converted the liquid into a red-brown solid, the composition of which was close to that of platinum tetrafluoride, but still containing small amounts of bromine.

Whether the black liquid represents a reaction product or not is difficult to ascertain. It may be that at 100°, the principal reaction is the thermal decomposition of platinum hexafluoride and the black liquid which forms is a solution of platinum tetrafluoride and platinum pentafluoride in bromine pentafluoride. This suggestion would accord with the findings of Weinstock, *et al.*,[3] that, although a black liquid forms, the stoichiometry of the reaction between platinum hexafluoride and bromine trifluoride corresponds only to fluorination to bromine pentafluoride.

The reaction of platinum hexafluoride with tetrafluorohydrazine gives nitrogen trifluoride and a reduced platinum fluoride. Stoichiometric measurements and chemical analyses of the solid products indicate that the reaction takes place in stepwise fashion according to the equations

$$2PtF_6 + N_2F_4 \longrightarrow 2PtF_5 + 2NF_3 \qquad (3)$$

$$2PtF_5 + N_2F_4 \longrightarrow 2PtF_4 + 2NF_3 \qquad (4)$$

When an excess of platinum hexafluoride was employed, the solid product was found to have a composition close to platinum pentafluoride as required by eq 3. Moreover, the melting point (80°) was near that reported for platinum pentafluoride by Bartlett and Lohmann.[1] When an equimolar mixture of platinum hexafluoride and tetrafluorohydrazine was used, the solid was of variable composition and appeared to be a mixture of platinum tetrafluoride and platinum pentafluoride, corresponding approximately to the composition $PtF_{4.5}$. The over-all stoichiometry was

$$2PtF_6 + {}^3/_2N_2F_4 \longrightarrow 2PtF_{4.5} + 3NF_3 \qquad (5)$$

The X-ray diffraction pattern of the solid did not show the pattern for platinum tetrafluoride.[1] It is thought that the $PtF_{4.5}$ may be a solid solution of platinum tetrafluoride and platinum pentafluoride. That such solid solutions can form has been noted previously by Bartlett and Lohmann.[1] When the reaction was carried out in a large excess of tetrafluorohydrazine, reduction to platinum tetrafluoride was not complete but compositions near to it ($PtF_{4.1}$ to $PtF_{4.3}$) were produced.

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The Thermal Decomposition of Ammonium Hexafluoroferrate(III) and Ammonium Hexafluoroaluminate. A New Crystalline Form of Aluminum Fluoride[1,2]

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Ammonium hexafluoroferrate(III), $(NH_4)_3FeF_6$, and ammonium hexafluoroaluminate, $(NH_4)_3AlF_6$, decompose on heating with an initial loss of 2 moles of ammonium fluoride, forming ammonium tetrafluoroferrate(III), NH_4FeF_4 (at *ca.* 140°), and ammonium tetrafluoroaluminate, NH_4AlF_4 (at *ca.* 170°). Further heating results in the gradual loss of ammonium fluoride, the final products being iron(III) fluoride mixed with oxide (at *ca.* 285°) and γ-aluminum fluoride, a new crystalline form (at *ca.* 300°). The structural relationships of the compounds are discussed. The intermediate, ammonium tetrafluoroferrate(III), was found to be tetragonal, $a = 3.78$, $c = 6.36$ A. It can also be prepared by direct reaction of iron(III) fluoride and ammonium fluoride at 180°.

Introduction

Many years ago, Poulenc[4] observed the formation of iron(III) fluoride when "ammonium iron fluoride" was heated carefully in a stream of inert gas. Thilo[5] has reported that heating ammonium hexafluoroaluminate, $(NH_4)_3AlF_6$, below 350° results in the formation of ammonium tetrafluoroaluminate, NH_4AlF_4, which at higher temperatures decomposes to aluminum fluoride. Thakur, Rock, and Pepinsky[6] studied the thermal behavior of aluminum fluoride, as did Roy,[7] but concluded that further investigation was needed.

The two hexafluoro compounds have been known for a long time, but much of the early work was put in doubt by the observations of Cox and Sharpe,[8] who

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[1] Taken in part from the M.S. thesis of D. B. Shinn.

[2] Supported in part by the U. S. Atomic Energy Commission.

[3] To whom communications should be addressed.

[4] C. Poulenc, *Compt. Rend.*, **115**, 941 (1892).

[5] E. Thilo, *Naturwissenschaften*, **26**, 529 (1938).

[6] R. L. Thakur, E. J. Rock, and R. Pepinsky, *Am. Mineralogist*, **37**, 695 (1952).

[7] R. Roy, *J. Am. Ceram. Soc.*, **37**, 581 (1954).

[8] B. Cox and A. G. Sharpe, *J. Chem. Soc.*, 1798 (1954).

were unable to prepare pure samples of ammonium hexafluoroferrate(III) from aqueous solution. It was subsequently found possible to prepare anhydrous fluorometallates from nonaqueous solution.[9] The structures of ammonium hexafluoroferrate(III) (cubic, a = 9.10 A)[10] and aluminate (cubic, a = 8.93 A)[10] have been reported, as have those of the corresponding fluorides, iron(III) fluoride (rhombohedral, a = 5.362 A, α = 57.99°)[11] and α-aluminum fluoride (rhombohedral, a = 5.026 A, α = 58.533°).[12] The intermediate tetrafluoroaluminate, NH_4AlF_4, was reported by Brosset (tetragonal, a = 3.587, c = 6.346 A).[13]

The incomplete knowledge of the thermal behavior of ammonium hexafluoroferrate(III) and hexafluoroaluminate, the uncertainties in chemical composition, and an opportunity to speculate on the structural relationships in a series of solid-state decompositions suggested a closer study of these two systems, using differential thermal analysis, thermogravimetry, X-ray diffraction, and infrared spectroscopy.

