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The magnetic properties of oxide spinel $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ solid solutions

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ABSTRACT

The exchange interactions (J_{BB} and J_{AB} are the intra and the inter-sublattice exchange interactions between neighbouring spins, respectively) are obtained by using the general expressions of canting angle and critical temperature obtained by mean field theory of $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$. The expression of magnetic energy of $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ is obtained for different spin configurations and dilution x. The saturation magnetisation of $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ is obtained with different values of dilution x. The magnetic phase diagram of $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ materials is obtained by high temperature series expansions (HTSEs). The critical exponent associated with the magnetic susceptibility of $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ is deduced.

1. Introduction

The crystallographic and magnetic characteristics of the lithium ferrite aluminates have been investigated [1,2] in an attempt to understand the site preference for Al^{3+} and the magnetic interactions in spinel lattice. The Mössbauer spectroscopic studies [3] of lithium aluminates have shown the central quadrupole doublet superimposed on a magnetic sextet and its intensity was sensitive to Al concentration. The spinel ferrites with S-block ions studied here are lithium ferrite [4]. The lithium ferrite of the composition $Li_{0.5}Fe_{2.5}O_4$ adopts an inverse spinel structure in which all the Li^+ ions and 3/5 of all Fe^{3+} ions occupy octahedral B-sites whilst the remaining Fe^{3+} ions occupy tetrahedral A-sites [5–11]. The material is extensively studied due to its technologically desirable electric and magnetic properties that are susceptible to modification on introducing suitable cationic substitutes for the Fe^{3+} ions at the *A*- or/and *B*-sub-lattice [1–7]. The magnitude and sign of the exchange constants have been examined using Anderson's theory of super-exchange [12]. The magnitudes of the transfer integrals for different exchange routes have been generally found to be in agreement with the chemical theory of covalency [12]. The $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ system exhibits canted spin structure and a central paramagnetic doublet was found superimposed on magnetic sextet in the Mössbauer spectra ($x>0.5$) [13].

In this work, we have used a critical temperature $T_C(K)$ and canting angle (α) to determine the J_{AB} and J_{BB} exchange interactions for a diluted spinels system $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$. The obtained results are given in Table 1 for $0 \le x \le 0.8$. The ferrimagnetic magnetic energy was calculated using the Becke's three parameter density functional [14]. The saturation magnetisation in cation $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ is given (see Fig. 1).

The High temperatures series expansion (HTSEs) combined with the *Padé* approximants methods are used to determine the critical temperatures of $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ systems. By applying this method to the magnetic susceptibility $\chi(T)$, we have estimated the critical temperature T_C. The value of critical exponents associated with the magnetic susceptibility is obtained.

2. Theories

2.1. Calculation of the values of the exchange integrals

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

$$H=-2J_{AA}\sum_{(i,i')}\vec{S}_i\vec{S}_{i'}-2J_{BB}\sum_{(j,j')}\vec{\sigma}_j\vec{\sigma}_{j'}-2J_{AB}\sum_{(i,j)}\vec{S}_i\vec{\sigma}_j-\mu_B h_{ex}\left(g_A\sum_i S_i^z-g_B\sum_j \sigma_j^z\right) \quad (1)$$

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Table 1
Critical temperature obtained by experiment and those obtained by mean field theory (MFT), the canting angle (α), the exchange interactions $J_{AB}(x)$, $J_{BB}(x)$, and $J_{AB}(x)/J_{BB}(x)$ for $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$.

x	≈ α [13]	$T_C(K)$ [13]	$J_{AB}(x)$	$J_{BB}(x)$	$T_C(K)$ MFT	$J_{AB}(x)/J_{BB}(x)$	$J_{AB}(x)/J_{BB}(x)$ [13]
0	0	945	61.40	40.94	943.67	1.50	–
0.4	17	662	74.84	55.31	658.38	1.35	1.36
0.5	26	572	79.80	63.47	567.14	1.28	1.25
0.6	27	530	95.70	78.32	522.30	1.22	1.21
0.8	33	398	173.80	159.53	363.68	1.09	1.08

