

# In situ time-resolved X-ray diffraction study of manganese trifluoride thermal decomposition

J.V. Rau<sup>a,\*</sup>, V. Rossi Albertini<sup>b</sup>, N.S. Chilingarov<sup>a</sup>, S. Colonna<sup>b</sup>, U. Anselmi Tamburini<sup>c</sup>

<sup>a</sup>Chemistry Department, M.V. Lomonosov Moscow State University, 119899 Moscow, Russia

<sup>b</sup>Istituto di Struttura della Materia/CNR, Via del Fosso del Cavaliere, 100-00133 Rome, Italy

<sup>c</sup>Dipartimento di Chimica Fisica, Università di Pavia, Viale Tramelli, 16-27100 Pavia, Italy

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## Abstract

The first in situ time-resolved X-ray diffraction study of  $\text{MnF}_3$  crystal structure evolution during its thermal decomposition was performed on the GILDA beam line at the European Synchrotron Radiation Facility (ESRF, France).  $\text{Mn}_2\text{F}_5(\text{s})$  was observed as intermediate phase during the process of decomposition of  $\text{MnF}_3(\text{s})$  to  $\text{MnF}_2(\text{s})$ . © 2001 Published by Elsevier Science B.V.

**Keywords:** In situ X-ray diffraction; Thermal decomposition; Manganese fluorides

## 1. Introduction

High valency metal fluorides ( $\text{MnF}_3$ ,  $\text{CoF}_3$ ,  $\text{TbF}_4$ , etc.) are interesting both from theoretical and from practical points of view. They are widely used as fluorinating agents in the synthesis of fluorinated derivatives of organic compounds [1] and are recently found to be promising fluorinating agents in synthesis of gaseous fluorides of transition metals in unusually high oxidation states [2]. Their thermal decomposition leads to the formation of the corresponding lower valency metal fluorides and the release of fluorine [3,4]. Although this is generally assumed to be a simple process, no deeper inspection has been done on the real mechanism hitherto. However, on the basis of mass spectrometric investigations, complex transformations were hypothesised for high valency metal fluorides decomposition [4,5].

The purpose of this work was to study in situ the evolution of the solid phase from  $\text{MnF}_3$  to  $\text{MnF}_2$  by time-resolved X-ray powder diffraction recorded during thermal transformation.

## 2. Experimental

A Ni capillary, previously passivated by keeping it for ~48 h at high temperature (400°C) in a fluorine atmosphere

( $P = 1$  atm), was used as the sample holder. On one hand, the sample holder has to be inert with respect to fluorine; on the other, it has to endure high temperatures (>500°C). Due to the latter constraint, a plastic container could not be used, although a metal capillary has the drawback of being rather opaque to X-rays. This applies to our Ni capillary, despite that the thickness of its walls was only 100  $\mu\text{m}$ . To reduce this effect and, simultaneously, to decrease the intensity of the higher harmonics present in the X-ray beam [6], high energy radiation (~24 keV) was utilised.

The diffraction measurements were performed on the GILDA beam line at the European Synchrotron Radiation Facility (Grenoble, France). The beam line monochromator was equipped with two Si(3 1 1) crystals, the first is flat, whereas the second is curved to focus the X-ray beam in the horizontal plane. A further reduction of the higher harmonics was obtained by a partial de-tuning of the monochromator. The calibration of the radiation energy was made by collecting the diffraction pattern of a standard  $\text{LaB}_6$  powder [7].

The capillary (~6 cm in length) containing the sample was mounted on a rotating system and connected to a pipe supplying an Ar flow during heating. The major problem in the preliminary measurements was connected to the use of the small volume closed capillary. Usually measurements, like gas phase IR spectroscopy or high temperature mass spectrometry, on thermal decomposition of this class of compounds are carried out under vacuum, so that fluorine developed during the decomposition is pumped away. In a

\* Corresponding author. Fax: +7-95-939-1240.

