

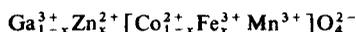
## Mössbauer effect studies of the $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ system

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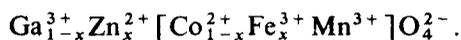
**Abstract.** Mössbauer studies have been carried out on the spinel system  $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$  at room temperature (294 K) for the values of  $X = 0, 20, 40, 50, 60, 80$  and  $100$  (where  $X$  denotes the mole percent of  $\text{ZnFeMnO}_4$  in  $\text{GaCoMnO}_4$ ). All the compounds showed well resolved quadrupole split doublets. Isomer shift values varied between  $0.26$  and  $0.48$  mm/sec. The value of quadrupole splitting increased with increasing  $u$  parameter. The increase in  $u$  parameter is attributed to the replacement of  $\text{Ga}^{3+}$  by  $\text{Zn}^{2+}$  ions at the A-site. From Mössbauer studies, the ionic configuration of the system is suggested as



**Keywords.** Spinel; isomer shift; quadrupole doublet;  $u$  parameter.

### 1. Introduction

One of the most exciting areas of the Mössbauer studies is the detailed study of spinel ferrites by changing the composition of solid solution in a controlled and continuous manner, along with the other experimental methods available. Literature survey (Sawatzky *et al* 1969; Mathur *et al* 1967; Jain and Darshane 1983) revealed that many workers have reported the ionic configuration of ferrites using Mössbauer spectroscopy. In the case of ferrites having  $\text{A}[\text{B}_2]\text{O}_4$  structure, their properties are mainly governed by the presence of cations which are located in two interstices between the oxygen ions. There are two types of interstices occupied by cations, called the tetrahedral (A) site and the octahedral (B) site. Origin of quadrupole splitting ( $\Delta E_q$ ) in oxidic spinels is considered to arise from asymmetric charge distribution at B-site. Similarly covalency effects and small distortions of oxygen tetrahedra ( $u$ -parameter) also contribute to the quadrupole splitting. The state of iron in compounds having two lattice-site spinel structure has been investigated by Mössbauer effect technique. Well established correlations between the measured isomer shift and the number of 'd' electrons in the valence band helps in determining the valence state of iron (Greenwood and Gibb 1971). We have already investigated (Jain and Darshane 1982) the crystallographic and electrical properties of the system  $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$  and reported its site distribution as



This paper deals with further work on the determination of the effect of distortion ( $u$ -parameter) on Mössbauer parameters and corroborates the distribution observed from x-ray and electrical conductivity data.

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## 2. Materials and methods

The end members of the system  $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$  were synthesized by standard ceramic techniques. High purity AR grade oxides *viz*  $\text{Ga}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\alpha\text{-Fe}_2\text{O}_3$  were mixed stoichiometrically and ground thoroughly in acetone. These two compounds were pelletized using polyvinylacetate as a binder and were then fired at 1173 K, sintering temperature, for a hundred hours. The samples were slowly cooled to room temperature in air (50 K/hr). The x-ray diffractometer patterns were taken on a Philips machine (pw 1051) using  $\text{Cu-K}_\alpha$  radiation with a Ni-filter. Both these compounds ( $\text{GaCoMnO}_4$  and  $\text{ZnFeMnO}_4$ ) were then mixed in different molar proportions for the values of  $X = 20, 40, 50, 60$  and  $80$  (where  $X$  denotes the mole percent of  $\text{ZnFeMnO}_4$  in  $\text{GaCoMnO}_4$ ) and these compositions were once again subjected to the same heat treatment. In all the cases, x-ray diffractometer patterns showed  $[hkl]$  reflections due to a single spinel phase only. Our Mössbauer spectra at room temperature also showed the absence of any unreacted  $\alpha\text{-Fe}_2\text{O}_3$ .

The oxygen parameter ( $u$ ) was calculated (Jain and Darshane 1982) from the  $[111]$  reflection since it is very sensitive to  $u$  parameter value. The intensity values were calculated by varying  $u$ -parameter from 0.375 to 0.395 at intervals of 0.002 and the value matching well with the observed intensity was taken as the  $u$  parameter.

Absorbers for Mössbauer measurements were made with the samples enriched with 25%  $^{57}\text{Fe}$  using the same procedure as above. The enriched samples also gave the same lattice parameters. Mössbauer spectra were taken with a conventional constant acceleration spectrometer operating in conjunction with a 1024-channel analyser. The calibration of the spectrometer was done with an  $\alpha\text{-Fe}$  foil using 5 mCi- $^{57}\text{Co}$  source in a copper matrix. The enriched sample of about 20 mg was spread over a 2.5 cm diameter disc and the spectra were recorded at room temperature (294 K). The isomer shift values are expressed as mm/sec with respect to iron metal.

