

$N_{C'-A} = P$  but  $n/m' = n_o/m'$  in (A2). For  $VEC_A > 8$ ,  $N_{C'-A} = P - [1 + 'x']C'C'/2$  and  $n/m' = n_o/m'$  in (A2). The definitions for equipartition given by both of us are very different and may lead to diverging results (for GeS there is non-equipartition while calculating  $PP_m$ , whereas equipartition is possible according to the calculation of  $C'AC'$ ). A strict correlation between (16) and (A1) in the case of structures with  $VEC_A \neq 8$  is therefore tedious and may lose any practical sense.

A simplified case is given by equation (16'). For this equation,  $k$  and  $a$  coincide, since no more than one  $C'AC'$  or two central cations through each apex are expected in the complexes and:

$$C'AC' = PP_m - AA(n_o/m') - 'x'C'C'. \quad (A3)$$

$C'AC'$  may also be derived from the general equation of  $PP_m$  (15) with (A3) and becomes incidently a general parameter!

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## A New Example of an Arrangement of Antiphase Domains: Investigation by Neutron Diffraction of Deuterated Manganese Fluosilicate

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### Abstract

Manganese hexafluorosilicate–deuterium oxide (1/6),  $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$ ,  $M_r = 317$ , hexagonal,  $P\bar{3}$  (No. 147),  $a = 9.678$  (11),  $c = 9.820$  (9) Å,  $V = 797$  (3) Å<sup>3</sup>,  $Z = 3$ ,  $D_x = 1.96$  g cm<sup>-3</sup>,  $\lambda = 0.8307$  (5) Å,  $\mu = 0.50$  cm<sup>-1</sup> (evaluated),  $F(000) = 32.38$ , room temperature, final  $R(F) = 0.118$  for 400 observed reflections. Above 244 K  $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$  is described by fitting the structural models previously proposed for  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  above 300 K and  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  above 240 K. The structure consists of an arrangement of domains of different octahedra orientations with equal volumes. The water molecule is perfectly determined: the D—O bond distances are 0.9287 (8) and 0.9351 (8) Å, and the D—O—D angle is 109.3 (1)°. The lengths of the H bonds are 1.852 (2) and 1.814 (2) Å for D(1)···F and D(2)···F, respectively. When the temperature is lowered from about 244 K,  $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$  undergoes a structural phase transition with hysteresis of ~4 K.

### Introduction

In the fluosilicates  $M\text{SiF}_6 \cdot 6\text{D}_2\text{O}$  ( $M$  = divalent metal), the two complex ions  $M(\text{H}_2\text{O})_6^{2+}$  and  $\text{SiF}_6^{2-}$

form octahedra, with a distribution between two orientations around the threefold axis. In the case of Co, Ni and Zn at room temperature, the disordered structure (space group  $R\bar{3}$ ) described by Ray, Zalkin & Templeton (1973) has recently been corroborated by neutron diffraction on  $\text{CoSiF}_6 \cdot 6\text{D}_2\text{O}$  at room temperature (Chevrier & Saint-James, 1990). The F sites of the disordered  $\text{SiF}_6$  octahedra were found to have equal occupation probability (0.5/0.5), instead of 0.43/0.57 as previously determined. In the case of  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  ( $T \geq 300$  K) and  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  ( $T \geq 240$  K) the superstructure reflections, inconsistent with the structural models (space group  $R\bar{3}m$ ) described by Syoyama & Osaki (1972) and Hamilton (1962), were explained in terms of an arrangement of antiphase domains. In the crystal, the juxtaposition of domains (space group  $P\bar{3}$ ) with two different octahedra orientations related by pseudo mirrors (11.0) and with equal volumes is sufficient to explain all the experimental observations. In  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  these domains are extensive (Jehanno & Varret, 1975; Chevrier & Jehanno, 1979), whereas in  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  the domain size is a function of temperature (Chevrier, Hardy & Jehanno, 1981).

At room temperature superlattice reflections are also observed for the  $\text{MnSiF}_6 \cdot 6\text{H}_2\text{O}$  fluosilicate, and

were first explained in space group  $P\bar{3}m1$  (Kodera, Torri, Osaki & Watanabe, 1972). At lower temperatures, and for the majority of these compounds (Chevrier & Saint-James, 1990), a structural phase transition is observed. The transition was first reported by Tsujikawa & Couture (1955) at about 223 K with hysteresis of 10 K; it has also been found at 225 K (Skjæveland & Svare, 1974), around 225 K with a large hysteresis ( $\sim 30$  K) (Jehanno & Varret, 1975) and at 236.2 K (Weir, Halstead & Staveley, 1985). The resulting structure is monoclinic ( $P2_1/c$ ) as determined by Syoyama & Osaki (1972) for  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ .

