FeAlF₅: Synthesis and Crystal Structure

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$FeAlF_5$ appears in the thermolysis products of $(TMA)M^{III}F_4 \cdot H_2O$—$(TMA) = [(CH_3)_4N]$, $M^{III} = (Fe_{0.5}Al_{0.5})$—and of FeAl $F_5 \cdot 7H_2O$. Its structure is solved ab initio from the X-ray powder diffraction pattern (S.G. *Immm*, $a = 7.4289(8)$ Å, $b = 6.203(1)$ Å, and $c = 3.5574(6)$ Å, $Z = 2$, $R_B = 0.10$). The network is constituted by two kinds of chains running along the c axis: AlF_6 octahedra form *trans*-chains whereas FeF_6 octahedra build edge sharing rutile-like chains. $FeAlF_5$ can be considered as the aristo-type structure from which derive some ABF_5 networks. The Mössbauer study characterizes two Fe^{2+} contributions involving respectively a small cationic inversion and a classical paramagnetic behavior down to 4.2 K due to the rutile type arrangement of the $Fe^{II}F_6$ octahedra. © 1994 Academic Press, Inc.

INTRODUCTION

Despite numerous efforts, it was not possible up to now to synthesize $FeAlF_5$. However, other ABF_5 fluorides are well known: $MnAlF_5$ (1), Cr_2F_5 (2), and $MnCrF_5$ (3) for instance. We describe here two preparation routes of $FeAlF_5$, its ab initio structural determination, based on the analysis of the X-ray powder diffraction pattern, and its magnetic characterization.

PREPARATION

$FeAlF_5$ has been obtained by thermal decomposition of $(TMA)Fe_{0.5}Al_{0.5}F_4 \cdot H_2O$ $(TMA = [(CH_3)_4N])$ under quasi-isobaric conditions at about 560°C or in vacuum at 500°C. Besides $FeAlF_5$, traces of α-AlF_3 and FeF_2 are formed. The starting compound was prepared according to (4).

Another possibility for the preparation of pure $FeAlF_5$ is the thermal dehydration of $FeAlF_5 \cdot 7H_2O$ under quasi-isobaric conditions at about 400°C. The starting compound $FeAlF_5 \cdot 7H_2O$ was prepared according to (5) by addition of solutions of 1 g Fe in 50 ml 20% HF and of 1 g Al in 50 ml 40% HF and subsequent crystallization. The thermoanalytical investigations were made with a Derivatograph Q-1500 D (MOM Budapest), sample mass 200 mg $((TMA)Fe_{0.5}Al_{0.5}F_4 \cdot H_2O)$ and 400 mg

$(FeAlF_5 \cdot 7H_2O)$, conical Pt crucible, heating rate 5 K/min, reference substance Al_2O_3, atmosphere N_2.

The decomposition of pure $FeAlF_5$ into α-AlF_3 and FeF_2 takes place above 600°C, but without any detectable thermal effects (the approximate decomposition temperature was determined by successive heatings).

The different quality of the $FeAlF_5$ samples is caused by their origin. The decomposition temperature of the TMA compound is relatively high compared with that of $FeAlF_5 \cdot 7H_2O$. Therefore, in the first case traces of α-AlF_3 and FeF_2 are always observed. Another point is the difficulty of obtaining the exact equimolar ratio of Fe and Al in the starting TMA compound. The advantage of the $FeAlF_5 \cdot 7H_2O$ route is the simple and reproducible preparation; the lower decomposition temperature leads to the formation of pure $FeAlF_5$ but also with lower crystallinity.

STRUCTURE DETERMINATION

The sample chosen for the crystal structure determination was coming from the TMA route. X-ray powder diffraction patterns were recorded at 295 K on a Siemens D501 diffractometer ($CuK\alpha$; graphite diffracted-beam monochromator), α-AlF_3 phase was easily recognized as the major impurity. The orthorhombic unit cell, $a = 7.4289(8)$ Å, $b = 6.203(1)$ Å, and $c = 3.5574(6)$ Å was obtained using the TREOR automatic indexing program (6) which gave very satisfactory figures of merit ($M(20) = 92$ and $F(20) = 65.(0.004711,65)$). The cell parameters were refined by a least-squares program.

