Mössbauer study of $Ni_{0.25}Zn_{0.75}Fe_2O_4$. I. Spin fluctuations

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A Mössbauer study of $Ni_{0.25}Zn_{0.75}Fe_2O_4$ has been made in the temperature range from 4.2 to 300 K, in the presence of longitudinal fields up to 80 kG. It is possible to distinguish between the effects of ionic spin relaxation and superparamagnetism on the shape of a Mössbauer spectrum using an external magnetic field, and effects of ionic spin relaxation are found to dominate the spectra of the ferrite. The Néel temperature is found to be higher than 350 K, although the collapse of the magnetic splitting in the absence of an external field occurs at ~250 K. Ionic spin relaxation cannot give rise to the collapse of the magnetic splitting below T_N. This is concluded to be due to superparamagnetism.

I. INTRODUCTION

The Mössbauer effect has been very useful in the study of spin fluctuations in mixed ferrites. It revealed[1–5] the presence of the ionic-spin-relaxation effect in the spectra of mixed ferrites at all temperatures below their magnetic transition temperatures. The relaxation frequency has been found to be temperature independent and low, in comparison to the value predicted from simple theoretical considerations, and thus showed that the magnetically coupled lattice behaves like a paramagnetic system under the influence of an external field as far as the relaxation process is concerned. In a paramagnetic or magnetically dilute lattice, under the influence of a sufficiently large magnetic field, the ionic Zeeman levels, broadened by the magnetic dipolar and exchange fields as well as spin-spin relaxation which gives the Zeeman level a finite lifetime, are discrete. When similar ions are brought closer, the exchange of energy between them becomes faster and leads to broadening of ionic Zeeman levels. Eventually, in a periodic magnetic lattice of similar ions, the propagation of spin waves due to the transverse part of the exchange interaction

$$J_{ij}(S_i^+S_j^- + S_i^-S_j^+) \ ,$$

give rise to the spin-wave bands. In this case spin relaxation occurs owing to the propagation of spin waves and transfer of energy between magnons and has a relaxation time of the order of 10^{-12} sec for $J_{ij} \sim 1$ K. The presence of a larger value of the spin-relaxation time in a mixed ferrite than is suggested by the strength of the exchange interaction showed that the exchange interaction merely provides a Weiss molecular field but is unable to transfer energy between neighboring ions in the manner described above through spin waves. This led to the conclusion[1] that in the mixed ferrites or oxides (or any other magnetic material with very low electrical conductivity) made up of magnetically dissimilar ions randomly distributed at equilvalent sites, the transverse part of the exchange interaction is unable to cause mutual spin flip of the neighboring ions and the propagation of spin waves. The exchange field merely produces Zeeman splitting but the levels remain discrete owing to localization of spin waves.

The presence of a different kind of fluctuation effect, in addition to the ionic spin relaxation, was found[1,2] in the Mössbauer spectra of the mixed ferrites with large concentration of Zn^{2+} ions. This led to a large disagreement between the magnetic transition temperatures determined using the Mössbauer effect and neutron diffraction,[6] which have characteristic times of 10^{-9} and 10^{-12} sec, respectively. The application of a field of 12.3 kG *reduced* the disagreement. However, the precise nature of this could not be ascertained in the earlier investigation[2] as the applied field was insufficient to *remove* the disagreement.

In the present investigation, the mixed ferrite $Ni_{0.25}Zn_{0.75}Fe_2O_4$ which shows the presence of these two effects simultaneously has been studied. Extensive measurement of the effect of the magnetic field on the shapes of the Mössbauer spectra at various temperatures permitted a clear separation of the two effects.

II. EXPERIMENTAL

The $Ni_{0.25}Zn_{0.75}Fe_2O_4$ sample employed in the present measurements was used in the earlier Mössbauer and neutron-diffraction measurements.[1–6] The finely ground powder was mixed with active charcoal and kept in an evacuated sample chamber at the center of the superconducting solenoid which provided the longitudinal field. A pair of thin films consisting of aluminum and aluminized mylar was

placed on both sides of the absorber to provide the radiation shield between the absorber and the helium and to ensure temperature uniformity. A 30-mCi source of ^{57}Co in Rh located 10 cm from the edge of the superconducting solenoid has been used for all the measurements. The calibration spectrum was recorded simultaneously using the other end of the electromagnetic transducer to take into account the small change in the calibration due to the change in the strength of the external field. The spectra have been obtained using a 1024 channel analyzer operated in the pulse-height analyzer (PHA) mode and using a sine wave to drive the spectrometer. The temperatures have been measured and controlled to within ±0.1 K using carbon resistors in the range from 4.2 to 40 K and copper constantan thermocouple at higher temperatures. The effect of the external magnetic field on the resistance of the carbon resistor used for the temperatures measurements has been taken into account using the relation[7]

$$R(H,T) = R(H=0,T)\,[1 + C(H^2/T^{3/2})],$$

$$C = 9.1 \times 10^{-5}\ \frac{\mathrm{K}^{3/2}}{\mathrm{kG}^2}\ ,$$

where $R(H,T)$ represent the resistance at temperature T in a field H. It has been assumed that the external field has no effect on thermocouple voltage at temperatures 70 K and above which is supported by the insensitivity of the power needed in the heater coil to the changes in the magnetic field in the range up to 80 kG.

