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The structure of solid dichlorodifluoromethane CF_2Cl_2 by powder neutron diffraction

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Abstract. The crystal structure of solid dichlorodifluoromethane has been solved from powder neutron diffraction data. A single solid phase exists between the melting point and 1.5 K. The structure is orthorhombic, *Fdd*2, $Z = 8$, with $a = 10.1676(3)$ Å, $b = 14.9638(4)$ Å, and $c = 5.1004(2)$ Å at 1.5 K. The molecules form columns with their dipole moments aligned ferroelectrically along the c direction.

Introduction

Dichlorodifluoromethane (CF_2Cl_2, Freon 12) has important uses as a refrigerant and spray-can propellant (Molina and Rowland, 1974). The molecule has been characterized by a number of techniques including electron diffraction (Livingstone and Lyon, 1956), microwave spectroscopy (Takeo and Matsumura, 1977; Su and Beeson, 1977; Davis, Gerry and Marsden, 1983; Booker and De Lucia, 1986), also infrared and laser spectroscopies (Morcillo, Zamorano and Heredia, 1966; Morillon-Chapey, Diallo and Deroche, 1981; Hyun, 1988; Jones and Morillon-Chapey, 1982;

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Nordstrom, Morillon-Chapey, Deroche and Jennings, 1979; Voitsekhovskaya, Kosichkin, Makushkin, Nadezhdinskii, Stepanov, Tishchenko, Trifonova and Cherepanov, 1987). The molecule has point symmetry C_{2v} with C – F and C – Cl distances of 1.347 Å and 1.744 Å, and F – C – F and Cl – C – Cl angles of 106.2° and 112.6°, respectively (Davis et al., 1983). The molecular dipole is reported in the range 0.51 to 0.55 D (Smyth and McAlpine, 1933; Fuoss, 1938; Epprecht, 1950). NMR studies have been conducted using ^{19}F (Jameson, Jameson and Oppusunggu, 1984), ^{13}C (Walker, Fox, De Marco and Moinz, 1979) and ^{35}Cl (Barlos, Kroner, Nöth and Wrackmeyer, 1978). Using molecular mechanics techniques Mountain and Morrison (1988) have developed site-site pair potentials for the liquid phase, which is stable between 115.37 K and 243.37 K at atmospheric pressure (L'Air Liquide, 1976). Below the melting point dielectric measurements have detected a single solid phase down to 77 K (Miller and Smyth, 1957). Powder neutron diffraction studies down to 1.5 K confirm the existence of a single solid phase. The structure has been solved ab-initio from the powder diffraction data.

Experimental

The experimental work was carried out using the neutron diffraction facilities of the Institut Laue Langevin, Grenoble, France. The sample of dichlorodifluoromethane, supplied by Fluorochem (Glossop, UK), was condensed in a 50-mm by 12/15-mm diameter silica-glass ampoule cooled by liquid nitrogen. The ampoule was sealed under vacuum and transferred to a standard I.L.L. orange cryostat precooled to 5 K mounted on the powder neutron diffractometer D1B. This instrument is equipped with a 400-wire multidetector covering an angular range of 80° in 2θ. Powder diffraction data were obtained whilst the temperature was raised from 1.5 K to 110 K at a rate of 0.8 K per minute. Diffraction patterns were measured from 5° to 85° 2θ at a wavelength of 2.52 Å and were stored every 160 s.

A high-resolution powder diffraction pattern was measured at 110 K on the powder diffractometer D2B in its high-flux mode at a wavelength of 1.595 Å. Data were collected in steps of 0.05° between 5° and 165° 2θ. The total data collection time was about 6 h. After solution and refinement of the structure it was evident that the sample had significant texture. A new sample was prepared by grinding solid CF_2Cl_2 in a pestle and mortar cooled in liquid nitrogen. The solid was very hard and only a coarse powder could be obtained. The sample was sealed in a standard 16-mm diameter vanadium sample can and diffraction patterns were measured on D2B at 1.5 K, 77 K and 110 K, using similar scan conditions to the earlier experiment.