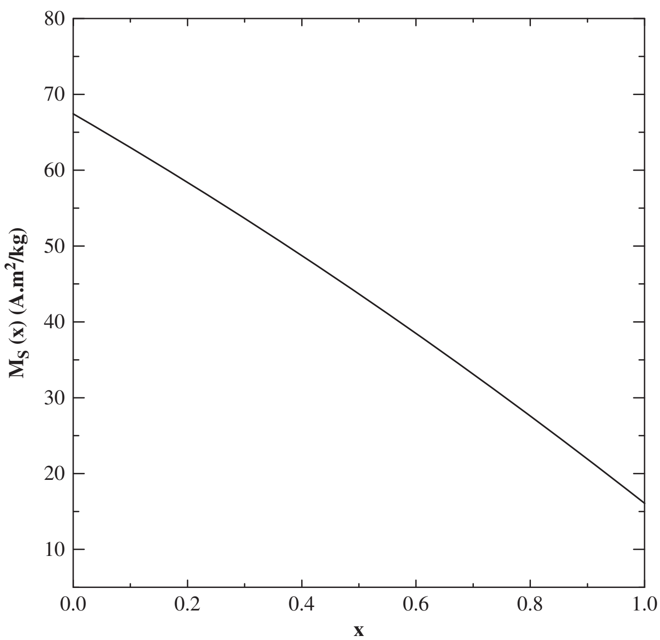

Fig. 1. Saturation magnetisation versus of dilution x for $[Fe^{3+}_{1-0.5x}Al^{3+}_{0.5x}]_A[Li^{+}_{0.5}Fe^{3+}_{1.5(1-x)}Cr^{3+}_{x}Al^{3+}_{0.5x}]_BO_4^{2-}$.

where $\vec{S}$ and $\vec{\sigma}$ are spin vectors of magnitudes $\vec{S}^2=S(S+1)$ and $\vec{\sigma}^2=\sigma(\sigma+1)$ in sublattice A and B respectively. g_A and g_B are the corresponding gyromagnetic factors and μ_B is the Bohr magneton. The values of gyromagnetic factors g_A and g_B are $g_{Fe}=2.1$ and $g_{Cr}=1.98$, respectively. h_{ex} is an external magnetic field (z direction) introduced in order to provide an easy determination of the magnetic susceptibility. The first summation is over all spin pairs nearest-neighbours in sublattice A, the second is over all spin pairs nearest-neighbours in sublattice B and the third is between all spin pair nearest-neighbours in A and B. J_{AA}, J_{BB} and J_{AB} are the intra and the inter-sublattice exchange interactions between neighbouring spins. In this work, we considered $J_{AA}=0$.

The magnetisation of the ferrimagnetic spinels systems is:

$$\vec{M}=\vec{M}_A-\vec{M}_B=\mu_B\left(g_A\sum_i\langle\vec{S}_i^z\rangle-g_B\sum_j\langle\vec{\sigma}_j^z\rangle\right). \quad (2)$$

Therefore, according to the mean field theory the magnetisation contributed by Fe^{3+} sublattice $\vec{M}_A$ is:

$[Fe^{3+}_{1-0.5x}Al^{3+}_{0.5x}]_A[Li^{+}_{0.5}Fe^{3+}_{1.5(1-x)}Cr^{3+}_{x}Al^{3+}_{0.5x}]_BO_4^{2-}$

$$\begin{aligned}\vec{M}_A&=NS_Ag_{Fe^{3+}}\mu_BB_{S_A}(S_Ag\mu_B(h_{ex})_{Fe}/k_BT)\\&\approx S_A(S_A+1)\{N(g_{Fe^{3+}}\mu_B)^2(h_{ex})_{Fe}-6J_{AB}(\vec{M}_{B_1}+\vec{M}_{B_2})-4J_{AA}\vec{M}_A\}/k_BT\end{aligned} \quad (3)$$

where $(h_{ex})_{Fe}$ is the effective field applied on Fe^{3+} local moment $B_{S_A}(S_Ag\mu_BH_{Fe}/k_BT)$ is the Brillouin function, $\vec{M}_{B_1}$ is the corresponding magnetisation for one Fe^{3+} sublattice B_1 and $\vec{M}_{B_2}$ for the other B_2.