III. RESULTS

A number of spectra were obtained in the temperature range from 4.2 to 77 K before polarizing the absorber in any way by the external field. The internal fields at Fe nuclei at A and B sites are equal at 4.2 K.

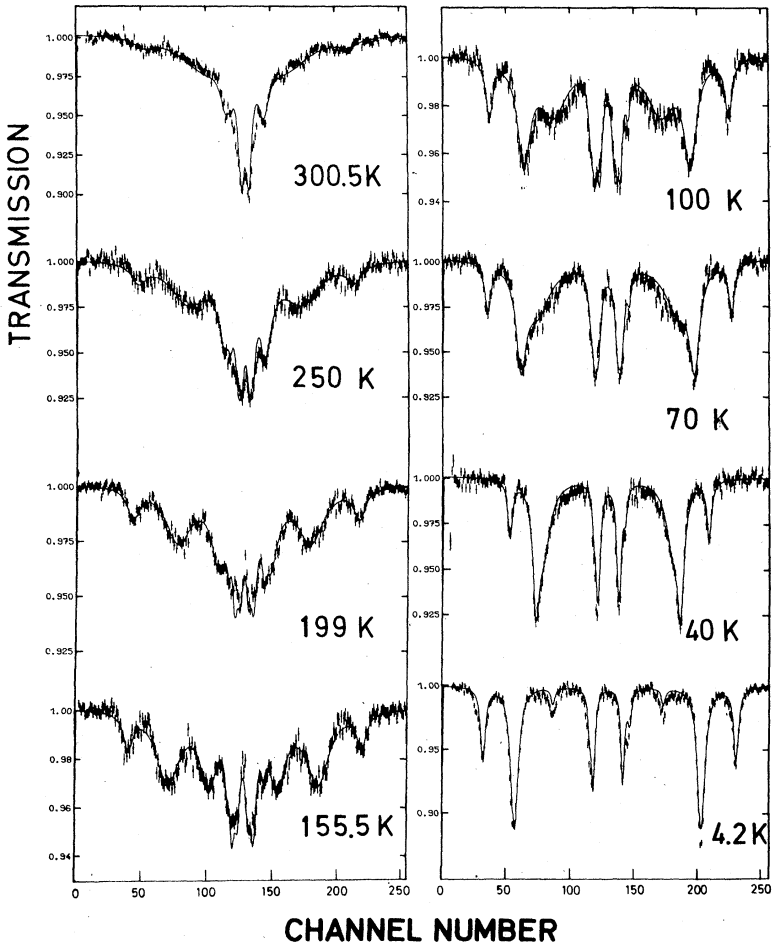

FIG. 1. Mössbauer spectra in the temperature range from 4.2 to 300 K in the presence of a longitudinal field of 80 kG. The solid curve represents the sum of three-component spectra A, B_1, and B_2 which are theoretically simulated using the stochastic model of ionic spin relaxation, described in the text. The change in velocity per channel ΔV, in all spectra except the spectrum at 40 K is 0.097 mm/sec.

The spectra in the temperature range from 4.2 to 80 K, in absence of the external field, show an anomalous increase in line broadening and decrease in the magnetic splitting with the increase in temperature. These spectra are shown in the following paper,[8] hereinafter referred to as Paper II. The zero-field spectra at higher temperatures were published earlier.[1,2] It is remarkable that the spectrum at 300 K in zero magnetic field which is quite similar[1,2] to a paramagnetic doublet is not due to the substance being in the paramagnetic state but due to the presence of fluctuation effects. This is borne out by the effect of the external field on the spectral shape at this temperature described below.