Experimental Section

Preparations.—Ammonium hexafluoroferrate(III) and ammonium hexafluoroaluminate were prepared by the reaction of the metal bromide with ammonium fluoride in methanol.[9] The hexafluoroaluminate was identified by X-ray powder diffraction. The hexafluoroferrate(III) was also identified by X-ray diffraction, and its purity was checked by elemental analysis. *Anal.* Calcd for $(NH_4)_3FeF_6$: NH_3, 24.16; Fe, 24.94; F, 50.90. Found: NH_3, 23.92, 23.81; Fe, 25.01, 24.98; F, 50.60, 50.90.

Iron(III) fluoride was prepared by the action of chlorine trifluoride on iron(III) chloride. Anhydrous iron(III) chloride, in a nickel boat, was heated gradually to 300° in a stream of chlorine trifluoride. The sample was removed, ground, and heated for 1 hr at 550° in ClF_3. This process was repeated until conversion was complete, as indicated by the absence of chloride in the product.

Ammonium tetrafluoroferrate(III) was prepared by heating an intimate mixture (3:1 mole ratio) of ammonium fluoride and iron(III) fluoride in a nickel boat to 180° in a stream of extra dry nitrogen, with a boat containing ammonium fluoride placed upstream from the sample. The sample was heated for several days to constant weight, taking care to keep the temperature at 180° maximum to prevent decomposition of the product. *Anal.* Calcd for NH_4FeF_4: NH_3, 12.04; Fe, 37.26; F, 50.70. Found: NH_3, 11.64, 12.04; Fe, 37.07, 37.33; F, 50.50, 50.10.

α-Aluminum fluoride was prepared by passing gaseous hydrogen fluoride over anhydrous aluminum chloride in an alundum boat at 800°.

γ-Aluminum fluoride from the thermal decomposition of the hexafluoroaluminate was analyzed for aluminum. Fluoride analysis was not done because of the resistance of the compound to digestion. The infrared spectrum showed no residual ammonium ion. Total weight loss for the reaction $(NH_4)_3AlF_6 \rightarrow AlF_3$ at 400° was 57.1%; the calculated loss is 57.0%. *Anal.* Calcd for AlF_3: Al, 32.13. Found: Al, 32.16 ± 0.04.

Analyses.—Iron and aluminum were determined gravimetrically as the oxides. Samples were digested for about 12 hr in nitric acid, followed by ignition in platinum crucibles at 800°. Ammonium was determined by distillation of ammonia from strongly alkaline solution into boric acid solution, followed by titration with hydrochloric acid, using methyl purple indicator. Fluoride was determined oscillometrically,[14] by titration with thorium nitrate after distillation.

Equipment.—X-Ray powder diffraction photographs were taken using 57.3- and 114.56-mm Philips cameras. Filtered iron radiation was used, and the samples were mounted in sealed 0.3-mm glass capillaries. Intensities were estimated visually for qualitative identification and read with a Welch Densichron connected to a Photovolt photometer for greater accuracy. The infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer, using Halocarbon and Nujol mulls. Thermogravimetric analyses were done on a recording balance similar to one described by Wendlandt[15] and modified by Kingston.[16] The differential thermal analysis apparatus was constructed in this laboratory.[17] Calcium fluoride was used as the reference material. The system was flushed continuously with extra dry nitrogen, passed through an Anhydrone tower and then over hot copper turnings.

Results

Thermogravimetric Analysis of $(NH_4)_3FeF_6$.—The results of the thermogravimetric analysis are shown in Figure 1. The initial reaction, the formation of ammonium tetrafluoroferrate(III), occurs in one step, giving an inflection at a weight loss of 33.3%. The calculated weight loss for the formation of NH_4FeF_4 is 33.1%. Isothermal analysis at 190° gives a constant weight at a loss value of 33.0%. There is no indication of an intermediate $(NH_4)_2FeF_5$. Dynamic analysis shows a second inflection at 36–42% weight loss, possibly analogous to the nonstoichiometric phase discussed later in the aluminum system. The X-ray diffraction pattern of this product is identical with that of the tetrafluoroferrate. Further decomposition is accompanied by the formation of iron oxide, with a weight loss of 64.4%. No stable iron(III) fluoride phase was observed. The compounds are extremely sensitive to oxide formation, and it was not practical to remove all traces of water and oxygen. The ammonium fluoride released reacts with glass in the apparatus to form ammonium hexafluorosilicate, possibly releasing oxygen in the process. Thermal decomposition could be done in an atmosphere of hydrogen fluoride to minimize this problem.

