Effect of magnesium substitution on the magnetic properties of diluted magnetic spinels Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$

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Abstract. The magnetic properties of Ni-Mg ferrites with compositions Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ have been studied using the mean field theory and high temperature series expansion theory (HTSE), extrapolated with the Padé approximants method. The nearest neighbour super-exchange interactions for intra-sites and inter-sites of the Ni-Mg ferrites in the range 0 ≤ x ≤ 1 have been computed using the distribution method of magnetic cations. The transition temperature $T_C$ is calculated as a function of Mg concentration. The critical exponent associated with the magnetic susceptibility was then deduced. The obtained results are in good agreement with experimental results and critical exponent values are consistent with those suggested by the universality hypothesis.

1. Introduction
Ni ferrite (NiFe$_2$O$_4$) and substituted ones are technologically important materials, which have been studied in many experimental and theoretical works [1-4]. NiFe$_2$O$_4$ is a typical soft ferromagnetic material crystallizing in a completely inverse spinel structure with all nickel ions located in the B-sites and ferrite ions occupying both A-sites and B-sites [5]. The compound, thus can be represented by the formula (Fe$^{3+}$)$_A$[$Ni^{2+}$Fe$^{3+}$]$_B$O$_4^{2-}$. MgFe$_2$O$_4$ has well known spinel structure [6]. The cations Mg$^{2+}$ and Fe$^{3+}$ are unequally distributed among the tetrahedral (A) and octahedral (B) lattice sites. The cations distribution in MgFe$_2$O$_4$ indicated that this ferrite is 86 % inverted as given by neutron scattering [7] and Mossbauer [8], for example (Fe$_{0.86}$Mg$_{0.14}$) in A and (Mg$_{0.86}$Fe$_{1.14}$) in B and this remained unchanged in the temperature range 90 – 700K, with $T_c = 665$ K [9].

The objective of this paper is to study the magnetic behavior of spinel compounds situated between the pure inverse spinel compounds NiFe$_2$O$_4$ and MgFe$_2$O$_4$ [10].The high temperature series expansions (HTSEs) extrapolated with the padé approximants (PAs) method are given to determine the critical $T_C$ versus $x$ and the critical exponent associated with magnetic susceptibility $\gamma$.

2. Theoretical methodologies

2.1. Exchange interactions calculations
Magnetic exchange interactions, inter and intra-sublattices ($J_{AB}$, $J_{BB}$, and $J_{AA}$) in [Mg$_{0.14x}$Fe$_{(1-0.14x)}$][Ni$_{(1-x)}$Mg$_{(0.86x)}$Fe$_{(1+0.14x)}$]O$_4$ diluted spinels, with different Mg concentrations, in the range $0 \leq x \leq 1$, were calculated. A probability law based on distribution of ions in A and B sublattices, given by neutron scattering (Table 2) [7] has been used. The interactions $J_{AA}^{Fe^{3+}-Fe^{3+}}$, $J_{AB}^{Fe^{3+}-Fe^{3+}}$, $J_{BB}^{Fe^{3+}-Fe^{3+}}$, $J_{AA}^{Fe^{3+}-Ni^{2+}}$, $J_{AB}^{Fe^{3+}-Ni^{2+}}$, $J_{BB}^{Fe^{3+}-Ni^{2+}}$, and $J_{BB}^{Ni^{2+}-Ni^{2+}}$, in the inverted pure spinel, given by Srivastava et al. [11], have also been used. The exchange interactions between B sites, between A and B sites and between A sites in the range $0 \leq x \leq 1$ are given by:

$$J_{AA}(x) = (1 - 0.14x)^2 J_{AA}^{Fe^{3+}-Fe^{3+}}$$
$$J_{AB}(x) = \frac{1}{2} [(1 + 0.14x)(1 + 0.14x) J_{AB}^{Fe^{3+}-Fe^{3+}} + (1 - x)(1 - 0.14x) J_{AB}^{Fe^{3+}-Ni^{2+}}]$$
$$J_{BB}(x) = \frac{1}{4} [(1 + 0.14x)^2 J_{BB}^{Fe^{3+}-Fe^{3+}} + (1 - x)(1 + 0.14x) J_{BB}^{Fe^{3+}-Ni^{2+}}]$$

\[+(1 - x)^2 J_{BB}^{Ni^{2+}-Ni^{2+}}\]  

\[(1)

\[Table 1. Exchange interaction ion-to-ion for the pure component NiFe$_2$O$_4$ [12].

