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**Abstract.** Nanostructured fluoride powders were prepared by the high-energy ball milling route. A combination of suitable techniques with complementary spatial scales was used for the first time to investigate both structural and microstructural properties: x-ray diffractometry, magnetic measurements and local probes such as $^{57}$Fe Mössbauer spectrometry and $^{19}$F, $^{69}$Ga and $^{71}$Ga NMR. The set of data allows us to describe these nanostructured powders on the basis of nanocrystalline grains and grain boundaries. The relevant hyperfine data support then modelling of the microstructure in terms of pseudo-cubic and random packing of corner sharing octahedral units corresponding to nanocrystalline grains ($\sim$15 nm diameter) and disordered grain boundaries (a few nanometres thick), respectively. Their different cationic topologies are consistent with the antiferromagnetic and speromagnetic behaviours, respectively, as evidenced by in-field Mössbauer spectrometry. They also support the temperature dependence of the magnetic properties which reveal a progressive magnetic decoupling of grains when the temperature increases, originating a superparamagnetic behaviour above a blocking temperature which is dependent on the thickness of the grain boundaries, i.e. the milling conditions.

(Some figures in this article are in colour only in the electronic version; see `www.iop.org`)

## 1. Introduction

During the last ten years, numerous studies have been devoted to nanostructured powders prepared by the high energy ball milling route. The growing interest is essentially due to their unusual and unexpected physical properties, which are strongly influenced by the confinement of microcrystalline into nanocrystalline structural domains, giving rise to an increasing contribution of grain boundaries [1]. Due to their high mixing efficiency at the atomic scale, mechanical alloying and mechanical milling techniques were widely applied to metallic and oxide systems. Interest was essentially devoted to ferromagnetic and ferrimagnetic nanostructured powders because of their promising technological applications deriving from mechanical and magnetic properties [2]. Nevertheless, very few studies were devoted to antiferromagnetic systems owing to their weak magnetization. Indeed in the case of nanometre size particles, it only originates from defects and non-compensated magnetic sublattices at the surface.

The main relevant questions which are currently open concern the estimate of the atomic proportion and the thickness of grain boundaries in nanostructured powders, as well as their dependence on both the milling time and the milling power. In addition their influences on the dynamic magnetic properties have to be modelled in the case of magnetic nanostructured powders.

Thus we have selected some ionic fluorides to reply to such questions. Indeed, previous studies have revealed the fundamental interest of ferric fluorides $FeF_3$ which exhibit three polymorphic crystalline phases and several amorphous varieties [3]. Indeed, most of these phases display original non-collinear magnetic arrangements resulting from the presence of triangular cationic platelets and antiferromagnetic interactions [3, 4]: the more stable crystalline rhombohedral r–$FeF_3$ phase is antiferromagnetically ordered below $T_N = 363$ K while the amorphous varieties display as speromagnets below $T_F \sim 30$–40 K [5, 6]. They behave thus as 'excellent model systems' for illustrating the topological magnetic frustration.

The present study deals with a better understanding of the physical properties of nanostructured fluoride powders and the structural nature of the grain boundaries and its role in transmitting magnetic interactions. A first simple picture can be established on the basis of some experimental features. It consists in an assembly of nanocrystalline grains which exhibit the $R\bar{3}c$ structure characteristic of the initial r–$FeF_3$ phase, welded each other by grain boundaries made of a random like packing of corner sharing octahedral units. Furthermore the simultaneous analysis of x-ray pattern using a two-phase model combined with that of Mössbauer spectra using a three-phase model allows a quantitative microstructural description of milled ferric fluoride powders to be proposed, that is well supported by Raman and NMR results. The experimental conditions and the fitting procedures will be detailed elsewhere [7, 8].

The present paper briefly reports on x-ray diffraction, $^{57}$Fe Mössbauer spectra and static magnetic results obtained on some ferric fluoride nanostructured powders milled under controlled atmosphere. In addition it clearly demonstrates that the combined analysis of different kinds of datum provides relevant and accurate information on both grains and grain boundaries and that the proposed description can be extended to other nanostructured powders. Such a consistent set of data and modelling approach of nanostructured powders have not yet been reported in the literature, to our knowledge.

