Mössbauer study of relaxation phenomena in zinc-ferrous ferrites

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The Mössbauer spectra for the $Zn_x Fe_{3-x} O_4$ system have been studied for $x = 0$, 0.2, 0.4, 0.6, and 0.8 at 77 and 300°K. For $x > 0.2$, the room-temperature spectra show relaxation effects similar to other zinc-substituted ferrite systems such as Ni-Zn and Co-Zn. As this effect occurs at temperatures far from the Néel temperature it cannot be accounted for by the critical point fluctuations in the spin system. Simultaneous study of magnetic relaxation has shown that the relaxation effects in the Mössbauer line shape arise owing to the domain-wall displacements. The line shape has been computed using Blume and Tjon's analysis of the Mössbauer spectra in a fluctuating environment and agreement with experimental data was found to be satisfactory. The variation of hyperfine field with zinc concentration has been explained qualitatively on the basis of supertransferred hyperfine interactions.

I. INTRODUCTION

The theory of Mössbauer line shapes in the presence of a fluctuating environment has been considered by a number of authors.[1-8] This theory has been successfully applied to problems involving hyperfine fields and electric field gradients in paramagnets. Its extension to ferromagnets was made by van der Woude and Dekker.[4] Using the stochastic model they showed that the spectra of some of the magnetically ordered materials near the transition temperature can be interpreted successfully.[9] The Mössbauer spectra of superparamagnetic particles have also been explained using the same model by comparing the reversal frequency of magnetization with the nuclear Zeeman frequency.[10]

In magnetically ordered materials, a hyperfine split spectrum is obtained at 0°K. As the temperature is increased the spin system initially has collective modes of excitation described by a spin-wave frequency ($\sim 10^{11}$ rad/sec) which is large compared to the nuclear Zeeman frequency ($\sim 10^8$ rad/sec). The nucleus, therefore, experiences a time-independent hyperfine field which is proportional to the average value of the spin $\langle S_z \rangle$. At higher temperatures the spin-wave approximation becomes increasingly poorer on account of interactions between thermally excited spin waves. It is then simpler to use the molecular-field approximation.[4,9] A single spin experiences the Weiss field due to the neighboring spins and the fluctuations in the spin system cause the hyperfine field to be time dependent. As the spin correlation time τ_c decreases with increase in temperature and becomes comparable to the nuclear Larmor period, ω_N^{-1}, the line shape undergoes rapid changes. The outer lines broaden while the inner lines grow in intensity at the cost of the former.

Finally when $\tau_c \ll \omega_N^{-1}$, there is only one central line which may be split due to the quadrupole interactions. This approach suffers from the fact that there is no definite way of describing the transition from the spin-wave to the molecular-field approximation.

In most ferromagnets the relaxation effects are observed close to T_c. However, in recent years for some of the Zn-substituted mixed ferrites like Ni-Zn, Co-Zn, Li-Zn, relaxed spectra have been reported for temperatures significantly lower than the transition temperature.[11-14] Since in the ordered phase at these temperatures there is a definite average value of $\langle S_z \rangle$, the nuclear spin should see a sharp hyperfine field. The existence of relaxed spectra cannot, therefore, be accounted for in terms of the critical-point spin fluctuations in the bulk of the material. So far no satisfactory explanation for this experimental observation has been offered. The present Mössbauer studies of $Zn_x Fe_{3-x} O_4$ have been undertaken primarily to investigate the origin of the relaxation phenomena in such systems. It has been shown that the Mössbauer relaxation is intimately connected with the magnetic relaxation processes and a satisfactory explanation for the relaxed spectra can be obtained when the correlation between the two is taken into account.

There is another significant result which has emerged from the Mössbauer studies of zinc substituted ferrites at 4°K.[15-17] In most cases the hyperfine field at the Fe^{3+} ions on the B site is largest when Zn is absent and begins to decrease as the Zn concentration increases. The explanation, so far offered, on the basis of the super-transferred A-B interaction is not wholly satisfactory as it does not account for the fact that A-site hyperfine field remains almost independent of the Zn concentration. It is shown in Sec. IV that

this failure arises on account of ignoring the contribution of the B-B supertransferred hyperfine interaction and a satisfactory explanation is obtained only when this is included.

