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THE CRYSTAL STRUCTURE OF SODIUM FLUOSILICATE

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THE CRYSTAL STRUCTURE OF SODIUM FLUOSILICATE

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The Crystal Structure of Sodium Fluosilicate*

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A study by x-ray diffraction showed that Na_2SiF_6 is hexagonal (trigonal) with $\underline{a}$ = 8.859, $\underline{c}$ = 5.038 Å (each ± 0.002 Å), $\underline{Z}$ = 3, $\underline{d_x}$ = 2.74 g cm^{-3}. The space group is $\underline{P}321$. The SiF_6 groups are almost regular octahedral with Si-F = 1.695 Å (corrected for thermal motion). Each sodium has 6 fluorine neighbors at the corners of a considerably distorted octahedron. Twinning which superimposes $\underline{hk\ell}$ and $\underline{kh\ell}$ is common. The structure was determined with data from a twinned specimen which contained unequal amounts of the two orientations.

Introduction

Sodium fluosilicate came to our attention as the result of hydrolysis of a sample of XeF_4 in a Pyrex vessel. The hexagonal crystals were found with

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orthorhombic crystals of $NaBF_4$ as a residue after evaporation of the solution. In seeking the identity of these crystals we discovered contradictions in the literature concerning sodium fluosilicate which lead us to undertake the determination of the structure. In this paper we report the result of a three-dimensional x-ray diffraction study of a twinned specimen of Na_2SiF_6.

According to x-ray powder diffraction data, sodium fluosilicate has the same crystal structure as Na_2GeF_6 (Cox, 1954; Cipriani, 1955), Na_2TiF_6, Na_2MnF_6, Na_2PtF_6, Li_2SiF_6 (Cox, 1954), Na_2PdF_6, Na_2RhF_6 (Cox et al., 1956), and Na_2IrF_6 (Hepworth et al., 1958). A determination of this structure was reported by Cipriani (1955), but we believe it to be in error because of incorrect choice of symmetry.

Crystals of Na_2SiF_6, found as crusts on lava at Vesuvius, are known as the mineral malladrite (Palache et al., 1951).

Experimental

Crystals of Na_2SiF_6 were prepared by dissolving $(NH_4)_2SiF_6$ in water, adding NaOH solution, and heating briefly. On cooling, numerous well-formed small crystals of sodium fluosilicate were obtained.

X-ray photographs using the Weissenberg technique and copper radiation yielded preliminary data. A "single crystal" (later found to be twinned) with the shape of a hexagonal prism and of approximate dimensions 0.08 x 0.08 x 0.08 mm was used for collecting the intensity data. The cell dimensions and intensities were measured with a General Electric XRD-5 goniostat equipped with a scintillation counter, using Mo $K\alpha$ radiation (λ = 0.70926 Å for Mo $K\alpha_1$).

The 270 independent reflections permitted by the space group in the sphere of reflection with $\sin\theta/\lambda$ less than 0.596 ($2\theta < 50^\circ$) were measured with counting times of 20 sec each. Of these, only 2 were recorded as zero intensity. No corrections were made for either absorption or extinction. We estimate the

linear absorption coefficient to be $\mu = 8.2$ cm^{-1} for molybdenum radiation. For the crystal used, μR is less than 0.03, and the absorption correction is unimportant. A correction for twinning is described later.

Calculations were made using an IBM-7090 computer using our version of the Gantzel-Sparks-Trueblood full-matrix least squares program which minimizes $\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2$. Atomic scattering factors were taken as the values given by Ibers (1962) for Na^{+1} and neutral Si and F. Dispersion is unimportant for these atoms with molybdenum radiation and was neglected.

After twinning was detected, another crystal was investigated in hope of finding less twinning. In fact, it contained the two orientations in more nearly equal amount than did the first specimen.

Results

Unit cell and space group

The primitive cell contains three formula units Na_2SiF_6 and is trigonal with dimensions:

$$\underline{a} = 8.859 \pm 0.002 \text{ Å}, \ \underline{c} = 5.038 \pm 0.002 \text{ Å}.$$

The density is calculated as 2.74 g cm^{-3}, compared with 2.755 measured by Stolba (1872). Axial dimensions and ratios are compared with other work in Table 1.

