Effect of substitution of In^{3+} ions on the electrical and magnetic properties and Mössbauer study of $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ ferrites

R. K. PURI
Department of Physics, Indian Institute of Technology, New Delhi 110016, India

M. SINGH, S. P. SUD
Department of Physics, Himachal Pradesh University, Shimla 171005, India

The effect of substitution of diamagnetic In^{3+} ions on the electrical and magnetic properties of Mg–Mn ferrites was studied in the ferrite series $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ where x varied from 0–0.8 in steps of 0.1. The incorporation of In^{3+} ions in place of Fe^{3+} ions resulted in an increase of lattice parameter owing to the larger size of the substituted ions, and an increase of d.c. resistivity owing to reduction of Verwey's hopping mechanism. It also resulted in improvement of saturation magnetization and produced a marked increase in the value of initial permeability, thus upgrading the bulk magnetic properties of these ferrites. These bulk magnetic properties improve due to substitution of diamagnetic In^{3+} ions, x, up to 0.5 only, whereas they deteriorate for a higher content of In^{3+} ions. The variations of saturation magnetization have been explained on the basis of modified cation distribution and their magnetic interactions. A large increase in the value of initial permeability has been attributed to its dependence on M_s and magnetocrystalline anisotropy constant. A comparison of bulk magnetic properties with the inferences drawn from Mössbauer studies of these samples shows a similar trend. It is concluded that the substitution of In^{3+} ions, x, up to 0.5 in Mg–Mn ferrites results in the production of a hyperfine field at A as well as B sites, followed by ferromagnetic relaxation and paramagnetic transition for higher concentrations of In^{3+} ions. These variations have been explained on the basis of the effect produced by In^{3+} ions on the magnetic interactions, supertransferred hyperfine fields and domain-wall oscillations.

1. Introduction

Mg–Mn ferrites are quite versatile from the point of view of their applications and the simplicity of their preparation. These ferrites have rectangular hysteresis loop characteristics, which renders them suitable for memory and switching circuits of digital computers, phase shifters and other applications [1, 2]. It has been shown that the magnetic and other properties of ferrites can be upgraded by incorporating suitable diamagnetic impurities in these ferrites [3, 4]. Kirichok and Antoschuk [5] have reported that when small amounts of diamagnetic In^{3+} ions are substituted in place of Fe^{3+} ions in Mg-ferrites, these ions preferentially occupy the A site, which improves its bulk magnetic properties. Amongst the different possible compositions of Mg–Mn ferrites, there is a minimum spin canting in $Mg_{0.9}Mn_{0.1}Fe_2O_4$ ferrites. In addition, there is a very low content of Mn^{2+} ions present in this ferrite which results in a minimum possibility of the formation of Mn^{3+} ions. $Mg_{0.9}Mn_{0.1}Fe_2O_4$ has, therefore, been used as the basic ferrite material in which diamagnetic ions can be

substituted to modify its properties. The present work aimed to successively substitute diamagnetic In^{3+} ions in place of Fe^{3+} ions in $Mg_{0.9}Mn_{0.1}Fe_2O_4$ ferrites to achieve a possible upgrading of their bulk magnetic properties and to study the effect of In^{3+} ions on their electrical and magnetic properties, apart from Mössbauer study of these ferrites.

2. Experimental procedure

The ferrite series was prepared with the composition $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ in which x varied from 0–0.8 in steps of 0.1. The analytical grade reagents MgO, MnO, In_2O_3 and Fe_2O_3 were weighed in proper proportions and thoroughly mixed by wet blending with deionized water in an agate mortar and pestle. The mixed powder was calcined at 1000 °C for 3 h in a platinum crucible to improve the homogeneity of the constituents. The reacted material was well milled by adding a small quantity of polyvinyl alcohol, to reduce the particle size. The pulverized powder was granulated through sieves of 85–120 mesh (BSS) and

compressed to form pellets and toroids. These were finally sintered at 1300 °C for 3 h in a platinum crucible and slowly annealed in air at the rate of 100 °C h^{-1}.