II. MÖSSBAUER SPECTRA OF Zn-SUBSTITUTED FERRITES

Amongst all the ferrites, the most extensively studied is $Zn_xNi_{1-x}Fe_2O_4$.[11,12,15,18] Low-temperature Mössbauer study of this system by Leung et al.[15] at 7 °K indicated that all the compositions $(0 \leq x \leq 1.0)$ investigated were magnetically ordered and the spectra consisted of the superposition of Zeeman lines from A and B Fe sites. In the first systematic study of this system Goldanskii et al.[18] reported the existence of two hyperfine fields corresponding to the two lattice sites and found that at room temperature the A-site field decreased more rapidly with Zn concentration than the B-site field but this was later contradicted by others.[12,15] Daniels and Rosencwaig[12] observed that at 294 °K the spectra were not relaxed for $x = 0$, 0.25, and 0.40 but for $x = 0.62$ it was relaxed, while for $x = 0.7$ and 1 there was only a quadrupole split central line arising from B site which was superimposed on an unsplit A-site line. Raj and Kulshreshtha[11] studied the system for $x = 0.5$ and 0.75 at different temperatures and observed that with the increase in temperature the hyperfine field decreased more rapidly than what was expected from the decrease in sublattice magnetization. They tried to explain their results by assuming the existence of collective spin flipping in the system like in the case of superparamagnetic relaxation. They also found that the line shapes for the two samples of the same composition $(Ni_{0.3}Zn_{0.7}Fe_2O_4)$ but different initial permeabilites were different. Their explanation was based on incomplete magnetic linkages and statistical models of Ishikawa[19] and Gilleo[20] and hence could not be correct for the following reasons. Neutron-diffraction[21] and Mössbauer studies[12,15] proved conclusively that there was canting among spins of the B-site ions which was responsible for the observed variation of saturation magnetization with Zn concentration and there was no evidence of the presence of paramagnetic Fe ions either as single ions or as clusters. Further, the ferromagnetic relaxation studies by Srivastava and Patni[22] showed that the room-temperature linewidth ΔH was almost independent of the Zn concentration for $x > 0.25$. The presence of superparamagnetic clusters would have resulted in an increase in ΔH with x since the clusters would act as additional centers for scattering of the uniform precession spin-wave mode to the degenerate mode manifold.

Bhargava and Iyengar[13] studied the $Zn_xCo_{1-x}Fe_2O_4$ system for $x = 0.25$, 0.5, and 0.7 in the temperature range 80–700 °K. They made use of the stochastic model to explain their data for all temperatures and compositions. The absence of velocity scale for the theoretical spectra makes it difficult to comment on their analysis. Further, no attempt was made to explain the result that the electronic relaxation time remains almost constant in the ordered phase over most of the temperature range and begins to decrease only near the Néel temperature. The application of the stochastic model in the magnetic phase far away from the Néel temperature has to be made in the spin-wave approximation for which the spin correlation time is much smaller ($\sim 10^{-13}$ sec) than the value reported by them ($\sim 10^{-9}$ sec). The origin of the observed electronic spin fluctuations with correlation time of the order of 10^{-9} sec remains therefore unexplained.

Mössbauer measurements on $Zn_xLi_{0.5-(x/2)}Fe_{2.5-(x/2)}O_4$ were reported by Young and Smit.[14] The spectrum for $x = 0$ at room temperature showed two superimposed six-line patterns due to Fe ions on A and B sites, respectively. However, the spectra for $0.2 \leq x \leq 0.6$ had rather complex structure exhibiting broad, asymmetric line shapes. For $x = 0.4$ and 0.6, a quadrupole split paramagnetic doublet was present along with the magnetically ordered six-line pattern. The simultaneous existence of para- and ferrimagnetic line patterns at temperatures 478 and 338 °C below the Néel temperatures for $x = 0.4$ and 0.6, respectively was explained by them on the basis of the presence of Fe ions on A and B sites with different numbers of A-site magnetic neighbors. We have shown already that a theory based on incomplete magnetic linkages cannot be applied to account for the relaxed Mössbauer spectra in the $Zn_xNi_{1-x}Fe_2O_4$ system. The same objections hold here also and it is difficult to accept the explanation offered by Young and Smit[14] for the complex nature of the Mössbauer spectra of Li-Zn ferrites.

Mössbauer studies of $Zn_xFe_{3-x}O_4$ were reported by Dobson et al.[23] They made room-temperature studies for the entire range of $0 \leq x \leq 1.0$. The spectra of samples with $x = 0.2$ and 0.4 were similar to Fe_3O_4 and consisted of the superposition of two six-line patterns from A and B sites. For $x = 0.6$ the spectrum showed typical relaxation features and could be analyzed in terms of the superposition of two sextets and a quadrupole split central line arising from a small fraction of iron ions. The existence of the quadrupole split spectrum was explained on the basis of broken magnetic linkages and the presence of paramagnetic

Fe ions. For the reasons given earlier this explanation is not correct. Further, the recent Mössbauer studies by Gapeev et $al.$[24] on $Mg_xFe_{3-x}O_4$ (which differs from $Zn_xFe_{3-x}O_4$ only in the nature of the nonmagnetic ion) also do not support this proposition. Gapeev et $al.$ found that for all the compositions in the range $0 \leq x \leq 1.0$ the Fe nuclei at both the sites A and B experienced sharp hyperfine fields at $296\,°K$. For Fe_3O_4 and $MgFe_2O_4$ the spectra could be resolved in terms of two sextets, one each from A and B sites. The remaining results were analysed in terms of superposition of four distinct sextets, one from A-site and three from B-site Fe ions. One of the B-site spectra was from the Fe^{3+} ions which did not partake in frequency exchange while the other two originated from Fe^{3+} and Fe^{2+} ions, respectively, which were linked by electron exchange $Fe^{3+} \rightleftharpoons Fe^{2+}$. It is improbable that the paramagnetic clusters are present in $Zn_xFe_{3-x}O_4$ while they are absent in $Mg_xFe_{3-x}O_4$. We therefore conclude that in both cases, below the Néel temperature, the spins are ordered at each iron site. However, the type of magnetic ordering in MgFe and ZnFe ferrites may not be the same as this depends on the distribution of the nonmagnetic metal ions on A and B sites, the exchange and anisotropy fields and similar other factors.

From the available experimental data regarding the relaxation phenomena in Zn substituted ferrites we are led to the following conclusions: (i) The relaxation effect is temperature dependent and vanishes as T approaches $0\,°K$. (ii) The effect occurs in some magnetic insulators particularly with high Zn concentration. It can be assumed therefore that this effect occurs in systems with low anisotropy energy and high initial permeability. It is shown that these experimental results follow from the explanation given in Sec. IV.

