JOURNAL OF MATERIALS SCIENCE 20 (1985) 3926–3930

Mössbauer studies of $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ system: canted spin alignment and cation distribution

S. K. KULSHRESHTHA
Chemistry Division, Bhabha Atomic Research Centre, Bombay 400085, India
G. RITTER
Physikalische Institut Abt II, Universitat Erlangen-Nurnberg, Gluck Strasse-10 D8520 Erlangen, Federal Republic of Germany

Based on ^{57}Fe Mössbauer effect studies conducted at 4.2 K with and without an external magnetic field of 40 kG, the exact distribution of Fe^{3+} between the octahedral and tetrahedral sites has been determined for the $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ system for $0.0 \leqslant x \leqslant 1.1$. Gallium ions show a slight preference for tetrahedral sites. The values of canting angle α_{yk} have been determined for octahedral Fe^{3+} ions using both relative intensity of different peaks and hyperfine field values. The effect of sintering on the values of hyperfine field, cation distribution and canting angle has been studied for $Li_{0.5}Fe_{1.4}Ga_{1.1}O_4$. The effect of gallium substitution on the values of hyperfine interaction parameters and the occurrence of a magnetically collapsed doublet is also discussed.

1. Introduction

Exact knowledge of cation distribution and spin orientation is essential to understand the magnetic characteristics of spinel ferrites and to synthesize the desired ferrites for specific application. Diamagnetically substituted lithium ferrite has attracted the attention of a number of research workers to help understand the exchange interactions in the spinel lattice, because only one type of magnetic ion, namely Fe^{3+} distributed between the octahedral and tetrahedral sites, is involved for this system which makes the analysis relatively simple and authentic. A variety of diamagnetic substitutions such as Li^{1+}, Zn^{2+}, Al^{3+}, Ga^{3+}, Ge^{4+}, Sn^{4+}, Ti^{4+} and Sb^{5+} etc, either alone or in combination have been investigated using ^{57}Fe Mössbauer spectroscopy [1–8] which has established its uniqueness for such studies by revealing the occurrence of a variety of phenomena such as the existence of paramagnetic and magnetically ordered Fe^{3+} in the same lattice, multiple sublattices for the octahedral sites, localized nearest neighbour effects on the values of internal hyperfine fields, canted spin alignment, spin flop processes and different types of relaxation process for these systems. Lithium ferrite is an inverse spinel ferrite with a cation distribution $Fe_{1.0}[Li_{0.5}Fe_{1.5}]O_4$. Recently, we have reported [9] our variable temperature ^{57}Fe Mössbauer effect experiments conducted under variable external magnetic fields for the lithium ferrite aluminate system to determine the exact Fe^{3+} distribution and to show the existence of superparamagnetic Fe^{3+} ions. The influence of these observations on the magnetic properties of this system was also discussed. Based on similar experiments, certain new observations for the lithium ferrite gallate system ($Li_{0.5}Fe_{2.5-x}Ga_xO_4$) are reported here to resolve some of the controversies about this system.

Before we present our results it is appropriate to summarize some of the relevant results for this system. Based on X-ray diffraction and magnetization experiments, Schulke and Blasse [10] reported a complete solid solution for this

0022–2461/85 \$03.00 + .12

system. From the observed values of magnetic moment and assuming a collinear spin alignment, they estimated the distribution of Fe^{3+} between the octahedral and tetrahedral sites for $x = 0.5$ and suggested a preferential occupation of tetrahedral sites by Ga^{3+} ions. Lopitaux and Linglet [11] based on X-ray and neutron diffraction studies of $Li_{0.5}Fe_{1.5}Ga_{1.0}O_4$, also arrived at similar conclusions. Zhilyakov and co-workers [12, 13] have investigated this system for different values of x using a variety of techniques such as neutron diffraction, thermal expansion, Mössbauer spectroscopy, etc, to understand the nature of exchange interactions and suggested the possibility of a canted spin alignment. Bashkirov *et al.* [14] investigated this sytem for $0.0 \leqslant x \leqslant 0.8$ using Mössbauer spectroscopy to find the effect of gallium substitution on the nature of superexchange interactions, and concluded that as the Ga^{3+} content is increased, the intrasublattice interactions become stronger and the intersublattice interactions weaken because of the reduction in lattice parameters and this facilitated a canted spin alignment at the octahedral sites. Later [15] they studied this system for $0.0 \leqslant x \leqslant 0.5$ using Mössbauer spectroscopy, X-ray diffraction and magnetization measurements, and suggested that the existence of Ga^{3+} and Fe^{3+} ions at the tetrahedral sites result in the fomation of magnetically inequivalent Fe^{3+} ions at the octahedral sites. They also suggested that the Ga^{3+} ions are involved in the chain of intersublattice interactions due to the transmittance of finite spin density from the Fe^{3+} ions into the empty 4s orbitals of Ga^{3+} ions. This conclusion was mainly derived from the results of Doroshev *et al.* [16] who showed the existence of significant transferred hyperfine fields at the Ga^{3+} sites from the ^{71}Ga and ^{69}Ga NMR studies of this system for $0.01 \leqslant x \leqslant 0.66$. Doroshev *et al.* [16] also suggested the existence of almost comparable amounts of Ga^{3+} ions at both the sites. In a recent study, Belov *et al.* [17] from the magnetization studies of $Li_{0.5}Fe_{1.23}Ga_{1.27}O_4$ have suggested the possibility of a canted spin alignment even for the tetrahedral sites. Thus it is apparent that there is a lot of controversy about this system and ^{57}Fe Mössbauer effect studies under large external magnetic fields can help in understanding some of these inconsistencies. Such studies are not available in the literature.

