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Mössbauer study of nano-particles of spinel ferrites $Li_xFe_{3-x}O_4$

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Mössbauer spectra have been recorded on three nano-particle samples in the series $Li_xFe_{3-x}O_4$ (for x = 0.1, 0.2 and 0.3) at 300K and 80K. Spectra could be resolved into two doublets attributed to two crystalline sites, viz., tetrahedral site and octahedral site. Li occupies the octahedral site with a complete preference as in the bulk particle size state. Analysis of Mössbauer spectra shows that electron hopping manifests at temperatures down to 80K implying the absence of a Verwey type transition. Magnetization measurements support this inference and are suggestive of no such transition occurring down to 20K.

Keywords: Mössbauer study, Nano-particles, Spinel ferrites, $Li_xFe_{3-x}O_4$

IPC Code: G01J3/28, H01F41/30

1 Introduction

Mössbauer studies on nano-particles of some spinel ferrites have shown that there is a redistribution[1,2] in site occupation of the cations as compared to in bulk particle sized samples. Work on lithium substituted spinel ferrite systems is available in Ref. 3. Unlike many other cations, Li^+ is a non-magnetic one. Merceron *et al*[3]. in their study of the bulk particles of Li substituted ferrites found that their three as prepared samples (of amounts of Li substitutions identical to in the series under study here), showed Verwey transitions[4] (associated with discontinuous change in magnetic anisotropy) at ~61, ~41 and ~35K ,respectively. In the following we present temperature dependent ^{57}Fe Mössbauer studies down to 80K on the nano-particle samples of identical compositions. Magnetization measurements down to 20K are also described to support Mössbauer results.

2 Experimental Details

The nano-particle ferrite samples were prepared using the method of chemical co-precipitation. Reactions were carried using solutions of $FeCl_3.6H_2O$ (0.2N), $FeSO_4.7H_2O$ (0.08N) and $Li_2(SO_4)$. H_2O (0.01N) and ammonia solution. Oleic acid was used for surface coating and the particles were dispersed in kerosene. For achieving a narrower size distribution of particle sizes, the prepared fluid was subjected to centrifuging at 12000 rpm and the decanted fluid which would have finer particles was used for further measurements. For obtaining the dried particles, portion of the fluid was repeatedly washed with acetone. The prepared samples $Li_{0.1}Fe_{2.9}O_4$, $Li_{0.2}Fe_{2.8}O_4$ and $Li_{0.3}Fe_{2.7}O_4$ are hereafter referred to as Li10, Li20 and Li30, respectively. For characterization of the samples, for single phase nature, powder X-ray diffraction (XRD) measurements have been recorded at 300K on Philips make powder diffractometer model PW 1840, using Fe K_α radiation (λ = 1.937355 Å).

^{57}Fe Mössbauer spectra have been recorded at 300K and 80K. For low temperature measurements, a flow type liquid nitrogen cryostat has been used. Spectra were recorded in transmission geometry and in constant acceleration mode using a ^{57}Co source of ~10 mCi strength embedded in rhodium matrix. Calibration was done using the spectrum of metallic natural iron (α-Fe) at 300K. A least square fitting based Mössbauer analysis program[5] was used for folding and analysis of the data. Temperature dependent magnetization measurements have been made using a Vibrating Sample Magnetometer (PARC Make, Model 155) and a closed helium cycle refrigerator cryostat.

3 Results and Discussion

Figure 1 shows the indexed XRD patterns of the sample Li10. Bragg reflections are indexed in Fe_3O_4

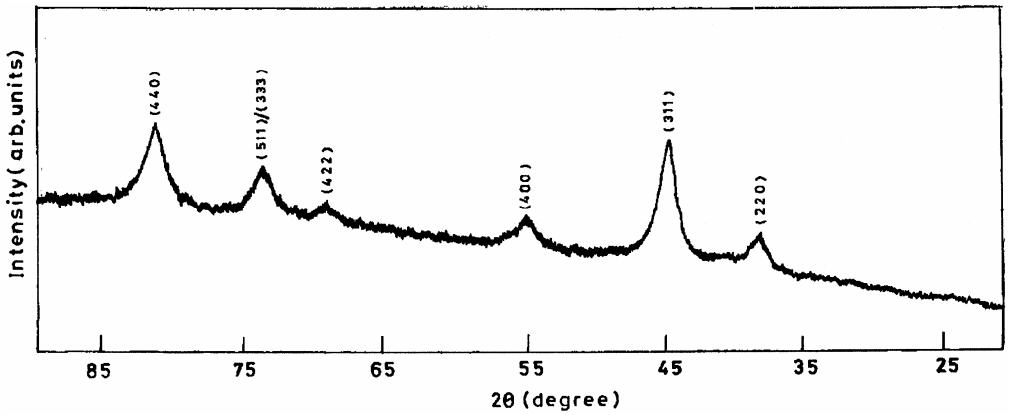

Fig. 1—Fe K_α X-ray powder diffraction pattern recorded at 300K for the sample $Li_{0.1}Fe_{2.9}O_4$

