

Mössbauer study of ferrite systems $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$

V K SINGH*, N K KHATRI and S LOKANATHAN

Department of Physics, University of Rajasthan, Jaipur 302 004, India

*On leave from SGRR (PG) College, Dehra Dun.

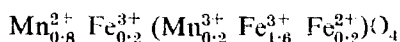
Abstract. Mössbauer spectra of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ferrites with x values ranging from 0.1 to 0.8 in steps of 0.1 have been recorded at room temperature. All spectra exhibit well-defined Zeeman hyperfine patterns. It has been observed that hyperfine field at Fe^{3+} nucleus increases more rapidly by nickel substitution than by cobalt substitution. This has been explained in terms of exchange interactions and cation distribution in the spinels. Hyperfine fields, isomer shifts and quadrupole splittings have been determined.

Keywords. Ferrites; Mössbauer spectra; octahedral sites; tetrahedral sites; super-exchange interaction; hyperfine field; isomer shift; quadrupole splitting; site preference energy.

1. Introduction

Ferrites are a broad class of complex magnetic oxides of considerable technological importance. They have the general formula $M\text{Fe}_2\text{O}_4$, where M stands for one- or two-metal cations. These cations are situated in the oxygen tetrahedron and octahedron. In each unit cell eight tetrahedral sites (A) and sixteen octahedral sites (B) are occupied by the cations in ferrites. Extensive studies of manganese-cobalt and manganese-nickel ferrites have been reported giving useful information about the influence of various exchange interactions on hyperfine fields, etc. (Tanaka *et al* 1963; Mizoghuchi and Tanaka 1963; Belov *et al* 1964; Weiser *et al* 1966; Hudson and Whitfield 1967; Yagnik and Mathur 1969; Evans *et al* 1971). Hyperfine field at ^{57}Fe nucleus in a magnetically-ordered system arises principally from the Fermi contact interaction due to interaction of spin-polarised s -electron magnetic moment with the nuclear magnetic moment (Watson and Freeman 1961). The time dependence of the nuclear magnetic field is therefore proportional to the time dependence of the atomic magnetic moments and the average nuclear magnetic field for all the ions in a particular sublattice is proportional to the average magnetization of that sublattice (Nangle *et al* 1960).

Cation distribution in MnFe_2O_4 has been determined using neutron diffraction (Hasting and Corliss 1961) and Mössbauer effect studies (Yasuoka and Hirai 1967) giving the arrangement



where cations in parenthesis occupy octahedral (*B*) sites. The observed values of hyperfine fields at *A* and *B* sites, are 483 kOe and 430 kOe respectively (Sawatzky *et al* 1967). Mössbauer studies of MnFe_2O_4 show that there is hardly any Fe^{2+} present in the *B* site (Yasuoka and Hirai 1967) in agreement with calculations by Lotgering (1964). The observed low magnetic moment ($0.5 \mu_B$ to $4.8 \mu_B$) in place of expected $5 \mu_B$ has been explained in terms of non-collinear spin arrangement (Sawatzky *et al* 1969). It has also been shown that $\text{Mn}_{(A)}^{2+} - \text{Fe}_{(B)}^{3+}$ super-exchange interaction is weaker than $\text{Fe}_{(A)}^{3+} - \text{Fe}_{(B)}^{3+}$ interaction (Marya 1964, 1965) and super-exchange interaction $\text{Fe}^{3+} - \text{O} - \text{Ni}^{2+}$ is weaker than $\text{Fe}^{3+} - \text{O} - \text{Fe}^{3+}$ (Geller *et al* 1962).

CoFe_2O_4 is not completely inverse. The cation distribution in the quenched compound is



where cations in parenthesis occupy octahedral sites (Sawatzky *et al* 1969) *A* and *B* sites are not well-resolved and one estimates an average value of hyperfine field as 516 kOe at *A* and *B* sites (Dezsi *et al* 1963). The magnetic moment of Co^{2+} ion in octahedral environment is considerably lower than the usually accepted value $3.5 \mu_B$ (Sawatzky *et al* 1968). This has been attributed to spin contribution and reduced orbital contribution due to covalency effect. The hyperfine field at *B* site has been found to decrease by about 8 kOe for each Fe (*A*) site nearest neighbour replaced by Co^{2+} ion. This has been explained in terms of supertransferred hyperfine interactions (Sawatzky *et al* 1969; Shrivastava *et al* 1976). The broadening of *B* site lines of Mössbauer spectra is interpreted as due to differences in hyperfine fields caused by a distribution of Co and Fe nearest *A* site neighbours (Sawatzky *et al* 1968).