III. EXPERIMENTAL

The preparation and the magnetic data of the $Zn_xFe_{3-x}O_4$ samples with composition $x = 0, 0.2, 0.4,$ $0.6, 0.8$ were given in the preceding paper[25] (hereafter referred as I). Before obtaining the Mössbauer spectra all the samples were ground to fine powders. The Mössbauer absorbers were prepared by mixing the powder with a thermosetting plastic powder, heating the mixture to $120\,°C$ under pressure in a mould and cooling to room temperature. The absorbers so prepared had the iron density of approximately 10 mg/cm². The room-temperature spectra were obtained with ferrite absorbers pressed firmly between two thin Mylar foils. The low-temperature spectra were obtained with the ferrite absorbers firmly pressed between two 0.001-in.-thick aluminium foils of the liquid-nitrogen cryostat holder.

The Mössbauer spectra were obtained using a conventional constant velocity electromechanical drive and a single channel analyzer. In this equipment the loudspeaker was coupled to a Hewlett Packard model 3LV A5 transducer. A square wave from a low-frequency function generator was integrated to provide a triangular signal. This triangular signal was amplified and used to drive the loudspeaker. The signal (square wave) induced in the coils of the transducer was used to provide the feed back. The design of this mechanical feedback system was an adaptation of the one used by Cohen et $al.$ with some modifications.[26] The source was 5-mCi Co^{57} plated on copper. All the spectra were obtained in transmission geometry and the 14.4-keV γ rays were monitored using an argon-methane filled proportional counter. The source-detector distance was always large enough that geometrical broadening of the absorption lines was negligible. The calibration spectra were taken with a natural iron foil using a value of 330 kOe for the effective nuclear hyperfine field at room temperature. All the isomer shifts (IS) were measured relative to the center of symmetry of the iron spectrum. The four inner lines of the iron spectrum had a Lorentzian shape with half-width of 0.42 ± 0.07 mm/sec. We used this as the standard line in constructing all the theoretical spectra for $Zn_xFe_{3-x}O_4$.

The Mössbauer results for 77 and $300\,°K$ are shown in Figs. 1(a) and 2(a), respectively. The spectra taken at $77\,°K$ show normal Zeeman-split sextets from A and B sites for $0 \leq x \leq 0.6$, while for $x = 0.8$ it shows a broad central line superimposed on a Zeeman-split sextet. The spectra for $300\,°K$ generally agrees with that reported by Dobson et $al.$[23] except that in our case the relaxation effects are present even for $x = 0.4$. This may be on account of the higher density of our samples (90% of x-ray density) compared to theirs (65%). The $300\,°K$ spectrum for $x = 0.8$ has a central doublet characteristic of the paramagnetic phase.

IV. DISCUSSION

The chemical and magnetic data for the Zn-Fe system were given in I.[25] The variation of the saturation magnetization with Zn concentration was explained on the basis of the presence of Yafet-Kittel angles on B site. The analysis of the permeability spectrum showed that for $0 \leq x \geq 0.2$ the resonance frequency ω_r was large compared to the relaxation frequency Ω, while for $x > 0.2$ the two were close to each other. It is shown below that noticeable relaxation effects in the Mössbauer
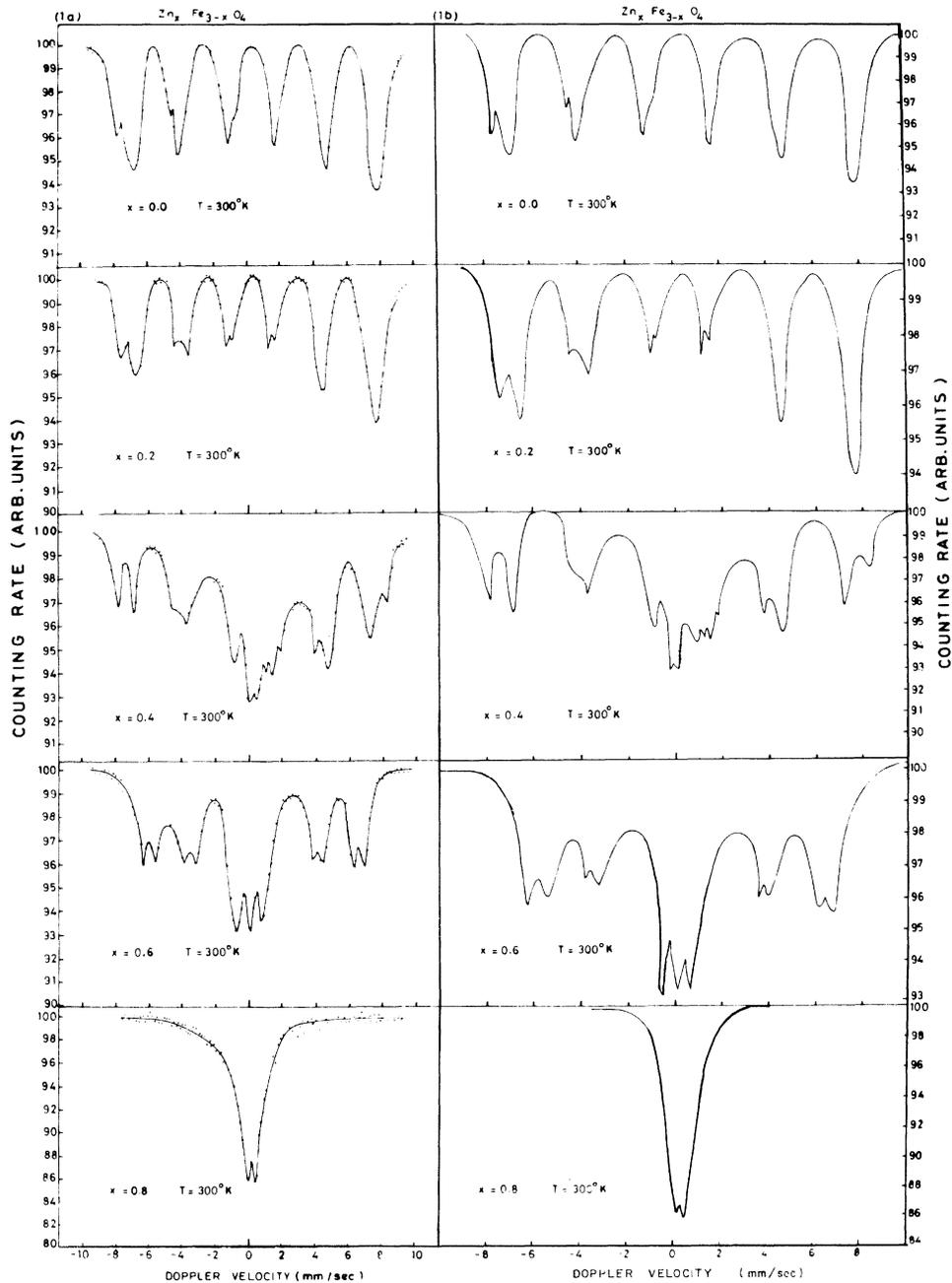
FIG. 1. Mössbauer spectra of $Zn_x Fe_{3-x}O_4$ at 77 °K; (a) experimental curves, (b) theoretical curves. Note that the scales are different for (a) and (b).

