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THERMAL DECOMPOSITION OF AMMONIUM FLUOROMANGANATES (III)

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ABSTRACT

The thermal decomposition of ammonium fluoromanganates (III) has been investigated in air and argon by simultaneous thermogravimetry and differential thermal analysis. Chemical analysis, X-ray powder data, and infrared spectra have been employed to characterise the intermediate and final products. The thermal decomposition can be described by the sequence $(NH_4)_3MnF_6 \rightarrow (NH_4)_2MnF_5 \rightarrow NH_4MnF_4 \rightarrow MnF_2$. Although penta- and tetra-fluoromanganates are well-defined compounds, the intermediate states could not be separated. In addition, a high temperature form of ammonium hexafluoromanganate has been observed.

INTRODUCTION

There are only a few studies on the thermal decomposition of ammonium fluorometallates (III) reported in the literature. For $(NH_4)_3MF_6$ (M = Al, Fe), Shinn et al.[1] have found NH_4MF_4 as intermediates and MF_3 as final products. In our study[2] on the decomposition of ammonium hexafluoro-aluminate, -gallate and -indate, the same intermediate and final compounds have been isolated. Thermal decomposition of $(NH_4)_3VF_6$[3] and $(NH_4)_3CrF_6$[4] at 500°C has been used as a preparative way of obtaining the respective trifluorides. In an investigation dealing with the complexes $(NH_4)_3MF_6$ (M = Sc, Ti, V, Cr)[5], tetrafluorometallates were found as intermediates for the first three compounds. In the case of titanium, the sublimation of NH_4TiF_4 was observed in addition to its decomposition. $(NH_4)_3CrF_6$ decomposed directly to CrF_3.

For manganese, two compounds are known in the literature, $(NH_4)_3MnF_6$[6] and $(NH_4)_2MnF_5$[7]. In addition, in a recent investigation on the system MnF_3–NH_4F–HF–H_2O ammonium tetrafluoromanganate (III) has been isolated[8].

EXPERIMENTAL

Ammonium fluoromanganates (III) isolated in the investigation already mentioned[8] have been used in this study. Thermogravimetric (TG), derivate thermogravimetric (DTG), and differential thermal analysis (DTA) data were obtained simultaneously by means of a Mettler thermoanalyzer with Pt/Pt–Rh thermocouples and Pt crucibles (TDI). Measurements were carried out in a dynamic atmosphere (5l h^{-1}) of dry argon and air at heating rates of 1 and 6°C min^{-1}, respectively, and sample masses of 100 mg.

Inert alumina was used as reference material for DTA.

Intermediate phases were obtained by heating the initial compounds at a heating rate of 6°C min^{-1} to the desired temperatures and cooling the samples.

Pyrolysis experiments were performed in a tube furnace supplied and regulated by a Mettler TM 16 digital-regulator. The samples of 100 mg were heated isothermally in a dynamic atmosphere of argon and air at a flow-rate of 2l h^{-1}. The amount of hydrogen fluoride given off was determined by passing the gases through a solution of N/10 sodium hydroxide.

Infrared spectra were measured using a Model 521 Perkin-Elmer grating spectrometer (4000–250 cm^{-1}). Crystallographic powder spectra were obtained with a Guinier–de Wolff and high temperature Lenne–de Wolff camera, respectively, using CuKα radiation.

RESULTS

The thermal decomposition of NH_4MnF_4 in argon begins at 170°C, as shown in Fig. 1. The process is accomplished in one step yielding MnF_2 as final product, as proved by X-ray powder photograph and chemical analysis. The experimental mass loss of 37.26% agreed with the theoretical value of 37.62%.

In a separate pyrolysis experiment carried out at 300°C, 0.73 moles HF/1.00 mol NH_4MnF_4 evolved. The composition of white sublimate deposited on the cooled part of the tube was approximately NH_4HF_2. It is known that thermal decomposition of NH_4F begins at about 100°C to give first NH_4HF_2, which further decomposes to NH_3 and HF[9].

In our case the complex starts decomposing at a higher temperature, consequently giving HF and NH_3, however the two gases recombine to form the most stable of the two fluorides. Because there is no sharp difference between the thermal stabilities of NH_4F and NH_4HF_2, the extent of recombination strongly depends on the experimental conditions. The decomposition of NH_4MnF_4 in an inert atmosphere can therefore be described by the equation:

$$3NH_4MnF_4 = 3MnF_2 + \tfrac{1}{2}N_2 + 2NH_3 + 6HF \qquad (1)$$

The simultaneously obtained DTA curve is endothermal and runs parallel to the DTG one. The peak temperatures are given in Table 1.

