Magnetic Properties of Magnesium Doped Li-Cr Ferrites

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Abstract   Mixed ferrites $Cr_{1.05} Li_{0.5} Mg_x Fe_{1.45-(2/3)x} O_4$ ($0 \leq x \leq 0.4$) doped with Magnesium have been studied using x-ray diffraction, Mössbauer spectroscopy and magnetic measurements. X-ray diffraction patterns show that all samples have single phase cubic spinel structure. The temperature-dependent magnetic measurements revealed that magnetic compensation disappears when Fe^{3+} in A-site is partially replaced by Mg^{2+}. Moreover, below the compensation temperature the observed magnetic moment of these ferrites increases with magnesium content. The magnetization data at all concentrations are discussed in the light of Néel's molecular field model taking into account the cations distribution obtained using the analysis of Mössbauer spectra.

Keywords   Magnetic Compensation, Crystal Structure, X-ray Diffraction, Mössbauer Spectroscopy, Cations Distribution

1. Introduction

$Li_{0.5}Fe_{2.5}O_4$ has been the subject to extensive technical and fundamental studies both in its pure form as well as its substituted form [1-3]. Various researchers have reported the effect of additions of divalent, trivalent and tetravalent ions in lithium ferrites and the different parameters have been measured depending on the desired application [4–6]. The reason behind these studies has been that the crystal structure and presence solely of Fe^{3+} ions in the host material has allowed detailed modelling of the exchange interactions giving rise to its ferrimagnetic order and secondly that subsequent substitution either with magnetic or with nonmagnetic cations has allowed studies of a variety of different magnetic states arising from the perturbed magnetic exchange interactions between ions.

The chromium-doped lithium ferrites $Li_{0.5}Fe_{2.5-x}Cr_xO_4$ are among the few systems exhibiting the effect of magnetic compensation and Gorter *et al* [7, 8] were the first to observe this phenomenon in $Cr_{1.25}Li_{0.5}Fe_{1.25}O_4$. These are ferrimagnetic materials in which the various temperature-dependent magnetizations of the spin-up and spin-down sublattices cross over at temperatures below the Curie temperature, resulting in a change of sign of the net spontaneous magnetization at that temperature. In a previous paper [9], we agreed with Kuznetsov *et al* [10] that $Li_{0.5} Fe_{2.5-x}Cr_xO_4$ ferrites have a completely inverted spinel structure for concentrations up to x = 1.25.

In this work, we report the effect of Mg^{2+} substitution for Fe^{3+} on the magnetic compensation of Li-Cr ferrite. Moreover, using a Mossbauer study of this system, we propose a cations distribution and investigate its relationship with the magnetic compensation effect.

2. Experimental

Five samples of the ferrite system $Cr_{1.05} Li_{0.5} Mg_x Fe_{1.45-(2/3)x} O_4$ ($0 \leq x \leq 0.4$) were prepared by the conventional double-sintering ceramic technique.The X-ray data were collected using a Philips PW1820 vertical goniometer with monochromator attached to a CuK_α PW1700 generator operating at a voltage of 40 kV.The Mössbauer spectra were collected in the transmission mode with α-Fe for calibration. The magnetization measurements were performed using a vibrating sample magnetometer (VSM) of 10^{-5} emu sensitivity in the magnetic field range of 0 kOe to 13.5 kOe and in the temperature range of 77 K to 600 K.

3. Results and Discussion

X-ray diffraction analysis showed the formation of single phase cubic spinel structure for all five samples. A representative diffraction of $Cr_{1.05}Li_{0.5}Fe_{1.45}O_4$is shown in Fig.1. The major peaks are indexed while the minor peaks indicate the presence of superlattice structures which suggest an ordered arrangement of Li^{2+} and Fe^{3+} cations on the octahedral sublattice.

The lattice parameter (a) was obtained by extrapolation to $\theta = 90^0$ for different indexed planes against the Nelson-Riley function. The lattice parameter value of $Cr_{1.05}Li_{0.5}Fe_{1.45}O_4$ agrees well with the literature taking into account our preparation technique. As can be seen in the inset of Fig.1,

within error barsthe lattice parameter increases slowly with magnesium content.