Differential Thermal Analysis of $(NH_4)_3FeF_6$.—The thermogram is shown in Figure 2 for a heating rate of 2°/min. The first peak represents the loss of 2 moles of ammonium fluoride to form the tetrafluoroferrate(III), isolated by stopping the reaction just beyond the break. Oxide formation again interfered, but iron(III) fluoride was identified in the final product. Samples heated through the second peak contained 1–2% ammonium ion but had powder patterns essentially like that of ammonium tetrafluoroferrate.

Thermogravimetric Analysis of $(NH_4)_3AlF_6$.—Am-

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[9] H. M. Haendler, F. A. Johnson, and D. S. Crocket, *J. Am. Chem. Soc.*, **80**, 2662 (1958).

[10] E. G. Steward and H. P. Rooksby, *Acta Cryst.*, **6**, 49 (1953).

[11] M. A. Hepworth, K. H. Jack, R. D. Peacock, and G. J. Westland, *ibid.*, **10**, 63 (1957).

[12] F. Hanic and D. Stempelova in "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., The Macmillan Co., New York, N. Y., 1964, p 429.

[13] C. Brosset, *Z. Anorg. Allgem. Chem.*, **239**, 301 (1938).

[14] C. L. Grant and H. M. Haendler, *Anal. Chem.*, **28**, 415 (1956).

[15] W. W. Wendlandt, *ibid.*, **30**, 56 (1958).

[16] D. W. Kingston, M.S. Thesis, University of New Hampshire, 1962.

[17] See D. B. Shinn, M.S. Thesis, University of New Hampshire, 1963, and H. M. Haendler, C. M. Wheeler, Jr., and D. W. Robinson, *J. Am. Chem. Soc.*, **74**, 2352 (1952).

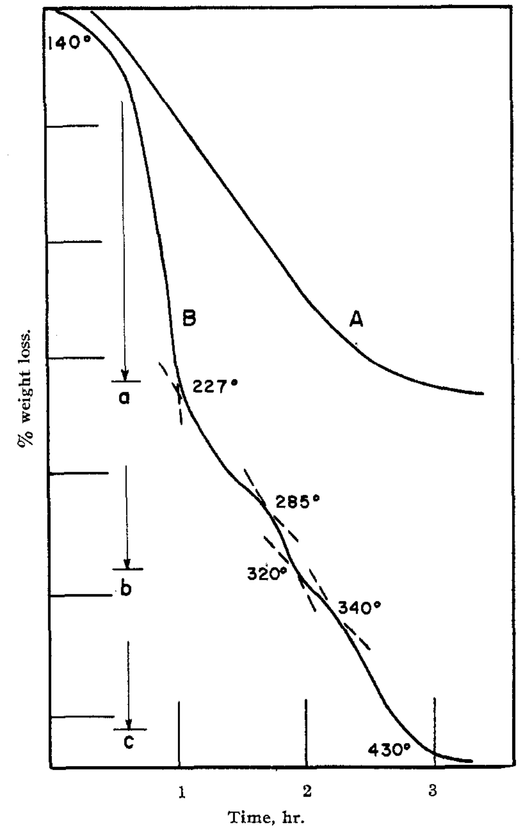

Figure 1.—Thermogravimetric analysis of $(NH_4)_3FeF_6$: A, isothermal decomposition at 190°; B, dynamic decomposition at 100°/hr; a, weight loss for conversion to NH_4FeF_4; b, weight loss for FeF_3; c, weight loss for Fe_2O_3.

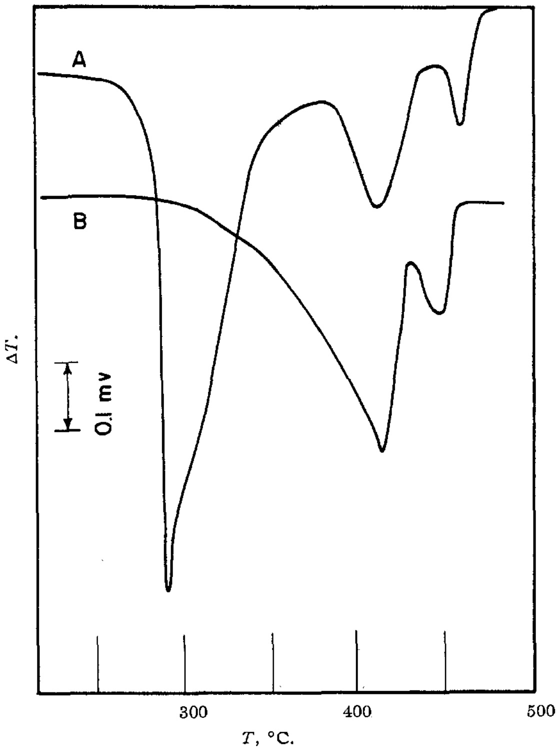

Figure 2.—Differential thermal analysis of $(NH_4)_3FeF_6$: A, $(NH_4)_3FeF_6$ as starting material; B, NH_4FeF_4 as starting material.

