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Magnetic phase diagrams of the spinels $AB_{2x}Ga_{2-2x}O_4$ (A = Zn, Co; B = Al, Cr) systems

M. Hamedoun [a,*], R. Masrour [a], K. Bouslykhane [a], A. Hourmatallah [a,b], N. Benzakour [a]

[a] *Laboratoire de Physique du Solide, Université Sidi Mohammed Ben Abdellah, Faculté des sciences Dhar Mahraz, BP 1796 Fes, Morocco*
[b] *Equipe de Physique du Solide, Ecole Normale Superieure, BP 5206 Bensouda, Fes, Morocco*

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Abstract

The magnetic properties of the spinels $CoAl_{2x}Ga_{2-2x}O_4$ and $ZnCr_{2x}Ga_{2-2x}O_4$ systems in the range $0 \le x \le 1$ have been studied by mean field theory and high-temperature series expansions. By using the first theory, we have evaluated the nearest neighbour and the next-neighbour super-exchange interaction $J_1(x)$ and $J_2(x)$, respectively, for the first systems in the range $0 \le x \le 1$ and $J_1(x=1)$, $J_2(x=1)$ for the second system. The intra-planar and the inter-planar interactions are deduced. The corresponding classical exchange energy for magnetic structure is obtained for the first system.

The second theory have been applied in the spinels $CoAl_{2x}Ga_{2-2x}O_4$ and $ZnCr_{2x}Ga_{2-2x}O_4$ systems, combined with the Padé approximants method, we have obtained the magnetic phase diagrams (T_N versus dilution x) in the range $0 \le x \le 1$. The obtained theoretical results are in agreement with experimental ones obtained by magnetic measurements and Mössbauer spectroscopy. The threshold percolation in the second system is $x_p \approx 0.4$. The critical exponents associated with the magnetic susceptibility (γ) and the correlation lengths (ν) are deduced in the range $0 \le x \le 1$.

Keywords: Spinel; Critical temperature; Exchange interactions; High-temperature series expansions; Padé approximants; Critical exponents; Magnetic phase diagram; Percolation threshold

1. Introduction

Materials with spinel structures, with the formula AB_2X_4 are of continuing interest because of their wide variety of physical properties and potential applications in nanoscience and technology. This is essentially related to (i) the existence of two types of crystallographic sublattices, tetrahedral (A) and octahedral (B), available for the metal ions; (ii) the great flexibility of the structure in hosting various metal ions, differently distributed between the two sublattices, with a large possibility of reciprocal substitution between them. Solid solutions of thiospinels and selenospinels have received considerable attention for their interesting electrical and magnetic properties, which can vary greatly as a function of composition [1–6].

In the $CoAl_{2x}Ga_{2-2x}O_4$ system, the Co^{2+} site distribution varies with dilution x, exhibiting the same trend as was observed for the previous system, i.e., the Co^{2+} octahedral occupation increases with the gallium content, giving rise to concomitant AA, BB and AB interactions. The antiferromagnetic spinels $CoAl_2O_4$ ($T_N = 5$ K) and $CoGa_2O_4$ ($T_N = 10$ K) have studied extensively [7]. In the system $ZnCr_{2x}Ga_{2-2x}O_4$ magnetic Cr^{3+} ions occupy octahedral sites only and the interactions are strongly antiferromagnetic $ZnCr_2O_4$ ($T_N = 13$ K; $\theta_P = -392$ K) [8]. A spin glass phase is predicted for such an antiferromagnetic octahedral spinel sublattice when a sufficient number of non-magnetic substitutional impurities are introduced [9]. This related to the removal of the high-ground state degeneracy present in the pure lattice itself in which nearest neighbour interactions prevail.

We have calculated the first and the second nearest neighbours exchange interactions $J_1(x)$ and $J_2(x)$ on the basis of magnetic results in $CoAl_{2x}Ga_{2-2x}O_4$ for $0 \le x \le 1$ [7] and $J_1(x=1)$, $J_2(x=1)$ for $ZnCr_{2x}Ga_{2-2x}O_4$ system [10]. The values of the intra-plane and inter-plane interactions J_{aa}, J_{ab} and J_{ac}; respectively, are deduced from the values of $J_1(x)$ and $J_2(x)$ for $0 \le x \le 1$. The interaction energy of the magnetic structure is

* Corresponding author.
E-mail address: hamedoun@hotmail.com (M. Hamedoun).

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obtained for the first system. In recent works [1,2], we have used the high-temperature series expansions (HTSE) to study the thermal and disorder variation of the short-range order (SRO) in the particular B-spinel $ZnCr_{2x}Ga_{2-2x}S_4$ compound. The Padé approximant (PA) [11] analysis of the HTSE of the correlation length has been shown to be a useful method for the study of the critical region [12,13]. The model that we used in this present work is valid in the case of a spinel structure. The percolation threshold is deduced in the $ZnCr_{2x}Ga_{2-2x}O_4$ system. We have used the HTSE technique to determine the Néel temperature T_N or the freezing temperature T_{SG} and the critical exponents γ and ν associated with the magnetic susceptibility χ and the correlation length ξ, respectively, in the range $0 \le x \le 1$ for the two systems.