In this context, the study of  $\text{MnSiF}_6 \cdot 6\text{H}_2\text{O}$  seemed of great importance in order first to determine precisely the structural relationship between the Mg, Mn and Fe compounds, with special attention to hydrogen bonding and, secondly, to follow the phase transition in detail.

### Experimental

Large crystals of the title compound, with an estimated deuteration rate of 60–80%, were prepared according to the technique described previously (Chevrier & Saint-James, 1990). Transparent white prism ( $2.2 \times 3 \times 2.5$  mm); neutron four-circle P110 diffractometer, Orphée reactor (CEN-Saclay), Cu(220) monochromator,  $\lambda = 0.8307(5)$  Å, 14 centered reflections for lattice parameters and orientation matrix ( $29 \leq 2\theta \leq 35^\circ$ ), space group  $P\bar{3}$ . Data collection at 295 K,  $3 \leq 2\theta \leq 75^\circ$ ,  $\omega$ -step scans [35 steps, 3–8 s per step as a function of  $I/\sigma(I)$ ] of scan widths according to the instrumental resolution ( $8 - 27\tan\theta + 44\tan^2\theta$ ) $^\circ$ ; standard reflections (03.0 and 00.3) stable over 10 days within 5% (no decay or crystal movement); index range  $h - 14$  to 14,  $k 0$  to 14,  $l - 14$  to 0, 2664 reflections measured, integrated intensities determined from resolution-adapted profile measurement of the peaks; background determined with an average of the first and the last six steps of each side; 1024 unique reflections ( $R_{\text{int}} = 0.051$ ) of which 400 with  $F^2 \geq 2\sigma(F^2)$  considered observed; no absorption correction; isotropic extinction correction by the method of Zachariasen (1967),  $g = 0.31(5)$ . Full-matrix least-squares refinement based on  $F^2$ ;  $R(F) = 0.118$ ,  $R(F^2) = 0.122$ ,  $S = 4.32$  for 45 parameters,  $(\Delta/\sigma)_{\text{max}} < 0.02$ . Computer programs used in the refinement: *XFLS* (Busing, Martin & Levy, 1977) and *XFLS* adapted to the treatment of antiphase domains. Computer used: Convex C1-XP. Neutron-scattering lengths:  $b(\text{Mn}) = -3.73$ ,  $b(\text{Si}) = 4.149$ ,  $b(\text{F}) = 5.65$ ,  $b(\text{O}) = 5.805$  and  $b(\text{D}) = 6.674$  fm.

For the temperature-dependent study, five reflections (30.0), (11.1), (22.3), (2.5 2.5 .3) and (33.3) were followed between 233 and 263 K in variable steps

adapted to the variation of intensity, using a close-cycle refrigerator;  $\omega$ -step scans (35 steps, 6 s per step), scan width  $\sim 0.13^\circ$ ; time between each temperature change: 10 min.

### Structure determination

For  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  we have already proposed a structure model based on a periodic alternation of elements of the low-temperature ( $P2_1/c$ ) structure (Chevrier & Jehanno, 1979): in this way a commensurate periodic arrangement of domains is found. The structure is described with a hexagonal cell (space group  $P\bar{3}$ ) consisting of one octahedron of *A* orientation and two octahedra of *B* orientation [the *A* and *B* orientations are related by the pseudo-mirror planes (11.0)] for the  $\text{O}^{2-}$  anions, and the opposite for the  $\text{F}^-$  anions [domain (I)]. Furthermore, these pseudo mirrors involve the presence of other domains where the state is opposite [domain (II)]. In a diffraction experiment, the whole crystal contributes in a coherent manner to the fundamental reflections ( $-h + k + l = 3n$ ). However, because of the lack of any periodic arrangement of the two domains (I) and (II), an incoherent superposition of the diffraction intensities for the superlattice reflections ( $-h + k + l = 3n \pm 1$ ) results (Chevrier & Jehanno, 1979).

