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Magnetic clustering phenomena observed on weak ferromagnets $Fe_xCr_{(1-x)}F_3$ ($0 \leqslant x \leqslant 1$)

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Abstract

Static magnetization measurements have been performed on the mixed fluoride series $Fe_xCr_{(1-x)}F_3$ ($0 \leqslant x \leqslant 1$). The evolution of the shape of the hysteresis loops reveals drastic changes as a function of the degree of concentration x and the temperature, whereas the coercive field and the magnetization exhibit singularities. These data are interpreted from a phenomenological model based on the existence of two uncompensated weak ferromagnetic sublattices randomly located on a cubic network. By including a spin relaxation process, such a mechanism explains well the presence of magnetic clustering phenomena, in agreement with ^{57}Fe Mössbauer spectrometry and magnetic susceptibility measurements.

1. Introduction

Some antiferromagnetic crystalline compounds possess a weak spontaneous magnetization: they exhibit a spin canted structure commonly designated as weak ferromagnetism. This behaviour has been extensively studied from the experimental point of view (in α-Fe_2O_3, $MnCo_3$, CrF_3, ...) and from the theoretical point of view on the basis of a thermodynamic approach proposed by Dzyaloshinsky [1]. It was shown that the weak ferromagnetism can be explained by the presence of an antisymmetrical spin–spin interaction, which is expressed by $D(S_A \times S_B)$. D is a constant vector (also called the Dzyaloshinsky vector) whereas $S_{A\ (B)}$ represents the spin characteristic of the A (B) sublattice. It has been established that this term when allowed in the thermodynamic potential of a sufficiently low-symmetry crystal favours a canted spin arrangement. The microscopic basis of the Dzyaloshinsky hypothesis was given by Moriya [2, 3], who suggested that the tensor describing the anisotropic superexchange

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interaction between two neighbouring spins S_i and S_j contains an antisymmetrical term which represents the anisotropic superexchange interaction.

During the last two decades, several studies have been devoted to the fundamental magnetic properties of crystalline and amorphous transition metal fluorides which can be considered as a 'cas d'école' of non-collinear magnetic systems. It is important to emphasize that these highly ionic insulating compounds exhibit a large variety of structural forms giving rise to non-collinear magnetic behaviours. Indeed, the nature of the cationic topology or the presence of single-ion anisotropy leads to non-collinear magnetic structures: geometrical magnetic frustration occurs when these structures exhibit competing interactions resulting from both specific (essentially triangular) coordination symmetry and short range antiferromagnetic interactions [4]. It is concluded that the presence of competing antiferromagnetic nearest neighbour interactions (superexchange term) leads to non-unique classical antiferromagnetic ground states, in the case of crystalline as well as of amorphous magnetic systems. Magnetic topological frustration may also be due to the competition between first and second nearest neighbour exchange interactions (superexchange and supersuperexchange terms, respectively). Thus, one can argue from Shekhtman *et al* [5] that the frustration is a necessary condition for the anisotropic superexchange interaction to explain the weak ferromagnetism. It is important to emphasize that the superexchange term is usually prevailing, but in the case of mixed crystalline fluorides containing several paramagnetic ions competition between first and second nearest neighbour exchange interactions is expected, leading to magnetic clustering effects when chemical disorder occurs.

From an experimental point of view, non-collinear magnetic behaviours can be investigated by neutron diffraction, static magnetic measurements and combined zero-field and high-field ^{57}Fe Mössbauer spectroscopy in the case of iron-based systems [6–8]. Moreover, susceptibility measurements allow an estimate of the degree of frustration in the case of antiferromagnetic systems through the ratio $|\theta_p/T_N|$, when it exceeds unity, according to Smart [9]. The quantities θ_p and T_N give the values of the Néel and Curie–Weiss temperatures, respectively, assuming $\theta_p = 2zS(S+1)J/3$, where z is the coordination number, S the spin quantum and J denotes the nearest neighbour exchange interaction.

Among the crystalline transition metal fluorides, r-MF_3 (M = Fe, Cr, Ga, V) compounds have received special attention because their chemical nature remains simple and they together exhibit a rhombohedral form (space group $R\bar{3}c$) which results from a corner sharing packing of octahedral units centred on a cubic lattice. In the frame of non-collinear antiferromagnets, FeF_3, CrF_3 and VF_3 compounds remain of particular interest because they behave as weak ferromagnets below $T_N = 363$, 80 and 19.4 K, respectively. So, we have recently focused our attention on several solid solutions $Fe_xM_{1-x}F_3$ (M = Fe, Cr, V and Ga; $0 \leqslant x \leqslant 1$) which were synthesized by solid state reaction. Let us remember that the spin values of Fe, Cr, V and Ga are $S = 5/2$, $3/2$, 1 and 0, respectively.

