcp) unit cell with c=16.4 Å is in error because the cell determination was based on powder diffraction that had even order ℓ indices only. If our fcc cell is re-indexed as hexagonal, one obtains lattice parameters of a=10.04 and c=24.6 Å and the same powder pattern as in [2].) Single-crystal x-ray diffraction shows that crystals have long range translational order with no evidence of stacking faults due to random packing of the close-packed planes. This demonstrates that at least at the inter-molecular level, there is no intrinsic disorder in these crystals.

DIFFRACTION RESULTS

Crystallographic x-ray diffraction data were collected at room temperature from a sublimed crystal. Cu K_α radiation and an Enraf-Nonius CAD4 diffractometer were employed using a crystal about 100 μm in diameter. From a set of 68 unique reflections in $Fm3m$, we observed 65 reflections with intensities greater than 2σ above background. The rapid intensity drop-off for the higher-angle reflections clearly indicates a large Debye-Waller factor and suggests considerable orientational disorder of the C_{60} molecules is present. The Patterson map was positive overall, but showed only three peaks including the origin. The prominent Patterson vector was 1.49 Å. The limited number of strong reflections impedes the application of direct methods. The best refinements on the data accumulated from several crystals were obtained in space group $Fm3$ with a twinning correction applied as described below.

The proposed C_{60} molecule has an icosahedral, non-crystallographic point symmetry, $m\overline{3}5$ (I_h).[4,5] In order to crystallize on a crystallographic space lattice, the lattice must necessarily adopt fewer symmetry elements than those present in the molecule. Since this loss of symmetry can be accommodated in multiple ways, there are potentially a number of symmetries that the solid can adopt. We first consider crystallization and twinning within cubic space groups. The highest point group symmetry of the C_{60} molecule consistent with cubic symmetry is a subgroup of the icosahedral point group, $m\overline{3}(T_h)$. From the size of the unit cell and the size of the C_{60} ball, we conclude that the structure is close-packed with four molecules per unit cell. This then leaves $Fm3$ as the highest symmetry space group consistent with F-centering and Z=4. The neighboring ball is obtained by F-centering, which in $Fm3$ amounts to a translation of the molecule along [110].
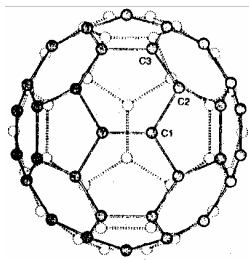
Figure 1: An idealized "soccer-ball" arrangement of atoms proposed for the C_{60} molecular structure. The dashed lines indicated an example of orientational disorder that can increase the apparent symmetry of a crystal.

A schematic view of an idealized C_{60} molecule is shown in Fig. 1. The view is down a two-fold axis with the origin chosen to be at the center of the ball. The three atom sites in $Fm\overline{3}$ are labeled C1, C2 and C3. The space group $Fm\overline{3}$ is susceptible to merohedral twinning which will increase the apparent symmetry of the solid. One merohedral twinning operation is depicted by the dashed lines that show the position of the molecule after a $\pi/2$ rotation about [100]. The effect of the rotation is to impose an apparent four-fold axis along a direction that was formerly two-fold and increase the apparent symmetry to $Fm\overline{3}m$. The rotation merges atoms C2 and C3 and introduces a large apparent thermal parameter on the combined atom in $Fm\overline{3}m$. Atom C1 is rotated into a new position by the twin operation, and therefore becomes two half-occupied sites in $Fm\overline{3}m$.

Alternatively, C_{60} may crystallize on a lattice that is metrically cubic but has rhombohedral symmetry. If we again retain the maximum symmetry possible, the highest symmetry space group will be $R\overline{3}m$. In this case the icosahedral molecule complies with crystallographic symmetry by retaining one three-fold axis and three mirror planes as in the case of boron icosahedra in β-B.[11,12] In $R\overline{3}m$ the layers follow (ABC...) stacking producing a pseudo-fcc unit cell. As in $Fm\overline{3}$, twinning and disorder can produce apparent $Fm\overline{3}m$ symmetry by three-fold twinning operations along the body diagonals of a cube.