NiFe_2O_4 is reported to have Néel collinear type sublattice (Slonczewski 1958) giving ferromagnetic Ni(*B*)—Fe(*B*) interaction as suggested by Morel (1967). It is an inverse spinel (Chappert and Frankel 1967) with magnetic moment $2.20 \mu_B$ (at 4.2K). The hyperfine fields at *A* and *B* sites are 506 kOe and 548 kOe respectively (Kedem and Rothen 1967; Eibschutz and Shtrikman 1968).

2. Experiment

The samples were prepared by dry ceramic method (Filote *et al* 1972). AR grade CoCO_3 , NiCO_3 , MnO and $\alpha\text{-Fe}_2\text{O}_3$ were taken in appropriate proportions, thoroughly mixed in distilled water, pelleted and then fired at 1200°C for 6 hr followed by quenching to preserve the single-phase structure. Samples of cobalt and nickel systems were prepared for $x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$. In order to prepare absorbers of proper thickness, pellets were ground to fine powder. The calculated amount of powder containing 0.01 mg/cm^2 of ^{57}Fe was thoroughly mixed with about 200 mg of lycopodium powder for homogenization and then placed in a circular hole of 1.5 cm^2 of an aluminium sheet pressed between two plastic sheets.

The Mössbauer spectrometer used is described elsewhere (Chandra and Lokanathan 1977). ^{57}Co in rhodium matrix was the source mounted on a drive operating in the constant acceleration mode and spectra were recorded on ND-1100 multi-channel analyzer.

3. Results and discussion

The recorded Mössbauer spectra of both the systems were analyzed with an IBM 360 computer using a standard programme (von Meerwal 1975). The relevant Mössbauer parameters are listed in tables 1 and 2.

3.1 Hyperfine fields

Room temperature spectra of both systems for values of $x=0.1$ to 0.8 exhibit well-defined Zeeman patterns as shown in figures 1 and 2 which have been resolved into two sextets. Mössbauer parameters of both the systems are listed in tables 1 and 2.

It is seen from these tables that the increase in octahedral hyperfine field $H(B)$ in both the systems is slower than the increase in tetrahedral hyperfine field $H(A)$ with increasing concentration of nickel and cobalt. $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$

Table 1. Mössbauer parameters of $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$.

Sample	$H(B)$ kOe	$H(A)$ kOe	$IS(B)$ mm/sec	$IS(A)$ mm/sec	$T(B)$ mm/sec	$T(A)$ mm/sec	$INT(B)$	$INT(A)$
$\text{Ni}_{0.1}\text{Mn}_{0.9}\text{Fe}_2\text{O}_4$	480(6)	436(6)	0.34(3)	0.22(3)	0.54(2)	0.46(2)	0.34(2)	0.64(2)
$\text{Ni}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$	483(6)	450(6)	0.32(2)	0.22(2)	0.61(2)	0.53(2)	0.42(2)	0.58(2)
$\text{Ni}_{0.3}\text{Mn}_{0.7}\text{Fe}_2\text{O}_4$	485(6)	466(6)	0.31(3)	0.23(2)	0.62(2)	0.46(2)	0.57(2)	0.43(2)
$\text{Ni}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$	486(6)	470(6)	0.31(2)	0.26(2)	0.61(2)	0.53(2)	0.53(2)	0.47(2)
$\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$	487(6)	481(6)	0.32(2)	0.24(2)	0.62(2)	0.62(2)	0.50(2)	0.50(2)
$\text{Ni}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$	489(6)	485(6)	0.32(2)	0.26(2)	0.61(2)	0.46(2)	0.49(2)	0.51(2)
$\text{Ni}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$	493(6)	489(6)	0.33(2)	0.24(2)	0.62(2)	0.64(2)	0.47(2)	0.53(2)
$\text{Ni}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$	515(6)	491(6)	0.32(2)	0.26(3)	0.53(2)	0.40(2)	0.31(2)	0.69(2)

Zero velocity channel 137.