From the observed reflection conditions, the space groups *Immm*, *Imm2* and *I222* are possible. Calculations were first made in the centrosymmetric *Immm* space group. Individual intensities were then extracted from the powder pattern by using a local cell-constrained whole pattern fitting program; its main originality is that the individual $|F_{obs}|$ are not refined in a least-squares sense, they are estimated from an iterative procedure based on the very simple principle which gives the so-called "$|F_{obs}|$" in all Rietveld-type refinement programs (7). Then the SHELXS program was used for structure solu-

TABLE 1
Conditions of the Structure Determination and Rietveld Refinement for FeAlF$_5$

Space group	*Immm*
Cell parameters (Å)	$a = 7.4289(8)$
	$b = 6.203(1)$
	$c = 3.5574(6)$
Volume (Å)^3	163.93
Z	2
2θ range (°)	10–130
Step scan (°2θ)	0.04
Time/step (sec)	16.5
Number of *hkl*	196 (+116 for AlF$_3$)
Total parameters	19
x, y, z coordinates	2 (+1 for AlF$_3$)
Thermal parameters	5 (+2 for AlF$_3$)
Profile parameters	8
Zero point (°2θ)	0.228(3))
Discrepancy factors	$R_B = 0.103$
	$R_w = 0.233$
	$R_{wp} = 0.243$
	$R_e = 0.074$

tion (8). Scattering factors and anomalous dispersion terms were taken from the "International Tables for X-Ray Crystallography" (9). The PATT option and further Fourier-difference calculations allowed us to locate all the five independent atomic sites from a reduced data set (94 reflections, eliminating those having a neighboring one at less than 0.04° 2θ, minimum R factor = 0.28). The final refinements were made by using a Rietveld program adapted to X-ray data (10), taking into account α-AlF$_3$ as a major impurity. The cell parameters were kept fixed at the previously refined values. The final conventional Rietveld reliabilities are $R_B = 0.10$, $R_p = 0.23$, $R_{wp} = 0.24$, and $R_e = 0.074$. Table 1 summarizes the conditions for the structural determination and Fig. 1 shows the re-

TABLE 2
FeAlF$_2$: Atomic Coordinates and Thermal Parameters

	x	y	z	B_{iso}(Å^2)^a
Fe	0	0	0	1.8(8)
Al	0	$\frac{1}{2}$	$\frac{1}{2}$	2(1)
F1	0.742(8)	0	0	3.0(9)
F2	0	0	0	3.0(9)
F3	0	0.209(9)	$\frac{1}{2}$	3.0(9)

^{a} B_{iso} was kept fixed at the same value for all the F atoms.

sults of the powder pattern refinement. Table 2 presents the atomic coordinates and thermal parameters and Table 3 gathers selected interatomic distances and angles. Calculations with the space groups *Imm2* and *I222* do not improve the results.

It can be noticed that the medium quality of the samples (rather broad diffraction lines, presence of unavoidable impurities) does not allow a very precise determination, but the simplicity of the refined model (two adjustable positional parameters and correct interatomic distances) reports strongly in its favor.

DESCRIPTION OF THE STRUCTURE

Figure 1 presents the projection of the structure on the (001) plane. It is built from two connected kinds of strictly linear chains of octahedra running along the c axis. AlF$_6$ octahedra form *trans*-chains by sharing opposite F2 corners, FeF$_6$ octahedra share F3–F3 edges and build rutile-like chains. One AlF$_6$ octahedron is connected to four

TABLE 3
FeAlF$_5$: Selected Interatomic Distances (Å) and Angles (°)

FeF$_6$ octahedron

Fe	F1	F1	F3	F3	F3	F3
F1	**1.92(6)**	3.83(8)	2.92(5)	2.92(5)	2.92(5)	2.92(5)
F1	180(5)	**1.92(6)**	2.92(5)	2.92(5)	2.92(5)	2.92(5)
F3	90(4)	90(4)	**2.20(3)**	3.56(2)	4.40(2)	2.59(8)
F3	90(4)	90(4)	108(1)	**2.20(3)**	2.59(8)	4.40(2)
F3	90(4)	90(4)	180(1)	72(4)	**2.20(3)**	4.40(2)
F3	90(4)	90(4)	72(4)	180(1)	108(1)	**2.20(3)**

$\langle$Fe–F$\rangle = 2.11$ Å

AlF$_6$ octahedron

Al	F2	F2	F1	F1	F3	F3
F2	**1.779(1)**	3.557(1)	2.53(4)	2.53(4)	2.53(4)	2.53(4)
F2	180.01(1)	**1.779(1)**	2.53(4)	2.53(4)	2.53(4)	2.53(4)
F1	90(3)	90(3)	**1.80(6)**	1.80(6)	2.55(6)	2.55(6)
F1	90(3)	90(3)	180(5)	**1.80(6)**	1.81(6)	3.61(8)
F3	90(3)	90(3)	90(5)	90(5)	**1.81(6)**	3.61(8)
F3	90(3)	90(3)	90(5)	90(5)	180(5)	**1.81(6)**