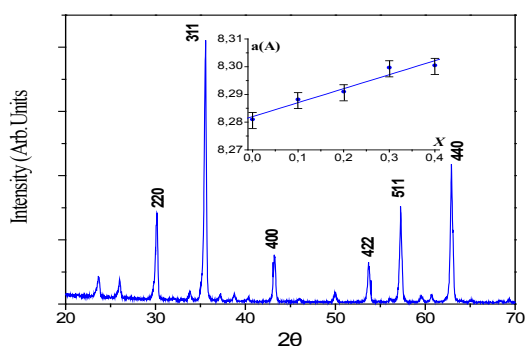**Figure 1.** X-ray representative spectrum of $Cr_{1.05}Li_{0.5}Fe_{1.45}O_4$. The inset shows the lattice parameter a (Angstroms) versus magnesium content

This variation reflects the larger radius of Mg^{2+} as compared to Fe^{3+}.

Figure 2 shows the Mössbauer spectra of $Cr_{1.05}Li_{0.5}Mg_xFe_{1.45-(2/3)x}O_4$ ($0 \leq x \leq 0.4$) at 77 K. The spectra were fitted with two magnetic sextet assigned to the octahedral [B] and tetrahedral (A) sites but constrained to have relative areas proportional to the occupancies stated in Table 1.

The line width of the outer absorption line of each spectrum shows a broadening and increases with magnesium content. This could give an estimate of the distribution of the hyperfine fields at each site. The 77 K spectra shows patterns similar to room temperature ones, but with less broadened outerlines. All the hyperfine interaction parameters except the relative areas, given in Table 1, were varying freely in the fitting process. Note that all the magnetic hyperfine fields are decreasing slowly with increasing magnesium content.
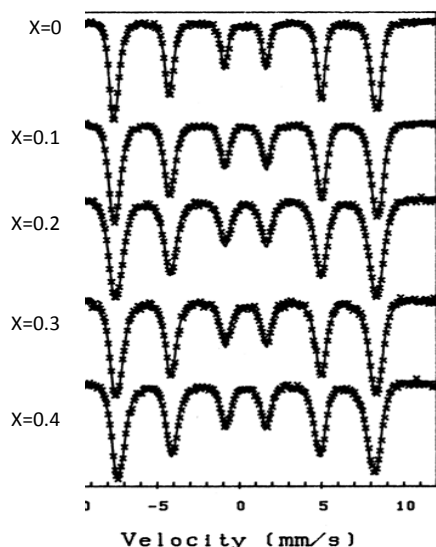

Figure 2. Mössbauer spectra of $Cr_{1.05}Li_{0.5}Mg_xFe_{1.45-(2/3)x}O_4$ at 77K

Taking the fitted absorption areas as proportional to iron site occupancies, Table 2 shows the proposed cation distrbutions. It is well known from previous studies that Mg^{2+} occupies A-sites [11] and Cr^{3+} occupies B-sites [12]. On the other hand from earlier reports, Lithium-Chromium ferrites [10] have been interpreted with Li^+ occupying preferentially the octahedral sites. The rest of the tetrahedral and octahedral sites have been filled with Fe^{3+} cations in accordance with our Mössbauer absorption areas results.

Table 1. Mössbauer parameters of Mg doped Li-Cr ferrites at 77 K

	Tetrahedral A-site				
X	IS mm/s	QS mm/s	LW mm/s	H(T)	A%
0.0	0.38	0.02	0.56	48.5	79.8
0.1	0.41	0.03	0.92	48.8	77.3
0.2	0.42	0.01	0.92	48.0	73.9
0.3	0.42	0.01	0.81	48.2	71.4
0.4	0.42	0.01	0.81	47.1	66.7
	Octahedral B-site				
X	IS mm/s	QS mm/s	LW mm/s	H(T)	A%
0.0	0.39	0.04	0.46	50.3	20.2
0.1	0.44	0.0	0.46	50.3	22.9
0.2	0.42	0.04	0.5	50.4	26.1
0.3	0.44	0.03	0.73	50.2	28.6
0.4	0.43	0.05	0.54	49.6	33.3

