A Mössbauer study of hyperfine interaction in the systems $Co_xMn_{3-x-y}Fe_yO_4$ and $Ni_xMn_{3-x-y}Fe_yO_4$

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Abstract. A Mössbauer study of systems $Co_xMn_{3-x-y}Fe_yO_4$ and $Ni_xMn_{3-x-y}Fe_yO_4$ for values of $x=0.1$, 0.5, 1.0 and y ranging from 0.1 to 2.0 in steps of 0.2 have been made. At room temperature samples for y values ranging in between 0.1 to 0.5 exhibit paramagnetic behaviour while all spectra for values of y between 0.6 to 0.8 show relaxation effects. Well-defined hyperfine Zeeman spectra are observed for all the samples with $y > 0.8$ and resolved in two sextets corresponding to octahedral and tetrahedral site symmetries and a central doublet probably due to the presence of super-paramagnetic particles in the system. The hyperfine field at ^{57}Fe nucleus reduces with decreasing iron cobalt and nickel concentration. These observations have been explained in terms of site preference of cations and exchange interactions.

Keywords. Hyperfine interaction; octahedral hyperfine field; tetrahedral hyperfine field; quadrupole splitting; isomer shift; octahedral site preference energy; super exchange interaction.

1. Introduction

Splinelic systems $Co_xMn_{3-x-y}Fe_yO_4$ and $Ni_xMn_{3-x-y}Fe_yO_4$ are solid solutions and may be prepared by usual dry ceramic technique (Filoti *et al* 1972a). In normal spinels, divalent cations occupy tetrahedral (A) and trivalent cations octahedral (B) interstitial sites of a face-centred cubic lattice of oxygen while in inverse spinel all divalent cations occupy octahedral (B) sites, one half of trivalent cations octahedral (B) and the other half tetrahedral (A) sites (Gorter 1954). Hausmannite (Mn_3O_4) is a normal spinel with divalent Mn^{2+} on tetrahedral (A) and trivalent Mn^{3+} on octahedral (B) sites (Goodenough 1955). Co^{2+} and Ni^{2+} due to large octahedral site preference energy produce deviation from normal distribution and give rise to inverse spinel structure by occupying octahedral sites (Driessens 1967).

In a magnetic field, the nuclear spin and hence the nuclear magnetic moment precesses around the field direction with Larmor frequency. In order to lift the degeneracy of nuclear levels completely in the field $\mathcal{H}$, the nuclear spins must succeed in making several rotations around the field direction during the life time of the excited state (Goldanskii and Makarov 1968). At a given temperature, the minimum field corresponding to a separation of the sublevels to give hyperfine pattern is of the order of hundreds of kOe. At lower field the velocity spectra observed exhibit no structure characteristic of a magnetic interaction and are known as relaxed spectra.

The magnetic state of the material (paramagnetic ferromagnetic and antiferro-

magnetic) governs the hyperfine structure of Mössbauer spectra by controlling the time of transition from one orientation of the net electron spin (S_L) to another. Both the dipolar contribution (H_D) and the Fermi contact term (H_C) of the internal magnetic field depend on the orientation of S_L. Thus from the point of view of the nucleus, the electron spin relaxation process can be considered as flipping the direction of an effective magnetic field and possibly changing its magnitude abruptly from $+ \mathcal{H}$ to $- \mathcal{H}$. In magnetically ordered materials ^{57}Fe nucleus experiences a time-independent field near 0 K. At higher temperatures lattice vibrations interact with the spin system which causes the field to be time dependent (Srivastava *et al* 1976). As the spin correlation time (t_c) decreases with increase in temperature and becomes comparable to nuclear Larmor period $(1/\omega_n)$, the line shape undergoes rapid changes. The outer lines broaden and the inner ones grow in intensity at the cost of the former. When $t_c \ll (1/\omega_n)$, only the central line is observed which however, may be split due to quadrupole interaction.

