Refinement of the structures of SrFCl and BaFCl. By M. Sauvage,* *Laboratoire de Cristallographie aux Rayons X, Université de Genève, 32 Bd d'Yvoy, CH-1211 Genève, Switzerland*

SrFCl and BaFCl belong to the tetragonal PbFCl structure type, space group $P4/nmm$; $a=4\cdot1259$ (8), $c=6\cdot9579$ (13) Å, for SrFCl; $a=4\cdot3939$ (6), $c=7\cdot2248$ (9) Å, for BaFCl. $Z=2$. The single crystals were grown by the Bridgman technique. Least-squares refinement based on 384 and 638 independent reflexions led to R values of 0·052 and 0·048 for SrFCl and BaFCl respectively.

Introduction

SrFCl and BaFCl are used as host crystals for e.p.r. measurements on defect centres (de Siebenthal, Bill & Lacroix, 1974; Bill, Moret & Lacroix, 1969; Cevey & Lacroix, 1970). The PbFCl structure type, a ternary ordered derivative of the Cu_2Sb (C38) structure type, was known from powder diffraction data (Frevel, Rinn & Anderson, 1946). Accurate cell parameters of SrFCl have been measured by Brixner & Bierlein (1974) and a preliminary determination of atomic parameters of BaFCl has been performed from $h0l$ Weissenberg photographs to give an R of 17·8% (Nicklaus & Fischer, 1972).

It was thus thought useful to obtain a better estimation of bond distances and angles to compare with the e.p.r. data.

Experimental

SrFCl

A single crystal ($96 \times 32 \times 8$ μm) was selected for the intensity measurements on a PW 1100 automatic diffractometer. 568 independent reflexions were recorded of which 384 had $I > 2\sigma(I)$ and were used in the refinement.

Data reduction and least-squares refinement were performed with the X-RAY system (1972) in which an absorption correction (De Meulenaer & Tompa, 1965) has been introduced. As the absorption coefficient is rather high ($\mu = 243\cdot5$ cm^{-1}) and the shape of the crystal easy to determine and very far from spherical, this method is the most

* Present address: Laboratoire de Mineralogie-Cristallographie associé au CNRS, 4 Place Jussieu, F-75230 Paris Cedex 05, France.

suitable. Anisotropic temperature factors have been used for all three atoms [exponential argument: $-2\pi^2(a^{*2}U_{11}(h^2+k^2)+c^{*2}U_{33}l^2)$] and data have been corrected for isotropic secondary extinction. Hartree–Fock scattering factors were used for F$^-$, Cl$^-$, Sr^{2+} (Cromer & Mann, 1968). Anomalous dispersion corrections f' and f'' were taken from *International Tables for X-ray Crystallography* (1968).

The final atomic parameters ($R=0\cdot052$) are listed in Table 1.

BaFCl

The same procedure was followed with a BaFCl single crystal ($130 \times 96 \times 50$ μm), absorption coefficient 153·7 cm^{-1}. 667 independent reflexions were collected, 638 of which had $I > 2\sigma(I)$ and were used in the refinement.†

The final atomic parameters are listed in Table 2 ($R=0\cdot048$). The values are compatible with the previous determination of Nicklaus & Fischer (1972).

The shortest interatomic distances are listed in Tables 3 and 4.

Discussion

This structure type is usually described as a stacking along the [001] direction of the following sequence of layers: F, Sr (Ba), Cl, Cl, Sr (Ba), F..., the weaker bonding between the two adjacent Cl layers being responsible for the easy cleavage parallel to the (001) plane (Fig. 1). The c/a ratios

† The tables of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30537 (8 pp.) Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic positional and thermal parameters in* SrFCl

Second setting of space group $P4/nmm$ with symmetry centre at origin.

Atom	Position	x	y	z	U_{11}(Å$^2 \times 10^2$)	U_{33}(Å$^2 \times 10^2$)
Sr	2(c)	0·25	0·25	0·2015 (2)	0·85 (4)	0·98 (6)
F	2(a)	0·75	0·25	0	0·86 (22)	1·08 (36)
Cl	2(c)	0·25	0·25	0·6429 (5)	1·20 (11)	0·39 (13)

Table 2. *Atomic positional and thermal parameters for* BaFCl

Second setting of space group $P4/nmm$ with symmetry centre at origin.