## 3. Results and discussion

For all the compositions of the system  $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$  (except  $\text{GaCoMnO}_4$ ), well resolved quadrupole doublets were observed at room temperature indicating that all are in the paramagnetic state. The Mössbauer spectra for  $X = 20, 50$  and  $80$ , are shown in figure 1. The isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E_q$ ) values are summarised in table 1. All the spectra have been fitted by the least-squares method and the solid line indicates the spectrum as given in figure 1. It is observed (table 1) that the system is cubic in the range  $0 \leq x \leq 60$  and tetragonal in the range  $80 \leq x \leq 100$ . The oxygen parameter ( $u$ ) value increases with the increasing value of  $X$  in the lattice.

The isomer shift and quadrupole splitting values for  $\text{ZnMnFeO}_4$  are found as  $0.48 \pm 0.02$  and  $0.62 \pm 0.02$  mm/sec relative to metallic iron respectively. Our values of isomer shift and quadrupole splitting are slightly higher than those reported earlier (Yagnik and Mathur 1968). The value of the isomer shift observed is typical of high spin ferric compounds and hence the true charge distribution of this spinel can be written as  $\text{Zn}^{2+}[\text{Fe}^{3+}\text{Mn}^{3+}]\text{O}_4^{2-}$ . The corresponding values of isomer shift for other compositions of the system  $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$  are also within the characteristic range (0.20 to 0.50 mm/sec) of high spin  $\text{Fe}^{3+}$  compounds as reported by a number of workers (Rabenau 1970; Van Loef 1966; Spencer and Scherrer 1974). Our values of

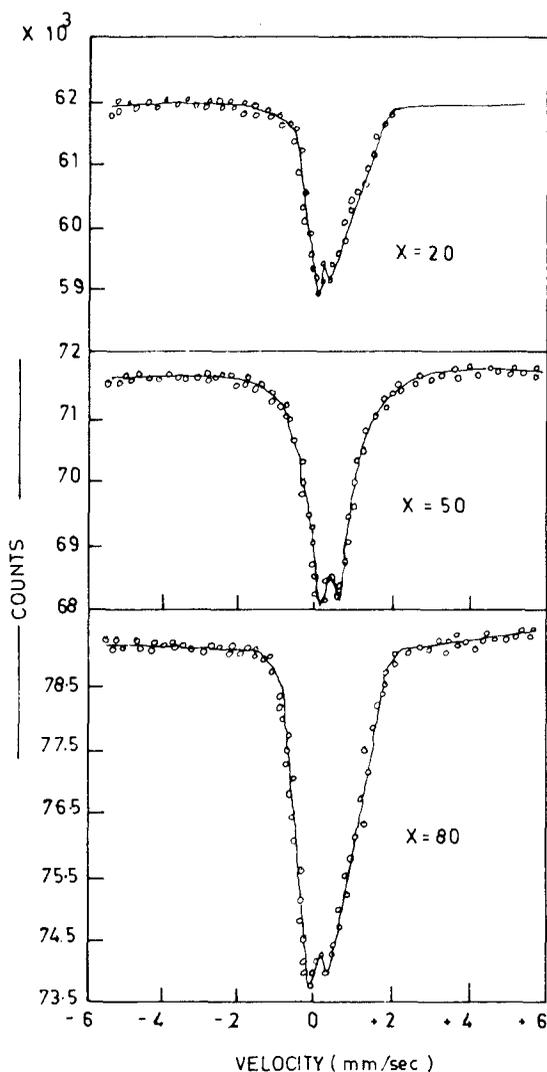


Figure 1. Mössbauer spectra at room temperature.

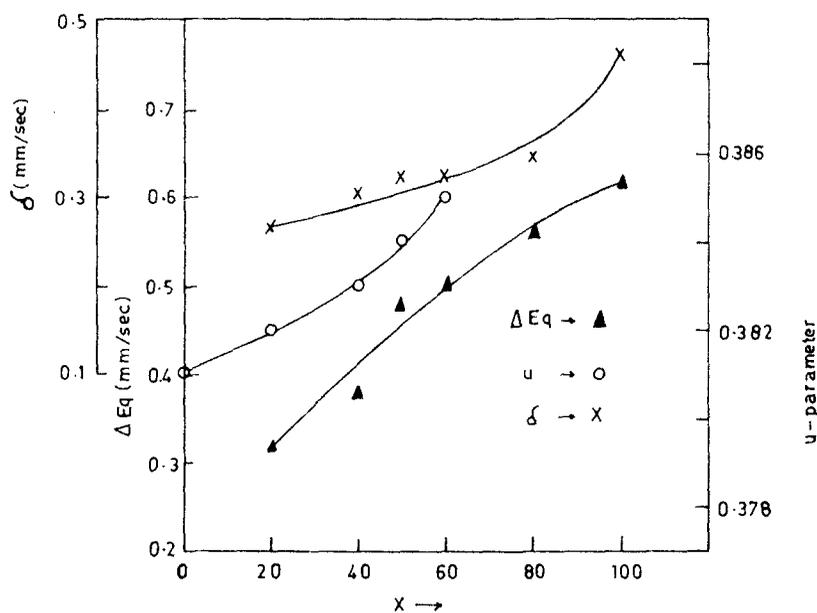
isomer shift varied between 0.26 and 0.48 mm/sec with respect to metallic iron. From x-ray intensity and electrical conductivity data (Jain and Darshane 1982) it was observed that  $\text{Fe}^{3+}$  ions are predominantly present at B-site only. In the present studies no line due to  $\text{Fe}^{3+}$  is observed at the tetrahedral site. However, even if very small concentrations of  $\text{Fe}^{3+}$  are present at A-site, it would lead to a very weak signal which is easily overshadowed by the quadrupole doublet due to octahedral  $\text{Fe}^{3+}$ . This suggests that  $\text{Fe}^{3+}$  ions are predominantly present at the B-site and this is consistent with our previous observations (Jain and Darshane 1982). Similarly, it has been reported (Murray and Linnet 1976) that ferrites in the paramagnetic state have been shown to have iron largely in the octahedral site. Cation distribution in similar compounds also suggests the presence of  $\text{Fe}^{3+}$  ion at the B-site only (Bongere 1957; Blasse 1965).