E-mail address: jrau@phys.chem.msu.ru (J.V. Rau).

closed container, decomposition was not observed even at more than 300°C above the expected temperature. Therefore, the capillary, heated by a hot air jet, was connected to the pipe so that an Ar flow passed through the powder to remove the released fluorine from the reaction zone, preventing the reverse reaction. The temperature of decomposition,  $T_d = 620^\circ\text{C}$ , was chosen on the basis of the mass spectrometric investigation of  $\text{MnF}_3$  evaporation [8]. The temperature was determined by measuring the shift of Bragg peaks of the Ni capillary, whose expansion coefficient is well known [9].

Diffraction patterns were collected by an imaging plate placed downstream of the capillary, with a sample-to-detector distance of 337 mm, allowing an angular collection of about  $50^\circ$ . The phase transformation was followed by the translating imaging plate technique [10], in which two vertical slits are placed in front of the detector plate that is translated during the sample heating. This allows collection of vertical stripes of the Debye–Scherrer rings and to follow their time variation. In spite of the high absorption of the capillary walls and of the reduced solid angle subtended by the detector, the counting statistics were still good for structural studies due to the high photon flux of the synchrotron radiation. The time resolution of each diffraction pattern was of the order of 3 min. The angular resolution depends on the capillary diameter [10]; the use of a 1.3 mm capillary in our experimental set up allowed resolution of the peaks of the various phases.

A reference measurement was carried out before the beginning of heating (see Fig. 1). The intensities are plotted as a function of the universal scattering parameter  $q = 4\pi \sin \theta/\lambda$ , where  $2\theta$  is the diffraction angle and  $\lambda$  is the (fixed) wavelength of the incident X-ray beam ( $0.5164 \text{ \AA}$ ). The diffraction pattern is in agreement with that of  $\text{MnF}_3(\text{s})$  [11]. Then the temperature was increased to  $T_d$ , and the kinetics of  $\text{MnF}_3(\text{s})$  decomposition was mon-

itored by collecting a sequence of diffractograms of the evolving system. A selection of diffractograms is plotted on Fig. 2. The region of interest is  $(1.5 < q < 3.6) \text{ \AA}^{-1}$ , where the compounds under study show their main peaks. The other less intense peaks, at higher  $q$  values, are not well resolved from the background noise. For this reason the scale is expanded and the peaks appear to be rather broad.

The lowest diffractogram on Fig. 2 corresponds to the composition of the solid phase when the temperature reached  $T_d$ , while the upper shows that the decomposition is complete. In the latter, as expected, the Bragg peaks of  $\text{MnF}_2$  only can be seen [11]. There is a  $q$ -interval where peaks that cannot be assigned to either  $\text{MnF}_3$  or  $\text{MnF}_2$  are present. The peaks appearing in this  $q$ -interval fit well with the diffraction pattern of  $\text{Mn}_2\text{F}_5$  [11] as can be seen in Fig. 3, where the first (lowest) diffractogram of the sequence in Fig. 2 is examined in detail. The  $[4\ 0\ 0]$ ,  $[2\ 2\ 0]$  and  $[0\ 0\ 2]$  reflexes of  $\text{Mn}_2\text{F}_5$  account for the presence of the three extraneous peaks in the low  $q$  region. Slight discrepancies in the peak positions can be explained by the difficulty in positioning the spinning Ni capillary that, suffering deformation due to the intense heating, may induce deviations from ideal geometry. On the other hand, the graphs are on an extended scale, so that small deviations are overemphasised.

As follows from Fig. 2,  $\text{Mn}_2\text{F}_5$  phase is already present in the system when the temperature reached  $T_d$ . It means that partial  $\text{MnF}_3$  decomposition takes place during the increase of temperature, and when it reaches  $T_d$  the solid phase consists of the mixture of  $\text{MnF}_3$  and  $\text{Mn}_2\text{F}_5$ .

