Mixed-valent Iron Fluoride Hydrates and Their Thermal-decomposition Products

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The mixed-valent iron fluoride hydrate $Fe_2F_5\cdot 7H_2O$ has been confirmed by chemical and thermal analysis. The unit cell has been found by powder and single-crystal diffractometry to be triclinic with a = 6·582, b = 8·988, c = 10·542 × 10^{-10} m, and α = 105·81, β = 123·28, and γ = 82·93°. Thermal analysis shows that at 75 °C in flowing nitrogen the heptahydrate loses water to form the dihydrate, $Fe_2F_5\cdot 2H_2O$. Further dehydration in nitrogen produces two phases (A and B) not previously reported and the two components FeF_2 and FeF_3. Phase B occurs in a very narrow temperature range, 190—230 °C, but gives sharp reflections which have been indexed according to the cubic unit cell, a = 10·37 × 10^{-10} m. Phase A is stable over a wider temperature range (190—400 °C) and gives broadened lines in the X-ray Guinier-powder photograph. These have been indexed on the basis of the hexagonal unit cell, a = 6·40, c = 7·56 × 10^{-10} m. The components FeF_2 and FeF_3 first appear at *ca.* 250 °C and above 500 °C are the only crystalline phases present. The two dehydration steps in the decomposition of the heptahydrate occur at much lower temperatures in flowing HF than in N_2. The first step also yields the dihydrate, but the second step gives an anhydrous product which contains a phase A′ with an X-ray pattern similar to that of A but no reflections of B are detected. No ferromagnetism is exhibited by any of the new phases.

CONTRARY to general belief, dissolution of iron in strong hydrofluoric acid in air followed by evaporation produces a single compound with a well defined composition. The compound is the mixed-valent iron fluoride hydrate $Fe_2F_5\cdot 7H_2O$. It was first prepared as pale yellow crystals by Weinland and Köppen[1] in 1899, but the only other mention of this compound in the literature is by Brauer and Eichner[2] who studied its thermal decomposition in nitrogen. They reported that at 100 °C a dark red intermediate hydrate, $Fe_2F_5\cdot 3H_2O$, was formed and at 180 °C complete dehydration to Fe_2F_5 took place. They also reported that the trihydrate could be prepared from a solution of FeF_2 and FeF_3 in hydrofluoric acid. Using Debye–Scherrer and Weissenberg X-ray cameras they obtained the following unit cells for these compounds: $Fe_2F_5\cdot 7H_2O$, tetragonal, $a = 12{\cdot}85$, $c = 6{\cdot}93 \times 10^{-10}$ m; $Fe_2F_5\cdot 3H_2O$, orthorhombic, $a = 10{\cdot}96$, $b = 6{\cdot}71$, $c = 7{\cdot}50 \times 10^{-10}$ m; Fe_2F_5, tetragonal, $a = 8{\cdot}06$, $c = 9{\cdot}56 \times 10^{-10}$ m.

The possible existence of a mixed-valent iron fluoride would be of particular interest in view of the electrical and magnetic properties it may possess, depending on the nature of the sites occupied by Fe^{2+} and Fe^{3+}. So far, high-temperature methods have failed to produce a mixed-valent fluoride[3] and it was, therefore, decided to investigate the method of Brauer and Eichner and examine in more detail the associated hepta- and trihydrates. In this paper it will be shown that the intermediate hydrate is in fact the dihydrate and that dehydration in N_2 leads to a mixture of the two fluorides FeF_2 and FeF_3 and two new unstable phases. Neither of these phases gave X-ray patterns corresponding to the anhydrous product of Brauer and Eichner.