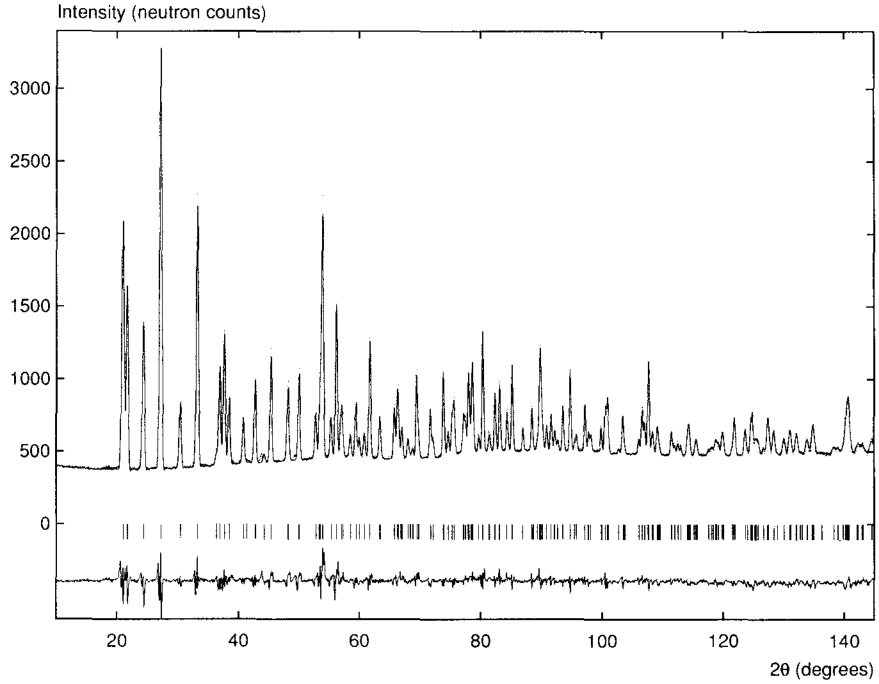

Fig. 1. Observed, calculated, and difference diffraction patterns for CF_2Cl_2 at 77 K with $\lambda = 1.595$ Å obtained on D2B at ILL, Grenoble. Vertical bars indicate calculated reflection positions.

Results

The D1B data revealed only one solid phase of CF_2Cl_2 between 1.5 K and 110 K. From the high-resolution diffraction pattern taken on D2B at 110 K, for the first (textured) sample in the silica-glass ampoule, the positions of twenty low-angle reflections were estimated and were input to the auto-indexing program FZON (Visser, 1969). The best solution with $M_{20} = 31$ was an A-face-centred triclinic cell. Cell reduction using the program TRACER (Lawton, 1967) yielded an F-centred orthorhombic cell whose refined parameters are $a = 10.2952(4)$ Å, $b = 15.2404(6)$ Å and $c = 5.1287(2)$ Å. The absence of the reflections 200 and 020 suggested the space group *Fdd*2 (No. 43). From the variation of the lattice parameters with temperature measured on D1B the thermal expansion coefficients were determined to be 0.00014(1), 0.00021(1) and 0.00008(1) along a, b and c, respectively, in the range 40 to 110 K.

The unit-cell volume indicates that there are eight molecules per unit cell. For an ordered structure there is only one position for the molecule in

Table 1. Final parameters for CF_2Cl_2 at 1.5 K, 77 K, and 110 K obtained from D2B data with $\lambda = 1.595$ Å. R factors are defined as follows: $R_{wp} = \{\Sigma w[y(\text{obs}) - y(\text{calc})]^2/\Sigma wy(\text{obs})^2\}^{1/2} \times 100\%$, $R_{exp} = \{(\text{N} - \text{P} + \text{C})/\Sigma wy(\text{obs})^2\}^{1/2} \times 100\%$, and $R_I = \{\Sigma|I(\text{obs}) - I(\text{calc})|/\Sigma I(\text{obs})\} \times 100\%$, where $w = 1/\sigma y(\text{obs})^2$ and y(obs) is the total profile intensity minus the estimated background intensity.