Literature data on  $\text{Mn}_2\text{F}_5$  are very limited: only two references [12,13] were found by us. Ehlert and Hsia [12] previously writing on this subject dedicated only a few lines in their paper and mentioned the conjecture concerning possible formation of a  $\text{Mn}_2\text{F}_5(\text{s})$  phase as a result of partial thermal decomposition of  $\text{MnF}_3(\text{s})$ . By means of a simple laboratory X-ray technique this  $\text{Mn}_2\text{F}_5$  phase was charac-

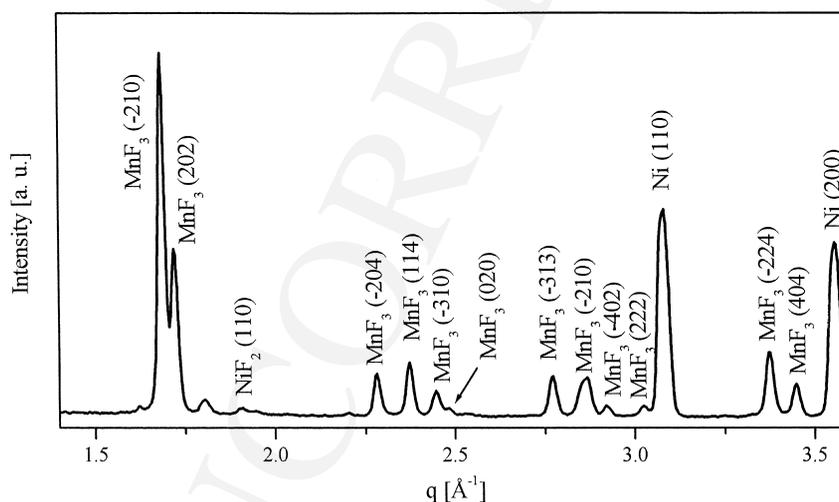


Fig. 1. Reference diffractogram of the  $\text{MnF}_3$  sample taken before the beginning of heating. The two peaks at  $3.08$  and  $3.55 \text{ \AA}^{-1}$  are produced by the Ni sample holder, the peak at  $1.90 \text{ \AA}^{-1}$  is due to  $\text{NiF}_2(\text{s})$  formed on the surface of the capillary during passivation. The two peaks at  $1.61$  and  $1.80 \text{ \AA}^{-1}$  are probably produced by impurities.

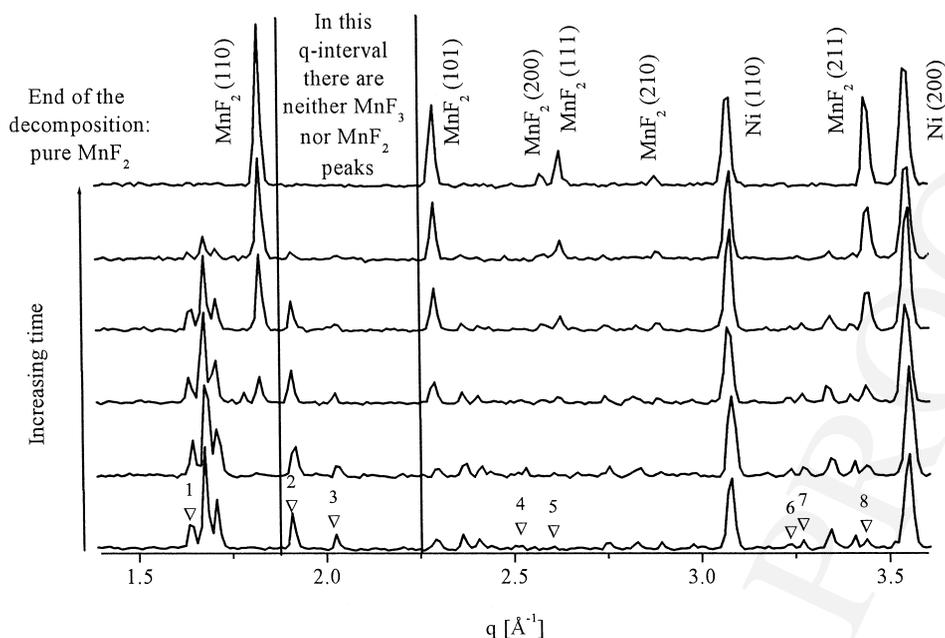
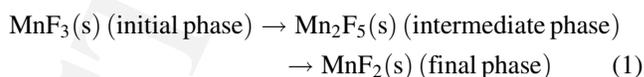


