

Crystal structure refinement of the inverse weberite $\text{MnFeF}_5(\text{H}_2\text{O})_2$

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Abstract. $\text{MnFeF}_5(\text{H}_2\text{O})_2$ is orthorhombic (S.G. *Imma*) with $a = 7.5635(2)$ Å, $b = 10.901(1)$ Å, $c = 6.7319(2)$ Å ($Z = 4$). The centrosymmetric space group of the inverse weberite was proved by ψ -rotation measurements. The structure was refined from 1029 independent reflections to $R(F) = 0.018$ ($R_w(F) = 0.028$).

Introduction

The concept of ordered magnetic frustration that we developed during the years (Férey et al., 1978, 1985a, b; Leblanc et al., 1986; Laligant et al., 1986b) describes the different arrangements adopted by spins in anti-ferromagnetic interaction when the corresponding cations form a triangular subnetwork. This geometry is encountered in the $\text{Na}_2\text{M}^{2+}\text{M}^{3+}\text{F}_7$ compounds with the weberite structure; although the crystal chemistry of this structural type is well established, its space group (*Imma* or *Imm2*) is still an open question in spite of four different structure refinements

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(Byström, 1944; Giuseppetti et al., 1978; Haegele et al., 1978; Knop et al., 1982) and the latter paper is indeed entitled "What is the true space group of the weberite?!" The answer to this question is especially important for the precise determination of the magnetic structure of weberites.

Recently, we pointed out (Férey et al., 1985b) that the crystal chemistry of the hydrated mixed valence fluoride $\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_5\text{H}_2\text{O}$, first described by Hall et al. (1977), is very close to that of the weberite, including, however, an inversion of the cationic sites M^{2+} and M^{3+} and a replacement of two trans F^- ions by two H_2O molecules on the divalent metal coordination octahedra. Therefore we expected the same ambiguity of space group to arise with the $\text{MM}'\text{F}_5\text{H}_2\text{O}$ compounds: this led us recently to reexamine the crystal structure of $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$ (Laligant et al., 1986a); the space group *Imma* was confirmed at room temperature. Moreover, the crystal structure at 60 K as well as the structure and magnetic ordering at 30 K were also refined from powder neutron diffraction data using the space group *Imma* rather than its subgroups (Laligant et al., 1986b); analysis of this magnetic structure enabled us to show the influence of the anisotropy of Fe^{2+} ions on the frustrated arrangement of the spins of Fe^{3+} (d^5) and Fe^{2+} (d^6).

It is now of interest to study the special situation which is encountered when all the cations have a d^5 electronic configuration, with no anisotropy. This case occurs when Mn^{2+} replaces Fe^{2+} and leads curiously to ferrimagnetism (Jones et al., 1985; Laligant et al., 1986c). The large size of Mn^{2+} ions may induce slight distortions and/or a lowering of the symmetry. A complete examination of the structure of $\text{MnFeF}_5(\text{H}_2\text{O})_2$ is therefore required. It is reported in this paper.

Experimental

$\text{MnFeF}_5(\text{H}_2\text{O})_2$ was obtained as single crystals by hydrothermal synthesis (Leblanc et al., 1984): a 5 M stoichiometric mixture of MnF_2 and FeF_3 in 10% aqueous HF was heated during 4 days at 380 °C under a pressure of 193 MPa. After cooling, the crystals were filtered, washed with ethanol and ether and air dried. A well shaped single crystal was selected by optical examination. Its dimensions and the Miller indices of its faces were carefully determined (Fig. 1). Laue and precession photographs using $\text{MoK}\alpha$ radiation confirm the orthorhombic symmetry. A second harmonic generation measurement gave a negative, and thus inconclusive, result. Data were collected on an Enraf Nonius CAD4 four-circle diffractometer (University of Caen). All reflection intensities within a half of the reciprocal space up to $\sin \theta/\lambda = 1 \text{ \AA}^{-1}$ were collected taking into account the tested *I*-centering; some experimental data are given in Table 1 and the characteristics of the measurement are summarized in Table 2. In order to test the existence of

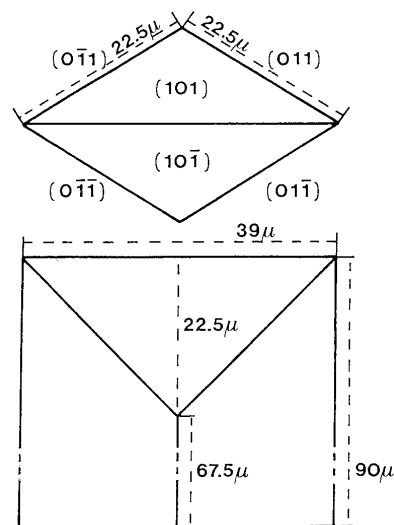


Fig. 1. Shape and size of the crystal used for data collection.

