Magnetic behavior of the oxide spinels: 
Li$_{0.5}$Fe$_{2.5-2x}$Al$_x$Cr$_x$O$_4$

U N TRIVEDI, K B MODI and H H JOSHI
Department of Physics, Saurashtra University, Rajkot 360 005, India

Abstract. In order to study the effect of substitution of Fe$^{3+}$ by Al$^{3+}$ and Cr$^{3+}$ in Li$_{0.5}$Fe$_{2.5}$O$_4$ on its structural and magnetic properties, the spinel system Li$_{0.5}$Al$_x$Cr$_x$Fe$_{2.5}$O$_4$ ($x =$ 0.0, 0.2, 0.4, 0.5, 0.6 and 0.8) has been characterized by X-ray diffraction, high field magnetization, low field ac susceptibility and $^{57}$Fe Mössbauer spectroscopy. Contrary to the earlier reports, about 50% of Al$^{3+}$ is found to occupy the tetrahedral sites. The system exhibits canted spin structure and a central paramagnetic doublet was found superimposed on magnetic sextet in the Mössbauer spectra ($x > 0.5$).

Keywords. Ferrites; canted spin structure; Mössbauer spectroscopy.

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1. Introduction

Lithium ferrites having high Curie temperatures and rectangular hysteresis loops have found extensive use in several microwave devices. Substituted lithium ferrites have attained considerable importance owing to their attractive magnetic and electrical properties. Titanium- and zinc-substituted lithium ferrites are the most widely used materials. 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. In this paper we focus our aim to study the influence of co-substitution of trivalent cations Cr$^{3+}$ and Al$^{3+}$ in Li$_{0.5}$Fe$_{2.5}$O$_4$ on its structural and magnetic properties through X-ray diffraction, high field magnetization, low field ac susceptibility and Mössbauer spectroscopic studies.

2. Experimental

The polycrystalline samples of the spinel solid solution series Li$_{0.5}$Al$_x$Cr$_x$Fe$_{2.5-2x}$O$_4$ were prepared by the double sintering ceramic method. All the samples were analyzed by X-ray powder diffractometry and the presence of only spinel structure was
Table 1. Lattice constant \( (a) \), magneton number \( (n_B) \), canting angle \( (\alpha_B) \), Curie temperature \( (T_c) \) and X-ray intensities ratios for LiFeAlCrO system.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( a (\text{Å}) ) ( ^* )</th>
<th>( n_B^N ) ( (77 \text{ K}) )</th>
<th>( \langle \alpha_B \rangle )</th>
<th>( J_{AB}/J_{BB} )</th>
<th>( T_c ) ( (\text{K}) )</th>
<th>( I(220) / I(440) )</th>
<th>( I(422) / I(400) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.318</td>
<td>2.45</td>
<td>2.5</td>
<td>0</td>
<td>945</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.2</td>
<td>8.298</td>
<td>2.10</td>
<td>2.1</td>
<td>0</td>
<td>808</td>
<td>0.83</td>
<td>0.68</td>
</tr>
<tr>
<td>0.4</td>
<td>8.271</td>
<td>1.45</td>
<td>1.7</td>
<td>17°02'</td>
<td>662</td>
<td>0.73</td>
<td>0.51</td>
</tr>
<tr>
<td>0.5</td>
<td>8.267</td>
<td>0.93</td>
<td>1.5</td>
<td>26°57'</td>
<td>572</td>
<td>0.65</td>
<td>0.55</td>
</tr>
<tr>
<td>0.6</td>
<td>8.251</td>
<td>0.75</td>
<td>1.3</td>
<td>27°41'</td>
<td>530</td>
<td>0.53</td>
<td>0.38</td>
</tr>
<tr>
<td>0.8</td>
<td>8.237</td>
<td>0.25</td>
<td>0.9</td>
<td>33°33'</td>
<td>398</td>
<td>0.43</td>
<td>0.28</td>
</tr>
</tbody>
</table>

\( ^* \text{Error=} \pm 0.002 \text{ Å}. \)

confirmed. The magnetization measurements of each sample at 77 K were carried out using hysteresis loop technique [4] and the Curie temperatures (table 1) were determined through ac susceptibility vs. temperature measurements using a double coil set up [5]. The Mössbauer spectra were obtained at 300 K for samples with \( x = 0.2, 0.5 \) and 0.8 using constant acceleration transducer interfaced to a PC-based multichannel analyzer.

3. Results and discussion

The values of lattice constant \( (a) \) are listed in table 1. The decrease in \( a \) with increase in Al–Cr content \( (x) \) is due to the substitution of smaller cations \( \text{Al}^{3+} \) (0.51 Å) and \( \text{Cr}^{3+} \) (0.63 Å) for \( \text{Fe}^{3+} \) (0.64 Å) in the system. The \( \text{Li}_0.5\text{Fe}_2\text{O}_4 \) \( (x = 0.0) \) is an inverse spinel with all \( \text{Li}^{1+} \) ions occupying octahedral sites [6]. The cation distributions for all the compositions were determined through X-ray diffraction intensity calculations using a computer program specially developed on the basis of the method suggested by Burger [7]. The normalized X-ray diffraction intensities, calculated and observed, for different Bragg planes by assuming various combination of cation distribution based on their site preferences were compared. The compositional dependence of observed and calculated intensity ratios of the planes considered to be sensitive to the cation distribution are given in table 1. It is well-known that the \( \text{Cr}^{3+} \) ions have marked preference for octahedral (B) sites and it was assumed that \( \text{Li}^{1+} \) ions preferentially occupies the B sites. The large difference between the values of atomic scattering factors of \( \text{Al}^{3+} \) and \( \text{Fe}^{3+} \) renders good contrast between them and it enables one to determine accurately the distribution of \( \text{Al}^{3+} \) and \( \text{Cr}^{3+} \) in the spinel lattice through X-ray diffraction. Contrary to the reports, we have found that the \( \text{Al}^{3+} \) ions are almost equally distributed among octahedral and tetrahedral sites. The general cation distribution formula can be written as