2. Theoretical method

2.1. Calculation of the values of the exchange integrals from mean field approximation

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

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

where J_{ij} is the exchange integral between the spins situated at sites i and j. $\vec{S}_i$ is the spin operator of the spin localised at the site i. In this work we consider the nearest neighbour (nn) and next nearest neighbour (nnn) interactions J_1 and J_2, respectively.

$$H = J_1\sum_{i,j}\vec{S}_i\vec{S}_j - J_2\sum_{i,k}\vec{S}_i\vec{S}_k \tag{2}$$

The sums over ij and ik include all (nn) and (nnn) pair interactions, respectively. In the case of spinels containing the magnetic moment only in the octahedral sublattice, the mean field approximation leads to a simple relations between the φ angle of helimagnetic ordering and the Néel temperature T_N, respectively, and the considered two exchange integrals J_1 and J_2.

The Néel temperature T_N and the φ angle of helimagnetic ordering are given by Hamedoun et al. [14]:

$$T_N = -\frac{5}{2K_B}[2J_1 + 4J_2] \tag{3}$$

$$\cos(\varphi) = -\frac{1}{4}\left[\frac{J_1 + 2J_2}{J_2}\right] \tag{4}$$

where K_B is the Boltzmann constant.

Using the experimental values of T_N and φ obtained by magnetic measurement for the spinel $CoAl_{2x}Ga_{2-2x}O_4$ [7] and $ZnCr_{2x}Ga_{2-2x}O_4$ [10]. We have deduced the values of exchange integrals $J_1(x)$ and $J_2(x)$. From these values, we have derived the variation of the intra-plane coupling and the coupling between nearest and next-nearest plane with the concentration x in the spinel $CoAl_{2x}Ga_{2-2x}O_4$ system with $0 \le x \le 1$. The values obtained of the exchange integrals are $J_1(x=1) = -1.3$ K, $J_2(x=1) = -0.65$ K for the $ZnCr_{2x}Ga_{2-2x}O_4$ system.

The obtained optimums values of $J_1(x)$ and $J_2(x)$ are given in Table 1. The values of corresponding classical exchange energy for the magnetic structure [14] and the values of the intra-plane and inter-plane interactions $J_{aa} = 2J_1$, $J_{ab} = 4J_1 + 8J_2$ and $J_{ac} = 4J_2$, respectively, are given in the same table in the range $0 \le x \le 1$ for the first system.

2.2. High-temperature series expansions

In this section we shall derive the high-temperature series expansions (HTSE) for both the zero field magnetic susceptibility χ to order six in β. The relation ship between the magnetic susceptibility per spin and the correlation functions may be expressed as follows:

$$\chi(T) = \frac{\beta}{N}\sum_{ij}\langle\vec{S}_i\vec{S}_j\rangle \tag{5}$$

where $\beta = 1/K_BT$ and N is the number of magnetic ion and

$$\langle S_iS_j\rangle = \frac{TrS_iS_j\,e^{-\beta H}}{Tr\,e^{-\beta H}}$$

is the correlation function between spins at sites i and j.

In ref. [1], a relation between the susceptibility and the three first correlation functions is given in the case of the B-spinel lattice with a particular ordering vector $Q = (0,0,k)$. In the ferromagnetic case we get $k = 0$. The high temperature series expansion of $\chi(T)$ gives the function:

$$\chi(T) = \sum_{m=-n}^{n}\sum_{n=1}^{6} a(m,n)y^m\tau^n \tag{6}$$

The high temperature series expansion of ξ^2 gives the function:

$$\xi^2(T) = \sum_{m=-n}^{n}\sum_{n=1}^{6} b(m,n)y^m\tau^n \tag{7}$$

where $y = J_2/J_1$ and $\tau = 2S(S+1)J_1/K_BT$. The series coefficients $a(m,n)$ and $b(m,n)$ are given in ref. [15].

Table 1
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 $CoAl_{2x}Ga_{2-2x}O_4$ as a function of dilution x

x	θ_P (K) [7]	T_N (K) [7]	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)	$\lvert E\rvert/K_BS^2$ (K)
1.00	97	5	−0.50	−0.25	−1.0	−4.00	−1.0	6.0
0.62	70	8	−0.80	−0.40	−1.6	−6.40	−1.6	9.6
0.50	65	8	−0.80	−0.40	−1.6	−6.40	−1.6	9.6
0.25	55	8	−0.80	−0.40	−1.6	−6.40	−1.6	9.6
0.00	65	10	−1.00	−0.50	−2.0	−8.00	−2.0	12.00