ESRF	**Experiment title:** Structural studies of fullerenes and heterofullerenes at high pressures and low temperatures	**Experiment number:** HS 145
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Report:

The origin of the faster depression of T_c with decreasing interfullerene separation in $Na_2(A,A')C_{60}$ (A, A'= alkali metals) has attracted considerable interest for a number of years. Empirically it appeared that the primitive cubic (Pa3) structure adopted could sensitively affect the electronic properties by modulating the electron hopping between neighbours and leading to a faster depression of $N(\varepsilon_F)$, and hence of T,, with reduced interfullerene separation. However, of particular importance was the observation that upon the application of pressure, 1 the sample with stoichiometry Na_2RbC_{60} appeared to undergo a symmetry- lowering transition to a phase which was described as orthorhombic and resembled the structure of the RbC_{60} polymer. Following our recent experimental work[2] on the $Na_2(A,A')C_{60}$ structures at ambient pressures, we identified the formation of a polymeric phase at low temperature with monoclinic symmetry (space group $P2_1/a$), comprising of C_{60}^{3-} chains bridged by single C-C bonds. As part of our present beam allocation on ID30, we performed angle dispersive X-ray diffraction measurements at pressures up to 10 GPa on Na_2RbC_{60}. We indeed identify the formation of the monoclinic polymeric phase which forms at pressures higher than 2 kbar (Fig. 1). The ambient pressure cubic phase appears very resilient and a large fraction of it appears to survive to pressures as high as 50 kbar. Fig. 2 shows the

pressure dependence of the lattice constants of the monoclinic (space group $P2_1/a$) Na_2RbC_{60} phase.

References

[l] Q. Zhu et al., Phys. *Rev. B* 1995,51, *3966.*

[2] Prassides, K. et al., J. ***Am. Chem. Soc.*** 1997, 119, 834; Cristofolini, L. et al., ***Chem. Commun.*** 1997, 375; Bendele, G. M. et al., submitted.

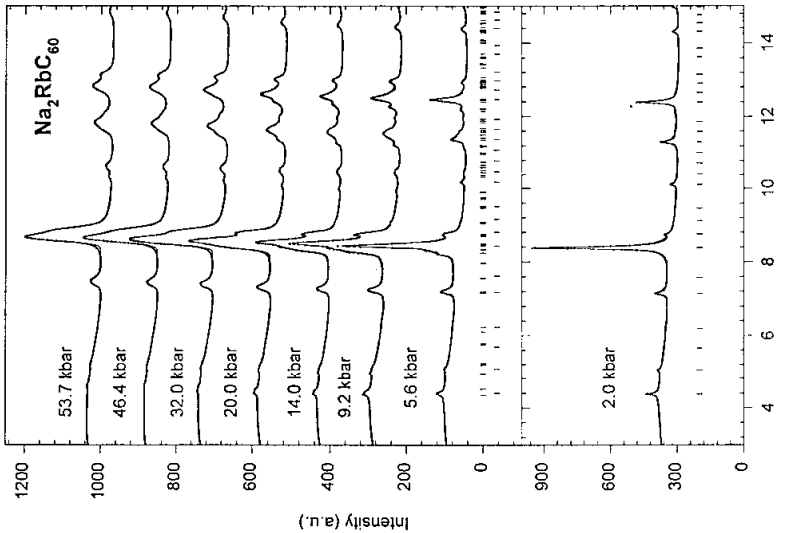

Fig. 1 Rietveld refinements of the high pressure synchrotron X-ray diffraction profiles of Na_2RbC_{60} (λ= 0.620 Å). The 2 kbar data show the presence of the Pa3 cubic phase, while at higher pressures a 2-phase refinement has been used, including a fraction of the monoclinic polymer phase that increases with increasing pressure.

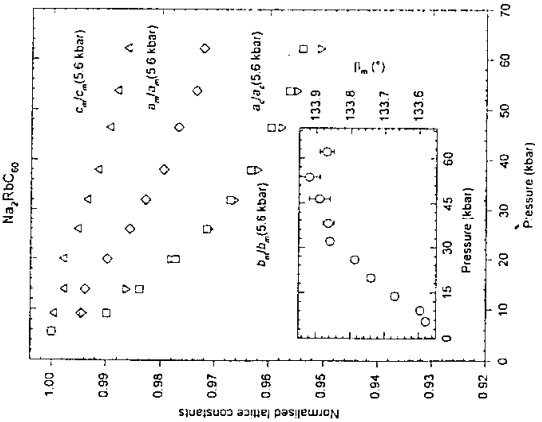

Fig. 2 Pressure dependence of the lattice constants of the monoclinic structure of Na_2RbC_{60}.