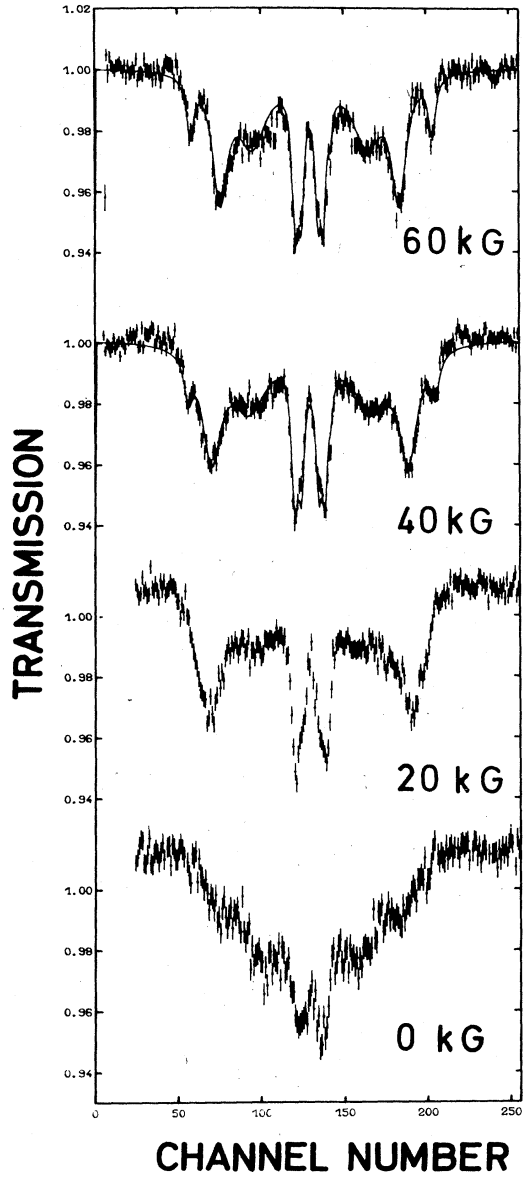

FIG. 2. Mössbauer spectra in the presence of longitudinal fields up to 80 kG at 100 K. The solid curve represents the sum of three-component spectra A, B_1, and B_2 which are theoretically simulated using the stochastic model of ionic spin relaxation and parameters described in Table I. $\Delta V = 0.097$ mm/sec.

The spectra obtained in presence of a longitudinal field of 80 kG at several temperatures in the range from 4.2 to 300 K are shown in Fig. 1. The most remarkable features of the spectra are the separation of A- and B-site component spectra which possess features characteristic of ionic spin relaxation, the larger values of Δ_{34} at all temperatures in comparison to the values in zero external field and the separation of the component spectrum due to B site into two component spectra (hereafter referred to as B_1 and B_2, respectively). Δ_{ij} refers to the separation between i th and j th lines in a Mössbauer spectrum. As we will discuss later, the splitting into A and B components which possess relaxation broadening is characteristic of ionic spin relaxation and cannot be accounted for by assuming the presence of any kind of collective fluctuation (e.g., superparamagnetism) which affect A- and B-site ions collectively and thus identically. The large increase in Δ_{34} of the spectra corresponding to both A- and B-site ions, which are oppositely oriented, at higher temperatures due to the application of the external field, however, shows the presence of a different kind of fluctuation effect in addition to the ionic spin relaxation. As discussed in Secs. IV and V, the presence of ionic spin relaxation cannot lead to a collapse of the hyperfine splitting below T_N seen experimentally.[1,2] The spectrum at 300 K in zero field has negligible magnetic splitting.[2] The splitting which characterizes A, B_1, and B_2 components, possessing large relaxation broadening, at 300 K in the presence of 80 kG corresponds to hyperfine fields of 373, 196, and 172 kG, respectively, which is much greater than the splitting which results from the addition of a field of 80 kG to a paramagnetic doublet. Thus it is seen that the spectrum at 300 K in zero field[2] is due to motional narrowing of the magnetic splitting by a fluctuation effect, which is different from ionic spin relaxation and causes a large disagreement between the magnetic transition temperatures determined using Mössbauer spectroscopy and the neutron-diffraction method.

In the final phase of the experiment, the dependence of the fluctuations on the external field has been determined at 100 K. The anomalous effect in the absence of the external field is large at this temperature. The experimental spectra are shown in Fig. 2.

A. Determination of the ionic spin-relaxation times

The procedure of the computation of the theoretical relaxation spectra has been described earlier.[1–5]

The computer program used in the earlier studies[1-5] was modified to take into account the presence of the longitudinal field which affects the splittings in the hyperfine spectra due to $\pm S_z$ levels oppositely. The rate of flipping between the pairs $\frac{5}{2} \rightarrow \frac{3}{2}$, $\frac{3}{2} \rightarrow \frac{1}{2}$, and $\frac{1}{2} \rightarrow -\frac{1}{2}$ of ionic Zeeman levels are given by $5\Omega_{SS}$, $8\Omega_{SS}$, and $9\Omega_{SS}$, respectively. Ω_{SS} has been treated as variable parameter. The spin-spin relaxation time τ_{SS} is related to the average of these flipping frequencies by the relation

$$\tau_{SS} = [7(1+s)\,\Omega_{SS}]^{-1} \quad . \tag{3}$$

In addition, the ratio of thermal population of successive ionic Zeeman levels s [$s = \exp(-2\mu_B H_a/kT)$, where H_a is the resultant of the Weiss and the external magnetic fields and μ_B represents Bohr magneton], which is related to $\langle S_z \rangle$ by the relation

$$\langle S_z \rangle = \frac{2.5 + 1.5s + 0.5s^2 - 0.5s^3 - 1.5s^4 - 2.5s^5}{1 + s + s^2 + s^3 + s^4 + s^5} \quad , \tag{4}$$

has been treated as a variable parameter.

The fitting of the zero-field spectra obtained in the range of temperature from 4.2 to 80 K with theoretically simulated relaxation spectra showed anomalous increase in s parameter as the temperature increases. The fitting of the zero-field spectra obtained at higher temperatures in the earlier study[1,2] also showed the anomalous temperature dependence of s.

