On two new K_2FeF_5 forms

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Two additional forms of K_2FeF_5 are disclosed and characterized by powder diffraction. One (form-IV) adopts a new A_2MF_5 structural type, space group $C2/m$, $a = 13.0919(2)$ Å, $b = 5.7311(1)$ Å, $c = 7.3114(1)$ Å, $\beta = 118.241(1)$, and $Z = 4$, it is obtained from the thermal evolution of form-III, isostructural with Rb_2FeF_5, space group $Pnma$, $a = 7.3964(2)$ Å, $b = 5.6779(1)$ Å, $c = 11.5445(3)$ Å, and $Z = 4$. Both forms are compared to two previously reported polymorphs. The III → IV transition is topotactic, conserving the same zigzag cis-connected octahedral $(FeF_5)_n^{2n-}$ chains after an ~90° rotation and 1/2*b* translation of half of them. © *2013 International Centre for Diffraction Data*.
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Key words: potassium iron fluoride, powder diffraction, crystal structure, polymorphism

I. INTRODUCTION

Thermolysis of hydrated and/or organometallic compounds is a well-known preparation route for new derivatives, intermediate or anhydrous forms of inorganic compounds, possibly metastable, usually obtained as fine powders. The full crystallographic characterization of such materials can be difficult, requesting expertise in the most up to date powder diffraction methodologies. Many crystal structures of new fluoride compounds that were prepared according to such routes or to more classical solid-state approaches, were determined *ab initio* from the powder diffraction data. The list includes fluoride compounds with a binary chemical formulation such as SF_6 (Cockroft and Fitch, 1988), τ-AlF_3 (Le Bail *et al.*, 1992), ReF_7 (Vogt *et al.*, 1994), and C_6F_{10} (Smrcok *et al.*, 2013). Such discoveries of new binary compounds are especially interesting owing to their rarefaction: the ReF_7 crystal structure being published in *Science*, τ-AlF_3 being later "post-predicted" together with other yet unknown possible AlF_3 polymorphs (Le Bail and Calvayrac, 2006). New ternary compounds are logically a bit more frequently produced, some crystal structures being also solved from the powder diffraction data, such as Li_2TbF_6 (Laligant *et al.*, 1988), β- and γ-$BaAlF_5$ (Le Bail *et al.*, 1990b), polymorphs of $CsAlF_4$ (Bentrup *et al.*, 1992), β-Ba_3AlF_9 (Le Bail, 1993) a complex one with 29 independent atoms, $ThZr_2F_{12}$ (Taoudi *et al.*, 1996), Ba_2ZrF_8 (Le Bail and Laval, 1998), θ-$KAlF_4$ (Le Bail, 2009a), and $NaAlF_4$ (Le Bail, 2009b), to give a few examples, and there is no place here for citing quaternary compounds. In the same A_2MF_5 family (A^I = K, Rb, Cs, and NH_4; M^{III} = Al, Cr, V, Fe, and Ga) as the title compounds, α- and β-$(NH_4)_2FeF_5$ (Fourquet *et al.*, 1989) were the results of the thermal decomposition of $(NH_4)_2FeF_5{\bullet}H_2O$, their structures were also solved from the powder diffraction data. On continuing such studies, the thermal dehydration of $K_2FeF_5{\bullet}H_2O$ was found to lead to two new K_2FeF_5 forms, one of them being characterized structurally *ab initio* in this paper by powder diffraction methodologies having demonstrated their efficiency during several recent blind tests (Le Bail *et al.*, 2009).

II. EXPERIMENTAL

The new K_2FeF_5 forms are the products of monohydrate thermolysis, which was reported by Bentrup (1991) to lead to an orthorhombic form at 135 °C. It is shown here that this orthorhombic form (noted III) is not the high-temperature solid-state one (Le Bail *et al.*, 1990a) belonging to the *Pbcn* space group (noted form-I), nor the hydrothermally synthesized form (Fourquet and Duroy, 1993) crystallizing in the *Pbam* space group (noted form-II), both these known phases being characterized from single crystal data. Moreover, a phase transition from form-III to a fourth form is observed at 412 °C, which finally undergoes a phase transition to the normal *Pbcn* HT form-I at 580 °C. The powder diffraction patterns of K_2FeF_5 forms III and IV could be recorded at room temperature. Note that form-II transforms at 190 °C irreversibly to $K_3FeF_6 + KFeF_4$ (Fourquet and Duroy, 1993).

III. INDEXING, STRUCTURE DETERMINATIONS, AND RIETVELD REFINEMENTS

A. K_2FeF_5 form-III

At the identification stage by search-match procedures applied to the powder diffraction pattern recorded at room temperature, by using the ICDD-PDF database, the best match was from $K_2VO_2F_3$ (see PDF entry 04-009-3298; PDF, 2012) (Ryan *et al.*, 1971). Rb_2CrF_5 (Jacoboni *et al.*, 1974) belongs to the same crystal structure type. Thus, the Rietveld (1969) refinement, using the *FULLPROF* software (Rodriguez-Carvajal, 1993) was made starting from the Rb_2CrF_5 atomic coordinates (*Pnma* space group), and readily converged to satisfy *R* values. In order to improve the sample crystallinity, it was maintained at 400 °C just before the form-III → form-IV transition, nevertheless, a small amount