## 2. Experimental section

Mechanically milled powders of $MF_3$ (M=Fe, Ga) were prepared from the rhombohedral crystalline phase of $MF_3$ using a commercial Fritsch Pulverisette 7 planetary ball-mill under an argon atmosphere. The present study concerns Fe and Ga containing powders milled for 20 h at power intensity $I = 10$ and 16 h at $I = 6$. Four zircon balls were used in each zircon vial with a powder-to-ball weight ratio of 1/30. Great attention has been paid to prevent any moisture from the powders during the different stages, owing to the high hygroscopic behaviour of fluorides and the high surface reactivity of final powders. X-ray patterns were obtained using a Phillips X'pert diffractometer (with monochromatized Cu K$\alpha$ radiation; $\lambda = 1.540\,56$ Å) using a special sample chamber under controlled atmosphere. Zero-field and in-field $^{57}$Fe Mössbauer spectra were recorded using a conventional transmission spectrometry, at different temperatures cooling the sample in a bath cryostat or a cryomagnetic device where the external field is oriented parallel to the $\gamma$-beam. The sample consists of 5 mg Fe cm$^{-2}$ milled $FeF_3$ powder mixed with dry $AlF_3$ to optimize the counting rate and to prevent hydrolysis.

## 3. Mechanical milling applied to crystalline fluorides

Before a detailed description of the microstructural model hereafter, it remains first important to emphasize some basic features which concern the mechanical process. Three different scenarios can be *a priori* expected: (1) a complete amorphization giving rise to amorphous

microparticles and nanoparticles, (2) only successive fragmentation of initial microcrystalline powder leading to a broad distribution of particle size ranging from nanometre to micrometre scale and (3) an iterative process consisting of successive fragmentation and welding, resulting in microcrystalline aggregates composed of nanocrystalline grains separated from each other by grain boundaries, so called nanostructured powders.

The structural and magnetic properties of amorphous powders, as prepared according to the mechanism assumed in the first situation, might be compared to those of previous amorphous phases [6]. The x-ray diffraction pattern, Mössbauer and NMR spectra give clear evidence of a crystalline phase, excluding the presence of pure amorphous particles. It is important to emphasize that the occurrence of a significant content of oxide and hydroxide for milling times of 100 hours prevents a complete amorphization process. In the second case, the particles can be described as a crystalline bulk and a disordered periphery by analogy to several kinds of particle prepared by the sol–gel method [9]. Consequently their average size is expected to be strongly dependent on the milling time and the increase of the surface contribution is expected to favour high chemical reactivity, with the occurrence of chemical and structural inhomogeneities and the presence of other surface ligands as O, OH. Nevertheless it is important to emphasize that the present experimental conditions (ball milling in dried atmosphere) do not favour the synthesis of only nanoparticles. The third scenario would lead to a low surface contribution but an extremely high grain boundary contribution in addition to a rather low crystalline contribution.

Owing to the hygroscopic behaviour of the present fluoride powders, no direct measurements of the particle size in liquid solution have been yet successively performed. In addition, the instability of fluorine containing material under an electron beam makes transmission electron microscopy inefficient to observe directly the grain and particle sizes of these nanostructured fluoride powders.

In other respects, a previous study of the recoilless factor temperature dependence from the absorption of transmission Mössbauer spectra revealed the presence of a small quantity of isolated ultra-fine particle or weakly welded ultra-fine grains [7, 10]. In addition, the values of the isomer shift characteristic of the different Mössbauer components are consistent with high-spin state $Fe^{3+}$ ions located in octahedral $FeF_6$ units, and are similar to those encountered in the usual crystalline and amorphous ferric fluorides. Besides, $^{19}F$, $^{69}Ga$ and $^{71}Ga$ NMR were performed using different acquisition procedures on milled powders of $GaF_3$, isostructural with $FeF_3$: the relevant values of chemical shift are consistent with the presence of corner-sharing $GaF_6$ octahedral units [11]. Consequently, such features would favour the dominant contribution of nanostructured grains, as suggested by scenario (3) previously described.