The asymmetry in the shape of the experimental spectra obtained in the range of temperature from 4.2 to 300 K in the presence of the longitudinal field of 80 kG, which is clearly visible at higher temperatures, is due to the splitting of A- and B-site components which have different isomer shifts. The external field of 80 kG separates the outer lines of the A-site spectrum clearly at all temperatures. The positions and widths of these outer lines are temperature dependent which shows that the relaxation frequency is greater than 10^7 Hz. The line shift and the broadening of these outer lines enables the determi-

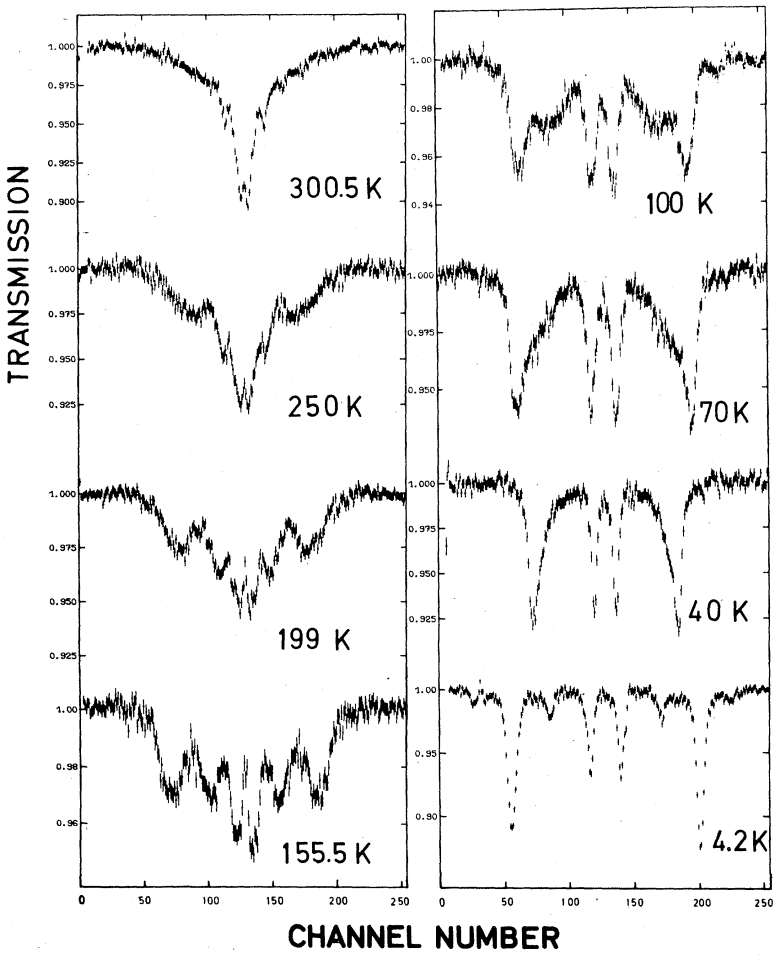

FIG. 3. Spectral shapes at temperatures in the range from 4.2 to 300 K in external field of 80 kG obtained after subtracting theoretical spectra corresponding to Fe^{3+} at A sites from the experimental spectra shown in Fig. 1.

TABLE I. Results obtained by fitting the experimental spectra of $Ni_{0.25}Zn_{0.75}Fe_2O_4$ with theoretical spectra simulated using the stochastic model of ionic spin relaxation as described in the text.

Absorber:	$Ni_{0.25}Zn_{0.75}Fe_2O_4$
Internal fields:	$H^A = 515.3$ kG, $H^{B_1} = 515.0$ kG, and $H^{B_2} = 520.0$ kG
Relative line intensities:	$I^{A,B}_{1,6} : I^{A,B}_{3,4} = 3:9$
Line widths (FWHM in mm/sec):	$\Gamma^A_{1,6}, \Gamma^A_{3,4} = 0.29, 0.22$, and $\Gamma^{B_{1,2}}_{1,6}, \Gamma^{B_{1,2}}_{3,4} = 0.42, 0.22$

Temperature (K)	External field, H (kG)	Difference in isomer shifts of A and B sites spectra (mm/sec)	A site $\langle S_z \rangle$	A site $0.10\Omega_{SS}$ (in MHz)	B_1 site $\langle S_z \rangle$	B_1 site $0.10\Omega_{SS}$ (in MHz)	B_2 site $\langle S_z \rangle$	B_2 site $0.10\Omega_{SS}$ (in MHz)
4.2	80	0.32	2.5	...	2.5	...	2.5	...
40	80	0.32	2.425	6	2.425	3	2.095	3
70	80	0.36	2.39	6	2.34	3	1.77	4
100	80	0.36	2.34	6	2.25	3	1.48	10
100	60	0.32	2.34	6	2.185	3	1.42	10
100	40	0.32	2.30	6	2.105	3	1.29	10
155.5	80	0.36	2.21	6	1.905	3	1.13	35
199	80	0.32	2.12	6	1.705	5	0.95	45
250	80	0.32	1.97	6	1.37	5	0.85	70
300.5	80	0.32	1.81	6	0.95	6	0.82	120

