



	Experiment title: Structural Studies of C ₆₀ and C ₇₀ -based Fullerides	Experiment number: CH-941
Beamline: BM16	Date of experiment: from: 6 December 2000 to: 11 December 2000	Date of report: 26/2/2001
Shifts: 15	Local contact(s): Dr. Andrew N. Fitch	<i>Received at ESRF:</i>
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Report:

Superconducting alkali fullerides with stoichiometry $A_2A'C_{60}$ ($A, A' = \text{Na, K, Rb, Cs}$) adopt cubic structures and their superconducting transition temperatures, T_c increase monotonically with increasing lattice constant up to a maximum of 33 K for $\text{Cs}_2\text{RbC}_{60}$. Co-intercalation of small molecules, like NH_3 , which coordinate with the alkali metals has allowed the synthesis of families of ammoniated alkali fullerides with composition $(\text{NH}_3)_x A_2 A' C_{60}$ which exhibit a variety of interesting structural and electronic properties. For this beamtime allocation, we focused on the family of salts, $(\text{NH}_3)_x \text{NaA}_2 \text{C}_{60}$ ($A = \text{K, Rb}$; $0.5 < x < 1$). The parent fullerides, $\text{NaA}_2 \text{C}_{60}$ are unstable but ammoniation stabilises a series of cubic superconductors with $T_c < 20$ K. However, the variation of T_c with interfullerene separation differs from that in all other fullerides with T_c decreasing with increased ammonia content, x and increased cubic lattice constant, a . This anomalous behaviour has been tentatively attributed to off-centring of the $\text{Na}^+ \text{-NH}_3$ units, which reside in the octahedral sites.

Data were collected at 10 K on two perdeuterated samples, $(\text{ND}_3)_x \text{NaRb}_2 \text{C}_{60}$ and $(\text{ND}_3)_x \text{NaKRbC}_{60}$ with $x \approx 1$. Combined refinements (Fig. 1) were performed together with powder neutron diffraction data obtained on D2b at the ILL (R_{wp} : 4.8% neutron, 5.0% X-rays, 4.9% total). Both samples are strictly cubic (space group $Fm\bar{3}m$). The $\text{Na}^+ \text{-ND}_3$ pairs are located in the octahedral interstices and their geometry and orientation were accurately determined (Fig. 2). Very importantly we find that the model described before in the

literature (H Shimoda *et al.*, *Phys. Rev. B* **1996**, 54, R15653), is totally inadequate to describe well the combined data. *The present results demonstrate how invaluable combined refinements of synchrotron X-ray and neutron diffraction data are in accurately determining the structures of these disordered ammoniated fulleride salts which contain both heavy and light elements.* We are currently investigating the implications of our structural findings in explaining the electronic and superconducting properties of these systems.