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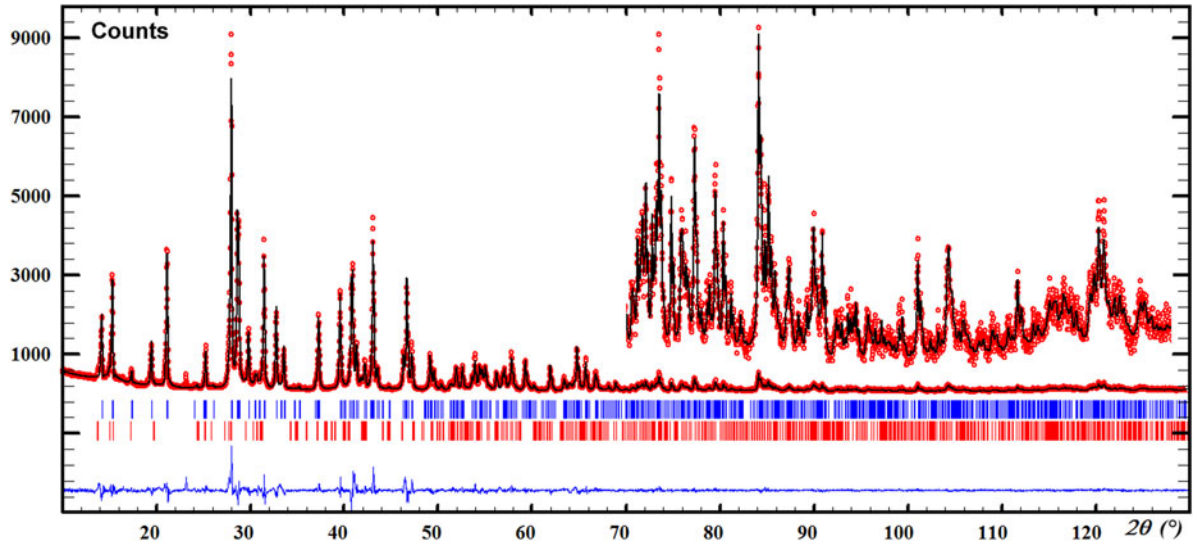


Figure 1. (Color online) Rietveld plot for K_2FeF_5 form-III (Cu$K\alpha$). The second phase corresponds to a 6.1(2)% contribution of form-IV starting to appear. A third phase remains unidentified, showing a main peak at 23.2° (2θ).

of form-IV had to be considered in the final Rietveld refinement (Figure 1), with fixed atomic coordinates, after the form-IV structure was solved. The Rietveld refinement details, the atomic coordinates, selected geometric parameters, and X-ray diffraction data are shown in Tables I–IV, respectively.

TABLE I. Experimental and Rietveld refinement details for the K_2FeF_5 forms III and IV.

Diffractometer	Siemens D500	
Geometry	Bragg–Brentano	
Goniometer	Vertical	
Radiation type	Cu$K\alpha$	
Wavelengths (Å)	1.540 56, 1.54 433	
Monochromator	Graphite	
Pattern refinement range (°2θ)	10–130	
Step size (2θ)	0.02°	
Temperature (°C)	23	
Chemical formula	K_2FeF_5	
Form	III	IV
Space group	*Pnma*	*C*2/*m*
Z	4	
Cell parameter (Å, °)		
a	7.3964(2)	13.0919(2)
b	5.6779(1)	5.7311(1)
c	11.5445(3)	7.3114(1)
β		118.241(1)
Volume (Å^3)	484.82(2)	483.28(1)
No. of contributing reflections	486	
No. of refined parameters (total)	70	55
No. of atomic coordinates parameters	13	
No. of restraints	none	
No. of isotropic thermal parameters	7	
No. of background parameters (interpolated from a set of points)	37	20
Profile shape	Pseudo-Voigt	
η	1.06(1)	0.67(2)
U	0.033(3)	0.27(2)
V	−0.020(3)	0.0002(17)
W	0.0169(7)	0.0013(3)
Conventional Rietveld reliability factors	(Rietveld, 1969)	
R_P (%)	13.1	14.0
R_{WP} (%)	15.3	17.0
R_{exp} (%)	8.69	9.02
R_B (%)	4.68	5.78
R_F (%)	3.11	4.50

B. K_2FeF_5 form-IV

The search-match process was negative for that sample quenched at 500 °C. Indexing was realized by using the *McMaille* software (Le Bail, 2004), leading to a C-centered monoclinic cell. The Figures of Merit (FoMs) were M_{20} = 55.9 (de Wolff, 1968), F_{20} = 79.5 (0.0043, 58) (Smith and Snyder, 1979), and McM_{20} = 169.9 (Le Bail, 2008). The cell volume was similar to that of form-III. On using Le Bail fitting (Le Bail, 2005) for evaluating the reliability of the indexing and for intensity extraction, the *C*2/*m*, *C*2, or *Cm* space groups were found to be the most probable. The structure solution was carried out in direct space by using the *ESPOIR* software (Le Bail, 2001), moving in the cell the appropriate number of K, Fe, and F atoms by a Monte Carlo process. A satisfying solution allowing us to recognize [FeF_6] octahedra was obtained in the *C2/m* space group, which was confirmed by a Rietveld refinement using *FULLPROF* (Figure 2). Traces of $KFeF_3$ were identified indicating some $Fe^{3+} \rightarrow Fe^{2+}$ disproportionation; another impurity in a very small proportion could not be defined. The Rietveld refinement details, the atomic coordinates, and selected geometric parameters are shown in Tables I–III, respectively, and the X-ray diffraction data are in Table V.

IV. STRUCTURE DESCRIPTION AND CORRELATIONS WITH RELATED COMPOUNDS

The form-III structure (Figure 3) is very common since it is adopted by $Rb_2M^{III}F_5$ (M^{III} = Cr, Fe, and Ga) and Cs_2FeF_5, as well as by some oxyfluoride compounds. MF_6 octahedra are connected by cis-corners to form infinite $(FeF_5)_n^{2n-}$ zigzag chains. Calculated bond valences reported in Table II for both forms III and IV are close to the expected values (maximum difference attaining 12%), indicating that the unrestrained Rietveld refinements from laboratory powder data have led to medium quality results. The bridging Fe–F

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TABLE II. Fractional atomic coordinates and isotropic displacement parameters (Å^2) at 23 °C for K_2FeF_5 forms III and IV in the *Pnma* and *C2/m* space groups, respectively; *BV* is the bond-valence calculated according to Brese and O'Keefe (1991).