An initial inspection of the film data gave the impression that a 6-fold symmetry axis was present. The superior precision of the counter measurements showed on the contrary that the crystal had Laue symmetry $\bar{3}\underline{m}$, in agreement with Cipriani (1955). The mirror symmetry of this Laue group is oriented with a plane perpendicular to the primitive $\underline{a}$ axis, as indicated by the full symbol $\bar{3}\underline{m}1$ rather than $\bar{3}1m$. With no reflections systematically absent, we have a choice of the three space groups $\underline{P}321$,

P3m1, and P$\bar{3}$m1. The space groups P312, P31m, and P$\bar{3}$1m are excluded by the orientation of the symmetry elements. Our final structure has the symmetry of space group P321.

Determination of the structure

We noted immediately that the cell could be filled with close-packed fluorine atoms arranged in octahedral (SiF_6) groups. One such group was placed with Si at the origin and the other two with Si at ±(1/3, 2/3, 1/2). The three space groups give diverse possibilities for the sodium positions.

We started refinement by least squares with the assumption (in this case ill-advised) of a center of symmetry, with the following atomic positions:

First (incorrect) trial structure in space group P$\bar{3}$m1

Si(1) in 1(a): 0, 0, 0.

Si(2) in 2(d): ±(1/3, 2/3, z); z = 0.51.

Na in 6(g): ±(x, 0, 0; 0, x, 0; $\bar{x}$, $\bar{x}$, 0); x = 0.34

F(1) in 6(i): ±(x, $\bar{x}$, z; x, 2x, z; 2$\bar{x}$, $\bar{x}$, z); x = 0.091, z = 0.805.

F(2) in 6(i): x = 0.424, z = 0.705.

F(3) in 6(i): x = 0.242, z = 0.315.

This arrangement placed the sodium atoms in octahedral holes and all at the same level, z = 0. Four cycles of refinement using all the data, each reflection with unit weight, and with an isotropic temperature factor $\exp(-B\lambda^{-2}\sin^2\theta)$ for each atom produced a conventional unreliability factor $R = \sum||F_o|-|F_c||/\sum|F_o| = 0.44$. Various combinations of sign changes for z parameters of the fluorine atoms and of moving the sodium atoms to z = 0.5 only reduced R to 0.35. At this stage the thermal parameter for sodium was larger than any other atom.

The above trial structure is nearly the same as the structure reported by Cipriani (1955) which came to our attention after our work was completed.

Cipriani reported $\underline{R}$ = 0.41 for Na_2SiF_6 and $\underline{R}$ = 0.31 for Na_2GeF_6 (in which incorrect sodium positions have less effect).

Because of our lack of success, we went to the non-centric group $\underline{P}321$. In this space group the sodium atoms are in two independent 3-fold sets, and each fluorine octahedron is free to rotate about its 3-fold axis. Continued refinement of the structure with this greater freedom reduced $\underline{R}$ to 0.28, and the thermal parameter of one sodium atom became very large. This result suggested that the offending sodium atom should be moved to $\underline{z}$ = 0.5, which is permitted in this space group. This change produced dramatic improvement with much better thermal parameters and $\underline{R}$ = 0.16.

At this point we realized that we had considered only one of the two independent ways that the structure can be oriented with respect to the coordinate system of the data. Rotation of the structure by 60° about the $\underline{c}$ axis gives the second structure. With this change the atoms were distributed in the final sets of positions:

Space group $\underline{P}321$

Si(1) in 1($\underline{a}$): 0, 0, 0.

Si(2) in 2($\underline{d}$): 1/3, 2/3, $\underline{z}$; 2/3, 1/3, $\bar{\underline{z}}$.

Na(1) in 3($\underline{e}$): $\underline{x}$, $\underline{x}$, 0; $\bar{\underline{x}}$, 0, 0; 0, $\bar{\underline{x}}$, 0.

Na(2) in 3($\underline{f}$): $\underline{x}$, $\underline{x}$, 1/2; $\bar{\underline{x}}$, 0, 1/2; 0, $\bar{\underline{x}}$, 1/2.

