

Coupled structural and magnetic properties of ferric fluoride nanostructures: part II, a Monte-Carlo Heisenberg study

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Abstract

We present a numerical study of the magnetic structure of nanostructured iron fluoride, using the Monte-Carlo-Metropolis simulated annealing technique and a classical Heisenberg Hamiltonian with a superexchange angle dependence. The parameters are adjusted on experimental results, and the atomic structure and topology taken from a previous atomistic model of grain boundaries in the same system. We find perfect antiferromagnetic crystalline grains and a disordered magnetic configuration (spromagnetic like) at the grain boundary, in agreement with experimental findings. Both the lowest magnetic energy and the rate of magnetic frustration are found to be dependent on the relative disorientation of crystalline grains, i.e. on the cationic topology. By simulating hysteresis loops, we find that the magnetization rotation is not spatially uniform. We conclude on possible extensions of the model.

Keywords: nanostructuration, iron fluoride, grain boundaries, Metropolis, magnetic frustration, Heisenberg

1. Introduction

During the last decade, strong efforts have been devoted studying the magnetic properties of nanostructures. This growing interest is due to their

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unusual and tunable physical properties, which are strongly influenced by the effect of confinement resulting in a large contribution of surface and interface effects [1]. Understanding the correlation between magnetic properties and nanostructure involves collaborative efforts between chemists, physicists and materials scientists to study both fundamental properties and potential applications [2]. This can be done experimentally using diffraction techniques, local probe techniques such as Mössbauer spectrometry, nuclear magnetic resonance, electron microscopies and magnetic measurements. In addition, one can use numerical modeling techniques based on *ab initio* or phenomenological calculations such as the classical Monte Carlo methods with the Heisenberg model, as in [3, 4, 5, 6] for instance. The key issue for understanding magnetic macroscopic properties, such as magnetization or susceptibility, would be to investigate the contributions arising from the nanograins and the role played by the nanograin surface and the interface between grains generally named grain boundary (GB). GBs in magnetic nanostructures feature a disordered atomic structure and a spin-glass-like behavior and have a chemical composition which might differ strongly from that of the corresponding nanograin [7, 8, 9].

To investigate the magnetic behavior of nanostructures and the mutual influence of the grains and grain boundaries, we selected ferric fluoride (FeF_3), because this ionic phase displays several advantages. Indeed, it exhibits a fascinating polymorphism with three different crystalline phases and two amorphous varieties, the structures of which result from ordered and disordered packing of corner-sharing octahedral units respectively. Those rather different cationic topologies originate collinear and non-collinear magnetic arrangements in conjunction with the antiferromagnetic nature of the superexchange interactions. Iron fluoride is therefore considered as an excellent simple model system to illustrate the concept of topological magnetic frustration. The more stable crystalline form of FeF_3 , which is the rhombohedral phase ($r\text{-}FeF_3$; SG $R\bar{3}C$) is antiferromagnetically ordered below $T_N = 363\text{K}$ while the amorphous varieties display a speromagnetic behavior below T_F 30-40K [10, 11, 12]. The presence of fluorine in those materials establishes superexchange magnetic interactions between magnetic ions. The strength of the coupling is linearly dependent on $\cos^2(\theta)$, where θ denotes the superexchange angle $Fe - F - Fe$ while the sign is given by the orbital configuration of the $FeFFe$ bond: for example, 180° ($Fe^{3+} - F^- - Fe^{3+}$) is characterized by a strong antiferromagnetic coupling according to Kanamori-Goodenough

rules [13, 14].

The magnetic properties of FeF_3 have been intensively studied during the past two decades and can be described in terms of iron ring statistics with induced magnetic frustration [7, 15].

- the rhombohedral phase $r-FeF_3$, which is a pseudo-cubic packing of weakly tilted octahedral FeF_6 units, is not frustrated;
- the hexagonal tungsten bronze HTB- FeF_3 which results from the superposition of magnetically frustrated planes composed of hexagonal and triangular octahedral units cycles ;
- and the pyrochlore pyr- FeF_3 phase which consists of a packing of octahedral units building corner-sharing tetrahedron is thus more frustrated than HTB- FeF_3 .

