Journal of Magnetism and Magnetic Materials 322 (2010) 301–304

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetic properties of $MnCr_2O_4$ nanoparticle

R. Masrour [a,b,*], M. Hamedoun [c,d], A. Benyoussef [b,c,d]

[a] Solid State Physics Laboratory, Sidi Mohammed Ben Abdellah University, Sciences Faculty, BP 1796, Fez, Morocco
[b] LMPHE, Faculté des Sciences, Université Mohamed V, Rabat, Morocco
[c] Institute for Nanomaterials and Nanotechnologies, Rabat, Morocco
[d] Académie Hassan II des Sciences et Techniques, Rabat, Morocco

ARTICLE INFO

Article history:
Received 19 March 2009
Available online 12 September 2009

PACS:
75.30.Et
75.40.Cx
74.25.Ha
75.30.Cr

Keywords:
$Mn_xZn_{1-x}Cr_2O_4$
Probability law
Exchange energy
High-temperature series expansion
Padé approximant
Magnetic phase diagram
Critical exponent

ABSTRACT

The exchange interactions and the magnetic exchange energies are calculated by using the mean field theory and the probability law of $Zn_{1-x}Mn_xCr_2O_4$ nanoparticles. The high-temperature series expansions have been applied in the spinels $Zn_{1-x}Mn_xCr_2O_4$ systems, combined with the *Padé* approximants method, to determine the magnetic phase diagram, i.e. T_C versus dilution x. The critical exponent associated with the magnetic susceptibility (γ) is deduced. The obtained value of γ is insensitive to the dilution ratio x and may be compared with other theoretical results based on the 3D Heisenberg model.

1. Introduction

Ferrites are ceramic materials formed by reacting metal oxides into magnetic materials. These are soft magnetic materials that can be both easily magnetized and demagnetized, so that it can store or transfer magnetic energy in alternating or other changing wave forms (i.e., sine, pulse, square, etc.). According to their structure, spinel-type ferrites are natural superlattices. It has tetrahedral *A* site and octahedral *B* site in AB_2O_4 crystal structure. It shows various magnetic properties depending on the composition and cation distribution. Various cations can be placed in *A* and *B* sites to tune its magnetic properties. Depending on *A* and *B* site cations, it can exhibit ferrimagnetic, antiferromagnetic, spin glass, and paramagnetic behavior [1,2]. Due to their remarkable behavior of magnetic and electric properties they are subjects of intense theoretical and experimental investigation for application purpose [2–6].

The system $Zn_{1-x}Mn_xCr_2O_4$ is particularly attractive because competitive antiferromagnetic interactions Cr–Cr, Mn–Cr, and Mn–Mn are present [7]. The two normal spinels $MnCr_2O_4$ and $ZnCr_2O_4$ form a solid solution throughout the whole range of composition: $MnCr_2O_4$ is a non-collinear ferrimagnet with T_C=43 K [8] while $ZnCr_2O_4$ orders antiferromagnetically with T_N=16 K [9]. Ledang et al. [8] reported NMR and low a.c. susceptibility of the $Zn_{1-x}Mn_xCr_2O_4$ mixed spinel system and for $x>0.6$ observed unidirectional anisotropy and remanent magnetization. The existence of a spin-glass state was proposed for a narrow range of compositions.

In this work, the values of the exchange interactions are calculated, by a probability law for the $MnCr_2O_4$ nanoparticle and $ZnCr_2O_4$ by using the mean field theory and probability law. The probability law is applied to the ferrite spinels $Zn_{1-x}Mn_xCr_2O_4$ systems to determine the exchange interaction J_{Mn-Cr} in the range of dilution $0\le x\le 1$. The results obtained are deduced by using the experimental results [10,11]. The *Padé* approximant (PA) [12] analysis of the high-temperature series expansions (HTSE) of the correlation functions has been shown to be a useful method for the study of the critical region [13,14]. We have used this technique to determine the critical temperatures $T_C(T_{FerriM})$ or the freezing temperature T_{SG} and the critical exponent γ associated with the magnetic susceptibility $\chi(T)$. The series expansions of the susceptibility $\chi(T)$ have been derived to the seventh order in the reciprocal temperature for spinels lattices including both nearest-neighboring (*nn*) and next-nearest-neighboring (*nnn*) interactions in the Heisenberg model [15]. We have applied this method to the spinel lattice. Estimate values of the

* Corresponding author. Tel.: +212 064317525.
E-mail address: rachidmasrour@hotmail.com (R. Masrour).