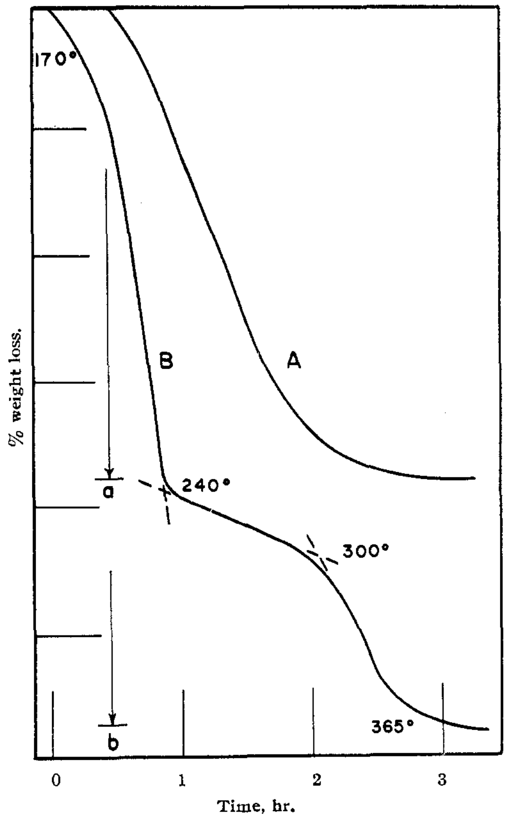

Figure 3.—Thermogravimetric analysis of $(NH_4)_3AlF_6$: A, isothermal decomposition at 205°; B, dynamic decomposition at 60°/hr; a, weight loss for conversion to NH_4AlF_4; b, weight loss for AlF_3.

monium hexafluoroaluminate decomposes as shown by the set of equations

$$(NH_4)_3AlF_6 \xrightarrow{170^\circ} NH_4AlF_4 + 2NH_4F$$

$$NH_4AlF_4 \xrightarrow{300^\circ} \gamma\text{-}AlF_3 + NH_4F$$

$$\gamma\text{-}AlF_3 \xrightarrow{720^\circ} \alpha\text{-}AlF_3$$

The initial stages are shown in Figure 3, for a heating rate of 1°/min. There is no indication of an intermediate $(NH_4)_2AlF_5$. The weight loss at 240° (dynamic) and at 205° (isothermal) is 37.4%. That for formation of NH_4AlF_4 is theoretically 38.0%. An inflection at about 300° corresponds to loss of 2.1–2.25 moles of ammonium fluoride, suggesting the possibility of a nonstoichiometric compound of variable composition $AlF_3 \cdot (0.75\text{–}0.90)NH_4F$. X-Ray patterns of several samples heated between 250 and 300° are identical with that of the tetrafluoroaluminate, in spacing and intensity, indicating maintenance of the NH_4AlF_4 structure during the initial loss of ammonium fluoride and prior to the formation of γ-AlF_3 above 300°.

Differential Thermal Analysis of $(NH_4)_3AlF_6$.—The thermogram, Figure 4, shows two major endothermic peaks, at about 325 and 460°. The first and larger peak represents the formation of ammonium tetrafluoroaluminate. The second peak represents formation of γ-aluminum fluoride. The splitting of the second peak may be attributed to the decomposition of

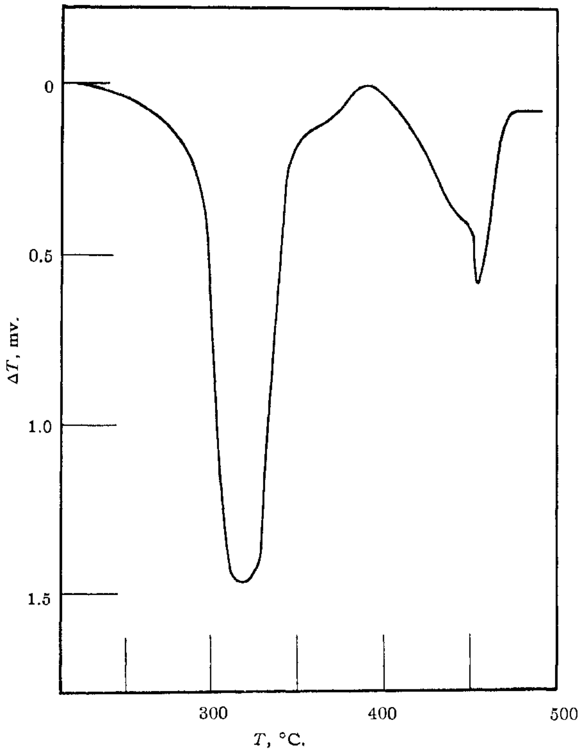

Figure 4.—Differential thermal analysis of $(NH_4)_3AlF_6$.

a nonstoichiometric intermediate, as indicated by the thermogravimetric analysis, or to a phase transition. A reversible phase transition in aluminum fluoride at 445° has been reported,[6] but repeated thermal cycling of a sample between 300 and 500° gave no evidence of change once the initial heating had occurred. Attempts to resolve the second peak to permit sampling were not successful. Difference in decomposition temperature for the two methods is inherent in the methods themselves. The loosely packed sample in thermogravimetry favors removal of the ammonium fluoride in the nitrogen stream.