## 4. Structural modelling of nanostructured fluoride powders

Independent fitting procedures were developed to analyse x-ray patterns, $^{57}Fe$ Mössbauer spectra versus temperature and $^{19}F$, $^{69}Ga$ and $^{71}Ga$ NMR spectra recorded on either Fe or Ga fluoride powders milled for different times. The successive results were then compared each other taking the sensitivity of the corresponding technique into account. The final refinements were into two main components due to crystalline grains and to disordered grain boundaries.

The structural and microstructural parameters were refined from the x-ray pattern using the RIETQUAN procedure which is based on the Rietveld method combined with Fourier analysis, well adapted for broadened diffraction peaks [12]. The present patterns are well reproduced using a nanocrystalline phase and a pseudo-amorphous phase where the long-range order is lost, attributed to the grain boundaries. Finally the refinement allows the crystallite size ($\langle d \rangle$)

**Table 1.** Structural and microstructural characteristics of some nanostructured fluoride powders obtained after milling under different conditions, as given in column 2. Corresponding atomic proportions of grains (G) and grain boundaries (GB) are given in columns 3 and 4 respectively while $\langle d \rangle$ and $\langle e \rangle$ are the mean diameter of crystalline grains and the mean thickness of grain boundaries.

| Sample | Milling conditions | At. % G | At. % GB | $\langle d \rangle$ (nm) | $\langle e \rangle$ (nm) | Investigation technique |
|--------|--------|------|------|------|------|--------|
| $FeF_3$ | 20 h; $I = 10$ | 57 | 43 | 16 | 3–4 | XRD |
|  |  | 58 | 42 |  |  | 0-field MS |
|  |  | 55 | 45 |  |  | In-field MS |
|  | 16 h; $I = 6$ | 83 | 17 | 16 | 1 | XRD |
|  |  | 85 | 15 |  |  | 0-field MS |
| $GaF_3$ | 20 h; $I = 10$ | 50 | 50 | 15 | 4 | XRD |
|  |  | 30 | 70 |  |  | NMR |
|  | 16 h; $I = 6$ | 21 | 79 | 16 | 1 | XRD |
|  |  | 40 | 60 |  |  | NMR |

and the r.m.s. microstrains to be first estimated. The grain boundary proportion gives an estimate of its thickness $\langle e \rangle$ assuming a spherical core–shell model.

In other respects, both the temperature dependence and the milling time dependence of the hyperfine structures were first examined. Then the Mössbauer spectra were decomposed into a sharp sextet attributed to crystalline grains and a broad magnetic component which progressively collapses into a large unresolved quadrupolar doublet, assigned to disordered grain boundaries. Only the proportions are listed in table 1 while the fitting procedure and the hyperfine characteristics will be detailed in a regular paper which is in progress [8]. Experimental conditions and fitting procedure of both $^{19}$F and $^{69;71}$Ga NMR spectra applied to gallium nanofluoride powders were recently reported in [11].
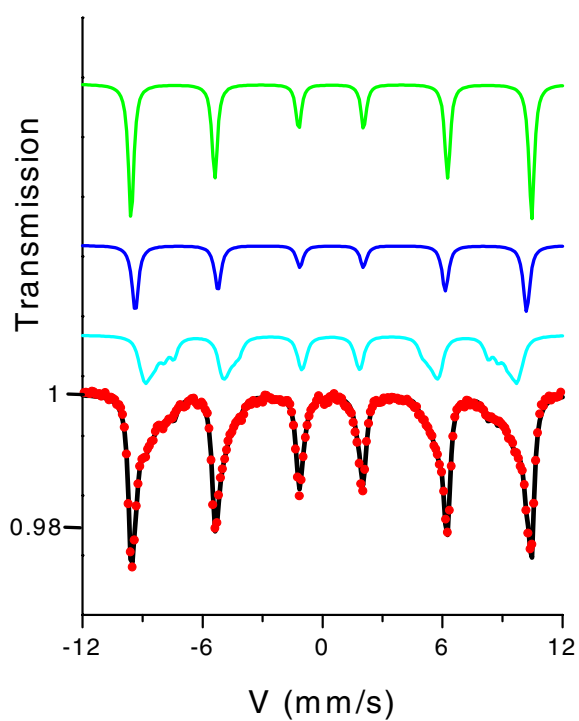
Typical x-ray pattern, $^{57}$Fe Mössbauer and $^{69}$Ga NMR spectra are presented in figure 1 and their decomposition as well. Table 1 lists the main structural characteristics in the case of fluoride powders milled for 16 h and 20 h at intensity 6 and 10, respectively. One observes a nice agreement of both the contents of crystalline grain and grain boundary estimated by x-ray diffraction and Mössbauer spectrometry in the case of $FeF_3$ while that estimated by x-ray diffraction in the case of $GaF_3$ significantly differs from that of NMR. Indeed the different short-range quadrupolar interactions can be clearly described by means of two distributions of quadrupolar parameter based on random packing of hard spheres as early proposed by Czjzek *et al* [13]: a narrow one attributed to crystalline grains and a broad one to grain boundaries, associated with low and high distorted Ga octahedral units, respectively [11]. So, because of their distortions, the octahedral units which structurally belong to the crystalline grains but located at the vicinity of the grain boundaries, are wrongly included in the grain boundaries, that consequently modify their respective contents.