	Wyckoff	*x*	*y*	*z*	B_{iso}	*BV*
Form-III						
K1	4c	0.1578(4)	1/4	0.4142(2)	1.99(8)	0.98
K2	4c	0.4873(3)	1/4	0.7283(3)	1.36(7)	1.05
Fe	4c	0.6693(3)	1/4	0.4368(2)	1.16(5)	2.97
F1	4a	1/2	0	1/2	0.89(12)	1.00
F2	4c	0.5236(8)	1/4	0.3050(6)	3.23(18)	0.99
F3	4c	0.7823(8)	1/4	0.5903(6)	2.88(19)	0.99
F4	8d	0.8257(7)	0.0119(6)	0.3869(3)	2.16(10)	1.01
Form-IV						
K1	4i	0.4773(2)	0	0.7516(4)	1.33(6)	1.02
K2	4i	0.1661(3)	0	0.7697(5)	1.32(7)	1.03
Fe	4i	0.1876(2)	0	0.2811(3)	1.05(5)	3.16
F1	4f	1/4	1/4	1/2	1.72(15)	1.04
F2	4i	0.0571(5)	0	0.3277(8)	1.51(16)	0.97
F3	4i	0.3397(5)	0	0.3069(8)	1.90(18)	0.96
F4	8j	0.1404(4)	0.2368(7)	0.0904(7)	1.93(12)	1.12

distance (2.029 Å in form-III and 2.011 Å in form-IV) is longer than the terminal ones $1.864 < Fe–F_{term} < 1.960$ Å in form-III and $1.831 < Fe\text{-}F_{term} < 1.909$ Å in form-IV; the bridging Fe–F–Fe angle is 180° in both forms. The same cis-chains of the FeF_6 octahedra are the characteristic of K_2FeF_5 form-II hydrothermally synthesized (Fourquet and Duroy, 1993) but the mutual orientation of the chains is different leading to a doubling of the longer axis ($b_{II} = 23.0897$ Å $\sim 2 \times c_{III} = 11.544$ Å), the two other cell parameters being very similar (Table VI). All of the potassium ions are tenfold coordinated in both forms II and III, with a clear cut of the K–F distances. In form-IV all of the potassium ions are also tenfold coordinated (they have coordination 9, 10, and 11 in form-I) and the same zigzag cis-connected $(FeF_5)_n^{2n-}$ chains (Figure 4) appear to present again a different mutual orientation (Figure 5). A topotactic reaction hypothesis looks highly plausible to explain the form-III → IV transition : it is sufficient to rotate half the chains accompanied by the potassium ions nearest neighbors by 90° along the *b*-axis (arrows in Figure 5), and to translate the chains by 1/2 ***b*** in order to make form-III appear back from form-IV (but since the reaction is irreversible, the inverse moves have to be considered). Polymorphic transitions were also proposed to be topotactic and a similar displacive mechanism was suggested for the α, β, and γ-$BaAlF_5$ phases characterized by the same cis-connected octahedral chains, some of these structures being also solved from the powder data (Le Bail *et al.*, 1990b). K_2FeF_5 form-II (Figure 6) may be described as containing kink-folded blocks related to form-IV, and if the junction zone between these blocks is examined, one recognizes similarities with form-III (Figure 3). All of the four K_2FeF_5 forms are characterized by cis-connected octahedral chains, and their *V/Z* ratios at room temperature (Table VI) are almost identical. The periodicity is of $N = 2$ octahedra for forms II, III, and IV, corresponding to the shortest cell parameter close to 5.7 Å (Table VI), whereas form-I shows $N = 8$ (Figure 7) so that the phase transition IV → I at 580 °C looks to require a much larger atomic displacement amplitude than for the III → IV transition. A different organization with $N = 4$ was established for α-$(NH_4)_2FeF_5$ (Fourquet *et al.*, 1989), also produced by dehydration and solved from the powder data, so that the current number of structure types for the A_2MF_5 compounds presenting cis-connected octahedral chains is five. Concerning K_2FeF_5, only form-I is yet characterized magnetically, however the three other forms should logically share the same characteristic one-dimensional antiferromagnetic model

TABLE III. Selected interatomic distances (Å) and angles (°) for the K_2FeF_5 forms III and IV at 23 °C.

