	Experiment title: Time resolved diffraction studies on the thermal decomposition of transition metal fluorides	**Experiment number**: 08-02-220
Beamline: BM08	**Date of experiment**: from: 19-07-2000 to: 21-07-2000	**Date of report**: 18-08-2000
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Report:

The fluorinating substances, i.e. compounds that may release gaseous fluorine, are interesting both from theoretical and from the practical point of view. In fact, they can be used to passivate metallic surfaces so that, after the treatment, they cannot suffer any other attach by aggressive chemical agents.

A particular attention is currently devoted to tri- fluorides of transition metals, whose overall thermal decomposition can be expressed as follows:

MeF_3 (solid) $\rightarrow$ MeF_2 (solid) + 1/2 F_2 (gas),

where Me =transition metal

Of course, this equation represents the passage from the initial compound to the final products only and does not take into account the possibility that more complex transformations involving temporary intermediate products occur. Indeed, mass spectrometric studies of the gas produced during the thermal decomposition provide the evidence that the reaction mechanism as described before is oversimplified. The purpose of the experiment is to observe the evolution of the solid phase from MeF_3 to MeF_2.

The compound chosen for this experiment was a sample of MnF_3 powder (a fraction of a milligram).

At our knowledge, this was the first time that a real-time observation of a thermal decomposition of a fluorine compound was observed by X-ray diffraction, so that the first part of the experiment had to be devoted to find the optimal set up. In fact, on one side, the sample holder has to be inert, i.e. it has not to react with gaseous fluorine released during decomposition; on the other side, it has to resist at the typical decomposition temperatures (about 400-500 °C). Due to the latter constrain, no plastic container could be used and the only suitable holders were Ni capillaries, previously passivated by keeping them in a high temperature (800° C). fluorine atmosphere (p=5atm)

As a drawback, despite the thickness of the Ni capillary walls (200 μm), soft X-rays are absorbed intensely and selectively, so that the higher harmonics can penetrate more easily producing spurious peaks in the

diffractogram. Therefore, an increase of the X-ray beam energy (about 24 keV) and a partial de-tuning of the monochromator were necessary to meet acceptable working conditions.

Another major problem was connected to the use of a closed capillary as sample holder. Usually, measurements on thermal decomposition of this class of compounds are carried out under vacuum, like gas phase FTIR or Mass Spectrometries, so that the small quantity of gas developed is immediately pumped away. In a closed container like the capillary, instead, the presence of gas inhibits the decomposition, which was not observed at more than 300° C above the expected temperature. The same happened after the capillary was drilled so that the gas, in principle, could escape from an orifice inside a suction pipe. It was necessary to make an Argon flux pass through the powder to remove the fluorine produced and to enable the decomposition that, in this condition, took place at about the usual temperature T_d~600° C.

After calibration measurements at a temperature just below T_d, the temperature was risen above T_d and the kinetic of decomposition of MnF3 was monitored by collecting a sequence of diffractogram of the changing compound. In fig. 1 a selection of diffractograms collected during the transition is plotted. The lower diffractogram represents an early stage of the decomposition, while the upper shows that the decomposition is complete. In the latter, the Bragg peaks of MnF_2 only are visible.

As indicated in the figure, there is a q interval inside which peaks that cannot be assigned to either MnF_3 or MnF_2 are present. This means that, during the decomposition, a temporary solid compound is formed, by which the two intense peaks in the (1.85, 2.20) $Å^{-1}$ range are produced.

On the base of mass spectrometric data on thermal decomposition of fluorides, a conjecture had been made about a possible production of compounds having an intermediate degree of fluorination, like Me_2F_5. In fig. 2, the Bragg reflexes MnF_3 (green) and of Mn_2F_5 (red) are overlapped to the lower spectrum of fig.1. Although the agreement is not perfect (but not even that of MnF_3 is very good), the Mn_2F_5 reflexes seem to account for the presence of the three extraneous peaks appearing the low q region. The discrepancies in the positions can be explained by the difficulty in positioning the (spinning) Ni capillary that, suffering deformations due to the intense heating, may induce deviations from the ideal geometry. On the other hand,

the graphs are drawn using an expanded scale (notice the peaks width), so that even small deviations are emphasised.

In any case, further measurements are required to sample more densely the crystalline structure during thermal decomposition and to investigate the other transition metal fluorides to study analogies and differences in their behaviours upon heating.

