

K₂FeF₅: Synthesis and Crystal Structure of a New Form

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Single crystals of a new form of K₂FeF₅ have been grown by hydrothermal synthesis in concentrated HF solutions. The structure is established from single crystal X-ray diffraction data: space group *Pbam*, *Z* = 8, *a* = 7.3591 (4) Å, *b* = 23.0897 (10) Å, and *c* = 5.7054 (2) Å (*R* = 0.0257, *R_w* = 0.0273 for 1530 independent reflections and 84 parameters). The network is built with infinite and single linked *cis*-chains of FeF₆ octahedra, running along the *c* axis, separated by 10 coordinated potassium ions. The structure is compared to those of Rb₂CrF₅ and of the previously known K₂FeF₅ form (*Pbcn*), showing respectively the same single linked and double linked chains of MF₆ octahedra. © 1993 Academic Press, Inc.

1. Introduction

Up to now, among the A₂BF₅-type compounds, three have been known to be made up with zigzag *cis*-chains of BF₆ octahedra: K₂FeF₅ (1) and α-(NH₄)FeF₅ (2) with double-linked chains and Rb₂CrF₅ (3) with single linked chains. We report here the structure of a new K₂FeF₅ form with single linked *cis*-chains, prepared from HF aqueous solutions.

2. Preparation

Single crystals were prepared by hydrothermal synthesis in concentrated HF solution (40%). Typically 2.14 g of KF were added to 1.5 g of Fe₂O₃ in 5 ml of HF solution in a 10 ml closed Teflon vessel. The bomb was heated at 175°C (heating rate 1°/min), maintained 1 day at this temperature, and then allowed to cool naturally. Transparent, needle-shaped crystals were filtered and air-dried. As shown by DSC ex-

periments, they transform at 190°C irreversibly to K₃FeF₆ + KFeF₄.

3. Structural Determination

A small needle of approximate size (0.3 × 0.06 × 0.08) mm was chosen for the structure determination. Table I gathers the experimental conditions of the data collection. The lattice parameters were refined from the positions of 36 reflections near 30° (2θ) by the double scan technique. Owing to the small size of the crystal and to the small value of the absorption coefficient, it was not judged necessary to apply an absorption correction. The intensity data show systematic absences characteristic of *Pbam* and *Pba2* space groups (*Ok*l: *k* = 2*n* + 1; *h0*l: *h* = 2*n* + 1).

All the calculations were performed with the SHELX-76 program (4). The atomic scattering factors for ions and the values of Δ*f*' and Δ*f*'' were taken from "International

TABLE I
CONDITIONS OF THE DATA COLLECTION (SIEMENS
AED2 FOUR CIRCLE DIFFRACTOMETER)

Symmetry	Orthorhombic
Space group	<i>Pbam</i>
<i>a</i> (Å)	7.3591 (4)
<i>b</i> (Å)	23.0897 (10)
<i>c</i> (Å)	5.7054 (2)
<i>V</i> (Å ³)	968.05
<i>Z</i>	8
Formula weight (g)	229.04
<i>D</i> _{calc} (g/cm ³)	3.14
Crystal volume (10 ⁻³ mm ³)	1.44
Radiation	MoK α (graphite monochromatized)
<i>T</i> (K)	293
Scanning mode	$\omega/2\theta$
Aperture (mm)	4 \times 4
Range registered:	
θ_{\max} (°)	35
<i>h, k, l</i> _{max}	11, 35, 9
Absorption coefficient	$\mu = 48.38 \text{ cm}^{-1}$
Absorption correction	none
Reflections as measured	two independent sets total 4974 (330 standards)
used in refinement (<i>I</i> > 3 σ (<i>I</i>))	1530
Number of refined parameters	84
Weighting scheme	$w = 1.3574/(\sigma^2(F))$ + $5.22 \times 10^{-4}F^2$
Secondary extinction coefficient	$\kappa = 36(2) \times 10^{-4}$
Election density in final Fourier difference map (max and min) (e ⁻ /Å ³)	+1.0, -1.18
<i>R</i>	0.0257
<i>R</i> _w	0.0273

Tables for X-ray Crystallography'' (5). With the *Pbam* space group, the direct methods facilities of the program revealed all the atoms of the unit cell on the best *E* map. The atomic coordinates and the anisotropic thermal parameters were then refined, the final model giving *R* = 0.0257 and *R*_w = 0.0273. The final Fourier difference map was featureless. Table II presents the atomic coordinates and thermal parameters (structure factor tables will be sent upon request). The main interatomic distances and angles are given in Table III.

Calculations with the *Pba2* space group did not significantly improve the results.