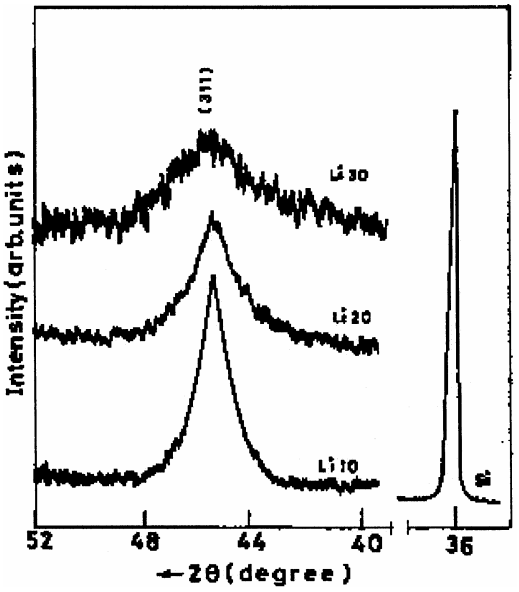

Fig. 2—311 reflection in the XRD pattern of the samples Li10, Li20 and Li30. One reflection in the pattern of a bulk particle sample of Si is also shown for the purpose of comparison

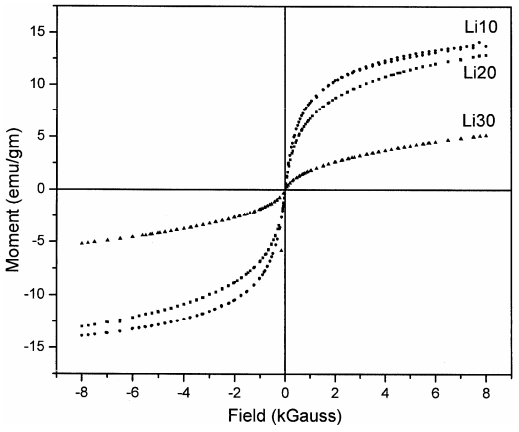

Fig. 3—*M* - *H* curves of the three samples Li10, Li20 and Li30 recorded at 300K

like cubic structure and the value of cell parameters have been estimated for the three lithium substituted samples, viz., Li10, Li20 and Li30 and is found to be ~8.37 Å. This is in good agreement with the cell constant for Fe_3O_4. The XRD lines are considerably broad which is suggestive of fine particle nature of the samples.

For determination of particle sizes, we have used the widths of 311 reflection lines in XRD patterns and that of a reflection of standard Si bulk particle sized sample. These are shown in Fig. 2. Estimated average particle (thicknesses) sizes, using these line widths in Debye-Scherrer equation, are ~80, ~70 and ~40 Å for Li10, Li20 and Li30, respectively.

Figure 3 shows the variation of magnetization[6] as a function of magnetic field (*M* - *H*) for the three dried particle samples Li10, Li20 and Li30, respectively at 300K. The three curves exhibit typical Langevin function type paramagnetic behaviour with zero remanance and coercivity. This shows that all the three samples are in superparamagnetic (SPM) state at 300K. Figure 4 shows the magnetization versus temperature (*M* – *T*) measurements[6] on the three samples recorded in zero filed cooling (ZFC) and field cooling (FC) modes. For measurements in ZFC mode, sample is first cooled from 300K down to 20K in the absence of any field, then a measuring field is applied and *M* – *T* measurements are made in warming cycle. For measurements in FC mode the samples are cooled from 300K down to 20K in the presence of the measuring field and then *M* – *T* variation is again recorded as a function of rising temperature. Departure between measurements in the two modes owes to magnetic relaxation behaviour of the nano-particles and confirm their SPM nature. Observed broad maxima in the ZFC curves