It has also been observed that super-exchange interaction in Fe^{3+}-O-Ni^{2+} or Fe^{3+}-O-Co^{2+} type of bond is weaker than that of Fe^{3+}-O-Fe^{3+} type of bond (Geller *et al* 1962; Moriya 1964, 1965; Streever *et al* 1963; Bennet and Streever 1962). Ordering temperature (T_c) is also known to decrease with increasing manganese concentration in such systems (Guilland 1951). The average normalised magnetization per Fe^{3+} ion in tetrahedral sublattice is found to be smaller than that in an octahedral sublattice. This is attributed to dipolar field resulting from cubic symmetry and the covalent nature of tetrahedral bond. Various spinel systems have been studied in which they observed that concentration of Fe^{3+}, Co^{2+} or Ni^{2+} determines the nature of Mössbauer spectra (Daniels and Rosencwaig 1970; Gupta and Mendiratta 1977; Sawatzky *et al* 1969; Srivastava *et al* 1976). In the present work, a room temperature Mössbauer study has been made to observe the effect of concentration of ferromagnetic cations Fe^{3+}, Co^{2+} and Ni^{2+} in the systems $Co_xMn_{3-x-y}Fe_yO_4$ and $Ni_xMn_{3-x-y}Fe_yO_4$. Changes in hyperfine fields for relative concentration of these cations are determined.

2. Experiment

The samples were prepared by dry ceramic method (Filoti *et al* 1972b); AR grade $CoCO_3$, $NiCO_3$, MnO and α-Fe_2O_3 were taken in appropriate proportion, thoroughly mixed in distilled water, pelleted and then fired at 1200° for 6 hr, followed by quenching, to preserve a single phase structure. Samples of cobalt and nickel systems were prepared for $y = 0·1, 0·3, 0·5, 0·7, 0·9, 1·1, 1·5, 2·0$ and $x = 0·1, 0·5, 1·0$.

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

3. Results and discussion

Samples were x-ray analysed and only lines of the spinel structure were observed in the x-ray diffraction pattern. The recorded Mössbauer spectra of both systems were

analysed with an IBM-360 computer using a standard programme (von Meerwal 1976). The relevant Mössbauer parameters are listed in tables 1 and 2.

Room temperature Mössbauer spectra of both the systems for values of y between 0·1 to 0·5 exhibit a quadrupole doublet indicating that the material is in a paramagnetic state. These paramagnetic Mössbauer spectra have been explored in detail and the Jahn Teller distortion in the systems has been studied (Singh *et al* 1981).

Mössbauer spectra for samples with y values between 0·6 to 0·8 exhibit relaxation effects. Since the line positions are not distinct, it is not possible to draw any quantitative conclusions about the internal magnetic field, quadrupole splitting, isomer shifts, etc.

Table 1. Mössbauer parameters of $Co_xMn_{3-x-y}Fe_yO_4$

Sample	H(B) kOe	H(A) kOe	IS(B) mm/sec	IS(A) mm/sec	τ(B) mm/sec	τ(A) mm/sec	INT(B)	INT(A)	INT(C)
$Co_{0.1}Mn_{2.0}Fe_{0.9}O_4$	371(6)	296(6)	0·35(2)	0·29(2)	0·64(2)	0·74(3)	0·46(2)	0·36(2)	0·18(2)
$Co_{0.1}Mn_{1.8}Fe_{1.1}O_4$	435(6)	384(6)	0·36(2)	0·29(2)	0·45(2)	0·69(2)	0·44(2)	0·36(2)	0·20(2)
$Co_{0.1}Mn_{1.4}Fe_{1.5}O_4$	443(6)	403(6)	0·37(2)	0·28(2)	0·71(3)	0·71(3)	0·42(2)	0·36(2)	0·22(2)
$Co_{0.1}Mn_{0.9}Fe_{2.0}O_4$	473(6)	428(6)	0·35(2)	0·29(2)	0·46(2)	0·65(2)	0·40(2)	0·53(2)	0·07(3)
$Co_{0.5}Mn_{1.6}Fe_{0.9}O_4$	406(6)	307(6)	0·39(3)	0·27(2)	0·58(2)	0·68(2)	0·63(2)	0·15(3)	0·22(2)
$Co_{0.5}Mn_{1.4}Fe_{1.1}O_4$	419(6)	337(6)	0·35(2)	0·29(2)	0·65(2)	0·68(2)	0·49(2)	0·24(2)	0·27(2)
$Co_{0.5}Mn_{1.0}Fe_{1.5}O_4$	441(6)	375(6)	0·34(2)	0·25(3)	0·49(2)	0·42(2)	0·37(2)	0·34(2)	0·29(2)
$Co_{0.5}Mn_{0.5}Fe_{2.0}O_4$	480(6)	386(6)	0·35(2)	0·26(2)	0·61(2)	0·74(3)	0·36(2)	0·61(2)	0·03(4)
$Co_{1.0}Mn_{1.1}Fe_{0.9}O_4$	411(6)	282(6)	0·38(3)	0·28(2)	0·70(3)	0·73(3)	0·43(2)	0·42(2)	0·15(2)
$Co_{1.0}Mn_{0.9}Fe_{1.1}O_4$	433(6)	320(6)	0·38(3)	0·29(2)	0·61(2)	0·64(2)	0·42(2)	0·42(2)	0·16(2)
$Co_{1.0}Mn_{0.5}Fe_{1.5}O_4$	460(6)	350(6)	0·37(2)	0·28(2)	0·62(2)	0·72(3)	0·40(2)	0·43(2)	0·17(2)

