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The Crystal Structure of Sodium Fluosilicate*

BY ALLAN ZALKIN, J. D. FORRESTER AND DAVID H. TEMPLETON

Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California, U. S. A.

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A study by X-ray diffraction showed that Na_2SiF_6 is hexagonal (trigonal) with $a = 8{\cdot}859$, $c = 5{\cdot}038$ Å (each $\pm 0{\cdot}002$ Å), $Z = 3$, $D_x = 2{\cdot}74$ g.cm^{-3}. The space group is $P321$. The SiF_6 groups are almost regular octahedra 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 *hkl* and *khl* 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 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 led 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, Sharp & Sharpe, 1956), and Na_2IrF_6 (Hepworth, Robinson & Westland, 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, Berman & Frondel, 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 with the use of 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 $0{\cdot}08 \times 0{\cdot}08 \times 0{\cdot}08$ 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 ($\lambda = 0{\cdot}70926$ 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 ($2\theta < 50°$) were measured with counting times of 20 sec each. Of these, only two were recorded as zero intensity. No corrections were made for either absorption or extinction. We estimate the linear absorption coefficient to be $\mu = 8{\cdot}2$ 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 on an IBM 7090 computer with our version of the Gantzel–Sparks–Trueblood full-matrix least-squares program which minimizes $\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2$. Atomic scattering factors were taken as the values given by Ibers (1962) for Na^+ 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:

$$a = 8{\cdot}859 \pm 0{\cdot}002,\ c = 5{\cdot}038 \pm 0{\cdot}002 \text{ Å}.$$

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 sixfold symmetry axis was present. The superior precision of the counter measurements

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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*

* 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 $c/a=0{\cdot}5626$, in agreement with the other values.

showed on the contrary that the crystal had Laue symmetry $\bar{3}m$, in agreement with Cipriani (1955). The mirror symmetry of this Laue group is oriented with a plane perpendicular to the primitive a axis, as indicated by the full symbol $\bar{3}m1$ rather than $\bar{3}1m$. With no reflections systematically absent, we have a choice of the three space groups $P321$, $P3m1$, 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 $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. 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*): $\pm(\frac{1}{3}, \frac{2}{3}, z)$; $z=0{\cdot}51$.
Na in 6(*g*): $\pm(x, 0, 0;\ 0, x, 0;\ \bar{x}, \bar{x}, 0)$; $x=0{\cdot}34$.
F(1) in 6(*i*): $\pm(x, \bar{x}, z;\ x, 2x, z;\ 2\bar{x}, \bar{x}, z)$; $x=0{\cdot}091$, $z=0{\cdot}805$.
F(2) in 6(*i*): $x=0{\cdot}424$, $z=0{\cdot}705$.
F(3) in 6(*i*): $x=0{\cdot}242$, $z=0{\cdot}315$.

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 index $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0{\cdot}44$. Various combinations of sign changes for z parameters of the fluorine atoms and of moving the sodium atoms to $z=0{\cdot}5$ 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 $R=0{\cdot}41$ for Na_2SiF_6 and $R=0{\cdot}31$ for Na_2GeF_6 (in which incorrect sodium positions have less effect).

Because of our lack of success, we went to the noncentric group $P321$. In this space group the sodium atoms are in two independent threefold sets, and each fluorine octahedron is free to rotate about its threefold axis. Continued refinement of the structure with this greater freedom reduced 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 $z=0{\cdot}5$, which is permitted in this space group. This change produced dramatic improvement with much better thermal parameters and $R=0{\cdot}16$.

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 c axis gives the second structure. With this change the atoms were distributed in the final sets of positions:

Space group $P321$

Si(1) in 1(*a*): 0, 0, 0.
Si(2) in 2(*d*): $\frac{1}{3}, \frac{2}{3}, z$; $\frac{2}{3}, \frac{1}{3}, \bar{z}$.
Na(1) in 3(*e*): $x, x, 0$; $\bar{x}, 0, 0$; $0, \bar{x}, 0$.
Na(2) in 3(*f*): $x, x, \frac{1}{2}$; $\bar{x}, 0, \frac{1}{2}$; $0, \bar{x}, \frac{1}{2}$.
F(1), F(2), and F(3) each in 6(*g*):
x, y, z; $\bar{y}, x-y, z$; $y-x, \bar{x}, z$;
$y, x, \bar{z}$; $\bar{x}, y-x, \bar{z}$; $x-y, \bar{y}, \bar{z}$.

Since refinement then reduced 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 sixfold symmetry.