2. Experimental details

The samples were prepared by standard ceramic techniques and were characterized by powder X-ray diffraction method using monochromatized Cu$K\alpha$ radiation. All samples showed the formation of a well-defined spinel lattice whose lattice parameter decreased systematically with increase in gallium substitution. Mössbauer spectra were recorded using a constant acceleration drive coupled with a multichannel analyser. The source used was ^{57}Co in a rhodium matrix and was kept at room temperature. The absorbers were kept immersed in liquid helium with and without external magnetic field parallel to the γ-ray direction. The parameters employed for least square fitting the observed spectra consisted of a hyperfine field, an axially symmetric quadrupole interaction, isomeric shift, width and intensity corresponding to both the crystallographic sites. The width and intensity of the two inner pairs of the magnetic sextet (say S_2S_5 and S_3S_4) of both the sites were related to the outermost pair S_1S_6 in terms of four adjustable parameters. This results in equal width and intensity of the two lines of any pair of a sextet.

3. Results and discussion

Mössbauer spectra for four samples with $x = 0.3$, 0.5, 0.7 and 1.1 were recorded at 298 and 78 K and at liquid helium temperature with and without an external magnetic field. The room temperature spectra showed a typical six-finger pattern with a superimposed central quadrupole doublet whose relative intensity increased with increase in gallium content. The magnetic pattern was broad and unresolved due to the superposition of two sextets arising from the octahedral and tetrahedral sites. With increase in gallium content, the width of the magnetic pattern showed an increase due to the distribution of hyperfine field values and the average value of the internal hyperfine field showed a systematic decrease. Because of the unresolved nature of the spectrum it was not possible to fit these spectra uniquely to obtain the information about individual sites. The spectra recorded at 78 K showed essentially similar features with some reduction in the intensity of the central doublet and an increase in the internal hyperfine field. The spectra recorded at 4.2 K are shown in Fig. 1 along with the least square fitted envelope. Fig. 2 illustrates the spectra recorded at 4.2 K

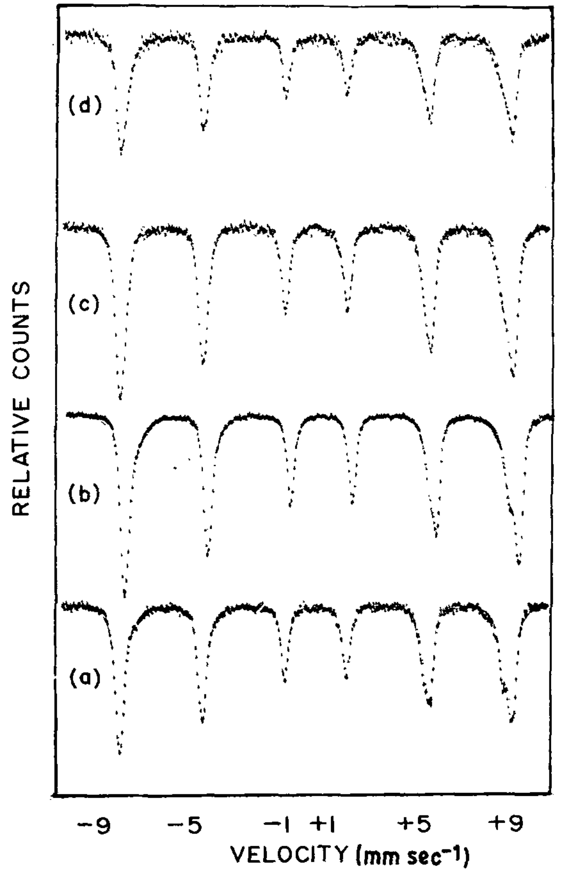

Figure 1 ^{57}Fe Mössbauer spectra recorded at 4.2 K for $Li_{0.5}Fe_{2.5-x}Ga_xO_4$; (a) $x = 0.3$; (b) $x = 0.5$; (c) $x = 0.7$; (d) $x = 1.1$.