Recent experimental and theoretical studies on the properties of FeF_3 nanostructures obtained by mechanical milling have shown that, at the nanoscale, this material is composed of two parts: the grain which behaves as the crystalline $r-FeF_3$ phase and a disordered grain boundary which remains composed of corner-sharing octahedral units [16, 17]. In terms of ring statistics, it has been numerically established that all odd rings are localized in the grain boundary of nanostructures, confirming the speromagnetic structure evidenced from in-field Mössbauer spectrometry. The Monte Carlo-Metropolis method has been successfully applied to study the surface and finite-size effects in nanostructures [18, 19, 20]. Nevertheless, no theoretical studies on the magnetic properties of ionic nanostructures which focus on the role of grain boundary by Monte Carlo simulation have yet been reported, to our knowledge. Unlike micromagnetic or molecular field calculations, the Monte Carlo simulation can take into account the atomic structure of the lattice and the nature of superexchange interactions for ionic materials such as FeF_3 .

The Monte Carlo-Metropolis simulated annealing technique is an effective approach in the study of a system with many degrees of freedom. During such a simulation, random numbers are used to sample conformations of the system with correct thermodynamical probabilities. A typical Monte Carlo simulation consists of two steps: thermalization and sampling. During thermalization, the system is led adiabatically to its thermodynamical

equilibrium. After the system reaches this equilibrium, properties of interest can be estimated by averaging over enough samples [21, 22]. Besides, in the simulated annealing method, it is possible to find heuristically the lowest energy state of the system.

We used, in this work, the standard Metropolis algorithm to simulate the magnetic behavior of iron fluoride nanostructure with an emphasis on the role of grain boundaries.

2. Magnetic model

Our sample model is chosen as a double grain boundary constrained in between grains which consists of pure perfectly crystalline FeF_3 with a size ranging from 8 to 12 nanometers as experimentally measured in iron fluoride prepared by high energy ball milling. Those samples are obtained by Voronoï tessellation and structurally relaxed with a scheme based on a modified Metropolis algorithm [17]. It has been shown both experimentally and numerically in such a system that the grain boundaries are disordered, but still remain composed of corner-sharing octahedral units with odd and even iron rings, thus leading to magnetic frustration. The macroscopic thermodynamic properties, such as the temperature dependence of the magnetization, the specific heat and the magnetic susceptibility for our system, are obtained from a Heisenberg-type Hamiltonian, which in general contains several terms corresponding to different energy contribution: exchange, Zeeman, dipolar, anisotropy, magnetostatic, magnetoelastic and thermal energy. In our study, we only consider the exchange energy for the first part of the work and then we add Zeeman contribution for the study of hysteresis loops. The Hamiltonian of the system is thus

$$H = \sum_{i=1}^N \left[-\frac{1}{2} \sum_{j \in V} J_{ij} \vec{S}_i \vec{S}_j - \mu_0 g_i \mu_B \vec{S}_i \vec{H}_{ext} \right] \quad (1)$$

V is the nearest neighborhood of site i , J_{ij} are the exchange coupling constant, \vec{S}_i and \vec{S}_j are spins corresponding to the i and j sites, μ_b is the Bohr magneton, g_i is the gyromagnetic ratio and H_{ext} is the external magnetic field.

The first step of our work consisted in the determination of the coupling constant J_{ij} which is related to the superexchange angle by the relation

$$J(\theta) = J_{180^\circ} \cos^2 \theta + J_{90^\circ} \sin^2 \theta \quad (2)$$

which can be written in the form

$$J(\theta) = J_{90^\circ} + (J_{180^\circ} - J_{90^\circ}) \cos^2 \theta \quad (3)$$

where J_{90° and J_{180° are respectively the coupling constant corresponding to the superexchange angle of 90° and 180° .

