Table 2. *Selected distances (Å) and angles (°) with s.u. values in parentheses for $Ca_2NaF(SiO_4)$*

Ca—*X* [*X* = O (× 4) or F (× 2)]

	Ca1	Ca2
Minimum	2.276 (3)	2.278 (4)
Maximum	2.458 (4)	2.454 (3)
Mean† (of 6)	2.39 (6)	2.36 (5)

X—Ca—*X* (*X* = O or F) - large angles (L)‡

	X—Ca1—*X*	*X*—Ca2—*X*
Minimum	138.3 (1)	141.7 (1)
Maximum	169.0 (1)	171.8 (1)
Mean (of 3)	150 (13)	152 (13)

X—Ca—*X* (*X* = O or F) - small angles (S)§

	X—Ca1—*X*	*X*—Ca2—*X*
Minimum	67.0 (1)	67.6 (1)
Maximum	124.0 (1)	120.6 (1)
Mean (of 12)	89 (17)	88 (16)

F—Ca distances and Ca—F—Ca angles

	F—Ca	Ca—F—Ca (L)	Ca—F—Ca (S)
Minimum	2.359 (3)	173.0 (1)	82.8 (1)
Maximum	2.454 (3)	174.1 (1)	94.5 (1)
Mean (of 6, 3, 12)	2.42 (4)	173.7 (5)	90 (4)

Silicate anion

	Si—O	O—Si—O
Minimum	1.625 (4)	108.1 (2)
Maximum	1.643 (5)	111.2 (2)
Mean (of 4, 6)	1.631 (7)	109.4 (14)

† The s.u. values associated with the mean values are calculated on the basis of *n* observations, where *n* is as stated. ‡ *X*—*Y*—*Z* angles at *Y* involving diagonally opposite *X* and *Y*. § *X*—*Y*—*Z* angles at *Y* where *X* and *Z* are adjacent.

Data collection used 2θ scan rates of 5.33 ($I_p > 150$) to 58.6° min^{-1} ($I_p > 2500$), where I_p is the prescan intensity. Scan widths were 2.4 to 2.8° 2θ. Refinement was by full-matrix least-squares techniques. All atoms were refined anisotropically. Ca1 and Ca2 sites were interpreted in a chemical sense as disordered Na and Ca in the ratio 1:2; they were initially refined as Ca but were later treated as Na/Ca atom pairs with common coordinates and anisotropic displacement parameters but independent site-occupancy factors summing to unity for each site. F was treated as fluorine. All computations were performed on the SUN SPARCserver (UNIX operating system) of the Computing Centre of the University of Aberdeen.

Data collection: Nicolet *P*3 software. Cell refinement: Nicolet *P*3 software. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *STRUPLO*82 (Fischer, 1982).

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Room-Temperature Form of Manganese Hexafluorosilicate Hexahydrate: a New Model with Submicroscopic Twinning

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Abstract

A new model of $MnSiF_6.6H_2O$ is presented which reproduces the 'weak' *h*0*l* reflections not explained with the 'antiphase domain' model by Chevrier [*Acta Cryst.* (1991), **B47**, 224–228]. Good agreement for the 'weak' reflections was obtained by assuming a sort of submicroscopic twinning. The average distances are Mn—O 2.15, Si—F 1.69 and O···F 2.78 Å.

Comment

In the preceding report (Kodera, Torii, Osaki & Watanabe, 1972), the title compound was assigned the space group $P\bar{3}m1$, based on the observed Laue symmetry and extinction rules obtained from Weissenberg and precession photographs. In a later study, however, it became clear that a reasonable structure consisting of the known polyhedra $Mn(H_2O)_6^{2+}$ and SiF_6^{2-} could not be constructed with this space group. It was then assumed that the true space group was $P\bar{3}$ and that the apparent symmetry plane must have been introduced by some kind of twinning. It was also realised that the crystal structure had a remarkable superperiodicity.

In order to record weak superstructure lines as well as possible, a new set of counter data was obtained for an apparently single crystal, using Ni-filtered Cu $K\alpha$ radiation from a 200 mA X-ray generator. This enabled us to record 451 independent reflections of which 349 were considered as observed [with $I > 3\sigma(I)$]. Among the weak $-h+k+l <> 3n$ type reflections, there are 45 of the $h0l$ or $0kl$ types. Since these 45 reflections are all calculated to be zero with the antiphase domain model by Chevrier (1991), we decided to try a new model which contains two independent octahedral ions for both $Mn(H_2O)_6^{2+}$ and SiF_6^{2-}.