The thermal decomposition of NH_4MnF_4 in dry air resulted in nearly the same TG curve having a weight loss of 37.40%. The endothermal reaction commences at the same temperature as in inert atmosphere and continues up to 310°C. At this

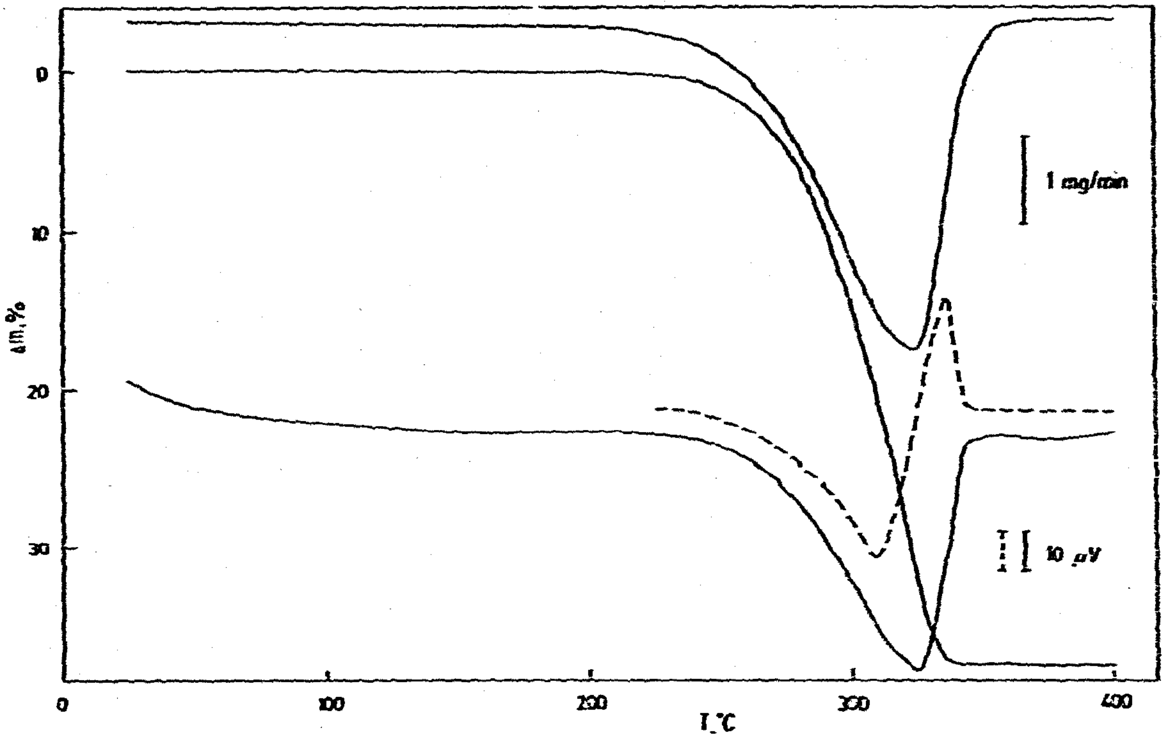

Fig. 1. Thermal decomposition of NH_4MnF_4 in flowing dry argon (solid lines) and flowing dry air (dashed line). Heating rate, 6°C min^{-1}; sample weight, 100 mg.

TABLE 1

PEAK TEMPERATURES FOR THE DECOMPOSITION OF AMMONIUM FLUOROMANGANATES IN ARGON

	Peak temp. (°C min^{-1})	*DTG*	*DTA*
NH_4MnF_4	6	320	323
	1	275	275
$(NH_4)_2MnF_5$	6	285, 323	285, 320
	1	245, 282	242, 282
$(NH_4)_3MnF_6$	6	115, 200, 240, 275, 318	92, 115, 203, 240, 275, 305
	1	160, 195, 235, 280	94, 160, 197, 235, 255, 280

temperature the exothermal reaction starts with a DTA peak at 336°C. The DTG curve shows the maximum reacting rate to appear at the same temperature as in argon.