CF_2Cl_2 at 1.5 K Space group *Fdd*2 (No. 43) $Z = 8$

Cell constants a,b,c (Å): 10.1676(3), 14.9638(4), 5.1004(2)

Volume per molecule (Å^3): 97.00(1), calculated density (g/cm^3): 2.070

Peak-width parameters U,V,W ($^{\circ 2}$): 0.21(1), −0.27(1), 0.24(1)

Atom	Site symmetry	X	Y	Z	B (Å^2)	N
C	8*a* ..2	0	0	0	0.51(5)	8
F	16*b* 1	−0.0407(2)	−0.0665(2)	−0.1543(7)	0.93(5)	16
Cl	16*b* 1	−0.1326(1)	0.0372(1)	0.1947(6)	0.63(2)	16

R factors: $R_{wp} = 11.3\%$, $R_{exp} = 5.0\%$, $R_I = 6.1\%$

CF_2Cl_2 at 77 K

Cell constants a,b,c (Å): 10.2422(3), 15.1137(4), 5.1173(1)

Volume per molecule (Å^3): 99.02(1) calculated density (g/cm^3): 2.027

Peak-width parameters U,V,W ($^{\circ 2}$): 0.12(1), −0.26(1), 0.23(1)

Atom	Site symmetry	X	Y	Z	B (Å^2)	N
C	8*a* ..2	0	0	0	1.5[a]	8
F	16*b* 1	−0.0407(3)	−0.0658(2)	−0.1518(9)	3.0[a]	16
Cl	16*b* 1	−0.1307(2)	0.0372(1)	0.1932(7)	2.0[a]	16

Atom	$B[1,1]$	$B[2,2]$	$B[3,3]$	$B[1,2]$	$B[2,3]$	$B[3,1]$ (Å^2)
C	1.5(1)	1.7(1)	1.3(1)	0.3(1)	0	0
F	2.9(1)	3.0(1)	3.1(1)	0.1(1)	−2.0(1)	−0.3(1)
Cl	1.38(5)	2.35(7)	2.19(7)	0.33(7)	−0.44(6)	0.40(7)

R factors: $R_{wp} = 9.6\%$, $R_{exp} = 3.6\%$, $R_I = 4.7\%$

CF_2Cl_2 at 110 K

Cell constants a,b,c (Å): 10.2952(4), 15.2404(6), 5.1287(2)

Volume per molecule (Å^3): 100.59(1) calculated density (g/cm^3): 1.996

Peak-width parameters U,V,W ($^{\circ 2}$): 0.15(1), −0.31(1), 0.24(1)

Atom	Site symmetry	X	Y	Z	B (Å^2)	N
C	8*a* ..2	0	0	0	2.1[a]	8
F	16*b* 1	−0.0402(3)	−0.0653(2)	−0.1497(10)	4.4[a]	16
Cl	16*b* 1	−0.1290(2)	0.0369(1)	0.1920(8)	2.9[a]	16

Atom	$B[1,1]$	$B[2,2]$	$B[3,3]$	$B[1,2]$	$B[2,3]$	$B[3,1]$ (Å^2)
C	2.1(2)	2.6(2)	1.6(1)	0.4(1)	0	0
F	4.2(2)	4.6(2)	4.2(2)	−0.0(1)	−2.5(1)	−0.5(1)
Cl	2.1(1)	3.3(1)	3.2(1)	0.5(1)	−0.4(1)	0.4(1)

R factors: $R_{wp} = 9.7\%$, $R_{exp} = 3.8\%$, $R_I = 5.4\%$

[a] Equivalent isotropic B values calculated from refined anisotropic B values.

The Bij's are expressed for $\exp - \frac{1}{4}\{B_{11}h^2a^{*2} + \ldots + 2B_{31}lhc^*a^*\}$.

Table 2. Bond lengths (Å), angles (°), and interatomic distances (Å) for CF_2Cl_2. Values in square brackets are the distances corrected for librational motion of the molecule.

	1.5 K	77 K	110 K
Intramolecular			
2 × C – F	1.334(3)	1.329(4) [1.345]	1.323(4) [1.345]
2 × C – Cl	1.765(2)	1.756(2) [1.770]	1.746(3) [1.765]
1 × F – F	2.155(3)	2.157(4)	2.156(5)
1 × F – Cl	2.543(4)	2.527(5)	2.509(5)
1 × F – Cl	2.538(4)	2.528(5)	2.516(6)
1 × Cl – Cl	2.917(2)	2.904(2)	2.884(3)
1 × F – C – F	107.7(2)	108.5(2)	109.1(3)
2 × F – C – Cl	109.3(1)	109.2(1)	109.4(1)
2 × F – C – Cl	109.5(1)	109.2(1)	108.8(2)
1 × Cl – C – Cl	111.5(1)	111.5(1)	111.3(2)
Intermolecular contacts			
1 × F – Cl	3.097(4)	3.143(5)	3.186(5)
2 × Cl – Cl	3.666(3)	3.713(4)	3.748(5)
2 × Cl – Cl	3.873(2)	3.903(3)	3.935(3)
2 × Cl – Cl	3.955(2)	3.991(3)	4.021(3)