In tables 1 & 2 the various abbreviations signify as follows:
H(B), H(A)-Hyperfine fields at octahedral(B) and tetrahedal(A) sites.
IS(B), IS(A)-Isomer shifts at B and A sites with respect to iron.
τ(B), τ(A)-Full width at half maximum (line widths) of Mössbauer lines corresponding to B and A site.
INT(B), INT(A) and INT(C)-Intensity of octahedral hyperfine field H(B), tetrahedral hyperfine field H(A) and central quadrupole doublet.
Number in parenthesis shows the standard deviation in the second digit of the figure obtained from computer fittings.

Table 2. Mössbauer parameters of $Ni_xMn_{3-x-y}Fe_yO_4$

Sample	H(B) kOe	H(A) kOe	IS(B) mm/sec	IS(A) mm/sec	τ(B) mm/sec	τ(A) mm/sec	INT(B)	INT(A)	INT(C)
$Ni_{0.1}Mn_{2.0}Fe_{0.9}O_4$	378(6)	320(6)	0·37(3)	0·28(2)	0·63(2)	0·71(2)	0·48(2)	0·33(2)	0·19(2)
$Ni_{0.1}Mn_{1.8}Fe_{1.1}O_4$	436(6)	378(6)	0·34(2)	0·28(2)	0·58(2)	0·73(2)	0·23(2)	0·60(2)	0·17(2)
$Ni_{0.1}Mn_{1.4}Fe_{1.5}O_4$	449(6)	410(6)	0·37(3)	0·27(2)	0·52(2)	0·68(2)	0·21(2)	0·57(2)	0·22(2)
$Ni_{0.1}Mn_{0.9}Fe_{2.0}O_4$	471(6)	428(6)	0·36(2)	0·28(2)	0·71(3)	0·73(3)	0·19(3)	0·77(2)	0·04(3)
$Ni_{0.5}Mn_{1.6}Fe_{0.9}O_4$	441(6)	371(6)	0·37(3)	0·28(2)	0·68(2)	0·65(2)	0·37(2)	0·35(2)	0·28(2)
$Ni_{0.5}Mn_{1.4}Fe_{1.1}O_4$	450(6)	384(6)	0·39(3)	0·24(3)	0·58(2)	0·74(3)	0·38(2)	0·51(2)	0·21(2)
$Ni_{0.5}Mn_{1.0}Fe_{1.5}O_4$	467(6)	429(6)	0·33(2)	0·25(2)	0·45(2)	0·71(2)	0·26(2)	0·51(2)	0·23(2)
$Ni_{0.5}Mn_{0.5}Fe_{2.0}O_4$	482(6)	463(6)	0·34(2)	0·23(3)	0·45(2)	0·72(3)	0·14(3)	0·83(2)	0·03(3)
$Ni_{1.0}Mn_{1.1}Fe_{0.9}O_4$	475(6)	450(6)	0·33(2)	0·24(2)	0·65(2)	0·63(2)	0·41(2)	0·27(2)	0·32(2)
$Ni_{1.0}Mn_{0.9}Fe_{1.1}O_4$	487(6)	467(6)	0·34(2)	0·29(2)	0·71(2)	0·71(3)	0·36(2)	0·30(2)	0·34(2)
$Ni_{1.0}Mn_{0.5}Fe_{1.5}O_4$	496(6)	471(6)	0·34(2)	0·30(3)	0·45(2)	0·64(2)	0·23(2)	0·36(2)	0·41(2)

