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BRIEF COMMUNICATION

A New Refinement of the Crystal Structure of the Inverse Weberite $Fe_2F_5(H_2O)_2$

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$Fe_2F_5(H_2O)_2$ is related to the weberite structure, whose space group is not clearly defined. A careful reexamination of the structure confirms and refines the previous results: $Fe_2F_5(H_2O)_2$ belongs to the space group *Imma* with cell parameters $a = 7.477(1)$ Å, $b = 10.862(2)$ Å, $c = 6.652(1)$ Å ($Z = 4$). The structure has been refined from 379 reflections to $R = 0.029$ ($R_w = 0.034$). $Fe_2F_5(H_2O)_2$ must be considered as an antiweberite structure since M^{2+} and M^{3+} positions are inverse of those of the weberite structure. © 1986 Academic Press, Inc.

Introduction

We observed that the crystal chemistry of the hydrated mixed valence fluoride $Fe^{2+}Fe^{3+}F_5 \cdot 2\ H_2O$ previously described by Hall *et al.* (*1*) is close to that of the weberite (hereafter noted Wb) structural type $Na_2M^{2+}M^{3+}F_7$ (*2–5*). However, M^{2+} and M^{3+} positions are inverse of those which exist in the weberite structure, and H_2O molecules replace two *trans* F^- ions of the divalent metal coordination octahedra. Consequently, the sites occupied by the alcali cations in Wb are empty in the hydrated mixed valence compound described here. For this reason, a notation $\square_2Fe_2F_5(H_2O)_2$ notation must be preferred to $Fe_2F_5 \cdot 2H_2O$ to take into account both the existence of vacancies and the fact that H_2O molecules belong to the octahedral skeleton of the structure.

Despite four structural determinations (*2–5*), the true space group of the weberite structure remains an open question: different authors describe Wb either in space group *Imma* (*hkl*: $h + k + 1 = 2n$ and *hk*0: $h = 2n$ ($k = 2n$)) or in *Imm*2 ($h + k + l = 2n$). The similarity between the Wb and $Fe_2F_5(H_2O)_2$ structures incited us to reexamine carefully the space group of the latter compound to see if the same question arised. The knowledge of the true space group is indeed necessary to undertake the study of the magnetic structure of $Fe_2F_5(H_2O)_2$ which is of interest to illustrate the concept of ordered magnetic frustration

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TABLE I

CONDITIONS OF INTENSITY DATA COLLECTION AND REFINEMENT

Lattice constants from 20 reflections: $a = 7.477(1)$ Å
$Z = 4$ $b = 10.862(2)$ Å
$c = 6.652(1)$ Å
$V = 540.24$ Å^3

Space group: *Imma*
Density: ρ exp = 2.95(2)g · cm^{-3}
ρ calc = 2.96 g · cm^{-3}
Systematic extinctions: hkl: $h + k + l = 2n + 1$
$hk0$: $h = 2n + 1$
Crystal size: 0.0225 × 0.0225 × 0.090 mm
Radiation: Mo$K\alpha$ (λ = 0.71069 Å)
Scan mode: $\omega - \frac{4}{3}\,\theta$
Scan angle (degrees): 1.00 + 0.035 tg θ
Aperture (mm): 1.00 + tg θ
Scanning speed max.: 0.33°/sec
θ_{max}: 45°
Range of measurement: $-13 \leq h \leq 12$
$-20 \leq k \leq 20$
$0 \leq l \leq 12$
Standard reflections: $-2\ -2\ \ 0$ measured every 2000 sec
$0\ -1\ -1$
$2\ -2\ \ 0$
Intensity variation max: 5%
Reflections measured: 862
Reflections rejected: none
Independent reflections: 379
R (from averaging): 0.0401
Absorption correction: Gaussian grid integration
Absorption coefficient: μ = 54.136 cm^{-1} (Mo$K\alpha$)
Transmission factors: A_{max} = 0.9239 A_{min} = 0.8535
F magnitudes used in least-squares refinement
Shift/e.s.d. mean: 0.00
max: 0.06
Secondary extinction coefficients (*16*):
Z_{11}: 1.7 (0.8) Z_{ij} are multiplied by 10^4
Z_{22}: 61. (42.)
Z_{33}: 0.02(0.5)

that we recently introduced (*6–8*). This paper reports a reexamination of the crystal structure of $Fe_2F_5(H_2O)_2$.