In the case of  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ , there are also two types of domain, but one ordered domain equivalent to domain (I) of  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  consists of an alternation along the hexagonal *c* axis of two types of areas, *a* and *b*, with one orientation of *A* octahedra and two orientations of *B* octahedra; the two hexagonal nets are then translated by  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ . In addition, the size of these domains [(I) and (II)] is a function of temperature (Chevrier *et al.*, 1981).

Above 244 K  $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$  exhibits the same behaviour as  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ : both main and superlattice reflections always keep the same peak shape when the temperature is decreased. In addition, the superlattice peaks are in perfect agreement with the condition  $-h + k + l = 3n \pm 1$ . The existence of mirror planes (11.0) is confirmed.

For these reasons, the model already used for  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  can be applied to the Mn compound. In each ordered domain, built from the low-temperature structure (monoclinic cell  $\mathbf{a}_m$ ,  $\mathbf{b}_m$ ,  $\mathbf{c}_m$ ; space group  $P2_1/c$ ), the antiphase boundaries cross  $\mathbf{a}_m$  at  $\pm \frac{1}{4}$  and the antiphase translation is  $(\mathbf{b}_m + \mathbf{c}_m)/2$  (Fig. 1). To calculate structure factors, we need first to consider the notation of Chevrier & Jehanno (1979) and Chevrier *et al.* (1981). In this notation,  $F_A$  is the form factor of 'right' octahedra  $\text{Mn}(\text{D}_2\text{O})_6^{2+}$ ,  $F_B$  is the form factor of 'left'  $\text{Mn}(\text{D}_2\text{O})_6^{2+}$  octahedra,  $F'_A$  is the form factor of 'right'  $\text{SiF}_6^{2-}$  octahedra,  $F'_B$  is the form factor of 'left'  $\text{SiF}_6^{2-}$  octahedra,  $F_{AB'} = F_A$

+  $F_B \exp[-2i\pi(1/2)]$ ,  $F_{BA'} = F_B + F_A \exp[-2i\pi \times (1/2)]$ , the quantity  $x$  is the volumetric proportion of ordered domains with two 'right'  $\text{Mn}(\text{D}_2\text{O})_6^{2+}$  octahedra and one 'left'  $\text{Mn}(\text{D}_2\text{O})_6^{2+}$  octahedron (and two 'left'  $\text{SiF}_6^{2-}$  octahedra and one 'right'  $\text{SiF}_6^{2-}$  octahedron), and the quantity  $(1-x)$  is the volumetric proportion of ordered domains where the situation is opposite. For the first domain, the structure factor is then (Fig. 1):

$$F_1 = F_{AB'} + F_{BA'} \{ \exp[-2i\pi(-h+k+l)/3] + \exp[-2i\pi(h-k-l)/3] \}$$

and for the second:

$$F_2 = F_{AB'} \{ 1 + \exp[-2i\pi(-h+k+l)/3] \} + F_{BA'} \exp[-2i\pi(h-k-l)/3].$$

The structure factor squared for the basic reflections ( $-h+k+l=3n$ ) is

$$F^2 = [xF_1 + (1-x)F_2]^2$$

$$F^2 = [x(F_{AB'} + 2F_{BA'}) + (1-x)(2F_{AB'} + F_{BA'})]^2$$

$$F^2 = [(2-x)F_{AB'} + (1+x)F_{BA'}]^2,$$

and for the superlattice reflections ( $-h+k+l=3n \pm 1$ ), without periodic alternation of the domains (I) and (II),

$$F^2 = xF_1^2 + (1-x)F_2^2$$

$$F^2 = x(F_{AB'} - F_{BA'})^2 + (1-x)(F_{AB'} + F_{BA'})^2$$

$$F^2 = (F_{AB'} - F_{BA'})^2.$$

For these superlattice reflections, a coherent superposition of the diffraction intensities leads to the structure factor,

$$F = [xF_1 + (1-x)F_2]$$

$$= (F_{AB'} - F_{BA'}) [\frac{1}{2}(1+x) + i(3^{1/2}/2)(1-x)]$$

and in this way to the expression of the structure factor squared,

$$F^2 = (F_{AB'} - F_{BA'})^2 (1 + x^2 - x) = y(F_{AB'} - F_{BA'})^2,$$

with  $\frac{3}{4} \leq y \leq 1$  when the volumetric proportion  $x$  varies between 0 and 1;  $y$  characterizes a 'rate of coherence'.