nation of[1-5] s and Ω_{SS} characterizing the A-site component uniquely, at all temperatures. The theoretical spectrum which fits the outer lines of the A-site spectrum was subtracted from the experimental data. This provides a highly symmetric component (hereafter referred to as R and shown in Fig. 3) at all the temperatures. The symmetry implies that the component R arises primarily from Fe^{3+} at B sites. Nevertheless, it is clear, even from a visual inspection, that R is composed of at least two component spectra. This is borne out by the positions and the widths of the second and fifth absorption lines in relation to the other pairs of lines. These lines are much closer to the outer lines at lower temperatures and gradually become closer to the inner lines as the temperature increases. Thus the experimental spectra have been fitted with a sum of three component spectra simulated theoretically using the stochastic model of ionic spin relaxation. All the experimental spectra could be fitted without including the spin-lattice relaxation frequencies. As has been described in another publication,[9] the spin-lattice relaxation allows $\Delta M = \pm 1$ and ± 2 ionic-spin transitions, unlike spin-spin relaxation, which allows only $\Delta M = \pm 1$ transitions. Thus the effect of the presence of spin-lattice relaxation on the shape of the Mössbauer spectra is quite distinguishable from the effect of the spin-spin relaxation.

The fitted spectra have been shown by solid curves in Fig. 1. The results thus obtained have been given in Table I. The temperature dependences of $\langle S_z \rangle$ characterizing the three component spectra have been shown in Fig. 4. The results show that whereas the temperature dependences of $\langle S_z \rangle$ characterizing A and B_1 components do not show anomalous behavior, the behavior of $\langle S_z \rangle$ corresponding to the B_2 component is anomalous, in presence of the field of 80 kG. Similarly, the relaxation frequencies Ω_{SS} characterizing the A and B_1 components are tempera-

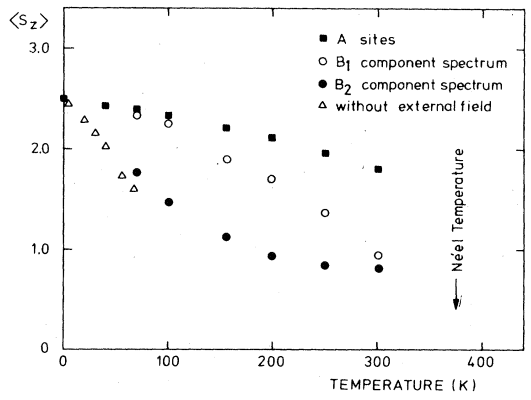

FIG. 4. Temperature dependences of $\langle S_z \rangle$ characterizing A, B_1, and B_2 component spectra in the field of 80 kG obtained using Eq. (4) given in the text.

ture independent at lower temperatures, the Ω_{SS} characterizing the B_2 component deviates from the value characterizing the B_1 component as the temperature increases.

A similar procedure has been adopted to fit the experimental spectra at 100 K in presence of the fields of 40, 60, and 80 kG. The fitted curves are shown in Fig. 2 and the results thus derived are given in Table I. It is found that whereas the relaxation frequencies are independent of the strength of the external field, the $\langle S_z \rangle$ characterizing the A and B_1 components depend on the field below 60 kG. The $\langle S_z \rangle$ characterizing the B_2 component increases with the increase in field even at 80 kG.

IV. DISCUSSION

A. Influence of the external magnetic field on spectral shapes due to ionic spin relaxation and superparamagnetism

The external magnetic field can be used to distinguish between the effects of ionic spin relaxation and superparamagnetism on the shape of Mössbauer spectra unambiguously. Spectral shapes due to superparamagnetism in substance with uniaxial and cubic anisotropies can be distinctly different and are discussed separately.

1. Uniaxial anisotropy

In presence of the superparamagnetic (spm) effect, the internal field at the nucleus fluctuates between $am\langle S_z \rangle$ and $-Am\langle S_z \rangle$ at a rate given by

$$\tau = \tau_0 \exp(KV/kT) \ ,$$

where K is the uniaxial anisotropy energy per unit volume, V is the volume of the magnetic domain, and $\tau_0 \sim 10^{-10}$ sec. Thus the separation of the lines corresponding to nuclear transitions $\pm(m_1 - m_0)$ cannot exceed the value $|2(A_1 m_1 - A_0 m_0)|\langle S_z \rangle$, hereafter referred to as $\Lambda_{m_1 m_0}$. Here, the subscripts 1 and 0 refer to the excited and ground nuclear levels, respectively. The lines corresponding to the transition $\pm(m_1 - m_0)$ move inward to the zero position in addition to broadening as τ_{spm} becomes smaller than $\Lambda^{-1}_{m_1 m_0}$. The number of lines in a spectrum cannot exceed six in absence of the external field for any value of the superparamagnetic relaxation frequency. In the presence of the longitudinal magnetic field, the intensities of the lines corresponding to the $\Delta m = 0$ nuclear transitions becomes zero and consequently the number of lines cannot exceed four, provided there is no canting in the spin structure. The lines corresponding to the transitions $\pm(m_1 - m_0)$ move to the zero position as τ_{spm} become smaller than $\Lambda^{-1}_{m_1 m_0}$ in the presence of the external field also. The spectral shape is extremely sensitive to T and H when $\Omega_{\text{spm}} \sim \Lambda_{m_1 m_0}$.

