CHAPTER IV:
CHEMICAL SHIFT STUDIES
4.1 INTRODUCTION

Since the first observation of chemical effects in x-ray absorption spectra by Bergengren\textsuperscript{1}, a large amount of work has been carried out by many workers\textsuperscript{2-5} to understand the chemical effects that affect the position and width of the absorption edge and extended fine structure near the absorption edge. The attempts have been made to correlate the effects with valence state of the absorbing atom, crystal structure, electronegativity, interatomic distances and binding energies of the atoms in different states. Various theories have appeared in literature\textsuperscript{6-9} regarding the K-absorption edge and extended fine structure observed in compounds, alloys and complexes.

Ballal and Mande\textsuperscript{10} have identified the valence state of Cu in CuCr\textsubscript{2}X (where X = O, S, Se, Te) having spinel structure from shifts in absorption edge. Also the chemical shifts have been studied and used by Kulkarni and Mande\textsuperscript{11} to establish ionic structure of copper manganates. A method has been discussed by Bandarev and Kirichokpp\textsuperscript{12} to correlate intensities of Fe-K absorption edge in iron with that given by the ionic state in ferrite. Vaingankar\textsuperscript{13} has correlated the degree of inversion with chemical shifts of Fe-K edges in different simple ferrites. Ghatikar et al.\textsuperscript{14} have carried out studies on chemical shifts, which were shown to be interrelated with effective charges on the absorbing atom in binary, ternary and complex systems.
Other workers have carried out similar type of studies for garnets and also studied the effect at different temperatures.\textsuperscript{15,16}

Thus, a study of the shifts of absorption edge can lead to important information about valance, ionic structure, degree of inversion and other aspects connected through the absorbing atom in the absorbing process. We have therefore, studied the chemical shifts of copper K and iron K absorption edges in the mixed ferrites $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$. The two types of absorbing atoms being studied in the same matrix of ferrite, provide for the possibility of obtaining complementary results about the material. In this chapter, we report our results on chemical shifts and discussion thereon preceded by a brief review of the work on chemical shifts reported in literature.

4.2 Chemical Shifts in K-absorption Edge and Chemical Bonding

Lindh\textsuperscript{17} has done large amount of work on the effect of chemical combination on K-absorption edge and has proved that the absorption spectrum of an element depends on its chemical state. Similar type of study has been done by Coster and Kiestra.\textsuperscript{18} These observations on the chemical shift of the wavelength of an X-ray absorption discontinuity were understood till Beeman and Bearden\textsuperscript{19} showed clearly that even the fine structure of an absorption edge could be explained making use of optical term values. This explanation led them to assume that $\text{Cu}^{2+}$, $\text{Ni}^{2+}$ and $\text{Zn}^{2+}$ ions in aqueous solutions absorb
X-rays as if these ions were in vacuum and that the fine structure was due to the excitation of K-electron into one of the optical levels of these ions. This gave the direct evidence in favour of valence effects in absorption spectra. Analysis of experimental work related to the shift of K-absorption discontinuities of atoms in different oxidation states has been carried out by Kunzl and according to him the absorption edge shifts are governed by valency of the atom. Recently Agrawal and Verma have given an empirical rule which states that "In general the chemical shifts is towards the high energy side of the metal edge, and it increases progressively with increase in the valency state of the cation, unless the shift is either suppressed by covalent character of the bond or enhanced by the formation of metal-metal bonding". It has been reported by Sapre and Mande that the chemical shift of an x-ray absorption edge may be positive or negative depending upon whether the absorbing ion has a positive or negative effective charge on it, which also depends on the effective ionic charge on the absorbing atom. K-absorption edge studies of the first transition series elements have been carried out by many workers. While the studies on 2nd transition series elements have been carried out by Bhide and Patki who have suggested a bond scheme for zirconium and its diselenides. Bhide and Bhat have carried out K-absorption edge studies of Yb and Nb and their compounds. Gupta and Nigam have reported their work on the K-absorption edge shift for a number of zirconium compounds and have related their bond lengths with the observed edge shifts. In general, ionic solids have been found to give rise to sharp edges, whereas
in covalent compounds they are somewhat broadened. The variation in intensity in different region of the absorption edge giving rise to the characteristic shape to the absorption coefficient curve has been co-related with many stereochemical features of the co-ordination complexes. Van Norstrand's classification of K-absorption curves of large number of transition metal ions into four groups, is very much useful to make specific deductions about bonding and co-ordination of the absorbing ions. The prominent features of the Van Nordstrand's curves have been explained by Sinha and Mande on the basis of ligand field theory. Studies on K-absorption edge widths by Nigam and Shrivastava led them to formulate an empirical correlation between edge width and coordination stoichiometry being expressed in terms of metal and nearest neighbour electronegativity difference. Nigam and Shrivastava have found that the edge width increases with increase in covalent character. Alok Kumar et al. have carried out studies on k-absorption edge shifts and edge widths of copper in nitrogen ligand complexes. They have discussed absorption edge shifts and edge widths in terms of the effective nuclear charge and the nature of the ligand.