On the basis of Neel's molecular field model [14] and the cation distributions given in Table 2, the magnetic moment in ferrites is mainly from the parallel-uncompensated electron spin of the individual ions, and the spin alignments in the two sub-lattices are arranged antiparallel. Also, the A–B exchange interaction is predominant over the A–A and B–B interactions. Hence the net magnetic moment of the lattice is given by the algebraic sum of the magnetic moments of A and B sub-lattices, i.e. $M_0 = M_B - M_A$. Given the electronic configurations of the B- and A-site cations Fe^{3+} ($3d^5$) and Cr^{3+} ($3d^3$), we can estimate the sublattice magnetizations (Fe^{3+} has no orbital momentum, whereas in Cr^{3+} it is crystal-field frozen). The calculated spin magnetic moments M_0 at 0 K are shown in Table 2 and appear to decrease with magnesium content.

Measured saturation magnetization M_S of all compositions against temperature are shown in Figure 3. At x=0, M_S values are in good agreement with those of Gorter *et al* [7] as well as the compensation temperature T_K (310K) and the Curie temperature T_C (500 K). The Curie temperatures were obtained using the method of the "intersecting tangents" to M_S against T curves. The inset shows T_C and T_K versus magnesium content.

It is interesting to point the gradual increase of M_S with the addition of magnesium at temperatures below T_K. This trend is consistent with the calculated M_0 values (Table 2) obtained using the cation distribution deduced from our Mössbauer analysis. We could not extract the experimental values of M_S at 0 K from our data because the long extrapolation from 77 K to 0 K would make the comparison

with the calculated M_0 unreliable.

As expected, the inset shows a decreasing T_C as more diamagnetic Mg^{2+} replaces Fe^{3+}. Moreover, Figure 3 shows that M_S decreases with magnesium content at temperatures between T_K and T_C, this is also expected since T_K gradually approaches T_C as the inset shows. Indeed, on extrapolating the compensation line, the intersection with the Curie line represents the point where compensation disappears, i.e. $x \approx 0.4$. This value is confirmed by our direct observation at this concentration.

Table 2. Cations distribution of $Cr_{1.05}$ $Li_{0.5}$ Mg_x $Fe_{1.45-(2/3)x}$ O_4 and calculated magnetic moments MA , MB and M0 in Bohr magnetons(μB). Round brackets stand for A-sites and square brackets stand for B-sites

X	Cation distribution	$M_B(\mu_B)$	$M_A(\mu_B)$	$M_0 = M_B - M_A$
0	$(Fe)[Li_{0.5} Cr_{1.05} Fe_{0.45}]$	5.4	5	0.4
0.1	$(Fe_{0.9} Mg_{0.1})[Li_{0.5} Cr_{1.05} Fe_{0.483}]$	5.6	4.5	1.1
0.2	$(Fe_{0.8} Mg_{0.2})[Li_{0.5} Cr_{1.05} Fe_{0.517}]$	5.7	4	1.7
0.3	$(Fe_{0.7} Mg_{0.3})[Li_{0.5} Cr_{1.05} Fe_{0.55}]$	5.9	3.5	2.4
0.4	$(Fe_{0.6} Mg_{0.4})[Li_{0.5} Cr_{1.05} Fe_{0.583}]$	6.1	3	3.1

This effect of the disappearance of magnetic compensation can be interpreted on the basis of Neel's molecular field model [14] and the concept of 'weak' magnetic sublattice as introduced by Belov[15]. In the case of $Cr_{1.05}$ $Li_{0.5}$ Mg_x $Fe_{1.45-(2/3)x}$ O_4, we may consider A-sites as the magnetically strong sub-lattice because of the relatively higher content of Fe^{3+} cations and the B-sites as the weak sub-lattice. As diamagnetic Mg^{2+} substitutes Fe^{3+} in A-sites only, exchange interactions A-A are modified in such a way that the magnetization M_A of A sub-lattice becomes weaker. This means that the decrease rate of M_A with temperature becomes higher and subsequently the compensation occurs at a point T_K approaching gradually T_C. The compensation disappears at a magnesium content as such that A sub-lattice has weakened enough so to disable the compensation of B sub-lattice over the whole temperature range up to T_C . Note that as Mg^{2+} substitutes Fe^{3+} in A-sites, the net moment $M = M_B - M_A$ increases because M_A decreases while M_B stays almost constant. This is due to the relatively unchanged content of the magnetic cations Fe^{3+} and Cr^{3+} in B-sites.