F(1), F(2), and F(3) each in 6($\underline{g}$): $\underline{x}$, $\underline{y}$, $\underline{z}$; $\bar{\underline{y}}$, $\underline{x}$-$\underline{y}$, $\underline{z}$; $\underline{y}$-$\underline{x}$, $\bar{\underline{x}}$, $\underline{z}$; $\underline{y}$, $\underline{x}$, $\bar{\underline{z}}$; $\bar{\underline{x}}$, $\underline{y}$-$\underline{x}$, $\bar{\underline{z}}$; $\underline{x}$-$\underline{y}$, $\bar{\underline{y}}$, $\bar{\underline{z}}$.

Since refinement then reduced $\underline{R}$ to 0.136, we retained the second orientation. The relatively small difference in agreement for the two orientations is related to the fact that the experimental intensities do not show large deviations from 6-fold symmetry.

We introduced anisotropic temperature factors of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}\ell^2 - 2\beta_{12}hk - 2\beta_{13}h\ell - 2\beta_{23}k\ell)$, with $4\beta_{ij} = a_i^* a_j^* B_{ij}$, a_i^* being the length of the ith reciprocal axis. With this notation, the anisotropic thermal parameters B_{ij} are in the units (Å^2) which are used for isotropic thermal parameters B in temperature factors of the form $\exp(-B\lambda^{-2}\sin^2\theta)$. Four cycles of least squares refinement with each atom having an anisotropic temperature factor reduced R to 0.116, but left serious discrepancies for certain reflections. A refinement with isotropic temperature factors in a space group of lower symmetry ($P3$), which provided considerably more independent coordinates, likewise had little effect on these discrepancies.

It was noticed that we were calculating much larger differences between $F(hk\ell)$ and $F(kh\ell)$ than were found in our experimental data. This fact suggested twinning such that $hk\ell$ and $kh\ell$ are interchanged in position. This can be accomplished by rotation about c or by reflection in (100). Because of the possibility that the crystals may be optically active, these twin laws in principle are distinguishable by optical methods, but we have no evidence for choosing between them. For such twinning we have the relations:

$$x\, I(hk\ell) + (1-x)\, I(kh\ell) = J(hk\ell),$$
$$(1-x)\, I(hk\ell) + x\, I(kh\ell) = J(kh\ell),$$

where x is the fraction of the specimen with the correct orientation, $I(hk\ell)$ is the intensity for an untwinned crystal, and $J(hk\ell)$ is the intensity for the twinned crystal.

If a value is assumed for x, the above equations can be solved to give the intensity data for the hypothetical untwinned crystal. By trial of various values of x, starting with 0.75 and with refinement with isotropic thermal parameters, we decided that 0.59 gave the optimum agreement. This value of x causes some of the corrected intensities to

vanish, and a smaller value gives some corrected intensities which are negative (i. e., physically impossible) by amounts which exceed the estimated experimental uncertainty.

With $\underline{x}$ = 0.59, $\underline{R}$ was 0.099. Four further cycles with anisotropic temperature factors reduced $\underline{R}$ to 0.085, using 44 parameters in all. In the last cycle, no parameter shifted as much as 3 percent of the estimated standard deviation.

While introduction of the correction for twinning made a substantial reduction in the largest discrepancies, it caused only small changes in the structure. No atom moved as much as 0.1 Å as a result of this correction. The change from isotropic to anisotropic temperature factors made little improvement in the agreement and moved no atom more than 0.01 Å.

The observed structure factors, after this correction for twinning, are compared with the calculated structure factors in Table 2. Coordinates for the atoms are listed in Table 3 and the thermal parameters in Table 4. The standard deviations of parameters were estimated assuming that the discrepancies of the structure factors represent random errors. Because of the symmetries of the special positions, several of the coordinates and thermal parameters are subject to constraints; e. g., $\underline{B}_{11} = \underline{B}_{22} = 2\underline{B}_{12}$ for each Si atom.

No attempt was made to refine the structure in space group P3m1 because this symmetry restricts the sodium atoms to a single z coordinate if they are to be in suitable holes in the fluorine packing. The results in group P321 show clearly that the sodium atoms are not so arranged.

