Cation distribution of the system $\text{Zn}_{1-x}\text{Co}_x\text{FeMnO}_4$ by x-ray, electrical conductivity and Mössbauer studies

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Abstract. Structural, electrical and Mössbauer studies were carried out for the system $\text{Zn}_{1-x}\text{Co}_x\text{FeMnO}_4$. It is observed that for $x \leq 0.6$, the ionic configuration of the system is $\text{Zn}^{2+}\text{Mn}^{2+}[\text{Co}^{2+}\text{Mn}^{3+}\text{Fe}^{3+}]\text{O}_4^-$ and for $x \geq 0.8$ Fe$^{3+}$ ions occupy tetrahedral site also. On the basis of electrical and Mössbauer studies a probable valence distribution of CoMnFeO$_4$ has been suggested. All the compounds showed positive values of thermoelectric coefficient and electrical conduction takes place by a hopping mechanism. Activation energy and thermoelectric coefficient values decreased with decrease in concentration of Zn$^{2+}$ ions. The compounds possess low mobility values varying between $10^{-5}$ and $10^{-6} \text{cm}^2/\text{V sec}$.

Keywords. Spinel; electrical conductivity; isomer shift; quadrupole splitting; hyperfine magnetic field; mobility; cation distribution.

1. Introduction

Oxidic spinels have been studied by several workers (Landolt Börnstein 1970) to determine the relationship between the structure, bonding and magnetic properties, because of intrinsic theoretical and commercial importance of these materials. In the oxidic spinel systems, particularly those containing cations of variable valency and which can occupy more than one possible site, one technique is not sufficient to depict the correct site distribution and oxidation state. In spinels containing elements of first transition series, the ionic distribution cannot be determined by x-ray investigation to any great accuracy because of the close atomic scattering powers. This paper attempts to overcome this problem by simultaneously using different techniques such as x-ray, electrical conductivity and Mössbauer effect.

The ionic configuration of CoMnFeO$_4$ has been studied by several workers. Magnetic measurements have shown that in the system CoMn$_x$Fe$_{2-x}$O$_4$, both Co$^{2+}$ and Fe$^{3+}$ may be present at A-site (Blasse 1965). Mössbauer studies (Yagnik and Mathur 1968) have shown that ionic configuration of cobalt-iron manganite is Mn$^{2+}$ Co$^{2+}$ Fe$^{3+}$ O$_4^-$. X-ray spectroscopic studies (Kulkarni 1974) on CoMnFeO$_4$ suggested a similar ionic configuration with Mn$^{2+}$ at A-site. The compound ZnFeMnO$_4$ possesses normal spinel structure (Goodenough 1966). The ionic configuration of CoMnFeO$_4$, therefore, requires further investigation using different techniques simultaneously since the elements possess close atomic scattering powers. This paper gives the results of our studies on the system $\text{Zn}_{1-x}\text{Co}_x\text{FeMnO}_4$ by x-ray,
electrical conductivity and Mössbauer techniques to arrive at the site distribution of CoMnFeO$_4$.

2. Materials and methods

2.1 X-ray analysis

The compositions of the system Zn$_{1-x}$Co$_x$FeMnO$_4$ were prepared by mixing the component oxides (GR grade) in acetone in appropriate molar proportions. The unreacted oxide mixture (after homogenizing) of each composition was subjected to TG analysis (using MOM derivatograph) up to 1273 K. The loss in weight in all the compositions of the system was negligible (< 0.03%) suggesting that the compounds were sufficiently stoichiometric. The pellets were prepared using 2% solution of polyvinylacetate as a binder. To remove the binder, the pellets were slowly heated at 773 K for 20 hr and fired at 1173 K, sintering temperature, for 100 hr. The samples were cooled in air at 50 K per hour. The loss or addition of an element was further checked by weighing the samples before and after heating and in all cases the change was negligible.