Form-III		Form-IV	
Fe–F2	1.865 (7)	Fe–F4…2*x*	1.831 (4)
Fe–F4…2*x*	1.870 (4)	Fe–F2	1.894 (8)
Fe–F3	1.959 (7)	Fe–F3	1.909 (8)
Fe–F1…2*x*	2.029 (2)	Fe–F1…2*x*	2.011 (1)
Fe–Fe	4.058 (4)	Fe–Fe	4.022 (2)
Fe–F1–Fe^{ix}	180.0	Fe–F1–Fe^{iii}	180.0
F2–Fe–F3	169.9 (3)	F2–Fe–F3	165.9 (3)
F2-Fe-F4	96.1 (2)	F2–Fe–F4	97.4 (2)
F1–Fe–F2	86.4 (2)	F1–Fe–F2	85.3 (2)
F3–Fe–F4	90.8 (2)	F3–Fe–F4	92.0 (2)
F1–Fe–F3	86.4 (2)	F1–Fe–F3	84.8 (2)
F1–Fe–F4	89.2 (1)	F1–Fe–F4	86.6 (2)
F1^{vii}–Fe–F4	176.8 (2)	F1–Fe–F4^{i}	176.2 (2)
F4–Fe–F4^{viii}	92.6 (2)	F4–Fe–F4^{i}	95.7 (2)
F1–Fe–F1^{vii}	88.8 (1)	F1–Fe–F1^{i}	90.9 (1)
K1–F2^{ii}	2.718 (7)	K1–F3^{iv}	2.625 (8)
K1–F4^{i}…2*x*	2.738 (4)	K1–F4^{ii}…2*x*	2.769 (6)
K1–F4^{iv}…2*x*	2.821 (5)	K1–F4^{v}…2*x*	2.822 (4)
K1–F3^{i}…2*x*	2.874 (1)	K1–F3	2.876 (6)
K1–F2	2.985 (7)	K1–F2^{ii}…2*x*	2.916 (9)
K1–F1…2*x*	3.066 (3)	K1–F1…2*x*	3.019 (2)
K2–F3^{vi}	2.585 (7)	K2–F2^{vi}	2.660 (2)
K2–F3	2.702 (7)	K2–F4^{ii}…2*x*	2.699 (5)
K2–F4^{v}…2*x*	2.734 (5)	K2–F2	2.849 (6)
K2–F2^{iii}…2*x*	2.866 (1)	K2–F4^{vii}…2*x*	2.863 (7)
K2–F1…2*x*	2.995 (3)	K2–F3^{ii}…2*x*	2.914 (3)
K2–F4^{i}…2*x*	3.057 (5)	K2–F1…2*x*	3.033 (4)

Symmetry codes – Form-III : (i) $-x+1$, $y+1/2$, and $-z+1$; (ii) $x-1/2$, $-y+1/2$, and $-z+1/2$; (iii) $-x+1$, $y-1/2$, and $-z+1$; (iv) $x-1$, y, and z; (v) $x-1$, $-y+1/2$, and z; (vi) $x-1/2$, $-y+1/2$, and $-z+3/2$; (vii) $-x+3/2$, $-y$, and $z+3/2$; (viii) $x+1/2$, y, and $-z+1/2$; (ix) $-x+3/2$, $-y-1$, and $z+3/2$; Form-IV : (i) x, $-y$, and z; (ii) $-x+1/2$, $y-1/2$, and $-z+1$; (iii) $-x+1/2$, $y+1/2$, and $-z+1$; (iv) $-x+1$, y, and $-z+1$; (v) $x+1/2$, $y-1/2$, and $z+1$; (vi) $-x$, y, and $-z+1$; (vii) x, y, and $z+1$; (*x*) x, $-y$, and $z+1$.

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TABLE IV. X-ray diffraction data for K_2FeF_5 form-III at 23 °C (Cu$K\alpha1$).

$2\theta_{obs}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{cal}$	d_{cal}	I_{cal}	$\Delta2\theta$
14.216	6.2248	16.4	1	0	1	14.209	6.2278	20.2	0.007
15.344	5.7697	26.7	0	0	2	15.337	5.7723	29.7	0.007
17.380	5.0981	3.9	0	1	1	17.391	5.0950	3.8	−0.011
19.481	4.5528	11.0	1	0	2	19.491	4.5505	14.3	−0.010
21.155	4.1961	37.7	1	1	1	21.157	4.1959	44.2	−0.002
25.268	3.5217	11.5	2	0	1	25.267	3.5219	12.5	0.001
27.994	3.1846	100.0	0	1	3	27.987	3.1855	100.0	0.007
28.640	3.1142	48.7	2	0	2	28.643	3.1139	47.6	−0.003
28.778	3.0996	44.9	2	1	0	28.786	3.0988	46.7	−0.008
29.820	2.9936	16.6	2	1	1	29.828	2.9929	18.3	−0.008
30.530	2.9256	3.7	1	1	3	30.530	2.9256	3.0	0.000
33.577	2.6668	11.3	2	0	3	33.581	2.6665	15.3	−0.004
37.282	2.4098	23.0	3	0	1	37.262	2.4111	12.2	0.020
			1	2	2	37.301	2.4086	15.9	−0.019
39.590	2.2745	29.9	2	0	4	39.577	2.2753	34.4	0.013
40.812	2.2092	32.5	2	2	1	40.791	2.2103	32.5	0.021
40.913	2.2040	28.4	1	0	5	40.912	2.2040	26.0	0.001
41.336	2.1824	13.8	1	2	3	41.328	2.1828	14.6	0.008
42.206	2.1394	9.0	0	1	5	42.218	2.1388	2.1	−0.012
43.089	2.0976	53.6	2	2	2	43.081	2.0979	56.0	0.008
43.565	2.0757	6.9	3	0	3	43.561	2.0759	7.0	0.004
46.326	1.9582	12.0	2	0	5	46.319	1.9585	12.2	0.007
46.706	1.9432	32.3	2	2	3	46.696	1.9436	42.0	0.010
47.207	1.9237	15.5	0	0	6	47.198	1.9241	12.0	0.009
49.170	1.8514	11.5	2	1	5	49.169	1.8515	12.9	0.001
49.575	1.8372	6.3	3	2	1	49.561	1.8378	7.0	0.014
50.345	1.8109	2.4	1	3	1	50.348	1.8109	2.2	−0.003
51.277	1.7802	2.1	3	1	4	51.280	1.7801	1.9	−0.003
51.941	1.7590	6.6	4	0	2	51.879	1.7609	4.1	0.062
			4	1	0	51.966	1.7582	6.4	−0.025
52.603	1.7384	7.1	4	1	1	52.611	1.7382	7.9	−0.008
53.656	1.7067	3.8	2	0	6	53.651	1.7069	4.2	0.005
53.949	1.6982	11.5	0	3	3	53.943	1.6983	11.4	0.006
52.603	1.7384	7.1	4	1	1	52.611	1.7382	7.9	−0.008
53.656	1.7067	3.8	2	0	6	53.651	1.7069	4.2	0.005
53.949	1.6982	11.5	0	3	3	53.943	1.6983	11.4	0.006
54.426	1.6844	7.2	2	3	0	54.412	1.6848	7.6	0.014
			4	1	2	54.513	1.6819	3.3	−0.087
54.728	1.6758	5.4	3	2	3	54.731	1.6757	6.2	−0.003
55.048	1.6668	7.1	2	3	1	55.036	1.6672	2.6	0.012
			4	0	3	55.054	1.6667	6.3	−0.006
56.226	1.6347	5.0	2	1	6	56.228	1.6346	6.4	−0.002
56.896	1.6170	4.9	2	3	2	56.883	1.6173	5.2	0.013
57.092	1.6119	4.9	2	2	5	57.084	1.6121	5.8	0.008
57.851	1.5926	12.2	0	2	6	57.844	1.5927	12.9	0.007
58.194	1.5840	2.7	0	1	7	58.203	1.5838	1.5	−0.009
59.303	1.5570	9.6	1	2	6	59.300	1.5571	8.4	0.003
			4	0	4	59.304	1.5570	4.3	−0.001
59.663	1.5484	2.3	1	1	7	59.654	1.5487	1.4	0.009
60.228	1.5353	2.1	4	2	1	60.211	1.5357	2.4	0.017
61.953	1.4966	7.7	4	2	2	61.960	1.4964	10.9	−0.007
63.422	1.4654	4.0	3	1	6	63.421	1.4654	4.7	0.001
64.528	1.4429	3.6	4	0	5	64.511	1.4433	2.6	0.017
64.811	1.4373	12.9	4	2	3	64.813	1.4373	18.7	−0.002
65.727	1.4195	10.3	0	4	0	65.728	1.4195	12.4	−0.001