Room temperature Mössbauer spectra of samples with values of y ranging from 0·9 to 2·0 show hyperfine Zeeman patterns which have, in general, been resolved in two sextets and a central doublet. Computer fitted spectra of both the systems for $x = 0·1$, $y = 0·9$, 1·5 and 2·0 are shown in figure 1. Mössbauer parameters of both the systems are listed in tables 1 and 2. In fact at least two sextets are expected in the system under investigation. One due to Fe^{3+} cations at tetrahedral sites and the other due to Fe^{3+} cations at octahedral sites. The central quadrupole doublet may be due to the presence of fine super-paramagnetic particles in the system. Such observations have been made by many authors in similar ferrimagnetic systems (Ishikawa 1962, 1964; Booth and Crangle 1962; Simkin 1965). The isomer shifts of Fe^{3+} at tetrahedral (A) site $\delta I(A)$ and octahedral (B) site $\delta I(B)$ show no significant variation indicating that s-electron charge distribution is negligibly influenced by Co^{2+}, Ni^{2+} or Fe^{3+} substitution. In spinel systems exhibiting a hyperfine Zeeman pattern, The
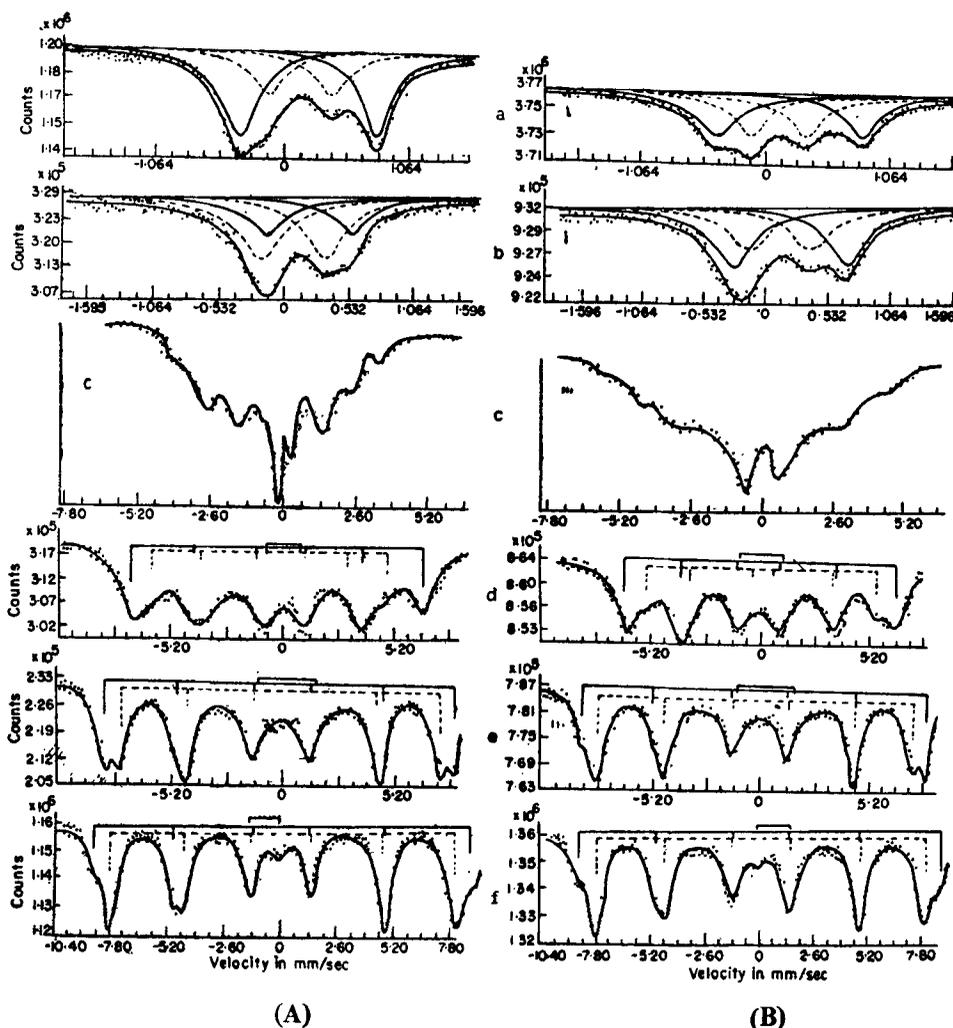

(A)   (B)

