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SYNTHESIS, CHARACTERIZATION AND CRYSTALLIZATION OF THE AMORPHOUS
IRON(III) FLUORIDE : $\text{FeF}_3 \cdot x\text{HF}$ ($0.4 < x < 1$)

M. Leblanc, G. Ferey, J.M. Greneche*, A. Le Bail, F. Varret*,
R. de Pape and J. Pannetier**

*Laboratoire des Fluorures, UA 449, Faculté des Sciences,
72017 Le Mans Cedex, France*

**Laboratoire Mössbauer, UA 807, Faculté des Sciences,
72017 Le Mans Cedex, France*

***Institut Laue Langevin, 156X, 38042 Grenoble Cedex, France*

Résumé - Un nouveau fluorure amorphe $\text{FeF}_3 \cdot x\text{HF}$ ($0.4 < x < 1$), obtenu par réaction de HF gazeux sur FeCl_3 à 80-100°C pendant 20 h, est mis en évidence. La perte de HF, qui intervient au dessus de 100°C, et la cristallisation en Rh- FeF_3 vers 250-300°C, ont été suivies par ATG, ATD, diffraction de neutrons et spectroscopie Mossbauer. Un essai de modélisation de l'amorphe $\text{FeF}_3 \cdot x\text{HF}$ est proposé à partir du spectre de rayons X à 20°C. Il conduit à un arrangement, en doubles feuillettes de type ReO_3 , d'octaèdres FeF_6 déformés qui s'accorde bien avec la cristallisation de $\text{FeF}_3 \cdot x\text{HF}$ en Rh- FeF_3 .

Abstract - A new amorphous fluoride $\text{FeF}_3 \cdot x\text{HF}$ ($0.4 < x < 1$), obtained from the reaction of gaseous HF with FeCl_3 at 80-100°C during 20 h, is evidenced. The HF loss, above 100°C, and the crystallization to Rh- FeF_3 were characterized by DTA, TGA, neutron diffraction and Mossbauer spectroscopy. An attempt to modelize the structure is proposed. The model, built from double ReO_3 type layers of FeF_6 octahedra, is in good agreement with the crystallisation of $\text{FeF}_3 \cdot x\text{HF}$ to Rh- FeF_3 .

I - INTRODUCTION

Several amorphous iron fluorides are known : FeF_2 /1/, FeF_3 /2/, NaFeF_4 and KFeF_4 /3/. All of them are prepared from high-temperature vapor deposition on a cold substrate. No attempt was made to use chemical reactions at very low temperature, leading sometimes to poorly crystallized or amorphous materials.

We report here the synthesis, the characterization and the crystallization of a new amorphous iron(III) fluoride: $\text{FeF}_3 \cdot x\text{HF}$ ($0.4 < x < 1$), obtained from a " soft chemistry " reaction.

II - SYNTHESIS, CHEMICAL AND THERMAL ANALYSES

A gaseous HF flow is passed in a monel tube over crystalline FeCl_3 , held in a gold boat. The reaction is achieved after 20 hours at 80-100°C and 10-15g of a beige powder can be obtained at one time. Care must be taken to avoid the presence of moisture. The HF content of the material slightly differs from one experiment to another; several results of chemical analyses are reported in Table 1. Then, the chemical composition can be preferably expressed as $\text{FeF}_3 \cdot x\text{HF}$ ($0.4 < x < 1$). No trace of iron(II) is evidenced, by contrast with the vapor deposits of amorphous iron fluorides precedently described /2,3/. The TGA and DTA curves appear in Fig. 1. The weight loss of sample 1 is approximately 12.3% between the room-temperature and 467°C; the estimate $x \approx 0.8$ can be given. The theoretical weight loss corresponding to one HF per FeF_3 molecule is 15.0%.

Table I - Chemical analyses (weight %) of $\text{FeF}_3 \cdot x\text{HF}$.