(Chelkowski and Wijn, 1995). Other A_2MF_5 structural types not considered here, characterized by trans-connections leading to linear octahedral chains, are described elsewhere (Babel and Tressaud, 1985).

V. CONCLUSIONS

Two additional K_2FeF_5 forms are disclosed: one belonging to the Rb_2FeF_5 type and the other establishing a new A_2MF_5 structural type. With four different forms, K_2FeF_5 appears to be the richest polymorphic composition of all of the $A^{I}_2M^{III}F_5$ (A^{I} = K, Rb, Cs, Tl, and NH_4; M^{III} = Al, Cr, Mn, Fe, and Ga) series. All of these forms are showing cis-connected $(FeF_5)^{2n-}_n$ octahedral chains. The role of powder diffraction in the elucidation of the crystal structures of such compounds obtained by thermolysis is absolutely pivotal since the possibility of suitable single crystal growth is generally excluded.

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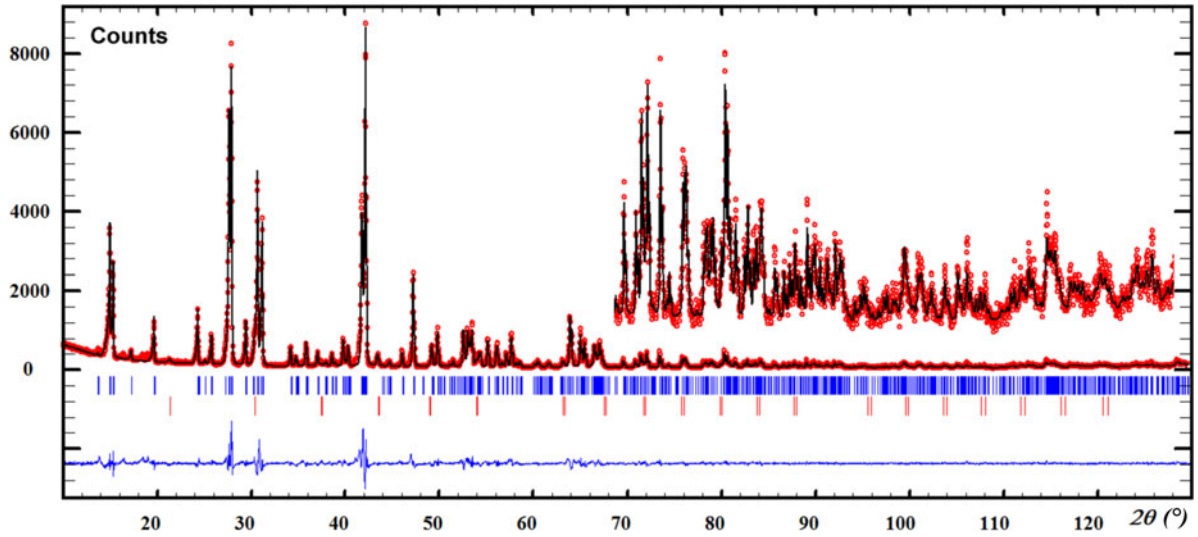


Figure 2. (Color online) Rietveld plot for K_2FeF_5 form-IV (Cu$K\alpha$). The second phase corresponds to 3.4(1)% of the cubic $KFeF_3$ phase. A third phase remains unidentified, showing weak reflections between ~15° and 20° (2θ).

TABLE V. X-ray diffraction data for K_2FeF_5 form-IV at 23 °C (Cu$K\alpha$1).