From previous studies several pieces of informations are available for $r\text{-FeF}_3$:

- The Néel temperature is approximatively $363K$ [15];
- The blank angle (angle for which the constant coupling is zero) is 115° [23];
- The superexchange angle in this phase is 153.15° [24].

Taking into account the fact that each iron atom has six F neighbors and that octahedral units are regular in pure perfectly crystalline $r\text{-FeF}_3$, we can use the relation giving the Néel temperature as a function of the coupling constant to determine the value of J_{θ_R} in units of the Boltzmann constant k_B

$$T_N = 1.45 \frac{Z |J_{\theta_R}| S^2}{6k_B} \quad (4)$$

where Z is the coordination number and S the spin. With $Z = 6$ and $S = 1$ $J_{\theta_R} = -250.35 K$

By combining relation 3 for the rhombohedral superexchange angle (θ_R) and the blank angle (θ_B), we obtain the system

$$\left\{ \begin{array}{l} J(\theta_R) = J_{90^\circ}(1 - \cos^2 \theta_R) + J_{180^\circ} \cos^2 \theta_R \\ 0 = J_{90^\circ}(1 - \cos^2 \theta_B) + J_{180^\circ} \cos^2 \theta_B \end{array} \right\} \quad (5)$$

The resolution of this system gives

$$J_{90^\circ} = \frac{J_{\theta_R} \cos^2 \theta_B}{\cos^2 \theta_B - \cos^2 \theta_R} \quad (6)$$

and

$$J_{180^\circ} = \frac{J(\theta_R)(\cos^2 \theta_B - 1)}{\cos^2 \theta_B - \cos^2 \theta_R} \quad (7)$$

which gives $J_{90^\circ} = 72.42K$ and $J_{180^\circ} = -333.07K$.

We can then deduce the relation giving the coupling constant as a function

of the superexchange angle. This relation is represented in figure 1. A comparison with the distribution of the superexchange angle in nanostructured FeF_3 obtained from previous studies [17] implies that all interactions in the GB remain antiferromagnetic. This is observed in figure 1 by the large peak centered around 160° , all angles being greater than 140° . It is thus concluded that the frustration in the GB does only originate from the cationic topology.

$$J(\theta) = 72.42 - 405.49 \cos^2 \theta \quad (8)$$

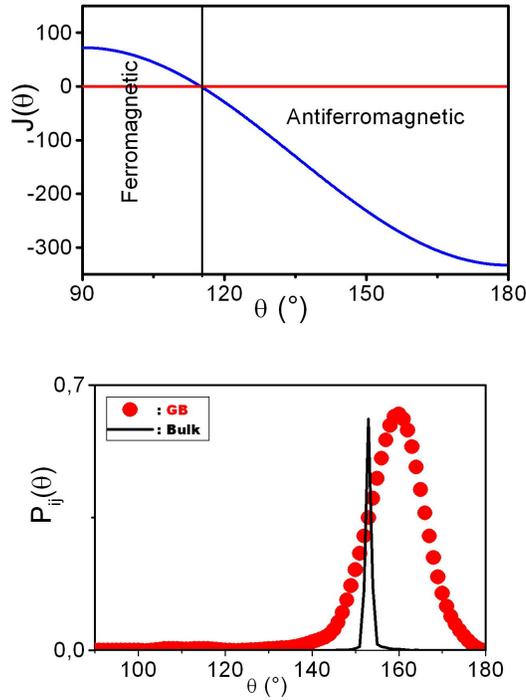


Figure 1: (a): Coupling constant as a function of the superexchange angle for iron fluoride. (b): Angular distribution function for the superexchange angle. GB is characterized by a large peak around 160° .