It is noteworthy to mention that the milling power does not influence the average size of the grains in contrast to the average thickness of grain boundaries: the higher is the power, the thicker are the grain boundaries. No data concern directly the distribution of sizes and the morphology of grains but one concludes that the morphology of grains is far from spherical at least for low power intensity.

In addition to a quantitative description in terms of the two phase model, the in-field Mössbauer spectrum applied to $FeF_3$ milled for 20 h at intensity 10 reveals the presence of two magnetic components as illustrated in figure 2: (i) a sextet with sharp lines whose intensities
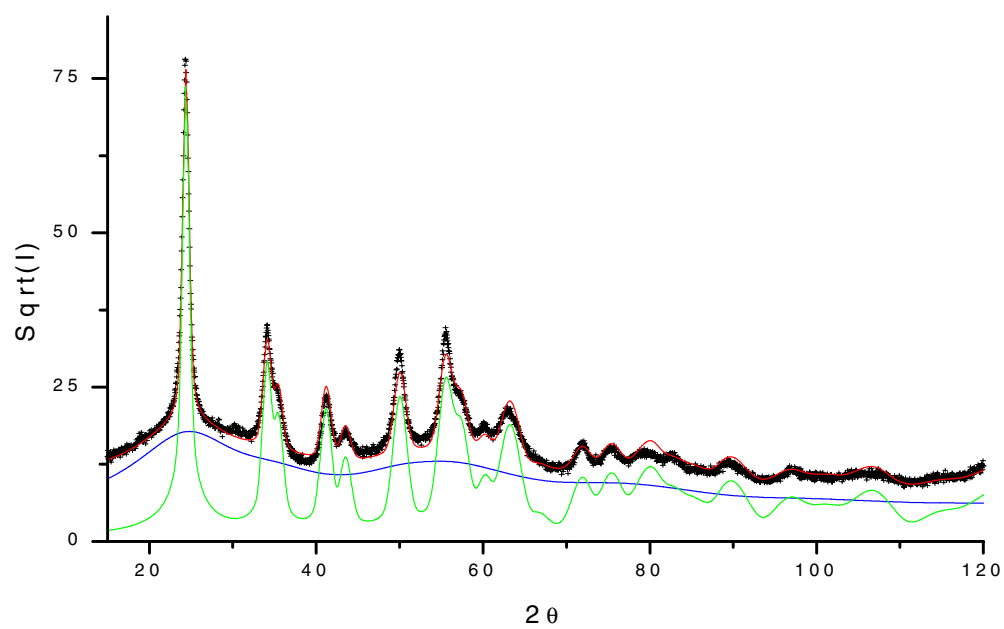
**Figure 1.** Typical x-ray pattern (a), [57]Fe Mössbauer spectrum (b) and [69]Ga RMN spectrum (c) and their decomposition into two components attributed to crystalline grains and grain boundaries (see text). Note the third component (middle one) for the Mössbauer spectrum that corresponds to the layer located at the periphery of the crystalline grain, in close contact with the grain boundary (see text).
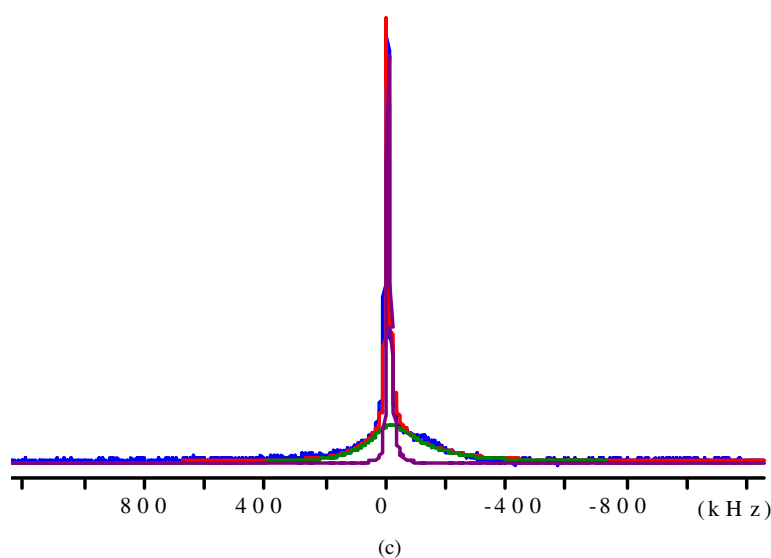
(c)