spectra should appear when ω_r is comparable to Ω.

A. Line shape

The observed Mössbauer spectra can be generally explained in terms of the superposition of two hyperfine-split sextets and a central doublet. The

existence of the central doublet at temperatures much lower than the critical temperature is due to the thermally excited domain wall oscillations. It was shown in I that such oscillations had a natural resonace frequency ω_r which was of the same order as the nuclear Zeeman frequency ω_N.[25] The ions lying within the range of domain-wall displacements would be subjected to rapid fluctuations
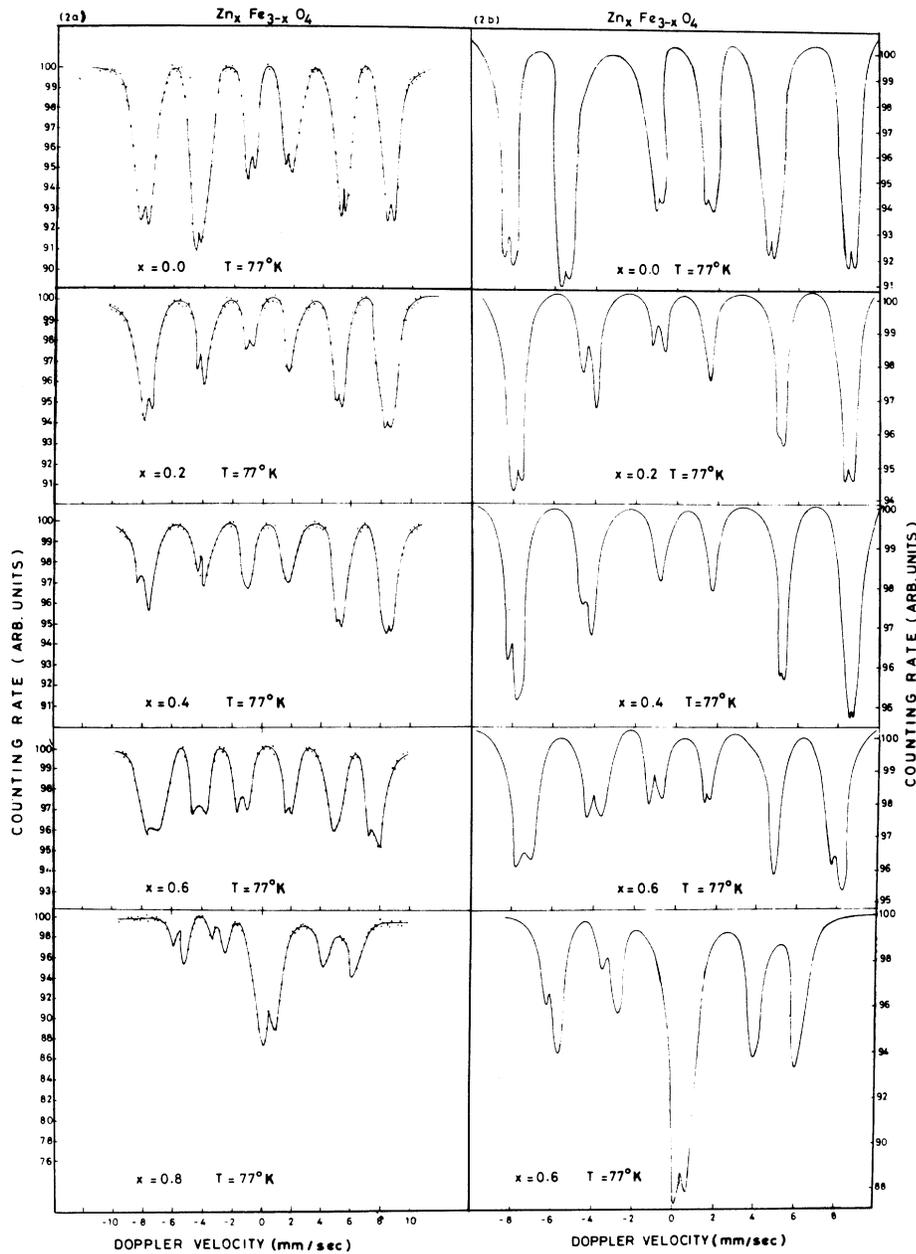
FIG. 2. Mössbauer spectra of $Zn_xFe_{3-x}O_4$ at 300 °K; (a) experimental curves, (b) theoretical curves. Note that the scales are different for (a) and (b).