Formation and Identification of γ-AlF_3.—The crystal structure of aluminum fluoride has been reported from X-ray powder diffraction data as rhombohedral by Ketelaar[18] and by Staritsky and Asprey[19] as rhombohedral. Wyckoff[20] recommended reinvestigation of this compound, and Hanik and Stempelova[12] have reported a modification of the originally proposed structure. Although details are not always explicit, it is our belief that in these cases preparation of the sample involved heating to above about 730°. This may have occurred in the reaction step, in a dehydration process, in a calcination to achieve a particular particle size, or in purification by sublimation. Other reported preparations of aluminum fluoride give no X-ray data[21] or involve high temperature.[6,7] An exception to this is the work of Muetterties and Castle,[22] who report the formation of a hexagonal aluminum fluoride in the reaction between liquid hydrogen fluoride and aluminum under pressure at 200°.

The new crystalline species of aluminum fluoride will be referred to as γ-aluminum fluoride; the common high-temperature form is designated as α-aluminum fluoride. γ-Aluminum fluoride can be formed by heating ammonium hexafluoroaluminate to 400°. Its composition has been established by analysis for aluminum, by thermogravimetric analysis of weight loss, and by the absence of ammonium ion. The γ-aluminum fluoride can also be formed by direct decomposition of the tetrafluoroaluminate. Upon heating γ-aluminum fluoride to 710–720°, an irreversible transition to α-aluminum fluoride occurs. The diffraction pattern of this product is identical with that obtained from the product of the hydrofluorination of aluminum chloride at 800° and with the reference pattern for aluminum fluoride in the "ASTM X-Ray Powder Diffraction File."

It has also been possible to prepare γ-aluminum fluoride, in an impure form, by the action of gaseous hydrogen fluoride on aluminum bromide and chloride, at temperatures from 150 to 500°, as indicated by X-ray pattern. In most instances a somewhat amorphous pattern is observed, which changes to that of α-aluminum fluoride when the sample is heated in nitrogen above 730°.

Since aluminum fluoride is used extensively as a catalyst, with a pronounced dependence of activity on crystallinity and particle size, some of the early work on this substance might bear reexamination.

Infrared Spectra of the Iron and Aluminum Fluorides.—Infrared data are listed in Table I. The similarity of the spectra of ammonium hexafluoroferrate(III) and hexafluoroaluminate reflect their isostructural nature. The appearance of the $\nu_4 + \nu_6$ combination frequency in ammonium tetrafluoroferrate(III) and tetrafluoroaluminate is indicative of hydrogen bonding, as described by Waddington.[23] The interaction between hydrogen and fluorine must be small, however, since the tetrafluoroaluminate is isostructural with the corresponding potassium and rubidium compounds. Of interest also is the fairly sharp line at 3325 cm^{-1} in the spectrum of ammonium tetrafluoroferrate(III). By analogy to ammonium chloride (see footnote *d* in Table I) this could be attributed to the $\nu_1 + \nu_5$ combination frequency, although somewhat more pronounced than in ammonium chloride. This band appeared in all samples of the compound regardless of the method of preparation.

The major absorption in the metal–fluorine vibration region has been assigned to ν_3. The band is fairly broad, but quite intense. The remaining frequencies are presumably combinations, since the first overtone of ν_4 is prohibited for octahedral point groups.

Peacock and Sharpe[24] have discussed trends affecting the ν_3 vibrations of octahedrally bound metal–

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[18] J. A. A. Ketelaar, *Z. Krist.*, **85**, 119 (1933).

[19] E. Staritsky and L. B. Asprey, *Anal. Chem.*, **29**, 984 (1957).

[20] R. W. G. Wyckoff, "Crystal Structures," Vol. 2, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1964, p 50.

[21] C. Wolf and C. B. Miller, U. S. Patent 2,673,139 (March 23, 1954).

[22] E. L. Muetterties and J. E. Castle, *J. Inorg. Nucl. Chem.*, **18**, 148 (1961).

[23] T. C. Waddington, *J. Chem. Soc.*, 4340 (1958).

[24] R. D. Peacock and D. W. A. Sharpe, *ibid.*, 2762 (1959).

TABLE I

INFRARED ABSORPTION SPECTRA[a]

	Ammonium vibrations						Metal–fluorine vibrations		
Compound		ν_3	$\nu_2 + \nu_4$	$2\nu_4$	$\nu_4 + \nu_6$	ν_4	ν_3		
$(NH_4)_3AlF_6$[b]		3250[b]	3060[b]	. . .	. . .	1428[b]	570[c]	. . .	
NH_4AlF_4		3230	3120	2905	1800	1435	610	. . .	537 w
γ-AlF_3		. . .	. . .	. . .	. . .	. . .	665	. . .	605 sh
α-AlF_3		. . .	. . .	. . .	. . .	. . .	675	642 w	566 s
$(NH_4)_3FeF_6$		3240	3035	2865 sh	. . .	1432	580	. . .	470 br
NH_4FeF_4	3325[d]	3195	3080	2850	1750 w	1425	575 sh	. . .	500 br
FeF_3		. . .	. . .	. . .	. . .	. . .	590 sh	. . .	530 br

[a] Halocarbon mulls were used between 1400 and 4000 cm^{-1}; Nujol between 400 and 1400 cm^{-1}; w, weak; sh, shoulder; s, sharp; br, broad. [b] Reported by Cox and Sharpe.[8] [c] This work. [d] Possibly the $\nu_1 + \nu_5$ combination frequency: K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 105.

fluorine systems in cryolites. They point out, using K_3AlF_6 and $KAlF_4$ as examples, that sharing of the fluoride ions at the corners of the M–F octahedron does not change the value of ν_3. From Table I, the data indicate a definite trend to higher wavenumber for ν_3 with increased sharing of the octahedral fluoride ions for the ammonium compounds. The spectrum of α-aluminum fluoride presents an interesting situation. A very sharp intense peak occurs at 566 cm^{-1}, and the ν_3 band appears split. This occurs regardless of the method of preparation of the fluoride, but does not appear in γ-aluminum fluoride, nor in the structurally similar iron(III) fluoride. The latest structure reported for aluminum fluoride[12] shows two almost perfect octahedra (AlF_6) in the rhombohedral unit cell, with different relative orientations. Presumably the splitting of the ν_3 band could occur, as mentioned by Peacock and Sharpe,[24] because of the presence of these two octahedra.