	Sample 1	$\text{FeF}_3 \cdot \text{HF}$	Sample 2	$\text{FeF}_3 \cdot 0.4\text{HF}$
Fe	42.2(1.4)	42.04	46.1(1.5)	46.21
F	56.7(2.3)	57.20	52.9(2.1)	53.45

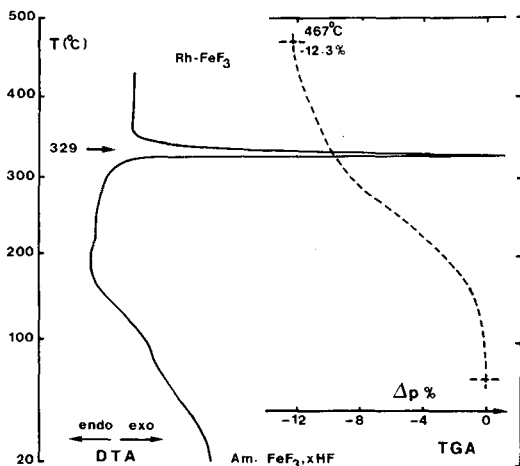


Fig. 1 - Thermal analysis of FeF_3, xHF (heating rate: $300^\circ C/h$, N_2 , $P=1$ Atm, Du Pont 9900).

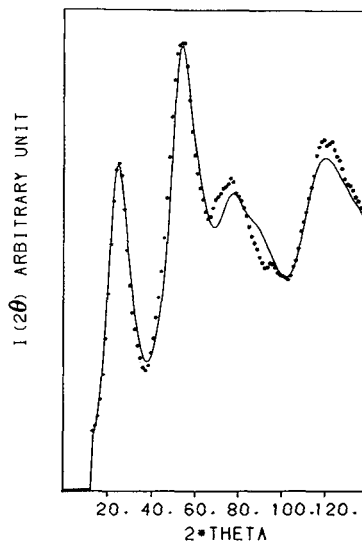


Fig. 2 - Observed (dots) and calculated (line) reduced interference functions of FeF_3, xHF ($Cu K\alpha$, $293K$).

III - X-RAY, NEUTRON AND MOSSBAUER CHARACTERIZATION.

The X-ray (λ $CuK\alpha$) (Fig. 2) and neutron ($\lambda=2.518$ A) diffraction spectra of FeF_3, xHF , at room-temperature clearly evidence the amorphous state of the material: only diffuse scattering is observed.

At room-temperature, the Mossbauer spectrum consists of a doublet with broad lines (Fig. 3). The data are fitted with a distribution of Lorentzian quadrupolar doublets centered around the mean value $IS=0.48$ $mm.s^{-1}$ *. The quadrupolar splitting distribution is given at Fig. 3b. At low temperature, the freezing of the spins extends over 10 degrees around 36 K. These two points corroborate the existence of an amorphous phase; the isomer shift is consistent with a six-fold coordination of Fe^{3+} . It must be noted that all the hyperfine Mossbauer data of FeF_3, xHF are close to those of the amorphous vapor deposited $FeF_3 / 2,4/$.

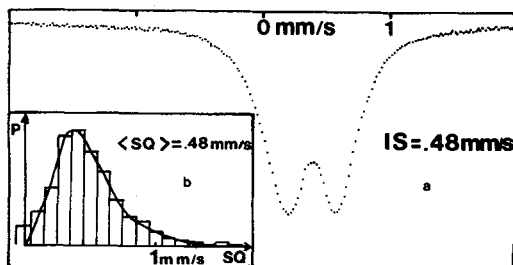


Fig. 3-a- Mossbauer spectrum of FeF_3, xHF at 295 K, -b- distribution of the quadrupolar splitting.

* Relative to metallic Fe at room-temperature

IV - CRYSTALLIZATION

The heating of the amorphous $\text{FeF}_3 \cdot x\text{HF}$ leads to the formation of the crystalline Rh-FeF_3 /5,6/. The crystallization was followed by TGA, DTA (Fig. 1), neutron diffraction (Fig. 4) and Mossbauer spectroscopy (Fig. 5).