EXPERIMENTAL AND RESULTS

Preparation. The heptahydrate $Fe_2F_5\cdot 7H_2O$ is obtained by several methods;[1,2] for example it may be crystallised from a concentrated hydrofluoric acid solution containing Fe^{2+} and Fe^{3+} in equal concentration or from hydrofluoric acid in which the mixed-valent oxide Fe_3O_4 has been dissolved. It was found, however, that the best crystals were obtained by crystallisation from 40% hydrofluoric acid (laboratory reagent grade; Fisons) in which iron powder (99·99%, Halewood Chemicals) had been dissolved, any excess of iron being removed by filtration. The preparation was carried out in air. Within a short time (or by cooling if a hot saturated solution was used), pale yellow crystals of $Fe_2F_5\cdot 7H_2O$ crystallised out. Further evaporation at room temperature increased the yield. Recrystallisation from 12% hydrofluoric acid (Analytical Reagent; Fisons) was carried out under nitrogen, because we found that in air β-$FeF_3\cdot 3H_2O$ was obtained.

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[1] R. Weinland and O. Köppen, *Z. anorg. Chem.*, 1900, **22**, 266.

[2] G. Brauer and M. Eichner, *Z. anorg. Chem.*, 1958, **296**, 13.

[3] G. Férey, M. Leblanc, C. Jacobini, and R. de Pape, *Compt. rend.*, 1971, **C273**, 700.

The heptahydrate separated out at room temperature or below *ca.* 60 °C. Brauer and Eichner reported that at higher temperatures the lower hydrate is obtained and so we attempted this method for its preparation using their conditions. A 40% solution of hydrofluoric acid containing equimolar concentrations of iron(II) and iron(III) was evaporated near the b.p. in a stream of dry nitrogen. The product consisted of very small, dark brown, crystals which were shown by *X*-ray analysis to be the dihydrate $Fe_2F_5 \cdot 2H_2O$ with minute amounts of $Fe_2F_5 \cdot 7H_2O$. The fact that the lower hydrate contains two and not three water molecules as reported by Brauer and Eichner is discussed later. Pure $Fe_2F_5 \cdot 2H_2O$ is best prepared by dehydration of the heptahydrate and samples for further investigation, especially for *X*-ray powder diffraction, were prepared this way.

Chemical Analysis of Di-iron(II,III) *Pentafluoride Heptahydrate.*—Since iron complexes with F^- in solution, the superior fluoride-titration method for determining fluorine content cannot be applied without first separating fluorine from iron. Dehydrated samples were heated with silicon at 900 °C (Portier and Roux [4]). The SiF_4 gas thus produced was decomposed by passing through water and neutralising the resulting solution of H_2SiF_6 with aqueous ammonia. The F^- ion thus released was titrated with $LaNO_3$ solution using a selective fluoride-ion electrode manufactured by Orion Research Inc. in conjunction with a calomel reference electrode and a digital voltameter. The method was checked on PbF_2 of extra pure grade from B.D.H. (minimum assay 99%). Determinations on four samples of the standard yielded values in the range 15·25—15·75% by weight with a mean value of 15·51% and a mean deviation of 0·13%, compared with the theoretical content of 15·5%. The titration procedure was frequently checked with standard 0·01M-NaF solution. The error in the fluorine determinations using the SiF_4 method is thus 0·2% or less in agreement with the value claimed by Portier and Roux. Samples of $Fe_2F_5 \cdot 7H_2O$ were first dehydrated (at 300 °C in flowing HF) as the SiF_4 method gave inconsistent results on the hydrated form.

The total iron content was determined by dissolving a sample in 50% HCl and reducing the iron(III) ions with excess of tin(II) chloride. After removing the excess of Sn^{2+} with mercury(II) chloride, the solution was titrated with cerium(IV) sulphate solution following the procedure of Vogel.[5] Weight losses during the dehydration of samples for fluorine analysis were used to calculate the water content. The following are mean values of three determinations given in percent by weight: F, 27·1; Fe, 33·2; H_2O, 38·1% (Calc. for $Fe_2F_5 \cdot 7H_2O$: F, 28·5; Fe, 33·6; H_2O, 37·8%).

X-*Ray Diffraction.*—Powder photographs were taken of the heptahydrate and all the products of thermal decomposition on a Guinier–De Wolff camera (ENRAF-Nonius Ltd., Delft) using Fe-K_α radiation. Single crystals, where obtainable, were examined on a Buerger's precession camera using Mo-K_α radiation and a zirconium filter. The intensities of the reflections as given in the Tables were estimated visually (maximum = 10).