space group *Fdd*2, situated at 8*a* (0,0,*z*) with site symmetry ..2 (C_2). A carbon atom was fixed at the origin of the unit cell, with fluorine and chlorine atoms on general positions 16*b* (*x*,*y*,*z*). Chemical restraints were employed (Cockcroft, 1990) to define a molecule with tetrahedral geometry and an arbitrary orientation about the twofold axis along *c*. Refinement of this model by the Rietveld (1969) method resulted in rapid convergence to a false minimum. A closer study of the model showed that 4 unique starting configurations are possible. Examination of the C – F and C – Cl distances showed that interchange of the F and Cl positions was necessary.

The final parameters at 1.5 K, 77 K and 110 K were obtained from data collected from the second sample ground at liquid-nitrogen temperature. The scale factor, lattice parameters and 2θ zero-point correction, three half-width parameters and an asymmetry parameter were refined. Six atomic positional parameters were varied for Cl and F along with a total of fifteen anisotropic temperature factors for all atoms. At 1.5 K a small quantity of solid nitrogen was apparent in the sample. This was taken into account by including a contribution to the profile from cubic nitrogen (space group *Pa*3, $a = 5.6582(4)$ Å, Botz, Boyd, Mauer and Peiser, 1959) using the multi-pattern refinement program MPROF (Thomas and Bendall, 1978; Fitch, Wright and Fender, 1982; Murray and Fitch, 1989). Only isotropic temperature factors were refined at 1.5 K. A Gaussian peak-shape function

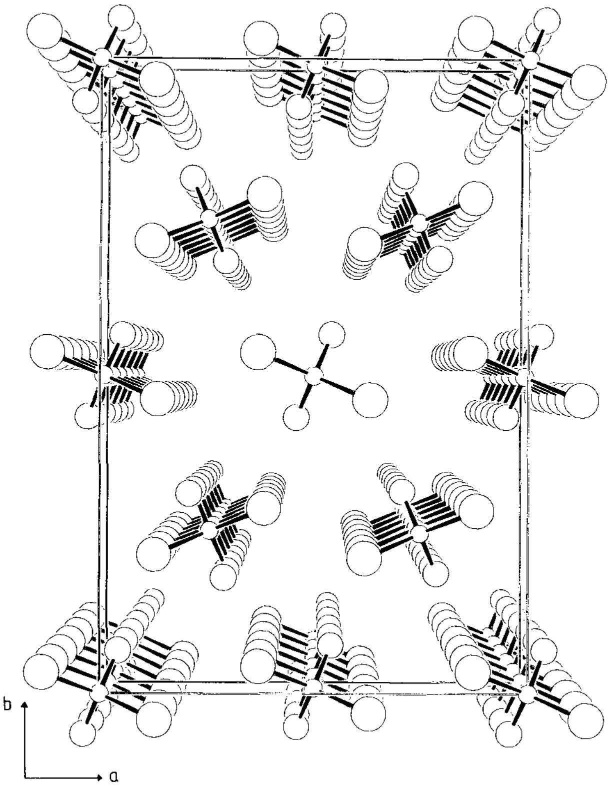

Fig. 2. SCHAKAL plot (Keller, 1989) of the structure of CF_2Cl_2 viewed down the *c* axis.

was used throughout and all chemical restraint functions were removed. Scattering lengths ($b_C = 6.6484$ fm, $b_F = 5.654$ fm and $b_{Cl} = 9.5792$ fm) were taken from Koester and Rauch (1983). Data up to 145° 2θ comprising 198 reflections were included in the refinements. The final parameters and *R* factors are given in Table 1, bond lengths and angles in Table 2, and the observed, calculated and difference profiles for CF_2Cl_2 at 77 K are plotted in Figure 1.