**Table 1.** Lattice constant, oxygen ion parameter ( $u$ ), isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E_q$ ) values for the system  $\text{ZnFeMnO}_4\text{-GaCoMnO}_4$ .

(Mole %)	$a$ (Å) $\pm 0.005$	$c$ (Å) $\pm 0.005$	$u$ $\pm 0.001$	$\delta$ (mm/sec) $\pm 0.02$	$\Delta E_q$ (mm/sec) $\pm 0.02$
0	8.37	8.37	0.381	—	—
20	8.36	8.36	0.382	0.26	0.32
40	8.36	8.36	0.383	0.30	0.38
50	8.38	8.38	0.384	0.32	0.48
60	8.37	8.37	0.385	0.32	0.50
80	8.27	8.65	—	0.34	0.56
100	8.28	8.78	—	0.48	0.62

The  $\text{Fe}^{3+}$  ( $3d^5$ ) ion will not contribute to the electric field gradient (EFG) because it is spherically symmetric. Hence quadrupole splitting should have been zero in all the compounds of the system studied. But it is gratifying to note that we have obtained sizeable quadrupole splitting in all the compounds. This is attributed to the presence of local distortion in the lattice ( $\text{Mn}^{3+}$ ,  $J-T$  ion). Similarly (Smit *et al* 1962) have also explained that the presence of a trigonal field at the octahedral site distorts the octahedron formed by six oxygen ions and changes the perfect cubic symmetry. This trigonal field would cause an EFG at the  $\text{Fe}^{3+}$  nucleus leading to quadrupole splitting.

The plot of quadrupole splitting ( $\Delta E_q$ ), isomer shift ( $\delta$ ), and  $u$  parameter *vs* composition is given in figure 2. It is seen that  $\Delta E_q$  value increases with increasing  $u$  parameter. It is observed from table 1 that  $u$  parameter increases with an increase in the concentration of  $\text{Zn}^{2+}$  ion at A-site. This may be due to the replacement of  $\text{Ga}^{3+}$  by

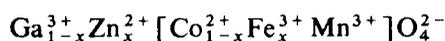
**Figure 2.** Plot of quadrupole splitting ( $\Delta E_q$ ), isomer shift ( $\delta$ ) and  $u$ -parameter values for the system  $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ .

Zn<sup>2+</sup> which is 20% larger in ionic radius (Shannon and Previtt 1970). In this case Ga<sup>3+</sup> ion has a tetrahedral site preference energy (Miller 1959) which is next to the Zn<sup>2+</sup> ion as compared to other ions in the lattice. In order to accommodate the Zn<sup>2+</sup> ion in place of the Ga<sup>3+</sup> ion at the A-site, tetrahedra consisting of oxygen ions expand by moving oxygen ions in the [111] direction away from their nearest A-site ideal position but maintaining the cubic point symmetry. This would result in a higher value of the *u* parameter in the lattice. At the same time, the six nearest oxygen ions around the B-site would deviate from the cubic symmetry. This would, therefore, account for the higher order of quadrupole splitting observed with increase in *X* (composition). A similar trend has also been reported by Jain *et al* (1981) in the case of the system ZnFe<sub>1-x</sub>Mn<sub>x</sub>CrO<sub>4</sub>.

The other possible combinations like Co<sup>3+</sup>, Fe<sup>2+</sup> or Fe<sup>2+</sup>, Mn<sup>4+</sup> at the B-site can be ruled out from our isomer shift values.

#### 4. Conclusions

Thus from the above discussion on Mössbauer effect studies, supported by site preference energy, x-ray intensity and electrical conductivity data as reported earlier, the site distribution of the system is given as



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