The powder diffraction pattern of $Fe_2F_5 \cdot 7H_2O$ was compared with that obtained by Brauer and Eichner (also listed in the J.C.P.D.S. Index [6] as file no. 12–52). Some lines in the latter's pattern were resolved into doublets by the higher resolving power of the Guinier camera, and many more additional reflections were observed. This more resolved pattern could not be indexed on the tetragonal unit cell proposed by Brauer and Eichner. A single crystal was therefore mounted and photographed on the precession camera and it was evident from this direct observation of the reciprocal lattice that the symmetry was triclinic. The dimensions of the unit cell were estimated from the precession photographs and the values thus obtained were refined by a successive-approximation method from the more precise powder data, which were calibrated with an ammonium alum standard. After conversion to real space the reduced unit cell was selected by Buerger's method.[7] The parameters of this reduced unit cell are as follows:

$$a = 6{\cdot}582 \times 10^{-10},\quad b = 8{\cdot}988 \times 10^{-10},\quad c = 10{\cdot}542 \times 10^{-10}\,\mathrm{m}$$
$$\alpha = 105{\cdot}81,\qquad \beta = 123{\cdot}28,\qquad \gamma = 82{\cdot}93^\circ$$

The *d* spacings calculated from the unit cell are listed in Table 1.

The powder pattern of the dihydrate $Fe_2F_5 \cdot 2H_2O$ yielded the *d* spacings and intensities listed in Table 2. This pattern may be compared to that obtained by Brauer and Eichner on the trihydrate $Fe_2F_5 \cdot 3H_2O$ which is included in the J.C.P.D.S. index [6] under file no. 12–53. We could not index the powder pattern nor could we obtain single crystals for examination on a precession camera. *X*-Ray diffraction observations on the new anhydrous phases are described in a separate section entitled *Phases A, A', and B.*

Thermal Decomposition.—*Thermal analysis.* Thermograms of $Fe_2F_5 \cdot 7H_2O$ were obtained on a Linseis thermoanalyser which was accurate to ±0·25 mg under the particular operating conditions selected. Sample weights in the range 30—50 mg, were heated at 10 °C min^{-1} in flowing nitrogen (99·999%, B.O.C.) and the t.g.a., d.t.g., and d.t.a. traces recorded simultaneously. A typical thermogram is shown in Figure 1. Loss of weight occurred in two stages, both of which are attributed to dehydration processes on the evidence of analysis of the products. In the first stage a weight loss of 27·1% occurred to yield an intermediate dihydrate which was dull red in colour; in the second stage further dehydration yielded a light grey anhydrous product, the overall loss in weight being 37·5%. The first loss in weight commenced at 75 °C, the second at 180 °C.

The first weight decrease corresponded to a loss of 5·01 mol of H_2O per mol of $Fe_2F_5 \cdot 7H_2O$. The intermediate product must therefore be the dihydrate, $Fe_2F_5 \cdot 2H_2O$. The thermogram indicated that the first dehydration was complete at 130 °C, and so one of the thermal-analysis runs was interrupted at this temperature to obtain a sample of the dihydrate, $Fe_2F_5 \cdot 2H_2O$, for examination by *X*-ray diffractometry. In the second dehydration process the dihydrate decomposed to yield two new phases which will be subsequently referred to as A and B. It was found that these two phases disappeared at higher temperatures, being replaced by a mixture of FeF_2 and FeF_3, and so a detailed survey was undertaken. Starting with the heptahydrate a series of thermoanalyses was carried out, each one terminating at different temperatures above the second

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[4] J. Portier and J. Roux, *Chim. analyt.*, 1968, **50**, 390.

[5] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, 1961, p. 322.

[6] Joint Committee on Powder Diffraction Standards, Swathmore, Pennsylvania, U.S.A.

[7] L. V. Azároff and M. J. Buerger, ' The Powder Method in *X*-Ray Crystallography,' 1st edn., McGraw-Hill, New York, 1958.

