

Structure Reinvestigation by Neutron Diffraction of Deuterated Magnesium Fluosilicate; Influence of the Metal Cation

G. CHEVRIER

Laboratoire Léon Brillouin (CEA-CNRS), CEN-Saclay,
91191 Gif-sur-Yvette Cedex, France

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The crystal structure of deuterated magnesium fluosilicate hexahydrate at 313 K has been refined using neutron diffraction ($F(000) = 40.38$, $D_x = 1.85 \text{ g cm}^{-3}$, $\mu = 0.30 \text{ cm}^{-1}$ (evaluated), space group $P\bar{3}$ (147), trigonal, $Z = 3$, $a = 9.556$ (15) Å, $c = 9.738$ (19) Å, $V = 770$ (4) Å³). A final R -factor of 0.117 was obtained with 646 observed structure factors. The structure of the high-temperature phase first determined by X-ray diffraction is confirmed: it presents an arrangement of domains of different octahedra orientations with equal volume parts. With decreasing temperature, $\text{MgSiF}_6 \cdot 6\text{D}_2\text{O}$ undergoes a structural phase transition with an hysteresis of about 1.5 K. A comparison of the structure analysis of all M -fluosilicates indicates that the nature of the M^{2+} cation drives the deformation of the $(M(\text{H}_2\text{O})_6)^{2+}$ octahedra and the choice of the space group symmetry. © 1992 Academic Press, Inc.

Introduction

In the fluosilicates $M\text{SiF}_6 \cdot 6\text{H}_2\text{O}$ ($M =$ divalent metal), the octahedral complex ions $M(\text{H}_2\text{O})_6^{2+}$ and SiF_6^{2-} can be distributed between two orientations around the 3-fold axis (1-3).

In the case of Co, Ni, and Zn fluosilicates, at room temperature, a disorder occurs and the space group $R\bar{3}$ used by Ray *et al.* (4) was corroborated by neutron diffraction for $\text{CoSiF}_6 \cdot 6\text{D}_2\text{O}$: the two fluorine sites of the SiF_6^{2-} octahedra were found to be equally occupied (5).

Besides this, the presence of superstructure reflections first observed by X-ray diffraction on Mg, Mn, and Fe compounds (6) is inconsistent with the structure models proposed before (space group: $R\bar{3}m$) (2-7). Therefore, we were led to build other models: the crystals show the presence of do-

main (space group: $P\bar{3}$) with two different octahedra orientations related by pseudo-mirrors (11.0), and with equal volume parts. In the case of Mg and Mn fluosilicates ($T \geq 300 \text{ K}$ (8); $T \geq 244 \text{ K}$ (9)), these domains are of great extension, whereas in Fe-fluosilicates ($T \geq 240 \text{ K}$ (10)), their size is a function of temperature.

For the majority of these compounds, when passing into the low-temperature phase in decreasing the temperature, a twinning is obtained in the monoclinic space group $P2_1/c$: the monoclinic cell is built from the hexagonal one from the matrix calculation

$$\begin{pmatrix} \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\ 0 & 1 & 0 \\ -\frac{2}{3} & -\frac{1}{3} & \frac{2}{3} \end{pmatrix}$$

and each of the three twin-orientations, is

TABLE I
ATOMIC PARAMETERS AND ISOTROPIC EQUIVALENT
TEMPERATURE FACTORS

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)^a$
Mg	0	0	0	1.92 1.26
Si	0	0	0.5	1.64 1.05
F _L	-0.1317(6)	-0.1534(5)	0.3997(4)	2.75 3.13
F _R	0.1534(5)	0.1317(6)	0.3997(4)	2.75 3.13
O _R	0.0603(6)	0.1964(5)	0.1244(4)	3.23 4.01
O _L	-0.1964(5)	-0.0603(6)	0.1244(4)	3.23 4.01
D(1) _R	0.0349(10)	0.1870(9)	0.2187(6)	4.28
D(1) _L	-0.1870(9)	-0.0349(10)	0.2187(6)	4.28
D(2) _R	0.1358(17)	0.3044(6)	0.1066(6)	3.99
D(2) _L	-0.3044(6)	-0.1358(17)	0.1066(6)	3.99

Note. Bold type, neutron diffraction study; Roman type, X-ray diffraction study (1-8). F_A is then calculated from Mg, O_R, D(1)_R and D(2)_R, F_B from Mg, O_L, D(1)_L and D(2)_L, F_A from Si and F_R, and F_B from Si and F_L. Also in the structure, the two other units are translated by 2/3 1/3 1/3 and 1/3 2/3 2/3, each of them have different orientations according to their own ordered domain.

