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Crystal Structure of the Higher Fullerene C$_{84}$

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The study of the structural and physical properties of fullerenes in the solid state has been attracting considerable interest in recent years. However, most of the structural work has concentrated on the most abundant fullerenes, C$_{60}$ and C$_{70}$. Solid C$_{60}$ displays a phase transition at ≈260 K from a high-temperature orientationally disordered face-centred-cubic (fcc) (space group $Fm\bar{3}m$) to an orientationally ordered primitive cubic (space group $Pa\bar{3}$) phase.[1] The structural behavior of solid C$_{70}$ as a function of temperature is more complicated, as its structure changes from fcc at high temperatures to rhombohedral at 340−350 K to monoclinic at 280 K.[2] Few details are known about the structures adopted by pristine higher fullerene solids. Most work has been performed on materials (e.g. C$_{76}$, C$_{82}$) crystallized from solution[3] when unavoidably either solvent molecules are included in the lattice spacings or cosolvates are formed; in such cases, the observed structures are monoclinic and evidently stabilized by the intervening solvent molecules. Heating the C$_{76}$ solid to 100 °C was found to partially remove the solvent, leading to the formation of a mixed fcc/hcp phase.[3]

C$_{84}$ fullerene was solvent extracted in macroscopic amounts very early. Among the 24 structural isomers obeying the isolated pentagon rule, it was found that it principally forms as a mixture of only two of them in a 2:1 abundance ratio (isomers with symmetry D_2(IV) and D_{2d}(II))[4]. A remarkable feature of these isomers is their quasispherical shape and their small aspect ratios, as derived from theoretical calculations (D_2(IV), d_x = 7.79 Å, d_y = 8.45 Å, d_z = 8.16 Å; D_{2d}(II), d_x = 7.90 Å, d_y = 8.30 Å, d_z = 8.50 Å).[5] In addition, they possess low-lying LUMOs[6] which may lead to their facile reaction with electron donors. Indeed it has been recently found that a potassium intercalation compound of stoichiometry, K$_{8+x}$C$_{84}$ can be isolated after doping with potassium to saturation.[7] These structural and electronic similarities with C$_{60}$ make an investigation of the properties of pristine C$_{84}$ highly desirable. At present, only low-resolution electron diffraction studies are available on crystalline C$_{84}$;[8] these provided evidence for a cubic structure with a lattice constant of a = 15.8-(1) Å. Finally, it has been recently possible to successfully isolate the two major isomers of C$_{84}$.[9]

The present C$_{84}$ sample was partially purified by single pass HPLC, employing a Cosmosil buckyprep column with the resulting fraction containing C$_{82}$, C$_{84}$, and C$_{86}$ fullerenes only. Repeated recycling HPLC using a Cosmosil 5PYE column led to complete removal of C$_{82}$, C$_{86}$, and the five minor isomers of C$_{84}$, leaving just the D_2(IV) and D_{2d}(II) isomers (Figure 1) in a ratio of 2:1. The sample was characterized by ^{13}C NMR spectroscopy using a 600 MHz JEOL JNM-A600 spectrometer. After recrystallization from toluene, the sample was heated at 200 °C under reduced pressure (∼10^{-5} Torr) for 12 h before sublimation at 650 °C. The sublimed sample (mass ≈ 2.1 mg) was very crystalline and displayed sharp reflections in its powder X-ray diffraction profile (collected on a Siemens D5000 diffractometer at ambient temperature). High-resolution synchrotron X-ray diffraction measurements (λ = 0.7993 Å) on the sample sealed in a thin-wall glass capillary 0.5 mm in diameter were performed between 5 and 295 K on the Swiss-Norwegian beamline (BM1B) at the European Synchrotron Radiation Facility, Grenoble, France. Data were collected in the 2θ range 4−26° at 20 K at a step of 0.01° for 20 h; at other temperatures, only the 2θ ranges incorporating the (111), (220), and (311) cubic reflections were measured. The capillary sample, which was contained within a He-flow cryostat (Janis Inc), was rotated continuously during the measurement. The long-term temperature stability of the cryostat was ±0.1 K and the sample was cooled from room temperature to 20 K in 280 min. The diffractometer was equipped with a Si(111) analyzer crystal. Data analysis was performed with the PROFIL[10] suite of Rietveld analysis programmes, incorporating form factors for spherically disordered molecules and the LeBail pattern decomposition technique.[11]