Structural Relationships

X-Ray Powder Diffraction of NH_4FeF_4.—The X-ray powder diffraction data for ammonium tetrafluoroferrate(III) can be indexed on the basis of a tetragonal unit cell. All of the intense reflections can be explained in terms of a cell directly comparable to that given by Brosset[13] for ammonium tetrafluoroaluminate. Some faint reflections indicate that a larger unit cell may be preferable, but in the absence of single-crystal data such a conclusion is tenuous. The data are given in Table II.

X-Ray Powder Diffraction of γ-AlF_3.—The powder diffraction pattern for γ-aluminum fluoride is remarkably similar to that of ammonium tetrafluoroaluminate, although the quality varies with the method of preparation. It is possible to index the pattern tentatively on the basis of a tetragonal cell, slightly smaller than that of the tetrafluoroaluminate. Comparison of these two, and the related α-aluminum fluoride, is shown in Table III.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR NH_4FeF_4

d, A	I/I_0[a]	hkl[b]	hkl[c]	d_{calcd}, A
6.368	100	001	001	6.363
3.777	78	100	200	3.735
3.250	78	101	201	3.253
3.179	16	002	002	3.181
2.670	27	110	220	2.676
2.331[d]	5	. . .	301, 212	2.345, 2.319
2.240	11	. . .	311	2.240
2.122	11	003	003	2.122
2.044	2	112	103, 222	2.043, 2.048
1.991	2	. . .	321	1.994
1.893	22	200	400	1.893
1.852	22	103	203	1.850
1.813	14	201	401	1.814
1.692	14	210	420	1.693
1.664	2	113	223	1.662
1.633[d]	24	211, 202	421, 402	1.636, 1.627
1.592	5	004	004, 412	1.591, 1.590
1.495	2	212	422	1.494
1.468	2	104	204	1.466
1.413	2	203	403	1.412
1.368	2	114	224, 432	1.367, 1.367
1.338	2	220	440	1.338
1.325	8	213	423, 314	1.323, 1.325
1.311	2	221	441	1.310
1.240[d]	1	301	601	1.238

[a] Densitometer measurement. [b] Based on tetragonal cell; $a = 3.785$; $c = 6.363$ A. [c] Based on tetragonal cell, $a = 7.570$, $c = 6.363$ A. [d] Broad line.

Topochemical Speculation.—There are few instances in which the structures of the members of a series of solid-state decomposition products are known in sufficient detail to permit speculation about the topochemical changes which occur. It has been suggested that the decomposition of solids may involve three distinct steps:[25] the breakdown of the initial structure, escape of product gas, and formation of the product structure. Any of these steps might be rate determining under different conditions.

Ammonium hexafluoroaluminate and ferrate have tetramolecular cubic unit cells. The space group has been chosen as O_h^5 (Fm3m)[26] with atoms in the positions: $NH_4(1)$: (4b) $^1/_2, ^1/_2, ^1/_2$; fc. $NH_4(2)$: (8c) $\pm (^1/_4, ^1/_4, ^1/_4)$; fc. Fe/Al: (4a), 0, 0, 0; fc. F: (24e) $\pm (x, 0, 0; 0, x, 0; 0, 0, x)$; fc ($x = 0.20$–$0.25$). This places a regular octahedron of fluorine atoms about each aluminum or iron atom, the octahedra being distributed in the positions of a face-centered-cubic lattice. There are two crystallographically nonequivalent kinds of ammonium groups, correlative to the observed loss of two ammonium fluorides during the initial thermal decomposition. The pertinent distances for these and the following compounds discussed are listed in Table IV.

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[25] J. Y. MacDonald, *Trans. Faraday Soc.*, **47**, 860 (1951).

[26] Reference 20, vol. 3, p 373.

