

## Observation of a New Co-F Compound Detected by Very-High-Energy X-ray Diffraction During Thermal Decomposition of $\text{CoF}_3$

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In situ diffraction studies of structural transformations occurring during thermal decomposition of a cobalt fluoride- $\text{CoF}_3$ -were performed using a very-high-energy (89 keV) synchrotron radiation. The real-time evolution of the crystal lattice was followed as a function of temperature. A new compound appearing as intermediate in the course of the decomposition from  $\text{CoF}_3$  to  $\text{CoF}_2$  was discovered.

High valency metal fluorides ( $\text{MnF}_3$ ,  $\text{CoF}_3$ ,  $\text{TbF}_4$  etc.) are used as solid fluorinating agents to produce fluorine derivatives of organic compounds<sup>1</sup> and gaseous higher fluorides of transition metals characterised by high value of electron affinity.<sup>2,3</sup> The mechanism of thermal decomposition of fluorinating agents is not well understood yet, although some hypotheses have been made.<sup>4</sup> The aim of this study is to follow the transformations taking place in the solid phase during thermal decomposition of a widely used fluorinating agent: cobalt trifluoride.

In a recent paper,<sup>5</sup> we reported a method we used to follow in real time the thermal decomposition of  $\text{MnF}_3$ . It consisted of placing a powdered sample inside a Ni capillary submitted to a temperature ramp. During heating, a sequence of diffraction patterns had been collected in order to observe the in situ evolution of the initial  $\text{MnF}_3$  compound.

This method, although successful, exhibited some drawbacks. First, the 100  $\mu$  thick Ni capillary walls are quite opaque to X-ray radiation of usual diffractometric energies and even the 24 keV X-ray beam we used was intensely absorbed, so that a low diffraction signal only could reach the detector. Furthermore, the higher energy harmonics present in the primary beam (having a greater penetrating ability than the fundamental) produced spurious peaks that complicated the data processing and refinement. Secondly, the shifting detector of the type generally used for time-resolved X-ray measurements,<sup>6</sup> allowed the collection of just a thin strip of the Debye-Scherrer rings, so that the statistical accuracy was low.

In the present letter we show how, by improving the experimental setup, even weak diffraction peaks of an intermediate compound appearing during the thermal decomposition from  $\text{CoF}_3$  to  $\text{CoF}_2$  could be detected.

To overcome the major problem coming from the X-ray absorption, the very-high-energy (89 keV) X-ray beam available at the ID15B beamline of the European Synchrotron Radiation Facility (Grenoble, France) was used. In this condition, the capillary walls become almost completely transparent and no remarkable intensity loss is suffered.

The shifting detector was replaced with a read-out image plate (model MAR 345) that allows a complete collection of the

Debye-Scherrer rings. In fact, in this case, the sequential acquisition of the diffraction patterns was performed. The radial integration of the entire rings provided high statistical accuracy diffractograms.<sup>7</sup>

Also the problem arising from the appearance of ghost peaks due to the higher harmonics was completely solved. Indeed, the intensity of the synchrotron beam at the energy of the harmonics (two or three times 89 keV) is very low and, furthermore, the efficiency of the detector falls rapidly down at energies higher than 120 keV.<sup>8</sup>

A  $\text{CoF}_3$  sample, purchased from Aldrich Chemical Co. (98% nominal purity, although a small amount of  $\text{CoF}_2$  impurity was found), was utilised for the measurements. Since cobalt trifluoride is hygroscopic, it was loaded inside the Ni capillary used as sample holder, in an Ar atmosphere dry box. The capillary has been preliminary passivated by  $\text{F}_2$  at high temperature (723 K) in order to prevent interactions between Ni and the trifluoride sample. The  $\text{NiF}_2$  layer formed on the surface of the capillary after passivation is rather inert in respect to trifluorides and too thin to produce visible Bragg peaks in the diffraction patterns.

After loading, the capillary was heated at a rate of 2 K per min by a hot air blower. Each experimental run lasted about 9 h. A sequence of diffraction patterns was collected upon heating by irradiating the capillary with 10 s long X-ray "flashes". A schematic view of the experimental set up is shown in Figure 1. Since the image storing and the detector reset took about 60 s, the structural evolution of the compound inside the capillary could be followed with a 70 s time sampling.