2. Experimental section

Such mixed iron crystalline fluorides were mainly investigated by means of ^{57}Fe Mössbauer spectrometry and magnetic susceptibility measurements [10–12]: the mainly significant results observed on the $Fe_xCr_{1-x}F_3$ series can be summarized as follows.

(i) The thermal evolution of the hyperfine properties was followed in the temperature range 4.2–300 K. One can observe a broadening of the line sextets which increases with the temperature. This broadening is essentially due to the magnetization distribution $\langle S \rangle$, originating from a distribution of exchange interactions, because of the cationic disorder

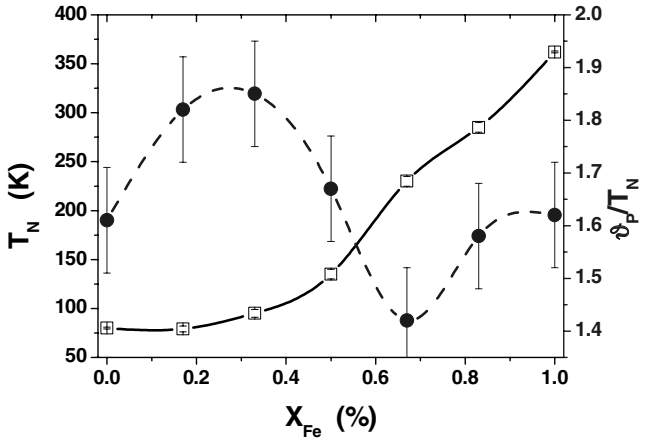

Figure 1. Evolutions of ratio $|\theta_p/T_N|$ (●) and T_N (□) versus iron concentration. Solid and dashed curves are guides for the eye.

between Fe^{3+} and Cr^{3+} ions around the iron probe. Furthermore, at least three different magnetic behaviours can be revealed depending on the chromium contents. A sharp magnetic transition is observed for $x = 0.83$, while a broad transition (a few degrees) is evidenced for $x = 0.17$ and 0.33. In the case of both $Fe_{0.67}Cr_{0.33}F_3$ and $Fe_{0.50}Cr_{0.50}F_3$, the Mössbauer spectra consist in a superposition of a paramagnetic singlet and an enlarged magnetic sextet over a 40 and 20 K temperature range, respectively, just below the magnetic ordering transition temperature. These different behaviours give clear evidence for the presence of anomalous magnetic properties in the iron–chromium series. In addition, from the Mössbauer experiments performed, the evolution of the hyperfine structure is associated with the presence of spin clusters with a distribution of relaxation times depending on the temperature.

(ii) The experimental magnetic susceptibility $\chi^{-1}(T)$ curves obtained with a 1 T applied magnetic field show that the paramagnetic Curie temperature appeared negative for the whole series $Fe_xCr_{1-x}F_3$ consistent with the presence of predominant antiferromagnetic interactions. In the low temperature range, the thermal evolution of the magnetic susceptibility strongly depends on the iron concentration. Reentrance properties can clearly be observed for $Fe_{0.17}Cr_{0.83}F_3$. From thermodynamic aspects, the magnetic susceptibility measurements as a function of temperature can provide the values of $|\theta_p/T_N|$ obtained as a function of concentration x, as plotted in figure 1. The minimum of $|\theta_p/T_N|$ corresponding to $x \cong 0.67$ confirms the pathological behaviour observed by ^{57}Fe Mössbauer spectrometry which is illustrated by the change of the slope curvature on the thermal evolution of the hyperfine field at around 210 K.