The idealized (or approximate) positions of the Mn and Si atoms are: Mn(1) at $1a$ 0,0,0; Mn(2) on $2d$ $\frac{1}{3},\frac{2}{3},z$, *etc.*, with $z \simeq \frac{2}{3}$; and Si(1) at $1b$ $0,0,\frac{1}{2}$; Si(2) on $2d$ $\frac{1}{3},\frac{2}{3},z$, *etc.*, with $z \simeq \frac{1}{6}$. In order to explain the observed F values for the 'weak' reflections mentioned above, it was found necessary to shift both the Mn(2) and Si(2) atoms from their idealized positions.

The formula of the structure factors used at this stage was

$$F_A(hkl) = [\{F(h,k,l)^2 + F(-k,-h,l)^2\}/2]^{1/2} \qquad (1)$$

because it was assumed that the crystal contained some sort of twinning to produce apparent $P\bar{3}m1$ symmetry. But the formula

$$F_B(hkl) = \{F(h,k,l) + F(-k,-h,l)\}/2 \qquad (2)$$

was not adopted because a submicroscopic twinning requiring formula (2) would show a higher diffraction symmetry.

Least-squares refinement at this stage converged at $R = 0.12$. In view of the value $R_{\text{int}} = 0.027$, the refinement was not considered sufficient. Assumption of a non-centrosymmetric space group $P3$ did not reduce the R value either.

Re-examination of the low-angle intensity data lead us to notice that many of the observed F values lie somewhere between F_A and F_B. It was taken to be an indication that some of the twin components are small enough to coexist within the same coherent range and the structure factors were calculated according to the formula

$$F_C(hkl) = [\{F(h,k,l)^2 + F(-k,-h,l)^2 + 2sF(h,k,l)F(-k,-h,l)\}/2]^{1/2}. \qquad (3)$$

Least-squares calculations using this formula were carried out for various values of s. The best agreement $R = 0.071$ was obtained for $s = 0.30$.

Extinction corrections applied to several very strong reflections, introduction of anisotropic displacement parameters for non-H atoms and anomalous scattering corrections for the Mn atoms reduced the R factor to 0.053. Incorporation of H atoms at calculated positions and subsequent refinements resulted in further reduction of R to 0.040. The R value for the 'weak' $h0l$ and $0kl$ reflections is 0.248 (see Table 4).

Bond distances and angles within the octahedral $Mn(H_2O)_6^{2+}$ and SiF_6^{2-} ions are given in Table 2. They all agree, within standard uncertainties, with the values reported for similar fluorosilicates (Jehanno & Varret, 1975; Chevrier & Jehanno, 1979; Chevrier & Saint-James, 1990; Chevrier, 1991; Hamilton, 1962; Ray, Zalkin & Templeton, 1973*a*,*b*; Syoyama & Osaki, 1972).

The unit cell of $MnSiF_6.6H_2O$ contains three columns of two kinds. The first kind (column A) extends along $(00z)$, while the second (column B) is situated along $(\frac{1}{3},\frac{2}{3},z)$ and $(\frac{2}{3},\frac{1}{3},-z)$, having an orientation around [001] different from that of column A (Fig. 1). Note that in fluorosilicates of this series crystallizing in $R\bar{3}$, all the columns have the same orientation.

Within each column, the neighbouring octahedra are linked through two sets of three O—H···F hydrogen bonds upwards and downwards along the column (Table 3). Each of these columns are again linked

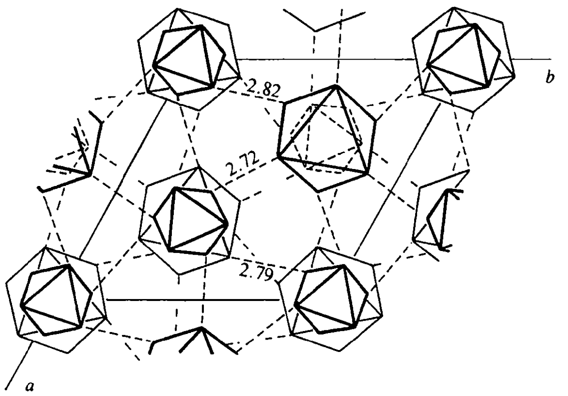

Fig. 1. View of a limited portion of the crystal structure.