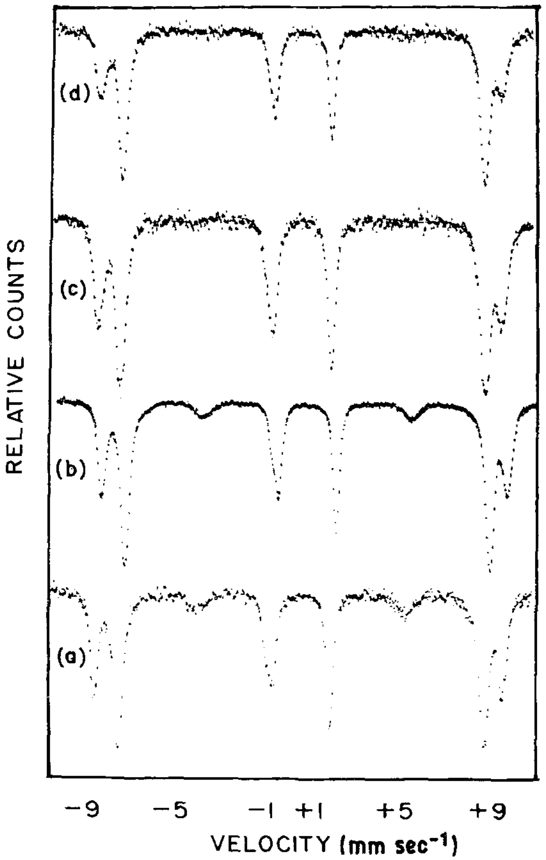

Figure 2 ^{57}Fe Mössbauer spectra recorded at 4.2 K with an external magnetic field of 40 kG for (a) $x = 0.3$, (b) $x = 0.5$, (c) $x = 0.7$ and (d) $x = 1.1$.

under an external magnetic field of 40 kG applied parallel to the direction of γ-rays. The central doublet, which was visible at room temperature, is not seen in these spectra. From Fig. 2 it is also clear that the peaks S_2 and S_5 have not disappeared completely. For $x = 0.3$ and 0.5 they are quite clearly seen. The position of these residual peaks corresponds to octahedral sites. It is also clear that the net magnetization is parallel to the octahedral site magnetization. The average values of effective hyperfine field (H_{eff}) for tetrahedral site is almost equal to ($H_{\text{int}} + H_{\text{ext}}$) but for the octahedral sites it is more than ($H_{\text{int}} - H_{\text{ext}}$). Both these features are arising due to the canting of octahedral site spins.

The results of the least square fitting of all these spectra are listed in Table I. From this table it is clear that as expected the values of isomeric shift (δ) and internal hyperfine field (H_{int}) are slightly less for the tetrahedral sites as compared to the octahedral sites. The value of quadrupole shift parameter

$$\varepsilon = \frac{e^2qQ}{2}\left(\frac{3\cos^2\theta - 1}{4}\right)$$

was found to be almost zero within experimental error for both the sites. These are the general observations for spinel ferrites. The other observation which is apparent from the table is the systematic decrease in the internal hyperfine field values for gallium substitution. This happens because the replacement of Fe^{3+} by Ga^{3+} influences the internal hyperfine fields at the nearest Fe^{3+} sites through supertransferred hyperfine fields.

The average value of the canting angle α_{yk} can be derived from the observed values of internal hyperfine fields using the expression

$$(H_{\text{eff}})^2 = (H_{\text{int}})^2 + (H_{\text{ext}})^2 - 2H_{\text{int}}H_{\text{ext}}\cos\alpha_{yk}$$

The derived values of α_{yk} are listed in Table I. For $x = 0.3$ and 0.5 where the peaks S_2 and S_5