$IS(A)$ and $IS(B)$ is isomer shifts of tetrahedral (A) and octahedral (B) sites with respect to iron, $QS(A)$ and $QS(B)$ quadrupole splitting of A and B sites are zero within experimental error, $T(A)$ and $T(B)$ are FWHM of Mössbauer lines corresponding to A and B sites, $INT(A)$ $INT(B)$ are intensities of A and B sites hyperfine patterns respectively.

Table 2. Mössbauer parameters of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$.

Sample	$H(B)$ kOe	$H(A)$ kOe	$IS(B)$ mm/sec	$IS(A)$ mm/sec	$T(B)$	$T(A)$	$INT(B)$	$INT(A)$
$\text{Co}_{0.1}\text{Mn}_{0.9}\text{Fe}_2\text{O}_4$	467(6)	422(6)	0.31(2)	0.23(2)	0.54(2)	0.44(2)	0.49	0.51
$\text{Co}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$	477(6)	427(6)	0.31(2)	0.22(3)	0.56(2)	0.51(2)	0.46	0.54
$\text{Co}_{0.3}\text{Mn}_{0.7}\text{Fe}_2\text{O}_4$	479(6)	437(6)	0.32(2)	0.24(2)	0.52(2)	0.49(2)	0.44	0.56
$\text{Co}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$	482(6)	451(6)	0.34(3)	0.25(2)	0.46(2)	0.43(2)	0.50	0.50
$\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$	483(6)	452(6)	0.34(2)	0.22(2)	0.46(2)	0.41(2)	0.50	0.50
$\text{Co}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$	484(6)	454(6)	0.35(3)	0.23(2)	0.46(2)	0.42(2)	0.50	0.50
$\text{Co}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$	486(6)	457(6)	0.35(2)	0.23(2)	0.54(2)	0.50(2)	0.49	0.51
$\text{Co}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$	490(6)	453(6)	0.34(2)	0.25(3)	0.46(2)	0.43(2)	0.42	0.58

Zero velocity channel 137.

$IS(A)$ and $IS(B)$ is isomer shifts of tetrahedral (A) and octahedral (B) sites with respect to iron, $QS(A)$ and $QS(B)$ quadrupole splitting of A and B sites are zero within experimental error, $T(A)$ and $T(B)$ are FWHM of Mössbauer lines corresponding to A and B sites, $INT(A)$ and $INT(B)$ are intensities of A and B sites hyperline patterns respectively.