**Figure 1.** (Continued)

are close to 3:4:1:1:4:3, typical of the antiferromagnetic arrangement of r–FeF$_3$ and (ii) a broad line component well described assuming a random distribution of iron hyperfine field directions as a speromagnetic model. It suggests that the grain boundaries behave as a highly frustrated behaviour originated from the cationic topology, by analogy to the amorphous phases [5, 6].

These different experimental features allow a structural modelling of nanostructured fluoride powders to be established. As shown in figure 3, the schematic 2D representation illustrates the ordered and disordered packing of corner-sharing octahedral units of nanocrystalline grains and grain boundaries, respectively. From a structural point of view, one expects that the grain boundaries originate some microstresses within the crystalline grains, as observed from the analysis of the x-ray pattern.

The connectivity of the octahedral units suggests that the values of both isomer shift and chemical shift have to be similar for the two components and to those observed in crystalline and amorphous varieties. In addition, the cationic topology has to favour a progressive reduction of the hyperfine field from the bulk of the grains towards the grain boundary through the presence of superexchange frustrated antiferromagnetic interactions. Such a reduction is consistent with the distribution observed at low temperatures by Mössbauer spectrometry. Furthermore, it justifies the third magnetic component which might be attributed to an intermediate octahedral layer located at the periphery of the crystalline grains, as illustrated in figure 1(b).

In other respects, Raman spectroscopy gives clear evidence for a progressive vanishing of the R$_5$ vibration octahedral tilt mode when the milling time increases. The disappearance of this specific mode is consistent with the small size of crystalline grains and the cationic topology suggested in the grain boundaries [7, 14].