TABLE 1

X-Ray powder data for $Fe_2F_5{\cdot}7H_2O$

hkl	$10^{10}d$/m Obs.	$10^{10}d$/m Calc.	I/I_1
$01\bar{1}$	7·00	7·00	1
$10\bar{1}$	6·48	6·48	2
011	5·44	5·44	2
$11\bar{2}$	4·802	4·803	10
$1\bar{1}0$	4·712	4·711	10
110	4·573	4·573	10
020	4·320	4·324	10
$01\bar{2}$ 002	4·269	4·270	10
$1\bar{1}\bar{2}$	3·853	3·853	10
012 022	3·500	3·500	8
$1\bar{2}0$	3·455	3·454	1
$1\bar{2}\bar{1}$	3·372	3·372	1
111	3·311	3·311	1
$20\bar{2}$	3·245	3·241	9
$20\bar{1}$	3·166	3·162	2
$12\bar{3}$	3·103	3·105	1
$21\bar{1}$	3·024	3·023	2
$21\bar{3}$	2·964	2·964	2
$01\bar{3}$	2·925	2·927	1
$1\bar{2}\bar{2}$	2·894	2·893	3
030	2·881	2·881	2
003	2·848	2·847	6
$22\bar{2}$	2·799	2·801	7
$13\bar{1}$	2·791	2·791	1
200	2·754	2·750	5
$1\bar{1}2$	2·745	2·747	4
022 $03\bar{2}$	2·718	2·720	2
$02\bar{3}$	2·704	2·704	3
121	2·677	2·678	1
$2\bar{1}0$	2·648	2·646	1
$22\bar{1}$	2·620	2·620	5
210	2·597	2·596	2
$1\bar{3}0$	2·590	2·588	2
031	2·546	2·546	1
130	2·518	2·518	7
$1\bar{3}\bar{1}$	2·499	2·498	1
112	2·486	2·485	3
$12\bar{4}$	2·477	2·475	3
$1\bar{3}1$	2·456	2·454	3
$20\bar{4}$	2·443	2·441	6
$22\bar{2}$	2·428	2·426	6
$22\bar{4}$	2·401	2·402	3
$1\bar{2}\bar{3}$	2·369	2·367	1
$03\bar{3}$ $23\bar{2}$	2·332	2·333	2
220	2·287	2·286	3
$1\bar{3}\bar{2}$	2·247	2·245	1
$04\bar{1}$	2·230	2·230	3
$2\bar{1}\bar{4}$	2·207	2·207	3
$1\bar{3}2$	2·182	2·182	3
040 $30\bar{3}$	2·161	2·161	3
032 $04\bar{2}$	2·152	2·154	4
$1\bar{1}3$	2·145	2·145	1
004 $02\bar{4}$	2·133	2·135	6
$14\bar{3}$	2·097	2·099	1
314	2·076	2·076	6
$3\bar{1}\bar{2}$	2·055	2·053	4
$3\bar{1}\bar{3}$	2·028	2·027	1

For all reflections, $\sin^2\theta$ values show an error limit $[(\sin^2\theta)_{calc.} - (\sin^2\theta)_{obs.}]/(\sin^2\theta)_{calc.} < 0{\cdot}33\%$.

TABLE 2

Observed X-ray powder data for $Fe_2F_5{\cdot}2H_2O$

$10^{10}d$/m	I/I_1	$10^{10}d$/m	I/I_1
5·70	10	1·895	6
4·97	8	1·872	6
3·70	8	1·837	8
3·34	1	1·812	2
3·19	9	1·775	6
3·13	9	1·707	3
3·08	9	1·691	3
2·841	8	1·678	2
2·724	2	1·666	2
2·496	1	1·660	2
2·434	2	1·632	2
2·390	5	1·616	4
2·336	5	1·593	4
2·205	6	1·586	1
2·149	7	1·560	5
2·129	4	1·554	2
2·110	2	1·542	3
1·985	4	1·515	3
1·964	3	1·470	5