of the Weiss field. The behavior of these magnetic ions could therefore be treated by the stochastic process.[2-4] The fraction p of such magnetic ions which lie in the range of the domain-wall oscillations has been calculated on a simple model and is given in I [Eq. (9)]. The remaining fraction $(1 - p)$ within the domain would experience a time-independent Weiss field.

To calculate the Mössbauer line shape in presence of domain-wall oscillations, we consider a 180° wall and assume the wall thickness to be small compared to the amplitude of oscillation, $\langle z^2 \rangle^{1/2}$. The fraction p of the ions fluctuates between the two states $\pm \langle S_z \rangle$, where $\langle S_z \rangle$ is the thermal average of the z component of the spin within the domain. These ions, therefore, experience a time-dependent hyperfine interaction, $g \mu_N H I_z f(t)$, where g is the g factor of the nuclear state, μ_N is nuclear magneton, H is the hyperfine field, I_z is the z component of the spin, and $f(t)$ is a random function of time which takes on the values ± 1 at a rate of ω_r/sec.

The fraction $(1 - p)$ of the ions within the domain which lies outside the range of domain-wall oscillations experiences a time-independent field. In spinels these ions are distributed over A and B sites and experience different hyperfine fields, quadrupole interactions, and isomer shifts.

The domain-wall oscillation leads to equal probability of "+" and "−" values of $\langle S_z \rangle$ so the explicit form of the solution for the stochastic model obtained by Blume and Tjon[2] is applicable for this case. Using it for Fe^{57} nuclear transitions in presence of quadrupole interaction, we obtain

$$I(\omega) \propto \sum_{i=A,B} \sum_{m_0, m_1} \xi_i (1-p) \frac{|\langle I_0 m_0 | H^+ | I_1 m_1 \rangle|^2}{\omega - \omega_{0i} - (g_1 m_1 - g_0 m_0)\mu_N H_i - Q_i(3m_1^2 - \frac{15}{4})^2 + \frac{1}{4}\Gamma_i^2}$$

$$+ \sum_{i=A,B} \sum_{m_0, m_1} \frac{2}{\Gamma_i} \xi_i p \operatorname{Re} |\langle I_0 m_0 | H^+ | I_1 m_1 \rangle|^2 \int_0^\infty dt \exp\{i[\omega - \omega_{0i} - Q_i(3m_1^2 - \frac{15}{4})]t - \frac{1}{2}\Gamma_i t\}$$

$$\times (\cos x \omega_r t + x^{-1} \sin x \omega_r t) \exp(-\omega_r t), \tag{1}$$

where ξ_i is the fraction of atoms on the ith $(i = A, B)$ site, ω_r is the resonance frequency of the domain wall given in I [Eq. (8b)], and the remaining terms are the same as in Ref. 2.

It follows from Eq. (1) that for $\omega_r \ll \omega_N$ the spectrum would be a superposition of only two sextets from A- and B-site ions even though some of the ions do experience spin fluctuations owing to domain-wall oscillations. On the other hand, for $\omega_r \gg \omega_N$ the spectrum would consist of two sextets from the ions within the domain and a central quadrupole split spectrum from the ions which lie within the range of domain-wall oscillations. The strength of the central quadrupole split line depends on p which has been calculated in I [Eq. (9)].

The initial permeability is a complicated function of temperature and goes to unity as $T \to 0$, so p is dependent on temperature. It is expected from the usual variation of μ with temperature that the central doublet would reduce in intensity as the temperature is lowered and would vanish at

low temperatures.

We have used Eq. (1) to analyze our experimental data for $0 \leq x \leq 0.6$ at 77 and 330 °K. We have assumed that $\omega_r \gg \omega_N$ so that the contribution from the ions which lie within the range of domain-wall displacements is a simple quadrupole split central line. The intensity parameter p has been adjusted to obtain the closest fit to the observed spectra. The results of the analysis are summarized in Table I and the theoretical curves are shown in Figs. 2(b) and 1(b) for 77 and 300 °K, respectively. The agreement for all the values of x at both the temperatures is fairly good.

The central doublet was observed only for $x \geq 0.4$. For this case we found from the study of the permeability spectrum in I that the ratio of the resonance to relaxation frequency was within the range 1–2. So under thermal excitation we expect that the domain walls would execute oscillations about their equilibrium position giving rise to the central doublet. The strength of the doublet

TABLE I. Results of data analysis based on the spectra shown in Figs. 1(a) and 2(a).