Initially, we tested the supergroup  $R\bar{3}m$ , which does not account for the superlattice reflections. We started from the Hamilton atomic positions for  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  (Hamilton, 1962) and obtained a reliability factor  $R(F) = 0.048$  using the 233 basic reflections with  $F^2 \geq 2\sigma(F^2)$ . The atomic positions and equivalent isotropic thermal parameters are shown Table 1. Then, secondly, we applied the model described before involving the extra parameter  $y$ , which characterizes the 'rate of coherence' between the two ordered [(I) and (II)] domains and leads to the expression  $F^2 = y(F_{AB'} - F_{BA'})^2$  for the

superlattice reflections. We started again from the atomic positions determined in space group  $R\bar{3}m$  (average structure) and obtained, using an adapted *XFLS* program, an  $R(F)$  factor of 0.118 for the 400 reflections with  $F^2 \geq 2\sigma(F^2)$ . The two parameters  $x$  and  $y$  are found to be 0.49 (2) and 0.73 (2), respectively.

## Discussion

The atomic positions and equivalent isotropic thermal parameters are shown Table 1, and bond distances and angles are given in Table 2.\* The use of neutron diffraction enabled the determination of the positions of the deuterium atoms (and thus the conformation of the water molecules) and the rate of deuteration of the crystal. The refinement confirms the estimated value from the preparation of the compound: 67 (1)% of D. Furthermore, the parameter  $x$  indicates the existence of mirrors (11.0), which are statistically distributed, and the parameter  $y$  shows a coherent superposition of the diffraction intensities for the superlattice reflections [ $y = 0.73$  (2) in comparison with the ideal value of  $\frac{3}{4}$ ].

\* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53709 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

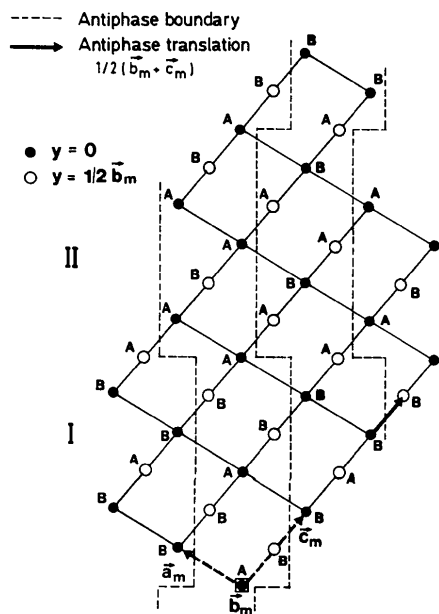


Fig. 1. Projection onto the  $1\bar{2}.0$  plane of the ideal structure of manganese fluosilicate above 244 K (only one octahedron type is drawn with its two A and B orientations). (I) is an antiphase domain in which there are two orientations of the B octahedra and one orientation of the A octahedra, and (II) is an antiphase domain in which the distribution of orientations is opposite.

Table 1. Atomic parameters and equivalent isotropic temperature factors with estimated standard deviations in parentheses

$$U_{eq} = \frac{1}{3}\{U(3,3) + \frac{2}{3}[U(1,1) + U(2,2) - U(1,2)]\}.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Supergroup $R\bar{3}m$				
Mn	0	0	0	0.0267
Si	0	0	0.5	0.0222
F	-0.1304 (2)	-0.1511 (2)	0.4013 (2)	0.0361
O	0.0668 (3)	0.2037 (2)	0.1307 (2)	0.0492
D(1)	0.0438 (5)	0.1917 (5)	0.2233 (3)	0.0601
D(2)	0.1372 (9)	0.3104 (4)	0.1121 (3)	0.0507
Group $P\bar{3}$ ('orientational' periodic antiphase)				
Mn	0	0	0	0.0271
Si	0	0	0.5	0.0226
$F_G$	0.1511 (7)	0.1304 (7)	0.4013 (2)	0.0365
$F_D$	-0.1304 (7)	-0.1511 (7)	0.4013 (5)	0.0365
$O_G$	0.0668 (9)	0.2036 (7)	0.1307 (5)	0.0497
$O_D$	-0.2036 (7)	-0.0668 (9)	0.1307 (5)	0.0497
$D(1)_G$	0.0437 (17)	0.1919 (16)	0.2232 (10)	0.0608
$D(1)_D$	-0.1919 (16)	-0.0437 (17)	0.2232 (10)	0.0608
$D(2)_G$	0.1404 (38)	0.3105 (12)	0.1120 (11)	0.0554
$D(2)_D$	-0.3105 (12)	-0.1404 (38)	0.1120 (11)	0.0554

