ESRF	**Experiment title:** The Solid Structures of HCFCs and HFCs	**Experiment number:** Ch503
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Report:

The aim of this experiment was to determine the crystal structures of a number of condensed HCFCs and HFCs by using high-resolution powder diffraction. The gases were condensed in situ into a 1.5 mm diameter evacuated thin-walled silica-glass capillary tube, cooled by a stream of cold nitrogen from a Cryostream cooler mounted coaxially with the sample. The gas line was disconnected, the sample was sealed mechanically, then spun about its axis as is standard for powder diffraction measurements. Our initial measurements indicated that the samples prepared by slow condensation in the capillary exhibited granularity problems, giving spotty diffraction patterns whose peak intensities showed sharp variations with the orientation of the sample. Considerable effort was put into improving the preparation of the samples to minimise this effect. Quite good powder specimens could be prepared by condensing the gas as a liquid in the capillary tube, which was then spun rapidly whilst liquid nitrogen was poured over the sample to cause abrupt crystallisation.

Good quality diffraction patterns were measured from 5 compounds (table 1), of which $CHClF_2$ has a known structure [1] and acted as a control to assess the performance of the sample preparation. Three of the unknown patterns have been indexed, and suggest that as many as 3 independent molecules may be present in the asymmetric units of these compounds. Attempts to solve the patterns by direct methods or by translating and rotating

the molecules around the unit cell by simulated annealing have not yet been successful. The quality of the diffraction patterns that can be measured from this type of compound is illustrated below in figure 1 for CF_2ClCH_3 (HCFC 142b). For CH_3CHF_2 (HFC152a) a previously unreported transition to a face-centred cubic phase was seen at around 108 K.

Table 1. Samples, temperature, indexed unit cells and probable space groups

Sample	T/K	a/Å	b/Å	c/Å	β/°	S/G
$CHClF_2$	80					
CF_2ClCH_3 HCFC 142b	90	7.552	8.747	6.148	90	$P2_12_12_1$
CH_3CHF_2 HFC 152a	100	8.669	7.688	7.944	113.57	*Pc* or *P2/c*
CH_2FCF_3 HFC 134a	100	9.119	9.359	8.805	106.57	$P2_1/a$
CF_3I (low-temp phase)	80	So far unindexed.				

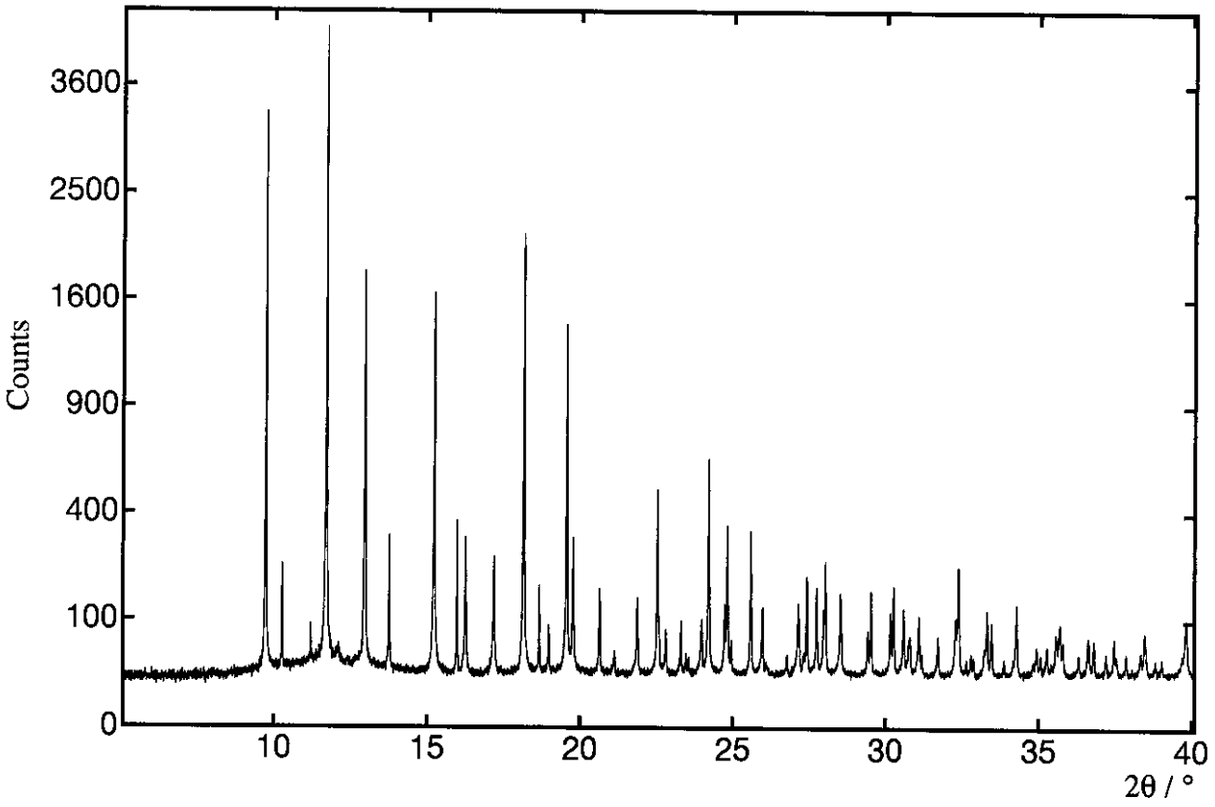

Fig 1. Powder diffraction pattern of solid CF_2ClCH_3 at 90 K. A square-root scale has been used for the intensities to show more clearly the higher-angle data.

The reason why the structures cannot be solved is perhaps linked to their complexity, or more likely with problems associated with persistent granularity in the samples. Oscillations in intensity are still seen on spinning. Work will continue to eradicate (or exploit) this effect as will attempts to solve the structures by direct methods or simulated annealing.

[1] O.S. Binbrek, B.H. Torrie, R. Von Dreele and B.M. Powell, Mol. Phys. 90, 49-54, (1997).