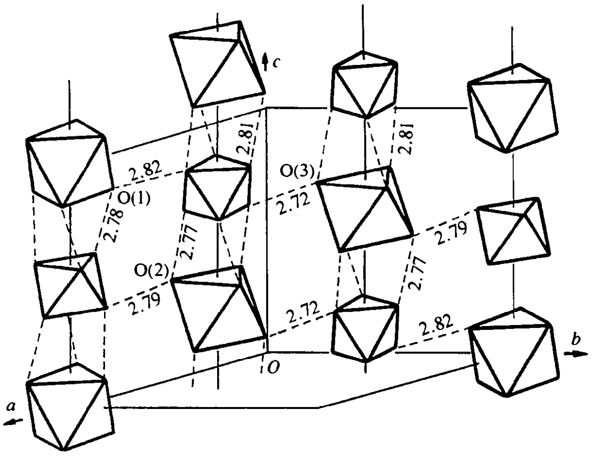

Fig. 2. Lateral hydrogen bonds connecting the columns. The bonds along the columns have been omitted for clarity.

through lateral hydrogen bonds to six neighbouring columns (Fig. 2). It is interesting to note that the shortest lateral hydrogen bond links the two *B*-type columns which are related by a crystallographic centre of symmetry.

The true meaning of the *s* parameter may not be simple, but the fact that formula (3) helped the reduction of *R* considerably suggests a possible effect of the size of the coherent region on X-ray scattering.

Experimental

Pale pink hexagonal prismatic crystals of $MnSiF_6.6H_2O$ were obtained by slow evaporation of a filtered solution of manganese carbonate and hydrofluoric acid.

Crystal data

$MnSiF_6.6H_2O$
$M_r = 305.10$
Trigonal
$P\bar{3}$
$a = 9.672\ (3)$ Å
$c = 9.834\ (3)$ Å
$V = 796.7\ (8)$ Å^3
$Z = 3$
$D_x = 1.91$ Mg m^{-3}
$D_m = 1.94$ Mg m^{-3}
D_m measured by flotation in $CHBr_3$/benzene solution

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 18 reflections
$\theta = 52$–$56°$
$\mu = 12.73$ mm^{-1}
$T = 298$ K
Hexagonal prism
0.14 × 0.07 × 0.07 mm
Pale pink

Data collection

Rigaku four-circle diffractometer
ω–2θ scans
Absorption correction: spherical
$T_{min} = 0.515$, $T_{max} = 0.556$
562 measured reflections
451 independent reflections
349 reflections with $I > 3\sigma(I)$

$R_{int} = 0.027$
$\theta_{max} = 67.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 10$
3 standard reflections every 50 reflections intensity decay: none

Refinement

Special refinement (see text)
$R = 0.040$
$wR = 0.040$
$S = 1.39$
349 reflections
101 parameters
All H atoms refined
Uniform weighting scheme

$(\Delta/\sigma)_{max} = 0.010$
Extinction correction: exponential form
Extinction coefficient: 7.7×10^{-5}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Mn(1)	0	0	0	0.0069 (4)
Mn(2)	1/3	2/3	0.6693 (3)	0.0063 (6)
Si(1)	0	0	1/2	0.0061 (2)
Si(2)	1/3	2/3	0.1715 (5)	0.0046 (3)
O(1)	0.0672 (10)	0.2025 (11)	0.1291 (7)	0.0125 (14)
O(2)	0.1993 (14)	0.4612 (11)	0.5411 (6)	0.0177 (17)
O(3)	0.1307 (8)	0.5940 (13)	0.8020 (6)	0.0131 (14)
F(1)	0.1509 (8)	0.0200 (7)	0.3998 (5)	0.0100 (9)
F(2)	0.1817 (8)	0.5350 (7)	0.2712 (5)	0.0091 (9)
F(3)	0.2017 (8)	0.6859 (7)	0.0754 (5)	0.0107 (10)

