

A glass capillary cell for *in situ* powder X-ray diffraction of condensed volatile compounds. Solid HCFC-123a and HCFC-124

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A rotating glass capillary cell with a gas handling system has been built to allow *in situ* studies by powder X-ray diffraction. The cell can be used to condense volatile compounds, or to follow solid-state chemical reactions under vacuum or at gas pressures up to around 7×10^5 Pa. Using the cell, cooled by a stream of helium gas, the solid phases of 1,2-dichlorotrifluoroethane (HCFC-123a) and 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124) have been investigated using powder synchrotron X-ray radiation. These were found to have disordered hexagonal structures, with $a = 4.018$ (5), $c = 6.553$ (1) Å and $a = 4.048$ (1), $c = 6.625$ (1) Å, respectively, at 64 K.

Keywords: hydrochlorofluorocarbons; synchrotron X-ray powder diffraction; *in situ* capillary cell.

1. Introduction

To enable high-resolution powder diffraction measurements to be carried out on the solid phases of the new HCFC and HFC refrigerants, which are highly volatile molecular compounds, a simple glass capillary cell has been built, to allow the gases to be condensed *in situ* on the powder diffractometer BM16 at ESRF, Grenoble. The motivation for this work was to investigate the interactions between the refrigerant molecules which ultimately control the thermodynamic and heat-transfer properties of these compounds. While these have been widely investigated (Dowdell & Matthews, 1993; Vega *et al.*, 1989), crystallographic information on the solid phases is scarce or non-existent because of the difficulties of growing single crystals at very low temperatures. Modern powder diffraction techniques should allow the solid structures of these materials to be investigated.

The cell is shown in Fig. 1. It attaches to a standard goniometer head and the sample can be cooled or heated with a stream of gas. A quick-release self-sealing coupling connects the cell to a gas handling system. After disconnecting the gas line, the cell can be spun on the axis of the diffractometer to improve the sampling of crystallites, as is normal for high-quality powder diffraction studies. Alternatively, for experiments under vacuum or under gas pressure, the cell can be oscillated with the gas line in place. For example, the thermal decomposition of AgCO_3 under CO_2 pressures of 4.5×10^5 Pa was recently reported from measurements made in the cell at temperatures up to 476 K (Norby *et al.*, 2002). The cell has been taken to pressures of 7×10^5 Pa without problems.

2. Experimental and results

To study HCFCs or other volatile compounds, the cell is first evacuated using a diaphragm pump, then the gas is transferred from its cylinder through the gas line at a pressure of up to 2 atm, and condenses as liquid in the capillary cooled by a cold gas stream. Typically, a 1.5 mm-diameter silica-glass capillary is used. Once filled,

the cell is sealed by disconnecting the gas line, and the temperature is lowered to crystallize the solid.

HCFC-123a (1,2-dichlorotrifluoroethane, 98%) and HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane, 99%) were supplied by Fluorochem, Glossop, UK. Both compounds have melting points below the boiling point of liquid nitrogen, so the capillary was mounted vertically on the diffractometer and was cooled by a coaxial stream of helium gas from an Oxford Cryosystems Helix cooler. In other studies (Brunelli & Fitch, 2002), the capillary has been mounted horizontally and a stream of cold nitrogen gas used. The use of a cryogenic gas stream offers the advantages of being able to follow visually what is happening as the sample solidifies and leaving free access for fine-tuning the alignment of the capillary *etc.*

High-resolution synchrotron X-ray powder diffraction patterns of the two compounds were collected using a wavelength of 0.401340 (2) Å at various temperatures down to 60 K. The temperature was calibrated from the reported melting points of the compounds, 78 K and 74 K, respectively. For each compound only a single crystalline phase was seen. Their diffraction patterns (Fig. 2) reveal similar hexagonal cells with $a = 4.018$ (5), $c = 6.553$ (1) Å for HCFC-123a, and $a = 4.048$ (1), $c = 6.625$ (1) Å for HCFC-124, at 64 K. The variation of the lattice parameters with temperature are shown in Fig. 3, giving linear thermal expansion coefficients of $1.1 \times 10^{-3} \text{ K}^{-1}$ along **a** and $1.0 \times 10^{-3} \text{ K}^{-1}$ along **c** for HCFC-123a, and $0.9 \times 10^{-3} \text{ K}^{-1}$ along **a** and $0.8 \times 10^{-3} \text{ K}^{-1}$ along **c** for HCFC-124. Systematic absences $P - c$ suggest the space groups $P6_3/mmc$, $P6_3mc$, $P\bar{6}2c$, $P\bar{3}1c$ or $P31c$, which have between 24 and six general positions.