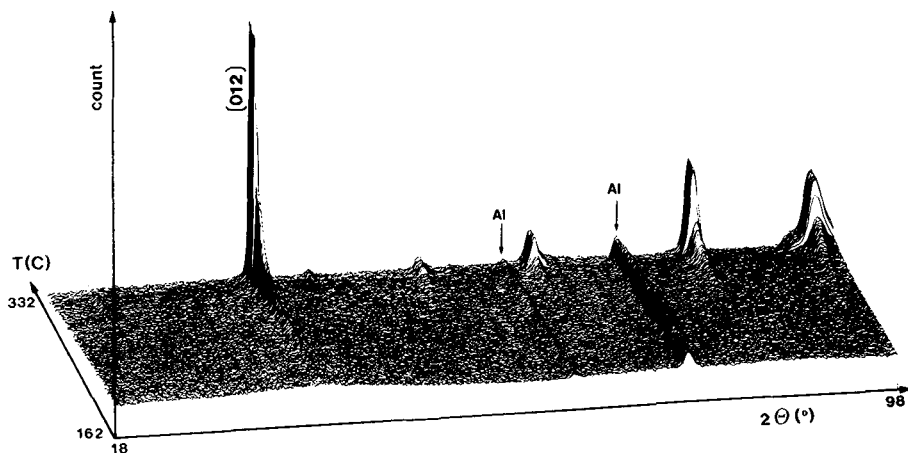


Fig. 4 - Temperature evolution of the transformation $\text{Am. FeF}_3 \cdot x\text{HF} \Rightarrow \text{Rh-FeF}_3$ under vacuum ($\lambda=2.518 \text{ \AA}$, $\Delta t=6\text{mn}$, $\Delta T=1^\circ\text{C}$, D1B (ILL Grenoble)).

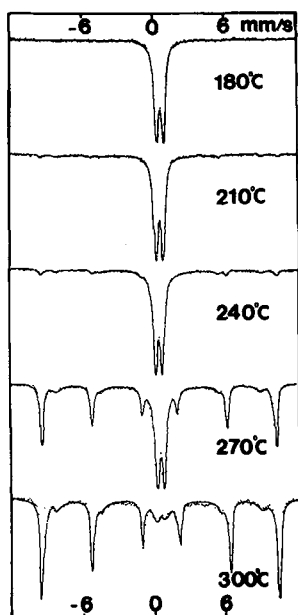


Fig. 5 - Mossbauer spectra obtained at 77 K after annealing $\text{FeF}_3 \cdot x\text{HF}$ at the mentioned temperatures during 6 hours under vacuum.

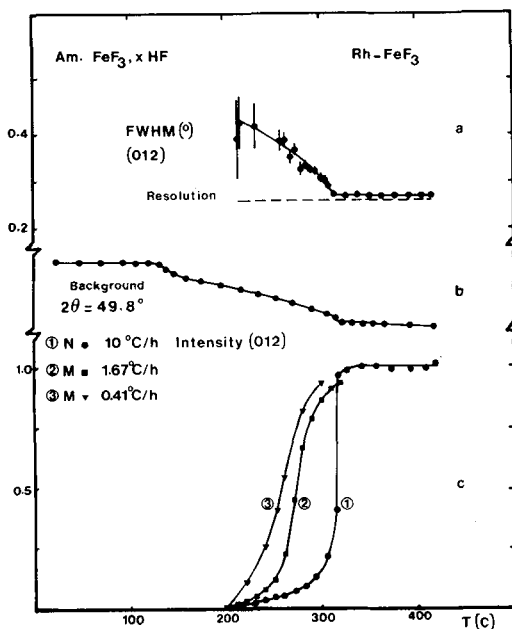


Fig. 6 - Background (b), intensity (c) and linewidth (a) of the (012) reflection in Fig. 4 (neutron spectra: N); Rh-FeF_3 rate from Mossbauer experiments (M).

The variations of the rate of crystalline Rh-FeF₃ are obtained :

- from the intensity, scaled to 1.00 at T>320°C, of the more intense (012) line of Rh-FeF₃ (hexagonal cell of R3c) in the neutron spectra;
- from the analysis of the Mossbauer spectra (Fig. 5) of samples quenched at 77 K after annealing at increasing temperatures during constant time intervals.

It is concluded that :

- the loss of HF, revealed by TGA or DTA (Fig. 1) and background variation of the neutron spectra (Fig. 6b), is endothermic and occurs above 100°C. TGA shows that the HF loss is not still complete after crystallization (Fig. 1);
- the crystallization of Rh-FeF₃ is exothermic (estimated to 10 kcal.mole⁻¹);
- both effects take place over large overlapping temperature ranges, depending on the experimental conditions. The temperature, corresponding to the maximum rate of Rh-FeF₃ formation, decreases with the heating rate: 316°C at 10°C/h, 270°C at 1.67°C/h (curves 1 and 2 respectively in Fig. 6c).

V - MODELLING

An attempt to modelize the structure of this new amorphous compound FeF₃.xHF is described, using the quasi-crystalline method proposed in section A19 of this conference /7/.