| $J_{AA}^{Fe^{3+}-Fe^{3+}}$ | $J_{AA}^{Fe^{3+}-Fe^{3+}}$ | $J_{BB}^{Fe^{3+}-Ni^{2+}}$ | $J_{BB}^{Fe^{3+}-Ni^{2+}}$ | $J_{BB}^{Fe^{3+}-Fe^{3+}}$ | $J_{BB}^{Ni^{2+}-Ni^{2+}}$ |
|---|---|---|---|---|---|
| -14 | -28 | -27.4 | -9 | -10 | +29.0 |

From Table 1, one can see that all exchange interactions are antiferromagnetic except $J_{BB}^{Ni^{2+}-Ni^{2+}}$ which is ferromagnetic. Furthermore, when increase in the Mg content all the interactions decrease except $J_{BB}^{Fe^{3+}-Fe^{3+}}$ which increases (Table 2). However, $J_{AB}(x)$ is stronger than the other two, which means that the interactions between A and B are higher than the interactions inside the sublattices A and B, but their value decreases with increase in Mg concentration x. This is due to the decrease in Ni concentration in B sites, and to the replacement of the magnetic ion Ni$^{2+}$ by the non-magnetic ion Mg$^{2+}$.

2.2. High-temperature series expansion (HTSE)

The Hamiltonian that describes the [Mg$_{0.14x}$Fe$_{(1-0.14x)}$][Ni$_{(1-x)}$Mg$_{(0.86x)}$Fe$_{(1+0.14x)}$]O$_4$ spinel, under an external field $h_{ex}$ within the Heisenberg model, may be written as follows:

$$H = -J_{AA}^{Fe^{3+}-Fe^{3+}} \sum_{(i,i')} S_i^z S_i'^z - J_{BB}^{Fe^{3+}-Fe^{3+}} \sum_{(i,j)} S_i^z S_j^z - J_{BB}^{Fe^{3+}-Ni^{2+}} \sum_{(i,j)} S_i^z \sigma_j^z$$
$$- J_{BB}^{Ni^{2+}-Ni^{2+}} \sum_{(i,j)} S_i^z S_j^z - J_{AB}^{Fe^{3+}-Fe^{3+}} \sum_{(i,j)} S_i^z S_j^z - J_{AB}^{Fe^{3+}-Ni^{2+}} \sum_{(i,j)} S_i^z \sigma_j^z$$
$$- \mu_B h_{ex} \left( g_F^S \sum_{i \in A} S_i^z - g_F^S \sum_{j \in B} S_j^z - g_N^S \sum_{j \in B} \sigma_j^z \right)$$

\[(2)\]

Where $S_i^z$ and $\sigma_j^z$ are spin vectors of $\vec{S}^z = S(S + 1)$ and $\sigma^z = \sigma(\sigma + 1)$ for Fe and Ni, respectively, $g_F^S = 2.091$ and $g_N^S = 2.183$ are the corresponding gyromagnetic factors. The symbol $<...>$ denotes
summation over nearest neighbours. $J_{AA}$, $J_{BB}$, and $J_{AB}$ are the intra- and the inter-sublattice exchange interactions in ferrimagnetic spinels.

The magnetization of the system is given by:

$$M = \mu_B \left( g^{Fe} \sum_{i \in A} \langle S_i^z \rangle - g^{Fe} \sum_{j \in B} \langle S_j^z \rangle - g^{Ni} \sum_{j \in B} \langle \sigma_j^z \rangle \right)$$  \hspace{1cm} (3)

Following the process in [12,13], we obtained the general expression of susceptibility for the collinear inverse ferrimagnetic spinel as follows.

$$\chi = \left( \frac{\mu_B^2}{3k_B T} \right) \left[ N_A^{Fe} g_A^2 S_A^2 + N_B^{Fe} g_B^2 S_B^2 + N_A^{Ni} g_B^2 S_A^2 + N_A^{Fe} g_A^2 \Gamma_{AB} S_A^2 \right.$$

$$+ \frac{N_B^{Fe} (N_B^{Fe} - 1) g_A^2 \Gamma_{BB} S_A^2}{(N_B^{Fe} + N_B^{Ni} - 1)}$$

$$+ \frac{N_B^{Fe} N_B^{Ni} g_A g_B \Gamma_{BB} S_A S_B}{(N_B^{Fe} + N_B^{Ni} - 1)}$$

$$- 2 \left( \frac{N_A^{Fe} N_B^{Ni} g_A g_B \Gamma_{AB} S_A S_B}{(N_A^{Fe} + N_A^{Ni})} \right) \right]$$