TABLE I Mössbauer effect parameters for $Li_{0.5}Fe_{2.5-x}Ga_xO_4$*

Composition	δ_{octa} (mm sec^{-1})	δ_{tetra} (mm sec^{-1})	Internal hyperfine fields		Effective fields with H_{ext}		$Fe^{3+}_{octa}/Fe^{3+}_{tetra}$	Average α_{yk} (deg)
			H_{octa} (kOe)	H_{tetra} (kOe)	H_{octa} (kOe)	H_{tetra} (kOe)		
$Li_{0.5}Fe_{2.5}O_4$	0.43	0.29	536	519	–	–	1.50	–
$Li_{0.5}Fe_{2.2}Ga_{0.3}O_4$	0.41	0.31	536	516	500	558	1.65	34
$Li_{0.5}Fe_{2.0}Ga_{0.5}O_4$	0.41	0.31	535	515	500	556	2.03	30
$Li_{0.5}Fe_{1.8}Ga_{0.7}O_4$	0.41	0.32	533	514	499	553	2.06	28
$Li_{0.5}Fe_{1.4}Ga_{1.1}O_4$ (Powder)	0.41	0.31	531	511	497	551	2.41	30
$Li_{0.5}Fe_{1.4}Ga_{1.1}O_4$ (Sintered)	0.40	0.31	529	503	493	543	2.50	25

*The errors in the estimation of isomeric shift and hyperfine field values are ± 0.02 mm sec^{-1} and ± 2 kOe, respectively.

are well defined, the values of α_{yk} have also been estimated from their area measurements and these values of α_{yk} are in good agreement with the values listed in Table I. For higher values of x the width of the S_2 and S_5 peaks is very large and their area measurement is not so precise to estimate the values of α_{yk}. This excessive width may arise due to the distribution of α_{yk} and the internal hyperfine field values, which is more likely to happen for higher concentrations of gallium. From these observations it is clear that the suggestion of Belov *et al.* [17] about the existence of a canted spin alignment for the tetrahedral sites is not correct.

The correct Fe^{3+} distribution between the octahedral and tetrahedral sites has been obtained from the analysis of the spectra recorded under an external magnetic field (i.e. Fig. 2) where the outermost peaks are well resolved and their areas can be measured with good accuracy. In this calculation, appropriate correction was made for the residual areas covered under peaks S_2 and S_6 which arise due to octahedral sites alone. These area ratios have been listed in Table 1. Since at 4.2 K the recoil free fraction for the octrahedral and tetrahedral sites can be treated as equal and if small saturation effects can be ignored, this area ratio represents the distribution of Fe^{3+} between the two sites. This distribution is slightly different from that derived from magnetization and neutron diffraction studies of earlier authors. The main reasons for this discrepancy are the possible existence of superparamagnetic Fe^{3+} species and the occurrence of canted spin alignment at the octahedral sites. If it can be assumed that all Li^+ ions remain at the octahedral sites as suggested from X-ray diffraction studies of this system [10], the complete cation distribution for different compositions can be written as

$$x = 0.0;\ Fe_{1.0}[Li_{0.5}Fe_{1.5}]O_4$$

$$x = 0.3;\ Fe_{0.83}Ge_{0.17}[Li_{0.5}Fe_{1.37}Ga_{0.13}]O_4$$

$$x = 0.5;\ Fe_{0.66}Ga_{0.34}[Li_{0.5}Fe_{1.34}Ga_{0.16}]O_4$$

$$x = 0.7;\ Fe_{0.59}Ga_{0.41}[Li_{0.5}Fe_{1.21}Ga_{0.29}]O_4$$

$$x = 1.1;\ Fe_{0.41}Ga_{0.59}[Li_{0.5}Fe_{0.99}Ga_{0.51}]O_4$$

From this it is clear that Ga^{3+} has a slight preference for tetrahedral sites which is in conformity with earlier suggestions.

In order to see the effect of sintering on the cation distribution we investigated one of the compositions, i.e. Ga = 1.1, which has favourable properties for certain applications. The sample was pressed in the form of a pellet and sintered at about 1350° C for a few hours. Mössbauer spectra recorded at room temperature for the sintered and powder sample showed the features characteristic of relaxation effects and were found to be slightly different. A broad sextet superimposed on a central quadrupole doublet was observed for both the samples. The spectrum for the sintered sample was more collapsed. However at 4.2 K the observed spectra were almost identical. The derived cation distribution and α_{yk} values for the sintered product are quite similar to that of the powder sample. However the value of internal hyperfine field for the tetrahedral site was found to be slightly less.