$$\begin{aligned}\vec{M}_{B_1}&=NS_Bg_{Cr^{3+}}\mu_BB_{S_B}(S_Bg\mu_B(h_{ex})_{Cr}/k_BT)\\&\approx S_B(S_B+1)\{N(g_{Cr^{3+}}\mu_B)^2(h_{ex})_{Cr}-2J_{BB}(\vec{M}_{B_2})-6J_{AB}\vec{M}_A\}/3k_BT\end{aligned} \quad (4)$$

where $(h_{ex})_{Cr}$ is the effective field felt by one Cr^{3+} sublattice B_2.

$$\begin{aligned}\vec{M}_{B_2}&=NS_Bg_{Cr^{3+}}\mu_BB_{S_B}(S_Bg\mu_B(h_{ex})_{Cr}/k_BT)\\&\approx S_B(S_B+1)\{-N(g_{Cr^{3+}}\mu_B)^2(h_{ex})_{Cr}-2J_{BB}(\vec{M}_{B_1})-6J_{AB}\vec{M}_A\}/3k_BT\end{aligned} \quad (5)$$

k_B is the Boltzmann's constant. $(h_{ex})_{Cr}$ is the effective field applied for the other Cr^{3+} sublattice B_2. After some simple treating of Eqs. (3)–(5) give:

$$\begin{aligned}&(1+4J_{AA}S_A(S_A+1)/3k_BT)\vec{M}_A+6J_{AB}S_A(S_A+1)(\vec{M}_{B_1}+\vec{M}_{B_2})/3k_BT\\&\quad=N(g\mu_B)^2S_A(S_A+1)h/3k_BT\end{aligned} \quad (6)$$

$$\begin{aligned}&-6J_{AB}S_B(S_B+1)\vec{M}_A/3k_BT-\vec{M}_{B_1}-2J_BS_B(S_B+1)\vec{M}_{B_2}/3k_BT\\&\quad=N(g\mu_B)^2S_B(S_B+1)h/3k_BT\end{aligned} \quad (7)$$

$$\begin{aligned}&-6J_{AB}S_B(S_B+1)\vec{M}_A/3k_BT-\vec{M}_{B_2}-2J_BS_B(S_B+1)\vec{M}_{B_1}/3k_BT\\&\quad=N(g\mu_B)^2S_B(S_B+1)h/3k_BT\end{aligned} \quad (8)$$

The transition is at the temperature at which the determinant of the coefficient matrix is zero. It is:

$$\begin{vmatrix}(1+4J_{AA}S_A(S_A+1)/3k_BT) & 6J_{AB}S_A(S_A+1)/3k_BT & 6J_{AB}S_A(S_A+1)/3k_BT\\ -6J_{AB}S_B(S_B+1)/3k_BT & -1 & -2J_{BB}S_B(S_B+1)/3k_BT\\ -6J_{AB}S_B(S_B+1)/3k_BT & -2J_{BB}S_B(S_B+1)/3k_BT & -1\end{vmatrix}=0 \quad (9)$$

The transition temperature $T_C(K)$ is:

$$T_C(K)\simeq\frac{\left(-2J_{AA}S_A(S_A+1)-J_{BB}S_B(S_B+1)+\begin{pmatrix}(-J_{BB}S_B(S_B+1)+2J_{AA}S_A(S_A+1))^2\\+72J_{AB}^2S_A(S_A+1)S_B(S_B+1)\end{pmatrix}^{0.5}\right)}{3k_B} \quad (10)$$

When Fe is partially substituted by Cr ions, the magnetism of A sublattice is weakend, which can be viewed as an effective decrease of the exchange energies. The critical temperature $T_C(K)$ of $Li_{0.5}Fe_{2.5-2x}Al_xCr_xO_4$ is:

$$T_C(K)\simeq\frac{\left(-2J_{AA}S_A(S_A+1)(1-x)^2-J_{BB}S_B(S_B+1)+\begin{pmatrix}(-J_BS_{BB}(S_B+1)+2J_{AA}S_A(S_A+1)(1-x)^2)^2\\+72J_{AB}^2S_A(S_A+1)(1-x)^2S_B(S_B+1)\end{pmatrix}^{0.5}\right)}{3k_B} \quad (11)$$

where $S_A=S_{Fe}^{3+}=5/2$ and $S_B=S_{Cr}^{3+}=3/2$.