



# The magnetic behaviour of the magnetically diluted spinel compound $\text{Fe}_{0.6}\text{Mg}_{1.6}\text{Ni}_{0.1}\text{Ti}_{0.7}\text{O}_4$ studied by Mössbauer spectroscopy

A.M. Alakrmi, R.E. Vandenberghe\*, E. De Grave

Department of Subatomic and Radiation Physics, Ghent University, Belgium

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## ABSTRACT

From a new magnetically diluted spinel oxide with composition  $\text{Fe}_{0.6}\text{Mg}_{1.6}\text{Ni}_{0.1}\text{Ti}_{0.7}\text{O}_4$  an as-prepared sample and one after reheating three times have been investigated with Mössbauer spectroscopy. The spectra of the as-prepared sample clearly show a typical superparamagnetic behaviour of magnetic clusters with diverging sizes. On the other hand, the reheated sample exhibits a sharp magnetic transition at 16 K. External-field Mössbauer measurements of the latter reveal spin canting to be exclusively present on the octahedral sites which disappears at the magnetic transition temperature. These results show that this spinel compound exhibits a transition to a spin-glass for which the random freezing only occurs on the octahedral sites.

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## 1. Introduction

The spinel structure  $\text{AB}_2\text{O}_4$ , in which A represents the tetrahedral sites and B the octahedral sites, is well known for its possibility to accommodate a large variety of magnetic structures, depending on the kind of cations, their magnetic interactions and the magnetic dilution [1,2]. Besides the common ferrimagnetic behaviour, triangular magnetic structures can appear when antiferromagnetic interactions between any two magnetic atoms cannot be satisfied simultaneously. This is possible if the antiferromagnetic intra-sublattice  $J_{\text{BB}}$  (or  $J_{\text{AA}}$ ) interaction is comparable to the antiferromagnetic inter-sublattice  $J_{\text{AB}}$  one. This can lead to an ordered non-collinear spin structure as has been demonstrated by Yafet and Kittel [3]. However, when one sublattice is magnetically diluted there is no longer a long-range ordering and localised spin canting states (LCS) [4–7] or spin-glass (SG) behaviour [7–11] may appear. In this respect, the canting of the spins originating from the antiferromagnetic  $J_{\text{BB}}$  (or  $J_{\text{AA}}$ )  $> J_{\text{AB}}$  interactions, leads to canted configurations or to frustration which together with disorder prevent magnetic ordering even though the magnetic interaction may be strong. Border lines between LCS and SG for spinel systems have been experimentally deduced and presented in compositional phase diagrams by Dormann and Nogues [2].

Another feature such as superparamagnetism (SPM) has also been reported in diluted spinel systems, even when the particle size is large. SPM in mixed ferrites has been explained by the

existence of magnetic clusters, i.e., diamagnetic isolation of ferrimagnetic areas in the crystals, as initially proposed by Ishikawa (1962) for Zn–Ni ferrites [12] and later by Pekoshevski et al. [13]. Otherwise, Bhargava et al. [10,14] showed from external-field Mössbauer measurements that in Ni–Zn ferrite SPM effects only play a role at high temperatures ( $> 250$  K), whereas at low temperatures LCS are dominant. A superparamagnetic cluster behaviour was also reported for the spinel solid solution  $\text{Mg}_{1+x}\text{Fe}_{2(1-x)}\text{Ti}_x\text{O}_4$  by De Grave et al. [15,16] and later in some particular compounds by Fayek et al. [17]. On the other hand, Brand et al. [8] studied the same Mg–Ti ferrite series with magnetic and Mössbauer measurements. Their results could rather be explained in terms of Villain's model [7] in view of the presence of frustration due to all negative  $J_{\text{AB}}$ ,  $J_{\text{BB}}$  and  $J_{\text{AA}}$  interactions in this system [18]. They proposed a magnetic phase diagram showing evidence for the presence of a SG region, in which the system exhibit a single transition from doublet to sextet for  $x \geq 0.7$  and an additional transition in a spin-glass-like (SGL) state for  $x \leq 0.6$ . These results have recently been confirmed via Monte Carlo calculations by Gibb [19].