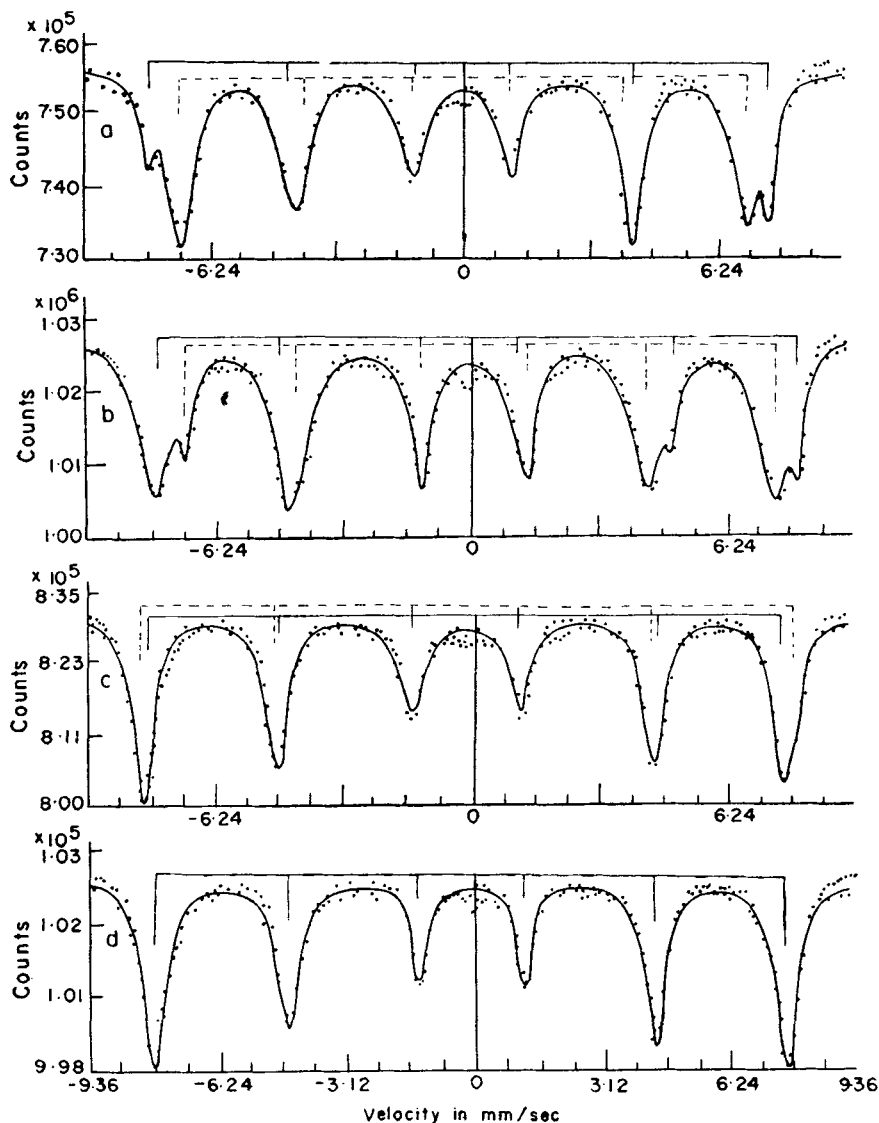


Figure 1. Room temperature Mössbauer spectra of $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$. (a) $x=0.1$, (b) $x=0.3$, (c) $x=0.5$, (d) $x=0.7$.

are ferrimagnetic spinels in which intersublattice magnetic interaction is stronger than either of intrasublattice interaction. The average hyperfine field at Fe^{3+} nucleus in each of the two sublattices is proportional to the average magnetization of the sublattice. It has been shown that the percent change of hyperfine field at octahedral site by replacing a tetrahedral Fe^{3+} cation by Co^{2+} cation is more than that of at tetrahedral site by replacing an octahedral Fe^{3+} cation because each octahedral Fe^{3+} cation is surrounded by six tetrahedral neighbours and each tetrahedral Fe^{3+} cation by twelve octahedral neighbours (Sawatzky *et al* 1969). Similarly it can be seen that the replacement of Mn^{2+} and Mn^{3+} cations by Co^{2+} or Ni^{2+} should result in