^a B_{eq} defined as $(8\pi^2/3) \cdot [u(3,3) + 4/3 \{u(1,1) + u(2,2) - u(1,2)\}]$.

TABLE II
BOND DISTANCES (Å) AND ANGLES (°) WITH
ESTIMATED STANDARD DEVIATIONS IN PAREN-
THESIS

Mg-O:	2.059 (2)	O-Mg-O:	88°9 (1)
Si-F:	1.686 (1)	O-Mg-O':	91°1 (1)
O-D(1):	0.943 (1)	Mg-O-D1:	123°0 (3)
O-D(2):	0.933 (1)	Mg-O-D2:	127°4 (4)
O...F :	2.775 (2)	F-Si-F:	89°8 (1)
O...F _⊥ :	2.688 (3)	F-Si-F':	90°2 (1)
D1...F :	1.842 (2)	D(1)-O-D2:	107°8 (1)
D2...F _⊥ :	1.810 (2)	F...O...F:	112°4 (1)
		O-D(1)...F:	169°8 (6)
		O-D(2)...F:	155°5 (6)

turned of 120°. The transition temperature is 300 K for Mg SiF₆ · 6H₂O (6-8), 240 K for FeSiF₆ · 6H₂O (6, 10), and 246 K (11), 230 K (12) for CoSiF₆ · 6H₂O, 223 K (13), 225 K (6, 14), and 236.2 K (15) for MnSiF₆ · 6H₂O. The substitution of H- by D-atoms increases slightly the values of these temperatures:

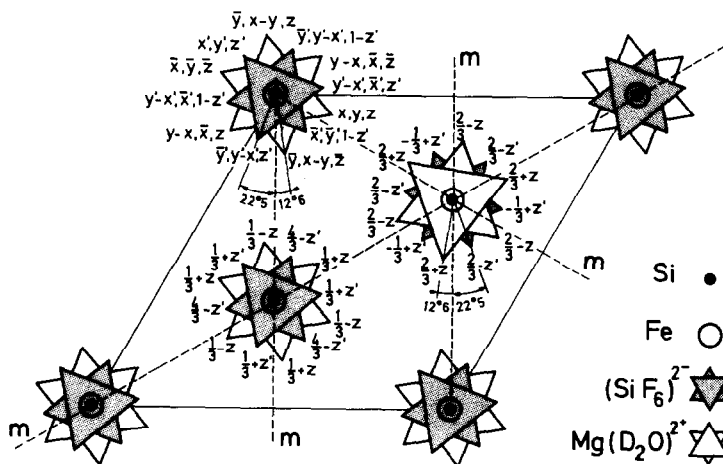


FIG. 1. Projection on the 00.1 plane of the cell corresponding to a domain where the structure factor is F_2 ; we can see the deviation and the orientation of $\text{Mg}(\text{D}_2\text{O})^{2+}$ and SiF_6^{2-} octahedra with the pseudo-mirrors (11.0) (deuterium atoms are not included so that to simplify the drawing). The atomic positions of Mg are 000, $\frac{2}{3} \frac{1}{3} \frac{1}{3}$, and $\frac{1}{3} \frac{2}{3} \frac{2}{3}$, and of Si, 00 $\frac{1}{2}$, $\frac{2}{3} \frac{1}{3} \frac{1}{3}$, and $\frac{1}{3} \frac{2}{3} \frac{1}{3}$. The atomic positions of O are $xyz\dots$ for a right orientation and $\bar{y}\bar{x}z\dots$ for a left one. For F they are respectively $\bar{y}'\bar{x}'z'$ and $x'y'z'$.

263 K (16), 261 K (5) for $\text{CoSiF}_6 \cdot 6\text{D}_2\text{O}$ and 244 K (9) for $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$.