Zinc content (x)	Absorber temperature (°K)	$H_{hf}(A)$ (kOe)	$H_{hf}(B)$ (kOe)	IS(A) [a] (mm/sec)	IS(B) [a] (mm/sec)	$\frac{1}{4}e^2qQ$ (A) (mm/sec)	$\frac{1}{4}e^2qQ$ (B) (mm/sec)	$\Gamma(A)$ (mm/sec)	$\Gamma(B)$ (mm/sec)	p [b]
0	77	550 ± 9	510 ± 9	0.42 ± 0.05	0.62 ± 0.05	$0 \quad \pm 0.02$	-0.40 ± 0.03	0.4 ± 0.15	0.5 ± 0.15	0
	300	509 ± 9	464 ± 9	0.40 ± 0.14	0.65 ± 0.14	0.025 ± 0.03	$+0.07 \pm 0.03$	0.6 ± 0.15	0.8 ± 0.15	0
0.2	77	530 ± 9	500 ± 9	0.42 ± 0.05	0.62 ± 0.05	$0 \quad \pm 0.02$	-0.40 ± 0.02	0.4 ± 0.15	0.5 ± 0.15	0
	300	491 ± 9	455 ± 9	0.44 ± 0.14	0.76 ± 0.14	$0 \quad \pm 0.03$	$0 \quad \pm 0.3$	0.6 ± 0.15	0.8 ± 0.15	0
0.4	77	530 ± 9	500 ± 9	0.42 ± 0.05	0.62 ± 0.05	$0 \quad \pm 0.02$	-0.20 ± 0.02	0.4 ± 0.15	0.6 ± 0.15	0
	300	506 ± 9	455 ± 9	0.44 ± 0.14	0.55 ± 0.14	$0 \quad \pm 0.03$	-0.07 ± 0.03	0.8 ± 0.15	1.2 ± 0.15	0.2
0.6	77	500 ± 9	460 ± 9	0.42 ± 0.05	0.62 ± 0.05	$0 \quad \pm 0.02$	-0.20 ± 0.02	0.4 ± 0.15	0.8 ± 0.15	0
	300	404 ± 9	374 ± 9	0.54 ± 0.14	0.61 ± 0.14	-0.05 ± 0.03	-0.07 ± 0.03	0.8 ± 0.15	1.6 ± 0.15	0.2
0.8	77	400 ± 9	365 ± 9	0.42 ± 0.05	0.62 ± 0.05	$0 \quad \pm 0.02$	-0.20 ± 0.02	0.4 ± 0.15	0.8 ± 0.15	0.4
	300	$\cdots$	$\cdots$	0.42 ± 0.14	0.52 ± 0.14	$0 \quad \pm 0.02$	0.20 ± 0.14	0.6 ± 0.15	1.0 ± 0.15	0

[a] With respect to Fe.
[b] Fraction of ions lying within the range of domain-wall displacements.

depends on p whose value at room temperature was 0.2 for both $x = 0.4$ and 0.6. At 77 °K the value of p was found to be zero. This is in agreement with the relation given in I [Eq. (9)], as at this temperature μ_0 tends to 1.

The spectrum for $x = 0.8$ at 300 °K was a quadrupole split central line from B-site ions superposed on a single line from A-site ions. As T_c was 340 °K, this occurred when the sample was in the magnetic phase. This can be understood in terms of the critical-point spin fluctuations in the bulk of the sample. The more interesting case is the spectrum of this sample at 77 °K. This could best be described as the superposition of a hyperfine field split spectra from A- and B-site ions and a broad central line spectrum from the atoms within the domain-wall displacements. Even at 77 °K the permeability of $x = 0.8$ appeared to be large compared to that of $x = 0.4$ and 0.6 which had $\mu_0 \sim 1$. This happens because the anisotropy energy for $x = 0.8$ is one order of magnitude smaller, while at this temperature T_c/T is only half compared to that of $x = 0.6$. Since permeability tends to increase exponentially as we approach T_c we expect that for $x = 0.8$, μ_0 is significantly different from unity. Such a variation has been observed[27] in $Zn_xCo_{1-x}Fe_2O_4$ and similar variation is most likely to occur in the $Zn_xFe_{3-x}O_4$ system also.

The effect of the presence of a longitudinal external dc magnetic field of 13.5 kOe on the nature of the line shape of the relaxed Mössbauer spectrum of $Zn_{0.7}Ni_{0.3}Fe_2O_4$ was found to be large by Daniels and Rosencwaig.[12] This field being small compared to the hyperfine field was not expected to change significantly any other factor in Eq. (1) except the fraction p of the number of ions within the range of domain-wall displacements. The

change in the line shape can be explained if it is assumed that in the presence of the field most of the domain walls are removed and p is close to zero. In order to have further check we used a transverse field of just 1 kOe obtained from a permanent magnet. The result for $Zn_{0.4}Fe_{2.6}O_4$ is given in Fig. 3. A theoretical curve with $p = 0.10$ is plotted also to show the significant changes in the line shape when the number of domain walls decreases. As expected the structure of the central peak changes significantly and the outer peaks grow in intensity in agreement with the observed spectrum. This agreement could have been further improved if other parameters like the linewidth and p could be slightly varied. However, this was not attempted as the main purpose was to show the influence of a relatively weak field which could alter only the number of domain walls.