X-ray powder diffractometer (Philips PW 1051) patterns were taken with Ni-filtered Cu-Kα radiation to study the compounds both for lattice parameters and intensity measurements. All the x-ray patterns showed no lines other than those belonging to spinel structure. To measure the intensity, the areas under different \{hkl\} peaks were determined by planimeter and values obtained in relation to the peak area for 311 reflection which was taken as 100. To ensure the reliability of the method, the specimens were subjected to x-ray diffractometry twice and after correcting for background a mean value of area was taken (reproducible within 2%).

To calculate the relative integrated intensity $I$ of a given \{hkl\} reflection, as seen in a diffractometer with a flat plate sample holder, the following formula (Bürger 1960) was used,

$$I = |F_{hkl}|^2 \cdot P \cdot L_p,$$

where $F$ is the structure factor, $P$ the multiplicity factor and $L_p$ = the Lorentz-polarisation factor. The atomic scattering powers for various ions were taken from International Tables (1959).

In spinel lattice the \{hkl\} reflections 220, 311, 222, 400, 422 and 440 are sensitive to cation distribution at both the sites. To determine the cation distribution and its variation with the composition, the intensity ratios ($I_{440}/I_{122}$, $I_{220}/I_{440}$, $I_{422}/I_{400}$, $I_{311}/I_{220}$ and $I_{220}/I_{322}$) for different possible models of cation distribution were calculated and compared with the observed intensity ratios. The maximum standard deviation in the observed intensity ratios was ± 0.02. According to Bertaut (1950) and Weil et al (1950), the best cation distribution is obtained when comparing experimental and theoretical intensity ratios for reflections whose intensities (i) are independent (or very slightly dependent) of oxygen parameter $u$ (ii) vary with the inversion parameter in the opposite sense and (iii) do not differ strongly. The above reflections and ratios were selected because they fulfil the requirements.
2.2 Mössbauer studies

Mössbauer spectrum for each sample was recorded using a constant acceleration drive in which the source can be moved with respect to a stationary absorber operating in conjunction with a 1024 channel analyzer. The spectrometer was calibrated with standard iron foil using $^{57}\text{Co}$ in copper matrix. About 20 mg of enriched sample was uniformly spread over 2.5 cm diameter disc. All the spectra were recorded at 294 K.

2.3 Electrical conductivity measurements

The DC resistivity was measured using LCR Marconi Bridge. The end faces of each pellet were coated with a thin layer of conducting silver paste and measured from room temperature to 773 K using the two-probe technique. Thermo electric coefficients were measured from room temperature to 573 K. The sign of the thermo electric coefficient value is designated as positive if the cold end is positive indicating p-type of semiconduction. The IR spectra were recorded on a double beam spectrophotometer (Beckman) from 1000 to 250 cm$^{-1}$ using KBr pellets.

3. Results and discussion

3.1 X-ray analysis

The results of x-ray analysis are given in table 1 and the lattice constant vs composition is plotted in figure 1. The system is tetragonal in the range $0 \leq x \leq 0.2$ and cubic in the range $0.4 \leq x \leq 1$. A plot of $V^{1/3}$ vs. composition showed a break near a critical composition region where there is a change in crystal structure. An inflexion near critical composition region can be explained according to the model of Goodenough and Loeb (1955). In the cubic region the distortion of the individual octahedron is suppressed by the strain energy of the lattice and when the critical concentration is reached, the cations at B-site get ordered in alternate planes perpendicular to C-axis producing tetragonal distortion. This causes an appreciable expansion of the lattice leading to an inflexion in $V^{1/3}$ vs. composition curve at the