DISCUSSION

The crystal structure is shown in Figure 1, and some of the interatomic distances are listed in Table 5. There are two independent kinds of SiF_6^{-2} ions, but their dimensions are equal and their shapes are regular-octahedral within the accuracy of the experiment. The mean Si-F bond distance is observed as 1.68 Å. Correction for thermal motion with the assumption that F rides on Si increases this distance to 1.695 ± 0.005 Å. Several measurements of this bond distance in other crystals have given values in the range 1.65 to 1.75 Å (Gossner and Kraus, 1934; Ketelaar, 1935; Hoard and Vincent, 1940; Hoard and Williams, 1942).

The F-Si-F bond angles are 90° or 180° within 2° or less, with standard deviations estimated as 1°.

Each sodium atom is in an "octahedral" hole, with six fluorine neighbors at distances which are only approximately equal. These distances range from 2.18 to 2.45 Å with standard deviations of 0.01 Å. The average Na-F distance is 2.32 Å. The F-Na-F angles deviate by nearly as much as 30° from the 90° or 180° values they would have if the coordination polyhedron were a regular octahedron.

This structure of Na_2SiF_6 is remarkably similar to that found by Stanley (1956) for $K_2S_2O_6$: a = 9.785 Å, c = 6.295 Å, c/a = 0.643, space group P321. If the pair of S atoms in each dithionate ion is considered as a single atom, then the two structures have atoms in the same sets of positions, with K corresponding to Na, S_2 corresponding to Si, and O corresponding to F.

References

CIPRIANI, C. (1955). Rend. soc. mineralog. ital. 11, 58.

COX, B. (1954). J. Chem. Soc. 1954, 3251.

COX, B., SHARP, D. W. A., & SHARPE, A. G. (1956). J. Chem. Soc. 1956, 1242.

GOSSNER, E. & KRAUS, O. (1934). Z. Kristallogr. 88, 223.

GROTH, P. (1906). Chemische Krystallographie. Leipzig: Wilhelm Engelman, vol. 1, p. 483.

HEPWORTH, M. A., ROBINSON, P. L., & WESTLAND, G. S. (1958). J. Chem. Soc. 1958, 611.

HOARD, J. L. & VINCENT, W. B. (1940). J. Amer. Chem. Soc. 62, 3126.

HOARD, J. L. & WILLIAMS, M. B. (1942). J. Amer. Chem. Soc. 64, 633.

IBERS, J. A. (1962). International Tables for X-ray Crystallography. Birmingham: Kynoch Press, v. 3, p. 202.

KETELAAR, J. A. A. (1935). Z. Kristallogr. 92, 155.

PALACHE, C., BERMAN, H. & FRONDEL, C. (1951). Dana's System of Mineralogy. New York: John Wiley and Sons, vol. 2, p. 105.

STANLEY, E. (1956). Acta Cryst. 9, 897.

STOLBA, (1872). Z. anal. Chem. 11, 199.

Table 1. Axial dimensions and ratios, Na_2SiF_6

	a	c	c/a
This work	8.859 Å	5.038 Å	0.5687
Cox (1954)	8.86	5.02	0.567
Cipriani (1955)	8.87	5.07	0.572
Groth (1906)			0.5635
Palache *et al.* (1951)			1.333[a]

[a]This value is calculated from a polar angle 56° 59.5' for $(10\bar{1}1)$. We think that a blunder has been made, since the complement of this angle corresponds to c/a = 0.5626, in agreement with the other values.

Table 2. Observed structure factor magnitudes (FOB) and calculated structure factor magnitudes (FCA), each multiplied by 10. The observed values have been corrected for twinning as described in the text. The phase angle (PHI) of the calculated structure factor is given as a fraction of a circle, multiplied by 1000.

