JOURNAL OF SOLID STATE CHEMISTRY 84, 408–412 (1990)

Reinvestigation of the Structure of K_2FeF_5

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Received July 21, 1989; in revised form October 16, 1989

The structure of K_2FeF_5 is reinvestigated: space group *Pbcn*, $Z = 16$, $a = 7.4059(4)$, $b = 12.8771(9)$, $c = 20.4282(13)$ Å (previous proposition: S.G. $Pn2_1a$ with c, a, b permutation). $R = 0.036$ ($R_w = 0.040$) for 1663 reflections and 149 parameters. All essential features of the previous description are maintained. © 1990 Academic Press, Inc.

1. Introduction

During a recent investigation of the thermal dehydration of $(NH_4)_2FeF_5 \cdot H_2O$, two phases were evidenced (*1*): β-$(NH_4)_2FeF_5$ which is isostructural with $(NH_4)_2MnF_5$ (*2*) and α-$(NH_4)_2FeF_5$ which exhibits a new structural type. The structure resolution of the α phase was realized by X-ray powder diffraction technique; strong structural correlations with the K_2FeF_5-type were observed. If α-$(NH_4)_2FeF_5$ crystallizes in the centrosymmetric space group *Pbcn* (unambiguously), then some doubt arises about the description of K_2FeF_5 in the noncentrosymmetric space group $Pn2_1a$ (*3*). Therefore, the structure was reinvestigated.

2. Experimental

Single crystals were prepared in a platinum crucible by the horizontal Bridgman method, from a mixture of 0.495 KF + 0.505 FeF_3. They were obtained together with $KFeF_4$ crystals from which they can be easily separated.

A colorless transparent crystal was selected. Data were collected on an AED2 Siemens-Stoe four circles diffractometer.

The systematic extinctions were not consistent with the previously retained space group $Pn2_1a$ (or *Pnma*) but with the nonequivocally centrosymmetric *Pbcn* space group, when an appropriate parameters permutation was performed. The experimental details of the data collection are given in Table I. Refinements were performed using the SHELX-76 program (*4*). Ionic scattering factors and anomalous dispersion terms were taken from *International Tables for X-ray Crystallography* (*5*). The refinements converge rapidly to $R = 0.059$ in the isotropic approximation (65 parameters) and $R = 0.036$ ($R_w = 0.040$)[1] with

[1] F_o and F_c values may be obtained by request from J. L. Fourquet.

0022-4596/90 $3.00

TABLE I

CONDITIONS OF DATA COLLECTION AND REFINEMENT FOR K_2FeF_5

Crystal data	
Space group	*Pbcn* (No. 60)
Cell dimensions, (from 40 reflections)	$a = 7.4059(4)$ Å, $b = 12.8771(9)$ Å, $c = 20.4282(13)$ Å
Z	16
Density (calcd)	3.123 g cm^{-3}
Crystal size	0.042 × 0.114 × 0.076 mm
μ (Mo$K\alpha$)	48.08 cm^{-1}
Intensity measurement	
T	20°C
Radiation	Mo$K\alpha$ (graphite monochromatized)
Scan mode	$\omega/2\theta$
Max 2θ	60°
Standard reflections	3 measured every 90 min
Reciprocal space explored	$0 \le h \le 10$ $-4 \le k \le 18$ $0 \le l \le 28$
Reflections measured	3383 total, 2367 unique
$R_{average}$	0.0266
Absorption correction	Gauss method
Min, max transmission	0.524, 0.784
Structure solution and refinements	
Reflections included	1663 with $I > 3\sigma(I)$
Parameters refined	149
Weighting scheme	$w = 0.966/[\sigma^2(F) + 0.0011\ F^2]$
Isotropic extinction	$F_c = F\ (1 - gxF^2/\sin\theta)$, $g = 5.0(8) \times 10^{-8}$
Agreement factors	$R = 0.036$, $R_w = 0.040$
$(\Delta\rho)$ max; $(\Delta\rho)$ min	0.7; −0.7 e/Å^3

anisotropic thermal motion for all atoms (149 parameters, 1663 reflections).

3. Results and Discussion

As shown in Fig. 1, all essential features of the previous structural description are maintained. The coordinates and anisotropic thermal parameters are given in Table II, selected interatomic distances and angles in Table III. Some understandable anomalies appearing in the previous study (Fe–F and K–F distances as short as 1.804 and 2.539 Å, respectively) are rectified. The usual shortening of the four Fe–F terminal bonds is confirmed. The K^+ coordinations were given as being 9 and 10. In fact, we observe a clear cut of the K–F distances near 3.25 Å, the next nearest F neighbors being at 3.5 Å, so the K^+ coordinations are 11 (K2, K4), 10 (K3, K5), and 9 (K1). However, K1 could be considered as eightfold coordinated because the 9th F is clearly at a very much longer distance than the others (0.35 Å more).

