

A Mössbauer study of octahedral site symmetries in systems $\text{Co}_x \text{Mn}_{3-x-y} \text{Fe}_y \text{O}_4$ and $\text{Ni}_x \text{Mn}_{3-x-y} \text{Fe}_y \text{O}_4$

V K SINGH* and S LOKANATHAN

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

*Present address: SGRR(PG) College, Dehradun 248 001

MS received 15 July 1982; revised 3 December 1982

Abstract. A Mössbauer study of cation distribution in systems $\text{Co}_x \text{Mn}_{3-x-y} \text{Fe}_y \text{O}_4$ and $\text{Ni}_x \text{Mn}_{3-x-y} \text{Fe}_y \text{O}_4$ has been made. It has been found that in both systems all specimens with $y < 0.6$ value exhibit quadrupole doublets corresponding to site symmetries $\text{Fe}^{3+}(\text{I})$ and $\text{Fe}^{3+}(\text{II})$ of octahedral site. As more and more cobalt or nickel is introduced into the matrix the intensity of the inner quadrupole doublet increases while on introducing iron that of the outer quadrupole doublet increases. After a certain concentration of iron the inner doublet starts becoming more intense. It is suggested that this arises possibly from the substitution of cations in the second co-ordination sphere of $\text{Fe}^{3+}(\text{I})$ and $\text{Fe}^{3+}(\text{II})$ sites. For $y > 0.6$ the Mössbauer spectra show relaxation effects.

Keywords. Octahedral sites; tetrahedral sites; quadrupole doublet; site preference energy; oxygen deviation parameter.

1. Introduction

Hausmannite (Mn_3O_4) forms a spinel structure with tetragonally-distorted lattice with axial ratio $c/a = 1.16$ (Mason 1947; Aminoff 1926). Due to large site preference energy, trivalent Mn^{3+} cation preferentially goes to octahedral sites and divalent Mn^{2+} cation occupies tetrahedral sites (Dunitz and Orgel 1957). The large tetragonal distortion present in the lattice is attributed to Jahn-Teller distortion due to Mn^{3+} cations which form square bonds in octahedral sites by hybridizing empty d_{sp^2} orbitals (Goodenough 1955). Satomi, by measuring the oxygen deviation parameter, has shown that only octahedral sites of Mn_3O_4 are distorted (Satomi 1961). $\text{Co}_x \text{Mn}_{2.9-x} \text{Fe}_{0.1} \text{O}_4$ and $\text{Ni}_x \text{Mn}_{2.9-x} \text{Fe}_{0.1} \text{O}_4$ are solid solutions in which divalent cations Ni^{2+} and Co^{2+} go into the lattice substitutionally. The large octahedral site preference energy of divalent cations Ni^{2+} and Co^{2+} force them to occupy first the vacant octahedral sites available and then the tetrahedral sites. Deviation from normal distribution in manganities has already been noticed (Driessens 1967).

The Mössbauer spectra of system $\text{Co}_x \text{Mn}_{2.9-x} \text{Fe}_{0.1} \text{O}_4$ are reported to exhibit two quadrupole doublets corresponding to two site symmetries of octahedral sites $\text{Fe}^{3+}(\text{I})$ and $\text{Fe}^{3+}(\text{II})$ (Filote *et al* 1977). Site $\text{Fe}^{3+}(\text{I})$ is considered to contain only Mn^{3+} cations in second co-ordination sphere while site $\text{Fe}^{3+}(\text{II})$ contains Mn^{3+} and other cations. Site $\text{Fe}^{3+}(\text{I})$ can be converted into site $\text{Fe}^{3+}(\text{II})$ by replacing at least one Mn^{3+} cation by Co^{2+} or Fe^{3+} in second co-ordination sphere of $\text{Fe}^{3+}(\text{I})$.

In the present work it has been observed that on increasing concentration of iron

from $y = 0.1$ to 0.5 , first the outer quadrupole doublet corresponding to site $\text{Fe}^{3+}(\text{I})$ is intensified indicating that more $\text{Fe}^{3+}(\text{I})$ sites have been created. After saturation, the introduced iron intensifies the inner quadrupole doublet due to conversion of $\text{Fe}^{3+}(\text{I})$ site into $\text{Fe}^{3+}(\text{II})$ site because of replacement of Mn^{3+} by Fe^{3+} in the second co-ordination sphere of $\text{Fe}^{3+}(\text{I})$ site. Increasing the concentration of Ni^{2+} or Co^{2+} increases the intensity of the inner quadrupole doublet, thereby showing that the $\text{Fe}^{3+}(\text{I})$ sites begin converting to $\text{Fe}^{3+}(\text{II})$ sites. After a certain concentration of Ni^{2+} or Co^{2+} the outer quadrupole doublet merges into the inner quadrupole doublet showing that all $\text{Fe}^{3+}(\text{I})$ sites have been converted into $\text{Fe}^{3+}(\text{II})$ sites. Mössbauer spectra beyond $y > 0.6$ show relaxation effects.