The detection of hydrogen fluoride evolved under the same conditions as previously, revealed 1.37 HF/1.00 NH_4MnF_4. Taking into account the oxidation of ammonia, the following equation can be written, having the same theoretical weight loss as the previous one

$$NH_4MnF_4 + \tfrac{1}{2}O_2 = MnF_2 + \tfrac{1}{2}N_2 + 2HF + H_2O \qquad (2)$$

If we consider the endothermal part of the TG curve (47.4%) to follow eqn (1) and the exothermal one to obey eqn (2), we get the ratio HF/NH_4MnF_4 of 1.37. This fairly good agreement of calculated and experimental values is only fortuitous, because the experimental conditions in both cases were different. Nevertheless, the increased amount of HF given off clearly indicates the nature of the exothermal reaction.

Thermoanalytical curves for the decomposition of $(NH_4)_2MnF_5$ are presented in Fig. 2. The compound undergoes a two-stage thermal decomposition. The formation of an intermediate phase is not evident from the TG curve. The use of a heating rate of 1 °C min^{-1} gives rise to splitting of the DTG curve, however, the two reactions still overlap.

If the complex is heated at 6 °C min^{-1} to the first peak temperature, the intermediate is obtained with a mass loss of 17.95%. The X-ray powder photograph of the isolated phase shows a mixture of $(NH_4)_2MnF_5$ and NH_4MnF_4. The final product is again MnF_2 with a mass loss of 49.30% (theor. 50.03).

The DTA curve is parallel to the DTG but shows a better resolution (Table 1).

TG and DTG curves for the decomposition of $(NH_4)_2MnF_5$ in dry air are the

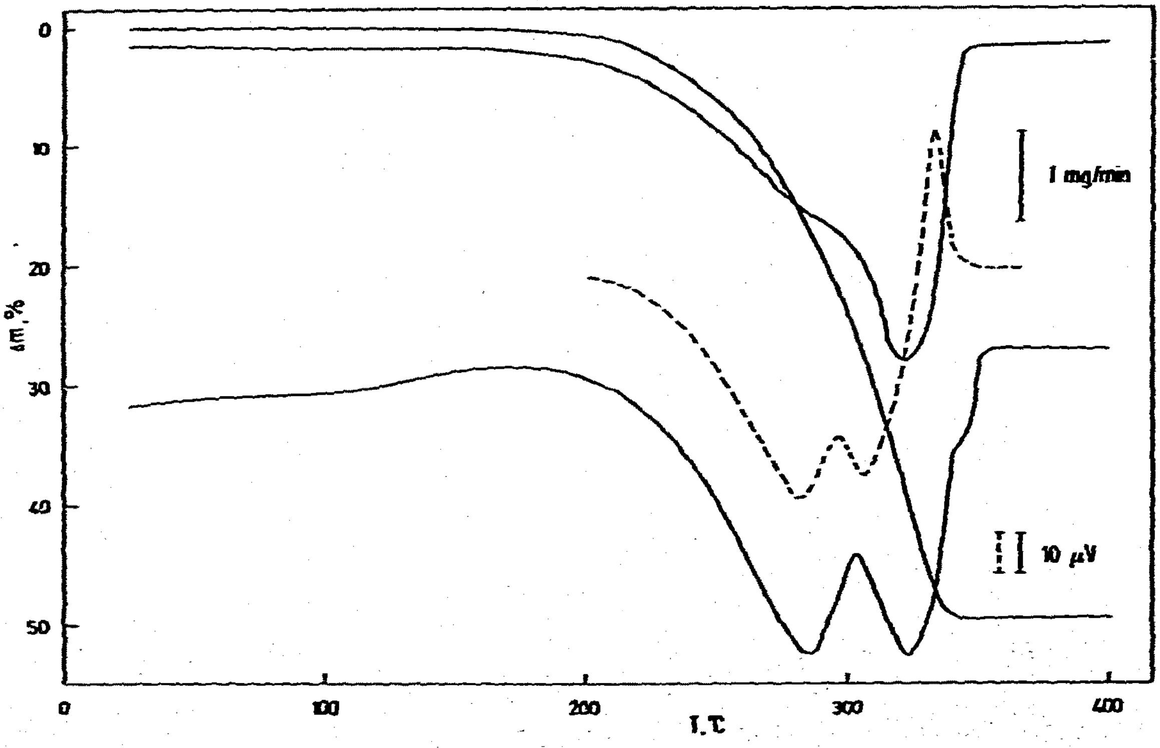

Fig. 2. Thermal decomposition of $(NH_4)_2MnF_5$ in flowing dry argon (solid lines) and flowing dry air (dashed line). Heating rate, 6 °C min^{-1}; sample weight, 100 mg.

same as in an inert atmosphere. The first DTA peak at 270°C corresponds to the one in argon. However, the second endotherm at 295°C and the exotherm at 322°C resemble the DTA curve of NH_4MnF_4 recorded in air.