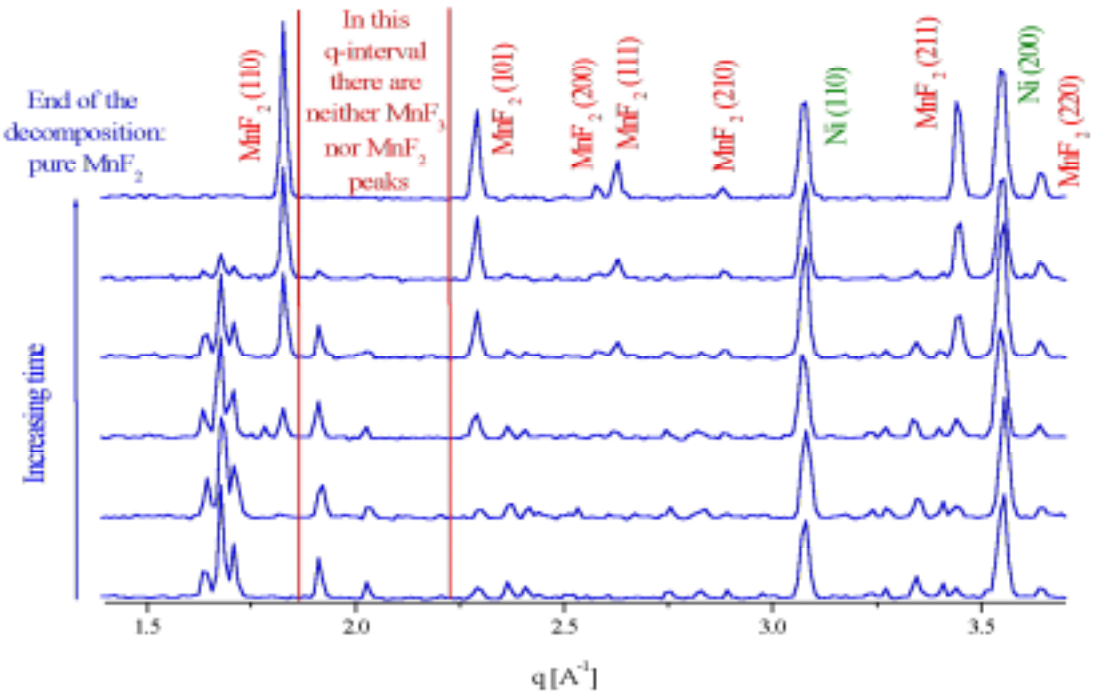

Figure 1
A selection of diffraction patterns collected during thermal decomposition.

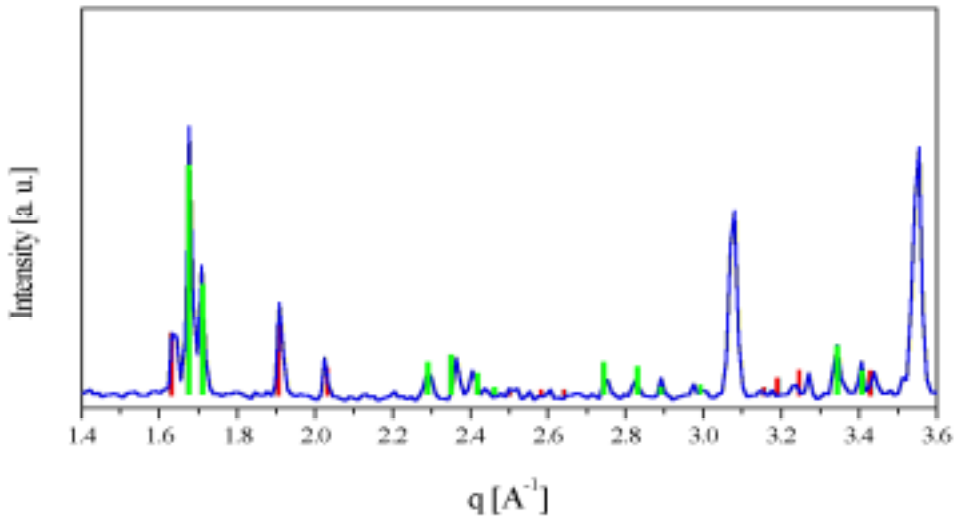

Figure 2
Comparison between the first diffractogram of the sequence and the reflexes of MnF_3 (green) and of Mn_2F_5 (red). The two peaks at about 3.08 and 3.55 $Å^{-1}$ are produced by the Ni sample holder.