TABLE III

X-RAY DIFFRACTION COMPARISON OF ALUMINUM FLUORIDE COMPOUNDS

NH_4AlF_4			γ-AlF_3				α-AlF_3[d]	
d, A	I/I_0[a]	hkl[b]	d, A	I/I_0[a]	hkl[c]	d_{calcd}, A	d, A	I/I_0
6.346	100	001	6.029	100	001	5.998	3.52	100
3.585	80	100	3.547	93	100	3.540	2.51	3
3.175	10	002	3.063	3	101	3.048	2.119	20
3.128	80	101	2.999	43	002	2.999	2.074	3
2.534	30	110	2.500	5	110	2.503	2.019	1
2.364	40	102	2.270	8	102	2.288	1.759	25
2.234	10	...	2.129	10	...	...	1.587	15
2.114	15	003	2.003	15	003	1.999	1.561	7
1.984	10	112	1.915	22	112	1.922	1.462	1
1.823	25	103	1.773	32	200	1.770	1.431	3
1.790	50	200	1.736	25	103	1.741	1.422	3
1.724	15	201, 113	1.707	5	201	1.698	1.355	1
1.603	15	210	1.582	8	210	1.583	1.257	3
1.585	7	004	1.532	13	211	1.531	1.233	1
1.557	20	202, 211	1.503	15	004	1.499	1.207	1
1.456	7	104, 212	1.379	7	104	1.381		
1.368	10	203	1.332	3	203	1.325		
1.347	3	114						
1.279	15	213						

[a] Densitometer measurement. [b] Based on tetragonal cell, $a = 3.585$, $c = 6.346$ A. [c] Based on tetragonal cell, $a = 3.54$, $c = 6.00$ A. "ASTM X-ray Powder Diffraction File."

TABLE IV

INTERATOMIC DISTANCES IN ALUMINUM AND IRON FLUORIDES

Compound	M–M, A	M–F, A	F–F, A[a]
$(NH_4)_3AlF_6$	6.31 (12)[b]	1.76 (6)	2.49
NH_4AlF_4	6.35 (2) 5.07 (4) 3.59 (4)	1.79 (6)	2.54
γ-AlF_3[c]	6.03 (2) 5.02 (4) 3.55 (4)	1.77 (4) ? (2)	?
α-AlF_3	3.52 (6)[d]	1.79 (6)	2.54
$(NH_4)_3FeF_6$	6.43 (12)	1.90 (6)	2.69
NH_4FeF_4	6.36 (2) 5.35 (4) 3.78 (4)	1.89 (6)	2.67
FeF_3	3.73 (6)	1.92 (6)	2.72

[a] Between neighboring fluorides in the octahedron. [b] Number of equivalent distances. [c] Based on a speculative structure. [d] Distance to neighboring octahedra.

Ammonium tetrafluoroaluminate and presumably the ferrate as well are tetragonal, with unimolecular cells. Atoms are in the special positions of D_{4h}^1 (P4/mmm):[27] NH_4: (1a) 0, 0, 0. Fe/Al: (1d) $^1/_2$, $^1/_2$, $^1/_2$. F(1): (2e) 0, $^1/_2$, $^1/_2$; $^1/_2$, 0, $^1/_2$. F(2): (2h) $^1/_2$, $^1/_2$, z; $^1/_2$, $^1/_2$, $\bar{z}$ ($z \approx 0.21$). This results in layers of regular octahedra like those in the hexafluoro compounds, sharing corners and separated by layers of ammonium groups, with both metal atoms and ammonium groups occupying positions of a primitive lattice.

α-Aluminum fluoride[12] and iron(III) fluoride[11] are rhombohedral, with space groups given as $R\bar{3}$ and $R\bar{3}c$, respectively. Here also, six fluorine atoms form a regular, or nearly regular, octahedron around the metal, and the octahedra are joined by sharing corners only.

The first thermal transition of $(NH_4)_3MF_6$ involves loss of two NH_4 and two F units from each mole of hexafluoro compound, presumably those related to the special positions of (8c). This would be followed by a contraction of the cubic lattice in two directions to form layers of MF_6 octahedra joined by shared corners. Layers of NH_4 groups would lie between these layers, both forming interpenetrating tetragonal arrays. The octahedral F–F distances and the M–F distances are nearly identical in the $(NH_4)_3MF_6$ and NH_4MF_4 structures, suggesting that the octahedra are relatively unaffected. The M–M distances show 12 nearest neighbors at 6.31 A for $(NH_4)_3AlF_6$ and at 6.43 A for $(NH_4)_3FeF_6$. In NH_4AlF_4 the four nearest neighbors (M–M) are at 3.59 A and in NH_4FeF_4 they are at 3.78 A, in the plane resulting from the contraction. The other two M atoms, normal to the plane, are at 6.35 and 6.36 A, distances similar to the shortest (not contracted) M–M distances in $(NH_4)_3MF_6$. These comparisons thus suggest that the [110] direction of the $(NH_4)_3MF_6$ unit cell becomes the [001] direction of the tetragonal unit cell of NH_4MF_4.

The second transition seems to occur in two stages: the escape of ammonium fluoride without appreciable structural alteration and the subsequent crystalline rearrangement to the normal high-temperature fluoride. The sensitivity of fluoroferrate decomposition to water or oxygen has precluded direct observation of the intermediate, as in the case of aluminum, but similarity of the thermal analyses suggests a similar mechanism. Removal of ammonium groups and the nearest nonbridging fluorides on alternate sides of the AlF_6 octahedra would lead to a tetragonal structure in which the Al–Al distances would remain about the same as those in NH_4AlF_4. This would result in layers of planar AlF_4 groups, sharing corners, each aluminum atom being connected to a single unshared fluorine. The symmetry would decrease from the P4/mmm of NH_4AlF_4 to P4mm, requiring a doubly primitive unit cell with $a = 5.02$, $c = 6.03$ A. This relationship

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(27) Reference 20, vol. 3, p 2.

is shown in projection in Figure 5. Qualitative comparison of X-ray powder intensities suggests that this interpretation is not unreasonable.