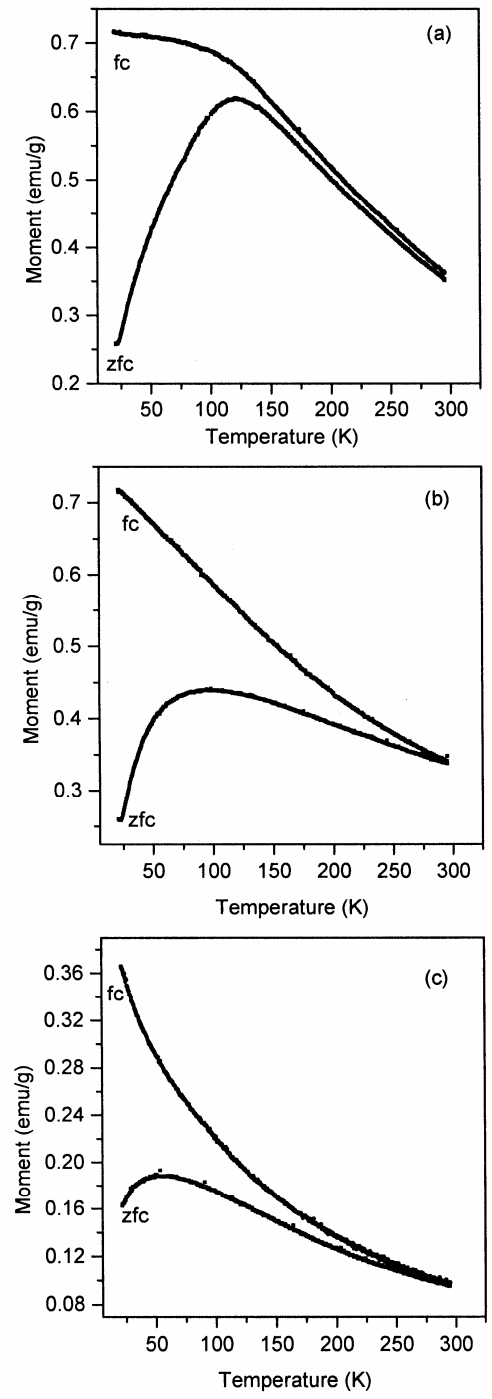

Fig. 4—*M* - *T* curves recorded in ZFC and FC modes for the samples (a) Li10 in 8.2 Oe, (b) Li20 in 8.1 Oe and (c) Li30 in 7.8 Oe

correspond to blocking temperatures for the SPM particles.

Figure 5 (a and b) show the Mössbauer spectra of the samples at 300K and 80K, respectively. The 300K spectra do not show any Zeeman splitting. The superparamagentic appearance is in line with *M-H* measurement at 300K. Also the spectra of Li20 and Li30 at 80K do not show Zeeman splitting. Spectrum of Li10 at 80K exhibits a very low field relaxed pattern.

Table 1—Mössbauer parameters* for the sample $Li_{0.3}Fe_{2.7}O_4$

	A-site	B-site	
T	IS dQ I	IS dQ I	Γ
300K	0.25 0.63 37	0.39 0.69 63	0.51
80K	0.32 0.67 37	0.48 0.71 63	0.52

*IS is isomer shift in mms^{-1} with respect to metallic iron at 300K; dQ is quadrupole splitting in mms^{-1}; I is relative intensity of different sub-spectra in percent and Γ is FWHM in mms^{-1}. The uncertainties in IS, dQ and Γ are ± 0.01 $mms^{-1}$and those in I are ± 1%.

Each of the 300K spectra and the 80K spectra of Li20 and Li30 could be resolved into two doublets – one each attributable to the two crystalline sites, i.e., tetrahedral site (A-site) and octahedral site (B-site). Table 1 presents the Mössbauer parameters of the sample Li30, viz., $Li_{0.3}Fe_{2.7}O_4$, at 300K. The ratios of the intensities of the doublets on the two sites show that in these samples Li occupies the B-site. This is in agreement with the reported[7] Mössbauer result on bulk particle sample $Li_{0.5}Fe_{2.5}O_4$. Based on the values of isomer shift (IS), one pattern in all the spectra is assigned to Fe^{3+} at A-site. The second doublet pattern would belong to B-site. The IS values for this pattern, in the spectra at both 300K and 80K, are suggestive of their arising from iron bearing valence of more than +2. Line widths in all the spectra are rather large which would owe to nano-particle nature and distribution in particle sizes. Further, the presence of Li ions in the lattice will make the environment of second coordination sphere at each Fe site to be randomly different contributing to large line widths.

Now, the question of Verwey transition in magnetite and its substituted analogues, though quite an old one, has been drawing attention even now[8-10]. In this context, our Mössbauer studies on the three nano-particle samples provide an important result. The B-site iron showing more than +2 valence, both at 300K and 80K which would result from electron hopping, between Fe^{2+} and Fe^{3+} states, continuing to occur at temperatures down to 80K. This implies the absence of a Verwey type transition down to 80K in these nano-particle samples. Another measurement where discontinuity is encountered at Verwey transition is the variation of magnetization with