$\langle$Al–F$\rangle = 1.796$ Å

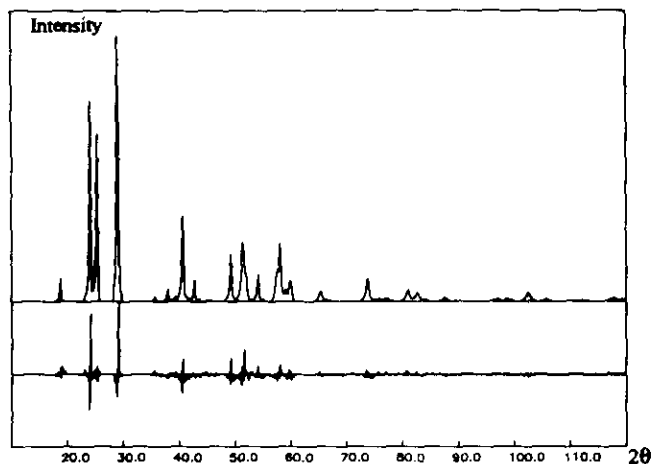FIG. 1. FeAlF$_5$: Comparison of the observed and calculated powder diffraction patterns; the difference is shown below at the same scale.

TABLE 4

FeAlF₅: Valence Bond Analysis[a]

	Fe	Al	Σ	Σ_expected
F1	0.49	0.50	**0.99**	1
	0.49	0.50		
F2	—	2 × 0.53	**1.06**	1
F3	2 × 0.23	0.49	**0.95**	1
	2 × 0.23	0.49		
Σ	**1.90**	**3.04**		
Σ_expected	2.0	3.0		

[a] Calculated from (11): $\nu_i = \Sigma_j \nu_{ij}$, with $\nu_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$, here $R_{Fe^{2+}-F^-} = 1.65$ Å and $R_{Al^{3+}-F^-} = 1.545$.

FeF₆ octahedra by two opposite F3 and two opposite F1 corners.

If the AlF₆ octahedron is quite regular, the FeF₆ one presents two short Fe–F1 (1.92 Å) and four long Fe–F3 distances (2.20 Å). This peculiarity was also noticed in the description of the closely related MnAlF₅ structure (1) where the MnF₆ octahedron exhibits four long and two short Mn–F distances.

This fact is imposed in both cases by the large F3–F3 distance which corresponds to the cell parameter related to the rutile type chains: $c = 3.557$ Å in FeAlF₅ and $a = 3.583$ Å in MnAlF₅. A satisfactory quantitative valence-bond analysis (11) is presented at Table 4.

Cr₂F₅(2) and MnCrF₅(3) structures can be described as monoclinic distortions of the FeAlF₅ one. The last represents the aristotype, the space group of which was previously theoretically predicted by Férey et al. (1).

MÖSSBAUER STUDY OF FeAlF₅

Experimental

⁵⁷Fe Mössbauer study has been performed using a classical way with a ⁵⁷Co source diffused into a rhodium matrix. Powder sample contained 10 mg of natural iron per cm². The hyperfine data were refined using the MOSFIT program (12). The studied sample is the same which was used for the structural determination.

Results and Discussion

Spectra at 300, 77, and 4.2 K are shown on Fig. 2. The 300 K spectrum presents a slightly asymetrical doublet, but at 77 K appears another component. In fact, these spectra were fitted using three components of iron: the most important (80%) corresponds to a very well resolved doublet with the following hyperfine parameters: isomer shift relative to iron-metal I.S. = 1.51 mm/sec and quadrupole splitting Q.S. = 2.30 mm/sec at 77 K; they are those of high-spin iron II (13). The Q.S. value remains
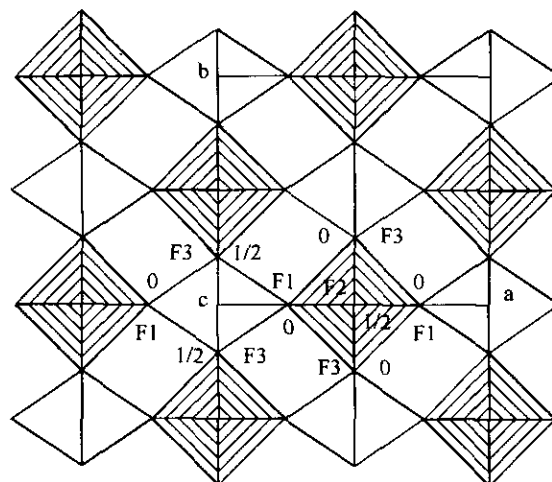

FIG. 2. FeAlF₅: Projection on the (001) plane. AlF₆ octahedra are hatched. Numbers refer to the z coordinates of the fluorine atoms.

surprisingly quasi-constant from 300 to 4.2 K. The second component (8%), visible at 77 and 4.2 K, gives also Mössbauer parameters typical for divalent iron (I.S. = 1.40 mm/sec and Q.S. = 3.64 mm/sec at 77 K). The last one (7%), which does not clearly appear on the spectra, is an iron III component (I.S. = 0.41 mm/sec and Q.S. = 0.85 mm/sec at 77 K). The spectrum at 4.2 K evidences a surprising small magnetic phase (see arrows), which is not present at 77 K.

