

Crystal structures of fluorinated fullerenes

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$C_{60}F_x$ and $C_{70}F_x$, respectively, prepared by the direct reactions of C_{60} and C_{70} powders with elemental fluorine form face-centered-cubic lattices with $a_0=17.19$ and 17.93 Å, in which rotational and/or orientational disorders of the $C_{60}F_x$ and $C_{70}F_x$ molecules prevail.

1. INTRODUCTION

Recent structural studies on solid C_{60} have established that it forms a face-centered-cubic (fcc) structure at room temperature and that the molecules execute rotational diffusion [1,2]. Structural studies of crystalline C_{70} have indicated that the equilibrium phase above room temperature is fcc, but that structural defects as well as residual solvent tend to stabilize the hexagonal-closest-packed (hcp) phase [3]. We have reported that fluorinated C_{60} , $C_{60}F_x$ ($20 < x < 45$), in which the fluorine atoms are bound to the carbon atoms, form an fcc lattice with $a_0 \approx 17.1$ Å [4].

In this paper the crystal structure of $C_{70}F_x$ is reported in connection with the crystal structure of C_{70} , and comparisons were made with the lattice parameters of C_{60} and $C_{60}F_x$.

2. EXPERIMENTAL

C_{60} and C_{70} powder samples, heat-treated for 2 days in a dynamic vacuum, were reacted with elemental fluorine of 1 atm at 200°C for 4 hours and at RT for 4 weeks, respectively. The compositions of the samples were determined by chemical analysis on F employing the oxygen flask combustion method with the fluoride ion electrode. The Debye-Scherrer (DS) X-ray powder diffraction (XRPD) patterns were obtained by loading powder samples in a quartz capillary ($\phi=0.7$ mm) using $\text{Cu-K}\alpha$ radiation on

the Shimadzu X-ray diffractometer XD-D1. The intensities were collected in 0.1° (2θ) steps in the range $5-35^\circ$ (2θ) using a pinhole slit ($\phi=2$ mm).

3. RESULTS AND DISCUSSION

The compositions of the products were *ca.* $C_{60}F_{45}$ and $C_{70}F_{32}$. The DS-XRPD patterns for C_{60} , $C_{60}F_{45}$, C_{70} and $C_{70}F_{32}$ are shown in Figures. 1(a)-4(a) and their lattice constants a_0 (and c_0) are summarized in Table 1.

The simulated pattern (Figure. 1(b)) for C_{60} was obtained assuming rotational and/or orientational disorders of C_{60} molecules, *i.e.*, spherical shell (SS) model [2,3] with the center to carbon-atom distance of 3.52 Å [2]. For the simulation the Gaussian function with an appropriate standard deviation was applied to

Table 1 Lattice constants for C_{60} , $C_{60}F_{45}$, C_{70} and $C_{70}F_{32}$

Sample	Lattice	$a_0/\text{Å}$	$c_0/\text{Å}$
C_{60}	fcc	14.19	
$C_{60}F_{45}$	fcc	17.19	
C_{70}	hcp	10.53	17.21
	fcc	14.90	
$C_{70}F_{32}$	fcc	17.93	

each calculated peak intensity.

The simulated pattern (Figure 2(b)) for $C_{60}F_{45}$ was obtained assuming a single unique center to carbon-atom distance of $3.87(=3.52 \times 1.1)$ Å and a single unique center to fluorine-atom distance of $5.23(=3.52 \times 1.1 + 1.36)$ Å, where the skeleton radius was expanded by the factor of 1.1, and the C-F distance of 1.36 Å was employed [5,6]. The sphere expands owing to the π -electron depletion. The atomic scattering factors of C

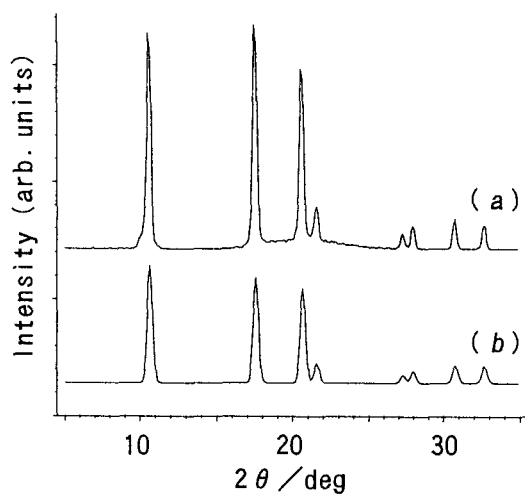


Figure 1. Observed (a) and simulated (b) diffraction patterns for C_{60} .