These experimental observations can be well described upon a spin cluster phenomenological approach as follows. Above the magnetic ordering temperature, the magnetic moments relax independently, in spite of the presence of magnetic exchange interactions. Then, as short range magnetic correlations appear when the temperature decreases, one can suppose the existence of very small spin clusters, magnetically independent of the cationic matrix, resulting from the frustration mechanism induced by the competition of nearest and next nearest antiferromagnetic exchange integrals. These behaviours are strongly dependent on the content of the transition metal ions. In order to complete these results

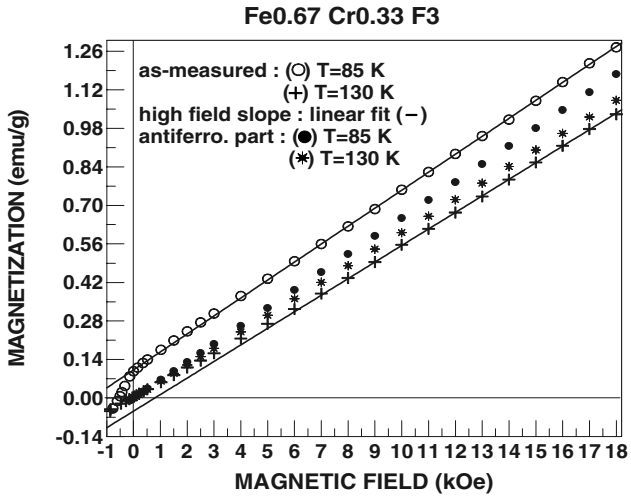

Figure 2. As obtained M–H hysteresis loops for $x = 0.67$.

described above, we have also investigated the magnetic characteristics of $Fe_xCr_{1-x}F_3$ by means of static magnetic measurements.

3. Static magnetic measurements

Hysteresis loop experiments were carried out with either a vibrating sample magnetometer (applied field up to 1.8 T) or a SQUID magnetometer (applied field up to 5.5 T) over the temperature range 4.2–350 K on $Fe_xCr_{1-x}F_3$ powder samples. Some significant examples of part of the as-obtained M–H loops are illustrated in figure 2. The M versus H behaviours are characteristic of the existence of two magnetic components:

(i) an antiferromagnetic component (AFC) is well observed at the highest fields as M varies linearly with H;
(ii) a hysteresis loop at low field which is characteristic of a weak ferromagnetic (WF) component superimposed with the antiferromagnetic matrix.

A more comprehensive description of our data consists in separating the two magnetic parts by subtracting the high field AFC from the as-obtained measurements. In figure 2, the high field linear part was fitted, then the linear law, crossing zero was represented. The difference between the as-measured data and the linear law gives rise to the hysteresis loop of the WF component illustrated in figure 3.

The extrapolated values at $H = 0$ of the high field fitted AFC magnetization correspond to the saturation magnetization M_{sat} of the WF loops. As a function of temperature, one can observe that the extrapolation presents alternately positive and negative values. This indicates that the WF component changes with regard to the AFC magnetization (more details and discussion are given below).

The WF coercive field and M_{sat} values vary with temperature and are given in figure 4 for the composition $x = 0.67$. The experimental results describing the thermal evolution of the remanent and saturation magnetizations and of the coercive field, for different values of concentration, are plotted in figures 5–7.

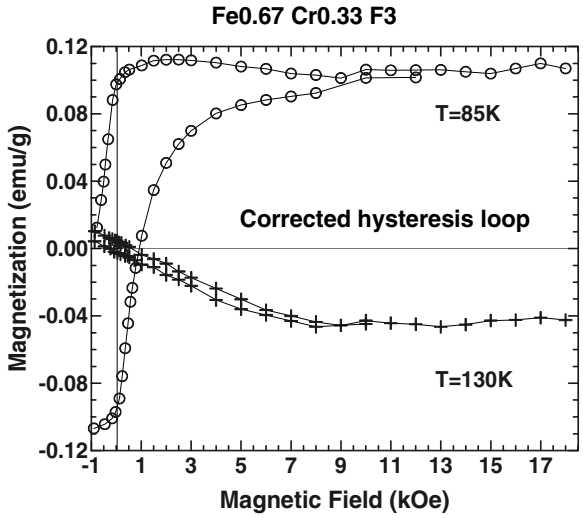

Figure 3. Corrected M–H hysteresis loops for $x = 0.67$.

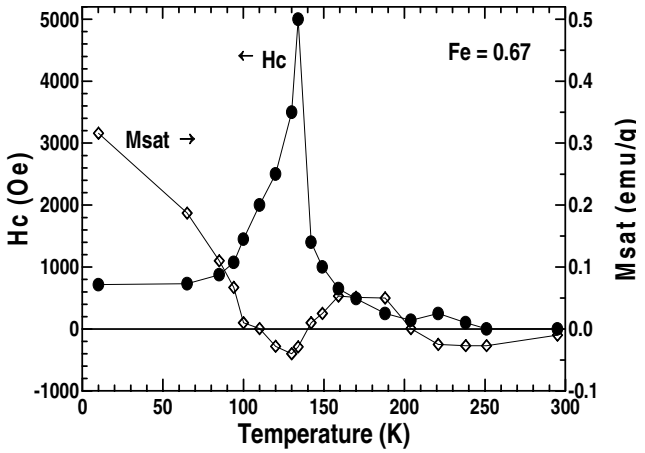

Figure 4. Temperature dependence of corrected coercive field (●) and saturation magnetization (◇) for $x = 0.67$.