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with estimated standard deviations in parentheses

Mn—O	2.162 (2)	O—Mn—O	88.4 (1)
Si—F	1.681 (1)	O—Mn—O'	91.6 (1)
O—D(1)	0.929 (1)	Mn—O—D(1)	117.3 (3)
O—D(2)	0.935 (1)	Mn—O—D(2)	120.4 (2)
O...F <sub>  </sub>	2.771 (2)	F—Si—F	90. (2)
O...F <sub>⊥</sub>	2.693 (3)	F—Si—F'	89.9 (1)
D(1)...F <sub>  </sub>	1.852 (2)	D(1)—O—D(2)	109.3 (1)
D(2)...F <sub>⊥</sub>	1.814 (2)	F...O...F	114.9 (1)
		O—D(1)...F	169.8 (12)
		O—D(2)...F	155.5 (6)

The manganese atom is octahedrally coordinated by water molecules. If the conformation of the water molecule is perfect [O—D(1) 0.929 (1), O—D(2) 0.935 (1)  $\text{\AA}$  and D(1)—O—D(2) 109.3 (1) $^\circ$ ] with its plane almost within the threefold axis [deviation 9.2 (1.4) $^\circ$ ], the elongation of the octahedra [(O—Mn—O') — (O—Mn—O)  $\leq$  3.2 $^\circ$ ] shows a significant deformation.

The shape of the F octahedra is almost regular [(F—Si—F) — (F—Si—F')  $\leq$  0.2 $^\circ$ ] and the bond length obtained from this neutron study [Si—F 1.681 (1)  $\text{\AA}$ ] is in perfect agreement with those obtained for the other  $M\text{SiF}_6 \cdot 6\text{H}_2\text{O}$  compounds [the average value for  $M = \text{Co}$  (Ray *et al.*, 1973; Chevrier & Saint-James, 1990),  $M = \text{Mg}$  (Chevrier & Jehanno, 1979) and  $M = \text{Fe}$  (Hamilton, 1962; Chevrier *et al.*, 1981) is 1.680  $\text{\AA}$ ].

To align the Mn—O and Si—F bonds with the pseudo-mirror planes, the related  $\text{Mn}(\text{D}_2\text{O})_6^{2+}$  and  $\text{SiF}_6^{2-}$  octahedra have to be turned by 11.2 and 22.7 $^\circ$ , respectively. The observed deviation of the Mn—O direction is more important than for  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  (9.7 $^\circ$ ), whereas the Si—F orientation is closer to the mirror planes (26.2 $^\circ$ ) (Hamilton, 1962; Chevrier *et al.*, 1981).

The hydrogen bonds D(1)...F and D(2)...F between the two  $\text{Mn}(\text{D}_2\text{O})_6^{2+}$  and  $\text{SiF}_6^{2-}$  ions are parallel and perpendicular, respectively, to the threefold axis. The bond lengths (Table 2) are of the same order as those given by Hamilton (1962) for  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  and those obtained for  $\text{CoSiF}_6 \cdot 6\text{D}_2\text{O}$  (Chevrier & Saint-James, 1990). It is possible to calculate a well-defined plane consisting of Mn, F, D(1), D(2) and O sites [maximum deviation from the plane -0.13 (4)  $\text{\AA}$  for D(2)]. The plane of the water molecule is inclined by 13 (2) $^\circ$  to this plane. The Mn atom is separated from the  $\text{D}_2\text{O}$  plane by 0.43  $\text{\AA}$ .

### Transition temperature

With slow temperature variations between the high- ( $P\bar{3}$ ) and low-temperature phases ( $P2_1/c$ ), a very small hysteresis was found for the transition: 242.2 (1) K with decreasing temperature and 245.9 (1) K with increasing temperature. Fig. 2 shows an example of a very good agreement for two measurements on the  $P\bar{3}$ -allowed (11.1) and -forbidden (2.5 2.5 .3) reflections.