(4)

Where $N_{A(B)}$ are the number of magnetic ions both A and B sites, and $S = 5/2$, $\sigma = 1$ are the spin values of $Fe^{3+}$ and $Ni^{2+}$, respectively. The spin correlation functions $\Gamma_{AA}$, $\Gamma_{BB}$ and $\Gamma_{AB}$ in terms of powers of $\beta = 1 / k_B T$ ($k_B$ is the Boltzmann constant) and mixed powers of couplings have been computed in ref. [14].

$$\Gamma_{AA} = \sum_{q=1}^{7} \sum_{m=0}^{q} \sum_{n=0}^{q-m-q} \sum_{p=0}^{q-m-q} a(m,n,p,q) \frac{\beta^n}{B_{AB}^{m,n} B_{AA}^{p,q}}$$

$$\Gamma_{BB} = \sum_{q=1}^{7} \sum_{m=0}^{q} \sum_{n=0}^{q-m-q} \sum_{p=0}^{q-m-q} b(m,n,p,q) \frac{\beta^n}{B_{BB}^{m,n} B_{AA}^{p,q}}$$

$$\Gamma_{AB} = \sum_{q=1}^{7} \sum_{m=0}^{q} \sum_{n=0}^{q-m-q} \sum_{p=0}^{q-m-q} c(m,n,p,q) \frac{\beta^n}{B_{BB}^{m,n} B_{AB}^{p,q}}$$

(5)

Non-zero coefficients $a(m,n,p,q)$, $b(m,n,p,q)$, and $c(m,n,p,q)$ up to order 7 in $\beta = 1 / k_B T$ are given in Ref. [15].

A PA [M, N] to a magnetic susceptibility $\chi(T)$ is a rational fraction $P_M / Q_N$, with $P_M$ and $Q_N$, polynomials of orders $M$ and $N$ in $\beta = 1 / k_B T$ ($k_B$ is the Boltzmann constant) such that $\chi(\beta) \approx P_M / Q_N + O(\beta^{M+N+1})$, $M$ and $N$ are the degrees of the $P$ and $Q$ polynomials, respectively. Estimates of $T_C$ and $\gamma$ for Mg$_x$Ni$_{1-x}$Fe$_2$O$_4$ have been obtained using the PA method [16]. The simple pole corresponds to $T_C$ and the residues to the critical exponent $\gamma$.

3. Results and discussions.

The powerful Padé approximants method has been used to estimate the critical temperature, and the critical exponent associated with magnetic susceptibility. The locations of singularities in the PA method to the HTSEs of the magnetic susceptibility determine the Curie point.
The high temperature series expansions extrapolated with the Padé approximants method [12-14] is shown to be a convenient method to provide valid estimations of the critical temperatures for real system. By applying this method to the magnetic susceptibility \( \chi (x) \), we have estimated the critical values of \( T_C \) for each dilution \( x \) in the \([\text{Mg}_{(0.14x)}\text{Fe}_{(1-0.14x)}]_A[\text{Ni}_{(1-x)}\text{Mg}_{(0.86x)}\text{Fe}_{(1-0.14x)}]_B\text{O}_4 \) system. The values of \( T_C \) obtained by HTSE are in good agreement with experiment measurements. The estimated magnetic susceptibility exponents are \( \gamma = 1.32 \) for \( \text{CoFe}_2\text{O}_4 \) and \( \gamma = 1.27 \) for \( \text{MgFe}_2\text{O}_4 \).

Figure 1 shows the phase diagram of the \( \text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4 \) systems. It contains the ferrimagnetic and paramagnetic (PM) phases, in the range \( 0 \leq x \leq 1 \), which cover the range between the opposite pure systems \( \text{NiFe}_2\text{O}_4 \) and \( \text{MgFe}_2\text{O}_4 \). The experimental results obtained by magnetic measurements [10] are also presented in Figure 1. They are in good agreement with theoretical results.