4. Description of the Structure

Figure 1 shows the projection on the (100) plane. The network can be described as built from infinite and single linked *cis*-chains of FeF₆ octahedra, running along the *c*-axis and separated by potassium ions. It is a superstructure of the Rb₂CrF₅ type (3) shown at Fig. 2.

TABLE II
K₂FeF₅ (*Pbam*): ATOMIC COORDINATES AND THERMAL PARAMETERS^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>B</i> _{eq} [Å ²]
K1	2983(1)	2610(1)	0	189(3)	146(3)	213(3)	41(2)	1.44(2)
K2	1333(1)	831(1)	0	209(3)	160(3)	187(3)	27(2)	1.46(2)
K3	4469(1)	1683(1)	$\frac{1}{2}$	238(3)	194(3)	179(3)	58(3)	1.61(2)
K4	2293(1)	4881(1)	$\frac{1}{2}$	170(3)	144(3)	186(3)	-18(2)	1.32(2)
Fe1	1201(1)	4063(1)	0	91(2)	82(2)	93(2)	4(1)	0.70(1)
Fe2	9558(1)	1556(1)	$\frac{1}{2}$	102(2)	91(2)	92(2)	-9(1)	0.75(1)
F1	8161(3)	2239(1)	$\frac{1}{2}$	309(12)	119(9)	292(12)	71(8)	1.90(8)
F2	1103(2)	1805(1)	2578(3)	262(7)	268(8)	155(7)	-111(6)	1.80(6)
F3	2823(2)	3732(1)	7490(3)	203(6)	227(6)	195(6)	37(5)	1.64(5)
F4	4652(2)	678(1)	7591(3)	169(6)	183(5)	151(6)	-26(5)	1.32(4)
F5	526(3)	783(1)	$\frac{1}{2}$	240(10)	162(9)	266(11)	100(8)	1.76(8)
F6	5078(3)	1692(1)	0	187(8)	111(7)	222(10)	45(6)	1.37(6)
F7	2819(3)	4704(1)	0	190(9)	126(8)	258(11)	-49(7)	1.51(7)

^a Standard deviations are given in parentheses and refer to the last digit, *x*, *y*, *z*, and *U*_{*ij*} are $\times 10^4$. The *U*_{*ij*} relate to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$. All *U*₁₃ and *U*₂₃ = 0.

TABLE III
 K_2FeF_5 (*Pbam*): SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Fe1F ₆ Octahedron (Fe1-F) = 1.937						
Fe1	F4	F4	F7	F6	F3	F3
F4	1.883(1)	2.749(2)	2.846(2)	2.733(2)	3.896(1)	2.703(2)
F4	93.8(0.2)	1.883(1)	2.846(2)	2.733(2)	2.703(2)	3.896(1)
F7	97.6(0.2)	97.6(0.2)	1.900(2)	3.802(3)	2.662(3)	2.662(3)
F6	91.6(0.2)	91.6(0.2)	166.5(0.2)	1.929(3)	2.663(2)	2.663(2)
F3	176.2(0.1)	87.7(0.2)	85.7(0.2)	84.9(0.2)	2.015(1)	2.864(2)
F3	87.7(0.2)	176.2(0.1)	85.7(0.2)	84.9(0.2)	90.6(0.2)	2.015(1)
Fe2F ₆ Octahedron (Fe2-F) = 1.935						
Fe2	F2	F2	F1	F5	F3	F3
F2	1.880(1)	2.764(2)	2.757(2)	2.767(2)	3.901(2)	2.714(2)
F2	94.6(0.2)	1.880(1)	2.757(2)	2.767(2)	2.714(2)	3.901(2)
F1	94.2(0.2)	94.2(0.2)	1.883(3)	3.786(3)	2.666(3)	2.666(3)
F5	93.4(0.2)	93.4(0.2)	168.7(0.2)	1.922(3)	2.689(2)	2.689(2)
F3	177.3(0.1)	88.1(0.2)	86.0(0.2)	85.9(0.2)	2.023(1)	2.841(2)
F3	88.1(0.2)	177.3(0.1)	86.0(0.2)	85.9(0.2)	89.2(0.2)	2.023(1)
Bridging angle Fe1-F3-Fe2 176.3 (1)						
K1 Polyhedron (K1-F) = 2.855			K2 Polyhedron (K2-F) = 2.865			
	K1-F6	2.621(3)	K2-F7	2.676(3)		
	K1-F6	2.677(3)	2× K2-F2	2.692(3)		
2×	K1-F2	2.744(3)	2× K2-F4	2.825(2)		
2×	K1-F1	2.877(1)	K2-F7	2.866(3)		
2×	K1-F3	2.962(3)	2× K2-F5	2.916(1)		
2×	K1-F2	3.043(2)	2× K2-F3	3.121(2)		
K3 Polyhedron (K3-F) = 2.867			K4 Polyhedron (K4-F) = 2.839			
	K3-F1	2.669(3)	K4-F5	2.629(3)		
2×	K3-F4	2.755(3)	2× K4-F4	2.760(2)		
2×	K3-F2	2.850(2)	2× K4-F4	2.762(2)		
2×	K3-F6	2.888(1)	K4-F5	2.830(3)		
2×	K3-F3	3.005(2)	2× K4-F7	2.908(1)		
	K3-F1	3.005(2)	2× K4-F3	3.035(3)		

Figure 3 presents the projection on the (001) plane and shows the mutual orientation of the chains.