The structural types commonly encountered for MF₃ or AMF₃ compounds (A= alkaline, M= transition metal) were tested : hexagonal tungsten bronze /8/, Rh-FeF₃ /6/, TlAlF₄ /9/ or KFeF₄ /10/ and pyrochlore /11/ types. After refinement of positional and cell parameters, only one model, deriving from the ReO₃ type, gives satisfactory results between calculated and observed interference functions (Fig. 2) (SG: P-1, R = 0.054 = (Σ(Iobs-Ical)²/ΣIobs²)^{1/2}). The final atomic positions and pseudo-cell dimensions are given in Table II (hydrogen atoms were not located). A projection of the model along b appears at Fig. 7.

Of course, this model has to be understood as the best mean local atomic arrangement able to reproduce the X-ray interference function and its Fourier transform. The simulated and experimental reduced atomic distribution functions are compared (Fig. 8) and the agreement factor is R = 0.174 = (Σ(Gobs-Gcal)²/ΣGobs²)^{1/2}.

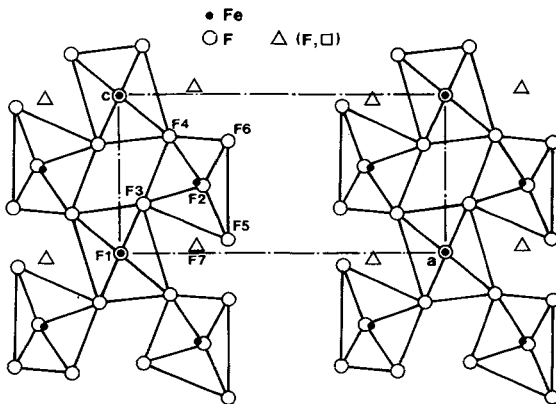


Fig. 7 - Representation of the model of the amorphous FeF₃.xHF

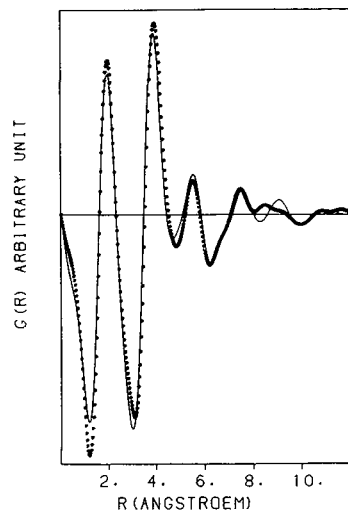


Fig. 8 - Observed (dots) and calculated (line) reduced atomic distribution functions G(r) of FeF₃.xHF (Cu Kα, 293 K).

Table II - Structural parameters of $\text{FeF}_3 \cdot x\text{HF}$ in the quasi-crystalline method
(e. s. d. in parentheses)

Cell dimensions: $a = 10.84(2)\text{Å}$ $b = 3.730(4)\text{Å}$ $c = 5.350(7)\text{Å}$
 $\alpha = 90.0(1)$ $\beta = 90.0(1)$ $\gamma = 85.0(1)$

Atomic positions:				x	y	z	
	x	y	z				
				F3	0.073(23)	0.083(90)	0.312(58)
Fe1	0	0	0	F4	0.153(27)	0.084(90)	0.741(27)
Fe2	0.238(14)	0.078(11)	0.448(27)	F5	0.333(23)	0.219(75)	0.088(77)
F1	0	0.5	0	F6	0.329(29)	0.227(76)	0.710(21)
F2	0.256(44)	0.570(66)	0.436(77)	(F7,□)	0.237(31)	0.600(69)	0.039(63)

Mean distances: $\langle \text{Fe1-F} \rangle = 1.986\text{Å}$ $\langle \text{Fe2-F} \rangle = 1.932\text{Å}$ $\langle \text{Fe-F} \rangle = 1.95\text{Å}$

VI - CONCLUSION

This new amorphous $\text{FeF}_3 \cdot x\text{HF}$, synthesized by "soft chemistry" reaction, crystallizes to Rh-FeF_3 : it differs from the previously described amorphous vapor deposited FeF_3 , crystallizing mainly to HTB-FeF_3 .

A modelization of $\text{FeF}_3 \cdot x\text{HF}$ is proposed, using a quasi-crystalline method. The model consists of separated double layers Fe_3F_{11} : it is figured out that the loss of HF molecules (corresponding to F5 or F6) allows to link the layers, in order to build the framework of corner-sharing octahedra in Rh-FeF_3 .

So, it is of interest to correlate the above structural results with the mechanism of formation and growth of Rh-FeF_3 particles. From this viewpoint, a kinetic study is undertaken by Mossbauer spectroscopy and neutron diffraction. A line profile analysis, suggested by the linewidth variations (Fig. 6a) in the neutron spectra, will be performed.

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