4. Conclusions

We may conclude from the study of the effect of Mg^{2+} on the magnetic compensation of Chromium-Lithium ferrites that:

1. The magnetic compensation in $Cr_{1.05}Li_{0.5}Fe_{1.45}O_4$ disappears when Fe^{3+} in A-site is partially replaced by Mg^{2+}.

2. Below the compensation temperature, the observed magnetic moment of these ferrites increases with magnesium content.

3. The magnetic moments calculated using a cations dis-

tribution consistent with the Mössbauer study of these ferrites show an increasing trend with magnesium content. This trend agrees with the magnetic measurements.
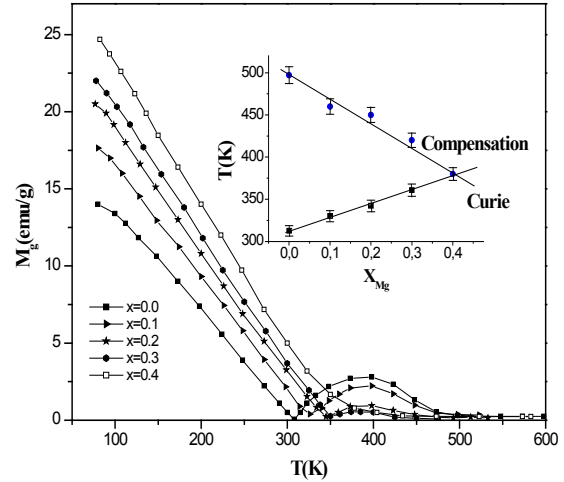

Figure 3. Saturation magnetizations versus temperature of $Cr_{1.05}$ $Li_{0.5}$ Mg_x $Fe_{1.45-(2/3)x}$ O_4. The inset shows the Curie and compensation temperatures versus magnesium content

REFERENCES

[1]　Krishnan R, Physica B 1977, 86-88, 1457.

[2]　Dormann J.L, Rev. Phys. Appl. 1980, 15, 1113.

[3]　Gill N.K and Puri R.K, Spectrochimica Acta 1985, A 41, 1005.

[4]　Deepika K, Sumitra P. and Baijal J S, J. Mater. Sci. 1990, 25, 5142.

[5]　Song J. M and Koh J. G., IEEE Trans. Magn. 1996, 32, 411.

[6]　Mazen S. A, Metawe F. and Mansour S. F., J. Phys. D:Appl. Phys. 2003, 30 1799.

[7]　Gorter E.W and Schulkes J.A, Phys.Rev. 1953, 89, 487.

[8]　Gorter E.W. Philips Res.Rep. 1954, 9, 295.

[9]　Rais A.M., Gismelseed A.M., and Al-Omari I.A., Phys. Stat. Sol. (b) 2005, 242, 2945 –2955.

[10]　Kuznetsov M, Pankhurst Q.A and Parkin I.P, J.Phys.D: Appl.Phys.2002, 31, 2886.

[11]　Fatseas G.A, Dorman J.L and Blanchard H, J.Phys. 1976, 12, 787.

[12]　Chen Y.L, Xu B.B and Chen J.G, Hyp.Int.1976, 70, 1029.

[13]　Kuznetsov M, Pankhurst Q.A and Parkin I.P, J.Phys.D: Appl.Phys. 2002, 31, 2886.

[14]　Neel L, Ann.Phys. 1948 3, 137.

[15]　Belov K.P, Phys.Usp. 1996, 39, 62