2. Cubic anisotropy

In the absence of an external field, the effects of the superparamagnetic fluctuations on the Mössbauer line shapes of particles with cubic and uniaxial anisotropies are similar. In the presence of the external

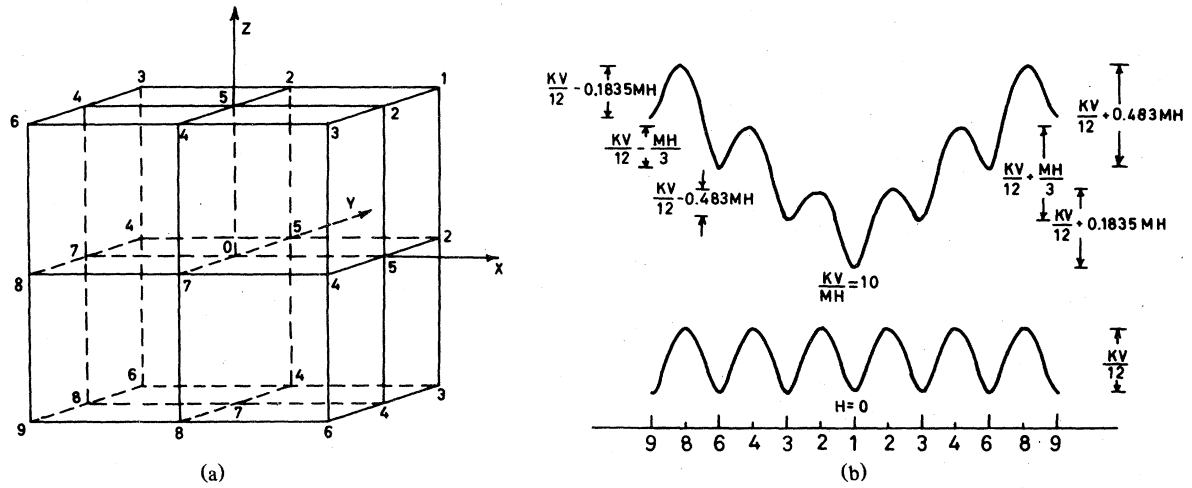

Fig. 5(a). Schematic representation of the enrgies when the spin located at 0 points along different directions in the cubic environments. The magnetic field H is along 01 and the anisotropy energy constant K is negative. The energy increases as the numericals labeling various directions on the cube increase for small values of the field H. The directions marked with identical numbers correspond to equal energies. (b) Changes in energy as the spin rotates along the edges of the cell. In the absence of H, the spin experiences minimum barrier when rotated along an edge, but this is not so when H is large such that (KV/MH) is smaller than 5.

field, the difference appears as the energy barrier takes the form shown in Fig. 5. The thermal energy causes fluctuations between the directions corresponding to the minima (3-3), (6-6), or (1-1). The fluctuations decreases the line separation from $\Lambda_{m_1 m_0}$ to $\Lambda_{m_1 m_0}\cos\theta$, where 2θ is the angle between the two directions of the minima. The number of lines is four only in absence of any fluctuation or when 2θ is 180°, but not more than six in any case.

On the contrary, in the presence of ionic spin relaxation the line positions are independent of temperature (or $\langle S_z \rangle$) when the spin-relaxation frequency is low, and the separation of lines corresponding to $\pm(m_1 - m_0)$ transitions cannot become lower than $\Lambda_{m_1 m_0}$ for any value of the relaxation frequency. When Ω_{SS} is small, the number of lines increases from 6 to 18 in absence of H and from 4 to 24 in the presence of H as the temperature increases from zero to T_N. This difference is due to the fact that whereas the line positions in the spectrum due to $\pm S_z$ ionic levels are same in absence of the external field, the line splitting in the two spectra are affected oppositely by the external field. Furthermore, the increase in the thermal population of higher ionic levels results in larger relative intensities of absorptions in the inner parts of the Mössbauer spectrum.

B. Spectral shapes when superparamagnetic and ionic spin-relaxation effects are simultaneously present

The exponential dependence of the superparamagnetic relaxation frequency Ω_{spm} on $-KV/kT$, which is highly temperature dependent, indicates that generally the component spectra are either characterized by $\Omega_{\text{spm}} > \omega_L$ or $\Omega_{\text{spm}} < \omega_L$ where ω_L is the Larmour precession frequency. The collapse of the magnetic splitting due to superparamagnetism occurs rapidly in a narrow range of temperature. On the contrary, the spin-spin relaxation frequencies (Ω_{SS}) are temperature independent and such a simplification is not valid.

In superparamagnetic fluctuations, the magnetization of the magnetic domain fluctuates from one direct of easy magnetization to another direction of easy magnetization without causing a change in the spin state $|M\rangle$ of any particular ion in the cluster. The transition from say $|M\rangle$ to $|M'\rangle$ Zeeman state of an ion can occur only through an exchange of energy with other spins in the magnetic domain or the lattice (called ionic spin relaxation). The direction of the nuclear spin is, however, not affected by the rapid changes in the directions of magnetizations either of the cluster or of an individual ion, only the magnitude of the internal field is changed. Thus, when $\Omega_{\text{spm}} \ll \omega_L$, the features of ionic spin relaxation on the shape are not affected by Ω_{spm} except through a small broadening and

