

Table 2. *The atomic positional and thermal parameters of SrO·2Al<sub>2</sub>O<sub>3</sub>*Positional error:  $\pm 0.0010$ . Temperature factor error:  $\pm 0.002$ .

	Sr	O(1)	Al(1)	Al(2)	O(2)	O(3)	O(4)
<i>X</i>	0	0	0.1686	0.1212	0.1188	0.1246	0.1899
<i>Y</i>	0.8099	0.5253	0.0873	0.4400	0.0374	0.2582	0.4446
<i>Z</i>	0.25	0.25	0.2939	0.2644	0.5442	0.1703	0.5965
$\beta_{11}$	0.00192	0.00151	0.00127	0.00138	0.00197	0.00260	0.00200
$\beta_{22}$	0.00332	0.00209	0.00267	0.00267	0.00363	0.00234	0.00451
$\beta_{33}$	0.00969	0.01169	0.00788	0.00852	0.00759	0.00698	0.00646
$\beta_{12}$	0	0	0.00018	-0.00001	0.00066	-0.00015	0.00012
$\beta_{13}$	0.00054	0.00051	0.00035	0.00072	0.00123	-0.00094	0.00062
$\beta_{23}$	0	0	0.00012	-0.00063	0.00050	-0.00074	-0.00052

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**An X-ray study of the low temperature form of MgSiF<sub>6</sub>·6H<sub>2</sub>O and the relation between the crystal lattices of low- and high-temperature forms.** By S. SYOYAMA and K. OSAKI, *Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto, Japan*

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A phase transition was found in MgSiF<sub>6</sub>·6H<sub>2</sub>O at about 25°C. The crystal lattices of the low- and high-temperature forms are closely related, and the space groups are *P*<sub>2</sub><sub>1</sub>/*c* and *R* $\bar{3}$ *m* respectively. The crystal structure of the low-temperature form is presented.

## Introduction

A number of hexahydrates of the type MGX<sub>6</sub>·6H<sub>2</sub>O have been reported to have a CsCl-like structure with one formula unit in the rhombohedral cell (Wyckoff, 1965), but atomic coordinates have been given for only NiSnCl<sub>6</sub>·6H<sub>2</sub>O (Pauling, 1930) and FeSiF<sub>6</sub>·6H<sub>2</sub>O (Hamilton, 1962). For the latter the crystal symmetry observed was *R* $\bar{3}$ *m*, in contrast to *R* $\bar{3}$  for the former, and was interpreted by Hamilton to be a result of disorder on a microscopic scale.

A phase transition in this series has been found by optical methods for MnSiF<sub>6</sub>·6H<sub>2</sub>O (Tsujikawa & Couture, 1955) and a monoclinic symmetry has been suggested for the low-temperature form of Mn- and CoSiF<sub>6</sub>·6H<sub>2</sub>O on the basis of the X-ray photographs taken at liquid nitrogen temperatures (Kodera, Torii, Osaki & Watanabé, 1972).

A description of some extra reflexions in an early report by Hassel & Salvesen (1927) led us to study MgSiF<sub>6</sub>·6H<sub>2</sub>O in detail, in the hope of finding a low-temperature form existing even at room temperature.

## Structure of the low-temperature form

Crystals of the low-temperature form were obtained by adding powdered MgCO<sub>3</sub> to an aqueous solution of H<sub>2</sub>SiF<sub>6</sub>

and evaporating the solution at about 20°C. Most of them were twinned, and the single crystals used for the X-ray analysis were first selected under a polarizing microscope and then checked by taking Weissenberg photographs. The single crystals became twinned very easily with the application of small uneven pressure and had to be handled with particular care.

Crystal data; MgSiF<sub>6</sub>·6H<sub>2</sub>O, space group *P*<sub>2</sub><sub>1</sub>/*c*, lattice constants, *a* = 6.460, *b* = 9.524, *c* = 8.460 Å (all  $\pm 0.005$  Å),  $\beta$  = 99° 24'  $\pm$  3', *D*<sub>o</sub> = 1.77, *D*<sub>c</sub> = 1.780 g.cm<sup>-3</sup>, *Z* = 2.

Intensities recorded with Cu *K* $\alpha$  radiation on Weissenberg photographs taken about the *b* axis (0 to 6 layers) were estimated visually. An absorption correction ( $\mu$ *r* = 2.0) was applied assuming a spherical shape for the crystal. The number of independent reflexions obtained was 709.