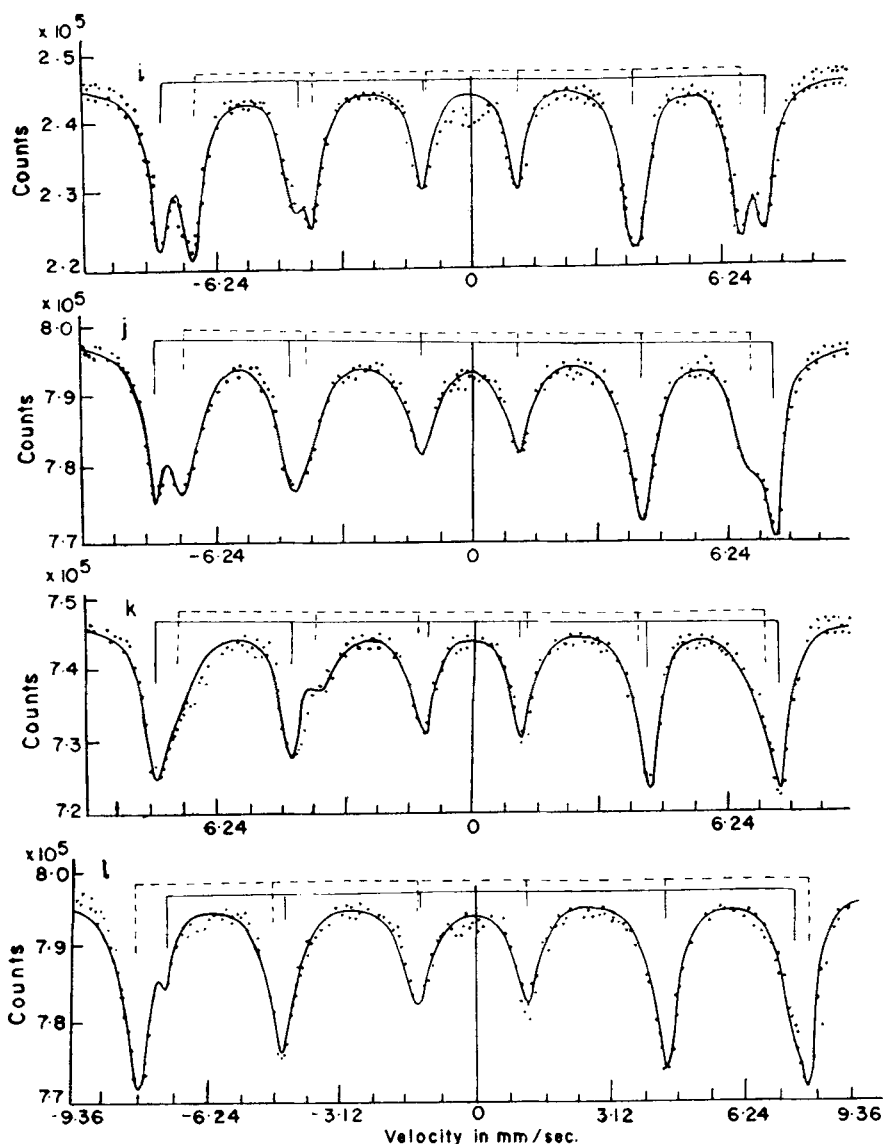


Figure 2. Room temperature Mössbauer spectra of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$. (i) $x=0.1$, (j) $x=0.3$, (k) $x=0.5$, (l) $x=0.7$.

increase of $|H(B) - H(A)|$. However, $|H(B) - H(A)|$ has been observed to decrease with increasing Ni^{2+} or Co^{2+} cation concentration. This has been attributed to large octahedral site preference energy of Ni^{2+} and Co^{2+} cations. The large occupation of octahedral sites by Ni^{2+} or Co^{2+} cations increase the tetrahedral hyperfine field $H(A)$ faster than that of octahedral hyperfine field $H(B)$.

It has also been observed that the substitution of Ni^{2+} cation produces a large percent change in $H(A)$ compared to that of Co^{2+} cation substitution. The line width in $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ was narrower than that of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$. These obser-

vations can also be explained on the basis of octahedral site preference energy of Ni^{2+} and Co^{2+} cations as follows.

Ni^{2+} , because of its large octahedral site preference energy is known to occupy exclusively octahedral sites (Dunitz and Orgel 1957; McClure 1957). Substitution of more and more Ni^{2+} increases the A site hyperfine field through ($A-B$) super-exchange interaction and the intensity of B site hyperfine field because of replacement of octahedral Mn^{3+} cations by Ni^{2+} cations. The B site hyperfine field increases because of increasing magnetization of the B sublattice. The observed narrow line width in nickel-doped manganese ferrite may be attributed to smaller distribution of magnetic fields due to different site symmetries created by octahedral substitutions of Fe^{3+} by Ni^{2+} cations. Co^{2+} , on the other hand, partially go in tetrahedral sites also. The increase of A and B hyperfine fields in cobalt-substituted manganese ferrites is, therefore, because of increasing sublattice magnetization and replacements of Mn^{3+} and Mn^{2+} cations by Co^{2+} in octahedral and tetrahedral sites. The observed large line width has been explained (Sawatzky *et al* 1969) in terms of larger distribution of magnetic fields due to the different site symmetries created at both tetrahedral and octahedral sites by replacements of Mn^{3+} and Mn^{2+} cations by Co^{2+} cation.