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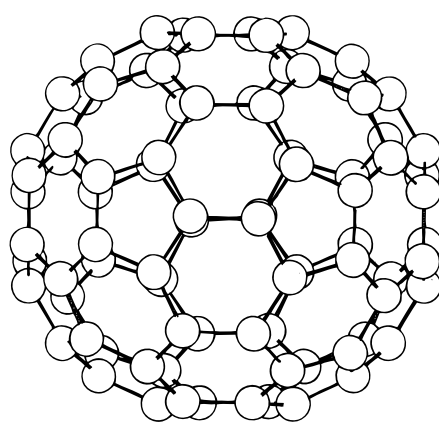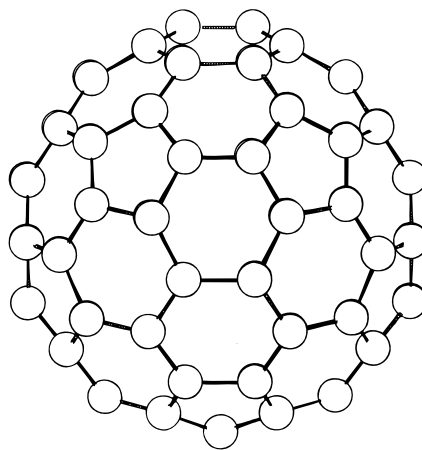
D2 (No.22)   D2d (No.23)

Figure 1. Molecular structures of the two major isomers of C_{84} with symmetry D_2(IV) and D_{2d}(II).
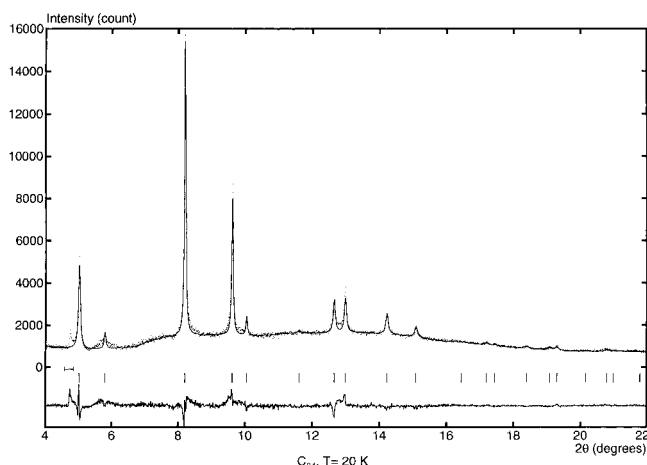

Figure 2. Rietveld refinement of the synchrotron X-ray powder diffraction profile of C_{84} at 20 K. The observed data are shown as points and the calculated fit as a solid line. The difference curve is included at the base of the figure with the ticks marking the positions of the Bragg reflections.

The synchrotron powder diffraction profile at 20 K showed that the crystal structure of C_{84} is fcc. All peaks observed to a momentum transer $Q = 3.54$ Å^{-1} (where $Q = 4\pi \sin \theta/\lambda$) indexed with Miller indices either all odd or all even. The only exception is a significant peak on the leading edge of the (111) reflection at $\approx 3.7°$; we ascribe this to the presence of hexagonal stacking faults in the fcc structure, an interpretation consistent with what has been observed in other fullerene solids.[1,2] Rietveld refinements of the profile were thus attempted in space group $Fm\bar{3}m$. This necessitates the presence of orientationally disordered quasispherical C_{84} molecules which are placed at the origin of the unit cell. Such an approach, in which the carbon atom motion is confined to the surface of a sphere, has been used before to describe the orientational disorder of C_{60} molecules in the high temperature fcc phase of C_{60}[1] and of $C_{60}{}^{3-}$ ions in the fcc phase of Li_2CsC_{60}.[12] Rietveld refinement