<table>
<thead>
<tr>
<th>$x$</th>
<th>Structure</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V^{1/3}$ (Å$^3$)</th>
<th>$\rho_{RT}$ (ohm-cm)</th>
<th>$\Delta E$ (eV)</th>
<th>$a(\mu V/K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>T</td>
<td>8.32</td>
<td>8.77</td>
<td>8.467</td>
<td>$1.3 \times 10^4$</td>
<td>0.51</td>
<td>230</td>
</tr>
<tr>
<td>0.2</td>
<td>T</td>
<td>8.37</td>
<td>8.47</td>
<td>8.403</td>
<td>$1.2 \times 10^4$</td>
<td>0.50</td>
<td>185</td>
</tr>
<tr>
<td>0.4</td>
<td>C</td>
<td>8.37</td>
<td>8.37</td>
<td>8.37</td>
<td>$7.1 \times 10^4$</td>
<td>0.47</td>
<td>175</td>
</tr>
<tr>
<td>0.5</td>
<td>C</td>
<td>8.37</td>
<td>8.37</td>
<td>8.37</td>
<td>$3.0 \times 10^4$</td>
<td>0.46</td>
<td>170</td>
</tr>
<tr>
<td>0.6</td>
<td>C</td>
<td>8.39</td>
<td>8.39</td>
<td>8.39</td>
<td>$1.0 \times 10^4$</td>
<td>0.45</td>
<td>140</td>
</tr>
<tr>
<td>0.8</td>
<td>C</td>
<td>8.40</td>
<td>8.40</td>
<td>8.40</td>
<td>$6.0 \times 10^4$</td>
<td>0.43</td>
<td>130</td>
</tr>
<tr>
<td>1.0</td>
<td>C</td>
<td>8.41</td>
<td>8.41</td>
<td>8.41</td>
<td>$4.2 \times 10^4$</td>
<td>0.42</td>
<td>95</td>
</tr>
</tbody>
</table>

C = Cubic; T = Tetragonal

Table 1. Lattice constant, room temperature resistivity, activation energy and thermo electric coefficient values for the system Zn$_{1-x}$Co$_x$FeMnO$_4$. 
transition region. A similar break has earlier been observed by the present authors (Jain and Darshane 1980) in ZnFeMnO₄-GaCoMnO₄ system.

The cation distribution at two sites in this system (Znₓ₋ₓCoₓFeMnO₄) is investigated by x-ray intensity calculations carried out at an interval of \( y = 0.05 \) (where \( y \) is the inversion parameter) for the compositions where \( x \leq 0.6 \). The various permutations and combinations of cationic arrangements between two sites were taken using the site preference energy data (Miller 1959; site preference energy in kcal/g. at.wt., \( \text{Zn}^{2+} \rightarrow -31.6 \), \( \text{Fe}^{3+} \rightarrow -13.3 \), \( \text{Mn}^{2+} \rightarrow -14.7 \) and \( \text{Co}^{2+} \rightarrow -10.5 \)). However, the observed and calculated intensity ratios which are comparatively closer are only summarised in table 2 for the following three models in which (i) \( \text{Zn}^{2+} \) and \( \text{Fe}^{3+} \) (ii) \( \text{Zn}^{2+} \) and \( \text{Co}^{2+} \) and (iii) \( \text{Zn}^{2+} \) and \( \text{Mn}^{2+} \) are present at tetrahedral (A) site.

The calculated intensity ratios of reflections \( I_{440}/I_{422}, I_{422}/I_{400}, I_{220}/I_{222}, I_{411}/I_{220} \) and \( I_{220}/I_{440} \) were determined for the compounds Zn₀.⁵ Co₀.⁵ FeMnO₄ and Zn₀.⁸ Co₀.₂ FeMnO₄ and compared with the observed ratios (table 2). It is seen that the model in which \( \text{Zn}^{2+} \) and \( \text{Mn}^{2+} \) occupy A-site and \( \text{Co}^{3+}, \text{Fe}^{3+} \) and \( \text{Mn}^{3+} \) occupy B-site shows better agreement. This model is further supported by site preference energy

