

Mössbauer study of spinel system $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$

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Abstract. Mössbauer effect of the system of spinels $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$ is studied for x having values 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0. These compounds show quadrupole splitting which increases with increasing Mn^{3+} ion concentration. It abruptly increases at Mn^{3+} ion concentration at which crystal structure also changes.

Keywords. Mössbauer effect; spinel structure; Jahn-Teller distortion; quadrupole splitting; isomer shift.

Recently there has been a renewed interest in phase transition phenomenon (Stanley 1971; Shenoy 1973). A variety of systems undergo structural transition at a critical temperature, pressure or critical composition. During the last decade the Mössbauer technique has been used as a tool to study such transitions (Preston *et al* 1962; Bhide and Bhasin 1967; Coey *et al* 1969; Umadikar 1970; Wertheim *et al* 1970; Bhide and Hegde 1972; Reich and Michaeli 1972). But there have been few studies of systems undergoing structural changes at critical composition.

$\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$ compounds exhibit bulk $J-T$ distortion for $x < 0.5$ (Deshpande *et al* 1974). This is accompanied by a change in the activation energy of carriers (Deshpande *et al* 1976). It is, therefore, of interest to study the system using a more sensitive probe like the Mössbauer effect. Three compounds *viz* those for which $x = 0, 0.5$ and 1.0 of the above series have been studied earlier (Singh and Srivastava 1975). Results of studies on the entire series which have not been made so far are reported in this paper.

All the Mössbauer spectra were taken using a multichannel analyser and a copper source from Radio Amersham, UK. Calibration of the spectrometer was checked at the beginning and at the end of each spectrum by taking a spectrum of enriched iron absorber. Spectra for $x = 0.4$ and $x = 0.5$ are presented in figure 1.

The Mössbauer spectra of these compounds show quadrupole splitting. The isomer shifts of cubic compounds are 0.39 ± 0.02 mm/sec at room temperature 294 K while those for tetragonal compounds are 0.34 ± 0.02 mm/sec with respect to iron (figure 2a). These values are characteristic of Fe^{3+} ions. The x-ray and Mössbauer study of spinels containing these ions have shown that Mn and Fe are in trivalent state (Mande *et al* 1969; Yagnik and Mathur 1968). For $x > 0.5$ the Mn concentration is small and spinels belong to the cubic system. On account of the symmetry of electronic configuration, there should be no quadrupole splitting.

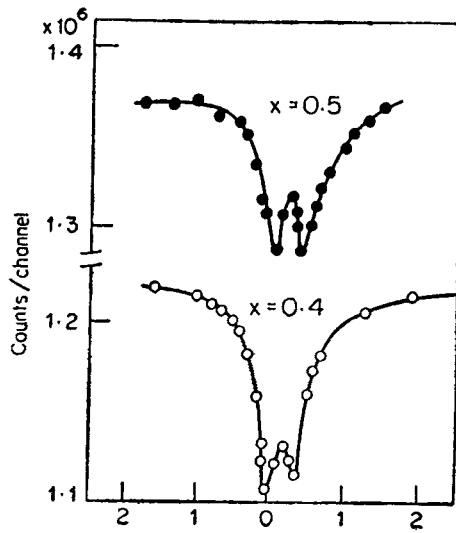


Figure 1. Mössbauer spectra for $x=0.4$ and $x=0.5$ of the system $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$.