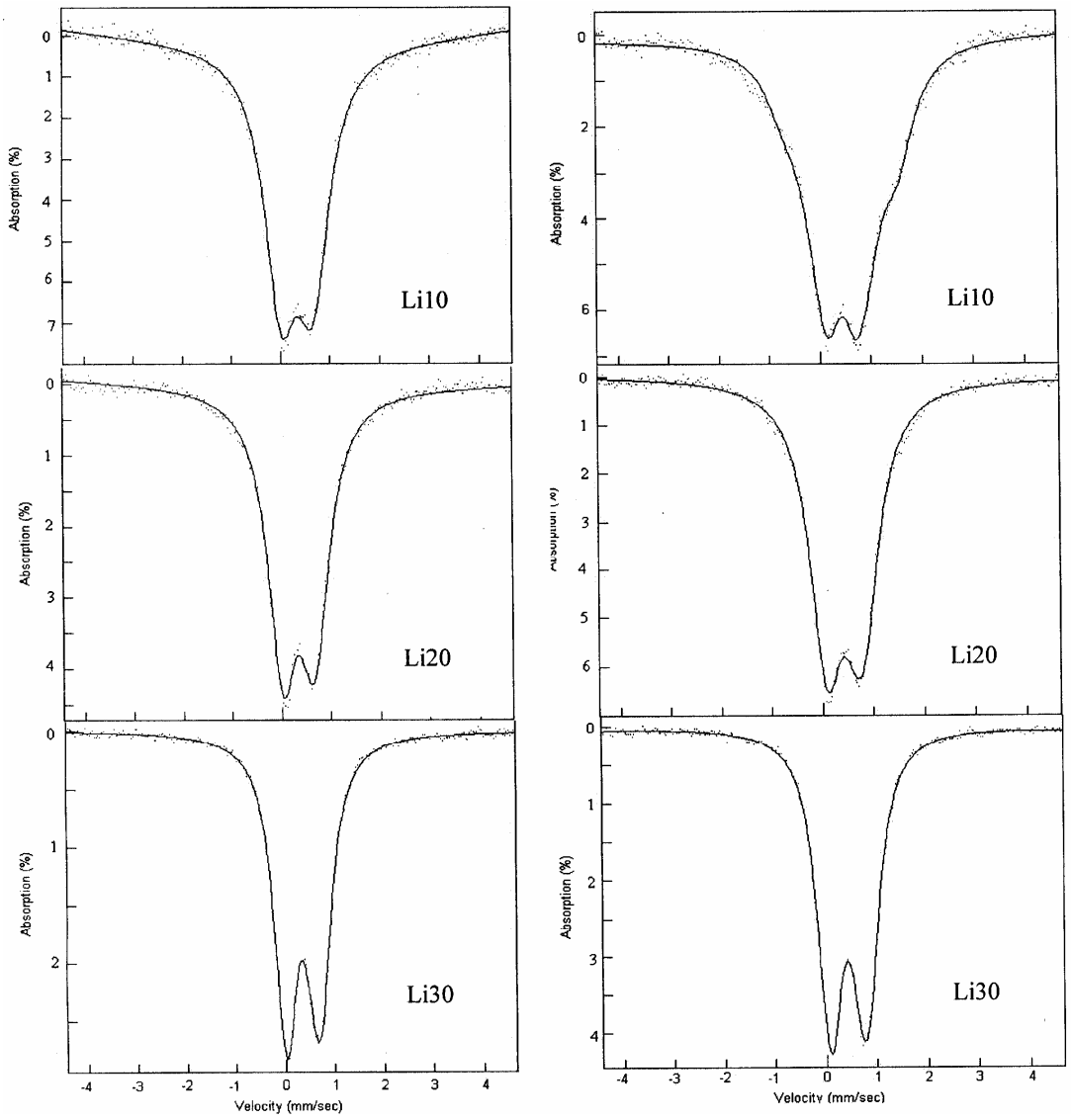

Fig. 5—Mössbauer spectra of the three samples Li10, Li20 and Li30 recorded at (a) 300K and (b) 80K. Fitted envelopes are also shown by continuous lines

temperature[9]. Our ZFC and FC measurements (Fig. 4) do not exhibit any such discontinuity or kink. This not only supports the Mössbauer result of absence of Verwey transition in the three nano-particle samples down to 80K but it also implies that such a transition does not occur down to 20K. It is to be noted that the bulk particle samples of identical compositions in the series $Li_xFe_{3-x}O_4$ are reported[4] to exhibit Verwey transitions at ~61, ~41 and ~35K. Our result on the transition not showing down to 20K would, thus, owe to nano-particle nature of the samples. This is an important result and supports similar findings in other nano-particle ferrites[9].

In conclusion, our study on nano-particle samples of Li substituted ferrites of the three compositions shows (i) that the samples are in superparamagnetic state at 300K, (ii) that Li^+ occupies the octahedral sites (site B) and the site occupancy remains the same as in bulk particle state, (iii) that electron hopping between Fe^{2+} and Fe^{3+} ions at B-sites continues at temperatures down to 80K, (iv) non-appearance of discontinuity or kink in magnetization – temperature curves down to 20K and (v) absence of Verwey type transition in these lithium substituted nano-particle ferrite samples down to 20K.

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