<table>
<thead>
<tr>
<th>A-site B-site</th>
<th>( I_{440}/I_{422} )</th>
<th>( I_{422}/I_{400} )</th>
<th>( I_{220}/I_{222} )</th>
<th>( I_{411}/I_{220} )</th>
<th>( I_{220}/I_{440} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Zn}^{2+} ) ( \text{Fe}^{3+} ) Fe( ^{3+} ) Co( ^{3+} ) Mn( ^{4+} )</td>
<td>3.86</td>
<td>0.82</td>
<td>4.26</td>
<td>0.82</td>
<td>3.16</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} ) Mn( ^{4+} ) Fe( ^{3+} ) Co( ^{3+} ) Mn( ^{4+} )</td>
<td>3.90</td>
<td>0.76</td>
<td>4.00</td>
<td>0.90</td>
<td>3.46</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} ) Co( ^{3+} ) Fe( ^{3+} ) Mn( ^{3+} )</td>
<td>3.69</td>
<td>0.88</td>
<td>4.82</td>
<td>0.63</td>
<td>3.30</td>
</tr>
</tbody>
</table>

Zn₀.⁵ Co₀.⁵ FeMnO₄

<table>
<thead>
<tr>
<th>A-site B-site</th>
<th>( I_{440}/I_{422} )</th>
<th>( I_{422}/I_{400} )</th>
<th>( I_{220}/I_{222} )</th>
<th>( I_{411}/I_{220} )</th>
<th>( I_{220}/I_{440} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Zn}^{2+} ) ( \text{Fe}^{3+} ) Fe( ^{3+} ) Co( ^{3+} ) Mn( ^{4+} )</td>
<td>3.55</td>
<td>0.93</td>
<td>5.59</td>
<td>0.85</td>
<td>3.12</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} ) Mn( ^{4+} ) Fe( ^{3+} ) Co( ^{3+} ) Mn( ^{4+} )</td>
<td>3.60</td>
<td>0.87</td>
<td>4.73</td>
<td>0.62</td>
<td>3.58</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} ) Co( ^{3+} ) Fe( ^{3+} ) Mn( ^{3+} )</td>
<td>3.46</td>
<td>0.99</td>
<td>5.02</td>
<td>0.90</td>
<td>3.16</td>
</tr>
</tbody>
</table>
values (Miller 1959). At the same time the model in which Zn$^{2+}$ and Mn$^{2+}$ occupy A-site (for $x \leq 0.6$) gives the least value of reliability factor ($R$),

$$R = \frac{\sum |I_{hkl}|_{\text{obs}} - \sum |I_{hkl}|_{\text{cal}}}{\sum |I_{hkl}|_{\text{obs}}}$$

where $R$ varied between 0.073 and 0.120. In this case we have taken 220, 311, 222, 400, 422, 511, 440, 533, 731, 555 and 844 planes to evaluate the $R$ factor.

In the case of intensity calculations the integrated intensities are valid at 0 K. Since we have noted the observed intensities at room temperature, a suitable correction to equation (1) is in principle necessary for precise comparison. However, as the spinels possess high melting points ($> 1773$ K), the thermal vibrations of the atoms at room temperature show negligible effect as compared to that at absolute zero. This has now been confirmed since the correction involved due to temperature factor in the intensity ratios of the present system, Zn$_{1-x}$Co$_x$FeMnO$_4$, was less than 2%. A similar observation has been made by Datta and Roy (1967) in NiAl$_2$O$_4$ and other spinels. Ohnishi and Teranishi (1961) and Bacon and Roberts (1953) reported the correction involved due to temperature factor and our value is consistent with their results.

From x-ray intensity calculations no precise ionic configuration can be suggested for the compositions Zn$_{0.2}$Co$_{0.8}$FeMnO$_4$ and CoMnFeO$_4$ ($x \leq 0.8$). In this case the concentration of Zn$^{2+}$ ion is appreciably less and the other ions present in the lattice possess close atomic scattering powers (for $\sin \theta/\lambda = 0.25$, Zn$^{2+} = 22.6$, Fe$^{3+} = 18.3$, Co$^{3+} = 19.5$, Co$^{4+} = 19.2$, Mn$^{3+} = 17.5$, Mn$^{4+} = 17.3$, Mn$^{5+} = 16.9$) and from intensity calculations we could not draw any conclusion since calculated intensity ratios were very close. The probable ionic configuration of these two compounds was, therefore, deduced with electrical conductivity, Mössbauer and site preference energy data.