Figure 1. Room temperature Mössbauer spectra of (A) $Co_xMn_{3-x-y}Fe_yO_4$, (B) $Ni_xMn_{3-x-y}Fe_yO_4$.
a. $x=0·1$, $y=0·1$, b. $x=0·1$, $y=0·5$, c. $x=0·1$, $y=0·7$,
d. $x=0·1$, $y=0·9$, e. $x=0·1$, $y=1·5$, f. $x=0·1$, $y=2·0$.

octahedral Fe^{3+} nuclei are subjected to both quadrupole and magnetic interaction. In a system having no chemical disorder, the tetrahedral or A sites have cubic point symmetry, and therefore experience no EFG. The octahedral or B sites, however, have different sources of contribution to EFG. The major contribution in the present system is due to tetragonal distortion produced by the Mn^{3+} (d^4), Jahn Teller ion. The second source is the trigonal symmetry at the octahedral sites owing to the pre-sence of different cations in second co-ordination sphere. EFG at octahedral sites arises not only due to metal cations but also from oxygen anions because of oxygen deviation parameter (Gorter 1954). It has been observed that spectra exhibiting hyperfine Zeeman pattern show zero QS for both tetrahedral and octahedral sites within experimental errors which infer the absence of EFG at both sites. However, as already discussed above samples with lower Fe concentration exhibit quadrupole doublet indicating the presence of EFG at octahedral sites. The origin of zero QS in the magnetic spectra may be attributed to the following reasons:

(i) Replacement of Mn^{3+} (d^4) Jahn Teller ion by Fe^{3+} weakens the tetragonal distortion of lattice thereby reducing the ligand field contribution of QS. Below a certain concentration of Mn^{3+} cations, co-operative JT distortion of the lattice ceases to occur and only Mn^{3+} cations experience local distortion.

(ii) The co-existence of octahedral sp^3d^2 and square coplanar dsp^2 bonds at octa-hedral sites, produces a chemical disorder resulting in distribution of EFG of varying magnitudes, direction, sign and symmetry (Daniels and Rosencwaig 1970). Consequently a distribution of quadrupole shifts results in broadening of individual lines in Zeeman pattern and no net shift of Zeeman lines is observed.

It is evident from tables 1 and 2 that the hyperfine field gradually decreases with decreasing Fe concentration. It is seen that the hyperfine field at (B) site is larger than hyperfine field at (A) site which has been attributed to dipolar field resulting from deviation from cubic symmetry and the co-valent nature of tetrahedral $Fe^{3+}-O$ bond (Watson and Freeman 1961). The large line widths of hyperfine spectra may be attributed to the distribution of magnetic fields at (A) and (B) sites due to random substitution of Fe in these sites.

The intensity of central doublet increases with iron concentration but after a certain concentration of Fe it diminishes indicating that the distribution of particle size of domains, giving rise to central doublet, increases with increasing ferromagnetic ions. Decrease of intensity of central doublet after a certain concentration of Fe is indica-tive of the fact that the magnetization of domains, formerly adding to the intensity of central doublet, has now started contributing to the hyperfine field because of enough domain magnetization.

Finally, we discuss an important observation that above a certain concentration of Fe^{3+} cation in ferrimagnetic spinels $Ni_xMn_{3-x-y}Fe_yO_4$ and $Co_xMn_{3-x-y}Fe_yO_4$ exhibit hyperfine Zeeman pattern and below another concentration they exhibit paramagnetic behaviour. In these ferrimagnetic systems the inter sub-lattice magnetic interaction (A-B) is stronger than either of intra sub-lattice interaction (A-A) or (B-B). As discussed above the average magnetic field at the nuclei of Fe^{3+} ions in each of the two sublattices is proportional to the average magnetization of the sublattice. Since super exchange interaction in Fe^{3+}-O-Ni^{2+} or Fe^{3+}-O-Co^{2+} type of bond is weaker

than that of Fe^{3+}-O-Fe^{3+} type of bond, it is clear that the average normalized magnetization of the sublattice will depend on relative population of Fe^{3+}-O-Ni^{2+} or Fe^{3+}-O-Co^{2+} and Fe^{3+}-O-Fe^{3+} types of bonds. Above a certain concentration of Fe ions the normalized magnetization becomes sufficient to create a hyperfine Zeeman pattern. This is equivalent to saying that the ordering temperature T_c increases with increasing iron concentration.

Acknowledgement

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