$2\theta_{obs}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{cal}$	d_{cal}	I_{cal}	$\Delta 2\theta$
13.709	6.4539	1.0	0	0	1	13.737	6.4411	1.2	−0.028
14.989	5.9055	29.5	−2	0	1	14.995	5.9033	37.6	−0.006
15.335	5.7730	23.2	2	0	0	15.352	5.7667	29.8	−0.017
17.249	5.1365	2.1	1	1	0	17.263	5.1323	3.0	−0.014
19.691	4.5047	9.7	−1	1	1	19.701	4.5025	13.0	−0.010
24.312	3.6579	14.2	1	1	1	24.324	3.6562	16.1	−0.012
25.798	3.4505	7.9	−3	1	1	25.798	3.4505	8.4	0.000
27.243	3.2707	4.2	−4	0	1	27.236	3.2716	2.2	0.007
27.676	3.2205	66.1	0	0	2	27.676	3.2205	61.4	0.000
27.920	3.1929	83.5	3	1	0	27.922	3.1927	84.8	−0.002
29.447	3.0307	11.8	−1	1	2	29.451	3.0303	13.1	−0.004
30.700	2.9098	48.5	−3	1	2	30.697	2.9101	56.2	0.003
31.181	2.8660	40.8	0	2	0	31.187	2.8655	41.6	−0.006
34.220	2.6180	5.4	0	2	1	34.220	2.6181	5.5	0.000
34.774	2.5777	2.4	−2	2	1	34.772	2.5779	2.8	0.002
35.877	2.5009	6.6	1	1	2	35.874	2.5011	7.1	0.003
37.090	2.4219	4.1	−2	0	3	37.099	2.4213	4.2	−0.009
38.613	2.3298	3.9	−4	0	3	38.625	2.3291	3.9	−0.012
39.814	2.2622	8.2	4	0	1	39.808	2.2626	8.1	0.006
40.345	2.2337	5.4	−3	1	3	40.340	2.2339	6.2	0.005
41.788	2.1598	46.8	−6	0	2	41.768	2.1608	34.3	0.020
41.909	2.1538	32.2	−4	2	1	41.874	2.1556	18.9	0.035
42.179	2.1407	100.0	0	2	2	42.177	2.1408	87.1	0.002
			−6	0	1	42.188	2.1403	12.9	−0.009
46.094	1.9676	5.0	−6	0	3	46.090	1.9678	4.4	0.004
47.260	1.9217	27.9	6	0	0	47.246	1.9222	9.6	0.014
			3	1	2	47.276	1.9211	18.2	−0.016
49.229	1.8493	6.4	−2	2	3	49.226	1.8495	6.4	0.003
49.836	1.8282	11.9	2	2	2	49.840	1.8281	11.0	−0.004
52.596	1.7386	10.2	−3	1	4	52.602	1.7384	12.2	−0.006
53.037	1.7252	10.9	−6	2	2	53.035	1.7253	11.5	0.002
53.280	1.7179	6.3	0	2	3	53.269	1.7182	5.3	0.011
53.521	1.7107	11.4	3	3	0	53.519	1.7108	9.6	0.002
54.256	1.6893	3.8	−6	0	4	54.266	1.6890	3.9	−0.010
54.441	1.6840	2.7	−1	3	2	54.427	1.6844	2.8	0.014
55.195	1.6627	8.7	−3	3	2	55.191	1.6628	9.2	0.004
56.174	1.6361	6.9	−8	0	2	56.184	1.6358	5.7	−0.010
57.164	1.6101	4.7	0	0	4	57.156	1.6103	4.7	0.008
57.692	1.5966	10.3	6	2	0	57.701	1.5963	9.9	−0.009
60.493	1.5292	2.1	−7	1	4	60.502	1.5290	2.2	−0.009
63.925	1.4551	15.5	−6	2	4	63.928	1.4550	18.6	−0.003
64.109	1.4514	3.6	1	1	4	64.098	1.4516	4.2	0.011
65.050	1.4326	12.2	0	4	0	65.043	1.4328	11.7	0.007
65.487	1.4241	8.6	6	2	1	65.479	1.4243	8.9	0.008

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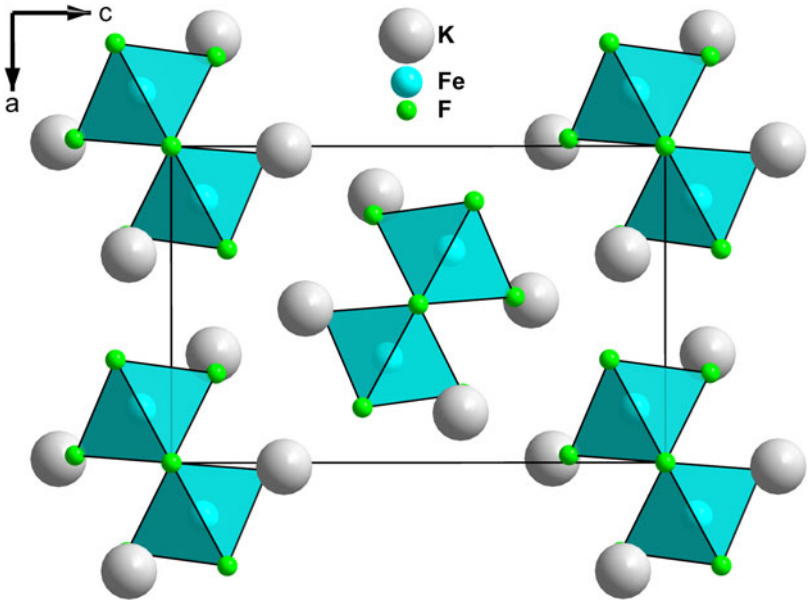


Figure 3. (Color online) Projection along the short *b*-axis of the structure of K_2FeF_5 form-III.

TABLE VI. Summary of the crystallographic details of the four K_2FeF_5 forms.