3.2 Mössbauer studies

The Mössbauer spectra for $x = 0.5$, 0.8 and 1 are given in figure 2. The six-line broad patterns were observed for $x \geq 0.8$ and for $x \leq 0.6$ spectra showed single quadrupole doublet. The six line spectrum was resolved graphically into two sets of quadrupole split spectra of unequal intensities by using the equation of Shirane et al (1962),

$$Y = \frac{Y_0}{1 + 0.75(x/\Gamma)^2 + 0.25 (x/\Gamma)^4},$$

where $Y_0 =$ length of absorption line at $x = 0$ and $2\Gamma$ is the full width at half maximum. The analysis of six-line spectrum with the above equation was carried out by the least square method. Different values of positions, linewidths and intensities were assumed to analyse the spectrum for a pair of Zeeman pattern assuming each line to be of Lorentzian shape. The analysis was continued till the synthetic curve gave the best possible visual fit to the experimental points as well as a minimum mean square deviation between the experimental points and the corresponding points on the synthetic curve. The values of isomer shift ($\delta$), quadrupole splitting ($\Delta E_Q$),
and magnetic hyperfine field \( (H_a) \) are listed in table 3. It is observed from table 3 that \( H_a \) (A) > \( H_a \) (B).

In order to determine the identification of components of the spectrum from Fe\(^{3+} \) ion located in two different crystallographic positions (for \( x \geq 0.8 \)), the Mössbauer spectrum was measured in an external magnetic field perpendicular to the beam of \( \gamma \)-rays. The magnetic moments of Fe\(^{3+} \) ions at octahedral site are then parallel to the magnetic field whereas those in the tetrahedral site are antiparallel. Hence the outer spectral components from tetra-and octahedral nuclei are shifted in the external field in opposite directions: the tetrahedral lines move towards higher fields and the octahedral one towards lower fields. The measurements were made for CoMnFeO\(_4\). Since the width of tetrahedral component in ferrite spinel is less than the octahedral one, it was concluded that the outer lines belonging to A-site are located on the outer side of the spectral components. A similar observation has been made by Belov et al. (1971) in cobalt iron chromite and by Sawatzky et al. (1969b) and Weiser et al. (1968) in iron manganite.

The quadrupole splitting \( (\Delta E_q) \) and isomer shift values for tetragonally-distorted ZnFeMnO\(_4\), found as 0.62 ± 0.02 mm/sec and 0.48 ± 0.02 mm/sec to metallic iron respectively, are slightly higher than the values reported by Yagnik and Mathur.
Table 3. Quadrupole splitting (QS), isomer shift (IS) and hyperfine magnetic field ($H_n$) values for the system Zn$_{1-x}$Co$_x$FeMnO$_4$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$H_n$ (kOe) ± 5</th>
<th>IS (mm/sec) ± 0.02</th>
<th>QS (mm/sec) ± 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A-site</td>
<td>B-site</td>
<td>A-site</td>
</tr>
<tr>
<td>0.0</td>
<td>—</td>
<td>—</td>
<td>0.48</td>
</tr>
<tr>
<td>0.2</td>
<td>—</td>
<td>—</td>
<td>0.48</td>
</tr>
<tr>
<td>0.4</td>
<td>—</td>
<td>—</td>
<td>0.48</td>
</tr>
<tr>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>0.48</td>
</tr>
<tr>
<td>0.6</td>
<td>—</td>
<td>—</td>
<td>0.46</td>
</tr>
<tr>
<td>0.8</td>
<td>386</td>
<td>344</td>
<td>0.24</td>
</tr>
<tr>
<td>1.0</td>
<td>438</td>
<td>407</td>
<td>0.27</td>
</tr>
</tbody>
</table>