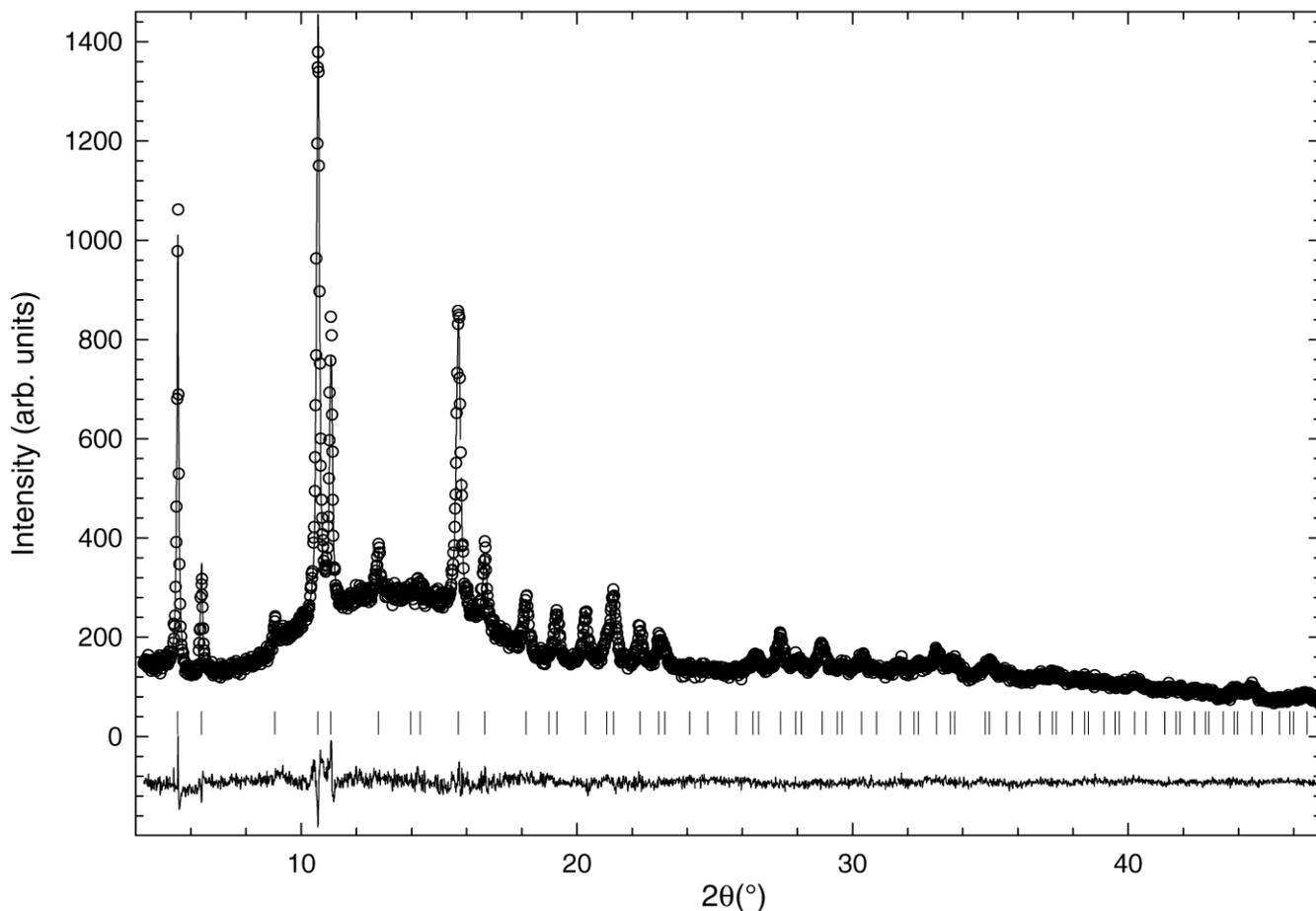


Fig. 1 Rietveld refinement of the synchrotron X-ray powder diffraction profile of $(\text{ND}_3)\text{NaKRbC}_{60}$ at 10 K ($\lambda = 0.80002 \text{ \AA}$) with the current model of Na^+ - ND_3 position and orientation in the octahedral interstices of the $Fm\bar{3}m$ structure.

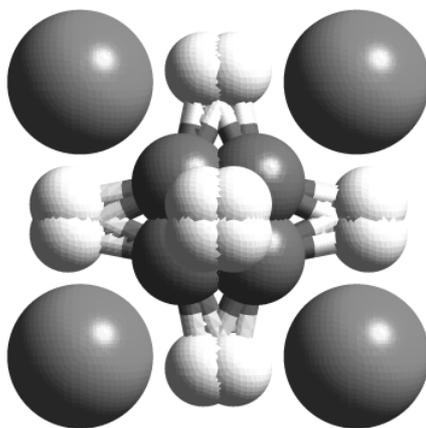


Fig. 2 Disordered geometry of the Na^+ - ND_3 pairs in the octahedral interstices. Each Na^+ ion (large sphere) and ND_3 molecule (small sphere) are disordered over the corners of cubes ($n = 1/8$).