The measurements for d.c. resistivity were made by a two-terminal d.c. method using spring-loaded copper electrodes connected to a Keithley Electrometer Model 610 C. The dielectric constant and initial permeability were determined using a Hewlett–Packard LCR Meter Bridge Model 4275 A. The saturation magnetization was determined using a Vibrating Sample Magnetometer E C and G Model 155. Mössbauer spectra of samples were obtained at room temperature using a Canberra Series 35 M.C.A. and a 50 mCi ^{57}Co source in a palladium matrix. The experimental data were computer analysed using a standard non-linear least squares fit program. The line shapes were assumed to be Lorentzian and the intensities and widths of sextets were allowed to vary freely subjected only to the constraints that $I_j = I_{7-j}$ and $\Gamma_j = \Gamma_{7-j}$ of the component spectrum where I_j and Γ_j correspond to the intensity and width, respectively, of the jth line. The computer fits were obtained with minimum chi-squares values.

3. Results and discussion

X-ray diffraction analyses confirmed single-phase spinel structure for all the compositions of these ferrite samples. The lattice parameter, obtained from X-ray diffraction analysis, for various samples of $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ ferrites, increased successively from 0.839 nm to 0.859 nm as the concentration of In^{3+} ions, x, was increased from 0–0.8, respectively, as shown in Fig. 1. Such an increase in the lattice parameter is expected, because Fe^{3+} ions of smaller radius, 0.067 nm, are being substituted successively with increasing amounts of In^{3+} ions of larger size, 0.091 nm.

D.c. resistivity increased sharply from 6.96 $\times 10^5$ Ωcm to 2.26×10^{10} Ωcm when the concentration of In^{3+} ions, x, was increased from 0 to 0.6, whereas it decreased with further increase of In^{3+} ions. It is well known [6] that Fe^{3+} ions are partially reduced to Fe^{2+} ions during sintering of such ferrites, which results in the formation of a small amount of Fe^{2+} ions in these samples. Also, a small fraction of Mn^{2+} ions reacts with Fe^{3+} ions to form Mn^{3+} [7, 8] and Fe^{2+} as per the following reaction

$$Mn^{2+} + Fe^{3+} \rightarrow Mn^{3+} + Fe^{2+} \qquad (1)$$

The presence of Fe^{2+}–Fe^{3+} and Mn^{2+}–Mn^{3+} ion pairs of the same element but of different valencies present at the equivalent crystallographic sites, results in an increase of conduction due to hopping of electrons in $Mg_{0.9}Mn_{0.1}Fe_2O_4$ ferrites. The addition of diamagnetic In^{3+} ions in place of Fe^{3+} ions limits the degree of conduction by blocking Verwey's hopping mechanism, resulting in an increase of resistivity. The decrease in resistivity for higher concentrations of In^{3+} ions, x, exceeding 0.6, is possibly due to a larger formation of Mn^{3+} and Fe^{2+} ions.

The variations of dielectric constant, ε, were studied as a function of frequency, f, of a.c. field in the fre-
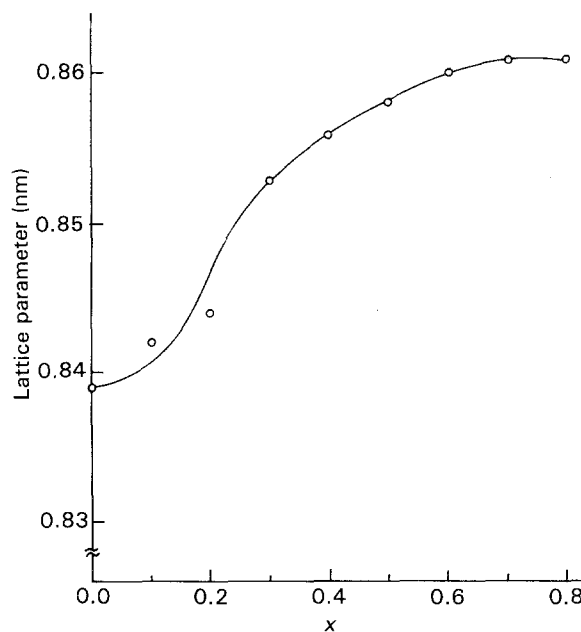