(1968) (table 3). The present value of isomer shift is typical of the high spin Fe$^{3+}$ ion at B-site and hence the true charge distribution of this spinel has been represented as Zn$^{2+}$[Fe$^{3+}$Mn$^{3+}$]O$_4^2^-$. The isomer shift values for other compositions of the system Zn$_{1-x}$Co$_x$FeMnO$_4$ are also within the characteristic range of high spin Fe$^{3+}$ complexes as reported by number of workers (Rabenau 1970; Bhide 1973; Spencer and Schroer 1974; van Loef 1966). The isomer shift values for all the cases varied between 0.21 and 0.48 mm/sec indicating the presence of only Fe$^{3+}$ ions in the lattice.

All the compounds studied showed sizable quadrupole splitting due to the presence of EFG in the lattice. The major EFG contribution in the present system is due to tetragonal distortion produced by Mn$^{2+}$ ($J - T$) ion. The second EFG source is the trigonal symmetry at the octahedral site owing to the presence of different cations in second co-ordination sphere. It has been observed that spectra exhibiting Zeeman pattern show quadrupole splitting at both the sites indicating the presence of EFG at both A and B sites. It is observed from table 3 that quadrupole splitting value suddenly increases at $x = 0.2$, i.e. Zn$_{0.8}$Co$_{0.2}$FeMnO$_4$ where crystal structure changes. A similar trend was observed earlier (Darshane et al 1981) in the system ZnFe$_{1-x}$Mn$_x$CrO$_4$.

Savatzky et al (1969) reported that the recoilless fraction of Fe$^{3+}$ ions at A and B sites are nearly equal and the degree of inversion $y$ (where $y$ is the fraction of Fe$^{3+}$ ion at A-site in the spinel lattice) is determined by the ratio of areas under the two resolved spectra due to Fe$^{3+}$ ions at two sites. Considering the area ratios of resolved spectra using equation (3), the amount of Fe$^{3+}$ ions present at A and B sites for $x = 1.0$ and $x = 0.8$ is 0.55 : 0.45 and 0.45 : 0.55 respectively. Here the accuracy of the least square method is of the order of ± 0.02. The above discussion on Mössbauer studies for $x \geq 0.8$ showed that Fe$^{3+}$ ions are distributed between A and B sites.

The hyperfine magnetic field at A-site is greater than B-site (table 3). The magnetic field at A-site is lowered by covalency effects. Superexchange interactions also influence magnetic field ($H_n$) at these sites. In the present system it appears that the superexchange interaction has a stronger influence over the magnetic field than the covalency effects. A similar observation was made by Sawatzky et al (1968), Weiser et al (1968) and Belov et al (1971) in FeMn$_2$O$_4$ and CoFeCrO$_4$ compounds respectively. It is observed from table 3 that magnetic hyperfine field at A and B
sites increases with increase in \( x \) value (cobalt concentration). This is because \( \text{Zn}^{2+} \) (diamagnetic ion), which is present at A-sub lattice in the composition \( x = 0.8 \) is completely replaced by the paramagnetic ion leading to increase in the magnetization at A-sublattice. This indicates the transfer of some \( \text{Co}^{2+} \) ions to A-site. Mössbauer studies on similar compounds suggested the presence of \( \text{Co}^{2+} \) at A-site. For example, in \( \text{CoFe}_2\text{O}_4 \) (Sawatzky et al 1969b) the ionic configuration was \( \text{Co}^{2+}_{0.97} \text{Fe}^{3+}_{0.93} \left[ \text{Co}^{3+}_{0.9} \text{Fe}^{3+}_{1.1} \right] \text{O}_4^{-} \) and for \( \text{CoFeCrO}_4 \) (Belov et al 1971) the distribution of cations is reported as \( \text{Co}^{2+}_{0.8} \text{Fe}^{3+}_{0.2} \left[ \text{Cr}^{3+} \text{Fe}^{3+}_{0.5} \text{Co}^{3+}_{0.5} \right] \text{O}_4 \). Thus, the transfer of \( \text{Co}^{2+} \) ions to A-site leads to increase in the magnetization at Fe\( ^{3+} \) nucleus and hence the magnetic field. The increase in magnetization (at A-site) also increases magnetic field at B-site through A–B interaction which is stronger in CoMnFeO\(_4\) than Zn\(_{0.2}\)Co\(_{0.8}\)FeMnO\(_4\). This is because every A-site cation is coupled by twelve exchange bonds with the nearest B-cations whereas B-cations have only six exchange bonds. The above discussion on magnetic field suggests the presence of both \( \text{Co}^{2+} \) and \( \text{Fe}^{3+} \) ions at A-site for the compositions \( x \geq 0.8 \). The detailed ionic configuration of these compositions was confirmed by studying electrical properties.

