ESRF	**Experiment title:** Structure of C84 intercalation compounds	**Experiment number:** CH-509
Beamline: BM16	**Date of experiment:** from: 15/12/98 to: 17/12/98	**Date of report:** 27/08/99
Shifts: 6	**Local contact(s):** Andrew Fitch	*Received at ESRF:*

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Report: Since the discovery of superconductivity[1] in K_3C_{60} the metal intercalation chemistry of C_{60} has been a topic of considerable interest. There is as yet no agreement on the aspects of C_{60} which are responsible for the onset of superconductivity in the A_3C_{60} phases; although the triply degenerate t_{1u} LUMO and spherical shape may be important contributing factors[2]. Of the higher fullerenes the D_{2d} isomer of C_{84} is nearly spherical and has a doubly degenerate LUMO, making it the natural starting point in the search for superconductivity in the higher fullerides. Following the recent success[3] in obtaining isomer pure D_2 and D_{2d} C_{84} and saturation doping[4] of these hosts with potassium it has become possible to synthesise isomer specific C_{84} intercalation compounds with lower doping levels.

The purpose of this experiment was to structurally characterise potassium intercalation compounds of isomer specific C_{84} hosts. Due to the small quantities (~5mg) of isomer pure C_{84} available, accurate control of the stoichiometry of K_zC_{84} during synthesis was not easy.

Using BM16 (λ=0.8350 Å) we performed high resolution powder diffraction measurements on a sample of potassium doped C_{84}-D_{2d} and a sample of potassium doped C_{84}-D_2. The diffraction data for both samples can be indexed on the basis of a cubic unit cell. Lebail extraction in the space group Fm3m gives lattice parameters of 16.27(2) Å and 16.34(1) Å for K_zC_{84}-D_{2d} and K_zC_{84}-D_2 respectively. Preliminary Rietveld refinements (Figures 1 and 2) confirm that these samples do indeed have a low potassium concentration. The refined compositions are $K_{2.872}C_{84}$-D_{2d} and $K_{2.444}C_{84}$-D_2. A summary of the crystallographic parameters from

the refinement of the data in Fm3m on the potassium doped C_{84}-D_{2d} is given in Table 1. The temperature factors of the carbon atoms were constrained to be the same while the temperature factors of the potassium cations were not refined.

	X	Y	Z	UISO / Å^2	Fractional occupancy
C	0.20521	0.87456	0.09205	0.073(16)	0.166667
C	0.13616	0.94830	0.21060	0.073(16)	0.166667
C	0.20233	0.94230	0.15293	0.073(16)	0.166667
C	0.03002	0.03002	0.26311	0.073(16)	0.166667
C	0.20197	0.13761	0.06263	0.073(16)	0.166667
C	0.26256	0.02867	0.98843	0.073(16)	0.166667
C	0.23678	0.11371	1.00443	0.073(16)	0.166667
C	0.11425	0.01056	0.23664	0.073(16)	0.166667
C	0.14672	0.08237	0.19610	0.073(16)	0.166667
C	0.20443	0.07596	0.13037	0.073(16)	0.166667
C	0.23675	1.01445	0.11436	0.073(16)	0.166667
K	0.25	0.25	0.25	0.025	0.465(15)
K	0.447(4)	0.447(4)	0.447(4)	0.025	0.205(16)
K	0.5	0.5	0.5	0.025	0.304(150)

Table 1. Crystallographic parameters for refinement of K_zC_{84}-D_{2d} data.

The model for the anion orientation in the refinement of the K_zC_{84}-D_{2d} data had the normals to the molecular mirror planes exclusively lined up along the <110> directions of the unit cell. In the space group Fm3m this produces a six-fold orientational disorder due to the lack of a three-fold axis in the C_{84}-D_{2d} molecule. The potassium cations partially occupy the octahedral, off octahedral and tetrahedral sites.

These experiments demonstrate that fcc phases with less than saturation occuancy of the possible interstitial sites in higher fullerides can be formed. The capability of BM16 to measure small poorly crystalline samples proved invaluable given the small quantities of isomer pure higher fullerenes currently available.