The thermal decomposition of $(NH_4)_3MnF_6$ is shown in Fig. 3. Under these experimental conditions the process occurs in a single step and the pathway of the TG curve does not permit the establishment of the stoichiometry of the decomposition reactions. On the other hand, there are five DTG peaks showing the process to be rather complicated. Employing a heating rate of 1 °C min^{-1} with all the other experimental conditions fixed, two slight breaks appear in the TG curve. The corresponding mass losses are 12.4 and 23.7%. The calculated values for the dissociation of one and two molecules of NH_4F, 16.61 and 33.21% respectively, do not agree with the experimental data.

Intermediate phases isolated by heating $(NH_4)_3MnF_6$ to the DTG-peak temperatures are given in Table 2. All stages of the thermal decomposition but the

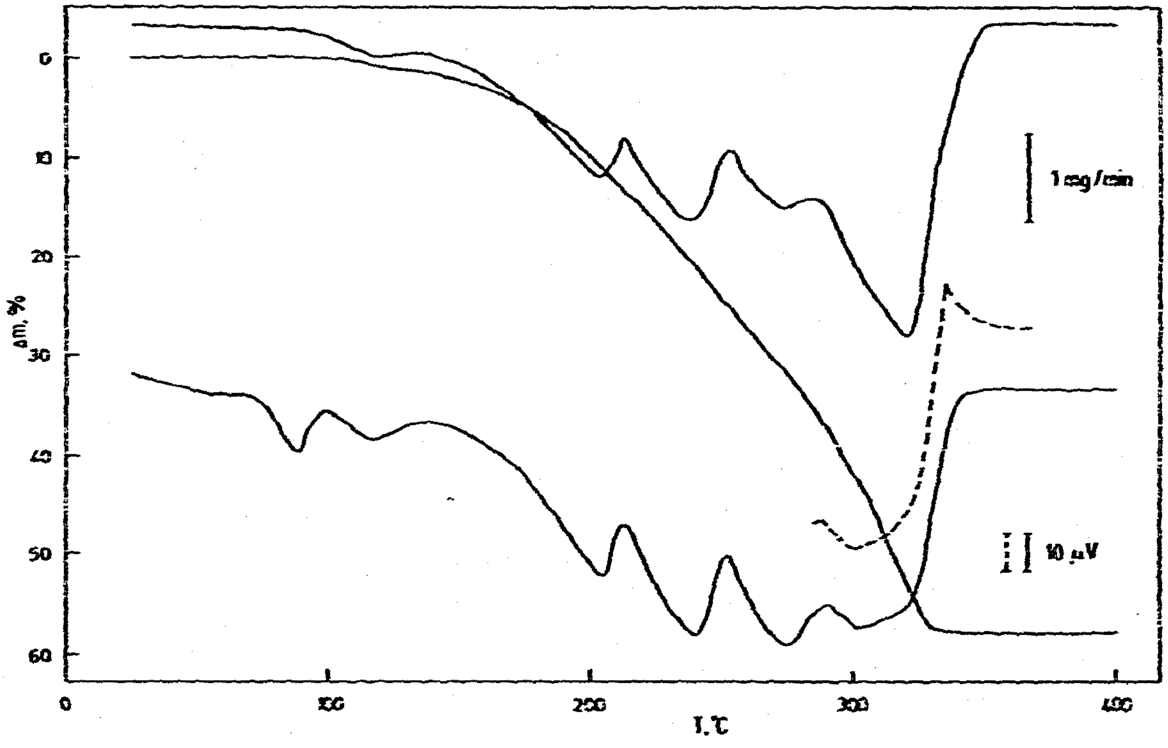

Fig. 3. Thermal decomposition of $(NH_4)_3MnF_6$ in flowing dry argon (solid lines) and flowing dry air (dashed line). Heating rate, 6°C min^{-1}; sample weight, 100 mg.