Figure 1 Variations of lattice parameter, a, with concentration of In^{3+} ions in $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ ferrites.
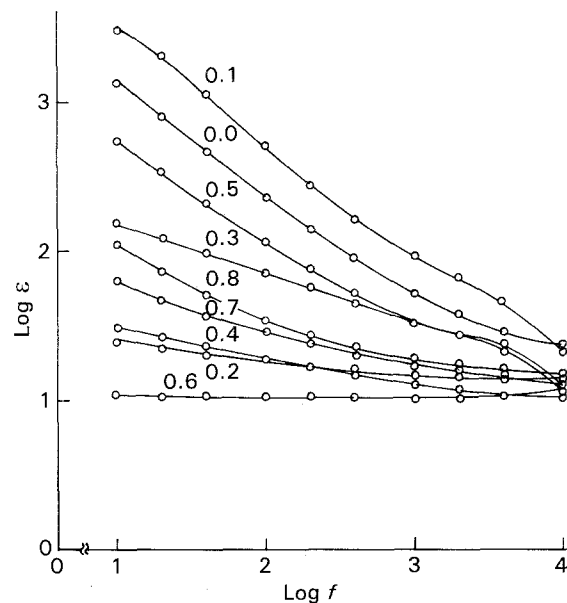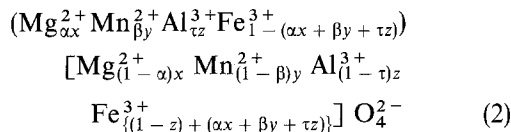

Figure 2 Variations of dielectric constant, ε, with the frequency of the a.c. field.
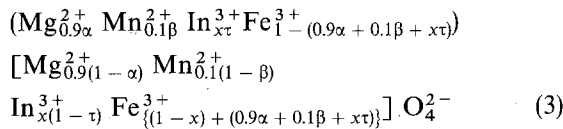
quency range 10 kHz–10MHz. The observed variations for all the samples, as shown in Fig. 2, did not show any systematic dependence but rather typical dispersion curves which result from space charge polarization due to the inhomogeneous dielectric structure. These variations, as explained by Wagner [9], are complex and are mainly governed by the number of space charge carriers and the resistivity of the samples. The dielectric constant may, therefore, possibly be affected due to (i) an inverse proportionality existing between resistivity and dielectric constant [10], and (ii) an increase in homogeneous dielectric structure when an increasing concentration of In^{3+} ions is successively incorporated in Mg–Mn ferrites.

The saturation magnetization, $4\pi M_s$, increases slowly for $0 \leqslant x \leqslant 0.3$ yielding a maximum value for $x = 0.3$ and decreases for $x > 0.3$. A similar trend had been observed for $MgIn_x Fe_{2-x} O_4$ ferrites [5] where $4\pi M_s$ initially increases up to $x = 0.4$ and then decreases as In^{3+} concentration x, was increased. The variation of $4\pi M_s$ with x can be explained from the difference in magnetic moments of A and B sublattices which depend upon their respective cation distributions. It has been conclusively shown by Kirichok and Antoshchuk [5] that when In^{3+} ions are substituted in place of Fe^{3+} ions in $MgIn_x Fe_{2-x} O_4$ ferrites, In^{3+} ions preferentially occupy the tetrahedral site for $0 \leqslant x \leqslant 0.3$, whereas for larger substitutions of In^{3+} ions, x, exceeding 0.3, a small fraction of In^{3+} ions also migrate to octahedral site. It has also been shown that Mg^{2+} ions primarily occupy the octahedral site and a small fraction of Mg^{2+} ions migrate to tetrahedral sites also when the content of In^{3+} ions, x, is increased. A similar type of the following cation distribution has been obtained for $Mg_x Mn_y Al_z Fe_{2-z} O_4$ where manganese ions exist in the divalent state as Mn^{2+} at A and B sites [11]

$$(Mg^{2+}_{\alpha x} Mn^{2+}_{\beta y} Al^{3+}_{\tau z} Fe^{3+}_{1-(\alpha x + \beta y + \tau z)})$$
$$[Mg^{2+}_{(1-\alpha)x} Mn^{2+}_{(1-\beta)y} Al^{3+}_{(1-\tau)z}$$
$$Fe^{3+}_{\{(1-z)+(\alpha x + \beta y + \tau z)\}}] O^{2-}_4 \qquad (2)$$

where α, β and τ are the distribution parameters which represent, respectively, the fractions of Mg^{2+}, Mn^{2+} and Al^{3+} ions present at the tetrahedral site.