Form	SG	*a*	*b*	*c*	*β*	*V*/*Z*	*Z*	Reference
I	*Pbcn*	7.4059(4)	12.8771(9)	20.4282(13)		121.76	16	Le Bail *et al.* (1990a)
II	*Pbam*	7.3591(4)	23.0897(10)	5.7054(2)		121.01	8	Fourquet and Duroy (1993)
III	*Pnma*	7.3964(2)	5.6779(1)	11.5445(3)		121.21	4	This work
IV	*C*2/*m*	13.0919(2)	5.7311(1)	7.3114(1)	118.241(1)	120.82	4	This work

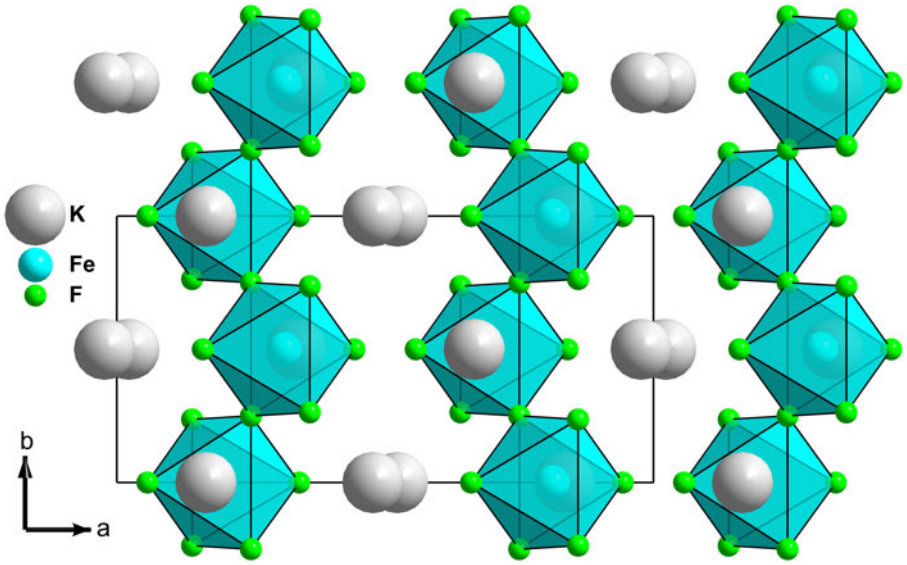


Figure 4. (Color online) View of the structure of K_2FeF_5 form-IV along the *c* axis, showing the infinite cis-connected octahedral chains. A view of form-III along its *a*-axis would be quite similar.

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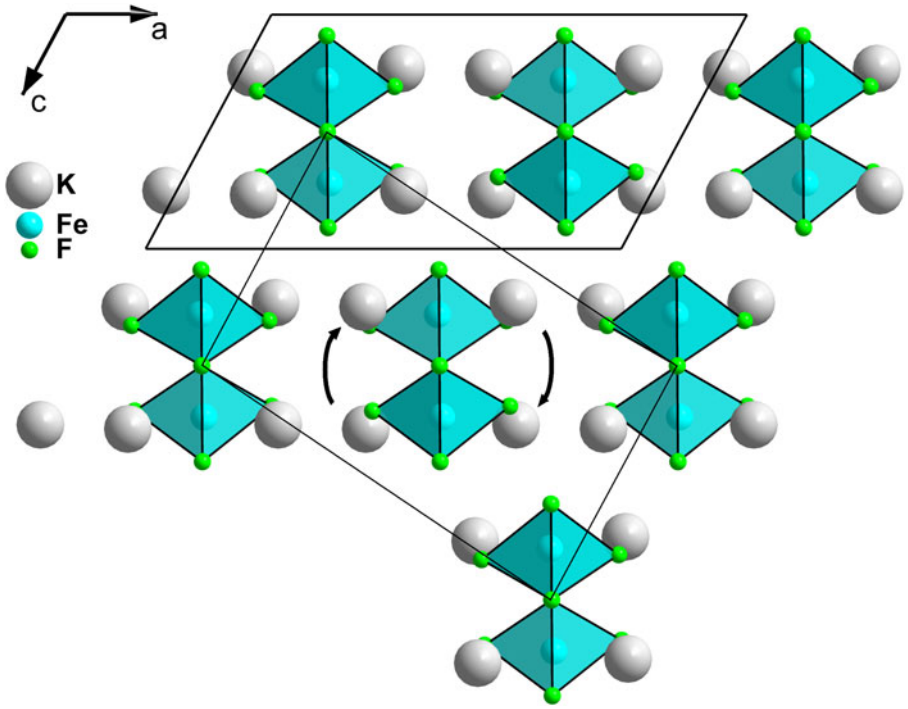


Figure 5. (Color online) Projection of the structure of K_2FeF_5 form-IV along the *b* axis, to be compared to Figure 3 in order to recognize how the rotation of half of the chains (see the arrows) and their translation of 1/2 ***b*** would allow us to rebuild the form-III structure (thin lines).