In order to gain some insight in this controversial problem, we have studied some spinel compounds with general formula  $\text{Mg}_{1+x-y}\text{Fe}_{2(1-x)}\text{Ni}_y\text{Ti}_x\text{O}_4$  with  $x = 0.5, 0.6$ , and  $0.7$  and  $y$  varying from 0.1 to 0.3. The  $\text{Ni}^{2+}$  was introduced to diminish slightly the frustration at the B sites because the  $\text{Ni}^{2+}\text{--Fe}^{3+}$  and  $\text{Ni}^{2+}\text{--Ni}^{2+}$  magnetic interactions are less negative than the  $\text{Fe}^{3+}\text{--Fe}^{3+}$  interactions [2]. It also affects the hyperfine field on octahedral Fe which results in some cases in better resolved sublattice spectra in the Mössbauer spectrum. In this paper, the results of a study on the particular compound  $\text{Fe}_{0.6}\text{Mg}_{1.6}\text{Ni}_{0.1}\text{Ti}_{0.7}\text{O}_4$  are reported. From this composition, an as-prepared sample (AP)

\* Corresponding author. Tel.: +32 9 264 65 66; fax: +32 9 264 66 97.

E-mail address: [robert.vandenberghe@ugent.be](mailto:robert.vandenberghe@ugent.be) (R.E. Vandenberghe).

and a sample after having been reheated for several times (RH) have been investigated by Mössbauer spectroscopy in order to determine whether the preparation methodology of such spinel compounds may play a role in the obtained magnetic behaviour.

## 2. Experimental

A sample with nominal composition  $\text{Fe}_{0.6}\text{Mg}_{1.6}\text{Ni}_{0.1}\text{Ti}_{0.7}\text{O}_4$  has been synthesized from the dried oxides by a conventional solid-state reaction sintering technique. The oxides in an approximate molar ratio were mixed in a rotating agate mortar during 12 h. The resulting mixture was then pressed into a rod under the pressure of  $5 \text{ ton/cm}^2$ . The material was then pre-fired at  $900^\circ\text{C}$  for 18 h. The as-prepared sample (AP sample) underwent a single sintering at  $1300^\circ\text{C}$  for 24 h in air and has been slowly cooled at a rate of  $5^\circ\text{C/min}$ . Part of the final product has been three times milled, pressed and re-sintered at  $1300^\circ\text{C}$  for 48 h (RH sample).

The structural properties were examined by X-ray powder diffraction (XRD) using  $\text{Cu-K}\alpha$  radiation and a slow scan (step =  $0.02$  degrees  $2\theta$  and  $7.5$  steps/min) to obtain a high-resolution pattern. The XRD pattern was further fitted by the Xfit-Koalariet program [20].

Mössbauer spectra were collected in 1024 channels (unfolded) with a conventional constant acceleration spectrometer using a  $^{57}\text{Co}(\text{Rh})$  source. Polycrystalline absorbers containing about  $10 \text{ mg/cm}^2$  of iron were used to avoid thickness effects. External-field Mössbauer measurements were performed in a superconducting magnet with a longitudinal field. The spectra have been fitted by conventional Lorentzian profiles and using hyperfine field distributions where necessary [21].

## 3. Results and discussion

The X-ray powder diffraction pattern of the AP sample shows the typical reflections of a pure cubic spinel structure belonging to  $\text{Fd}\bar{3}m$  space group (Fig. 1). All lines are close to instrumental broadening and no other reflections or shoulders on the lines could be observed. The lattice parameter was found to be  $a = 8.4318 \text{ \AA}$ .