In the A_2BF_5-type compounds, three are

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS OF K_2FeF_5

	x	y	z	$U11$	$U22$	$U33$	$U23$	$I13$	$U12$	B_{eq} [Å^2]
K1	0	729(1)	2500	164(7)	162(7)	147(6)	0(0)	13(6)	0(0)	1.24(5)
K2	0	5374(1)	2500	189(8)	164(7)	293(8)	0(0)	−59(7)	0(0)	1.70(6)
K3	1593(2)	216(1)	4163(1)	252(6)	290(6)	174(5)	−35(4)	−20(5)	73(6)	1.88(4)
K4	1472(2)	7881(1)	1634(1)	257(6)	247(6)	235(5)	75(5)	−44(5)	−62(5)	1.95(4)
K5	4886(2)	2321(1)	−65(1)	172(5)	178(6)	186(4)	−21(4)	7(4)	25(4)	1.41(4)
Fe1	6684(1)	20(0)	4219(0)	89(3)	99(3)	91(3)	−1(2)	10(3)	−3(3)	0.73(2)
Fe2	3372(1)	8030(1)	3286(0)	89(3)	116(3)	86(3)	−1(2)	4(3)	−6(3)	0.76(2)
F1	−59(5)	1986(2)	1406(1)	293(18)	187(14)	220(14)	−14(12)	103(14)	90(14)	1.84(12)
F2	4957(5)	9046(2)	3767(1)	214(16)	218(14)	246(14)	−72(12)	−41(13)	−79(13)	1.78(12)
F3	0	5000	0	206(23)	289(25)	187(19)	31(16)	−153(19)	2(18)	1.79(17)
F4	0	3218(3)	2500	188(22)	279(22)	155(18)	0(0)	−116(17)	0(0)	1.64(16)
F5	2978(4)	2057(2)	2790(1)	243(17)	265(16)	163(13)	−36(12)	11(13)	122(13)	1.77(12)
F6	2223(4)	8801(2)	402(1)	186(16)	176(14)	248(14)	−40(11)	−14(12)	−43(12)	1.60(11)
F7	4724(5)	1098(2)	1119(2)	324(20)	219(15)	325(15)	−77(13)	−50(15)	−126(15)	2.28(13)
F8	1817(5)	9925(2)	1518(1)	310(18)	280(16)	182(13)	46(12)	165(14)	59(15)	2.03(12)
F9	1791(4)	9098(2)	5299(1)	258(17)	263(16)	185(12)	−38(12)	−20(13)	−159(14)	1.86(12)
F10	2070(5)	9199(2)	2966(1)	242(18)	247(16)	254(14)	44(13)	−13(13)	128(14)	1.96(13)
F11	3098(4)	2986(2)	4038(1)	209(16)	350(16)	146(12)	−31(12)	−94(13)	80(14)	1.86(12)

Note. 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 $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23})]$.

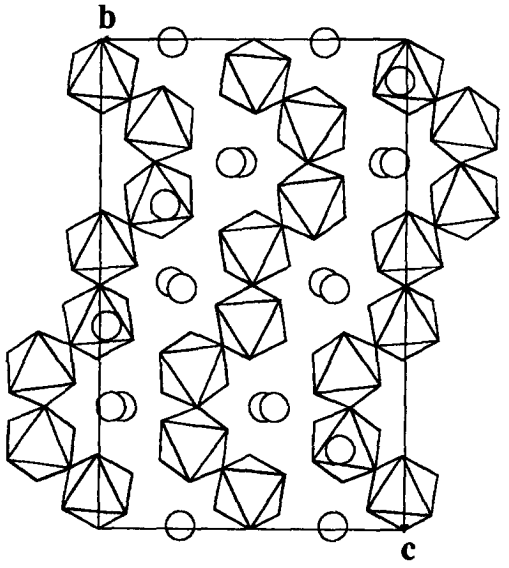

FIG. 1. Projection of the K_2FeF_5 structure on the (100) plane (K atoms are those of the unit cell only).

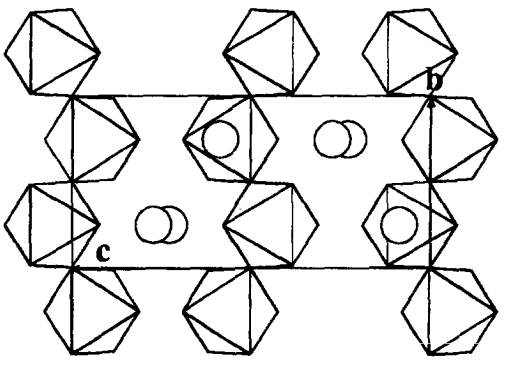

FIG. 2. Projection of the Rb_2CrF_5 structure on the (100) plane (Rb atoms are those of the unit cell only).