The observation of a central doublet along with the magnetic sextet at temperatures far below T_N, has been reported for a number of diamagnetic substitutions in lithium ferrite. Some authors believe that the method of preparation is an important factor in deciding the origin of these lines. In a previous publication [9] we have given a detailed explanation of the origin of the central doublet in terms of nearest neighbour diamagnetic configurations of any Fe^{3+} ion. However, the existence of finite spin density at the gallium sites as seen from the NMR experiments [16] can create some difference and weaken the effect of diamagnetic substitution. The fact that the observed line widths for the octahedral and tetrahedral sites are almost comparable ($\Gamma_{oct} \simeq \Gamma_{tetra} \simeq 0.45 \pm 0.05\,\text{mm sec}^{-1}$) implies that there is no multiple sublattice formation for the octahedral sites as seen for some other diamagnetically substituted spinel ferrites [18, 19]. This observation also suggests that the spread in the value of hyperfine field for both the sites is also comparable for both the sites. Owing to the existence of spin density at the gallium sites, the effect of a varying number of Ga^{3+} as the nearest neighbours on the value of internal hyperfine field at the Fe^{3+} sites may be less pronounced than that of Al^{3+} substitution. For both Al^{3+} [9] and Ga^{3+} substitution the decrease in the internal hyperfine field at the tetrahedral sites is more pronounced than the octahedral sites. Both these features are apparent from the comparison of present results and the results reported earlier for the $Li_{0.5}Fe_{2.5-x}Al_xO_4$ system [9]. For a number of diamagnetically substituted ferrites [18–21] the existence of localized spin canting instead of Yaffet–Kittel type average spin canting has been suggested from the analysis of the broad magnetic pattern into multiple components. This arises either due to the formation of superlattice on octahedral sites or due to a varying number of diamagnetic nearest neighbours for Fe^{3+} ions. The observed line widths for this system are not so excessive (see Fig. 2) and our attempt to fit these spectra in terms of localized spin canting characteristics of varying nearest neighbour configurations, did not give unique and consistent results for different compositions.

In conclusion, we have shown that the spin canting exists only for the octahedral sites. The average value of spin canting and the distribution of Fe^{3+} between the octahedral and tetrahedral sites has been determined. The effect of sintering on these parameters has also been studied for the $Li_{0.5}Fe_{1.4}Ga_{1.1}O_4$ composition.

References

1. J. L. DORMANN, *Rev. Phys. Appl.* **15** (1980) 1113.
2. J. W. YOUNG and J. SMIT, *J. Appl. Phys.* **42** (1971) 2344.
3. P. RAJ and S. K. KULSHRESHTHA, *J. Phys. Chem. Solids* **31** (1970) 9.
4. C. F. DIONNE, *J. Appl. Phys.* **45** (1974) 3621.
5. J. L. DROMANN, *J. Phys. C-1* **41** (1980) 175.
6. C. R. ABELEDO and R. B. FRANKEL, *ibid.* **38** (1977) 135.
7. M. ROSENBERG, P. DEPPE, S. DEY and U. JANSON, *IEEE Trans. Mag.* **18** (1982) 1616.
8. B. J. EVANS and L. J. SWARTZENDRUBER, *J. Appl. Phys.* **42** (1971) 1628.
9. S. K. KULSHRESHTHA and G. RITTER, *J. Mater. Sci.* **20** (1985) 821.
10. J. A. SCHULKE and G. BLASSE, *J. Phys. Chem. Solids* **24** (1963) 1651.
11. J. LOPITAUX and M. LINGLET, *Phys. Status Solidi (a)* **35** (1976) K141.
12. S. M. ZHILYAKOV, V. V. IVOLGA and E. P. NAIDEN, *Sov. Phys. Solid State* **20** (1978) 1980.
13. S. M. ZHILYAKOV and E. P. NAIDEN, *ibid.* **17** (1975) 113.
14. Sh. Sh. BASHKIROV, R. A. ISKHAKOV, A. B. LIBERMAN, V. I. SINYAVSKII, Yu. A. MEMALUI and N. N. EFIMOVA, *ibid.* **18** (1976) 1498.
15. *Idem*, *Ukr. Fiz Zh.* (*USSR*) **21** (1976) 543.
16. V. D. DOROSHEV, V. A. KLOCHAN, N. M. KOVTUM and V. N. SELEZNOV, *Phys. Status Solidi (a)* **26** (1974) 77.
17. K. P. BELOV, A. N. GORYAGA and A. I. KOKOREV, *Sov. Phys. Solid State* **25** (1983) 1022.
18. G. A. PETITT and D. W. FORESTER, *Phys. Rev.* **B4** (1971) 3912.
19. A. ROSENCWAIG, *Can. J. Phys.* **48** (1970) 2857.
20. G. O. WHITE, C. A. EDMONDSON, R. B. GOLDFARB and C. E. PATTEN, *J. Appl. Phys.* **50** (1979) 2381.
21. S. C. BHARGAVA and N. ZEMAN, *Phys. Rev.* **B21** (1980) 1726.

Received 29 October
and accepted 22 November 1984