We have undertaken a new neutron diffraction study at 313 K on $\text{MgSiF}_6 \cdot 6\text{D}_2\text{O}$ in order to determine precisely the H-positions in the structure. Furthermore, the phase transition was followed properly with the monitoring of special reflections.

Last, we report here an attempt to explain how the nature of the metallic cation affects the structural chemistry of these compounds.

Experimental

Large crystals of $\text{MgSiF}_6 \cdot 6\text{D}_2\text{O}$ with an estimated degree of deuteration of about 80% were obtained by a saturated solution technique, described elsewhere (5).

The neutron diffraction experiment was performed with a transparent white prism ($3 \times 2.2 \times 5.1$ mm) on the 4-circle diffractometer P110 at the Orphée Reactor (C.E.N.—Saclay), using a wavelength of $\lambda = 0.8307$ (5) Å.

The centering of 19 reflections gave the lattice parameters and the orientation matrix ($29^\circ < 2\theta < 37^\circ$). The reflection intensities were collected in the $3^\circ < 2\theta < 75^\circ$ range using ω -step scans (35 steps, 2 to 10 sec per step as a function of $I/\sigma(I)$). Then 2071 reflections were measured in the Miller index range: $0 \leq h \leq 13$, $\bar{13} \leq k \leq 13$, $0 \leq l \leq 14$. The intensity variation of the standard reflections (300) and (003) over 6 days was within 3%, indicating a good stability of the data measurement.

The integrated intensities were determined from resolution adapted profile measurement of the peaks: the background was calculated from an average of the first and the last six steps of each side; from the measured reflections, 1666 were independent ($R_{\text{int}} = 0.026$) and 646 with $F^2 \geq 3\sigma$ (F^2) were used in the refinement.

Due to the small linear absorption coefficient $\mu = 0.30 \text{ cm}^{-1}$ (estimated), we did

not perform an absorption correction. An isotropic extinction correction by the method of Zachariasen (17) led to $G = 0.248$ (20). The full matrix least square refinement method, based on F^2 was used. The final factors $R(F^2) = 0.135$ and $R(F) = 0.117$, the goodness of fit 5.46 for 45 parameters and $(\Delta/\sigma) \text{ max} < 0.02$ were obtained.

The computer program used in the refinement was XFLS (18) adapted to the treatment of antiphase domains and the computer was CONVEX C1-XP. The neutron scattering lengths were: $b_{\text{Mg}} = 0.5375 \times 10^{-12}$, $b_{\text{Si}} = 0.4149 \times 10^{-12}$, $b_{\text{F}} = 0.565 \times 10^{-12}$, $b_{\text{O}} = 0.5805 \times 10^{-12}$, and $b_{\text{D}} = 0.6674 \times 10^{-12} \text{ cm}$ (19).

The phase transition was followed between 297 and 313 K by the study of four reflections (23.3, 1.5 3.3, 13.3, and 03.3) with steps adapted to the variation of intensity using a close-cycle refrigerator. The intensities were computed as before from ω -step scans (35 steps, 2 to 6 sec per step) of width $\sim 0.07^\circ$. The time between each temperature change was chosen as 10 min.

Results and Discussion

The structural model developed before, involving a special arrangement of antiphase domains, leads us, with the same definitions described elsewhere (9) to a reliability factor $R(F) = 0.117$ for the 646 reflections with $F^2 \geq 3\sigma$ (F^2).

Let us now calculate the structure factors. With the same notation as before (8–10) we have

$$F_{AB'} = F_A + F_{B'} \exp[-2i\pi(\frac{1}{2})]$$

and

$$F_{BA'} = F_B + F_{A'} \exp[-2i\pi(\frac{1}{2})],$$

if F_A is the form factor of the “right” $\text{Mg}(\text{D}_2\text{O})_6^{2+}$ octahedra, F_B is the form factor of the “left” $\text{Mg}(\text{D}_2\text{O})_6^{2+}$ octahedra, $F_{A'}$ is the form factor of the “right” SiF_6^{2-} octahe-

dra, and F_B is the form factor of the "left" SiF_6^{2-} octahedra.