As shown in Table III, the FeF₆ octahedra are quite regular, the mean Fe-F distances

being very close to the sum of the ionic radii: 1.930 Å (6). Classically and as in the structure of the previously known K_2FeF_5 form (*Pbcn*), the four Fe-F terminal bonds are shortened while the bridging Fe1-F3

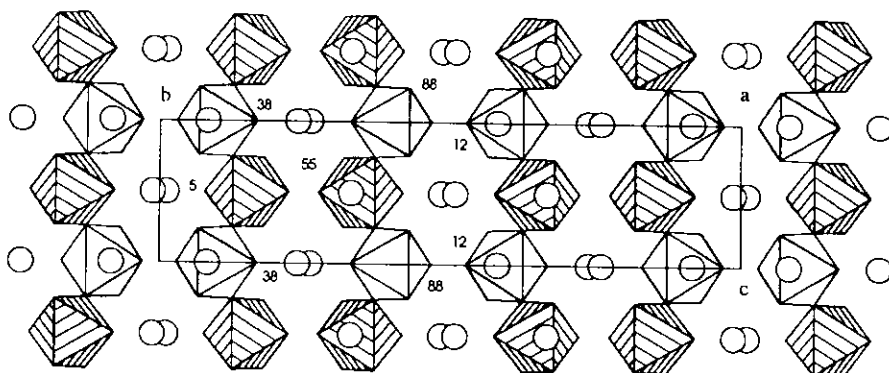


FIG. 1. K_2FeF_5 (*Pbam*). [100] projection of the structure. K atoms are circles. Fe2 octahedra are hatched. Numbers are x coordinates for the Fe atoms (centers of octahedra).

and Fe2–F3 distances are significantly longer.

All the potassium ions are tenfold coordinated; we observe a clear cut of the K–F distances near 3.12 Å, the next nearest F neighbors being at 3.4 Å.

It is interesting to compare this structure first to those of Rb_2CrF_5 (3) and Rb_2FeF_5 (7), which exhibit the same single-linked *cis*-chains of MF_6 octahedra running along the b axis as shown in Fig. 2 and Fig. 4. In the title structure, the mutual orientation of the chains is different (see Fig. 3) and enforces the doubling of the b axis (perpendicular to the chains) while the values of the a and c parameters agree very well respectively with those of the a and b parameters for Rb_2CrF_5 and Rb_2FeF_5 as shown in Table IV.

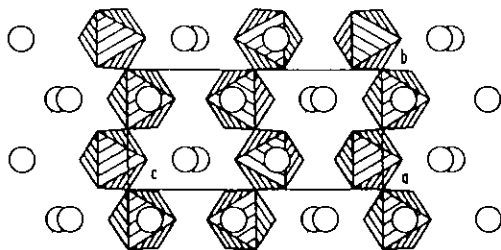


FIG. 2. Rb_2CrF_5 (*Pbam*). [100] projection of the structure. Rb atoms are circles.

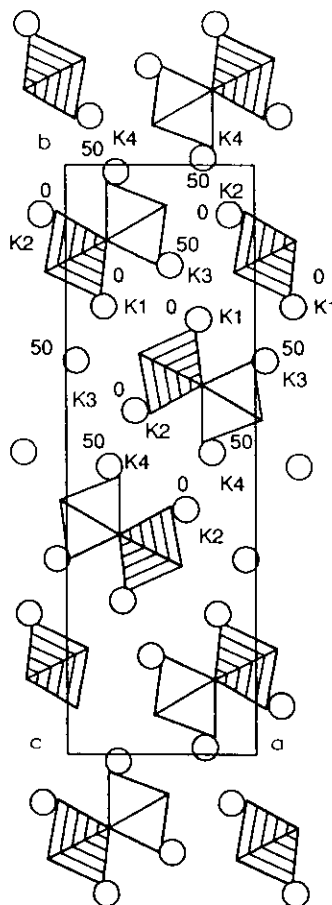


FIG. 3. K_2FeF_5 (*Pbam*). [001] projection of the structure. K atoms are circles. Fe2 octahedra are hatched. Fe1 are at $z = 0$, Fe2 at $z = \frac{1}{2}$. Numbers refer to the z coordinate for K atoms.