3. Discussion

The unit-cell volumes of the two compounds are small, 90.37 and 93.66 Å³, with the larger molecule (HCFC-123a) having the smaller cell. The density of the liquids at 60 K extrapolated from thermodynamic data at higher temperatures (Defibaugh & Moldover, 1997) would be around 1.9 g cm⁻³ for HCFC-123a and around 1.7 g cm⁻³ for HCFC-124, suggesting 0.6–0.7 molecules per cell. Whatever the exact number, given the very high symmetry, it is clear that there must be substantial disorder in the structures, furthermore indicated by a broadening of the diffraction profile: the peak widths are about twice those found, for example, in solid HFC-134a which is fully ordered (Brunelli & Fitch, 2002).

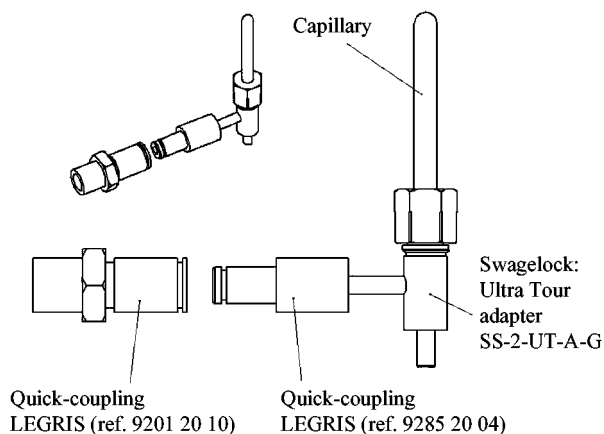


Figure 1

Schematic drawing of the glass capillary cell. The capillary is glued with quick-setting epoxy resin into a brass sample holder, which is sealed with a rubber O-ring in the modified Swagelok piece.

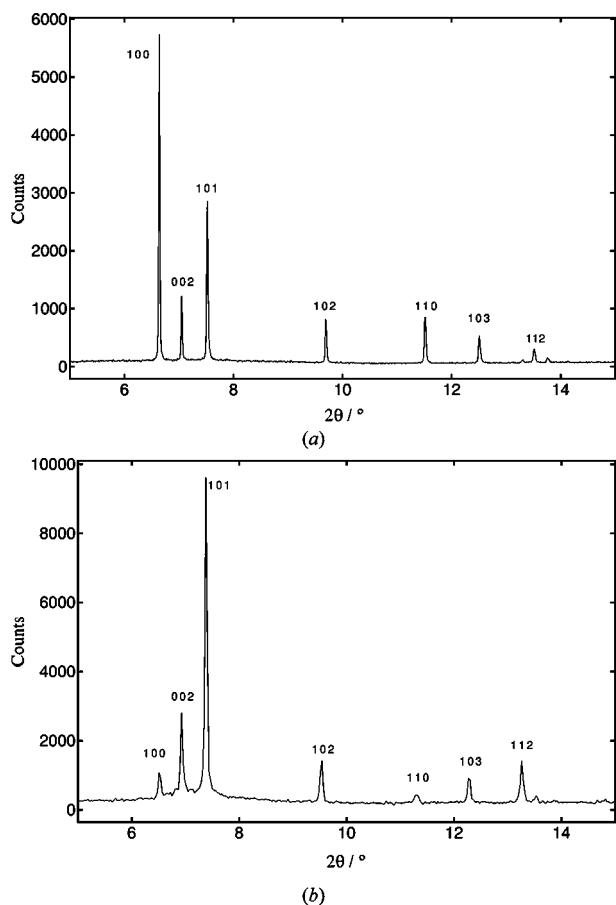


Figure 2
 Powder diffraction pattern of (a) 1,2-dichlorotrifluoroethane, HCFC-123a, collected at 60 K, corresponding to a hexagonal unit cell with $a = 3.998$ (1), $c = 6.5199$ Å, and (b) 2-chloro-1,1,1,2-tetrafluoroethane, HCFC-124, collected at 62 K, corresponding to a hexagonal unit cell with $a = 4.0436$ (1), $c = 6.6127$ (1) Å. The peak intensities for this compound were poorly reproducible showing marked fluctuations owing to granularity of the sample. Both data sets were collected on BM16 at the ESRF with a wavelength of 0.401340 (2) Å.