4. Discussion

Such magnetic data combined with Mössbauer results give clear evidence for the existence of different magnetic regimes which are strongly temperature and composition dependent. Let us first consider $x = 0$, 0.17 and 0.33: they behave as only a single type of magnetic regime where WF prevails, while for $x = 0.50$ a tiny change seems to occur above 100 K.

The composition $x = 0.67$ exhibits clearly four different magnetic regimes according to the temperature. They can be described as the following.

(1) Below $T = 110$ K, both experimental and corrected hysteresis loops exhibit a classical shape; the corrected saturation magnetization decreases as the temperature increases whereas the corrected coercive field increases with temperature.

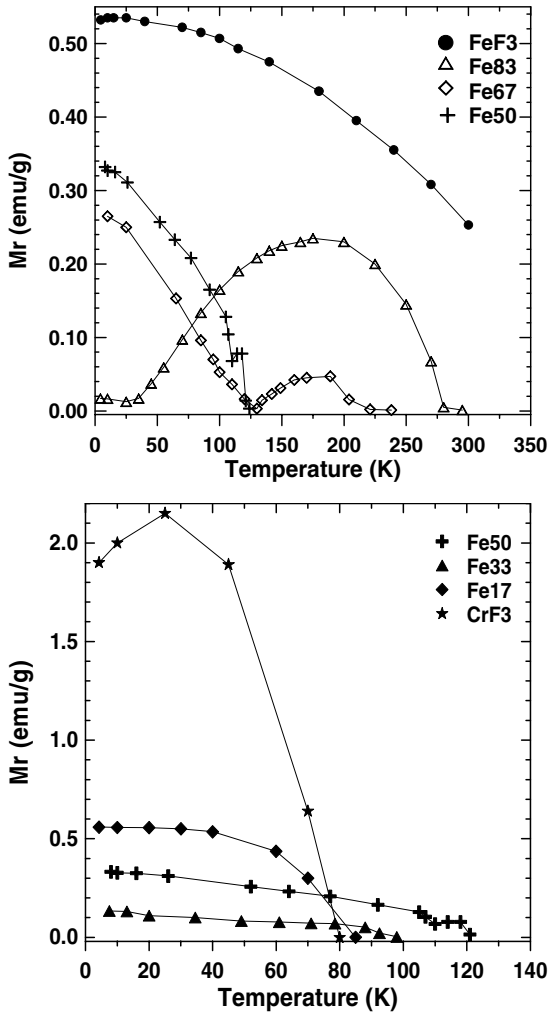

Figure 5. Evolution of the remanent magnetization M_r versus temperature for $0 \leqslant x \leqslant 1$.

(2) For 115 K $\leqslant T \leqslant$ 140 K, one can observe that the extrapolation of the high field slope is negative whereas this value is usually positive: consequently, the corrected hysteresis loops are reversed, that is rather original. In addition, the WF H_c values increase drastically with T, like a divergence, which is consistent with the existence of a compensation point in the M_{sat} behaviour versus T.

(3) For 145 K $\leqslant T \leqslant$ 205 K, the hysteresis loops exhibit a classical shape while both H_c and M_{sat} decrease with temperature.

(4) For $T \geqslant$ 205 K, loops are again observed as reversed due to negative M_{sat} values. The WF hysteresis disappears progressively until $T = 240$ K. For $T \geqslant 240$ K, the sample behaves as a paramagnet, confirming previous Mössbauer results.

The last composition $x = 0.83$ is rather similar to the previous one, except that the coercive field diverges at around 45 K. In the following, we concentrate our discussion on $x = 0.67$ because of its greater interest.