It is observed that hyperfine field at both sites, in the materials under study, lies between the extrapolated end members for $x=0$ and $x=1$. There is a systematic increase in H_{hpf} as x increases from $x=0$ to $x=1$ *i.e.* from MnFe_2O_4 to CoFe_2O_4 or NiFe_2O_4 . It has also been noticed that the increase in $H(A)$ and $H(B)$ hyperfine fields in $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ with increasing nickel concentration is larger than that of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ with cobalt substitution. This is attributed to exclusive octahedral site occupation of Ni^{2+} cations. Co^{2+} , on the other hand, partially occupy tetrahedral sites also. The large replacements of Mn^{3+} cations by Ni^{2+} cations at octahedral sites increase $H(B)$ more in the $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ system than in the $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ system because the super-exchange interactions $\text{Fe}^{3+}\text{-O-Ni}^{2+}$ is larger than $\text{Fe}^{3+}\text{-O-Mn}^{3+}$. The larger increase of $H(A)$ in the system $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ than in $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ on the other hand is due to the reason that each tetrahedral Fe^{3+} is surrounded by twelve octahedral neighbours and more octahedral sites are populated by Ni^{2+} in the nickel system than Co^{2+} in the cobalt system thereby increasing the $H(A)$ through A - B exchange interaction.

3.2 Isomer shifts

The isomer shifts of Fe^{3+} at tetrahedral (δ_A) and octahedral (δ_B) sites do not show any significant variation with x indicating that the s -electron charge distribution of the Fe^{3+} cation is negligibly influenced by substitution. Moreover, the isomer shifts in both the systems $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ were found to be the same within experimental error showing that the chemical environment was the same. The weighted average room temperature isomer shifts at both sites are

$$\delta E_A = + 0.24 (2) \quad \delta E_B = + 0.32 (2) \text{ for } \text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4 \text{ system,}$$

and
$$\delta E_A = + 0.24 (2) \quad \delta E_B = + 0.32 (2) \text{ for } \text{Co}_x \text{Mn}_{1-x}\text{Fe}_2\text{O}_4 \text{ system.}$$

The isomer shift of octahedral Fe^{3+} ions were found 0.08 mm/sec more positive than that of isomer shift for tetrahedral Fe^{3+} ions, which may be attributed to the covalency of tetrahedral sites (Goodenough 1955).

3.3 Quadrupole interaction

Origin of quadrupole splitting (QS) at a Fe^{3+} nucleus is considered to arise from (i) non-cubic point symmetry of neighbouring ions and (ii) trigonal symmetry, known to be experienced by octahedral cations due to oxygen deviation parameter. In a magnetically ordered spinel ferrite exhibiting a hyperfine pattern the octahedral Fe^{3+} nuclei should be subjected to both quadrupole and magnetic interaction. An axially symmetric EFG with its principal axis making an angle θ with the magnetic axis and assuming that magnetic interaction is much stronger than quadrupole interaction, the Zeeman lines are shifted by an amount (Mathias *et al* 1962)

$$\delta = \frac{1}{2} \delta_0 (3 \cos^2 \theta - 1), \quad (1)$$

where δ_0 is the magnitude of shift when magnetic interaction tends to zero. Daniels and Rosencwaig (1970) have shown that octahedral Fe^{3+} cations in magnetically ordered system such as these spinel ferrites should exhibit a quadrupole shift which they failed to observe. We also observed Zeeman hyperfine patterns of zero quadrupole splitting within experimental error for both tetrahedral and octahedral sites. Following the work of Daniel *et al*, this has been attributed to the distribution of EFG's of varying magnitude direction sign and symmetry due to chemical disorder resulting in distribution of QS as given by equation (1). This would also lead to a small line broadening.

4. Conclusions

The systematic increase in H_{hpf} field at both sites and the rapid increase at tetrahedral site as compared to that at octahedral site, in $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$, with increasing value of x , is because of the larger occupation of octahedral sites which as a consequence increases the A - B exchange interaction. The larger change in H_{hpf} in the case of $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$, than in $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ is attributed to exclusively B site occupation of Ni^{2+} cations, whereas Co^{2+} partially goes to A site also. The observed large line width in Co^{2+} mixed ferrite is due to the larger distribution of site symmetries at both A and B sites.

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