TABLE 2

INTERMEDIATE PHASES OBTAINED BY HEATING $(NH_4)_3MnF_6$ IN ARGON

T(°C)	*Mass loss (%)*	*X-ray pattern*
195	13.2	$(NH_4)_3MnF_6$
235	23.1	$(NH_4)_2MnF_5$
275	34.8	$(NH_4)_2MnF_5$ + NH_4MnF_4

last are therefore accompanied by sublimation of NH_4F. In the course of the decomposition of $(NH_4)_3MnF_6$ both previously mentioned compounds appear as intermediates. In the last step, disproportionation of NH_4MnF_4 occurs to yield MnF_2. The final mass loss is 58.50%, in good agreement with the calculated value of 58.34%.

The DTA curve, which is parallel to the DTG one, has an additional peak at 92°C (Table 1). There is no weight change, so it can be ascribed to a polymorphic transition.

The curves run in dry air reveal the same feature as in the former cases. The

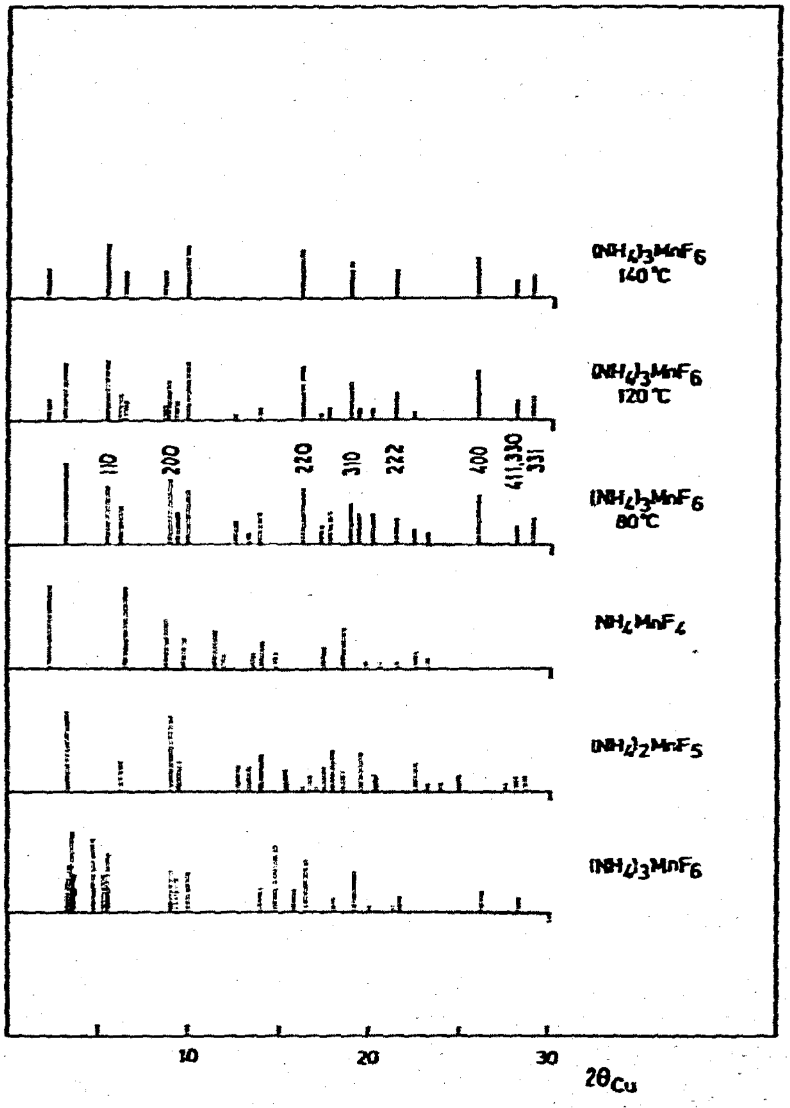

Fig. 4. X-ray patterns of pure substances and of $(NH_4)_3MnF_6$ at 80, 120 and 140°C. Indices of HT-$(NH_4)_3MnF_6$ are indicated.

DTA again shows an exothermal reaction in the last stage of pyrolysis, whereas the TG and DTG remain almost unchanged.