As the number of manganese ions in $Mg_{0.9} Mn_{0.1} In_x Fe_{2-x} O_4$ ions is very small, they will mainly exist in the divalent state, Mn^{2+}, at A as well as B sites. Thus the cation distribution of Mg^{2+}, Mn^{2+} and In^{3+} ions with their respective distribution parameters α, β and τ, can be similarly given by

$$(Mg^{2+}_{0.9\alpha} Mn^{2+}_{0.1\beta} In^{3+}_{x\tau} Fe^{3+}_{1-(0.9\alpha+0.1\beta+x\tau)})$$
$$[Mg^{2+}_{0.9(1-\alpha)} Mn^{2+}_{0.1(1-\beta)}$$
$$In^{3+}_{x(1-\tau)} Fe^{3+}_{\{(1-x)+(0.9\alpha+0.1\beta+x\tau)\}}] O^{2-}_4 \qquad (3)$$

where the cations in the parentheses represent A sites and cations in square brackets represent B sites. As the magnetic moment for Mg^{2+} and In^{3+} is zero, the saturation magnetic moment, μ_0, is given by the difference of magnetic moments of B- and A-site ions

$$\mu_0 = \mu_B - \mu_A$$
$$= \mu_{Mn^{2+}}[0.1(1-\beta) - 0.1\beta]$$
$$+ \mu_{Fe^{3+}}[(1-x) + (0.9\alpha + 0.1\beta + x\tau)$$
$$- 1 + (0.9\alpha + 0.1\beta + x\tau)] \qquad (4)$$

As $\mu_{Mn^{2+}} = 5\mu_B$ and $\mu_{Fe^{3+}} = 5\mu_B$, the saturation magnetic moment, μ_0, is given by

$$\mu_0 = 5[1.8\alpha + (2\tau - 1)x + 0.1]$$

Bohr magneton $\qquad (5)$

Because the distribution parameter, α, for Mg^{2+} ions is very small and τ is close to 1.0 for In^{3+} ions, the saturation magnetic moment, μ_0, increases slowly as x increases up to 0.3. As the In^{3+} concentration, x,

exceeds 0.3, a small fraction of In^{3+} ions also occupy octahedral sites and τ decreases, which results in a decrease of μ_0. Thus preference for In^{3+} ions to occupy the A sublattice results in an increase of magnetic moment of the B sublattice and a decrease in magnetic moment of the A sublattice, so that the net magnetic moment increases up to $x = 0.3$. A further increase in the number of In^{3+} ions with $x > 0.3$ in these ferrites weakens the A–B interaction because the In^{3+} (A)–Fe^{3+} (B) interaction is weaker than the Fe^{3+} (A)–Fe^{3+} (B) interaction. It results in a reduction of the resultant magnetization, as x exceeds 0.3. Because $4\pi M_s$ is directly proportional to μ_0, $4\pi M_s$ increases slowly for $0 \leqslant x \leqslant 0.3$ and decreases sharply for x exceeding 0.3. The variations of initial permeability, μ_i, with x are shown in Fig. 3 which indicate that μ_i increases when the amount of In^{3+} ions is increased up to 0.5 in $Mg_{0.9} Mn_{0.1} In_x Fe_{2-x} O_4$ ferrites. It yields a marked increase in initial permeability up to a high value of 13 920 for $Mg_{0.9} Mn_{0.1} In_{0.5} Fe_{1.5} O_4$ ferrites. The value of μ_i, however, decreases sharply when the amount of In^{3+} ions is further increased. These variations can be explained from the following dependence of μ_i