The collapse of this structure along the *c* axis to the α-AlF_3 structure follows readily, forming an almost cubic structure, with the Al–Al distance of 3.52 A directly comparable to the 3.55 and 3.59 A of its precursors. The fluorides revert to a complete octahedral configuration, the Al–F distances having remained at 1.76–1.79 A during the series. Comparison is simplified if the sixfold primitive hexagonal cell, $a = 4.914$, $c = 12.449$ A, is used for α-AlF_3. The edges of the pseudo-cube (the Al–Al directions) then lie along the $[2\bar{2}1]$, $[42\bar{1}]$, and $[241]$ directions of the hexagonal cell. The vacancies in γ-AlF_3 correspond to those in α-AlF_3, the latter lying at the centers of the pseudo-cubes.

It is interesting to note that there is a report of different forms of gallium fluoride, one obtained by thermal decomposition of ammonium hexafluorogallate and one by fluorination of oxide at 600°.[28]

NOTE ADDED IN PROOF.—We have recently become aware of a patent[29] on the synthesis of vinyl fluoride, in which one of the claims is for the preparation of a new catalytic form of aluminum fluoride by dehydration of α-aluminum fluoride trihydrate. The powder pattern cited is quite similar to that for the γ-aluminum fluoride presented in this paper but contains a number of lines not present in our material, including a strong line at 3.465 A. The low calculated density indicates an open structure, and it is believed that the product reported in the patent is the open γ-AlF_3 of this paper with a small amount of water remaining in the holes. No analysis is given in the patent, and there is no evidence to indicate complete removal of water.

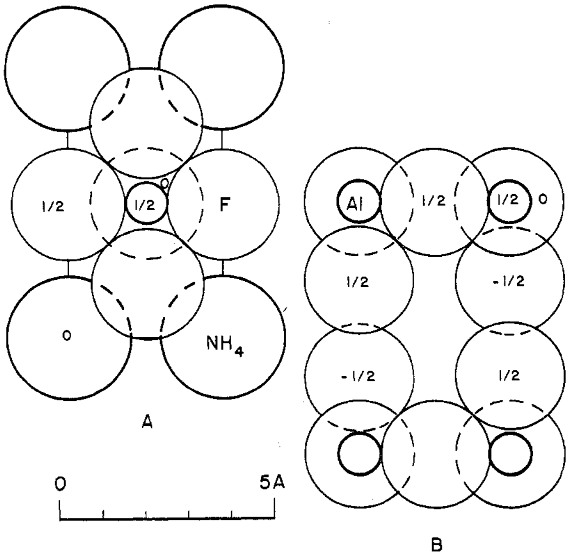

Figure 5.—Structural relation between NH_4AlF_4 and γ-AlF_3: A, NH_4AlF_4; B, γ-AlF_3. The figures are projected along the *a* axis; numbers within the circles give the fractional distances in terms of cell axes of atoms above (or below) the plane of protection. Note that the drawing of γ-AlF_3 is not that of the unit cell.

[28] O. Hannebohn and W. Klemm, *Z. Anorg. Allgem. Chem.*, **229**, 337 (1936); R. Hoppe, unpublished work, 1955–1956; Dissertation, Münster, 1958. See C. Hebecker and R. Hoppe, *Naturwissenschaften*, **53**, 104 (1966).

[29] F. J. Christoph, Jr., and G. Teufer, U. S. Patent 3,178,483 (1965).

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The Sodium Fluoride–Scandium Trifluoride System[1]

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The equilibrium phase diagram of the condensed system NaF–ScF_3 was constructed from data obtained using standardized methods of thermal analysis and thermal gradient quenching, and also by direct observation of crystallizing melts. Crystallographic properties of the solid phases were measured by petrographic and X-ray diffraction techniques. Equilibria among the condensed phases in the system were established through the temperature interval from the liquidus to approximately 400°. Two equilibrium compounds were observed to form from NaF and ScF_3—the cryolite-like phase, $3NaF \cdot ScF_3$, and a hexagonal phase, $NaF \cdot ScF_3$, with lattice constants $a = 12.97$ A, $c = 9.27$ A. Four invariant points were found to occur in the system NaF–ScF_3: the eutectic at 17 mole % ScF_3 and at 800°, a peritectic at 35 mole % ScF_3 and at 680°, associated with a solid-state transition in $3NaF \cdot ScF_3$, a eutectic at 38 mole % ScF_3 and at 650°, and a peritectic at 42 mole % ScF_3 and at 660°. The equilibrium character of the system NaF–ScF_3 is contrasted with that of NaF–AlF_3 and with those of the sodium fluoride–rare earth trifluoride systems.

Introduction

Variability in stoichiometry, structure, and stability among the complex compounds formed in the binary systems of the alkali fluorides and the lanthanide trifluorides is influenced chiefly by two factors: (a) disparity in size between the monovalent and trivalent ions[3] and (b) relative charge density of the lanthanide ions. Results of the recent investigation of the sodium fluoride–lanthanide trifluoride systems[4] showed

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[2] Summer Research Participant, 1964–1965.

[3] R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

[4] R. E. Thoma, G. M. Hebert, and H. Insley, *ibid.*, **5**, 1222 (1966).