Structural Phase Transformations in C_{70}

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Powder X-ray diffraction shows that on sublimation, solvent free C_{70} crystallizes in a hexagonal close packed (HCP1) arrangement with small admixture of a second hexagonal close placked (HCP2) phase as well as a face centred cubic (FCC) phase, the proportions of which are progressively transformed by annealing *in vacuo* at 300 °C *via* HCP2 to FCC.

The discovery of a method of producing large amounts of fullerenes[1,2] and the possibility of separating these all-carbon closed shell units,[3] has opened up new fields of research in the synthesis of novel materials, and the characterization of their physical properties. It is now clear that the solid-state properties of the fullerenes, and in particular their phase relationships,[4] are as intriguing as the shapes of the molecules themselves. Thus, early reports on C_{60} suggested that the solid consisted of a mixture of HCP and FCC phases [1,5,6] a result that was shown to be solvent dependent, as is the crystal morphology.[7] However, drying or sublimation under vacuum eliminates the intercalated solvent yielding an FCC (Fm3m) phase. In the FCC phase, stable above 260 K, the C_{60} units are orientationally disordered. Below 260 K the units librate between nearly degenerate orientations[8] until at 90 K a complete freezing of the balls occurs and optimization of the C_{60}–C_{60} interaction places the bonds joining two pentagons on the unit over a hexagonal ring, in a neighbouring one.

In contrast the phase relations of C_{70} have proved more difficult to unravel. Firstly, separation of high purity C_{70} from C_{60} and higher fullerenes is not as effective on a normal alumina column as it is for C_{60}. Retention of around 10–15% C_{60} in C_{70} is common. Secondly, intercalated solvent cannot be removed from C_{70} by heating the solid under vacuum.[9] Sublimation is necessary to remove all traces of solvent but has the advantage of yielding a microcrystalline product on condensation from the vapour. There is evidence[9] for the coexistence of HCP and FCC phases in C_{70}, but little is known about the conditions under which they are stable. We have therefore examined the structural evolution of a solvent-free microcrystalline sample of C_{70} after annealing it for increasing periods of time *in vacuo*. In contrast to previous work[9] we find two HCP phases which transform one into another and then into an FCC phase. The whole process takes 17 days at 300 °C but only 5 days at 450 °C.

Mixtures of fullerenes were prepared at the Tokyo Metropolitan University by arc heating of graphite rods, HPLC being used to separate the constituent fractions as reported in ref. 10. The C_{70} powder was placed in a 30 cm long silica tube under a 10^{-1} to 10^{-2} Torr (1 Torr = 133.3 Pa) dynamic vacuum, and sublimed at 700 °C. Single crystals (around 0.5 × 0.3 × mm) condensed in the cold zone of the tube outside the furnace. Scratches on the inside of the tube served to seed the growth. About half the material sublimed under these

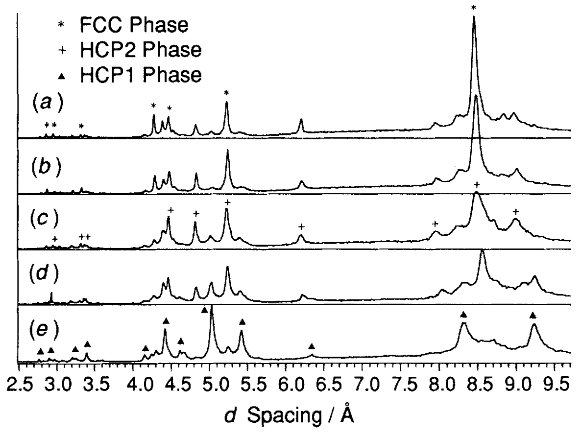

Fig. 1 Powder X-ray diffraction patterns of C_{70} as a function of annealing time at 300 °C, from top to bottom (*a*) no annealing, (*b*) 3 days, (*c*) 7 days, (*d*) 14 days, (*e*) 17 days

conditions but the remainder, which was non-crystalline, could be recovered by recrystallisation in CS_2 and resublimed. In the IR and Raman spectra of the sample employed, no peaks due to C_{60} or other fullerenes were observed, the estimated detection limit being 1%. The C_{70} crystals were ground, placed on an amorphous silicon substrate and powder X-ray diffraction profiles recorded at room temperature by a Siemens D500 diffractometer at the Royal Institution, using Cu-Kα-radiation. The sample was then placed in a furnace at 300 °C under a vacuum of 10^{-1} to 10^{-2} Torr. After 3, 7, 14 and 17 days annealing, it was removed from the furnace, cooled to room temperature, and the powder diffraction profile remeasured.

Fig. 1 shows the X-ray powder diffraction profiles of C_{70} measured following different anealing times. The scan (*a*) is dominated by peaks assigned (Table 1) to a hexagonal close packed phase (HCP1) [a = 10.776(1), c = 20.33(4) Å] with minor admixture of a second hexagonal close packed (HCP2) phase [a = 10.553(8) Å], and a face centred cubic phase (a = 14.96 Å, Table 1). It is noteworthy that the peaks of the two HCP phases could not be indexed to a single orthorhombic cell and furthermore, annealing at 300 °C modifies the proportions of the three phases in the sample. The HCP1 phase transforms first to the HCP2 and FCC phases, so that after 3 days, intense HCP1 reflections such as (004) and (101) (*d* spacings 5.05 and 8.36 Å, respectively) lose most of their intensity. The FCC reflections coincide with those of the HCP2 phase. However, a number of reflections unique to the latter, such as (100), (101) and (103) (*d* spacings 9.00, 7.15 and 4.82 Å, respectively) increase in intensity with up to 7 days annealing, and then decrease steadily to reach a limiting intensity corresponding to a mole fraction of about 10%, the remaining reflections being from the FCC phase. The presence of a majority FCC phase was further confirmed by X-ray diffractioin of a single crystal that had been fully annealed.[11] Furthermore, on resubliming the FCC sample at 700 °C it transformed back to the original HCP1 phase with small admixture of HCP2 and FCC. Calculations[12,13] of the relative stability of different modes of packing C_{70} in crystal lattices further confirm the small difference in free energy between HCP and FCC structures, making it plausible that such phases may coexist.

The lattice parameters determined by us for HCP2 and FCC phases of C_{70} are in good agreement with those of Vaughan *et al.*[9] It is significant that the c:a ratio for HCP1 is 1.89. This deviation from the ideal value of 1.63 may be an indication of a degree of orientational ordering similar to that seen in C_{60} at low temperature. If analogous transitions do occur in C_{70}, they would be expected to occur at higher temperature than in C_{60} because of the higher molecular symmetry of the latter.

In summary, we have demonstrated that C_{70} forms two HCP phases and an FCC one. Prolonged annealing at high temperature is needed to effect transformation between them. Details of the orientational order and structures of the three phases remain to be worked out.[14]

Table 1 X-ray powder diffraction peaks for the HCP1, HCP2 and FCC phases of C_{70}

	d Spacing/Å (observed)	*d* Spacing/Å (calculated)	*hkl*
HCP1	9.27	9.33	100
	9.36	8.48	101
	5.45	5.48	103
	5.05	5.08	004
	4.64	4.67	200
	4.45	4.46	104
	3.42	3.44	204
HCP2	9.00	9.14	100
	8.48	8.61	002
	7.95	8.07	101
	6.21	6.27	102
	5.23	5.28	110
	4.82	4.86	103
	4.27	4.30	004
	3.32	3.34	114
	2.95	2.96	213
FCC	8.45	8.64	111
	5.23	5.29	220
	4.46	4.51	311
	4.27	4.32	222
	3.32	3.34	420

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