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 proportion thoroughly mixed in distilled water, pelleted and then fired at 1200°C for 6 hr, followed by quenching, in order to preserve single phase structure. Samples of cobalt and nickel system were prepared for $y = 0.1$ $x = 0.1, 0.5, 1.0$, $y = 0.3$ $x = 0.1, 0.5, 1.0$ $y = 0.5$ $x = 0.1, 0.5, 1.0$. In order to prepare thin absorbers, the pellets were ground to fine powder 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 so that the absorber contained 0.01 mg/cm^2 ^{57}Fe .

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

3. Results

The samples were x-ray analyzed. Only lines of the spinel structure could be observed in the x-ray diffraction patterns of both the systems. The recorded Mössbauer spectra of both systems were analyzed with an IBM 360 computer using a standard program (von Meerwal 1975). The computer fitted spectra are shown in figures 1 to 4. In the cobalt system two quadrupole doublets were observed for $y = 0.1$ $x = 0.1, 0.5$ and 1 , $y = 0.3$ $x = 0.1, 0.5$ and 1 and $y = 0.5$ $x = 0.1, 0.5$ but only one doublet was observed for $y = 0.5$ $x = 1.0$.

In nickel system two quadrupole doublets were observed for $y = 0.1$ $x = 0.1$ and $y = 0.3$ $x = 0.1$ and only one doublet for $y = 0.1$ $x = 0.5, 1$, $y = 0.3$ $x = 0.5, 1$, $y = 0.5$ $x = 0.1, 0.5, 1$.

The variation of intensity of the doublets corresponding to sites $\text{Fe}^{3+}(\text{I})$ and $\text{Fe}^{3+}(\text{II})$ with respect to Co^{2+} , Ni^{2+} and Fe^{3+} concentration has been shown in figures 1, 2, 3 and 4.

4. Discussion

The isomer shift of the resolved doublets matches with that of Fe^{3+} in octahedral site suggesting that both quadrupole doublets arise due to two inequivalent positions of

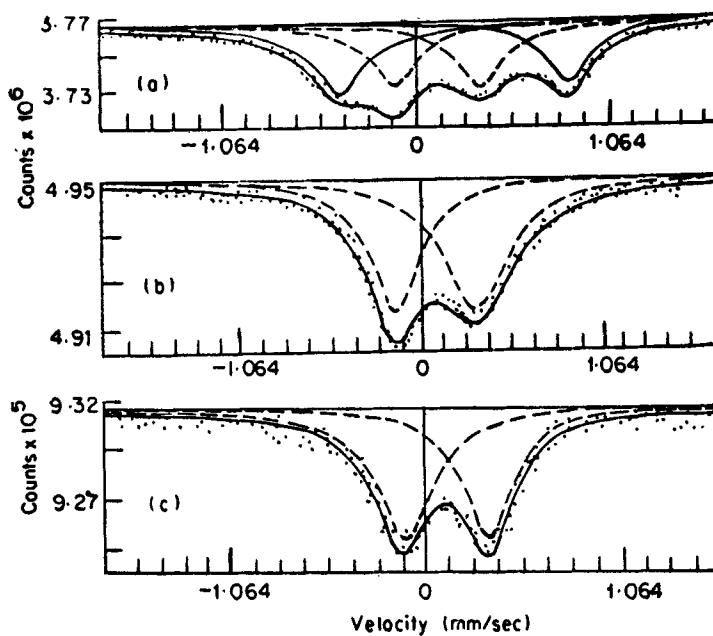


Figure 1. Room temperature Mössbauer spectra of $\text{Ni}_x\text{Mn}_{3-x-y}\text{Fe}_y\text{O}_4$. a. $x=0.1$, $y=0.1$; b. $x=0.5$, $y=0.1$; c. $x=1.0$, $y=0.1$.