TABLE IV
CRYSTALLOGRAPHIC DATA FOR SOME A_2BF_5 *cis*-CHAIN STRUCTURES

Compound	S. G.	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	Z	$V/2(\text{\AA}^3)$	Type of chain	Ref.
Rb_2CrF_5	<i>Pnma</i>	7.515(5)	5.724(4)	11.985(6)	4	128.88	Single link	(3)
Rb_2FeF_5	<i>Pnma</i>	7.565(1)	5.810(1)	12.002(4)	4	131.88	Single link	(7)
K_2FeF_5	<i>Pham</i>	7.3591(4)	23.0897(10)	5.7054(2)	8	121.14	Single link	this work
$\alpha\text{-(NH}_4)_2FeF_5$	<i>Pbcn</i>	7.6223(5)	13.4408(8)	10.4167(6)	8	133.39	Double link	(2)
K_2FeF_5	<i>Pbcn</i>	7.4059(4)	12.8771(9)	20.4282(13)	16	121.76	Double link	(1)

Figure 5 presents the projection of the previously known form of K_2FeF_5 (*Pbcm*). The *cis*-chains are different and present double links. These chains are also encountered in $\alpha\text{-(NH}_4)_2FeF_5$ (2) as shown in Fig. 6.

5. Conclusions

The existence of two structural forms of K_2FeF_5 , differing by the nature of the links

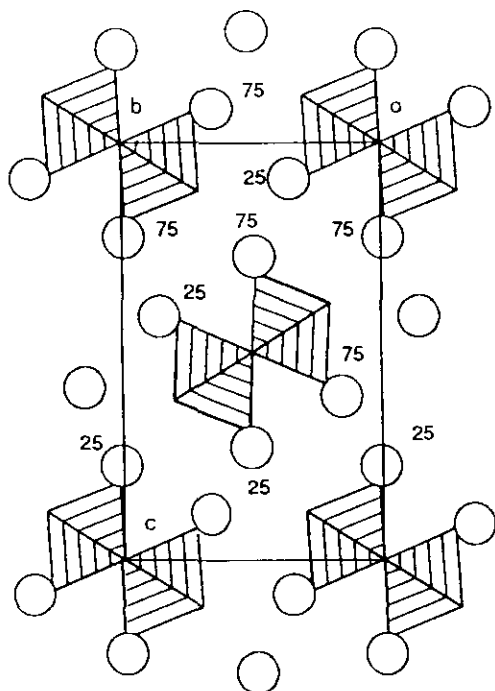


FIG. 4. Rb_2CrF_5 . [010] projection of the structure. Rb atoms are circles. Numbers refer to y coordinate for Rb atoms.

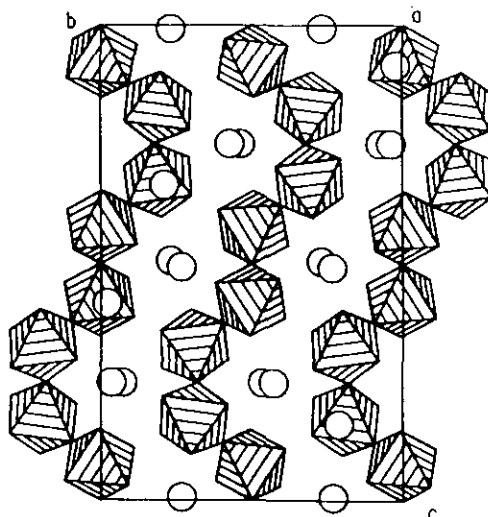


FIG. 5. K_2FeF_5 (*Pbcm*). [100] projection of the structure. K atoms are circles.

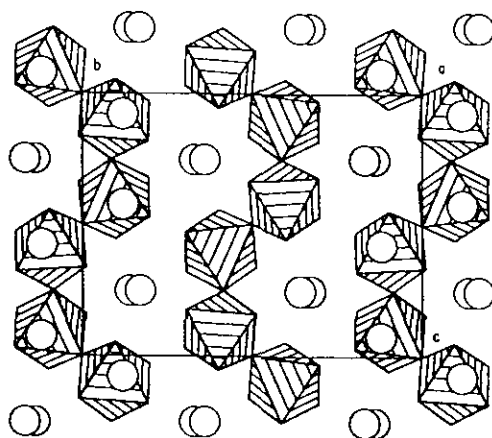


FIG. 6. $\alpha\text{-(NH}_4)_2FeF_5$. [100] projection of the structure. N atoms are circles.

of the *cis*-chains of FeF_6 octahedra, is interesting from the magnetic point of view. It is easy to predict that the title compound constitutes a new one-dimensional antiferromagnetic model. Further study is now in progress in this direction.

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