The phase transition for our deuterated sample ( $\sim 244$  K) is again at a higher temperature than that reported for the undeuterated compound ( $\sim 225$  K); this significant difference ( $\Delta T \approx 19$  K) is of the same order of magnitude as that for  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$  [ $\Delta T \approx 17$  K (Ghosh, Chatterjee, Das, Dutta Roy &

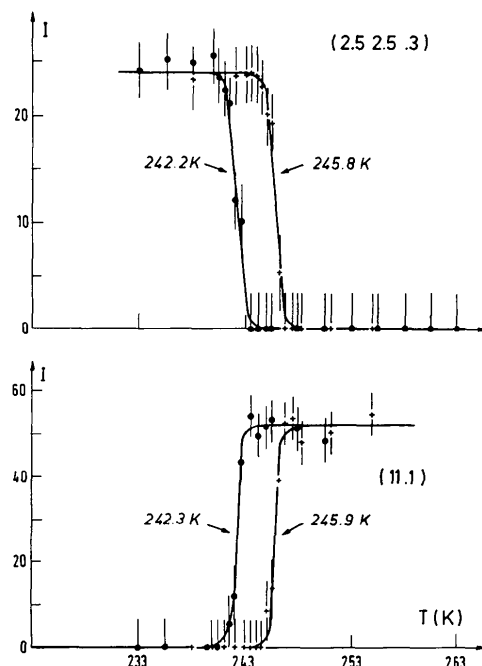


Fig. 2. Intensity of (2.5 2.5 .3) and (11.1) peaks in the high-temperature phase of  $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$  as a function of temperature.

Pal, 1977),  $\Delta T \approx 15$  K (Chevrier & Saint-James, 1990)]. Another important effect of the deuteration is the temperature width of hysteresis: 3.6 K for a 67 (1)% deuteration compared with 10–30 K for  $\text{MnSiF}_6 \cdot 6\text{H}_2\text{O}$ .

### Concluding remarks

From Table 1 it can be seen that the atomic positions are perfectly determined in the average structure (space group  $R\bar{3}m$ ). Therefore the bond distances and the angles between atoms are already well known with this approximation. The 'orientational' antiphase model explains the unusual features of the structure (when the space group  $P\bar{3}m1$  with an  $R$  factor of  $R(F) = 0.41$  cannot be used), *i.e.* the existence of superlattice reflections and statistical mirrors.

We now have three correlated models to describe the structure of the  $M$  fluosilicates ( $M = \text{Mg}, \text{Mn}, \text{Fe}$ ). In going from  $\text{Mg}^{2+}$  to  $\text{Fe}^{2+}$ , the two ordered domains become slightly more complex. Studies on  $\text{Mg}_{1-x}\text{Fe}_x\text{SiF}_6 \cdot 6\text{D}_2\text{O}$  are now in progress in order to understand this evolution.

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## Structures and Phase Transition in the Ferroelectric Crystal of Pentakis-(methylammonium) Undecachlorodibismuthate(III): $[\text{NH}_3(\text{CH}_3)]_5\text{Bi}_2\text{Cl}_{11}$

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### Abstract

$[\text{NH}_3(\text{CH}_3)]_5\text{Bi}_2\text{Cl}_{11}$ ,  $M_r = 968.3$ ; for  $T = 294$  K, orthorhombic,  $Pca2_1$ ,  $a = 12.924$  (2),  $b = 14.034$  (2),  $c = 15.364$  (2) Å,  $V = 2786.6$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.31$  g cm<sup>-3</sup>,  $R = 0.032$  ( $wR = 0.033$ ) for 2197 unique reflections; for  $T = 349$  K, orthorhombic,  $Pcab$ ,  $a = 13.003$  (2),  $b = 14.038$  (3),  $c = 15.450$  (2) Å,  $V = 2820.1$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.28$  g cm<sup>-3</sup>,  $R = 0.044$  ( $wR = 0.037$ ) for 1219 unique reflections. In the high-temperature phase ( $T = 349$  K),  $\text{Bi}_2\text{Cl}_{11}^{5-}$  anions are centrosymmetric biotahedra and three of the five methylammonium cations are disordered. In the ferroelectric phase ( $T = 294$  K),  $\text{Bi}_2\text{Cl}_{11}$  biotahedra are severely distorted and two of the methylammo-

nium cations are still disordered. The packing is strengthened by N—H...Cl hydrogen bonds between anions and cations. Ordering of the methylammonium cations in the ferroelectric phase leads to new hydrogen-bond formation which is responsible for the high dipolar properties of this compound.

### Introduction

Alkylammonium halogenoantimonate(III) and bismuthate(III) salts show a number of interesting properties arising from the possibility of rotational motion of the cations. Most of these compounds display a sequence of phase transitions and some