4.3.a) Results on Fe-K edge:

In Table 4.1 data on energies of K-absorption discontinuity in metallic iron and in mixed ferrites Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Mg$_{1-x}$Fe$_2$O$_4$ are presented. The photographs of original microphotometer traces of K edge in these samples are shown in Plate 4.1. It is seen from the table that the wavelength of
<table>
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<th>Sr. No.</th>
<th>Absorber</th>
<th>Energy in eV ± 0.35 eV</th>
<th>ΔE in eV</th>
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<td>Fe metal (Present author)</td>
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<td>14.51</td>
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<td>8</td>
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<td>Cu$<em>{0.8}$Mg$</em>{0.2}$Fe$_2$O$_4$</td>
<td>7129.16</td>
<td>17.41</td>
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* Not taken in the present discussion.
Figure 4.1: Variation of $\Delta E$ (eV) of Fe K-edge with Copper content.
K-absorption edge of pure iron, found out in our studies agrees well with that reported by other workers.\textsuperscript{34, 35} For Cu-Zn mixed ferrite system with $x = 0.2, 0.4, 0.6, 0.8$ Cu, the Fe-K edge shift goes on decreasing with increase in copper content. Also for Cu-Mg mixed ferrite system with $x = 0.2, 0.4, 0.6$ Cu, the shift goes on decreasing with increase in copper content (the sample $\text{Cu}_0.9\text{Mg}_{0.1}\text{Fe}_2\text{O}_4$ exhibiting tetragonal structure shows enhanced shift). The graphs of $\Delta E$ against composition of Cu in Cu-Zn and Cu-Mg mixed ferrite are shown in Fig. 4.1. The nature of the graph is a straight line having negative slope in both the cases, slope being more negative for $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ system.

4.3.b) \textbf{Results on Cu-K edge}:

In Table 4.2 data on energies of K-absorption discontinuity in metallic copper and in mixed ferrites $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ are presented. The photographs of original microphotometer traces of K-edge in these samples are shown in Plate 4.2. It is seen from the table that the wavelength of K-absorption edge of pure copper, found out in our studies agrees well with that reported by other workers.\textsuperscript{36, 35} For $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ system with $x = 0.2, 0.4, 0.6, 0.8$ Cu, the Cu-K edge shift goes on increasing. For $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ system with $x = 0.2, 0.4, 0.6$ Cu, the shift goes on decreasing with increase in copper content. The graphs of $\Delta E$ versus composition for both the systems are shown in Fig. 4.2. The slope of the graph for Cu-Zn system is positive while that for the system $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ system it is negative.
Table 4.2: Chemical shift of Cu-K-Absorption edge in 
\( \text{Cu}_x \text{M}_{1-x} \text{Fe}_2 \text{O}_4 \) (where \( M = \text{Zn, Mg and} \),
\( x = 0.2, 0.4, 0.6, 0.8 \))

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<tr>
<th>Sr. No.</th>
<th>Absorber</th>
<th>Energy in Ev ( \pm 0.35 \text{ eV} )</th>
<th>( \Delta E ) in Ev</th>
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<td>1</td>
<td>Cu metal (Present author)</td>
<td>8980.37</td>
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<td>2</td>
<td>( \text{Cu}_0.2 \text{Zn}_0.8 \text{Fe}_2 \text{O}_4 )</td>
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<td>4.93</td>
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<td>( \text{Cu}_0.4 \text{Mg}_0.6 \text{Fe}_2 \text{O}_4 )</td>
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<td>2.03</td>
</tr>
<tr>
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<td>( \text{Cu}_0.6 \text{Mg}_0.4 \text{Fe}_2 \text{O}_4 )</td>
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<td>( \text{Cu}_0.8 \text{Mg}_0.2 \text{Fe}_2 \text{O}_4 )</td>
<td>8980.64</td>
<td>2.75</td>
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</table>

* Not taken in the present discussion.
Figure 4.2: Variation of $\Delta E$ (eV) of Cu K-edge with Copper content.