From a macroscopic point of view, the magnetization of the crystalline grains is expected to be blocked at low temperature because the grain boundaries are also magnetically ordered. When the temperature increases, the cationic topology of the grain boundaries favours a progressive unfreezing of iron magnetic moments at temperatures ranging between 50 and 150 K, in any case much lower than the Néel temperature of the crystalline grains. In addition
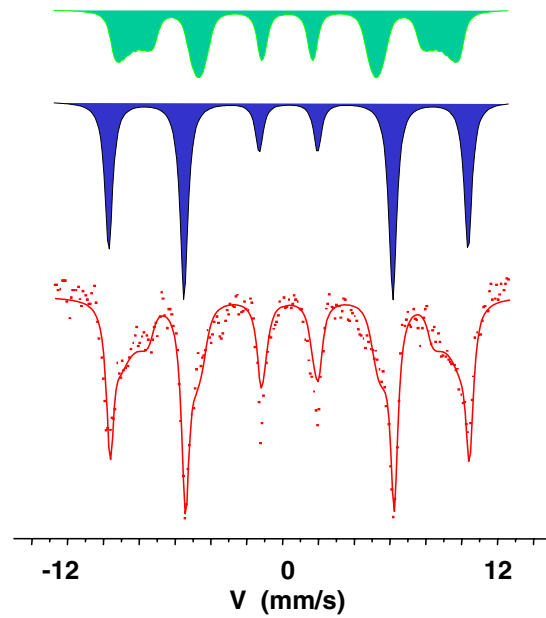
**Figure 2.** In-field Mössbauer spectrum of 20 h $I = 10$ milled fluoride powder recorded at 7 K and 60 kG (applied field parallel to the $\gamma$-beam) and its decomposition: the lower and the upper components correspond to crystalline grains and grain boundaries which display as an antiferromagnet and speromagnet, respectively.
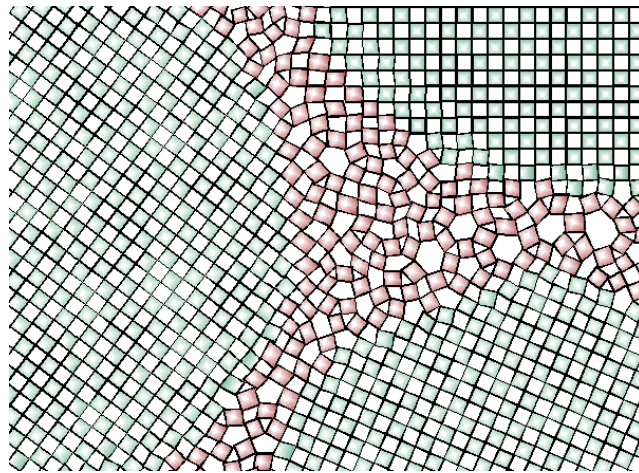


**Figure 3.** Schematic 2D representation of the microstructure of crystalline and grain boundaries in nanostructured fluoride powder.

to the small size of crystalline grains propitious to the onset of thermal fluctuations, thick grain boundaries speed up the magnetic decoupling of grains while narrow grain boundaries favour the magnetic coupling between grains thanks to superexchange interactions together with dipolar interactions. Such predictions are fairly well supported by FC and ZFC magnetic measurements which clearly evidence a mean blocking temperature at around 250 K for the highest milling intensity, i.e. the thickest grain boundaries [7, 15]. It is also important to note

that the temperature dependences of the coercive field agree fairly well with Pfeiffer's relation established in the case of an assembly of non-interacting magnetic particles dominated by thermal fluctuations [16], with superparamagnetic blocking temperatures estimated at 320 and 360 K for powders milled for 20 and 16 h, respectively [7, 15].

## 5. Conclusions

In spite of experimental difficulties, different complementary techniques were successfully applied to some nanostructured fluoride powders obtained by high energy ball-milling. We developed appropriate fitting procedures independently to analyse the different results and the structural and hyperfine parameters were refined after mutual comparison and after consideration of the sensitivity of each technique. Such an analysis allows a consistent set of structural and microstructural parameters to be estimated. These data suggest a modelling approach which consists of nanocrystalline grains welded to each other through grain boundaries, described on the basis of cubic ordered and random packing of corner sharing octahedral units, respectively. The microstructural model supports the experimental magnetic data, including the temperature evolution of magnetization and of coercive field, giving evidence for the role of grain boundaries in coupling the magnetic grains. Both the methods of analysis which were applied to these antiferromagnetic nanostructured systems and the modelling approach have to be extended to ferrimagnetic and ferromagnetic nanostructured systems.

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