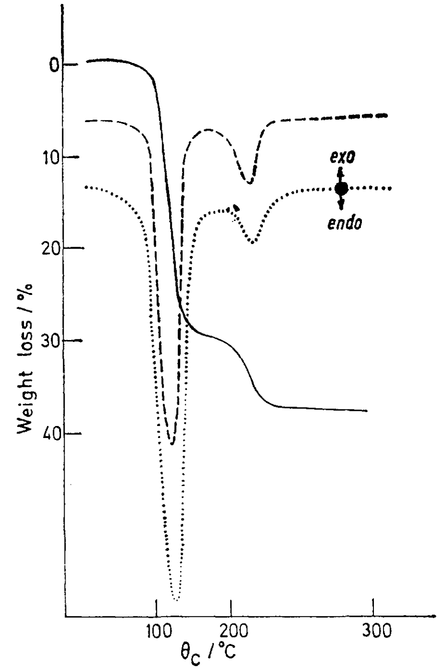

FIGURE 1 Thermogram of $Fe_2F_5{\cdot}7H_2O$: (— — —), d.t.g.; (· · · ·), d.t.a.; and (——), t.g.a.

TABLE 3

Phases produced at different temperatures

θ_c/°C	Phases	Colour
	(*a*) During thermal analysis (10° min^{-1} in N_2)	
100	$Fe_2F_5{\cdot}2H_2O$ and $Fe_2F_5{\cdot}7H_2O$	Dull red
200	B and A	Off white
220	B, some A, little FeF_2	Purple-grey
250	A, some FeF_2, little FeF_3	Purple-grey
300	A, some FeF_2, little FeF_3	Brown
400	A, FeF_2, some FeF_3	Brown
500	FeF_3 and FeF_2	Brown
600	FeF_3, some FeF_2, little α-Fe_2O_3	Brown
	(*b*) During isothermal heating in flowing HF	
30	$Fe_2F_5{\cdot}7H_2O$ and trace of $Fe_2F_5{\cdot}2H_2O$	Yellow
60	$Fe_2F_5{\cdot}2H_2O$ and some A′	Purple-grey
90	A′, Fe_2F_5, and FeF_3	Purple-grey
120	A′, FeF_2, and FeF_3	Purple-grey
200—700	FeF_2 and FeF_3	Off white

dehydration-temperature range. In each case the products were analysed by X-ray diffraction and the results are shown in Table 3. Phases A and B were characterised by their diffraction patterns, being distinguished from one another by the fact that the reflections of one set (phase B) disappear simultaneously at one temperature (230 °C) while those of the second set (phase A) disappear together at another temperature (>400 °C).

X-Ray photographs of anhydrous mixtures obtained on terminating the heating at 200 and 220 °C showed reflections of phases A and B whereas the product obtained at 250 °C recorded reflections of A but none of B. The latter also exhibited reflections of FeF_2 (J.C.P.D.S., file no. 17–768) and FeF_3 (J.C.P.D.S., file no. 2–327) but the intensities were rather low. As the terminal temperature was raised, phase A reflections diminished while those of FeF_2 and FeF_3 increased and between 400 and 500 °C phase A reflections disappeared altogether, and only those of FeF_2 and FeF_3 remained. The disappearance of phase B reflections, however, was accompanied by an increase in the intensities of reflections of phase A.

The totally dehydrated products varied from purple-grey to an off white colour below 300 °C but above this temperature they exhibited a brown colour. Although no phases containing oxide ions were observed by *X*-ray diffraction below 600 °C, the fact that traces of the oxide α-Fe_2O_3 could be detected above this temperature suggests that the brown colour was due to a thin film of the oxide. These traces of oxide were probably due to oxygen contamination of the nitrogen. This explanation is supported by the fact that the brown colour did not appear when the dehydration was carried out under hydrogen fluoride as described in the next section.