(Table to be reproduced photographically)

H	K	L	FOB	FCA	PHI
1	0	0	22	9	000
2	0	0	33	20	000
3	0	0	163	185	000
4	0	0	82	84	000
5	0	0	80	66	000
6	0	0	138	131	000
7	0	0	91	79	000
8	0	0	83	81	000
9	0	0	35	46	000
0	1	0	16	9	000
1	1	0	476	456	005
2	1	0	164	172	287
3	1	0	135	135	751
4	1	0	33	28	430
5	1	0	96	95	388
6	1	0	49	41	477
7	1	0	58	58	990
8	1	0	72	73	362
0	2	0	28	20	000
1	2	0	164	172	287
2	2	0	252	236	477
3	2	0	196	196	770
4	2	0	276	268	298
5	2	0	339	334	005
6	2	0	140	154	735
7	2	0	111	103	333
0	3	0	165	185	000
1	3	0	131	135	751
2	3	0	197	196	770
3	3	0	610	610	986
4	3	0	127	130	835
5	3	0	73	62	138
6	3	0	129	134	932
7	3	0	60	55	964
0	4	0	82	84	000
1	4	0	23	28	430
2	4	0	270	268	298
3	4	0	133	130	835
4	4	0	473	471	009
5	4	0	68	69	382
6	4	0	0	8	849
0	5	0	82	66	000
1	5	0	100	95	388
2	5	0	336	334	005
3	5	0	66	62	138

H	K	L	FOB	FCA	PHI
4	5	0	60	69	382
5	5	0	87	100	094
0	6	0	142	131	000
1	6	0	49	41	477
2	6	0	143	154	735
3	6	0	137	134	932
4	6	0	24	8	849
0	7	0	89	79	000
1	7	0	58	58	990
2	7	0	99	103	333
3	7	0	60	55	964
0	8	0	86	81	000
1	8	0	63	73	362
0	9	0	43	46	000
0	0	1	281	267	500
1	0	1	373	373	000
2	0	1	377	377	000
3	0	1	660	620	000
4	0	1	151	138	500
5	0	1	245	248	000
6	0	1	169	165	500
7	0	1	30	23	500
8	0	1	94	100	000
0	1	1	322	347	000
1	1	1	436	435	695
2	1	1	177	170	086
3	1	1	197	186	700
4	1	1	325	308	937
5	1	1	195	202	948
6	1	1	109	76	791
7	1	1	230	232	490
8	1	1	142	130	853
0	2	1	356	379	000
1	2	1	166	194	887
2	2	1	252	244	270
3	2	1	348	349	089
4	2	1	161	161	951
5	2	1	122	127	443
6	2	1	190	178	021
7	2	1	112	103	158
0	3	1	705	715	500
1	3	1	83	60	412
2	3	1	274	298	987
3	3	1	95	93	485
4	3	1	103	103	908

H	K	L	FOB	FCA	PHI
5	3	1	235	238	026
6	3	1	20	46	468
7	3	1	35	48	842
0	4	1	151	153	500
1	4	1	448	457	553
2	4	1	149	167	035
3	4	1	79	78	963
4	4	1	148	143	506
5	4	1	99	113	004
6	4	1	98	84	817
0	5	1	289	286	000
1	5	1	174	161	983
2	5	1	0	31	015
3	5	1	224	220	007
4	5	1	112	113	984
5	5	1	42	38	803
0	6	1	60	60	000
1	6	1	128	132	798
2	6	1	233	235	139
3	6	1	58	45	473
4	6	1	0	21	873
0	7	1	30	46	500
1	7	1	93	112	015
2	7	1	58	54	949
3	7	1	35	16	126
0	8	1	122	109	000
1	8	1	62	93	991
0	0	2	104	87	500
1	0	2	53	57	000
2	0	2	192	159	000
3	0	2	655	633	000
4	0	2	263	278	000
5	0	2	168	159	000
6	0	2	261	268	000
7	0	2	0	28	500
8	0	2	51	5	500
0	1	2	28	20	500
1	1	2	144	142	520
2	1	2	164	144	172
3	1	2	238	209	942
4	1	2	151	163	998
5	1	2	218	200	303
6	1	2	160	183	667
7	1	2	216	230	011
8	1	2	72	77	373