### 3.3 Electrical conductivity

The DC resistivity of all the compounds, when measured as a function of temperature varied between \( 10^8 \) and 10 ohm-cm and log \( \rho \) vs \( 10^3/T \) plots obeyed Wilson's law. The activation energy calculated from the slopes of above plots for different compositions varied between 0.51 and 0.42 eV. Activation energy values were quite reproducible and the maximum deviation was within the range of 0.01 eV. It is observed (figure 3) that the values of activation energy, thermoelectric coefficient and room temperature resistivity decrease with decrease in zinc ion concentration. This is attributed to increase in the number of charge carriers at B-site. All the compounds now studied showed \( \rho \)-type semiconductivity.

![Figure 3](image)

**Figure 3.** Plot of room temperature resistivity, activation energy and thermoelectric coefficient vs composition for the system Zn\(_{1-x}\)Co\(_x\)FeMnO\(_4\).
The electrical conductivity, \( \sigma \), is related to the number of charge carriers \( p \) and their mobility \( \mu \) at room temperature by the relation:

\[
\sigma = p.e.\mu
\]

where \( e \) is the electronic charge. Taking the average unit cell volume \((8.4)\)\(^3\), the value of hole concentration would be \(10^{22}\) per cc and the mobility value varies between \(10^{-7}\) and \(10^{-9}\) cm\(^2\)/V sec. It can also be calculated using the equation (Heikes and Johnston 1957):

\[
\mu = \frac{ed^2 \nu \exp \left(\frac{-\Delta E}{kT}\right)}{kT}
\]

where \( \Delta E \) is the activation energy, \( k \) the Boltzman constant, \( d \) the jump length and \( \nu \) the lattice frequency. The mobility value thus calculated is \(10^{-9}\) cm\(^2\)/V-sec. Infrared studies indicated the presence of two strong absorption bands at 450 and 600 cm\(^{-1}\). These bands are due to the intrinsic vibration of octahedral cations (Tarte 1965; Jain and Darshane 1980). However, the band at 600 cm\(^{-1}\) being stronger than 450 cm\(^{-1}\) was considered for our calculation of lattice frequency in equation (5).

All the compounds of the system \( \text{Zn}_{1-x}\text{Co}_x\text{FeMnO}_4 \) possess low mobility values and it increases exponentially with increasing temperature following the relationship:

\[
\mu = \mu_0 \exp \left(\frac{-\Delta E}{kT}\right)
\]

where \( \mu_0 \) is a constant representing the mobility at \( T = \infty \). In the case of low mobility semi-conductors and its exponential temperature dependence, the charge carriers are localised to particular site and electrical conduction involves the hopping of charge carriers from one site to another during lattice vibrations and, therefore, mobility shows exponential temperature dependence.

Thermoelectric coefficient measurements carried out between 300 and 573 K showed that all the compounds are \( p \)-type semiconductors. In all the compositions the plots of \( aT \) vs \( T \) were linear obeying the equation suggested by Honig (1966):

\[
a_+ = \frac{k}{e} \left[ \ln \frac{1-S}{S} + \frac{S_R}{k} \right]
\]

where \( S \) is the probability of cationic site for an extra charge carrier and \( S_R \) = lattice relaxation entropy term. The \( a \) values varied between + 95 and + 230 \( \mu V/k \) (table 1).

