ESRF	Experiment title: Anion orientational ordering in the first fcc – related A_3C_{70} phases.	Experiment number: CH-508
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Report: The observation of superconductivity[1] in fcc A_3C_{60} phases has led to extensive study of the intercalation chemistry of C_{60}. The mechanism of superconductivity is as yet not understood but the triply degenerate nature of the C_{60} t_{1u} LUMO may be an important factor[2]. To test this experimentally it is necessary to synthesise and structurally characterise A_3C_{2n} phases based on fullene hosts other than C_{60}. A natural choice to start with is C_{70} as it has a non-degenerate LUMO. A structural study[3] of C_{70} indicated a more complicated phase diagram than for C_{60}. There are three different phases based on cubic close packing associated with different degrees of freedom of the C_{70} molecules.

The purpose of this experiment was to examine the extent of anion orientational ordering and its variation with temperature in the novel fullerides Na_2CsC_{70} and Na_2C_{70}. High resolution powder diffraction measurements were performed on powder samples at temperatures between 295 K and 645 K on BM16 (λ=0.85075 Å).

Data collected at 295 K proved difficult to index due to severe peak overlap but it is clear the crystal structure is based on fcc packing of the C_{70} anions. If the anions are fully ordered the highest metric symmetry consistent with both the ABC stacking sequence and the D_{5h} symmetry of the molecule is monoclinic.

On heating the Na_2CsC_{70} sample a phase transition is observed to a cubic phase with a lattice parameter of 14.984(3) Å at 645 K which was confirmed by Lebail extraction in the space group Fm3m. We associate this

phase transition with the freeing up of molecular rotation modes such that the C_{70} tumbles isotropically. A Rieveld refinement[4] (Figure 1) on the data from the high temperature phase required the use of a molecular form factor appropriate for a plastic crystal in which the molecules are completely dynamically disordered. In C_{70} there are carbon atoms at five unique radii from the centre of the molecule giving a molecular form factor based on five concentric spherical shells of electron density (N_i is the number of carbon atoms at radius R_i):

$$f_{mol}(q) = f_c(q)\sum_{i=1}^{5} N_i \frac{\sin(qR_i)}{qR_i}$$

The refinement places the Na^+ cations on the tetrahedral sites and the Cs^+ cations on the octahedral sites of the cubic close packed structure. Collection of data after the sample had been cooled to room temperature indicated it remained cubic implying that considerable supercooling of the high temperature phase is possible.

Heating the Na_2C_{70} sample again induced a phase transition to a high temperature cubic phase. However on cooling the extensive hysteresis observed for the Na_2CsC_{70} sample was not observed; Instead the sample tranformed reversibly to the low temperature phase. The evolution with temperature of a selected range of the diffraction pattern is shown in Figure 2.

These experiments conclusively demonstrate the existence of A_3C_{70} structural analogues to the A_3C_{60} superconducting phases; the possibility of supercooling the high temperature cubic phase will allow detailed comparison with the electronic properties of the C_{60}^{3-} phases.

References

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4. Fullprof Version 3.5. Juan Rodriguez-Carvajal.

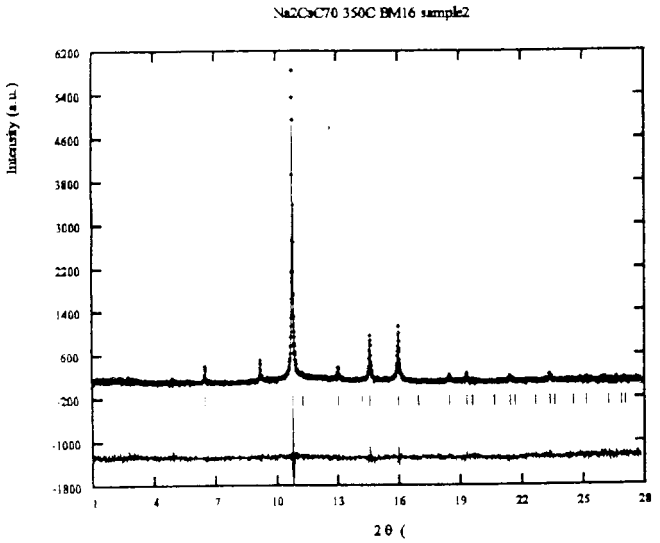

Figure 1. Rietveld refinement of data from Na_2CsC_{70} sample at 350 °C (BM16).

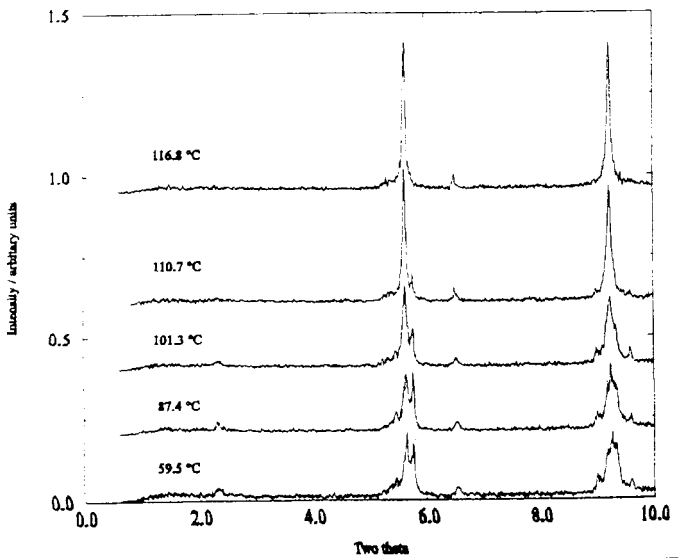

Figure 2. Evolution of the diffraction pattern of Na_2C_{70} with temperature (BM16).