$$h(V,T)\left(=\frac{H_{\text{int}}(V,T)}{H_{\text{int}}(\infty,T)}\right),$$

less than unity due to superparamagnetism, if Ω_{spm} is not too small.[10] But when the direction of magnetization of the cluster M change rapidly from one easy direction of magnetization to another oriented at an angle 2θ, such that $\Omega_{\text{spm}} \gg \omega_L$, the ion in the spin state $|M\rangle$ give rise to a hyerfine field $H_{\text{int}}^M \cos\theta$ instead of H_{int}^M resulting in absence of superparamagnetism. The ionic spin relaxation from $|M\rangle$ to $|M'\rangle$ state of the ion thus changes the internal field from $H_{\text{int}}^M \cos\theta$ to $H_{\text{int}}^{M'} \cos\theta$ in presence of the fast superparamagnetic fluctuations. As the population of any spin state $|M\rangle$ of an ion is unchanged by Ω_{spm}, the s parameter of the spin-relaxation spectra is unaffected.

C. Interpretation of experimental results

Experimentally, the external field has been found to split the spectrum into three component spectra A, B_1, and B_2. The shapes of the component spectra show presence of large fluctuation effects even in the field of 80 kG and can be very satisfactorily fitted using the stochastic model of ionic spin relaxation at all temperatures. The spin-relaxation frequencies Ω_{SS} characterizing A and B_1 component spectra has been found to be independent of temperature and $\langle S_z \rangle$ characterizing A and B_1 components thus determined show normal temperature dependence in presence of the field of 80 kG. The A and B_1 components can be identified with Fe^{3+} at A and B sites, respectively. These features unambiguously rule out the presence of appreciable effects of any collective spin-flip process like superparamagnetism in A and B_1 components at 80 kG. The temperature independence of Ω_{SS} characterizing A and B_1 components is similar to the behavior found[1–5] in other mixed ferrites with lower concentrations of Zn^{2+} ions. This behavior of Ω_{SS} is consistent with the interpretation given earlier[1] for the large values of τ_{SS} in these magnetic materials.

We consider the possibility of the simultaneous presence of superparamagnetism and ionic spin relaxation to explain the anomalous temperature and magnetic field dependences of Δ_{34}, described earlier in Sec. III and in Paper II. When $\Omega_{\text{spm}} < \omega_L$, superparamagnetism does not affect the line positions. Also, when $\Omega_{\text{spm}} > \omega_L$, the superparamagnetic fluctuations do not affect the shape of the spectrum showing ionic spin relaxation except through a decrease in hyperfine field corresponding to state $|M\rangle$ from H_{int}^M to $H_{\text{int}}^M \cos\theta$, where 2θ is the angle between

the two directions of easy magnetizations ($2\theta = 180°$ in case of uniaxial anisotropy). In particular, superparamagnetic fluctuations with the frequency appreciably greater or smaller than ω_L cannot change s and Ω_{SS} parameters and consequently cannot contribute to line widths and change the temperature dependences of Δ_{16}/Δ_{34} and Δ_{25}/Δ_{34}. But the zero-field experimental spectra in the lower-temperature range, do not show a decrease in the hyperfine field corresponding to an ionic state but an anomalous increase in s parameter and a consequent increase in Δ_{16}/Δ_{34}, Δ_{25}/Δ_{34}, and in the relative intensities of absorptions in different parts of the spectrum as the temperature increases from 4.2 to 70 K. As the Néel temperature is much higher, a normal behavior of $\langle S_z \rangle$ can result in only a small increase in s as temperature increases from 4.2 to 70 K.

All the experimental spectra[2] could be fitted with theoretical relaxation spectra. In an ionic spin-relaxation spectrum, linewidths, relative intensities of absorptions in different parts of the spectrum, and the ratios Δ_{16}/Δ_{34} and Δ_{25}/Δ_{34} uniquely fixes s and Ω_{SS} parameters. The large changes in Δ_{16}/Δ_{34}, Δ_{25}/Δ_{34} and the relative intensities of absorptions in the inner parts of the spectrum which accompanies the line broadenings due to ionic spin relaxation can distinguish it from the broadening due to other sources (For example, a spread in hyperfine fields).