B. Hyperfine field

The observed variation of the A- and B-site hyperfine fields with the Zn concentration is shown in Fig. 4. Similar variations[15,17] were observed in NiZn and MnZn systems also. Attempts[15,17] were made to explain this observation on the basis of the mechanism of the supertransferred hyperfine fields. Although this qualitatively explained the variation of B-site hyperfine field with x, the independence of the A-site hyperfine field of the zinc concentration was not explained.

The presence of Yafet-Kittel angles indicates that A-B and B-B superexchange interactions are comparable in strength. It is therefore necessary that along with A-B, B-B supertransferred hyperfine interactions should also be considered. Further, since these interactions are strongly
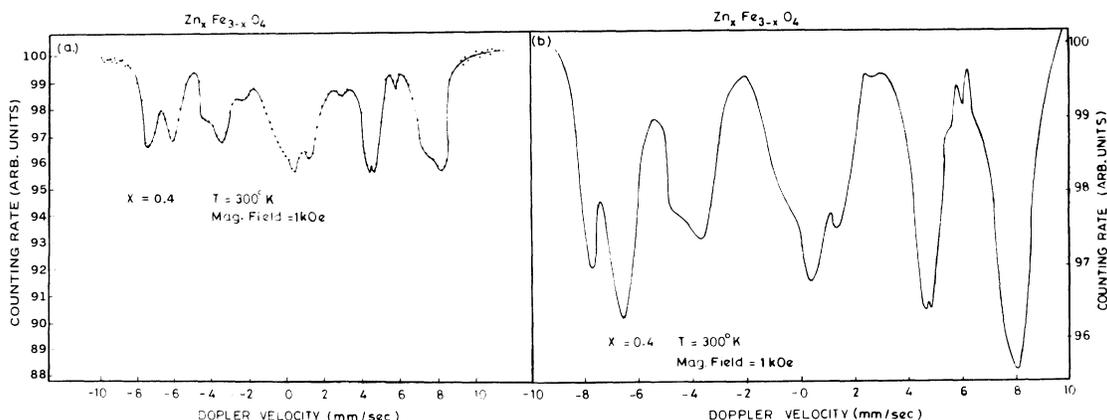
FIG. 3. Mössbauer spectra of $Zn_{0.4}Fe_{2.6}O_4$ with an external field of 1 kOe perpendicular to the direction of propagation of the γ rays; (a) experimental curve, (b) theoretical curve. Note that the scales are different for (a) and (b).

dependent on the angle between the two spins, the angular dependence of the supertransferred hyperfind field should also be taken into account.

The supertransferred hyperfine interaction (STHI) for Fe^{3+} compounds was discussed for the linear chain by Owen and Tayler[28] and Huang et al.[29] As far as we are aware there has not been any attempt to analyze the contribution from the $90°$ B-B STHI on similar lines. One of the possibilities that exists for this type of interaction involves the use of s orbital of $Fe^{3+}(2)$, p_z of the ligand O^{2-} and t_{2g} of $Fe^{3+}(1)$. A certain fraction of the unpaired spin density is transferred from a t_{2g} orbit on $Fe^{3+}(1)$ to the $2p_z$ orbit on the ligand by constructing a π-bonding molecular orbital. This unpaired spin density on the O^{2-} orbit can be partly transferred to the unoccupied s orbital on $Fe^{3+}(2)$ through orthogonalization giving an unpaired s-electron spin density with the same spin direction as the t_{2g} orbital of $Fe^{3+}(1)$. Thus this covalent transfer process leads to a decrease in the absolute value of the hyperfine field. Similar result can be obtained by another mechanism. Let us consider a direct transfer from e_g of Fe^{3+} on a B site to an unoccupied $4s$ orbital of Fe^{3+} on the nearest-neighbor B site. Since the charge transfer Hamiltonian is spin independent, and as the spins on the B sites are parallel, this would again lead to a decrease in the absolute value of H_{hf}. We thus conclude that B-B supertransferred hyperfine interaction tends to reduce the net hyperfine field at the Fe^{3+} ion if the B spins are parallel.

In the presence of Yafet-Kittel angles it is nec-

essary to know the dependence of A-B and B-B STHIs on the angle between spins of the interacting ions. This however cannot be obtained unless a detailed calculation is carried out.

The variation of the hyperfine field with Zn concentration for $Zn_xFe_{3-x}O_4$ can be approximately expressed in terms of A-B and B-B STHIs in the following form:

$$\langle H_{hf}(x)\rangle_A = H_{0A} + \sum_{n=0}^{12} \eta_{AB}(n,x)\Lambda_{AB}(n)f_n(\theta_{AB}),$$

$$\langle H_{hf}(x)\rangle_B = H_{0B} + \sum_{n=0}^{6} \eta_{BA}(n,x)\Lambda_{AB}(n)f_n(\theta_{AB}) \quad (2)$$

$$- \sum_{n=0}^{3} \eta_{BB}(n,x)\Lambda_{BB}(n)[1+g_n(\theta_{BB})],$$

where H_{0A} and H_{0B} are the hyperfine fields in the absence of STHIs. $\Lambda_{AB}(n)$ and $\Lambda_{BB}(n)$ are the strengths of the A-B and B-B STHI, respectively, with n $(Fe^{3+}- Fe^{3+})$ near neighbors. $f_n(\theta_{AB})$ and $g_n(\theta_{BB})$ are the functions denoting the dependence of STHI on the angles between the spins of the Fe^{3+} ions on different sublattices. η_{AB} denotes the relative frequency of occurrence of an A-site Fe^{3+} ion having n B-site Fe^{3+} neighbors when the Zn concentration is x and is given by