References

1. Hebard, A. F. ; Rosseinsky, M. J. ; Haddon, R. C. ; Murphy, D. W. ; Glarum, S. H. ; Palstra, T. T. M. ; Ramirez, A. P. ; Kortan, A. R. *Nature* **1991**, 350, 600.
2. Gunnarsson, O. *Rev. Mod. Phys.* **1997**, 69, No. 2, 575.
3. Dennis, T. J. S. ; Tsutomu Kai; Tetsuo Tomiyama; Hisanori Shinohara *Chem. Commun.* **1998**, 619.
4. Allen, K. M. ; Dennis, T. J. S. ; Rosseinsky, M. J. ; Shinohara, H. *J. Am. Chem. Soc.* **1998**, 120, 6681-6689.

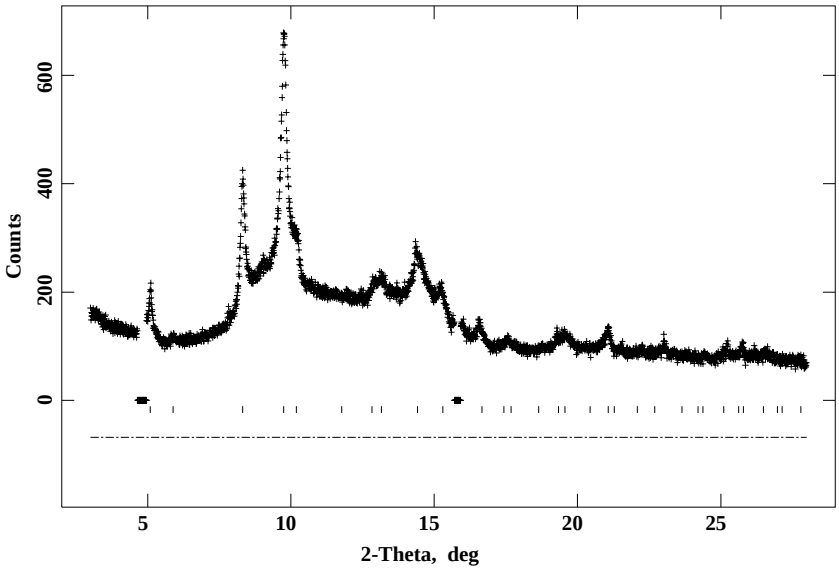

Figure 1. Rietveld refinement of data from $K_{2.872}C_{84}$-D_{2d} sample at 295 K (BM16)

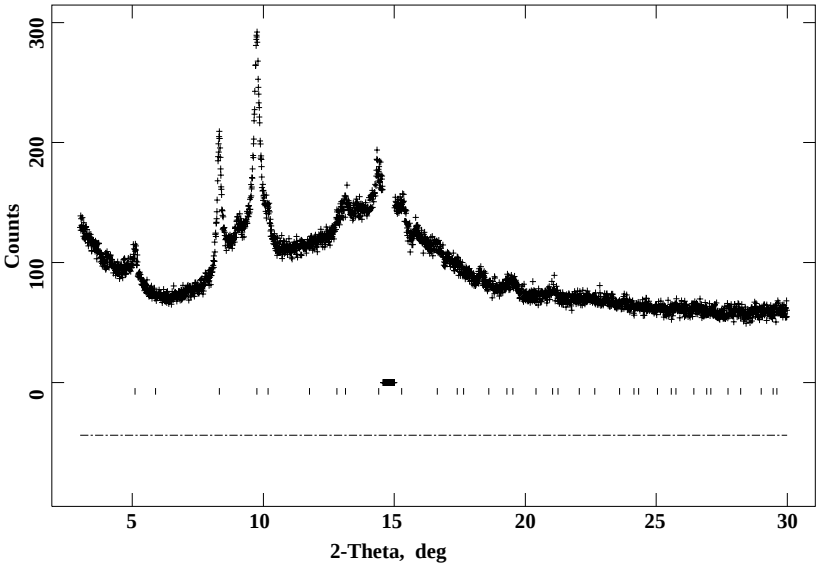

Figure 2. Rietveld refinement of data from $K_{2.444}C_{84}$-D_2 sample at 295 K (BM16)