The graph shows the variation of $\Delta E$ (eV) with Copper content for two systems: $Cu_x Zn_{1-x}Fe_2O_4$ and $Cu_x Mg_{1-x}Fe_2O_4$. The $\Delta E$ values are plotted on the y-axis, while the Copper content is on the x-axis.
4.4 Discussion:

It is found that the chemical shifts in the x-ray absorption studies have been correlated to a large number of parameters such as effective nuclear charge, electronegativity, coordination number of chemical bonds and particularly in ferrites on the degree of inversion, cation distribution etc. Details of the exact correlation of these parameters has not yet been attempted from x-ray spectroscopic study of ferrite materials. It has been reported that the chemical shift is either suppressed or enhanced by the effective ionic charge on the absorbing ion. Ballal et al. have carried out studies on chemical shift of copper and cobalt k-absorption discontinuities of the cobalt and copper mixed spinels in which anions were replaced by other elements. This study revealed that there exists a linear relationship between the chemical shift and the fractional ionicity calculated according to Levine's method of the ionocovalent bond. In case of ferrite spinels the cation distribution plays an important role as many electrical and magnetic properties are governed by this distribution. The magnitude of the effective charge on the absorbing ion, which is responsible for many electrical and magnetic properties has been attempted by Ghatikar et al. using Gianturco and Coulson's method of charge calculations. However, it can be easily seen that the effective charge (q) values do not vary significantly with the variations of compositions of mixed ferrite samples. Therefore, Ghatikar et al. were
conclude that the chemical shift could be explained on the basis of cation distribution rather than the effective charge.

The present studies on chemical shifts in mixed ferrites thus, affords information on the distribution of cations on A and B sites of the spinel lattice from which the degree of inversion can be inferred. The dependence of fractional covalency on charge $q$ has already been studied by Ballal and Mande\(^{39}\) for spinel structure compounds. Vaingankar\(^{13}\) has reported from his studies on simple ferrites that there exists an inverse relationship between covalent character and chemical shifts of Fe-K absorption discontinuities. Thus, the chemical shifts are directly or indirectly related to the cation distribution, degree of inversion, covalency and the effective charge on the absorbing ion in ferrite spinels, in as much as all these aspects are reflected in the situation on the absorbing atom during the absorbing process.

The shifts of Fe-K absorption edge in Cu\(_x\)Zn\(_{1-x}\)Fe\(_2\)O\(_4\) where $x = 0.2, 0.4, 0.6, 0.8$ Cu exhibit a trend as follows:

$$\Delta E_{Cu_{0.2}Zn_{0.8}Fe_2O_4} > \Delta E_{Cu_{0.4}Zn_{0.6}Fe_2O_4} > \Delta E_{Cu_{0.6}Zn_{0.4}Fe_2O_4} > \Delta E_{Cu_{0.8}Zn_{0.2}Fe_2O_4}$$

The ferrites are well known ionic compounds and the observed Fe-K edge shifts in the mixed ferrites also indicate the same. The gradual change in the chemical shift of Fe-K edge with copper and zinc concentration in the mixed ferrites cannot be easily explained in view of the relatively unchanged surroundings.
of Fe ions and the continued manifestation of the overall ionic nature of the ferrite. In the similar way the gradual change in the shift of Fe-K edge in Cu-Mg ferrite system with changing copper concentration has been observed as follows:

\[
\Delta E \text{Cu}_{0.2} \text{Mg}_{0.8} \text{Fe}_2\text{O}_4 \lor \Delta E \text{Cu}_{0.4} \text{Mg}_{0.6} \text{Fe}_2\text{O}_4
\]

\[
\Delta E \text{Cu}_{0.6} \text{Mg}_{0.4} \text{Fe}_2\text{O}_4
\]