$$\mu_i \propto \frac{M_s^2 D_m}{K_1} \qquad (6)$$

where D_m is the average grain diameter and K_1 is the magnetocrystalline anisotropy constant. It has been observed that the average grain diameter, D_m changes insignificantly due to the substitution of In^{3+} ions in $Mg_{0.9} Mn_{0.1} In_x Fe_{2-x} O_4$ ferrites. As μ_i is proportional to M_s^2, the variations of μ_i with x should be affected in a manner similar to that of variations of M_s^2 with x, which can be obtained from Fig. 4. The variations of μ_i with x show a much larger change than that produced by M_s^2. This implies that variations of the magnetocrystalline anisotropy constant, K_1, mainly affects these variations. The variations of K_1 can be qualitatively explained on the basis of the single-ion anisotropy model [12] which shows that Fe^{3+} ions present at A as well as B sites contribute to
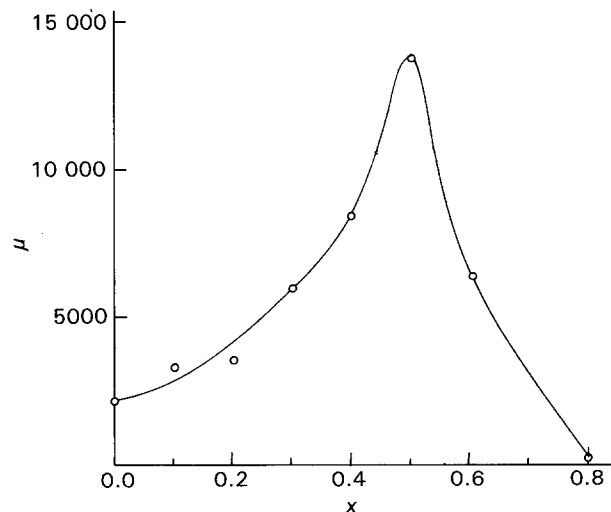

Figure 3 Variations of initial permeability, μ_i, with the concentration of In^{3+} ions in $Mg_{0.9} Mn_{0.1} In_x Fe_{2-x} O_4$ ferrites.
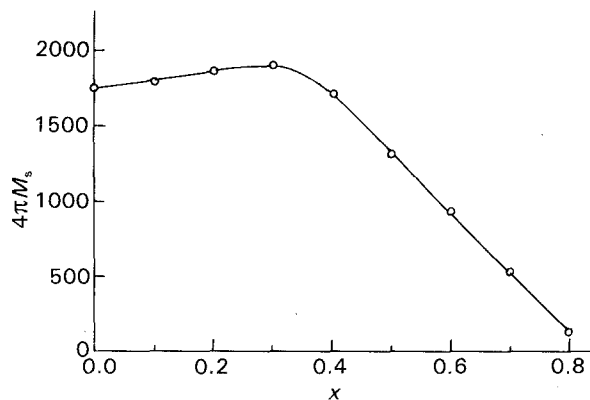
Figure 4 Variations of saturation magnetization, $4\pi M_s$, with x for $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ ferrites.

the anisotropy energy. The net value of K_1 is given by the relative contribution of the positive anisotropy of Fe^{3+} ions at the tetrahedral site which is compensated by the negative anisotropy of Fe^{3+} ions at the octahedral site. As the concentration of In^{3+} ions is increased, the cation distribution of Fe^{3+} ions becomes modified as given by Equation 3 which yields a different number of Fe^{3+} ions present at both the sites, which eventually affects K_1. This implies that the net anisotropy constant K_1 is reduced to its minimum value when the concentration of In^{3+} ions, x, is equal to 0.5, yielding a marked increase to a maximum value of μ_i. The net value of K_1, however, increases with further addition of In^{3+} ions which results in a sharp reduction of μ_i.

The analysis of Mössbauer spectra of these samples at room temperature for increasing values of In^{3+} concentration, x, showed that a magnetic hyperfine field is present at A and B sites, followed by ferromagnetic relaxation and a sharp paramagnetic transition with further increase of In^{3+} ions. The typical spectra for $x = 0.0, 0.1, 0.3, 0.5$ and 0.8 are shown in Fig. 5, in which the solid line shows the best fit with the minimum chi-squares value. Mössbauer spectra of samples with x up to 0.5 showed pure Zeeman splitting which could be resolved into two sextets, each of which has been assigned A or B sites on the basis of their isomer shifts and hyperfine magnetic fields. The isomer shifts of Fe^{3+} ions at both the tetrahedral and octahedral sites are given in Table I which show an insignificant variation for all the samples, indicating that the s electron charge density is influenced by an insignificant amount due to the substitution of In^{3+} ions. The electric quadrupole splitting is negligibly small for all the samples, which shows the presence of cubic symmetry at both the sites.