0304-8853/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jmmm.2009.08.051

$T_C(T_{FerriM})$ or T_{SG} and critical exponent γ for the systems $Zn_{1-x}Mn_xCr_2O_4$ are given in the range order $(0 \le x \le 0.1)$ and $(0.9 \le x \le 1)$.

2. Theory

2.1. Calculation of the values of the exchange integrals

2.1.1. Mean field theory

Starting with the well-known Heisenberg model, the Hamiltonian of the system is given by

$$H = -2\sum_{i,j} J_{ij}\vec{S}_i\vec{S}_j \quad (1)$$

where J_{ij} is the exchange integral between the spins situated at sites i and j. $\vec{S}_i$ is the spin operator localized at the site i. In this work, we consider the nearest neighbouring (nn) and next nearest neighbouring (nnn) interactions. To deduce the value of exchange interaction of $MnCr_2O_4$ and $ZnCr_2O_4$, I have used the expression of the Néel temperature T_N in order phase given in Ref. [16].

Using the experimental values of T_N obtained by Bhowmiket al. [10] for the $MnCr_2O_4$ nanoparticles and by Leccabue et al. [11] for the $ZnCr_2O_4$ to determine the exchange interactions J_{Mn-Cr} in the $MnCr_2O_4$ system, and the nearest neighbor and the next-neighbour super-exchange interaction $J_1(x)$ and $J_2(x)$ respectively, the intra-planar and the inter-planar interactions are deduced and the corresponding classical exchange energy for magnetic structure for the $ZnCr_2O_4$ system. The obtained results are given in Tables 1 and 2.

2.1.2. Probability law

In the last work, the authors [17] used the probability law to calculate the exchange integrals. In this work, we have applied the probability law in the diluted spinels systems $Zn_{1-x}Mn_xCr_2O_4$, only the random placement of the ions A and B leads to the spatial fluctuations of the signs and magnitudes of the super-exchange interaction between the magnetic ions A and B. Due to the nature of dilution problem we choose a probability law permitting us to determine exchange integral $J_{AB}(x)$ for each concentration x. The exchange integral of the opposite pure compound AB_2X_4 of the bound random spinel is denoted J_{AB}. The occupation probability $p(i)$ of the two ions A or B induced in the interaction is $p(i) = C_n^i x^{n-i}(1-x)^i$, where n is the total number of lattice sites inside a sphere with the volume $(4/3)\pi R_i^3$ (R_i denotes the distance between the sites i and j, n is the number of cations the Pth coordination sphere around a given cation chosen as the central one, for this structure $n=3$), while i varies from 0 to 3. The exchange integral for such an occupation is assumed to be $J_{AB}^i = (J_A^{n-i}J_B^i)^{1/n}$. The expression obtained is [18]:

$$J_{AB}(x) = \sum_{i=0}^{3} C_3^i x^{3-i}(1-x)^i (J_A^{3-i}J_B^i)^{1/3} \quad (2)$$

where J_{AB} correspond to the exchange interactions of the opposite pure systems AB_2X_4.

$Zn_{1-x}Mn_xCr_2O_4$ is diluted ferrimagnetic spinels $MnCr_2O_4$ with the value of the exchange integral J_{AB}, J_{BB} and J_{AA} being given by Ref. [19]. The magnetic exchange energies E_i ($i=1-3$) are deduced using the expressions $E_1=E_2=5J_{AA}-3J_{AB}$ and $E_3=3J_{BB}-3J_{AB}$ given by Ref. [20].