In that manner $F_1 = F_{AB'} + F_{A'B}$ $\{\exp[-2i\pi(-h + k + l)/3] + \exp[-2i\pi(h - k - l)/3]\}$ is the structure factor of the first ordered domain with one "right" $\text{Mg}(\text{D}_2\text{O})_6^{2+}$ octahedron and two "left" $\text{Mg}(\text{D}_2\text{O})_6^{2+}$ octahedra (and one "left" SiF_6^{2-} octahedron and two "right" SiF_6^{2-} octahedra). For the second ordered domain where the situation is opposite the structure factor becomes

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

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

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

and with x the volumetric proportion of the first domain, that leads to

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

For the superlattice reflections ($-h + k + l = 3n \pm 1$) a coherent superposition of the diffraction intensities leads to

$$F = [xF_1 + (1 - x)F_2] \\ = (F_{AB'} - F_{A'B})\left[\frac{1}{2}(1 + x) + i(3^{1/2}/2)(1 - x)\right],$$

and then for the structure factor squared to $F^2 = y(F_{AB'} - F_{A'B})^2$, with y the rate of coherence.

In real space, the model used presents two types of ordered domains, built from the low-temperature cell (1-8). The value of the x parameter indicates, when an equal volume proportion of each domain is obtained, that the observed mirrors (11.0) are statistical ones.

The atomic positions and equivalent isotropic thermal parameters are shown Table I and bond distances and angles are given in Table II. In the X-ray case, the number of electrons of Mg, Si, F, and O is 10 with Mg^{2+} , Si^{4+} , F^- , and O^{2-} ions, and respec-

tively 12, 14, 9, and 8 with neutral atoms. It is reasonable to use unequal values for the scattering factors and we can think that a neutron analysis will not be more accurate than an X-ray one. But, contrary to the neutron scattering lengths, the X-ray scattering factors decrease with $\sin \theta/\lambda$. The neutron study does not present this drawback and furthermore, it enables the determination of the D positions and the rate of deuteration of the crystal: the refinement corroborates the estimated value from the preparation of the compounds 81.0 (7) % of D. The parameter $x = 0.497$ (8) confirms the existence of pseudo-mirrors (11.0), statistically distributed (1-8), and $y = 0.76$ (1) indicates a coherent superposition of the diffraction intensities for the superlattice reflections (ideal value $y = \frac{2}{3}$ (9)).

Once more, the magnesium atom is octahedrally coordinated by water molecules ($\text{O}-\text{D}(1) = 0.943(1)$, $\text{O}-\text{D}(2) = 0.933(1)$ Å, and $\text{D}(1)-\text{O}-\text{D}(2) = 107.8(1)^\circ$) with its plane almost within the 3-fold axis (deviation $11.1(8)^\circ$); the conformation of the octahedron ($(\text{O}-\text{Mg}-\text{O}')-(\text{O}-\text{Mg}-\text{O}) \leq 2^\circ$) shows a significant deformation. (Along the z -axis, unprimed atoms lie on the up side and primed ones on the down side of the cation).

On the other hand, the SiF_6^{2-} octahedron is more regular ($(\text{F}-\text{Si}-\text{F}')-(\text{F}-\text{Si}-\text{F}) \leq 0.4^\circ$) and the bond length ($\text{Si}-\text{F} = 1.686(1)$ Å) is in agreement with the values obtained before with the other $\text{MSiF}_6 \cdot 6\text{H}_2\text{O}$ compounds (average value: 1.680 Å).

As for the Fe and Mn compounds, the $\text{Mg}(\text{D}_2\text{O})_6^{2+}$ and SiF_6^{2-} octahedra have to be turned to align the Mg-O and Si-F directions with the pseudo-mirrors planes; the deviations are respectively 12.6° and 22.5° (Fig. 1), they are of the same order as those of $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$ (9). In the same way, the hydrogen bond lengths (Table II) between the two $\text{Mg}(\text{D}_2\text{O})_6^{2+}$ and SiF_6^{2-} ions are comparable with those of Fe(2), Co(5) and Mn-compounds (9). A well-defined plane consisting of Mg, F, D(1), D(2), and O atoms