We introduced anisotropic temperature factors of the form

$$\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl),$$

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 $F(hkl)$ and $F(khl)$ than were found in our experimental data. This fact suggested *twinning* such that hkl and khl 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:

$$xI(hkl)+(1-x)I(khl)=J(hkl)\,,$$
$$(1-x)I(hkl)+xI(khl)=J(khl)\,,$$

where x is the fraction of the specimen with the correct orientation, $I(hkl)$ is the intensity for an untwinned

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

H K L	FOB	FCA	PHI	H K L	FOB	FCA	PHI	H K L	FOB	FCA	PHI	H K L	FOB	FCA	PHI	H K L	FOB	FCA	PHI	H K L	FOB	FCA	PHI
1 0 0	22	9	000	4 5 0	60	69	382	5 3 1	235	238	026	0 2 2	97	131	500	2 1 3	276	279	974	3 1 4	175	169	623
2 0 0	33	20	000	5 5 0	87	100	094	6 3 1	20	46	468	1 2 2	267	276	341	3 1 3	120	128	024	4 1 4	128	135	016
3 0 0	163	185	000	0 6 0	142	131	000	7 3 1	35	48	842	2 2 2	304	297	992	4 1 3	278	250	568	5 1 4	84	77	384
4 0 0	82	84	000	1 6 0	49	41	477	0 4 1	151	153	500	3 2 2	124	118	838	5 1 3	180	155	925	6 1 4	77	53	980
5 0 0	80	66	000	2 6 0	143	154	735	1 4 1	448	457	553	4 2 2	95	96	284	6 1 3	36	48	958	0 2 4	80	92	000
6 0 0	138	131	000	3 6 0	137	134	932	2 4 1	149	167	035	5 2 2	56	54	103	7 1 3	47	13	560	1 2 4	117	87	067
7 0 0	91	79	000	4 6 0	24	8	849	3 4 1	79	78	963	6 2 2	78	71	450	0 2 3	208	209	000	2 2 4	69	69	103
8 0 0	83	81	000	0 7 0	89	79	000	4 4 1	148	143	506	7 2 2	60	53	620	1 2 3	224	220	021	3 2 4	78	68	574
9 0 0	35	46	000	1 7 0	58	58	990	5 4 1	99	113	004	0 3 2	831	857	000	2 2 3	189	197	348	4 2 4	104	99	357
0 1 0	16	9	000	2 7 0	99	103	333	6 4 1	98	84	817	1 3 2	268	285	600	3 2 3	231	245	997	5 2 4	98	97	033
1 1 0	476	456	005	3 7 0	60	55	964	0 5 1	289	286	000	2 3 2	39	35	508	4 2 3	96	106	268	0 3 4	208	196	000
2 1 0	164	172	287	0 8 0	86	81	000	1 5 1	174	161	983	3 3 2	126	117	941	5 2 3	19	30	940	1 3 4	125	137	955
3 1 0	135	135	751	1 8 0	63	73	362	2 5 1	0	31	015	4 3 2	40	35	970	6 2 3	113	123	065	2 3 4	139	132	823
4 1 0	33	28	430	0 9 0	43	46	000	3 5 1	224	220	007	5 3 2	116	122	804	0 3 3	94	53	000	3 3 4	163	162	986
5 1 0	96	95	388	0 0 1	281	267	500	4 5 1	112	113	984	6 3 2	95	96	928	1 3 3	155	170	936	4 3 4	42	44	787
6 1 0	49	41	477	1 0 1	373	373	000	5 5 1	42	38	803	0 4 2	169	149	500	2 3 3	226	212	050	0 4 4	165	188	000
7 1 0	58	58	990	2 0 1	377	377	000	0 6 1	60	60	000	1 4 2	308	299	001	3 3 3	0	3	435	1 4 4	53	17	026
8 1 0	72	73	362	3 0 1	660	620	000	1 6 1	128	132	798	2 4 2	115	118	401	4 3 3	151	141	566	2 4 4	88	104	304
0 2 0	28	20	000	4 0 1	151	138	500	2 6 1	233	235	139	3 4 2	63	55	960	5 3 3	96	85	150	3 4 4	42	38	828