Table 1. Experimental data for $\text{MnFeF}_5(\text{H}_2\text{O})_2$ crystals¹.

Symmetry: orthorhombic	Cell parameters* (<i>Z</i> = 4)
Systematic extinctions:	<i>a</i> = 7.5635(2) Å
<i>hkl</i> <i>h</i> + <i>k</i> + <i>l</i> = 2 <i>n</i> + 1	<i>b</i> = 10.901(1) Å
<i>hk0</i> <i>h</i> = 2 <i>n</i> + 1	<i>c</i> = 6.7319(2) Å
Space group: <i>Imma</i>	<i>V</i> = 555.04 Å ³
$\rho_{\text{exp}} = 2.87(3) \text{ g} \cdot \text{cm}^{-3}$	
$\rho_{\text{calc}} = 2.89 \text{ g} \cdot \text{cm}^{-3}$	
Temperature of the lattice constants determination: 20 °C	

* Refined and calibrated with Si internal standard.

ten very weak (*hk0*) reflections with *h* = 2*n* + 1 and *I* > 3 $\sigma(I)$, we performed further measurements on a Siemens-Stoe AED-2 four-circle diffractometer (Kernforschungszentrum Karlsruhe).

The intensities were corrected for Lorentz-polarization effects and absorption. The structure refinement was performed with the program system PROMETHEUS (Zucker et al., 1983); secondary extinction

Table 2. Conditions of intensity data collection and refinement.

Crystal size: 0.250 × 0.045 × 0.0265 (mm)
Radiation: MoK α (λ = 0.71069 Å)
Scan mode: ω -4/3 θ
Scan angle (degrees): 1.00 + 0.35 tg θ
Aperture (mm): 1.00 + tg θ
Scanning speed max.: 0.33°/s
θ_{\max} : 45°
Lattice constants refined from 20 reflections (see Table 1)
Range of measurement: $-15 < h < 15$
$-21 < k < 21$
$0 < l < 13$
Standard reflections: 3 $-2-2$ 0
0-1-1 measured every 2000 s
2-2 0
Intensity variation max: 5%
Reflections measured: 3491
Reflections rejected: ($\sigma(I)/I \geq 0.33$): 7
Independent reflections: 1039
$R_{\text{int}} = 0.0145$
Absorption correction: Gaussian grid integration
Absorption coefficient: 46.75 cm $^{-1}$
Transmission factors: $A_{\text{max}} = 0.914$; $A_{\text{min}} = 0.814$
F magnitudes used in least-squares refinement
Shift/e.s.d. mean: 0.00
max: 0.25

parameters were included, using an anisotropic Lorentzian mosaic-spread distribution (Becker and Coppens, 1974). Ionic scattering factors and anomalous dispersion parameters were taken from *International Tables for X-Ray Crystallography* (Vol. 4, 1974). Starting from the structural model of Fe $_2$ F $_5$ (H $_2$ O) $_2$ (Laligant et al., 1986a), refinements in *Imma* converged rapidly to the values given in Table 3. The hydrogen atoms were localized on difference Fourier maps and included in the last stages of the refinement¹.

Discussion

As mentioned in the introduction, the space group of weberite has been questioned in the recent years. From a careful investigation of a natural weberite Na $_2$ MgAlF $_7$ both at room temperature and 133 K, Knop et al. (1982) arrived at the conclusion that the true space group is probably *Imm2* or *I2 $_1$ 2 $_1$ 2 $_1$* , but that the deviation from *Imma* is so slight that "the

¹ Additional material to this paper can be ordered referring to the no. CSD 52718, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 3. Refined atomic coordinates and thermal parameters (a, b) of MnFeF $_5$ (H $_2$ O) $_2$. ($R_{\text{FP}} = 0.018$; $R_{\text{wFP}} = 0.028$).

Atom	site	x	y	z	U $_{11}$	U $_{22}$	U $_{33}$	U $_{12}$	U $_{13}$	U $_{23}$	B $_{\text{eq}}$ [Å $^{-2}$]
Mn	4a	0	0	0	105(1)	115(1)	152(1)	0	0	-33(1)	0.98
Fe	4c	1/4	1/4	1/4	73(2)	75(1)	113(1)	0	-8(1)	0	0.69
F1	16j	2924(1)	1252(1)	4444(1)	167(2)	175(2)	229(3)	43(2)	21(2)	88(2)	1.50
F2	4c	0	1/4	3237(2)	76(4)	210(5)	215(5)	0	0	0	1.32
O	8h	1/2	5711(1)	2000(2)	220(5)	443(8)	177(5)	0	0	75(5)	2.21
H	16j	0.080(2)	0.096(1)	0.650(3)	—	—	—	—	—	—	2.6(6) ^a

^a Standard deviations are given in parenthesis and refer to the last digit.