The crystal structure of ammonium pentafluoromanganate consists of MnF_6^{3-} octahedra, sharing their trans vertices to form endless chains.[7] There are two crystallographically non-equivalent nitrogen atoms in the unit cell, both possessing C_s sites. The crystal structures of hexa- and tetra-fluoro compounds are unknown. On the basis of infrared spectra it was suggested[8] that both $(NH_4)_3MnF_6$ and NH_4MnF_4 have octahedral coordination of manganese. In the first case the octahedra are isolated; in the second one, they share their fluorine atoms to form a layer-like structure.

The changes in X-ray powder pattern were followed up to 150°C (Fig. 4). The powder patterns of pure substances are also shown for comparison. At about 80°C some of the lines of the initial compound disappear, clearly indicating the increase in symmetry. The temperature of this polymorphic change is somewhat lower than that determined by DTA. Such transitions are known for similar compounds, e.g.,

TABLE 3

INTERPLANAR SPACINGS, INTENSITIES AND INDICES OF REFLECTIONS OF $(NH_4)_3MnF_6$ AT 80, 120 AND 140°C

Key No.[a]	*hkl*	*80°C*		*120°C*		*140°C*	
		d	*I*	*d*	*I*	*d*	*I*
1	001			6.32	2	6.33	2
2	101/002	5.40	10	5.41	8		
3	110	4.25	7	4.27	8	4.27	8
2	020	3.98	4				
1	200			3.90	2	3.90	3
1	201			3.29	2	3.29	3
2	022	3.20	8	3.21	5		
2	200	3.12	4	3.13	2		
3	200	3.00	6	3.01	7	3.01	7
2	031	2.56	2	2.57	1		
2	220	2.47	1				
2	221	2.38	3	2.39	2		
3	220	2.12	7	2.13	7	2.13	7
2	105/204	2.03	3	2.04	1		
2	230	1.997	2	2.00	1		
3	310	1.900	5	1.900	6	1.900	6
2	312	1.870	2	1.875	1		
2	224/321	1.820	2	1.822	1		
3	222	1.735	4	1.739	4	1.740	4
2	116	1.681	2	1.685	1		
2	304	1.642	1				
3	400	1.501	5	1.505	5	1.507	5
3	411/330	1.414	2	1.415	2	1.415	2
3	331	1.380	3	1.382	3	1.383	3

[a] 1 NH_4MnF_4 tetragonal $a = 7.752(6)$ Å $c = 6.153(12)$ Å; 2 $(NH_4)_2MnF_5$ orthorombic $a = 6.20(3)$ Å $b = 7.94(1)$ Å $c = 10.72(1)$ Å; 3 HT-$(NH_4)_3MnF_6$ cubic $a = 6.02$ Å

$(NH_4)_3M^{III}F_6$ (M = Al[10], In[2], Sc, Ti[5]). Comparison of the X-ray powder photograph between 80 and 120°C to that of pure $(NH_4)_2MnF_5$ reveals a close relationship between them. The pattern, in fact, consists of $(NH_4)_2MnF_5$ lines together with some additional lines already present in the initial pattern. These extra lines, which may be attributed to a high temperature form of ammonium hexafluoromanganate, can be indexed on the basis of a cubic unit cell (Table 3). The lines of $(NH_4)_2MnF_5$ disappear at about 140°C, but before that, the strongest reflections of NH_4MnF_4 appear. Between 120 and 140°C there are three phases, HT-$(NH_4)_3MnF_6$, $(NH_4)_2$ MnF_5 and NH_4MnF_4, present at the same time. It is interesting that the lines of HT-$(NH_4)_3MnF_6$ are preserved over the whole temperature range.

It should be added that heating of $(NH_4)_3MnF_6$ isothermally at 200°C for two days, resulted in complete decomposition to MnF_2 with weak lines in its X-ray powder photograph.

Heating the sample at 150°C for 25 days yielded MnF_2 as well, having extremely weak lines in its X-ray powder photograph.

The sublimation of NH_4F as well as disproportionation of tervalent manganese are obviously competitive processes so that the overall reaction heavily depends upon the experimental conditions.

The infrared spectra of several intermediate stages closely resemble those of pure substances. A representative part of the spectrum given in Fig. 5 shows the splitting of the NH_4^+ deformation mode and Mn–F streching mode, respectively.