H	K	L	FOB	FCA	PHI
0	2	2	97	131	500
1	2	2	267	276	341
2	2	2	304	297	992
3	2	2	124	118	838
4	2	2	95	96	284
5	2	2	56	54	103
6	2	2	78	71	450
7	2	2	60	53	620
0	3	2	831	857	000
1	3	2	268	285	600
2	3	2	39	35	508
3	3	2	126	117	941
4	3	2	40	35	970
5	3	2	116	122	804
6	3	2	95	96	928
0	4	2	169	149	500
1	4	2	308	299	001
2	4	2	115	118	401
3	4	2	63	55	960
4	4	2	44	51	408
5	4	2	57	87	368
0	5	2	54	22	500
1	5	2	154	186	278
2	5	2	27	37	189
3	5	2	103	99	858
4	5	2	125	115	354
0	6	2	233	231	000
1	6	2	152	121	834
2	6	2	0	41	828
3	6	2	110	88	918
0	7	2	183	181	000
1	7	2	179	159	020
2	7	2	60	61	368
0	8	2	95	109	000
1	8	2	41	14	357
0	0	3	171	157	000
1	0	3	228	209	500
2	0	3	204	213	000
3	0	3	281	299	500
4	0	3	163	151	000
5	0	3	229	264	000
6	0	3	58	47	500
7	0	3	39	58	000
0	1	3	180	195	500
1	1	3	263	260	731

H	K	L	FOB	FCA	PHI
2	1	3	276	279	974
3	1	3	120	128	024
4	1	3	228	250	568
5	1	3	180	155	925
6	1	3	36	48	958
7	1	3	47	13	560
0	2	3	208	209	000
1	2	3	224	220	021
2	2	3	189	197	348
3	2	3	231	245	997
4	2	3	96	106	268
5	2	3	19	30	940
6	2	3	113	123	065
0	3	3	94	53	000
1	3	3	155	170	936
2	3	3	226	212	050
3	3	3	0	3	435
4	3	3	151	141	566
5	3	3	96	85	150
0	4	3	46	87	000
1	4	3	101	80	792
2	4	3	83	54	200
3	4	3	160	163	578
4	4	3	41	23	519
5	4	3	67	55	921
0	5	3	315	279	000
1	5	3	173	182	911
2	5	3	56	36	283
3	5	3	111	100	134
4	5	3	33	45	878
0	6	3	58	78	500
1	6	3	84	65	973
2	6	3	139	123	948
0	7	3	68	66	000
1	7	3	137	139	484
0	0	4	479	488	000
1	0	4	55	55	500
2	0	4	65	47	500
3	0	4	406	388	000
4	0	4	172	164	500
5	0	4	71	13	500
6	0	4	106	121	000
0	1	4	0	19	000
1	1	4	88	89	985
2	1	4	135	155	380

H	K	L	FOB	FCA	PHI
3	1	4	175	169	623
4	1	4	128	135	016
5	1	4	84	77	384
6	1	4	77	53	980
0	2	4	80	92	000
1	2	4	117	87	067
2	2	4	69	69	103
3	2	4	78	68	574
4	2	4	104	99	357
5	2	4	98	97	033
0	3	4	208	196	000
1	3	4	125	137	955
2	3	4	139	132	823
3	3	4	163	162	986
4	3	4	42	44	787
0	4	4	165	188	000
1	4	4	53	17	026
2	4	4	88	104	304
3	4	4	42	38	828
0	5	4	88	116	000
1	5	4	84	75	311
2	5	4	139	128	991
0	6	4	165	163	000
1	6	4	97	108	576
0	0	5	153	141	500
1	0	5	235	214	000
2	0	5	148	120	000
3	0	5	38	34	500
4	0	5	40	49	500
5	0	5	100	86	000
0	1	5	118	143	000
1	1	5	158	155	655
2	1	5	56	55	015
3	1	5	68	56	613
4	1	5	16	63	620
0	2	5	127	166	000
1	2	5	56	46	021
2	2	5	53	65	281
3	2	5	130	115	047
0	3	5	67	53	000
1	3	5	39	38	647
2	3	5	116	110	041
0	4	5	69	58	500
1	4	5	84	61	691
0	5	5	100	99	000

Table 3. Final coordinates and estimated standard deviations.[a]

	$\underline{x}$	$\sigma(\underline{x})$	$\underline{y}$	$\sigma(\underline{y})$	$\underline{z}$	$\sigma(\underline{z})$
Si(1)	(0)	---	(0)	---	(0)	---
Si(2)	(1/3)	---	(2/3)	---	0.5062	0.0012
Na(1)	0.3790	0.0010	(0.3790)	---	(0)	---
Na(2)	0.7143	0.0009	(0.7143)	---	(1/2)	---
F(1)	0.0870	0.0018	-0.0918	0.0017	0.8099	0.0014
F(2)	0.4442	0.0012	-0.4006	0.0013	0.7007	0.0014
F(3)	0.2299	0.0015	-0.2599	0.0015	0.3098	0.0014

[a]Parentheses indicate coordinates which are not independent parameters.