We expect, therefore, that twinning (or disorder) will disguise the true symmetry of C_{60}. Consequently, we have refined the data using assumptions about the twinning operation present. A first-order refinement was performed using one carbon site per molecule. We note that if we include only one atom in $Fm\overline{3}m$ symmetry (the merged C2/C3 positions of $Fm\overline{3}$), the cubic symmetry will produce 48 equivalent atoms/molecule and hence, 80% of the scattering power. We placed the atom in an arbitrary position near the origin with no constraints on its movement. The refinement used isotropic thermal parameters initially and anisotropic parameters for the final refinement. The results showing thermal ellipsoids are shown in Fig. 2. This preliminary refinement gives an R-factor of about 20% and shows that the data require electron density at a radius of about 3.5 Å from the origin. A second atom with half occupancy can be added to the refinement. The result is a structure that qualitatively reproduces the twinned C1 position shown in Fig. 1. Again, the distance of this second atom from the origin independently refines to a radius of about 3.5 Å. These results give us confidence that the molecule is indeed spherical with the predicted size.

The large thermal ellipsoids in Fig. 2 could occur because of rapid molecular motion or static disorder, but could also result from a twinning operation that imposes a four-fold axis on a direction that is actually two-fold. A better refinement (R=10%) can be obtained by assuming complete and equal twinning in the $Fm\overline{3}$ space group where we no longer require the coincidence of the positions of C2 and C3. The results with fixed, isotropic thermal parameters are schematically shown in Fig. 3 and summarized in Table I. The
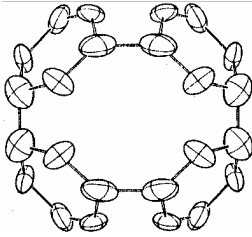
Figure 2: The results of a one-atom refinement of C_{60} in space group $Fm3m$ with anisotropic thermal parameters. The atom position refines to a sphere with the expected radius.

final refinement results in a structure that is qualitatively a "soccer ball", but highly distorted with large estimated errors. Some of the bond distances are unphysical, but the average is consistent with theoretical estimates and with the observed Patterson vector.

Table I
C_{60} Structural Parameters
Face-Centered Cubic Lattice, $a = 14.1981(9)$ Å
Space group: $Fm3$ (Twinned), Z=4, R = 10%

atom	position	x	y	z	U
C1	48h	0	0.252(2)	0.042(3)	.204
C2	96i	0.218(3)	0.125(3)	0.083(5)	.204
C3	96i	0.139(3)	0.213(3)	0.044(5)	.204

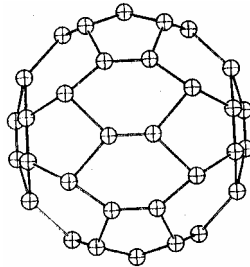| Bond Distances (Å)					
C1	C1	1.19(8)	C1	C2	1.73(6)
C2	C3	1.39(8)	C2	C3	1.76(6)
C3	C3	1.25(14)			
Avg.		1.46(26)			

Figure 3: The results of refinement of three atoms in $Fm3$ assuming equal twinning and fixed, isotropic thermal motion.

CONCLUSIONS

The following conclusions can be drawn from the data. First, C_{60} is a hollow sphere and it crystallizes on a close-packed fcc lattice when free of solvent. The highest possible space groups for a fully ordered structure of C_{60} are $Fm\bar{3}$ or $R\bar{3}m$. (The rhombohedral space group may be metrically cubic.) Both merohedral twinning and rotational disorder will increase the apparent symmetry to $Fm\bar{3}m$. Refinement of our crystallographic data using a model in $Fm\bar{3}$ with twinning applied adequately reproduces the observed intensities, but the refinement lacks precision in bond distances. While hints of the soccer-ball structure arc apparent, a complete crystal structure with accurate bond lengths will have to await a better crystal. Better structural data can be collected by (a) finding a crystal with less static disorder or (b) minimizing dynamic disorder by collecting data at low temperatures or high pressure. At the present time it is not clear which of these approaches is the more important. Even if the structure had no dynamic disorder, static disorder and twinning could easily account for all of the problems we encountered.

ACKNOWLEDGMENTS

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