2.2. High-temperature series expansions

In order to deduce the expression of the susceptibility of the system with two sublattices, the Hamiltonian of the Heisenberg with extern field h_{ex} may be put in the form

$$H = -2J_{AA}\sum_{\langle i,i'\rangle}\vec{S}_i\vec{S}_{i'} - 2J_{BB}\sum_{\langle j,j'\rangle}\vec{\sigma}_j\vec{\sigma}_{j'} - 2J_{AB}\sum_{\langle i,j\rangle}\vec{S}_i\vec{\sigma}_j - \mu_B h_{ex}(g_A\sum_i S_i^z - g_B\sum_j \sigma_j^z) \quad (3)$$

where $\vec{S}$ and $\vec{\sigma}$ are spin operators of ions in sublattice A and B, respectively. g_A and g_B are the corresponding gyromagnetic factors. The symbol $\langle \dots \rangle$ denotes summation over nearest neighbors. J_{AA}, J_{BB} and J_{AB} are the intra- and the inter-sublattice exchange interactions in ferrimagnetic spinels.

The susceptibility for the collinear normal ferrimagnetic spinel is as follows:

$$\chi = \frac{\mu_B^2}{3k_BT}(N_A g_A^2\overline{S}^2 + N_B g_B^2\overline{\sigma}^2 - g_A^2\sum_{i\neq i'}\langle\vec{S}_i\vec{S}_{i'}\rangle - g_B^2\sum_{j\neq j'}\langle\vec{\sigma}_j\vec{\sigma}_{j'}\rangle - 2g_Ag_B\sum_{i,j}\langle\vec{S}_i\vec{\sigma}_j\rangle) \quad (4)$$

where (N_A, N_B) and ($S=5/2$, $\sigma=3/2$) are the number of ion and the spin value of each type of spin, respectively.

Finally, we obtain simple form

$$\chi = \frac{\mu_B^2}{3k_BT}(N_A g_A^2\overline{S}^2 + N_B g_B^2\overline{\sigma}^2 - N_A g_A^2\gamma_{AA} - N_B g_B^2\gamma_{BB} - 2N_B g_A g_B\gamma_{BA}) \quad (5)$$

Following the procedure in Refs. [20–27], we compute the expressions of spin correlation functions γ_{AA}, γ_{BB} and γ_{AB} in terms of power of $\beta=1/k_BT$ (k_B is the Boltzmann's constant) and mixed powers of $J_1 = 2J_{BB}\,\overline{\sigma}^2$, $J_2 = 2J_{AB}\,\overline{S}\overline{\sigma}$ and $J_3 = 2J_{AA}\,\overline{S}^2$ with $\overline{S} = \sqrt{S(S+1)}$,

$$\overline{\sigma} = \sqrt{\sigma(\sigma+1)} \quad (6)$$

Table 1
The different sizes L (nm), the Néel temperature T_N (K) and the values of the exchange interactions $|J_{AB}(K)/k_B|$ of $MnCr_2O_4$ nanoparticle.

L (nm) [10]	T_N (K) [10]	$\lvert J_{AB}$ (K)$/k_B\rvert$
11	52	6.93
16	47	6.26
19	46	6.13
Bulk	45	6.00

Table 2
The Curie—Weiss temperature θ_P (K), the Néel temperature T_N (K), the values of the first, second, intra-plane, inter-plane exchange integrals and the energy of $ZnCr_2O_4$.

θ_P (K) [11]	T_N (K) [11]	J_1/k_B (K)	J_2/k_B (K)	J_{aa}/k_B (K)	J_{ab}/k_B (K)	J_{ac}/k_B (K)	$(J_{ab}+J_{ac})/J_{aa}$ (K)	$\lvert E\rvert/k_B\,S^2$ (K)
−424	16	−10.66	−6.93	−21.32	−98.08	−27.72	5.90	−147.12