The absence of any effect of superparamagnetism in the low-temperature range is also borne out by the effect of the external field on spectral shape at 100 K discussed below. The presence of the superparamagnetic effects in addition to the ionic spin relaxation at higher temperatures ($T > 200$ K) is, however, strongly indicated by the collapse of the splitting of the zero-field spectrum at temperatures (~250 K) lower than T_N. Ishikawa studied[11] hysteresis loops of $Ni_xZn_{1-x}Fe_2O_4$, $x = 0.1$, 0.2, and 0.4. The composition $x = 0.1$ showed the presence of superparamagnetic behavior at 20 K, and finite area of the hysteresis loop at 2 K. This was interpreted[11] to be due to diamagnetic isolation of ferrimagnetic clusters consisting of 13 (one magnetic ion on A site coupled to 12 ions on B sites through J_{AB}) and 23 (two magnetic ions on A sites coupled to 21 ions on B sites through J_{AB}) magnetic ions in the lattice by Zn^{2+} ions on the A sites. The hysteresis curve at 2 K showed that the superparamagnetic blocking temperature, T_{spm}, of these clusters is greater than 2 K. The shapes and areas of the hysteresis loops of the ferrite with composition $x = 0.2$ at 5 and 201 K have strong resemblance to the hysteresis loop of the composition $x = 0.1$ at 2 K but is remarkably different from the area of the hysteresis curve of the composition $x = 0.4$, in which the long-range magnetic ordering due to J_{AB} interactions exist, and thus indicate cluster formation in $x = 0.2$. The finite area of the hysteresis curve at 201 K, however, showed that the ferrimagnetic clusters in $x = 0.2$ are large such that the blocking temperature T_{spm} is higher than 201 K. The sizes of the clusters composed of 13 and 23 magnetic ions as visualized in the model of Ishikawa are too small ($r < 10$ Å) and should not give $T_{spm} > 10$ K. The larger cluster possessing $T_{spm} > 201$ K could result from magnetic coupling between the small clusters proposed by Ishikawa through magnetic ions on the A sites. The superparamagnetic fluctuation of the large cluster and a uniaxial superparamagnetic particle would give similar temperature dependences of Δ_{34}. This can explain the collapse of magnetic splitting at 250 K ($< T_N$) but cannot give the rapid decrease of Δ_{34} at $T < 30$ K in view of the exponential dependence of τ_{spm} on (KV/kT), in agreement with the conclusions derived above.

D. Influence of the external magnetic field at 100 K

The most significant objection to the interpretation of the anomalous increase in the line broadening and decrease in the magnetic splitting with the increase in temperature at low temperatures to be due to superparamagnetism appears from the spectra at 100 K in fields of 80, 60, 40, and 20 kG. The spectrum splits into three components. A and B_1 can be easily identified with Fe^{3+} ions at A and B sites, respectively. The component B_2 can be fitted using the stochastic model of ion spin relaxation and shows anomalous behavior of s even in the field of 80 kG. If this component B_2, which has same isomer shift as B_1, is due to a part of the Fe^{3+} ions at B sites, it implies that the interpretation of the anomalous behavior of Δ_{34} to be due to superparamagnetism is not correct because this collective fluctuation influence the spectra of A and B sites identically. On the other hand, if it is assumed that the quantitative fits with the theoretically simulated ionic-spin-relaxation spectra obtained above are accidental and the B_2 component is due to superparamagnetic clusters with negligible moment such that Ω_{spm} is weakly affected by H, the inconsistency in this interpretation is immediately obvious. The effect of the external field on a spectrum showing superparamagnetic effects occurs in two distinct steps. First, the unfolding of the spectrum occurs[12] as the external field is increased. After the unfolding is complete, the increase in the external field narrows the lines in the split spectrum. Experimental spectra at 100 K, however, show that the increase in the external field above 20 kG does not increase the splittings of the component spectra but only narrows the broadened lines (Fig. 2). Thus line separations in the B_2 component above 20 kG cannot have any motional narrowing due to superparamagnetism which shows that the anomalous behavior of Δ_{34} characterizing the B_2 component even in the presence of 80 kG at $T < 100$ is not due to super-

paramagnetism. The quantitative fits of the spectra of $Ni_{0.25}Zn_{0.75}Fe_2O_4$ in the presence of a field of 12.3 kG described earlier are not significant because the analysis does not take into account the presence of three components A, B_1, and B_2 which have been seen in the present investigation using larger H.

The application of the external field suppresses the fluctuations, which cause the collapse of the magnetic splitting of the zero-field spectra at $T \sim 250$ K.

V. CONCLUSIONS

An extensive investigation of the mixed ferrite $Ni_{0.25}Zn_{0.75}Fe_2O_4$ has been made in the present study. The presence of ionic-spin-relaxation effects in the Mössbauer spectra of the ferrite has been established and has been related to the presence of disorder in the arrangement of magnetically similar ions. In substances like $Ni_xZn_{1-x}Fe_2O_4$, $0 < x < 1$, the presence of ions like Zn^{2+} cuts off the propagation of magnetic wave completely. The exchange interactions of an ion with the neighboring magnetic ions do give rise to the Weiss field, but the formations of magnetic waves which critically depend on the widths of Zeeman levels in comparison to the differences in the Zeeman splittings of the neighboring ions do not occur.[13] The small temperature-independent value of the relaxation frequency observed experimentally indeed show that Zeeman levels remain discrete, as in a paramagnetic system in the presence of an external magnetic field. The spin relaxation is not due to mutual spin flip between neighboring ions coupled by exchange interaction but between more distant ions interacting through magnetic dipolar fields.

In addition, superparamagnetic effects have been concluded to be present at higher temperatures ($T > 200$ K), though the magnetic clusters formed in the lattice should be much larger than the clusters of 13 and 23 magnetic ions suggested in the model of Ishikawa.[11]

Whereas the assumption of the presence of superparamagnetism satisfactorily explains the collapse of magnetic splitting at $T \sim 250$ K ($< T_N$), it is found to be an incorrect explanation for the anomalous decrease of Δ_{34} at lower temperatures ($T < 100$ K). The interpretation for the low-temperature behavior of Δ_{34} has been provided in Paper II.

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