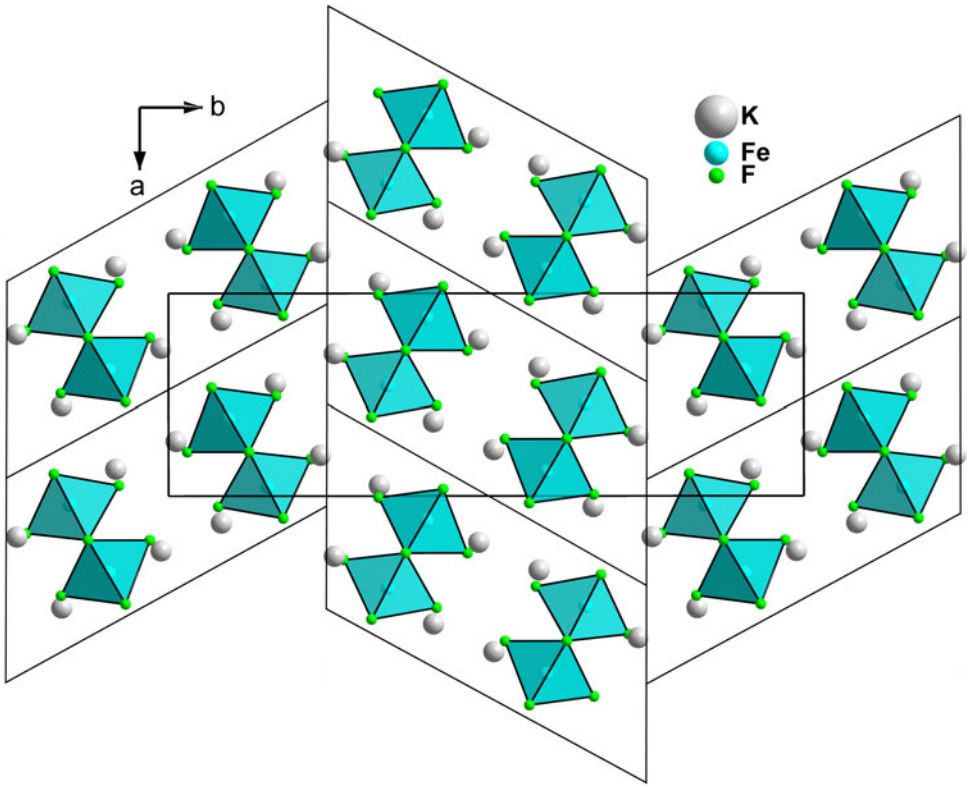


Figure 6. (Color online) Projection of the structure of K_2FeF_5 form-II along the *c* axis, to be compared to Figure 5 in order to recognize kink folded blocks of the form-IV monoclinic cell (thin lines) which reproduce also the form-III arrangement at their junctions.

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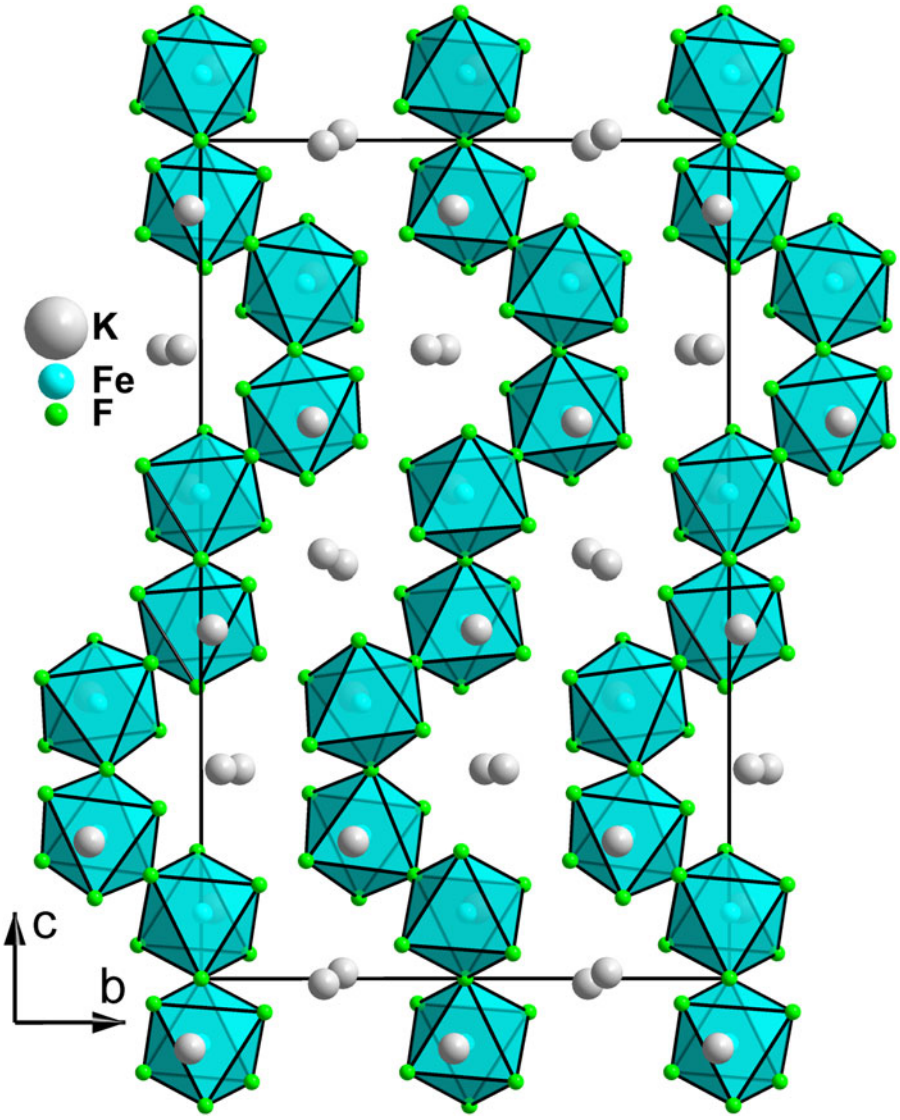


Figure 7. (Color online) Projection of the structure of K_2FeF_5 form-I along the *a* axis, showing a $N = 8$ periodicity along the octahedral chains, to be compared to Figure 4 showing $N = 2$ for form-III (and also for forms II and IV).

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SUPPLEMENTARY MATERIALS AND METHODS

The supplementary material referred to in this article can be found online at http://www.journals.cambridge.org/pdj.

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