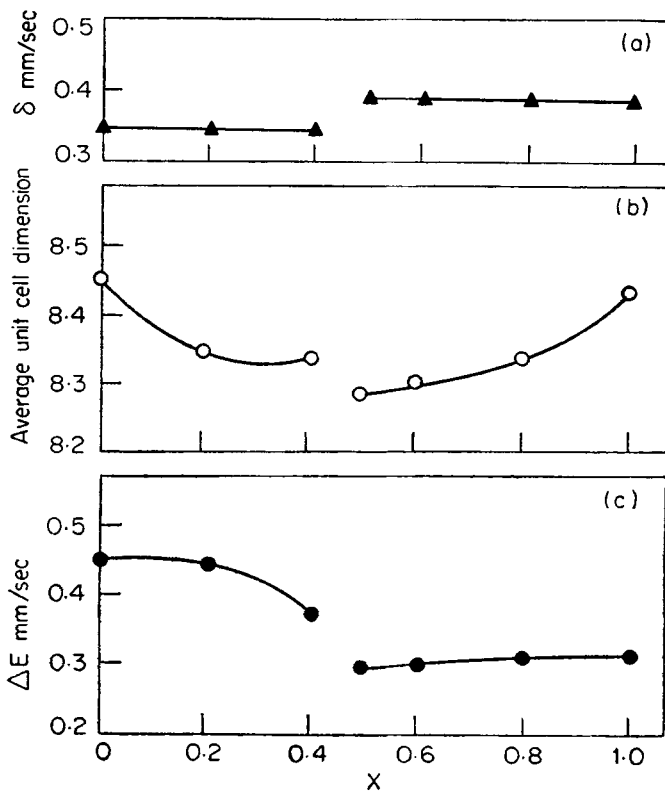


Figure 2 a. Isomer shift δ versus x at room temperature (294 K). b. Average unit cell dimension versus x at room temperature (294 K). c. Quadrupole splitting ΔE versus x at room temperature (294 K).

Table 1. Lattice parameters of $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$.

x	Symmetry	Lattice parameters in Å		Distortion $\frac{c}{a} - 1$
		a	c	
0	Tetragonal	8.30	8.73	0.052
0.2	Tetragonal	8.33	8.39	0.007
0.4	Tetragonal	8.33	8.36	0.003
0.5	Cubic	8.29	8.29	0.000
0.6	Cubic	8.31	8.31	0.000
0.8	Cubic	8.35	8.35	0.000
1.0	Cubic	8.44	8.44	0.000

However, the Mössbauer effect data show ΔE values grouped around 0.33 ± 0.02 mm/sec at room temperature (294 K). It is apparent that this quadrupole splitting stems from the trigonal field as Fe^{3+} is spherically symmetric.

The x-ray diffraction patterns of the compounds of the series recorded on 114.6 mm (diameter) Debye-Scherrer camera using filtered copper radiation, showed a single phase of spinel structure. Lattice parameters calculated using the x-ray data are given in table 1.

The replacement of Mn^{3+} ions by Cr^{3+} ions reduces the distortion of unit cell and at $x = 0.5$ i.e. when one of the octahedral (B) sites is equally shared by Mn^{3+} ($3d^4$) and Cr^{3+} ions, the distortion disappears. The average unit cell dimension versus x shows a break when $x = 0.5$ (figure 2b) at which the crystal symmetry changes from tetragonal to cubic (Deshpande *et al* 1974). It is well known that Mn^{3+} ($3d^4$) ion at B site in a spinel structure causes a co-operative distortion (Jahn-Teller 1937). The fact, that Mn^{3+} ions occupying more than a critical fraction (f) of B sites in a spinel structure produces distortion, has been well established (O'Keeffe 1961; Irani *et al* 1960). The critical fraction f depends on the nature of ions in the neighbourhood of Mn^{3+} ions at B sites (Goodenough 1966).

The distortion of $\text{Mn}^{3+} - \text{O}^{2-}$ octahedra affects the $\text{Fe}^{3+} - \text{O}^{2-}$ octahedra which is reflected in the quadrupole splitting. It can be seen (figure 2c) that the quadrupole splitting increases abruptly at $x = 0.5$ when $f > 0.25$. The splitting increases as the tetragonality of the cell increases. Our values of quadrupole splitting are in general lower than those for the three compounds in this series reported earlier (Singh and Srivastava 1975). Our ΔE value of $\text{Zn}(\text{MnFe})\text{O}_4$ is also slightly lower than those obtained by Yagnik and Mathur (1968) ($\Delta E = 0.5$ mm/sec) and by Singh and Srivastava (1975) ($\Delta E = 0.52$ mm/sec).

The spinels of this series in the range $x = 0.4$ to $x = 0.5$ are being studied to determine the composition at which the structural change takes place.

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