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR K_2FeF_5

Fe 1 octahedron ⟨Fe–F⟩ = 1.932

Fe1	F7	F8	F9	F6	F2	F3
F7	1.869(3)	2.754(4)	2.755(4)	3.785(3)	2.664(4)	2.695(3)
F8	94.7(3)	1.876(3)	2.791(3)	2.718(3)	2.708(4)	3.897(3)
F9	94.6(3)	96.0(3)	1.880(3)	2.733(3)	3.893(2)	2.715(3)
F6	170.9(2)	91.2(3)	91.7(3)	1.928(2)	2.710(4)	2.700(3)
F2	86.5(3)	88.1(3)	175.7(2)	86.8(3)	2.015(3)	2.802(2)
F3	87.5(2)	175.3(2)	88.0(2)	86.1(2)	87.8(2)	2.025(0)

Fe2 octahedron ⟨Fe–F⟩ = 1.934

Fe2	F11	F1	F5	F10	F2	F4
F11	1.883(2)	2.747(4)	2.818(3)	2.693(3)	2.699(4)	3.901(4)
F1	93.6(3)	1.885(3)	2.717(4)	3.780(3)	2.676(3)	2.740(3)
F5	96.4	91.8	1.897(3)	2.782(4)	3.908(2)	2.729(3)
F10	90.7(3)	172.3(2)	94.1(3)	1.903(3)	2.700(4)	2.686(3)
F2	87.6(3)	86.6(3)	175.8(2)	87.1(3)	2.013(3)	2.800(3)
F4	174.7(3)	89.0(2)	88.2(2)	86.3(2)	87.8(2)	2.023(0)

Bridging angles

Fe1–F2–Fe2	176.2(1)	Fe1–F3–Fe1	180.0(1)	Fe2–F4–Fe2	166.3(2)

K Polyhedrons K–F < 3.5 Å

K1		K2	
2 × F8	2.628(3)	2 × F5	2.700(3)
2 × F10	2.671(3)	F4	2.777(4)
2 × F1	2.760(3)	2 × F10	2.812(3)
2 × F5	2.853(3)	2 × F7	2.979(3)
F4	3.205(4)	2 × F2	3.103(3)
		2 × F8	3.149(3)
⟨K1–F⟩	2.781	⟨K2–F⟩	2.933

K3		K4		K5	
F9	2.734(3)	F5	2.621(3)	F6	2.642(3)
F10	2.797(3)	F8	2.654(3)	F6	2.673(3)
F1	2.800(3)	F7	2.677(3)	F11	2.715(3)
F6	2.868(3)	F6	2.836(3)	F9	2.731(3)
F9	2.875(3)	F11	2.836(3)	F1	2.881(3)
F11	2.893(3)	F1	2.933(4)	F7	2.888(3)
F8	2.908(4)	F5	3.035(3)	F11	2.897(3)
F7	3.010(4)	F2	3.149(3)	F2	2.965(3)
F2	3.022(4)	F4	3.186(2)	F3	2.993(1)
F3	3.061(2)	F10	3.229(4)	F9	3.024(3)
		F10	3.237(3)		
⟨K3–F⟩	2.897	⟨K4–F⟩	2.946	⟨K5–F⟩	2.841

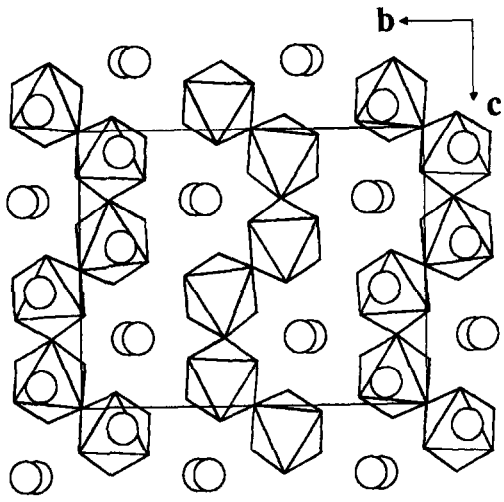

FIG. 3. Projection of the α-$(NH_4)_2FeF_5$ structure on the (100) plane.

now known to be made up with octahedral zig-zag *cis* chains: K_2FeF_5, Rb_2CrF_5 (*6*) (Fig. 2), and α-$(NH_4)_2FeF_5$ (*1*) (Fig. 3). These three structural types provide an interesting series for the intercomparison of one-dimensional magnetic behavior.

4. Acknowledgments

One of the authors (A.D.) would like to thank Professor J. Nouet and G. Niesseron for providing her with single crystals of K_2FeF_5.

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