In the first step of the simulations we only considered the exchange contribution to the magnetic Hamiltonian of the system. We have then neglected other phenomenological contributions such as dipolar, Zeeman or anisotropy terms, in order to clarify the influence of the exchange coupling on the magnetic behavior. All samples, with sizes ranging from 8 to 12 nanometers and

different orientations of grains (tilted, twisted etc) were first structurally relaxed. The energy given in equation 1 is minimized by means of the Monte Carlo/Metropolis simulated annealing procedure. During the simulation, Monte Carlo steps are applied on individual magnetic moments ("spins") with a random walk while solid angles are uniformly distributed over 4π . Starting with a random spin configuration at a temperature T_{start} much higher than T_N (600K), the energy is minimized using the simulated annealing scheme with a decreasing power law for temperature $T = T_{\text{start}}0.97^i$ where i is the step number, while the thermodynamic quantities, such as magnetization, susceptibility and specific heat, can be derived as a function of the temperature. In each simulation, the final temperature is lower than 1K and the number of Monte Carlo steps per spin (MCS) is 10^5 .

3. Results

We first determine the magnetization, susceptibility and specific heat of the system as a function of temperature. Figure 2 represents the specific heat and one can observe a transition around 360 K which is the Néel temperature of r-FeF₃. The magnetization of the system is uniformly zero due to antiferromagnetic behavior. The magnetic configuration after annealing is composed of two antiferromagnetic grains separated by a transition zone with disordered spin structure as illustrated on figure 2. Each change in simulation conditions (number of MCS, orientation of initial grains, final temperature, etc) leads to a different orientation of magnetic moments of grains and then a different coupling of GB moment.

We can conclude that the system is not in the magnetic equilibrium state. This can be easily understood by considering the fact that the GB is magnetically frustrated. The present single spin flip we used is not appropriate for finding the magnetic equilibrium state in a reasonable time of simulation. New conditions have to be applied to reach this magnetic equilibrium state. A constraint can be added by considering the fact that there is one orientation of the relative global moment of each grain for which the magnetic energy is minimal. We used fixed boundary conditions to constrain magnetic moments of the two grains to form an angle θ and then relaxed the interface. Figure 3 represents the relative energy of the system for an angle varying

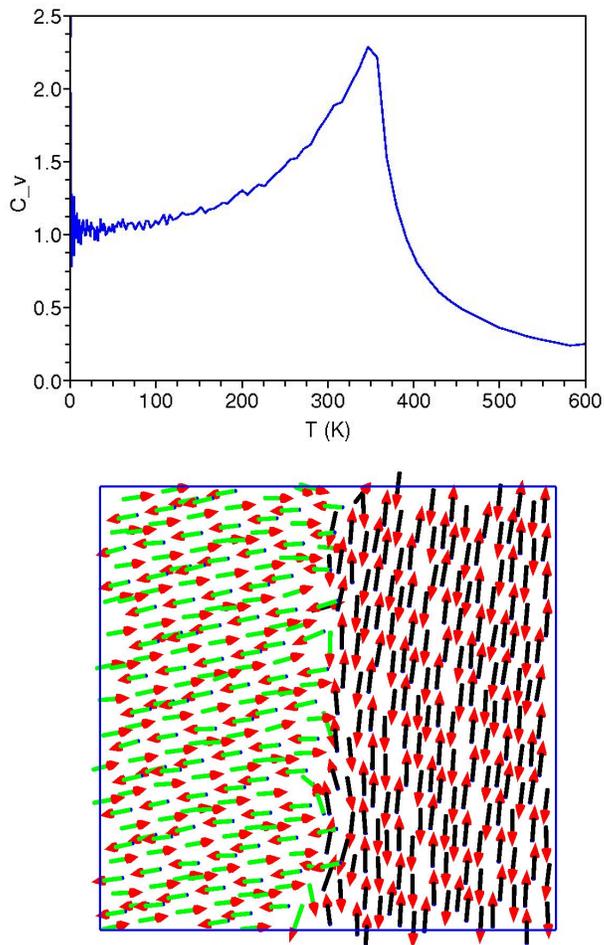


Figure 2: (a): specific heat of the system as a function of temperature (Néel temperature is around 360K). (b): Magnetic configuration after annealing: each change in simulation conditions would give a different orientation of the total moment of the grain.

from 0° to 360° . We can clearly distinguish two magnetic states with minimal energy around 90° and 270° .