Table 2. The values of critical temperature obtained by HTSE and the exchanges integrals \( J_{AB} \), \( J_{BB} \) and \( J_{AA} \) for the ferrites \( \text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4 \) \( (0 \leq x \leq 1) \) with the cation distribution \([\text{Mg}_{(0.14x)}\text{Fe}_{(1-0.14x)}]_A[\text{Ni}_{(1-x)}\text{Mg}_{(0.86x)}\text{Fe}_{(1-0.14x)}]_B\text{O}_4 \).

| \( x \) | Distribution ion in A site [9] | Distribution ion in B site [9] | \( J_{BB}(K) \) | \( J_{AB}(K) \) | \( J_{AA}(K) \) | \( T_C(K) \) exp.[6] | \( T_C(K) \) HTSE |
|---|---|---|---|---|---|---|---|
| 0 | (Fe\(_1\))\(_A\) | (Ni\(_1\)Fe\(_1\))\(_B\) | ---- | -27.70 | -14.00 | 860 | 866 |
| 0.1 | (Fe\(_{0.96}\)Mg\(_{0.04}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.06}\)Fe\(_{0.94}\))\(_B\) | -0.80 | -25.96 | -13.61 | ---- | 850 |
| 0.2 | (Fe\(_{0.97}\)Mg\(_{0.03}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.07}\)Fe\(_{0.93}\))\(_B\) | -1.70 | -24.26 | -13.22 | 831 | 838 |
| 0.3 | (Fe\(_{0.94}\)Mg\(_{0.04}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.25}\)Fe\(_{0.75}\))\(_B\) | -2.44 | -22.59 | -12.84 | ---- | 827 |
| 0.4 | (Fe\(_{0.84}\)Mg\(_{0.16}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.34}\)Fe\(_{0.66}\))\(_B\) | -3.02 | -20.97 | -12.47 | 809 | 815 |
| 0.5 | (Fe\(_{0.9}\)Mg\(_{0.1}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.43}\)Fe\(_{0.57}\))\(_B\) | -3.45 | -19.39 | -12.10 | ---- | 802 |
| 0.6 | (Fe\(_{0.91}\)Mg\(_{0.09}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.51}\)Fe\(_{0.49}\))\(_B\) | -3.72 | -17.84 | -11.74 | 786 | 793 |
| 0.7 | (Fe\(_{0.9}\)Mg\(_{0.09}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.6}\)Fe\(_{0.4}\))\(_B\) | -3.84 | -16.33 | -11.39 | ---- | 774 |
| 0.8 | (Fe\(_{0.88}\)Mg\(_{0.12}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.68}\)Fe\(_{0.32}\))\(_B\) | -3.80 | -14.86 | -11.03 | 759 | 763 |
| 0.9 | (Fe\(_{0.87}\)Mg\(_{0.13}\))\(_A\) | (Ni\(_{1}\)Mg\(_{0.74}\)Fe\(_{0.26}\))\(_B\) | -3.60 | -13.43 | -10.69 | ---- | 738 |
| 1 | (Fe\(_{0.8}\)Mg\(_{0.1}\))\(_A\) | (Mg\(_{0.82}\)Fe\(_{1.18}\))\(_B\) | -3.24 | -12.04 | -10.35 | 719 | 725 |
Figure 1 Magnetic phase diagram for the Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ ferrite with [Mg$_{(0.14x)}$Fe$_{(1-0.14x)}$]$_A$[Ni$_{(1-x)}$Mg$_{(0.86x)}$Fe$_{(1+0.14x)}$]$_B$O$_4$ cations distribution

4. Conclusions

The general expression of exchanges integrals $J_{AB}$, $J_{BB}$ and $J_{AA}$ of the cation distribution [Mg$_{(0.14x)}$Fe$_{(1-0.14x)}$]$_A$[Ni$_{(1-x)}$Mg$_{(0.86x)}$Fe$_{(1+0.14x)}$]$_B$O$_4$ are given. The magnetic properties of spinel ferrites depend on the magnetic interaction and cation distribution in the two sublattices i.e. tetrahedral (A) and octahedral (B) lattice sites.

The HTSEs combined with the Padé approximants methods are applied to the [Mg$_{(0.14x)}$Fe$_{(1-0.14x)}$]$_A$[Ni$_{(1-x)}$Mg$_{(0.86x)}$Fe$_{(1+0.14x)}$]$_B$O$_4$ system, to obtained the critical temperature for different values of $x$. The value of critical exponent associated with magnetic susceptibility has been estimated.

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