Conclusions

In the solid state the molecular point symmetry is reduced from C_{2v} to C_2, but with only a slight distortion of the molecule. A view of the structure down [001] (Fig. 2) shows the molecules stacked one above the other with

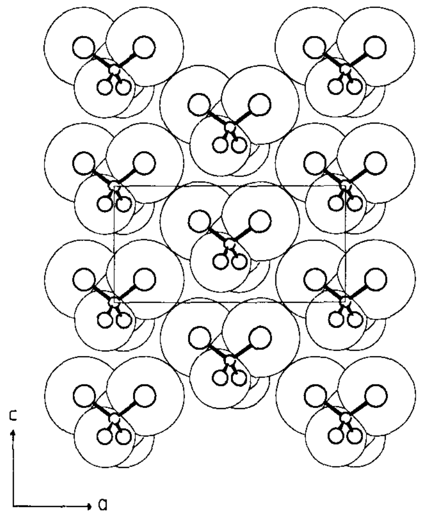

Fig. 3. A space filling figure of the structure of CF_2Cl_2 viewed down the *b* axis showing the intermolecular Cl—Cl contacts between columns.

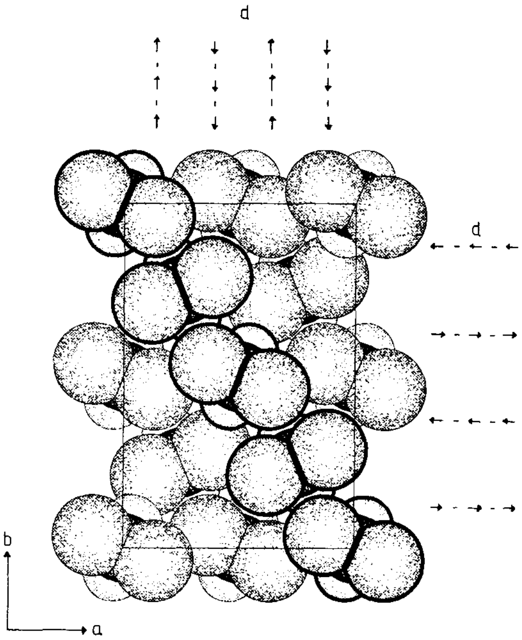

Fig. 4. A space filling figure of the structure of CF_2Cl_2 viewed down the *c* axis, showing the close contacts between the Cl atoms of molecules related by the *d*-glide planes (heavy outlines), and also the contact between molecules in adjacent columns whose carbon atoms are related by (1/4,1/4,−3/4) (or equivalent). This can most easily be seen for the molecule in the centre of the *C* face.

the dipoles aligned ferroelectrically to form columns along the twofold axis in the *c* direction. The distances between a Cl atom of one molecule and the two F atoms of the molecule are 3.782(4) Å and 3.785(4) Å which are longer than the sum of the van-der-Waals radii (F 1.35 Å, Cl 1.80 Å, Pauling, 1970). There is therefore no direct contact between molecules aligned in the columns, Figure 3. The intermolecular distances are determined by the packing of adjacent columns in the *ab* plane via intermolecular Cl – Cl and Cl – F contacts.

Along *a* the columns lie side by side with neighbouring molecules displaced by (1/2,0,1/2) with a C – C separation of 5.6876(2) Å, Figure 3. This arrangement leads to close packing of the Cl atoms in adjacent columns with an intermolecular Cl – Cl distance of 3.666(3) Å, which is close to the sum of the van-der-Waals radii.

The shortest intermolecular C – C distance (4.6991(1) Å) occurs for molecules related by the *d*-glide planes as illustrated in Figure 4. The Cl – Cl distances are slightly longer here at 3.873(2) Å and 3.955(2) Å. In addition, there is contact between F and Cl atoms of molecules whose carbon atoms are related by (1/4,1/4, – 3/4) (or equivalent). This contact of 3.097(4) Å also helps define the separation between molecules in the individual columns and can clearly be seen in Figure 4.

The solid structure of CF_2Cl_2 shows certain similarities to that of phase II of CH_2I_2 (Prystupa, Torrie, Powell and Gerlach, 1989) in that in both structures the molecules align ferroelectrically in columns along the twofold axis of an orthorhombic cell. However in the latter the molecules retain their full molecular point symmetry (C_{2v}) and are situated on the mirror planes in space group *Fmm*2, whereas in CF_2Cl_2 rotation of the columns about the twofold axis (Fig. 4) leads to a reduction in the molecular symmetry to C_2. The packing of the columns in the *ac* plane in CF_2Cl_2 (Fig. 3) is essentially the same as in the *bc* plane in CH_2I_2 and is determined by contacts between the chlorine or iodine atoms. Owing to the need to accomodate the larger fluorine atoms in CF_2Cl_2 compared with the hydrogen atoms in CH_2I_2, the arrangement of columns is different in the two compounds along the C – F and C – H directions, respectively.

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