The same behavior of the magnetic energy was obtained for different grain orientations, but the angle corresponding to the minimal energy was not the same. Figure 3 compares the same results obtained with non-tilted, tilted and twisted samples : it clearly appears that the angle corresponding to the

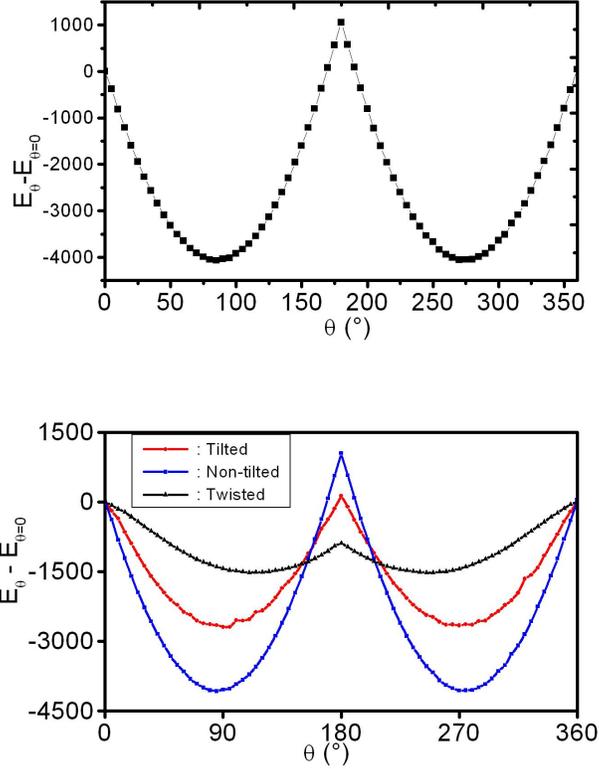


Figure 3: (a):Magnetic energy as a function of fixed angle boundary condition. There are two magnetic states of lower energy around 90° and 270° . (b): The same behavior is obtained for tilted, twisted and non-tilted system but with different angles.

minimum energy depends on the initial relative crystallographic orientation of grains. It has recently been shown [17] that the only difference between those samples is the rate of frustration in the GB, suggesting that the angle corresponding to the minimum energy depends on the rate of frustration. To verify this dependence, we first considered a simple model consisting of a cubic cluster with all interactions being antiferromagnetic, then we changed some antiferromagnetic in ferromagnetic interactions at the interface to create locally a bond frustration. Frustration rate can be thus defined as $\tau = NJ_F / (NJ_{AF} + NJ_F)$, where NJ_F and NJ_{AF} respectively represent the number of ferromagnetic and antiferromagnetic bonds. For each rate, the

system is relaxed and the angle between the moments of both sides of interface is measured: a certain rate of frustration gives rise to a non collinear orientation of the moments as evidenced on figure 4.

Therefore, we can assume that the non collinear orientation observed in ferric fluoride nanostructures is due to the magnetic frustration of the grain boundary. We conclude that the angle between the total momenta of the two grains depends on the rate of frustration, which suggests the possibility to tune the final orientation of the grains. To achieve the study of this system,