Atom	Position	x	y	z	U_{11}(Å$^2 \times 10^2$)	U_{33}(Å$^2 \times 10^2$)
Ba	2(c)	0·25	0·25	0·2049 (1)	1·05 (5)	1·11 (4)
F	2(a)	0·75	0·25	0	1·52 (64)	1·35 (42)
Cl	2(c)	0·25	0·25	0·6472 (7)	1·67 (25)	1·45 (18)

Table 3. *Interatomic distances in* SrFCl

		Number of equivalent distances
F—Sr	2·4944 (10) Å	4
F—F	2·9175 (4)	4
F—Cl	3·2291 (25)	4
Sr—Cl	3·0715 (37)	1
Sr—Cl	3·1117 (13)	4
Cl—Cl	3·5312 (26)	4

Table 4. *Interatomic distances in* BaFCl

		Number of equivalent distances
F—Ba	2·6491 (7) Å	4
F—F	3·1070 (3)	4
F—Cl	3·3649 (41)	4
Ba—Cl	3·1959 (55)	1
Ba—Cl	3·2856 (18)	4
Cl—Cl	3·7655 (43)	4

for SrFCl (1·68) and BaFCl (1·64) are in agreement with the predictions of Johnson & Jeitschko (1973) for PbFCl-type compounds with no intralayer bonding.

E.p.r. measurements of Mn^{2+} substituting Sr^{2+} in SrFCl (Cevey & Lacroix, 1970) have shown a superhyperfine structure due to an interaction with the four F neighbours at 2·49 Å whilst no influence of the almost equivalent five Cl neighbours (3·07 and 3·11 Å) has been detected.

Another e.p.r. experiment on a V_k centre, Cl_2^-, (Bill, Moret & Lacroix, 1969) led to a value of $52·5° \pm 1°$ for the angle between the $(Cl-Cl)^-$ bond and the c axis; the present determination gives 55·71 (6)° for the same angle, the ions being in a non-excited state. This discrepancy might be due to a bond distortion due to the perturbation of the charge distribution (Bill, 1974).

Fig. 1. Unit cell of SrFCl.

References

BILL, H. (1974). Private communication.

BILL, H., MORET, J. M. & LACROIX, R. (1969). *Colloque Ampère* XV, pp. 323–325. Amsterdam: North Holland.
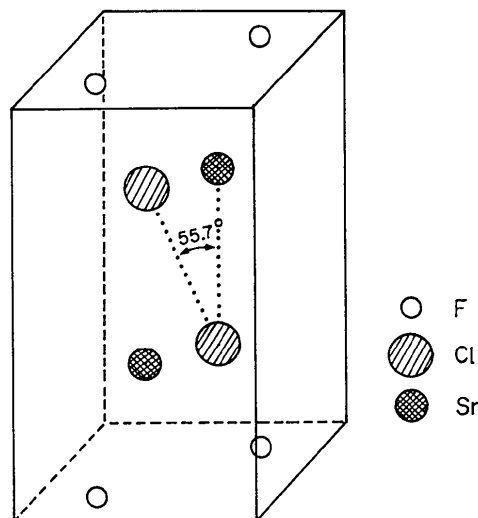
BRIXNER, L. H. & BIERLEIN, J. D. (1974). *Mat. Res. Bull.* **9**, 99–104.

CEVEY, D. & LACROIX, R. (1970). *Helv. Phys. Acta*, **43**, 304–306.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324

DE MEULENAER, J. & TOMPA, M. (1965). *Acta Cryst.* **19**, 1014–1018.

FREVEL, L. K., RINN, H. W. & ANDERSON, H. C. (1946). *Ind. Eng. Chem.* **18**, 83–93.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

JOHNSON, V. & JEITSCHKO, W. (1973). *J. Solid State Chem.* **6**, 306–309.

NICKLAUS, E. & FISCHER, F. (1972). *J. Cryst. Growth*, **12**, 337–338.

SIEBENTHAL, J. M. DE, BILL, H. & LACROIX, R. (1974). *Solid State Commun.* **14**, 167–168.

X-RAY system (1972). Technical report TR 192 of the Computer Science Center, Univ. of Maryland, U.S.A., June 1972.