The internal magnetic field for tetrahedral and octahedral sites is given in Table I which shows that the internal magnetic field decreases as the concentration of In^{3+} ions, x, is increased up to 0.5. Because the internal magnetic field depends upon dipolar magnetic field, H_{dip}, and supertransferred hyperfine field, H_{STHF}, the decrease in the internal magnetic field can be explained from the effect produced by the substituted In^{3+} ions on H_{dip} and H_{STHF}. As In^{3+} ions have a strong affinity to occupy the tetrahedral site for
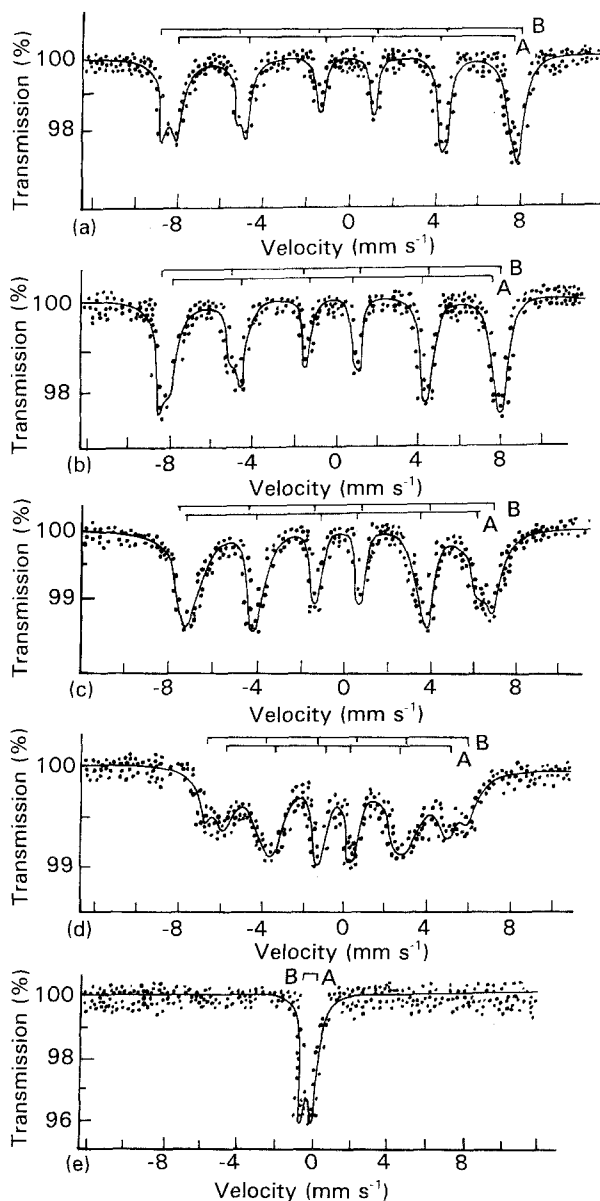

Figure 5 Mössbauer spectra of $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ ferrites for $x = $ (a)0.0, (b)0.1, (c)0.3, (d)0.5 and (e)0.8.

$x < 0.3$ and these ions partly occupy tetrahedral and octahedral sites for x exceeding 0.3, the replacement of Fe^{3+} ions of higher magnetic moment by diamagnetic In^{3+} ions effectively decreases the dipolar magnetic field, H_{dip}. The variation in supertransferred hyperfine field, H_{STHF}, is known to result from overlap and covalent spin charge transfer interaction between the next nearest neighbour cation d orbitals, the nearest neighbour ligand orbits and 4s orbitals of the ions [13]. The net magnetic field is mostly due to dominant $Fe_A^{3+}-O-Fe_B^{3+}$ linkages, because AB interactions are stronger than AA or BB interactions. In^{3+} and Mg^{2+} ions, being diamagnetic, do not directly participate in the exchange interactions, whereas $Fe_A^{3+}-O-In_B^{3+}$ bonds are weak. The replacement of Fe^{3+} ions by diamagnetic In^{3+} ions thus leads to an average net reduction of the number of $Fe_A^{3+}-O-In_B^{3+}$ bonds which A and B site ions will experience. As the two sublattices should be treated as a coupled system, the decrease in average magnetization at either site weakens AB interactions. In addition, AA and BB super-