1 2 0	164	172	287	5 0 1	245	248	000	3 6 1	58	45	473	4 4 2	44	51	408	0 4 3	46	87	000	0 5 4	88	116	000
2 2 0	252	236	477	6 0 1	169	165	500	4 6 1	0	21	873	5 4 2	57	87	368	1 4 3	101	80	792	1 5 4	84	75	311
3 2 0	196	196	770	7 0 1	30	23	500	0 7 1	30	46	500	0 5 2	54	22	500	2 4 3	83	54	200	2 5 4	139	128	991
4 2 0	276	268	298	8 0 1	94	100	000	1 7 1	93	112	015	1 5 2	154	186	278	3 4 3	160	163	578	0 6 4	165	163	000
5 2 0	339	334	005	0 1 1	322	347	000	2 7 1	58	54	949	2 5 2	27	37	189	4 4 3	41	23	519	1 6 4	97	108	576
6 2 0	140	154	735	1 1 1	436	435	695	3 7 1	35	16	126	3 5 2	103	99	858	5 4 3	67	55	921	0 0 5	153	141	500
7 2 0	111	103	333	2 1 1	177	170	086	0 8 1	122	109	000	4 5 2	125	115	354	0 5 3	315	279	000	1 0 5	235	214	000
0 3 0	165	185	000	3 1 1	197	186	700	1 8 1	62	93	991	0 6 2	233	231	000	1 5 3	173	182	911	2 0 5	148	120	000
1 3 0	131	135	751	4 1 1	325	308	937	0 0 2	104	87	500	1 6 2	152	121	834	2 5 3	56	36	283	3 0 5	38	34	500
2 3 0	197	196	770	5 1 1	195	202	948	1 0 2	53	57	000	2 6 2	0	41	828	3 5 3	111	100	134	4 0 5	40	49	500
3 3 0	610	610	986	6 1 1	109	76	791	2 0 2	192	159	000	3 6 2	110	88	518	4 5 3	33	45	878	5 0 5	100	86	000
4 3 0	127	130	835	7 1 1	230	232	490	3 0 2	655	633	000	0 7 2	183	181	000	0 6 3	58	78	500	0 1 5	118	143	000
5 3 0	73	62	138	8 1 1	142	130	853	4 0 2	263	278	000	1 7 2	179	159	020	1 6 3	84	65	973	1 1 5	158	155	655
6 3 0	129	134	932	0 2 1	356	379	000	5 0 2	168	159	000	2 7 2	60	61	368	2 6 3	139	123	948	2 1 5	56	55	015
7 3 0	60	55	964	1 2 1	166	194	887	6 0 2	261	268	000	0 8 2	95	109	000	0 7 3	68	66	000	3 1 5	68	56	613
0 4 0	82	84	000	2 2 1	252	244	270	7 0 2	0	28	500	1 8 2	41	14	357	1 7 3	137	139	484	4 1 5	16	63	620
1 4 0	23	28	430	3 2 1	348	349	089	8 0 2	51	5	500	0 0 3	171	157	000	0 0 4	479	488	000	0 2 5	127	166	000
2 4 0	270	268	298	4 2 1	161	161	951	0 1 2	28	20	500	1 0 3	228	209	500	1 0 4	55	55	500	1 2 5	56	46	021
3 4 0	133	130	835	5 2 1	122	127	443	1 1 2	144	142	520	2 0 3	204	213	000	2 0 4	65	47	500	2 2 5	53	65	281
4 4 0	473	471	009	6 2 1	190	178	021	2 1 2	164	144	172	3 0 3	281	299	500	3 0 4	406	388	000	3 2 5	130	115	047
5 4 0	68	69	382	7 2 1	112	103	158	3 1 2	238	209	942	4 0 3	163	151	000	4 0 4	172	164	500	0 3 5	67	53	000
6 4 0	0	8	949	0 3 1	705	715	500	4 1 2	151	163	998	5 0 3	229	264	000	5 0 4	71	13	500	1 3 5	39	38	647
0 5 0	82	66	000	1 3 1	83	60	412	5 1 2	218	200	303	6 0 3	58	47	500	6 0 4	106	121	000	2 3 5	116	110	041
1 5 0	100	95	388	2 3 1	274	258	987	6 1 2	160	183	667	7 0 3	39	58	000	0 1 4	0	19	000	0 4 5	69	58	500
2 5 0	336	334	005	3 3 1	95	93	485	7 1 2	216	230	011	0 1 3	180	195	500	1 1 4	88	89	985	1 4 5	84	61	691
3 5 0	66	62	138	4 3 1	103	103	908	8 1 2	72	77	373	1 1 3	263	260	731	2 1 4	135	155	380	0 5 5	100	99	000