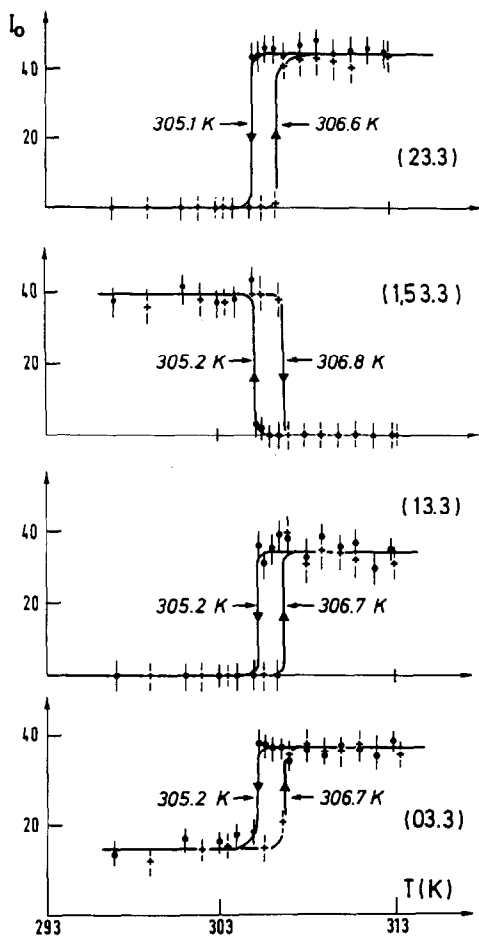


FIG. 2. Intensity of (23.3), (1,5 3.3), (13.3) and (03.3) peaks corresponding to space group $P\bar{3}$ in the high-temperature phase of $\text{MgSiF}_6 \cdot 6\text{D}_2\text{O}$ as a function of temperature.

(maximum deviation from the planes: $-0.15(2)$ Å for D(2)) is inclined by $14(1)^\circ$ to the water molecule plane (the deviation of Mg from this plane is 0.42 Å).

Transition Temperature

The first-order transition between the low-temperature ($P2_1/c$) and high-temperature phase ($P\bar{3}$) shows only a small hysteresis: 306.8 K with increasing and 305.2 K

with decreasing temperature. In Fig. 2 examples of basic (03.0), superlattice (23.3, 13.3) and forbidden (1.5 3.3) reflections corresponding to space group $P\bar{3}$ are shown.

As for the other deuterated fluosilicates, the phase transition (~ 306 K) occurs at a higher temperature than that of hydrogenated compounds ($\Delta T \sim 6$ K), but the difference is smaller than in the case of Co and Mn compounds (~ 15 to 19 K) (5, 9, 16).

Influence of the Metal Cation

The results of the structure analysis of all fluosilicates indicate that these compounds can be separated into essentially two series. The first one with $M = \text{Co}, \text{Ni}, \text{Zn}$ and the second with $M = \text{Mn}, \text{Mg}, \text{Fe}$. According to these series, the structure of the high temperature phase is described either in the $R\bar{3}$ or in the $P\bar{3}$ space group.

A gathering of all the known information allows to show the importance of the nature of the metal cation M^{2+} (Table III):

(i) The deformation (O-M-O')-(O-M-O) in degrees is a function of the radius of the metal ion (20) (Fig. 3-I): it is rather weak in the case of Ni, Co and Zn ($\sim 1^\circ$) and more important in the case of Mg, Mn and Fe ($\sim 3^\circ$). Besides this, the deformation of the SiF_6^{2-} octahedron is very weak with no difference between the compounds of the two series (Fig. 3-II).

(ii) As shown in Fig. 4, the M-O bond length is a function of the M^{2+} ionic radius. At a given radius, it is longer in the case of the second series ($P\bar{3}$ space group).

(iii) The cation lies practically in the mean least square plane O, H/D(1), H/D(2), F in the case of Mg, Mn, and Fe (maximum deviation 0.58 Å: $M = \text{Fe}$), whereas it is out of the two possible planes (O, H/D(1), H/D(2), F(1) and O, H/D(1), H/D(2), F(2)) in the case of Co, Ni and Zn (minimum deviation 1 Å: $M = \text{Co}$) (Table IV).