Isothermal studies. To ascertain whether a better defined product is obtained if the dehydration is performed in hydrogen fluoride, samples of $Fe_2F_5 \cdot 7H_2O$ were heated isothermally in flowing HF at various temperatures in a furnace controlled to ±5 °C. Platinum boats were used throughout. The results are shown in Table 3 and it may be seen that the brown colouration was suppressed at all temperatures up to 700 °C, the highest temperature used. The dehydration in HF was similar to that in N_2 but there were other more significant differences. It was observed, for example, that dehydration to the dihydrate takes place at a lower temperature commencing at *ca.* 30 °C and is complete at *ca.* 60 °C. The dihydrate in turn decomposed to an anhydrous product between 60 and 90 °C. The most outstanding difference, however, is in the anhydrous product. This was not initially a mixture of phases A and B but mainly one phase, A′, which had an *X*-ray pattern similar to phase A [see Figure 2(*b*)], along with traces of FeF_2 and FeF_3. This new phase disproportionated directly into FeF_2 and FeF_3 as the temperature was raised. The concentration of phase A′ reached a maximum at *ca.* 90 °C. Phase B thus never appears at the temperatures at which isothermal runs were carried out. Disproportionation was complete between 120 and 200 °C; the product of the isothermal runs at the latter temperature showed no traces of phase A′. Thus disproportionation as well as dehydrations occur at much lower temperatures in flowing HF. A general feature of the HF experiments was that the reflections of all the decomposition products were sharp indicating larger crystallite size than in the products of decomposition in N_2.

Phases A, A′, and B.—The occurrence of phases A, A′, and B is described in the previous section. The separate *X*-ray patterns of A, A′, and B are each shown schematically in Figure 2(*a*), (*b*), and (*c*) respectively. They do not correspond to the pattern of any known compound listed in the J.C.P.D.S. index [6] including Brauer and Eichner's *X*-ray pattern of Fe_2F_5 (file no. 12–54) which is reproduced in Figure 2(*d*). Although phase B exists over a narrow temperature range, its reflections are sharper than those of A which are considerably broadened. The reflections of phase A′ are sharper than those of A, in agreement with the general observation that the reflections of products obtained in flowing HF are sharper than those obtained in flowing nitrogen. The pattern of phase A was indexed according to the hexagonal unit cell, $a = 6{\cdot}40$, $c = 7{\cdot}56 \times 10^{-10}$ m (see Table 4), and that of B was indexed according to the face-centred-cubic unit cell, $a = 10{\cdot}37 \times 10^{-10}$ m (see Table 4). The diffraction pattern of phase A′, although similar to that of A, could not be indexed on the basis of a hexagonal unit cell. Attempts to index with other unit cells were equally unsuccessful. Measured *d* spacings and intensities of reflections of phase A′ are listed in Table 5.

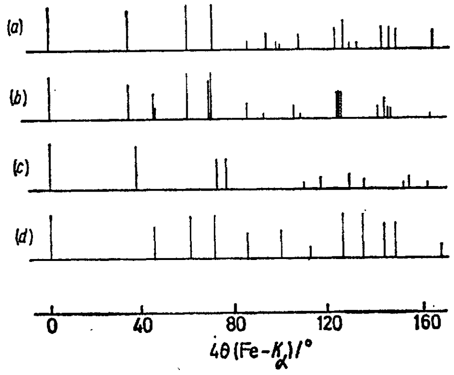

FIGURE 2 Representations of the *X*-ray powder patterns of phases A (*a*), A′ (*b*), B (*c*), and the anhydrous phase reported by Brauer and Eichner (*d*)

TABLE 4

X-Ray powder data of phases A and B

Phase A				Phase B			
hkl	Obs.	Calc.	I/I_1	*hkl*	Obs.	Calc.	I/I_1
100	6·42	6·40	9	111	5·99	5·99	10
002	3·78	3·78	10	311	3·13	3·13	7
200	3·20	3·20	10	222	2·996	2·995	7
112	2·643	2·643	2	422	2·118	2·117	2
202	2·438	2·443	3	511	1·997	1·996	3
103	2·345	2·346	1	400	1·833	1·834	3
211	2·307	2·304	1	531	1·752	1·753	3
300	2·133	2·134	3	533	1·582	1·583	2
004	1·889	1·891	5	622	1·563	1·564	3
220	1·849	1·848	7	444	1·497	1·497	2
104	1·812	1·812	1				
310	1·775	1·775	1				
222	1·649	1·660	5				
303	1·627	1·628	5				
400	1·601	1·600	5				
402	1·476	1·474	4				

For all reflections $\sin^2\theta$ values show an error limit of $[(\sin^2\theta)_{calc.} - (\sin^2\theta)_{obs.}]/(\sin^2\theta)_{calc.} < 0{\cdot}5\%$ for phase A and $< 0{\cdot}2\%$ for B.