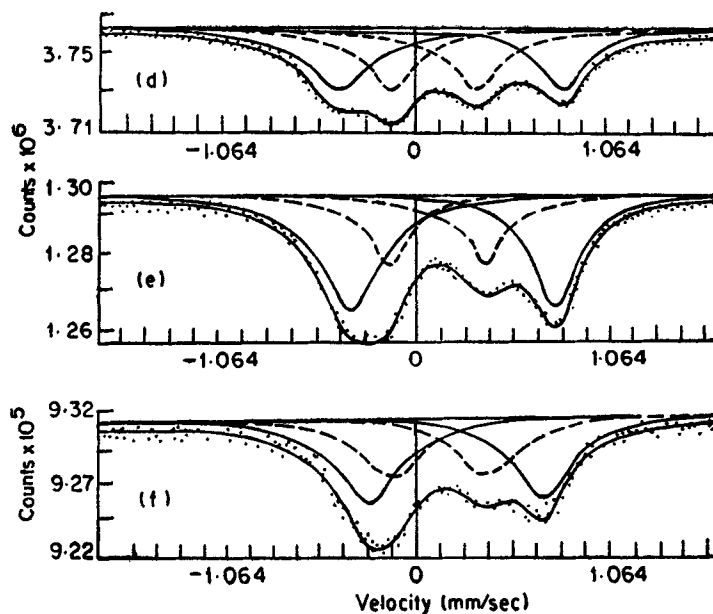


Figure 2. Room temperature Mössbauer spectra of $\text{Ni}_x\text{Mn}_{3-x-y}\text{Fe}_y\text{O}_4$. d. $x=0.1$, $y=0.1$; e. $x=0.1$, $y=0.3$; f. $x=0.1$, $y=0.5$.

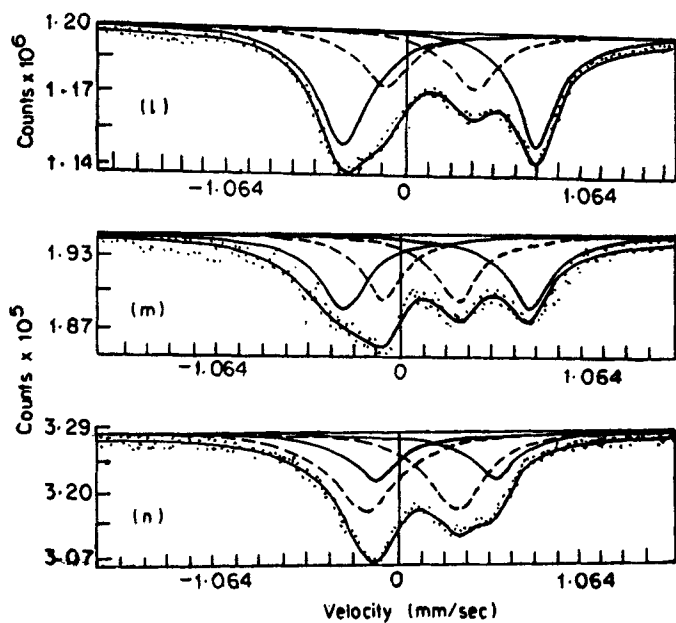


Figure 3. Room temperature Mössbauer spectra of $\text{Co}_x\text{Mn}_{3-x-y}\text{Fe}_y\text{O}_4$. l. $x = 0.1$, $y = 0.1$; m. $x = 0.5$, $y = 0.1$; n. $x = 1.0$, $y = 0.1$.