From the x-ray results it is observed that Mn\(^{2+}\) ions are present at A-site along with Zn\(^{2+}\) for the compositions \( x \leq 0.6 \). The presence of Fe\(^{3+}\) and Co\(^{3+}\) ions at A-site is also observed from the Mössbauer studies (\( x \geq 0.8 \)). Similar compounds studied earlier like CoMn\(_4\)O\(_4\) (Ikou Aoki 1962) and CoFe\(_2\)O\(_4\) (Sawatzky et al 1969b) also show the presence of Mn\(^{2+}\), Co\(^{3+}\) and Fe\(^{3+}\), Co\(^{3+}\) at A-site respectively. The presence of these three cations at A-site is further supported by site preference energy data (Miller 1959).
Generally in spinels electrical conduction takes place through hopping of charge carriers at B-site via the following process,

\[ \text{Mn}^{3+} + \text{Mn}^{4+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{3+}. \]

The motion of Mn\(^{4+}\) ions in the lattice of Mn\(^{3+}\) ions can be visualised as a motion of hole. The other possible mechanism of conduction like Co\(^{3+}\) + Co\(^{4+}\) \rightarrow Co\(^{4+}\) + Co\(^{3+}\) can be ruled out on the basis of ionisation energy values (Huheey 1972; Mn\(^{3+}\) \rightarrow 17.5 eV and Co\(^{3+}\) \rightarrow 17.8 eV). It is seen from table 1 and figure 3 that activation energy and room temperature resistivity values decreased with decrease in concentration of zinc ions. Comparatively low values of activation energy and room temperature resistivity for the compositions \(x \geq 0.8\) suggested the presence of cations of two different charges at B-site (Mn\(^{3+}\), Mn\(^{4+}\)).

The above discussion suggests the need for calculating Mn\(^{3+}\), Mn\(^{4+}\) concentration at B-site in Zno.\(x\) Co0.8 FeMnO\(_4\) and CoFeMnO\(_4\) compounds. To calculate the ratios of Mn\(^{3+}/\text{Mn}^{4+}\) from thermoelectric coefficient values, the following equation suggested by Honig (1966) for \(p\)-type material was used,

\[ a = \frac{k}{e} \ln \left[ \frac{\text{Mn}^{3+}/\text{Mn}^{4+}}{A/kT} \right], \quad (8) \]

where \(A\) is the kinetic energy term for transport. In the above equation, usually the first term in bracket predominates and determines the sign of thermo-electric coefficient. From the values of \(a\), the ratios of Mn\(^{3+}/\text{Mn}^{4+}\) at B-site for \(x = 0.8\) and \(x = 1.0\) are found as 0.70 : 0.15 and 0.60 : 0.20 respectively.

Thus, from Mössbauer and electrical conductivity studies supported by site preference energy data, the following site distribution of Zno.\(x\) Co0.8 FeMnO\(_4\) is proposed

\[ \text{Zn}_{0.20}^{2+} \text{Fe}_{0.45}^{3+} \text{Mn}_{0.15}^{2+} \text{Co}_{0.20}^{2+} [\text{Fe}_{0.65}^{3+} \text{Mn}_{0.70}^{3+} \text{Mn}_{0.15}^{4+} \text{Co}_{0.60}^{3+}] \text{O}_4^{2-} \]

and for CoMnFeO\(_4\) as,

\[ \text{Fe}_{0.65}^{3+} \text{Mn}_{0.20}^{2+} \text{Co}_{0.35}^{2+} [\text{Fe}_{0.45}^{3+} \text{Mn}_{0.60}^{3+} \text{Mn}_{0.20}^{4+} \text{Co}_{0.75}^{3+}] \text{O}_4^{2-}. \]

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