Table 4. Final thermal parameters and estimated standard deviations.[a]

	Si(1)	Si(2)	Na(1)	Na(2)	F(1)	F(2)	F(3)
$\underline{B}_{11}$	1.3	1.1	2.4	1.6	3.6	1.6	1.9
$\sigma(\underline{B}_{11})$	0.2	0.1	0.3	0.2	0.5	0.4	0.4
$\underline{B}_{22}$	(1.3)	(1.1)	(2.4)	(1.6)	2.7	1.9	2.5
$\sigma(\underline{B}_{22})$	---	---	---	---	0.5	0.4	0.4
$\underline{B}_{33}$	1.9	1.3	1.3	2.5	3.1	2.3	2.3
$\sigma(\underline{B}_{33})$	0.4	0.2	0.3	0.4	0.3	0.3	0.3
$\underline{B}_{12}$	(0.6)	(0.5)	0.9	0.7	2.1	1.2	1.3
$\sigma(\underline{B}_{12})$	---	---	0.3	0.3	0.3	0.4	0.3
$\underline{B}_{13}$	(0)	(0)	0.1	-0.1	0.9	0.5	-0.4
$\sigma(\underline{B}_{13})$	---	---	0.2	0.2	0.5	0.3	0.4
$\underline{B}_{23}$	(0)	(0)	(-0.1)	(0.1)	-0.4	1.3	-0.2
$\sigma(\underline{B}_{23})$	---	---	---	---	0.5	0.3	0.4

[a]Parentheses indicate parameters which are not independent.

Table 5. Interatomic distances and standard deviations in Na_2SiF_6.

Atom	Neighbors	Distance, Å
Si(1)	6 F(1)	1.673 ± 0.012
		(1.690 corrected[a])
	3 Na(1)	3.357 ± 0.009
Si(2)	3 F(3)	1.685 ± 0.011
		(1.694 corrected)
	3 F(2)	1.693 ± 0.009
		(1.701 corrected)
	3 Na(2)	3.185 ± 0.005
mean corrected Si-F		1.695 ± 0.005
Na(1)	2 F(2)	2.30 ± 0.01
	2 F(3)	2.36 ± 0.01
	2 F(1)	2.45 ± 0.02
	Si(1)	3.357 ± 0.009
Na(2)	2 F(1)	2.18 ± 0.01
	2 F(3)	2.31 ± 0.01
	2 F(2)	2.31 ± 0.01
	2 Si(2)	3.185 ± 0.005
F(1)	F(1)	2.34 ± 0.02
	2 F(1)	2.38 ± 0.02
	F(1)	2.38 ± 0.02
	F(2)	3.15 ± 0.02
	F(3)	3.28 ± 0.02
	F(1)	3.35 ± 0.02
F(2)	F(3)	2.37 ± 0.01
	2 F(2)	2.39 ± 0.02
	F(3)	2.43 ± 0.01
	F(2)	3.12 ± 0.02

	F(1)	3.15 ± 0.02
	F(3)	3.23 ± 0.02
	F(3)	3.34 ± 0.01
	F(3)	3.35 ± 0.02
F(3)	2 F(3)	2.36 ± 0.02
	F(2)	2.37 ± 0.01
	F(2)	2.43 ± 0.01
	F(2)	3.23 ± 0.02
	F(1)	3.28 ± 0.02
	F(2)	3.34 ± 0.01
	F(2)	3.35 ± 0.02

[a]Corrected for thermal motion with assumption that F rides on Si.

Figure caption:

Fig. 1. Crystal structure of Na_2SiF_6. The z coordinates (x 100) are indicated for some of the atoms, and the lengths (in Å) are given for some of the interatomic distances.

