ESRF	**Experiment title:** Structural studies of higher fullerenes and endohedral metallofullerenes	**Experiment number:** CH-434
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Report: Work on the structural and physical properties of fullerenes in recent years has principally concentrated on C_{60} and its derivatives and, to a lesser extent, on C_{70}. 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 [I] when unavoidably either solvent molecules are included in the lattice spacings or cosolvates are formed. 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:l abundance ratio (isomers with symmetry D_2(IV) and D_{2d}(II)[2]). A particular feature of interest of these isomers is their quasi-spherical shape, reminiscent of the shape of C_{60} itself. High-resolution synchrotron X-ray diffraction measurements on a sublimed C_{84} sample, which was a mixture of the two major isomers D_2 and D_{2d}, were performed between 5 and 295 K on BMlB (Fig. 1). The results show that the C_{84} molecules remain disordered at all temperatures (*fcc*; space group $Fm3m$) with 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 [3]. Following our recent success in obtaining isomer-pure, D_2 and D_{2d}, sublimed C_{84} samples [4], we performed high resolution diffraction measurements between 5 and 295 K on *BM16* (λ= 0.8499 A), as part of our beam allocation. The results show that while at room temperature both isomers crystallise in an orientationally-disorderedfcc

structure, on cooling both materials undergo phase transitions to low symmetry structures of different symmetry. Our preliminary data analysis, which is at a more advanced stage for the D_{2d} isomer, shows that at room temperature the crystal structure is *fcc* (a= 15.817(4) Å), comprising of orientationally disordered quasi-spherical units. However, at 20 K the structure is monoclinic with lattice dimensions a= 15.926(l) Å, *b*= 11.140(1) Å, c= 11.224(l) Å, β= 90.980(5)° (Fig 2) and comprises of orientationally ordered C_{84} molecules. The order-disorder phase transition takes place at about -200 K. The structural analysis of our data on the D_2 isomer is still in progress but the presence of a cubic to low sysmmetry structural phase transition is again evident unambiguously.

These results demonstrate the importance of studying isomer pure samples of the higher fullerenes and show the extreme sensitivity of their properties on the isomer form involved.

References

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Fig 1. Rietveld refinement of the synchrotron X-ray powder diffraction profile of C_{84} (sublimed mixture of D_2 and D_{2d} isomers) at 20 K (BMlB).

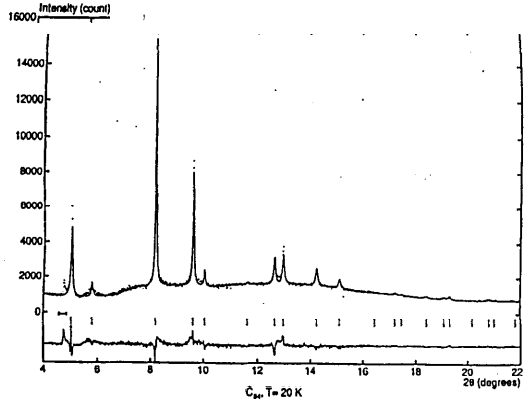

Fig 2. LeBail refinement of the synchrotron X-ray powder diffraction profile of C_{84} D_{2d} isomer at 20 K (BM16).