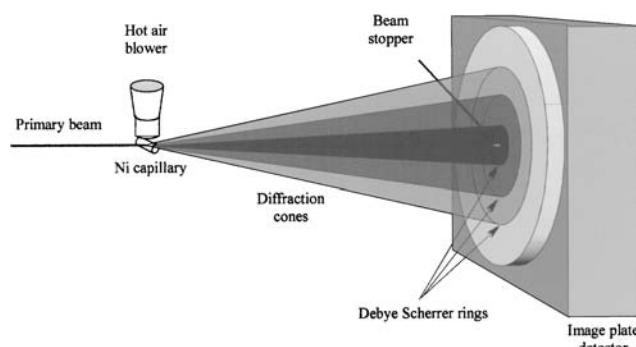
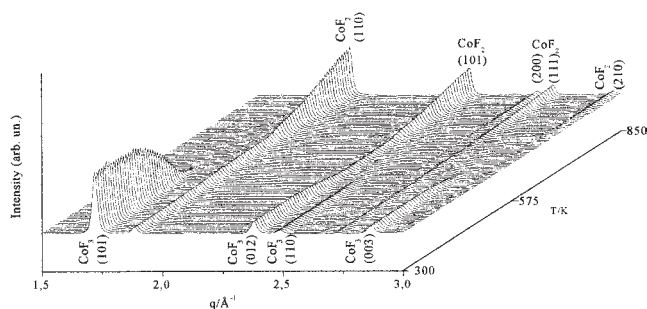


Figure 1. Sketch of the experimental set-up.

The results of the measurements are summarized on the maps of diffraction patterns in Figure 2 and 3, which show the pattern sequence in the  $(1-3) \text{ \AA}^{-1}$  reciprocal space range. The first pattern in both the Figures represents the initial structure of  $\text{CoF}_3$ .<sup>9</sup>

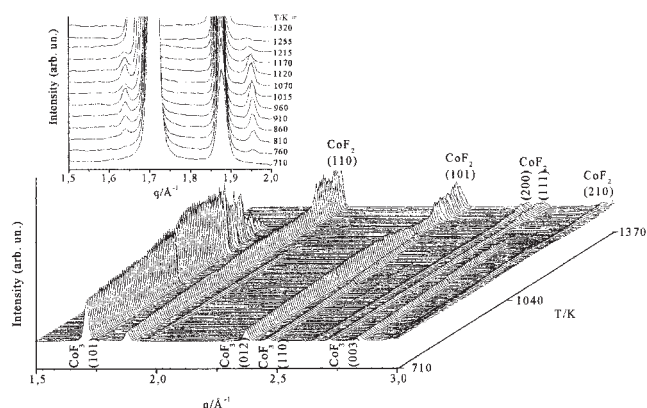
Figure 2 describes the thermal decomposition observed when



**Figure 2.** Sequence of the diffraction patterns acquired upon thermal decomposition of  $\text{CoF}_3$ , submitting the sample to an Ar flux during heating.

a small Ar gas flux ( $3.5 \text{ cm}^3/\text{min}$ ) is kept inside the capillary during heating. In this case, the transition occurs directly from  $\text{CoF}_3$  to  $\text{CoF}_2$  (namely, without any intermediate phase) and, starting from a certain temperature, the Bragg peaks of  $\text{CoF}_3$  progressively disappear and new peaks belonging to  $\text{CoF}_2$  replace them. For instance, the intensity of the  $\text{CoF}_3$  [101] reflection begins to decrease at about 600 K while, simultaneously, the [110] reflection of  $\text{CoF}_2$  appears.

The map on Figure 3, instead, shows the diffraction patterns sequence collected upon decomposition in the case when no Ar flux passes through the capillary during heating. In this condition, a more complex process takes place in the 760–1250 K



**Figure 3.** Sequence analogous to that in Figure 2, but collected with no Ar flux. Due to the instability of the X-ray beam, some variations in the height of peaks at the end of the acquisition can be noticed. In the insert, the  $(1.5, 2.0) \text{ \AA}^{-1}$ –(710–1320) K region is shown in detail.

temperature interval, where extraneous peaks not belonging either to  $\text{CoF}_3$  or to  $\text{CoF}_2$  can be observed at  $q = 1.64 \text{ \AA}^{-1}$  and  $1.95 \text{ \AA}^{-1}$  (see the box, where the  $q = 1.5\text{--}2.0 \text{ \AA}^{-1}$  range is magnified). Those extraneous peaks are the fingerprint of an intermediate short-living phase like that already observed in analogous conditions during thermal decomposition from  $\text{MnF}_3$  to  $\text{MnF}_2$ .<sup>5</sup>

The difference between the sequences in Figures 2 and 3 is that, in the former case, the fluorine released during the decomposition is removed from the reaction zone by the Ar flux, so that the reaction is faster and no intermediate can be observed.

In conclusion, by analogy with the  $\text{Mn}_2\text{F}_5$  phase<sup>5</sup> formed upon  $\text{MnF}_3$  thermal decomposition, we can affirm that this compound is likely  $\text{Co}_2\text{F}_5$ , whose existence was never reported before, and that the method we proposed is suitable for detailed studies of decomposition kinetics.

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