Table 3. *Final coordinates and estimated standard deviations**

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Si(1)	(0)	—	(0)	—	(0)	—
Si(2)	$(\frac{1}{3})$	—	$(\frac{2}{3})$	—	0·5062	0·0012
Na(1)	0·3790	0·0010	(0·3790)	—	(0)	—
Na(2)	0·7143	0·0009	(0·7143)	—	$(\frac{1}{2})$	—
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

* Values in parentheses indicate coordinates which are not independent parameters.

Table 4. *Final thermal parameters and estimated standard deviations**

	Si(1)	Si(2)	Na(1)	Na(2)	F(1)	F(2)	F(3)
B_{11}	1·3	1·1	2·4	1·6	3·6	1·6	1·9
$\sigma(B_{11})$	0·2	0·1	0·3	0·2	0·5	0·4	0·4
B_{22}	(1·3)	(1·1)	(2·4)	(1·6)	2·7	1·9	2·5
$\sigma(B_{22})$	—	—	—	—	0·5	0·4	0·4
B_{33}	1·9	1·3	1·3	2·5	3·1	2·3	2·3
$\sigma(B_{33})$	0·4	0·2	0·3	0·4	0·3	0·3	0·3
B_{12}	(0·6)	(0·5)	0·9	0·7	2·1	1·2	1·3
$\sigma(B_{12})$	—	—	0·3	0·3	0·3	0·4	0·3
B_{13}	(0)	(0)	0·1	−0·1	0·9	0·5	−0·4
$\sigma(B_{13})$	—	—	0·2	0·2	0·5	0·3	0·4
B_{23}	(0)	(0)	(−0·1)	(0·1)	−0·4	1·3	−0·2
$\sigma(B_{23})$	—	—	—	—	0·5	0·3	0·4

* Values in parentheses indicate parameters which are not independent.

crystal, and $J(hkl)$ 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 valuc gives some corrected intensities which are negative (*i.e.*, physically impossible) by amounts which exceed the estimated experimental uncertainty.

With $x=0·59$, R was 0·099. Four further cycles with anisotropic temperature factors reduced R to 0·085, using 44 parameters in all. In the last cycle, no parameter shifted as much as 3% 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.*, $B_{11}=B_{22}=2B_{12}$ 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 Fig. 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±0·006 Å. Several measurements of this bond distance in other crystals have given values in the range 1·65 to 1·75 Å (Gossner & Kraus, 1934; Ketelaar, 1935; Hoard & Vincent, 1940; Hoard & Williams, 1942).

Table 5. *Interatomic distances and standard deviations in* Na_2SiF_6

Atom	Neighbors	Distance
Si(1)	6 F(1)	1·673±0·012 Å
		(1·690 corrected*)
	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±0·006†
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

* Corrected for thermal motion with assumption that F rides on Si.

† Standard deviation of the mean, estimated from the standard deviations of the separate distances.

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 $K_2S_2O_6$:

$$a=9·785,\ c=6·295\ \text{Å},\ c/a=0·643\ ,$$

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

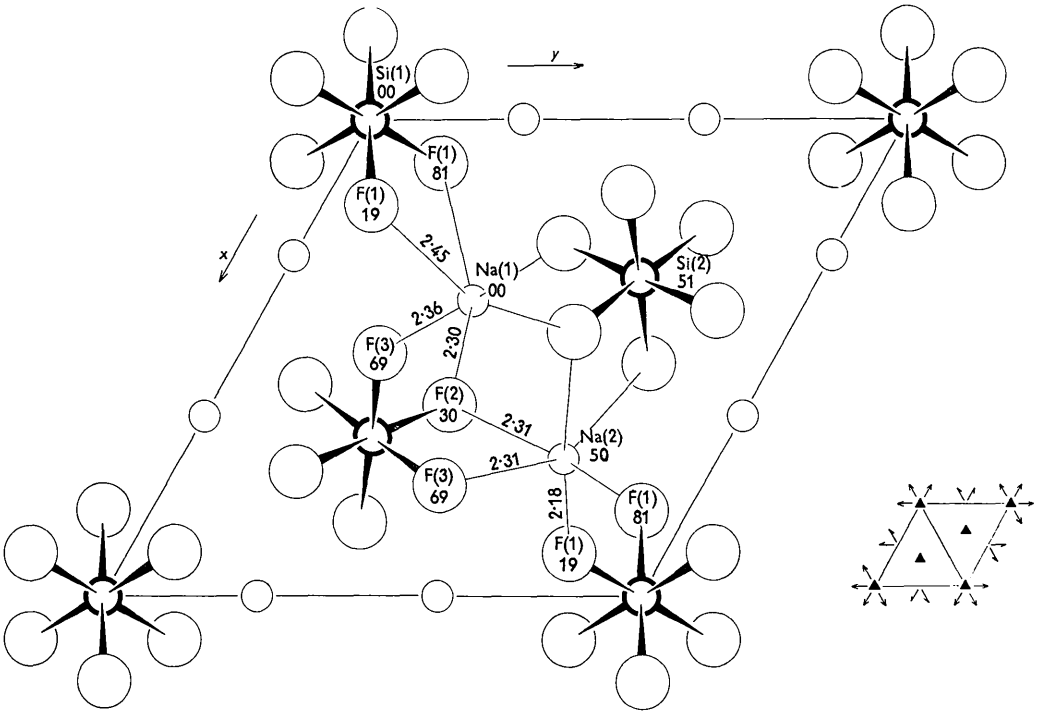

Fig. 1. Crystal structure of Na_2SiF_6. The z coordinates ($\times 100$) are indicated for some of the atoms, and the lengths (Å) are given for some of the interatomic distances.

positions, with K corresponding to Na, S_2 corresponding to Si, and O corresponding to F.

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