TABLE I Values of d.c. resistivity, isomer shift, quadrupole splitting and hyperfine magnetic field

x	D.c. resistivity, $\rho(\Omega\,cm)$	Isomer shift (w.r.t. natural iron) ($\pm\,0.01$ mm s^{-1})		Quadrupole splitting ($\pm\,0.02$ mm s^{-1})		Hyperfine field ($\pm\,5$ kOe)	
		I. S. (A)	I. S. (B)	Q. S. (A)	Q. S. (B)	H_A	H_B
0.0	7×10^5	-0.33	-0.42	-0.04	-0.02	473	499
0.1	1×10^7	-0.31	-0.37	0.05	-0.00	462	487
0.2	2×10^8	-0.31	-0.32	-0.07	-0.01	447	472
0.3	7×10^8	-0.34	-0.38	-0.03	-0.06	403	442
0.4	3×10^9	-0.30	-0.31	0.00	0.04	363	405
0.5	8×10^9	-0.40	-0.44	0.01	-0.02	308	363
0.6	2×10^{10}	-0.25	-0.55	$-$	$-$	$-$	$-$
0.7	5×10^9	-0.22	-0.48	$-$	$-$	$-$	$-$
0.8	3×10^8	-0.11	-0.51	$-$	$-$	$-$	$-$

transferred hyperfine interactions, which are strongly dependent on the angles between the spins, tend to reduce the internal magnetic field. Thus the decrease in various magnetic linkages due to substitution of In^{3+} ions mainly reduces H_{dip} and H_{STHF} and results in a net decrease of internal magnetic field at A as well as B sites. As the concentration of In^{3+} ions exceeds 0.5, line shapes and intensities of both the sextets become modified, yielding a relaxed spectra each of which finally collapses to a singlet. This can be explained on the basis of model of domain-wall oscillations and displacements [14]. The Mössbauer spectrum initially consists of two sextets which are produced by ions distributed over A and B sites which lie within the range of domain walls. These domain walls would be bound to their equilibrium position and their motion becomes damped. The shape of relaxed Mössbauer spectra changes significantly due to thermal excitation of these oscillations which will be produced due to those Fe^{3+} ions which lie within the range of domain-wall oscillations. The spectra for $x = 0.8$ can be understood in terms of critical point spin fluctuations in bulk samples [14], which is contributed by atoms due to domain-wall displacements.

References

1. W. N. PAPIAN, *Proc. Metal Powder Assoc. Lond.* **2** (1955) 183.
2. CARL HECK, "Magnetic Materials and their Applications" (Butterworth, London, 1974).
3. NAVDEEP K. GILL and R. K. PURI, *Solid State Commun.* **52** (1985) 579.
4. USHA VARSHNEY and R. K. PURI, *IEEE Trans Magn.* **25** (1989) 3109.
5. P. P. KIRICHOK and A. I. ANTOSHCHUK, *Inorg. Mater.* **13** (1977) 1073.
6. J. B. GOODENOUGH and A. L. LOEB, *Phys. Rev.* **98** (1955) 391.
7. Z. SIMSA, *Czech. J. Phys.* **B15** (1965) 435.
8. A. WITHOP, *IEEE Trans. Magn.* **14** (1978) 439.
9. K. W. WAGNER, *Annal. Phys.* **40** (1913) 817.
10. F. G. BROCKMAN, P. H. DOWLING and W. G. STENECK, *Phys. Rev.* **75** (1949) 1440.
11. S. A. CHO, *J. Mater. Sci.* **9** (1974) 1949.
12. R. F. PEARSON and A. D. ANNIS, *J. Appl. Phys.* **39** (1968) 1338.
13. L. K. LEUNG, B. J. EVANS and A. H. MORRISH, *Phys. Rev.* **B8** (1973) 29.
14. C. M. SRIVASTAVA, S. N. SHRINGI and R. G. SRIVASTAVA, *ibid.* **B14** (1976) 2041.