The  $^{57}\text{Fe}$  Mössbauer spectra for the as-prepared sample collected at different temperatures between 4 K and room

temperature (RT) are displayed in Fig. 2. The spectra were all fitted with a sextet and a doublet. For the sextet, a hyperfine field distribution has been considered in which the hyperfine field was linearly correlated with the isomer shift to account more or less for the two sites with different isomer shift. The hyperfine data are summarised in Table 1. One can readily observe that in the spectra there is above 4 K a significant increase of the doublet at the expense of the sextet up to 15 K (Fig. 3). This is a spectral feature comparable with that of a non-uniform nanoparticle system. Therefore, this behaviour clearly fits in the picture of superparamagnetism and points rather to the existence of magnetic clusters in this compound with varying volume  $V$  and corresponding blocking temperature  $T_B$  given in the idealised case by the well-known relaxation formula

$$\tau_{\text{MS}} = \tau_0 \exp \frac{K_{\text{eff}} V}{kT_B}$$

with  $K_{\text{eff}}$ , an effective anisotropy constant;  $\tau_{\text{MS}}$  the characteristic Mössbauer time ( $\approx 2.5 \times 10^{-8} \text{ s}$ ) and  $\tau_0$  approximately a constant of the order  $10^{-9} \text{ s}$ . Although no quantitative information is provided here, this relaxation formula shows that  $T_B$ , i.e., the temperature at which a magnetic particle becomes superparamagnetic, increases with the cluster volume.

Above 20 K, there is still a fraction of the spectrum (20% of Fe) that remains a sextet and that only disappears at relatively high temperature ( $> 150 \text{ K}$ ). The evolution up to 40 K of the hyperfine field distributions derived from the spectra are displayed in Fig. 4. Several maxima are observed and above 15 K the high-field component diminishes only slowly with increasing temperature. Because neither additional lines nor shoulders on the XRD lines have been noticed which could point to a second spinel phase, this persisting sextet infers that also large clusters are intrinsically present in the compound. All these features suggest that the AP sample has a very inhomogeneous cation distribution leading to a variety of magnetic clusters.

The  $^{57}\text{Fe}$  Mössbauer spectra for the RH sample collected at different temperatures between 4 K and RT are shown in Fig. 5. The spectrum at 4 K could even be fitted with two distributed sextets and a weak Lorentzian quadrupole doublet. The first sextet showed a maximum-probability hyperfine field  $H_{\text{hf,p}} = 43.4 \text{ T}$  and an isomer shift  $\delta_{\text{Fe}} = 0.23 \text{ mm/s}$  which could be roughly attributed to  $\text{Fe}^{3+}$  on A sites, whereas the second sextet with  $H_{\text{hf,p}} = 46.8 \text{ T}$  and  $\delta_{\text{Fe}} = 0.51 \text{ mm/s}$  could arise from  $\text{Fe}^{3+}$  on B

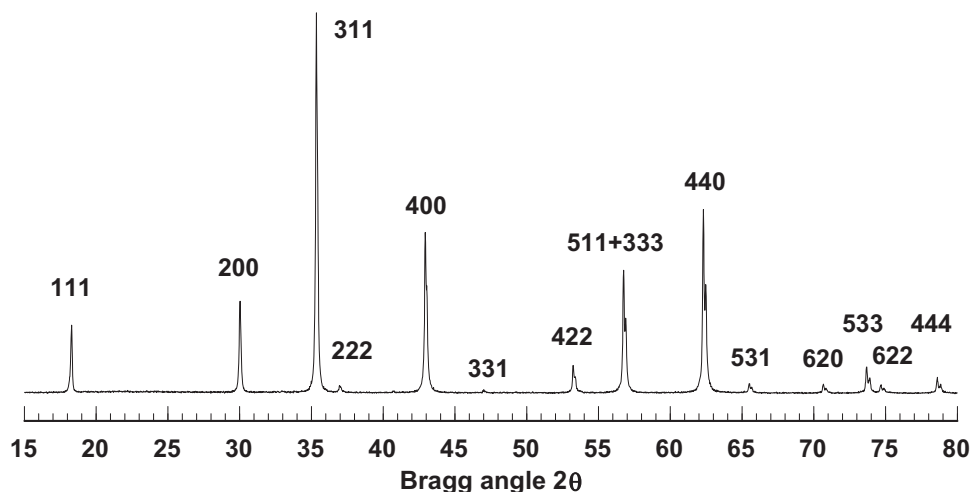


Fig. 1. XRD pattern of the AP sample.

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