Table 2. *Selected geometric parameters (Å, °)*

Mn(1)—O(1)	2.144 (9)	Si(1)—F(1)	1.690 (7)
Mn(2)—O(2)	2.154 (10)	Si(2)—F(2)	1.693 (7)
Mn(2)—O(3)	2.159 (8)	Si(2)—F(3)	1.668 (7)
O(1^{i})—Mn(1)—O(1^{ii})	88.5 (5)	F(1)—Si(1)—F(1^{iii})	89.4 (4)
O(1^{i})—Mn(1)—O(1^{iii})	180	F(1^{iii})—Si(1)—F(1^{vi})	180
O(2)—Mn(2)—O(2^{iv})	89.2 (6)	F(2)—Si(2)—F(2^{iv})	89.9 (5)
O(3)—Mn(2)—O(3^{v})	87.2 (6)	F(3)—Si(2)—F(3^{v})	91.1 (5)
O(2^{iv})—Mn(2)—O(3^{iv})	91.4 (4)	F(2)—Si(2)—F(3)	89.4 (3)
O(2^{iv})—Mn(2)—O(3)	92.2 (4)	F(2^{iv})—Si(2)—F(3)	89.7 (3)
O(2^{iv})—Mn(2)—O(3^{v})	178.5 (4)	F(2^{v})—Si(2)—F(3)	179.1 (4)

Symmetry codes: (i) $y, -x + y, -z$; (ii) $-x, -y, -z$; (iii) $-y, x - y, z$; (iv) $-x + y, 1 - x, z$; (v) $1 - y, 1 + x - y, z$; (vi) $y, -x + y, 1 - z$.

Table 3. *Contact distances (Å)*

O(1)···F(1^{i})	2.774 (9)	O(1)···F(3^{iii})	2.816 (13)
O(2)···F(2)	2.776 (8)	O(2)···F(1^{iv})	2.793 (13)
O(3)···F(3^{ii})	2.808 (8)	O(3)···F(2^{v})	2.727 (11)

Symmetry codes: (i) $-y, x - y, z$; (ii) $x, y, 1 + z$; (iii) $1 - y, 1 + x - y, z$; (iv) $x - y, x, 1 - z$; (v) $-x, 1 - y, 1 - z$.

Table 4. *Observed and calculated structure factors for 'weak' h0l and 0kl reflections (×10)*

h	*k*	*l*	F_o	F_c	ΔF	*h*	*k*	*l*	F_o	F_c	ΔF
0	0	2	35	52	17	1	0	5	60	67	7
1	0	2	26	37	11	4	0	5	27	24	3
0	2	2	55	48	7	6	0	5	32	23	9
0	3	2	32	25	7	0	2	5	39	45	6
0	6	2	39	28	11	2	0	6	73	54	19
0	8	2	45	16	29	4	0	6	26	50	24
0	4	3	29	13	16	5	0	6	44	29	15
0	0	4	55	83	28	0	4	6	42	22	20
2	0	4	32	29	3	0	0	7	86	86	0
3	0	4	59	65	6	0	1	7	51	49	2
6	0	4	28	10	18	0	0	8	78	91	13
8	0	4	33	34	1	2	0	9	30	25	5
0	3	4	73	70	3	0	4	9	49	37	11
0	4	4	47	53	6	0	0	10	99	111	12
0	0	5	40	67	27	0	1	10	112	82	30

Note: $R = \Sigma\Delta F/\Sigma F_o = 366/1475 = 0.248$.

A scan speed of 2° min^{-1} and a scan width of $(1.4 + 0.35\tan\theta)°$ were used. Out of 451 independent reflections possible within $(\sin\theta)/\lambda < 0.60$, 349 were actually observed $[I > 3\sigma(I)]$ and were reduced to F_o values after absorption and other corrections. The low reflections-to-parameters ratio comes from the high Laue symmetry imposed on the diffraction due to twinning, not from limitations in measurement. 149 reflections (99%), 103 (68%) and 97 (65%) of the possible data (451 reflections in all) were measured for the index conditions $-h + k + l = 3n$, $3n + 1$ and $3n - 1$, respectively. All computations were made on a personal computer using local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1098). Services for accessing these data are described at the back of the journal.

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