Experimental

$Fe_2F_5(H_2O)_2$ was obtained as single crystals by heating a solution prepared by reacting iron wire with 49% aqueous HF at 110°C for 1 hr. A well shaped single crystal was selected. Its dimensions and Miller indices of faces were carefully determined.

Laue and precession photographs using Mo$K\alpha$ radiation confirm both the orthorhombic symmetry and cell parameters. A second harmonic generation measurement[1] did not give any significant signal, thus strongly suggesting a centrosymmetric space group. Moreover, the absence of $hk0$ reflections with h and k odd, which would characterize the space group *Imm2*, was carefully verified both by long exposures of the precession pattern photógraphs and by long scans on these expected reflections during the collection of intensities on an Enraf Nonius CAD 4 diffractometer. The structure was then refined in the group *Imma*. Table I summarizes the characteristics of the crystal and the experimental conditions of data collection. The intensities were corrected for Lorentz and polarization effects and absorption corrections were applied. The structure refinement was performed with the program PROMETHEUS (*9*); anisotropic secondary extinction parameters were included in

TABLE II

ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS OF $Fe_2F_5(H_2O)_2$[a,b]

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B_{eq.}$
Fe^{2+}	4*a*	0	0	0	81(5)	103(6)	172(7)	0	0	−31(6)	0.937
Fe^{3+}	4*c*	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	57(4)	75(5)	151(7)	0	−12(5)	0	0.745
F1	16*j*	0.2024(3)	0.1252(2)	0.0544(4)	121(11)	167(12)	273(16)	−44(9)	15(10)	−83(12)	1.476
F2	4*e*	0	$\frac{1}{4}$	0.3343(8)	61(20)	201(26)	205(29)	0	0	0	1.229
O	8*h*	$\frac{1}{2}$	0.5690(5)	0.2034(8)	205(21)	354(27)	154(27)	0	0	59(22)	1.877

[a] Standard deviations given in parenthesis. U_{ij} are ×10^4.

[b] The vibrational coefficients relate to the expression: $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

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[1] Experiment performed at Laboratoire de Chimie des Solides, University of Montpellier (France).

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN $Fe_2F_5(H_2O)_2$[a]

Fe^{2+} octahedron					
4 × Fe–F1	2.066(2)	[2.060(6)]	F1–Fe–F1	85.8(1) 94.2(2)	[85.4(3)] [94.6(3)]
2 × Fe–O	2.111(5)	[2.13(1)]			
4 × F1–F1	2.815(3)	[2.793(9)]			
			F1–Fe–O	86.0(1) 94.0(1)	[87.2(3)] [92.8(3)]
4 × F1–O	2.849(5)	[2.87(1)]			
4 × F1–O	2.875(6)	[2.89(1)]			
Fe^{3+} octahedron					
4 × Fe–F1	1.912(2)	[1.932(7)]	F1–Fe–F1	89.7(2) 90.3(3)	[89.3(3)] [90.7(3)]
2 × Fe–F2	1.951(2)	[1.960(4)]			
2 × F1–F1	2.711(3)	[2.749(9)]			
2 × F1–F1	2.698(4)	[2.714(9)]	F1–Fe–F2	89.0(6) 91.0(6)	[88.7(4)] [91.3(4)]
4 × F1–F2	2.709(3)	[2.720(8)]			
4 × F1–F2	2.756(4)	[2.78(1)]			
Superexchange angles and metal–metal distances					
Fe^{3+}–F2–Fe^{3+}	146.6(1)	[145.7(8)]	Fe^{2+}–F1–Fe^{3+}	136.2(2)	[136.1(4)]
Fe^{3+}–Fe^{3+}	3.739(2)	[3.744(2)]	Fe^{2+}–Fe^{3+}	3.692(2)	[3.702(2)]