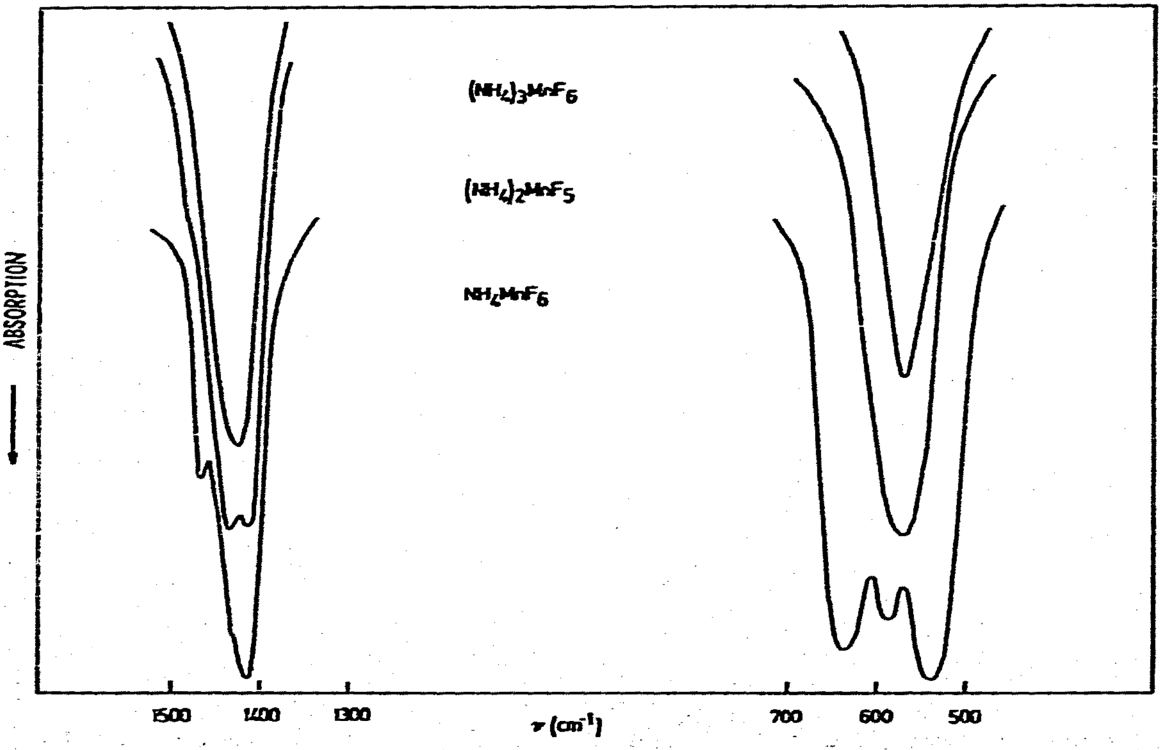

Fig. 5. Changes in (MnF) stretching and (HNH) deformation bands during decomposition in argon.

The changes in ammonium band were attributed to increasing hydrogen-bonding in the sequence hexa-, penta-, and tetra-fluoromanganates[8]. Similar splitting was observed in decomposition of ammonium metavanadate[11]. It was ascribed to a disordered structure in terms of NH_4^+ ion arrangement. Such a disordered state, formed by random removal of NH_4^+ ions, may appear in our case too, but the mentioned similarity of the spectra of the initial substances and intermediate phases, supports the former explanation.

REFERENCES

1 D. B. Shinn, D. S. Crocket and H. H. Haendler, *Inorg. Chem.*, 5 (1966) 1927.

2 P. Bukovec and J. Šiftar, in H. G. Wiedemann (Ed.), *Thermal Analysis*, Vol. 2, Birkhäuser, Basel and Stuttgart, 1972, p. 321.

3 B. I. Sturm and C. W. Sheridan, in J. Kleinberg (Ed.), *Inorganic Synthesis*, Vol. 7, McGraw-Hill, New York, 1963, p. 87.

4 B. I. Sturm, *Inorg. Chem.*, 1 (1962) 665.

5 P. Bukovec and J. Šiftar, *Monatsh. Chem.*, 105 (1974) 510.

6 W. Massa, *Z. Anorg. Allg. Chem.*, 415 (1975) 254.

7 D. R. Sears and J. L. Hoard, *J. Chem. Phys.*, 50 (1969) 1066.

8 P. Bukovec and J. Šiftar, *Monatsh. Chem.*, 108 (1977) 387.

9 L. Erdey, S. Gál and G. Liptay, *Talanta*, 11 (1964) 913.

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

11 M. E. Brown and B. V. Stewart, *J. Therm. Anal.*, 2 (1970) 287.