\[
(\text{Fe}^{3+}_{x} \text{Al}^{3+}_{0.5x} \text{Li}^{1+}_{0.5})^{\wedge} \text{Li}^{1+}_{0.5} \text{Fe}^{3+}_{1.5(1-x)} \text{Cr}^{3+}_{x} \text{Al}^{3+}_{0.5x} \text{O}_5^{2-}.
\]

The values of saturation magnetization \( (\sigma_s) \) and the saturation magnetization per formula unit, i.e., magneton number \( (n_B) \) measured at 77 K and in the peak field of 5 kOe are listed in table 1. The \( \sigma_s \) value decreases with increase in Al–Cr content \( (x) \). According to the Néel’s two sub-lattice collinear spin model [8] the magneton number \( n_B^N \) is defined as

\[
n_B^N = M_B(x) - M_A(x),
\]

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Figure 1. Mössbauer spectra of spinel system LiFeAlCrO at 300 K.

where $M_B$ and $M_A$ are octahedral and tetrahedral site moments, respectively. These site moments have been calculated using the cation distribution and the free ion magnetic moments of the cation involved. The variation of $n_B$ at 77 K as a function of $x$ follows the Néel’s collinear spin model [8] up to $x = 0.2$, thereafter it decreases with faster rate for further magnetic dilution (table 1). The observed decrease in the $n_B$ on increasing Al–Cr contents is attributed to the fact that the rate of decrease of the B-site moment is faster than that of the A-site moment. This happens because on B-site Fe$^{3+}$ (5 $\mu$B) is replaced simultaneously by nonmagnetic Al$^{3+}$ (0 $\mu$B) and magnetic Cr$^{3+}$ (3 $\mu$B) while an A-site Fe$^{3+}$ is replaced by Al$^{3+}$ only. The deviation of $n_{\text{obs}}^B$ from $n_{\text{N}}^B$ indicates the evolution of canted (non-collinear) spin structure for the samples with $x > 0.2$. The initial composition i.e., $x = 0.0$; Li$_{0.5}$Fe$_{2.5}$O$_4$ is an inverse spinel and a collinear ferrimagnet with $J_{AB}/J_{BB} = 3.63$ [9]. On Al$^{3+}$ substitution the number of A-B superexchange interactions is reduced and the BB interaction is made stronger due to the reduction in unit cell dimension [10]. This induces non-collinear spin alignment in octahedral (B) sites. Since the actual spin canting depends on the number of non-magnetic nearest neighbors and spatial arrangement, the statistical model proposed by Rosencwaig [11] should be used. According to his model, the B-site magnetic ions can be considered to be canted with an average angle $\langle \alpha_B \rangle$ due to
non-magnetic substitution (Al$^{3+}$) in A sites which in average nearest neighbor approximation is estimated to be

$$\cos(\alpha_B) \sim [(5 - 2.5x)/(7.5 - 4.5x)] \left(\frac{J_{AB}}{J_{BB}}\right).$$

The $J_{AB}$ and $J_{BB}$ are exchange integrals. The experimental values of the canting angle $\langle \alpha_B \rangle$ have been obtained from the measured $n_B$ at 77 K (table 1). The exchange integral ratio $J_{AB}/J_{BB}$ approaches unity with magnetic dilution (table 1).

The Mössbauer spectrum for $x = 0.2$ (figure 1) is a superposition of two Zeeman sextets while the spectrum for $x = 0.5$ exhibits a central paramagnetic doublet on magnetic sextets (figure 1). The spectrum for $x = 0.8$ shows features of relaxation effects with sharp central enhancement. The reported values of A-site and B-site hyperfine fields at 300 K for pure Li-ferrite ($x = 0.0$) are 495 kOe and 480 kOe, respectively [12]. The values of hyperfine fields from the Mössbauer spectral analysis, for $x = 0.2$; $H_n(A) = 432$ kOe, $H_n(B) = 460$ kOe; and for $x = 0.5$, $H_n(A) = 405$ kOe, $H_n(B) = 379$ kOe. The direct proportionality between the sublattice magnetization and the nuclear hyperfine field can be exploited, and the net magnetic moment $n_M$ (through Mössbauer study) by imposing the ratio of site-hyperfine fields [$H_n(x)/H_n(o)$] on the Néel’s equation, can be deduced. It has been suggested that [13] the discrepancy between $n_M$ and the observed moment is an indirect indication for the non-collinear spin structure.

The iron distribution deduced through Mössbauer data for $x = 0.2$ agrees well with the value found from X-ray diffraction. The central doublet may be attributed to those Fe$^{3+}$ ions which are magnetically isolated and did not participate in long range magnetic ordering due to large number of non magnetic nearest neighbors [14]. In the present system, the B site has Li$^{1+}$ and Al$^{3+}$ both non-magnetic ions and Fe concentration is continuously reduced. Therefore, A-site Fe$^{3+}$ ions having large number of non-magnetic ions as its nearest neighbors produce the central doublet.

References