The structure was solved using three-dimensional Patterson and Fourier syntheses and was refined by full-matrix least-squares calculations to an *R* value of 0.138, at which stage the refinement was terminated because of the unfavourable shape of the crystals used. The structure obtained consists of octahedral ions [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> and [SiF<sub>6</sub>]<sup>2-</sup> arranged in a slightly distorted CsCl structure. Fig. 1 shows the arrangement of the two ions in the *b*-axis projection. The atomic coordinates are given in Table 1 and correspond closely to those given for FeSiF<sub>6</sub>·6H<sub>2</sub>O by Hamilton if the

latter are transformed to the appropriate coordinate system. Fig. 2 is a projection along the pseudo-trigonal axis, corresponding with Fig. 2 of Hamilton (1962), and shows that the  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  ions in this case are surrounded by  $[\text{SiF}_6]^{2-}$  ions with two different orientations. The structure here determined explains the appearance of 'six inequivalent  $\text{Mn}^{2+}$  ions' in a p.m.r. study by Arakawa (1954) if it is assumed that the specimen used there consisted of threefold twins of the low temperature form.

Table 1. Positional and thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Mg	0.0	0.0	0.0	0.81
Si	0.500	0.500	0.0	0.60
O(1)	0.267	-0.131	0.050	2.12
O(2)	0.186	0.173	0.090	1.90
O(3)	-0.064	-0.036	0.230	1.66
F(1)	0.380	0.140	0.412	1.42
F(2)	0.275	-0.085	0.472	1.52
F(3)	0.549	-0.055	0.323	1.33

#### Relation between the crystal lattices of low- and high-temperature forms

Crystals obtained at about 30°C were found, from Weissenberg photographs, to have a rhombohedral lattice containing one formula unit with  $a_h = 6.43 \text{ \AA}$ ,  $\alpha = 96^\circ 3'$ . The space group observed is  $R\bar{3}m$ , which is the same as that observed by Hamilton for  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  and the crystals may be expected to have a disordered structure of a type similar to that of the latter.

The lattice vectors corresponding to the low-temperature form can be derived from those for the high-temperature form by the transformation matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 1 & 1 \end{bmatrix}$$

from which the following relations are derived,

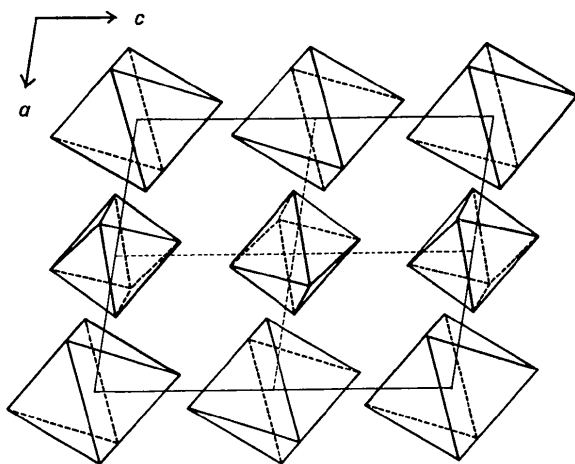


Fig. 1. The arrangement of cations,  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  (larger octahedra), and anions  $[\text{SiF}_6]^{2-}$  (smaller octahedra), in  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  as viewed down the *b* axis.

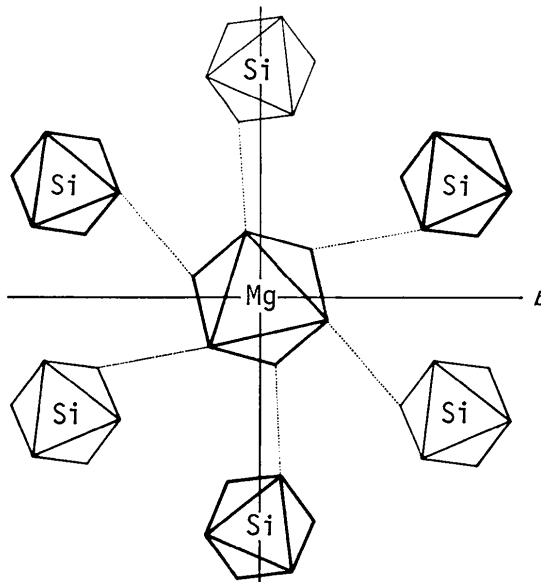


Fig. 2. The arrangement of anions surrounding a cation in  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  as viewed down the pseudo-trigonal axis. The two anions directly above and below the central cation have been omitted.

$$a' = a_h, \quad b' = 2a_h \sin\left(\frac{\alpha}{2}\right),$$

$$c' = 2a_h \cos\left(\frac{\alpha}{2}\right), \quad \cos \beta' = \frac{\cos \alpha}{\cos\left(\frac{\alpha}{2}\right)}$$

where  $a_h$  and  $\alpha$  are the lattice constants of the high-temperature form and  $a'$ ,  $b'$ ,  $c'$  and  $\beta'$  are those corresponding to the low-temperature form. The calculated values of  $a'$ ,  $b'$ ,  $c'$  and  $\beta'$  are 6.43, 9.56, 8.60 Å and  $99^\circ 5'$  respectively, which are close to the observed values for the low-temperature form.

The transition point between the low- and high-temperature forms was found, by using a differential scanning calorimeter (DSC), to be about 25°C.

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