[a] Values in brackets from Hall (*1*).

the refinement, using a Lorentzian mosaic-spread distribution. Scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-Ray Crystallography" (*10*). Starting from the positions published by Hall (*1*), the reliability factor for 379 reflections (248 for Hall) and 28 refined parameters converges to $R_w = 0.034$ (to be compared to the value $R_w = 0.053$ obtained by Hall) with aniso-

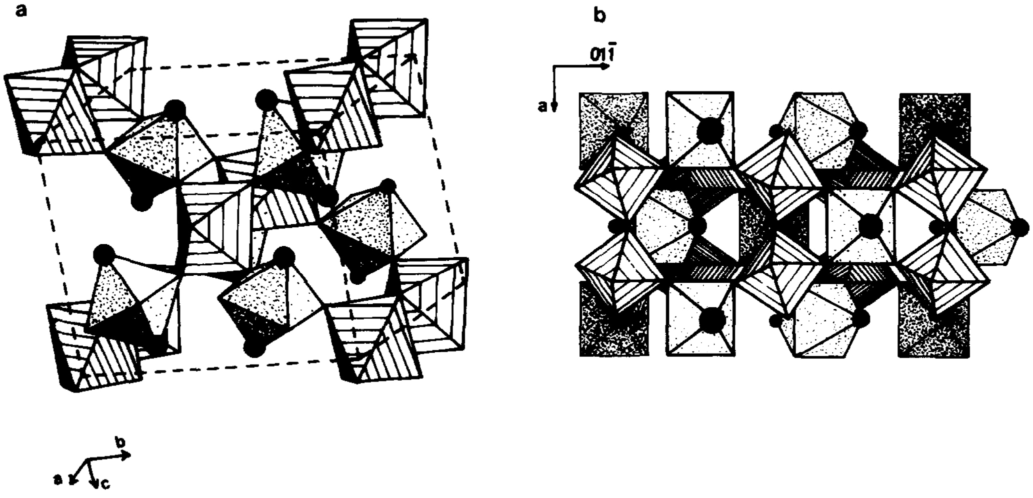

FIG. 1. (a) Perspective view of $Fe_2F_5(H_2O)_2$ · Fe^{3+} octahedra are hatched and Fe^{2+} octahedra are dot shaded. (b) Projection of the structure along (011), showing the hexagonal tungsten bronze planes.

tropic thermal parameters. The final refined atomic coordinates of nonhydrogen atoms are given in Table II. A subsequent difference Fourier synthesis does not clearly evidence the hydrogen atoms of the water molecules. They will be located accurately from the data of the neutron diffraction study which is in progress. Moreover, an attempt to refine the structure in the group *Imm*2 gave a worse reliability factor (R_w = 0.041). A table of structure factors using the *Imma* space group will be supplied by G.F. upon request.

Description of the Structure

In this structure, Fe^{2+} and Fe^{3+} ions are octahedrally coordinated. Interatomic distances and bond angles are given in Table III. They do not depart significantly from Hall's results but they are closer to the ionic radii (*11*). Fe^{3+}–F^- distance (1.913 Å) is close to the ideal value (1.922 Å) which is found in the Rh–FeF_3 structure (*12*).

The perspective view of Fig. 1a shows that the crystal chemistry of the antiweberite structure is verified. Two *trans* chains of corner-sharing Fe^{3+} octahedra, which run along [100], are linked together by isolated $FeF_4(H_2O)_2$ octahedra and form hexagonal tungsten bronze layers (*13*) in the (011) plane (Fig. 1b). Triangular cycles of octahedra are occupied in an ordered way by two Fe^{3+} and one Fe^{2+} ions, whose magnetic superexchange interactions are predicted to be antiferromagnetic by the Kanamori-Goodenough rules (*14, 15*). The magnetic structure, which is in progress, will describe the frustrated arrangement adopted by the spins of Fe^{2+} and Fe^{3+} in the triangular cycles of the structure.

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