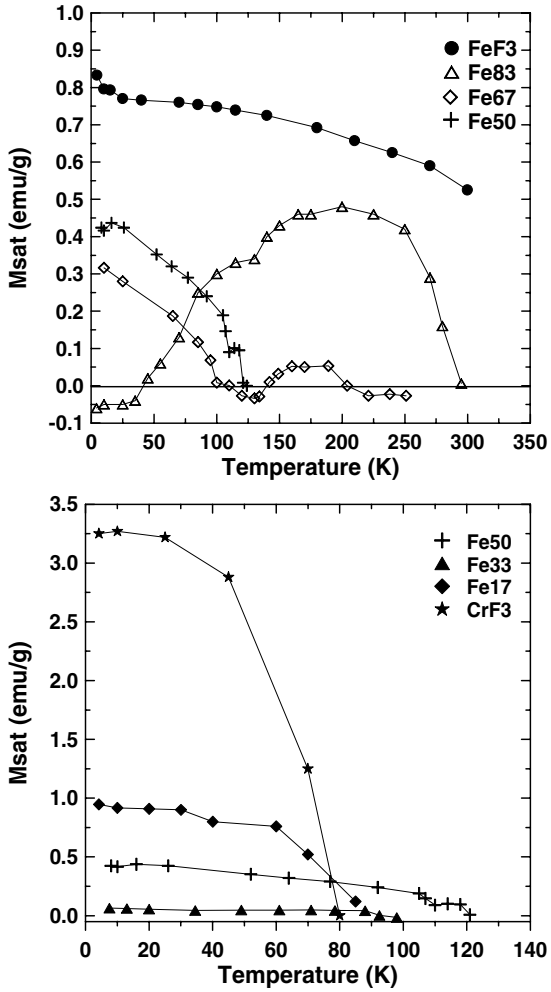

Figure 6. Evolution of the saturation magnetization M_{sat} versus temperature for $0 \leqslant x \leqslant 1$.

The different magnetic behaviours observed for the composition $x = 0.67$ can be described with a phenomenological model based on the existence of two uncompensated weak ferromagnets randomly distributed on a cubic lattice and antiferromagnetically coupled. In addition, this description suggests that the transverse spin components can follow a relaxation process. Consequently, it involves the existence of two minima which are strongly dependent on the temperature and on the relative magnitudes of the exchange interactions.

In the case of two independent weak ferromagnetic sublattices, the application of a magnetic field adds to the transverse component: consequently, it tends to increase the canting angle. Let us assume that these two sublattices are similar and antiferromagnetically coupled: this interaction will favour the existence of two opposite transverse components and consequently induces spin fluctuations.

In the case of two different sublattices, the transverse component of the magnetically dominant sublattice will be oriented parallel to the applied field whereas that of the second sublattice will be aligned antiparallel. At a critical applied field, this contribution will flip towards its direction.

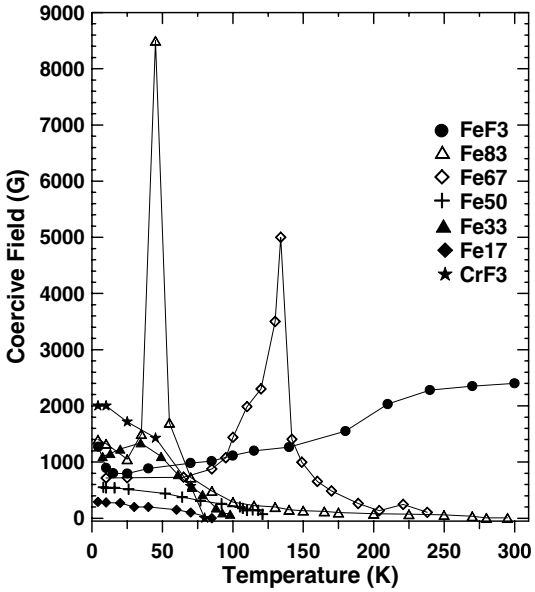

Figure 7. Evolution of the coercive field versus temperature for $0 \leqslant x \leqslant 1$.

In these models, the coupling of the magnetic moments results from the both nearest and next nearest neighbour exchange antiferromagnetic interactions, thus originating the magnetic frustration phenomena. Consequently, a numerical approach based upon the Metropolis algorithm was developed by simulation of the magnetic Ising and Heisenberg structures in the case of a cubic lattice, as a function of J_2/J_1, where J_1 and J_2 are the superexchange integrals between first and second nearest neighbours, respectively. At absolute zero Kelvin, two kinds of magnetic configuration were evidenced which exhibit the presence of frustrated antiferromagnetic interactions [13]. A magnetic phase transition is observed and the calculations on the bulk and surface spin-waves on these systems were performed in order to corroborate the simulation results [14]. Such calculations were applied to the case of r-FeF_3 and the values of J_1 and J_2 obtained are in agreement with the presence of frustration phenomena in the case of a cubic system. We can assume that the cationic disorder associated with the similarity of the superexchange J_{Cr-Cr} and J_{Fe-Cr} with supersuperexchange J_{Fe-Fe} interactions justify explaining the experimental magnetic behaviours in terms of spin clusters.