Besides this, the importance of the SiF_6^{2-} octahedra for the specific space group sym-

TABLE III
M-FLUOSILICATE INFORMATIONS

	Mg	Ni	Co	Fe	Zn	Mn
$[(O-M-O)-(O-M-O')]^\circ$	-3.6 (1) -2.2 (*)	1.0 (4)	-1.2 (4) -1.2 (5)	-3.2 (1) -2.8 (2)	-0.2 (4)	-3.2 (9)
$[(F-Si-F)-(F-Si-F')]^\circ$	2.4 (1) -0.4 (*)	0.2 (4) -1.2 (4)	-0.8 (4) -0.8 (4) -0.4 (5) -0.7 (5)	-0.2 (1) -0.4 (2)	-0.4 (4) -0.8 (4)	0.1 (9)
M-O (Å)	2.074 (1) 2.059 (*)	2.047 (4)	2.084 (5) 2.081 (4)	2.143 (1) 2.146 (2)	2.078 (4)	2.162 (9)
Si-F (Å)	1.668 (1) 1.686 (*)	1.671 (4) 1.683 (4)	1.665 (5) 1.680 (5) 1.674 (4) 1.678 (4)	1.691 (1) 1.706 (2)	1.671 (4) 1.680 (4)	1.681 (9)

Additional M-fluotitanates informations (21)

$[(O-M-O)-(O-M-O')]^\circ$	1	-1
$[(F-Ti-F)-(F-Ti-F')]^\circ$	-1.6	-1.2
M-O (Å)	2.082	2.163

Note. References are in parenthesis; * this study.

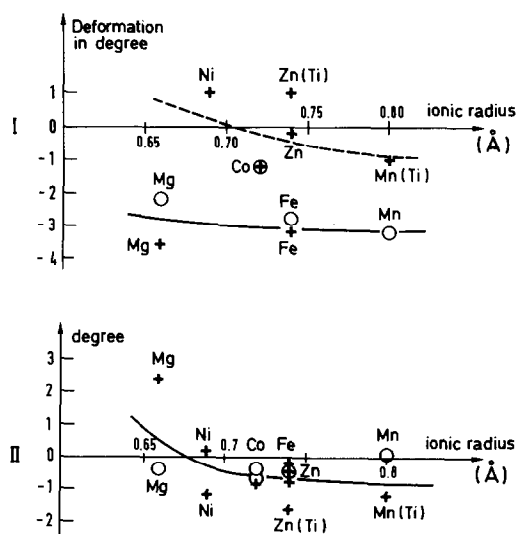


FIG. 3. Deformation of the two types of octahedra. (I), water octahedra; (II), fluorine octahedra; +, X-ray diffraction; o, neutron diffraction; M(Ti), fluotitanates results (21).

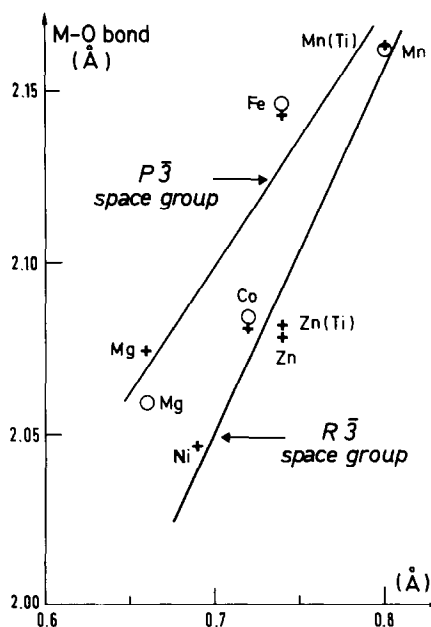


FIG. 4. Evolution of the M-O bond as a function of the metal ion radii. +, X-ray diffraction; o, neutron diffraction; M(Ti), fluotitanates results (21).

TABLE IV
M-FLUOSILICATES CALCULATIONS MEAN-LEAST-SQUARE PLANE OH₁(D₁)H₂(D₂)F

	Mg (*)	Mn (9)	Fe (2)	Co (5)	Ni (4)	Zn (4)
Chi squared	491	143	11	933	397	3082
Deviation of M ²⁺ (Å)	0.16	0.08	0.58	1.27 -1.00	2 1.51 1.39	588 1.49 -1.28

Note. References are in parenthesis; (*) this study.

metry can be seen from a comparison of SiF₆²⁻ and TiF₆²⁻ compounds: MnTiF₆·6H₂O as well as ZnTiF₆·6H₂O belongs to the second series with R $\bar{3}$ space group (21).

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