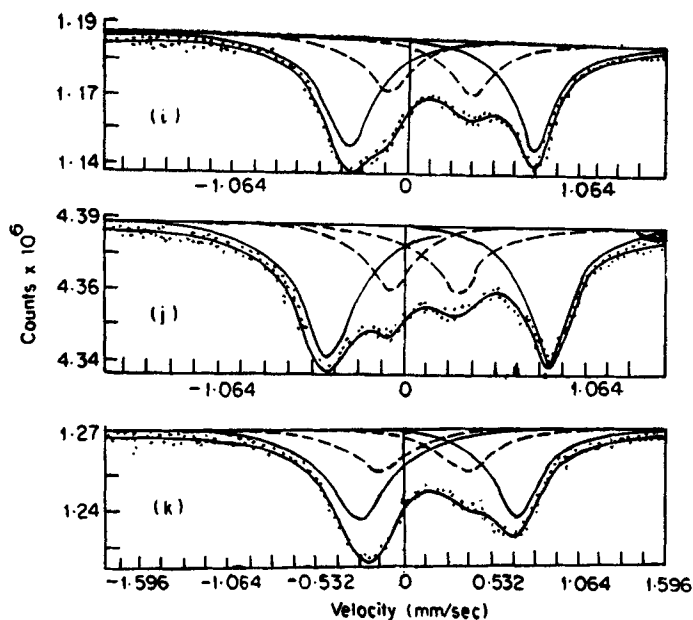


Figure 4. Room temperature Mössbauer spectra of $\text{Co}_x\text{Mn}_{3-x-y}\text{Fe}_y\text{O}_4$. i. $x = 0.1$, $y = 0.1$; j. $x = 0.1$, $y = 0.3$; k. $x = 0.1$, $y = 0.5$.

iron ion in octahedral sites. The outer doublet with large quadrupole splitting is considered to be due to $\text{Fe}^{3+}(\text{I})$ site, the second co-ordination sphere of which contains Mn^{3+} cations only while the inner doublet is ascribed to $\text{Fe}^{3+}(\text{II})$ site, the second co-ordination sphere of which, contains Mn^{3+} and other cations (Singh *et al* 1981). The other cations can be Fe^{3+} in normal spinel, divalent Co^{2+} and Ni^{2+} in partially inverted spinels.

One expects that on increasing the iron concentration, the Fe^{3+} cations will go in octahedral sites creating more $\text{Fe}^{3+}(\text{I})$ sites. Thus the population of $\text{Fe}^{3+}(\text{I})$ sites will increase which would explain the increase in the intensity of the outer quadrupole doublet (figures 2 d, c and 4 i, j) After a saturation value the substituted Fe^{3+} will start converting $\text{Fe}^{3+}(\text{I})$ site into $\text{Fe}^{3+}(\text{II})$ site by replacing Mn^{3+} by Fe^{3+} in the second co-ordination sphere of $\text{Fe}^{3+}(\text{I})$ site. Therefore, the intensity of the inner doublet starts increasing (figures 2 f and 4 k). Introduction of Co^{2+} and Ni^{2+} into the matrix increases the intensity of inner doublet showing that all $\text{Fe}^{3+}(\text{I})$ sites convert into $\text{Fe}^{3+}(\text{II})$ sites due to replacement of Mn^{3+} in second co-ordination sphere of $\text{Fe}^{3+}(\text{I})$ site until the outer doublet merges into the inner one indicating that all $\text{Fe}^{3+}(\text{I})$ sites have been converted into $\text{Fe}^{3+}(\text{II})$ sites (figures 1a, b, c and 3 l, m, n). The quadrupole splitting in both systems decreases with increasing Fe^{3+} , Co^{2+} or Ni^{2+} concentration because of replacement of Mn^{3+} Jahn-Teller cation by non Jahn-Teller cations. The chemical isomer shift of the two doublets are significantly different and roughly constant for all concentrations. Both systems have the same order of isomer shifts for outer and inner doublets indicating that chemical environment in both cases is same.

Acknowledgement

The authors are specially thankful to Shri Ram Narain Diwedee of Materials Division, NPL, New Delhi for help in material preparation. Thanks are due to Dr M V N Murthy, Geological Survey of India, Jaipur, for permission to use x-ray diffraction facility and to Dr G L Diwedee of Geological Survey of India, Jaipur for x-ray analysis of the material. One of the authors (vks) wishes to thank UGC, New Delhi for financial assistance.

References

- Aminoff G 1926 *Z. Krist.* **64** 475
- Chandra R and Lokanathan S 1977 *Phys. Status Solidi* **B83** 273
- Dunitz J D and Orgel L E 1957 *J. Phys. Chem. Solids* **3** 311
- Driessens F C M 1967 *Inorg. Chem. Acta* **1** 193
- Filote G, Gelberg A, Gomella V and Rosenberg M 1972 *Int. J. Magnetism* **2** 65
- Filote G, Gelberg A, Rosenberg M, Spanu V and Telnic P 1977 *Phys. Status Solidi* **B83** 273
- Goodenough J B 1955 *Phys. Rev.* **98** 391
- Mason B 1947 *Am. Miner.* **32** 426
- Singh V K, Chandra R and Lokanathan S 1981 *Phys. Status. Solidi* **B105** K13
- Satomi K 1961 *J. Phys. Soc. Jpn.* **16** 258
- von Meerwal E 1975 *Computer Phys. Commun.* **9** 117