TABLE 5

Observed *X*-ray powder-diffraction data for phase A′

$10^{10}\,d$/m	I/I_1	$10^{10}\,d$/m	I/I_1
6·54	7	2·115	1
4·97	5	1·867	6
4·87	2	1·855	6
3·75	10	1·842	6
3·23	8	1·658	3
3·21	10	1·629	5
2·614	3	1·616	3
2·450	1	1·602	2
2·169	3	1·460	1

DISCUSSION

The most notable feature of our observations is that they differ considerably in some respects from those of Brauer and Eichner. Whereas both the composition of and X-ray patterns for the heptahydrate agree with our findings, there are marked differences in the case of the dihydrate. The composition they report for the heptahydrate is based on chemical analysis but no analytical data are given for their lower hydrate; the authors simply state that the heptahydrate loses four molecules of water on heating in N_2 at 100 °C. This discrepancy in the number of water molecules suggests the possibility of a third hydrate intermediate between the hepta- and di-hydrates, but in none of our thermal analyses of the heptahydrate was the existence of a trihydrate revealed. Another explanation is that dehydration was incomplete in their case; our thermal analyses indicate that even in flowing N_2 dehydration is not complete at 100 °C, which could account for the higher water content but not the differences in the X-ray powder patterns. If dehydration to the dihydrate was incomplete to this extent, heptahydrate reflections though weak would still be observable. The X-ray powder patterns of Brauer and Eichner for the lower hydrate do not contain reflections of the heptahydrate. The very different patterns for the partially dehydrated products favour the first explanation, whereas the absence of a secondary peak in the d.t.a. and d.t.g. curves immediately following the main large peaks and the absence of another plateau at *ca.* 24% weight loss in the t.g.a. curve favour the second explanation. In the absence of additional evidence no progress can be made in explaining these discrepancies.

The differences between Brauer and Eichner's anhydrous products and those obtained by us are also difficult to explain. Even the chemical properties differ. They report a well characterised single-phase anhydrous product consisting of small dark blue-grey platelets which are so hygroscopic that they reversibly rehydrate to the trihydrate in air and if placed in water form the yellow, very soluble, heptahydrate. In contrast to this we observed the dehydration to be irreversible, neither the dihydrate nor the heptahydrate being formed on exposure to water. No hygroscopic tendencies could be detected when weighed samples of the A and B mixture were exposed to moist air.

In addition to the chemical properties, the X-ray powder patterns differed markedly as may be seen by comparing Brauer and Eichner's pattern shown in Figure 2(d) with those of phases A, A′, and B which are shown in Figure 2(a), (b), and (c), respectively. There is some resemblance to Figure 2(b) but there are significant reflections in one and not in the other and there are so many differences in intensity and d values in the remainder that one must conclude that they are different phases. In addition we obtained a mixture of phases in contrast to the single phase which they report; their reflections can be indexed on the basis of one unit cell, although there are inconsistencies between some calculated $\sin^2\theta$ values.

A comparison of the powder patterns of phases A [Figure 2(a)] and A′ [Figure 2(b)] indicates that, in addition to being structurally similar to each other, phase A′ is more ordered. The lower symmetry of phase A′ is probably the reason why we could not index it, whereas the phase A pattern was readily indexed. The more ordered structure of phase A′ is in agreement with its lower temperature of formation. The fact that the powder patterns of neither phase A nor A′ bear any resemblance to that of the dihydrate suggests that there is considerable structural change on dehydration unlike that of $CoFeF_5\cdot7H_2O$ in which seven water molecules are lost, and yet the X-ray pattern of the parent hydrate remains with only minor contraction of the d values.[8]

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[8] K. J. Gallagher and M. R. Ottaway, unpublished work.