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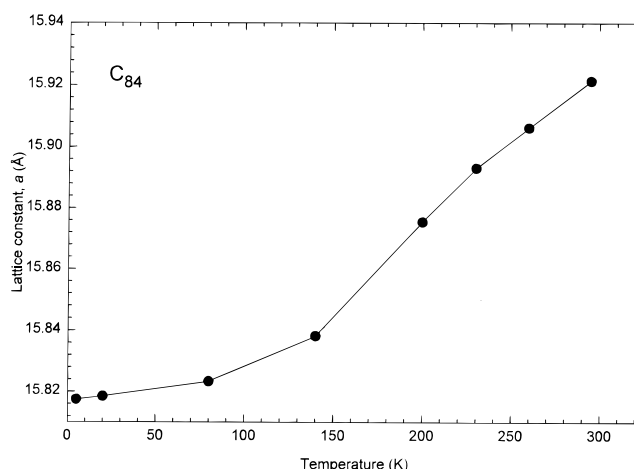

Figure 3. Temperature evolution of the cubic lattice constant, a, of C_{84} as extracted from the LeBail refinements of the synchrotron X-ray powder diffraction profiles. The line is a guide to the eye.

of the data (Figure 2), assuming a form factor for the spherical C_{84} shell of radius R of the form: $f(Q) = (84/\sqrt{4\pi})f_C[\sin(QR)/QR]$, where Q is the momentum transfer and f_C the carbon atom form factor, proceeded smoothly with the refined value of the lattice constant, $a = 15.817(4)$ Å, and the diameter of the spherical shell, $d = 8.35(1)$ Å ($2\theta = 4-22°$, $R_{wp} = 20.1\%$, $R_{exp} = 7.5\%$). The values of the R factors reflect the presence of anisotropic peak broadening effects which are not taken into account in the present refinements. No full profile refinements were performed for the restricted range datasets measured at other temperatures. Instead LeBail refinements were employed to extract accurate values of the cubic lattice parameter as a function of temperature (Figure 3). The cell is found to contract almost linearly from room temperature down to 140 K with an expansion coefficient of $da/dT = 5.4(3) \times 10^{-4}$ Å K^{-1}. Below 140 K, the rate of contraction decreases markedly and the lattice constant essentially flattens off at temperatures below 80 K.

Several points arising from the results of the present refinements are of particular interest. First, the C_{84} molecules remain disordered at all temperatures with

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neither an orientational ordering transition (cf. C_{60}) nor a phase transition to a low-symmetry structure (cf. C_{70}) observed on cooling. While the lack of a symmetry lowering transition can be safely ascribed to the quasi-spherical molecular shape, the coexistence of the two isomers should be responsible for the absence of orientational ordering effects, as static disorder is dominant at all temperatures. We did not consider it physically meaningful at this stage to describe the scattering density of C_{84} in terms of symmetry-adapted spherical harmonic (SASH) functions, even though the inclusion of SASH functions in the Rietveld refinements improves the R factors considerably. Structural data on isomer-pure C_{84} solids are needed to perform such an investigation of the orientational disorder effects. We stress that the observed structural behavior with temperature is strongly encouraging with respect to the existence of a broad intercalation chemistry of C_{84}, in an analogous fashion to C_{60}. The structure always remains fcc with large octahedral (~2.32 Å at 20 K) and tetrahedral (~1.26 Å at 20 K) voids which can be occupied by metal ions while cubic crystal symmetry is retained. It is also noteworthy that the expansivity of C_{84} is more than twice as large as that of the fcc phase of C_{60} (da/dT =

2.30(5) $\times$ 10^{-4} Å K^{-1}), reflecting a weaker intermolecular bonding in the lattice of the large C_{84} molecules.

In conclusion, we have employed temperature-dependent high-resolution synchrotron X-ray powder diffraction to characterize the structural properties of pristine C_{84} for the first time. The solid remains fcc in the temperature range 5−295 K, making it a highly promising candidate as a host for the synthesis of intercalation compounds with exciting electronic and conducting properties, as those of their C_{60} antecedents.

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