Fig. 2. A selection of the diffraction patterns collected during thermal decomposition ( $T_d = 620^\circ\text{C}$ , time of decomposition  $\sim 3$  h). The peaks indicated by progressive numbers can be assigned to the following  $\text{Mn}_2\text{F}_5$  Bragg reflections: 1 (4 0 0), 2 (2 2 0), 3 (0 0 2), 4 (3 1 2), 5 (5 2 0), 6 (4 3 1), 7 (8 0 0), 8 (4 0 3).

terised. Data were essentially refined in [13], where  $\text{Mn}_2\text{F}_5(\text{s})$  was obtained as a stable phase by submitting a mixture of  $\text{MnF}_3(\text{s})/\text{MnF}_2(\text{s})$  to 1.25– to  $300^\circ\text{C}$  and  $P = 4$  bars.

Apparently in our case the  $\text{Mn}_2\text{F}_5(\text{s})$  formation by the reaction between  $\text{MnF}_3(\text{s})$  and  $\text{MnF}_2(\text{s})$  might be excluded, because  $\text{MnF}_2(\text{s})$  was not present either on the first (lower) diffractograms on Fig. 2, which correspond to the beginning of decomposition, nor on heating up to  $T_d$ . Another process for  $\text{Mn}_2\text{F}_5(\text{s})$  formation seems to be more likely in our case. The depletion of the  $\text{MnF}_3$  phase in fluorine takes place upon heating. The decrease in stoichiometric amount of fluorine leads to the formation of a new crystalline phase —  $\text{Mn}_2\text{F}_5$ . A further depletion in fluorine leads to the formation of the

final product of decomposition —  $\text{MnF}_2(\text{s})$ . Therefore, the process of  $\text{MnF}_3(\text{s})$  thermal decomposition is a consecutive chemical transformation from the initial structure to the final according to the following sequence:



### 3. Conclusions

In the present work, the consecutive chemical transformations (1) taking place during  $\text{MnF}_3(\text{s})$  thermal decomposition were followed in situ. To our knowledge, this is the first

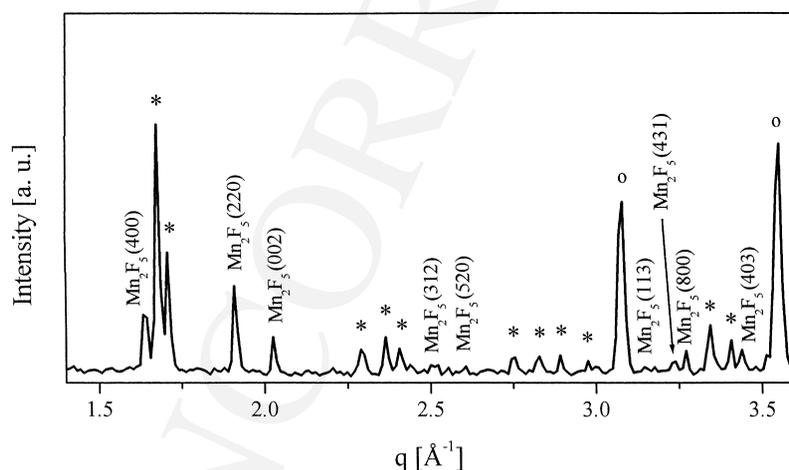


Fig. 3. Detailed view of the first (lowest) diffractogram of Fig. 2, which shows the onset of new peaks. To these new peaks Miller indexes of  $\text{Mn}_2\text{F}_5$  reflections are assigned. The remaining reflections due to  $\text{MnF}_3$  and to the Ni capillary are indicated by asterisks and circles, respectively.

real-time X-ray diffraction measurement of phase transitions taking place during thermal decomposition of a transition metal fluoride. The application of a modern technique — synchrotron radiation facility — to study such processes was shown. The experimental procedure could be used to study the thermal stability and the mechanism of decomposition of other high valency metal fluorides.

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