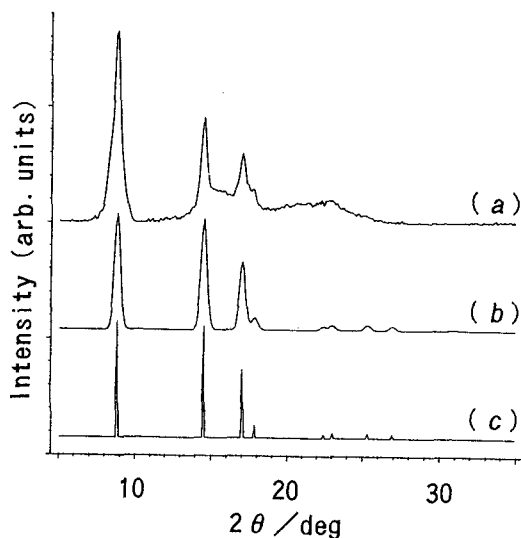


Figure 2. Observed (a), simulated (b) and calculated (c) diffraction patterns for $C_{60}F_{45}$.

and F were weighted by 60 and 45, respectively, to match the composition. The molecule consists of two concentric shells: one made of carbon atoms and the other of fluorine. It is noted that any $C_{60}F_x$ molecule except $C_{60}F_{60}$ will have several non-equivalent carbon atoms, and some non-equivalent fluorine atoms depending on the molecular symmetry. As a consequence a rotating $C_{60}F_x$ becomes essentially equivalent

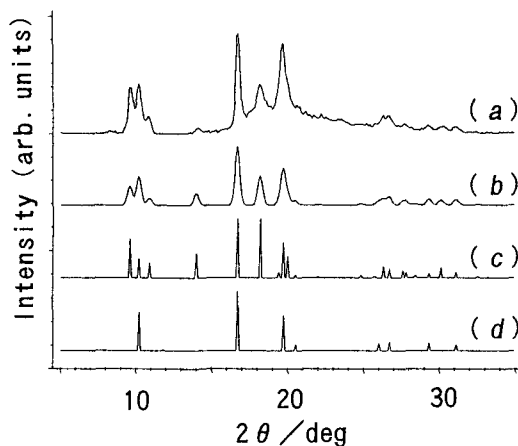


Figure 3. Observed (a) and simulated (b) diffraction patterns for C_{70} , and calculated patterns for hcp (c) and fcc (d).

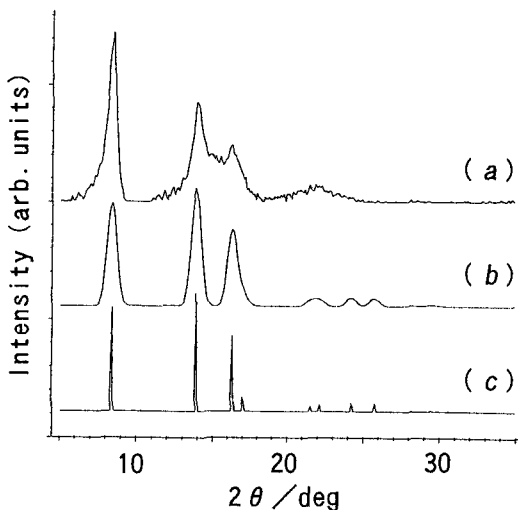


Figure 4. Observed (a), simulated (b) and calculated (c) diffraction patterns for $C_{70}F_{32}$.

to multi-shells of carbon and fluorine atoms. However, the satisfactory fit in Figure. 2 indicates that the differences in their radii are not significant.

The structure of C_{70} is more subtle. Recent studies have indicated that heat-treatment of C_{70} is not sufficient to remove the trapped solvent completely [3]; sublimation and the subsequent annealing of C_{70} is necessary to obtain an fcc crystal of pure C_{70} . Our C_{70} sample was found to be an admixture of hcp and fcc phases, indicating that there remained a certain amount of solvent in the C_{70} sample. Figure 3 shows the calculated patterns based on the hcp (c) and fcc (d) structures and the simulated pattern (b) with a 2:1 mixture of the hcp and fcc phases. The calculation was done assuming the SS model. There are five unique center to carbon-atom distances; 4.172 Å (10 atoms), 4.029 Å (10), 3.876 Å (20) 3.663 Å (20) and 3.565 Å (10) [7].

The XRPD (Figure. 4(a)) of $C_{70}F_{32}$, on the other hand, indicates that it forms an fcc lattice. The structural change from hcp to fcc for C_{70} upon fluorination is intriguing. The pattern was simulated (Figure. 4(b)) in the same manner as above; the C_{70} skeleton was enlarged by the ratio 1.1 and 70 fluorine atoms were attached 'normal' to the spheroid. The C-F bond length of 1.36 Å was used. The atomic scattering factors of C and F were weighted by 70 and 32, respectively. The molecule consists of ten concentric shells: five of carbon atoms and five

of fluorine.

In Table 2 the effective radii of spherical C_{60} , $C_{60}F_{45}$, C_{70} and $C_{70}F_{32}$ are summarized. For C_{70} the hexagonal c_0/a_0 ratio is 1.63, suggesting an ideal hcp structure made of perfect spheres. The same differences of ca. 1.07 Å in the radii of the pristine fullerenes and the fluorinated ones indicate that the fluorinations of C_{60} and C_{70} bring about similar changes in the molecular as well as in the crystal structures of the fullerenes.

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Table 2 Effective radii of spherical C_{60} , $C_{60}F_{45}$, C_{70} and $C_{70}F_{32}$, and the increments upon fluorination

System	Radius/Å	Increment/Å
C_{60}	5.02	
$C_{60}F_{45}$	6.08	1.06
C_{70}	5.27	
$C_{70}F_{32}$	6.34	1.07