^b U $_{ij}$ are multiplied by 10 4 . The U $_{ij}$ relate to the expression: $T = \exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2klb^* c^* U_{23})]$.

^c Restricted isotropic refinement of the temperature factor.

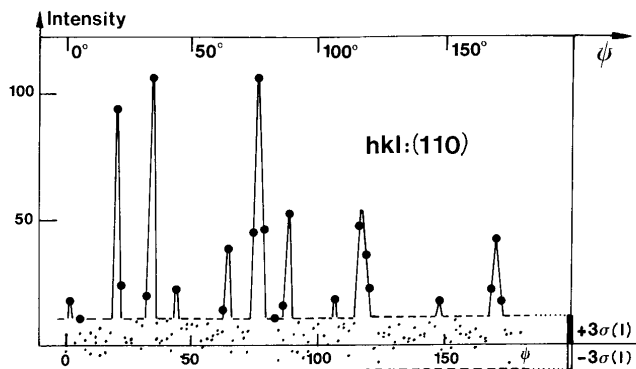


Fig. 2. Integrated background corrected intensities of the (110) reflection from ordinary $\omega/2$ θ -scans as a function of ψ -rotation.

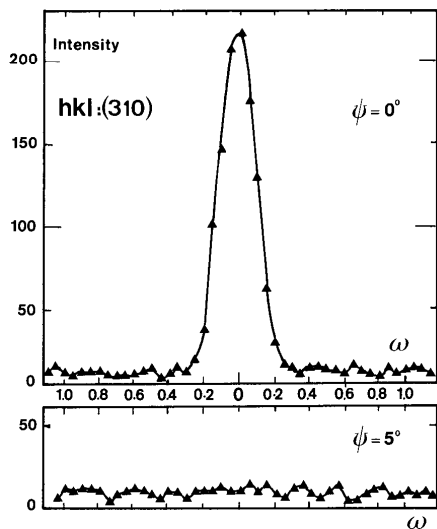


Fig. 3. Profile (ω -scan) of a typical ($hk0$) reflection with $h = 2n + 1$ (true counts scaling, 10 s/step). The Bragg peak (clearly visible at $\psi = 0^\circ$) has completely vanished for $\Delta\psi = 5^\circ$.

descriptions of the weberite structure in the three space groups must be regarded as practically indistinguishable". The physical argument supporting the non-centrosymmetric space groups was the observation, mainly on $\text{Na}_2\text{NiFeF}_7$ (Haegele et al., 1978), of several very weak ($hk0$) reflections with $h = 2n + 1$. Our routine intensity collection on the inverse weberite $\text{MnFeF}_5(\text{H}_2\text{O})_2$ produced also 10 very weak ($hk0$) reflections with $h = 2n + 1$ and $I/\sigma(I) > 3$; the existence of these reflections is the only physical evidence which would imply a non-centrosymmetric space group. However, one may not rule out the possibility of double reflection (Renninger, 1937), a point which has not been considered by Haegele et al. (1978) and Knop et al. (1982).

As the occurrence of a specific double reflection requires a combination of particular wavelength with an orientation of the reciprocal lattice, the existence of a Renninger effect can be checked either, for a given orientation, by changing the wavelength, or, alternatively, for a given wavelength, by changing the orientation of the crystal. A series of ($hk0$) reflections with $h = 2n + 1$ was then tested by so-called ψ -scan rotation on a AED-2 four-circle diffractometer, and we were able to prove that there is some probabil-

Table 4. Interatomic distances (\AA) and bond angles ($^\circ$) in $\text{MnFeF}_5(\text{H}_2\text{O})_2$.

<i>Mn²⁺ octahedron</i>			
4 × Mn—F1	2.114(1)	F1—Mn—F1	84.1(1) 95.9(1)
2 × Mn—O	2.163(1)		
4 × F1—F1	2.830(1)	F1—Mn—O	86.2(1) 93.8(1)
4 × F1—O	2.863(1)		
4 × F1—O	2.923(1)		
<i>Fe³⁺ octahedron</i>			
4 × Fe—F1	1.915(2)	F1—Fe—F1	89.4(1) 90.6(1)
2 × Fe—F2	1.955(1)		
2 × F1—F1	2.695(1)	F1—Fe—F2	89.3(1) 90.7(1)
2 × F1—F1	2.721(1)		
4 × F1—F2	2.721(1)		
4 × F1—F2	2.752(1)		
<i>Superexchange angles and metal-metal distances</i>			
Fe ³⁺ —F2—Fe ³⁺	150.58	Mn—F1—Fe ³⁺	134.75
Fe ³⁺ —Fe ³⁺	3.782	Mn ²⁺ —Fe ³⁺	3.719
<i>Water molecule</i>			
O—H	0.74(2)		
H—O—H	108.9(1)		