Let us reconsider these situations described above in the case of the mixed ferric crystalline fluoride $Fe_xCr_{1-x}F_3$ ($0 \leqslant x \leqslant 1$) for which Fe and Cr magnetic moments are randomly distributed on the crystal lattice. When $x = 0$ and 1, the magnetic order is given by the superexchange interactions Cr–Cr and Fe–Fe, respectively. Increasing values of x originate the emergence of Fe–Cr superexchange and Cr–Cr supersuperexchange interactions, while Fe–Cr superexchange and Fe–Fe supersuperexchange interactions occur on the opposite side of the diagram, both leading to two compensation points. This unusual phenomenon is clearly illustrated in figure 8 which shows the composition dependence of the remanent and saturation magnetization.

In addition, the cationic neighbours of both types of cation differ, giving rise to different temperature dependences of the magnetic behaviour, as previously observed for $x = 0.67$ by Mössbauer spectroscopy on the Fe sublattice. The critical value of 110 K evidenced in the above section can be associated with a compensation temperature at which the magnetic

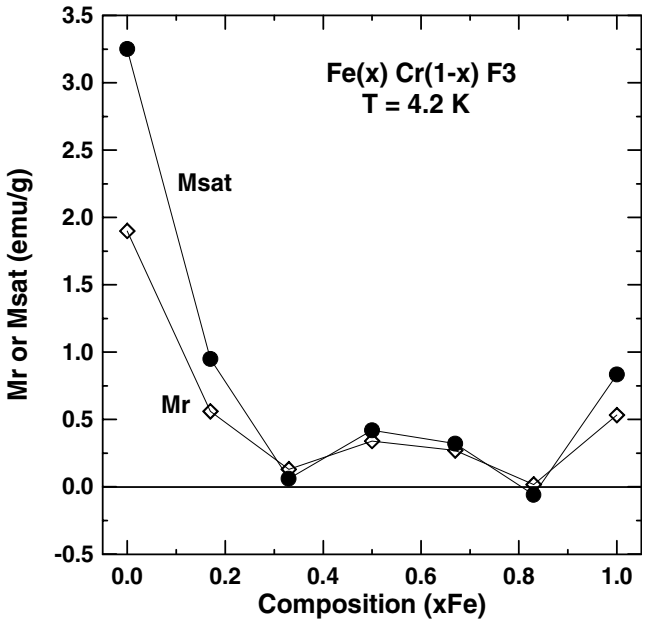

Figure 8. Composition dependence of the magnetization and remanent magnetization.

transverse component of the Cr sublattice flips towards the applied field, whereas $T = 240$ K corresponds to the magnetic ordering temperature on the Fe sublattice. These phenomena result from the existence of Cr and Fe magnetic moments which can be described from the presence of magnetic and/or structural inhomogeneities with the coexistence of both competition of magnetic interactions. Such a phenomenological approach was developed first by Malozemoff *et al* [15, 16] in order to describe the thermal evolution of the magnetic resonance lines for $Gd_{0.37}Al_{0.63}$ spin glasses and observed several years later by Nogues *et al* [17] with regard to magnetic measurements of the substituted spinel system $Zn_xCd_{1-x}Cr_2S_4$ ($0.3 \leqslant x \leqslant 0.4$).

5. Conclusion

In addition to previous results obtained using Mössbauer spectrometry on the mixed chromium–iron trifluorides, the present experimental approach based on the static magnetic measurements revealed a variety of magnetic properties, such as reentrance and spin clustering. These behaviours are strongly dependent on the nature and the concentration of transition metal ions. The presence of magnetic clustering phenomena and magnetic frustration is suggested, due to the simultaneous presence of competing antiferromagnetic interactions, between nearest and next nearest neighbours. The next work will be focused on the complementary dynamic magnetic measurements on the other mixed trifluoride compounds $Fe_xM_{1-x}F_3$ (M = Ga, V; $0 \leqslant x \leqslant 1$) in order to understand their own magnetic behaviours and finally to suggest a magnetic phase diagram for iron–gallium, iron–chromium and iron–vanadium systems.

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