At this step, we can say that our FeAlF₅ sample, identical to that used for the X-ray study, contains as expected iron II. Owing to its Q.S. value, the second iron II component cannot be attributed to the presence of FeF₂ traces (15); consequently we suppose that it belongs to the title
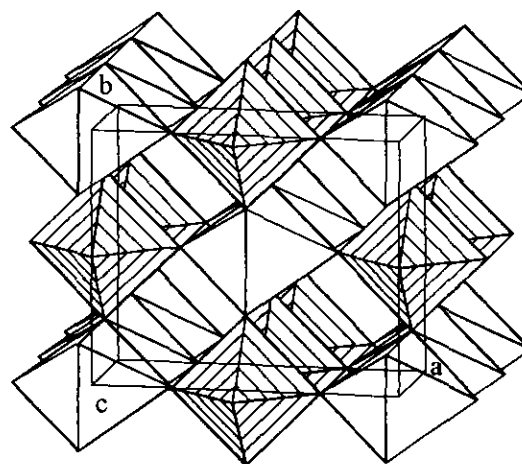

FIG. 3. FeAlF₅: Perspective view showing the trans-chains of AlF₆ octahedra, the rutile type chains of FeF₆ octahedra and their connections. AlF₆ octahedra are hatched.
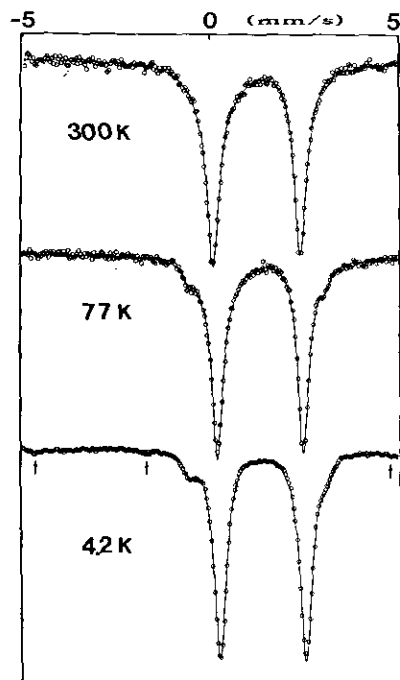
FIG. 4. FeAlF$_5$: Mössbauer spectra at different temperatures.

compound. The existence of the two contributions can be explained as a consequence of a partial inversion on the Fe/Al sites. In this case, the main contribution should correspond to iron in its normal site, the second contribution being then associated to iron substituted to aluminum, the local environment of which becoming perturbed as shown by a larger quadrupole splitting. Unfortunately, profile refinements are not very sensitive to this hypothesis and calculations in this way do not improve the results. The case of the iron III is more complex and the existence of a magnetic contribution at very low temperature is very typical of superparamagnetism in oxides as for Fe$_2$O$_3$ in small particles (14). So we can assume that Fe III is only present in form of oxides and not included in the fluoride.

The quadrupole splitting of the main contribution of iron II in the aluminofluoride is surprisingly not temperature dependent between 300 and 4.2 K. Such a behavior has

already been observed in other fluorides as the rutile FeF$_2$ (15).

The observed paramagnetic state at 4.2 K is in agreement with the structure which presents isolated rutile chains of Fe^{II}F$_6$ octahedra. If we consider the Fe^{2+}–Fe^{2+} coupling constants given for the rutile FeF$_2$ (16), particularly for the super-superexchange, a three-dimensional ordering is not expected before about 1 K.

CONCLUSION

FeAlF$_5$ is obtained by dehydration of complex hydrated fluorides. Its simple crystal structure may be considered as the aristotype from which derive the structures of many ABF$_5$ fluorides. The Mössbauer spectroscopy characterizes a small possible cationic inversion and a paramagnetic state down to 4.2 K in agreement with the low values of the Fe^{2+}–Fe^{2+} coupling constants for the rutile type arrangement of the Fe^{II}F$_6$ octahedra.

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