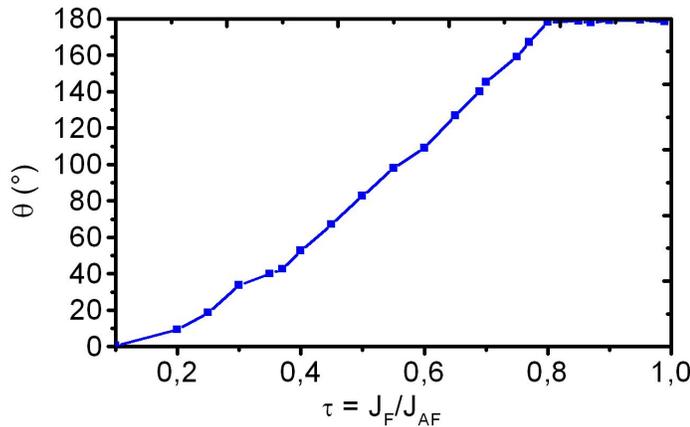


Figure 4: *Coupling angle between grains as a function of frustration rate. Non collinear coupling appears for a rate comprised between 0.2 and 0.8.*

we have performed a simulation of hysteresis loops. It is well established that crystalline $r\text{-FeF}_3$ is antiferromagnetic and that the GB behaves as a speromagnet giving rise to zero magnetization : therefore we do not expect any remanence on the hysteresis loops. The goal of the study is to analyze the influence of disorder in the GB on the spin rotation under a magnetic field.

The hysteresis loops have been computed starting from a saturated state achieved after the application of a high enough field (2700 T) along the z-axis (orthogonal to the GB plane) and decreasing the field in constant steps $\delta h = 10T$, during which the magnetization was averaged over 5000 MC steps after thermalization. The temperature was sufficiently low (10^{-3} K) to avoid thermal fluctuations. The result for a sample with a 12 nm size is presented

in figure 5. As expected, there is no remanent magnetization in hysteresis loops, but the spin rotation from a configuration parallel to the magnetic field to an antiferromagnetic configuration is not uniformly done: the moments far away from the interface are decoupling first due to their strong coupling compared to those of the GB.

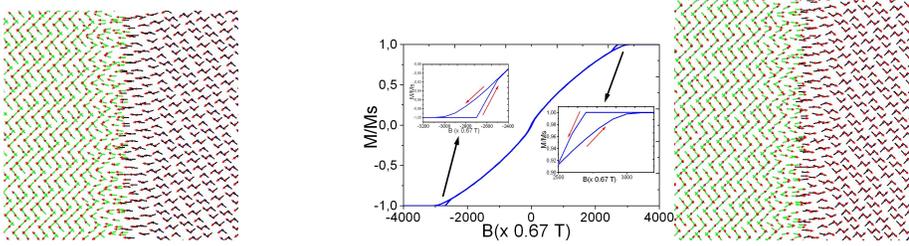


Figure 5: *Hysteresis loops and snapshots of the magnetic configuration during spin rotation for a 12nm size nanostructure. As expected, there is no remanent magnetization but a non uniform spin rotation in the area in inset. As the strength of the magnetic coupling far from the GB is greater than the one in the GB, magnetic moments in the GB are still in the direction of applied field after the spins far from the GB have rotated.*

4. Conclusion

We presented a Monte Carlo study of nanostructured ferric fluoride by coupling a previously established structural atomistic modeling to a magnetic modeling. As experimentally evidenced, at the nanoscale, this compound is composed of two parts: A perfect antiferromagnetic configuration in the grain and a disordered magnetic configuration (speromagnetic like) at the grain boundary. The present numeric study has shown that the magnetic configuration at the grain boundaries is governed by the cationic topology which results from the disorientation of crystalline neighboring grains. Consequently, the lowest magnetic energy of the total system is strongly correlated to the rate of magnetic frustration in the GB, opening the possibility to tune the final orientation of the magnetic moments of the grains by modulating the frustration rate.

From the careful simulation of hysteresis loops, the magnetization reversal is not uniform under a magnetic field ; in addition it is dependent on the strength of the magnetic coupling which is related to the superexchange

angle. It is finally important to emphasize that such an approach to numerically model structural and magnetic structures can easily be extended to ionic nanostructures, particularly to multilayers composed of different oxide species in order to follow the dependence of their properties on their topological ordering, the thickness of the interfaces and the mismatch between layers.

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