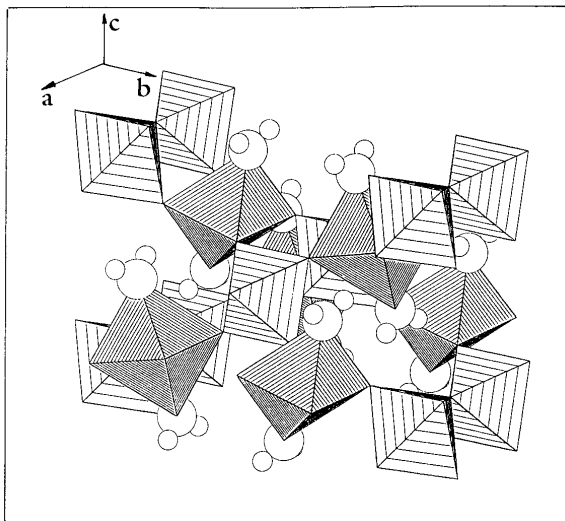


Fig. 4a. Perspective view of $\text{MnFeF}_5(\text{H}_2\text{O})_2$ structure drawn using program STRUPL0 (Fischer, 1985). Fe^{3+} octahedra are slightly hatched, and Mn^{2+} octahedra, strongly hatched, bear water molecules.

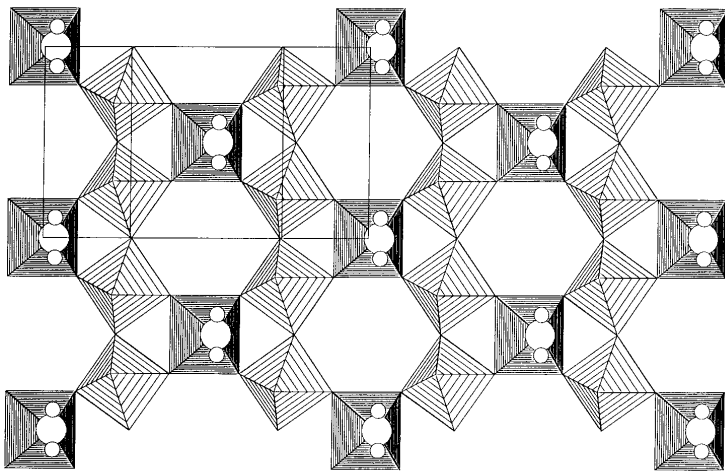


Fig. 4b. Projection of the structure along (011), showing the hexagonal tungsten bronze planes.

ity for Renninger effect in the case of the weberite structure and $\text{MoK}\alpha$ radiation. In Figure 2, the integrated background corrected intensity of the (110) reflection is drawn as a function of ψ -rotation. It is obvious that there are many configurations where the observed intensity is much higher than the marked limit of $3\sigma(I)$. In all cases, a small ψ -rotation around the scattering vector yields a complete disappearance of any significant Bragg peaks (an example is given in Figure 3). In this way, we have shown for the inverse weberite $\text{MnFeF}_5(\text{H}_2\text{O})_2$ that the true space group is centrosymmetric: *Imma*. One may suspect that the same conclusion holds also for direct weberite compounds.

Description of the structure

In the structure of $\text{MnFeF}_5(\text{H}_2\text{O})_2$, Mn^{2+} and Fe^{3+} ions are octahedrally coordinated. Interatomic distances and bond angles are given in Table 4. There is no significant deviation from the sum of ionic radii (Shannon, 1976). The $\text{Fe}^{3+}-\text{F}^-$ distance (1.928 Å) is close to the value of 1.922 Å which is found in the rhombohedral FeF_3 structure (Leblanc et al., 1985).

The perspective view of Figure 4a illustrates the crystal chemistry of the inverse weberite structure. Two trans chains of corner-sharing Fe^{3+} octahedra, which run along [100], are linked together by isolated $\text{MnF}_4(\text{H}_2\text{O})_2$ octahedra and form hexagonal tungsten bronze layers (*Magneli*, 1953) in the (011) plane (Fig. 4b).

Magnetic superexchange interactions between Mn^{2+} and Fe^{3+} cations are predicted to be antiferromagnetic by the Kanamori (1959) Goodenough (1963) rules and it is only the frustrating triangular topology which will be able to explain the observed ferrimagnetism, as already noted in the direct weberite $\text{Na}_2\text{NiFeF}_7$ (Heger, 1972). The refinement of the magnetic structure is in progress. It will allow to describe the corresponding frustrated spin arrangement in $\text{MnFeF}_5(\text{H}_2\text{O})_2$.

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