$$\eta_{AB}(n,x) = \binom{12}{n}(1+x)^n(1-x)^{12-n}. \quad (3)$$

Similarly $\eta_{BA}(n,x)$ and $\eta_{BB}(n,x)$ are the relative frequencies of occurrence of a B-site Fe^{3+} ion having n A-site and n B-site Fe^{3+} neighbors, re-
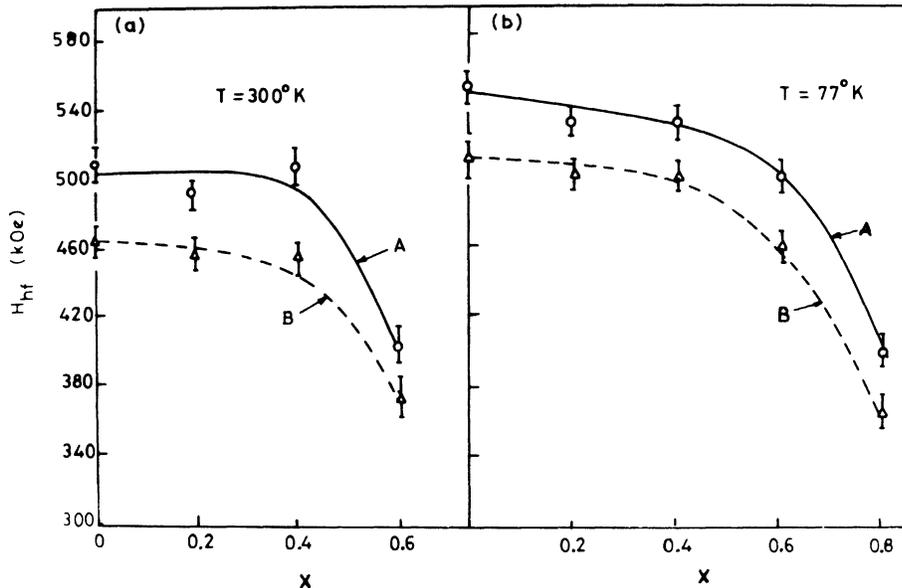
FIG. 4. Hyperfine fields corresponding to A and B sites vs x in $Zn_xFe_{3-x}O_4$; (a) data for 300 °K, (b) data for 77 °K.

spectively, and are given by

$$\eta_{BA}(n,x) = \binom{6}{n}(1-x)^n x^{6-n} \qquad (4)$$

and

$$\eta_{BB}(n,x) = \binom{3}{n}(1+x)^n(1-x)^{3-n}. \qquad (5)$$

As $x \to 0$, $\eta_{BA}(n,x) \to 0$ for all $n \le 5$. For $n = 6$ this tends to 1 as expected.

It is possible to account qualitatively for the variation of the hyperfine field with Zn concentration on the basis of Eq. (2). Consider the hyperfine field at the A site. As x increases the contribution tends to increase due to the factor $\eta_{AB}(n,x)$. However, $f_n(\theta_{AB})$ is certainly going to decrease as Yafet-Kittel angles appear on the B sublattice and θ_{AB} departs from π. On account of the two opposing factors the hyperfine field may remain substantially constant as x is varied. The decrease in the $H_{hf}(B)$ occurs since both $\eta_{BA}(n,x)$ and $f_n(\theta_{AB})$ decrease while η_{BB} increases as x is increased. The factor $g_n(\theta_{BB})$ may reduce to some extent the fall in $H_{hf}(B)$ but its effect is generally expected to be small compared to the rest of the factors. Similar arguments also explain qualitatively the observed variation of the hyperfine fields in NiZn and MnZn systems. It is expected that low-temperature Mössbauer studies may yield the functions $f_n(\theta_{AB})$ and $g_n(\theta_{BB})$ and lead to a better understanding of the supertransferred hyperfine interactions in Zn-substituted spinel systems.

V. CONCLUSION

The Mössbauer spectra of $Zn_xFe_{3-x}O_4$ for $x \ge 0.4$ show relaxation effects at temperatures much smaller than the critical temperature. Such effects had been observed by others in several other Zn-substituted ferrites also. It has been shown that these effects arise due to magnetic relaxation processes associated with the domain-wall oscillation. The correlation between the Mössbauer and magnetic relaxation effects has been studied and the temperature dependence of the Mössbauer line shape is satisfactorily explained on the basis of the thermal excitation of domain-wall oscillations. The changes in the Mössbauer spectra in presence of a small steady magnetic field of 1 kOe are shown to be in agreement with the theory proposed here.

The observed variation of the Fe^{57} hyperfine field on A and B sites with Zn concentration is found to be similar in nature to that of $Zn_xNi_{1-x}Fe_2O_4$. Earlier attempts to explain this effect on the basis of the A-B super-transferred hyperfine interaction were not very successful. It has been shown that in the presence of Yafet-Kittel angles, the effect of B-B supertransferred hyperfine interaction as well as the canting of the spins have also to be considered. On taking proper account of these two effects a satisfactory qualitative explanation has been obtained.

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