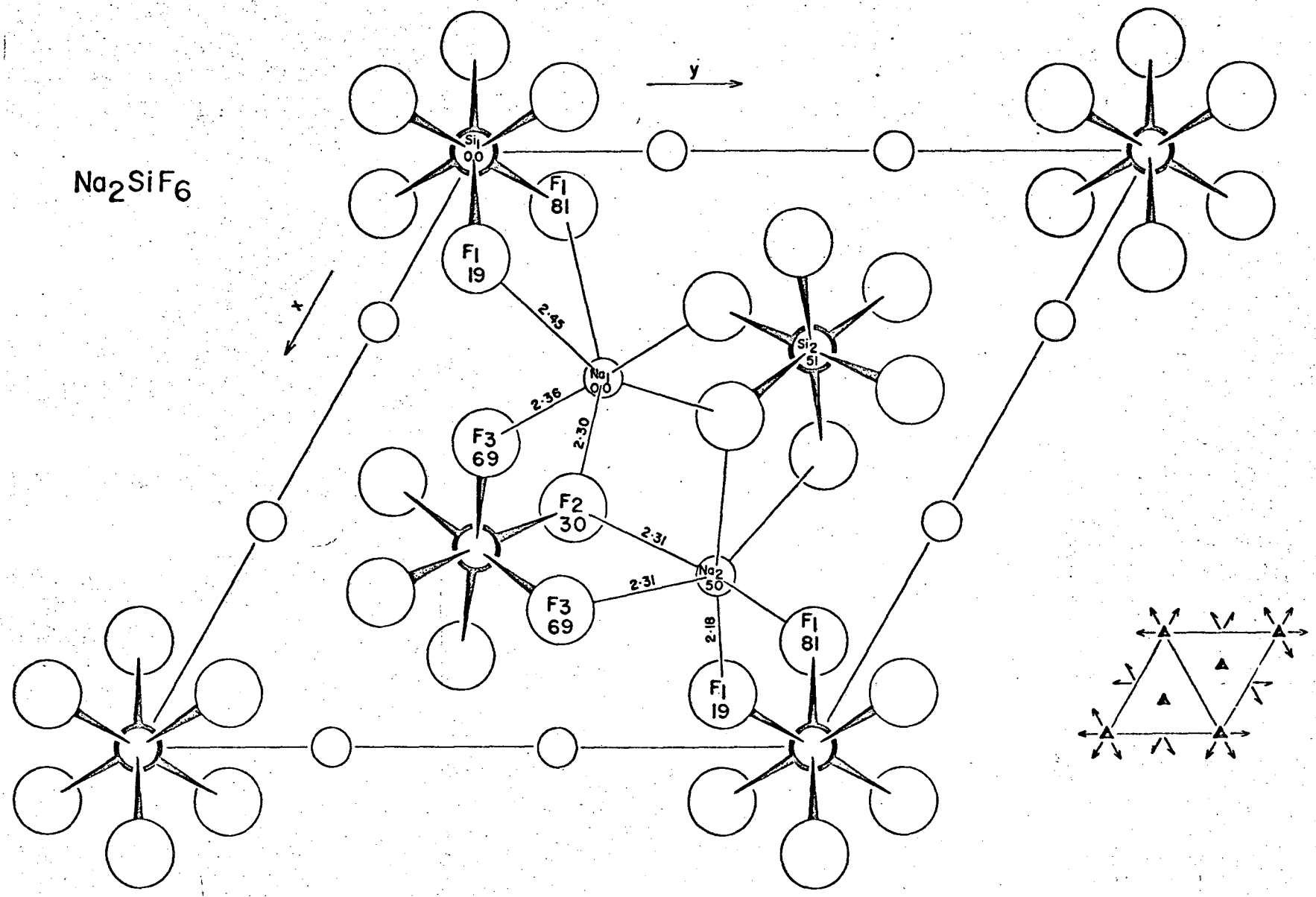
Na_2SiF_6
y
x
Si1
00
F1
81
F1
19
2·45
Na1
00
2·36
2·30
F3
69
F2
30
2·31
Na2
50
2·31
F3
69
2·18
F1
81
F1
19
Si2
51
MUB-1964

Fig. 1

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