ESRF	**Experiment title:** The Solid Structures of HCFCs and HFCs	**Experiment number**: CH-736
Beamline: ID11 BM16	**Date of experiment**: from: 09.07.99 to: 15.07.99 from: 04.09.99 to: 09.09.99	**Date of report**: 29 February 2000
Shifts: 15 on ID11 (16 bunch) 12 on BM16	**Local contact(s)**: G. Vaughan A. N. Fitch	*Received at ESRF:*

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Report:

This experiment was a continuation of our attempts to solve the crystal structures of a number of condensed HCFCs and HFCs using powder X-ray diffraction. The gases are condensed *in situ* into 0.3 to 1.0 mm diameter evacuated silica-glass capillary tubes, cooled by a stream of cold nitrogen from a Cryostream cooler mounted coaxially with the sample.

Our initial measurements on BM16 suggested that these samples have granularity problems, giving diffraction patterns with peak intensities showing sharp variations. The irreproducibility and hence the unreliability of the observed intensities impeded the refinement and sometimes even the determination of the crystal structures using direct methods.

The idea was to use a 2-dimensional detector system to obtain a better powder average because individual frames containing a small part of the powder ring can be combined to recreate the rings. This leads to a higher proportion of the diffracted radiation being recorded with respect to BM16 data where only the vertical strip defined by the horizontal receiving slits is sampled.

Powder diffraction rings were recorded on ID11 using the 2-dimensional Smart CCD detector system. Preliminary analysis of the images collected, before full integration of the

powder rings, revealed the quite poor powder averages in some of the samples. The diffraction rings exhibited spots, which confirmed the strong granularity of the powders as suggested from our previous measurement on BM16.

We ran the following set of samples:

HCFC-142b ($CClF_2CH_3$) HFC-134a (CFH_2CF_3) HFC-152a (CF_2HCH_3)
HCFC-141b ($CFCl_2CH_3$) HCFC-123 (CF_3CCl_2H) HCFC-132b ($CClF_2CClH_2$)

For all of them the structure have been determined using direct methods and the results validate those obtained with BM16 data.

We assessed the granularity effects, then put more effort into improving the preparation of the samples to minimise this problem. Further measurements on BM16 gave better quality data and Rietveld refinements have been carried out.

On BM16 we ran the following set of samples:

HCFC-142b ($CClF_2CH_3$) HFC-134a (CFH_2CF_3) HFC-152a (CF_2HCH_3)
HCFC-141b ($CFCl_2CH_3$) HCFC-123 (CF_3CCl_2H)

Some of these compounds were found to undergo solid-state phase transitions at low temperatures, passing from a disordered plastic phase to an ordered phase at lower temperature. This has not previously been reported! By cycling the samples through the transition, powdered samples with less granularity could be produced, because the volume change associated with the transition breaks up the larger crystalites.

For HFC-134a and for HFC-152a phase transitions to a cubic phase were seen at around 112 K and at 108 K, respectively. For HCFC-142b and for HCFC-141b no intermediate solid-solid phase transition has been observed. HCFC-123 presents a complicate phase diagram with a suspected mixture of phases.

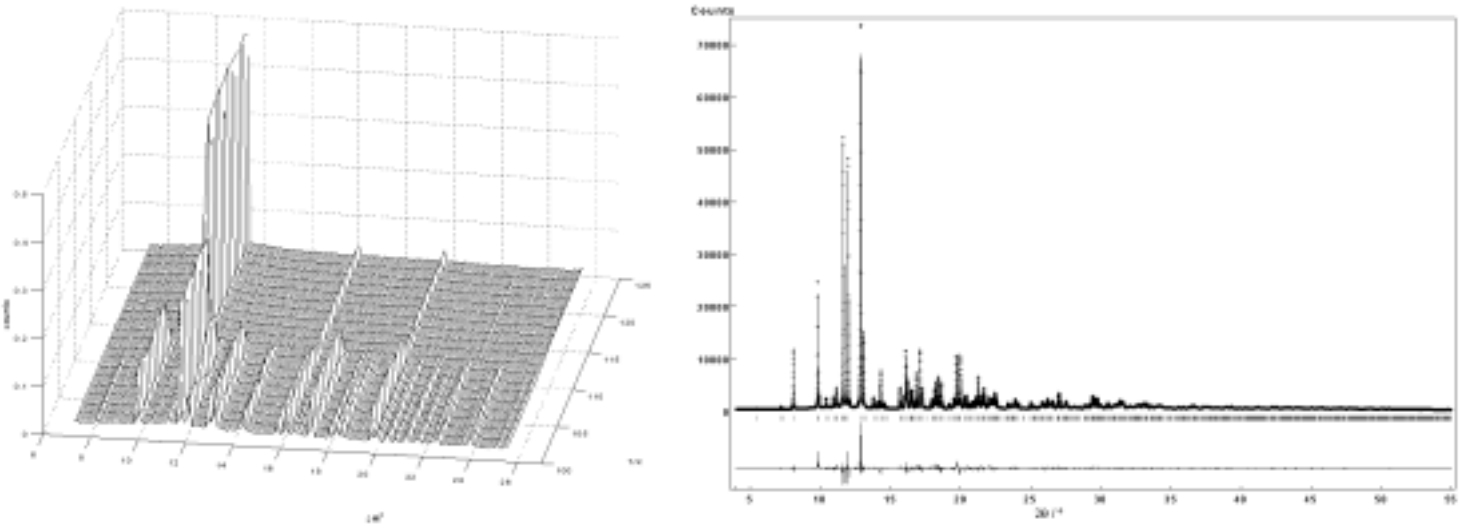

Fig. 1. (on the left) The temperature evolution of the diffraction pattern of HFC-134a shows the solid-solid phase transition at about 112 K on cooling.

Fig. 2. (on the right) Observed, calculated and difference plot of the Rietveld refinement of the low temperature monoclinic phase of HCFC-134a at 80 K. Final refinement converged to R_{wp} = 11.4%.