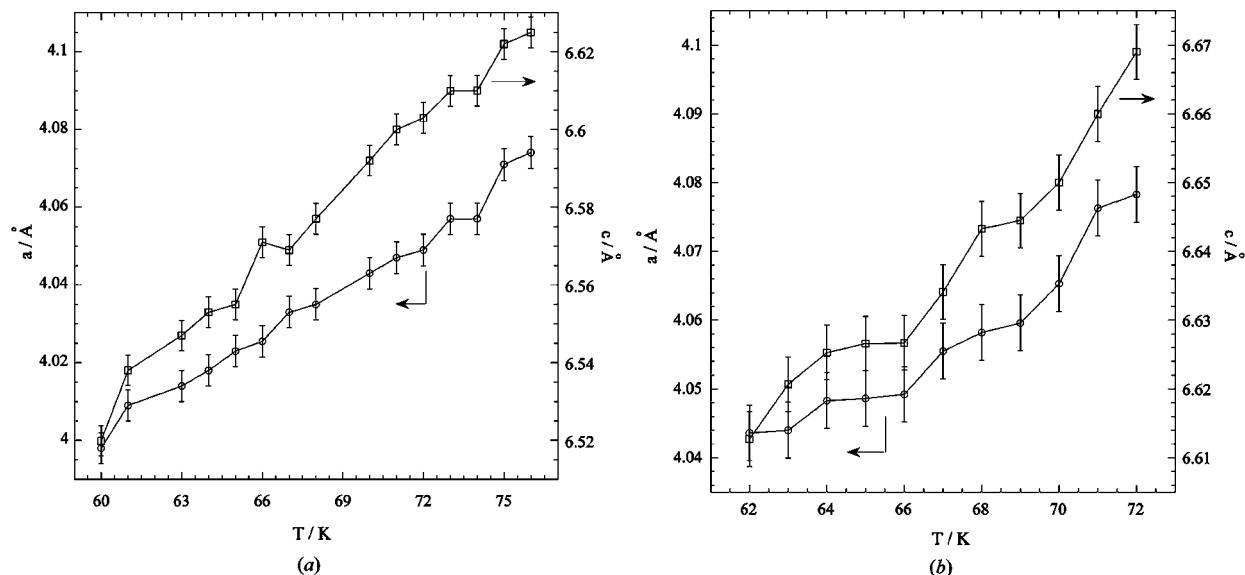


Figure 3
 Variation of the unit-cell parameters of (a) 1,2-dichlorotrifluoroethane, HCFC-123a, and (b) 2-chloro-1,1,1,2-tetrafluoroethane, HCFC-124, determined as a function of temperature on warming at 30 K h^{-1} for HCFC-123a, and on cooling at 30 K h^{-1} for HCFC-124.

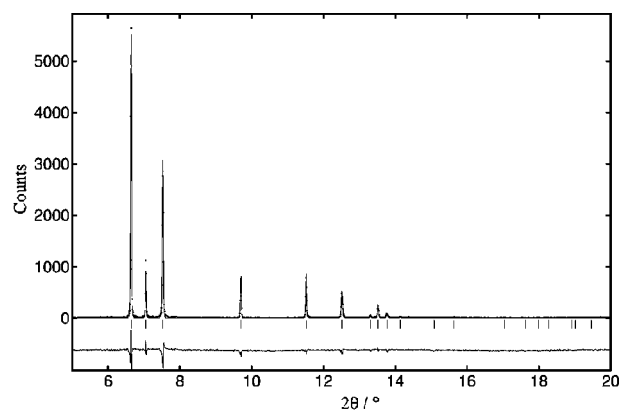


Figure 4
 Observed (dotted line) and calculated (solid line) diffraction patterns for the model of 1,2-dichlorotrifluoroethane, HCFC-123a, obtained from *Dash* in space group $P6_3/mmc$. Reflection positions are shown as vertical lines.

Just to enquire how much information such a simple pattern might contain, attempts were made to locate the whereabouts of the molecules in the unit cell of HCFC-123a using the simulated annealing computing program *Dash* (David *et al.*, 2001). This was attempted in each of the above-mentioned hexagonal or trigonal space groups (the possible lower-symmetry orthorhombic or monoclinic space groups were not investigated). A molecule of fixed conformation with a Cl—C—C—Cl torsion angle of 179° , indicating the minimum from *Gaussian94* (Frisch *et al.*, 1995) molecular orbital calculation, was used. The different space groups gave a similar general (x, y, z) position of the molecule and comparable values of the quality of the agreement between observed and calculated data, resulting in a χ^2 value of around 2.9 (Fig. 4). The minimum seems to be a real one, as moving the molecule leads to a marked decrease in the quality of the fit. Given the extensive disorder present, interpretation of the structure is difficult. Any single molecule has numerous overlaps with its symmetry-generated neighbours. The average structure has alternating C, F and Cl layers, with the C—C bond almost parallel to the ab plane. It may be that this approximates

to the real situation in the low-temperature phases of these compounds.†

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: KV2001). Services for accessing these data are described at the back of the journal. Alternatively, these data may be obtained from the Cambridge Crystallographic Data Centre (reference: CCDC 209201) via www.ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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