In Fig. 4.1, data on shifts of Fe-K edge are summarized for Cu-Zn and Cu-Mg mixed ferrite systems with variation of copper concentration. The slopes of the supposedly straight line graphs in these two cases are different. If the overall ionicity of the crystal structure is not affected differently in these two systems, the surroundings of the absorbing atom being more or less the same, this variation of chemical shifts with copper concentration will be rather difficult to explain. However, the most important consideration in explaining the chemical shift would be the ionicity or covalency of the bonds from or to the absorbing atom in its immediate neighbourhood as induced by the different concentrations of the divalent cations namely copper, zinc, magnesium. Here it should be remembered that the behaviour of the pairs of Cu-Zn and Cu-Mg in mixed ferrite systems will be different, although copper is common to both, because of the tendencies of zinc and magnesium and in occupancy of A or B sites are different. These tendencies are associated with the formation of $\text{Sp}^3$ and $\text{Sp}^4$ orbitals on zinc and the ionic size of Mg$^{+2}$. In addition copper also has a
tendency of formation of $d^2p^2$ square planer orbitals and going into B site, the detailed cation distribution having its origin in the statistical weightage of these different factors besides the thermophysical history. Thus, in copper-zinc ferrite system the contribution to the total stabilization energy of the structure due to covalency of bonds around zinc and copper is considerable, allowing the bonds around iron to go more ionic in order to balance the overall ionicity of the structure approximately for keeping Madelung energy favoured for the stabilization of the structure. An argument on similar lines regarding Cu-Mg system would then explain the different slopes of the straight line in Fig. 4.1.

In Fig. 4.2 data on shifts of copper K-edge are summarized for Cu-Zn, Cu-Mg ferrite systems. Two important observations stand out clearly which require detailed explanations. Firstly, the shift shows decreasing trend in Cu-Mg ferrite system with increasing copper concentration in the region of cubic ferrite the tetrahedral composition $Cu_{0.8}Mg_{0.2}Fe_2O_4$ showing increased shift again. Secondly, the chemical shift of Cu K-edge in Cu-Zn ferrite system shows increasing trend with increasing copper concentration. The explanation of these observations cannot be successfully given on the lines of explanation given for the chemical shifts of Fe K-edge earlier, as copper is itself unlike $Fe^{+3}$ ion has to undergo through the situation for setting down with certain occupancy of A and B sites as dictated by the free energy considerations. In case of Cu-Zn ferrite system, the stabilization energy involving zinc ion with $d^3$
hybridized orbitals on A site pins down copper ions to B site, not necessitating copper ions to resolve to $d\sigma^2$ orbitals to a large extent. This is exemplified by nonoccurrence of tetrahedral phase in the copper-zinc system and even for a very small concentration of zinc the poisoning type effect of ruling out the tendency of tetrahedral distortion due to $d\sigma^2$ or other hybridized type of orbitals. Thus, on an inclusive energy consideration the increasing trend of shift in Cu K-edge most probably indicates that the copper ion is more or less left as an ion through the indirect effect of bonding with oxygen. In case of Cu-Mg ferrite system, the shifts in copper K-edge need to be explained, taking into consideration the mutually inclusive tendencies of Cu and Mg ions as to the occupancy of the A or B site, besides the tendency of copper ion for the formation of $d\sigma^2$ orbitals. In fact, such suggestion was made by Romeijn because of the fact that Mg ions are less compressible than Cu ions as Mg ions have noble gas configuration and consequently more Cu ions can accommodate in tetrahedral A site. In this case Mg ions, although complete with the copper ions towards the occupancy of B site does not forestall the formation of $d\sigma^2$ type orbitals on copper as indicated by the occupancy of tetrahedral composition $\text{Cu}_0.8\ \text{Mg}_0.2\ \text{Fe}_2\text{O}_4$. It may be mentioned here that the shifts of Cu K-edge in the present study do not indicate the valency state of copper on the lines of clearly divalent or monovalent copper compounds. However, for the cubic compositions of Cu-Mg system the decreasing trend of Cu K-edge with increasing copper
concentration might indicate the co-existence of Cu$^{+1}$ and Cu$^{+2}$ in the structure taking into consideration its non-stoichiometry on account of oxygen. Notwithstanding, the observation of very very low shift of Cu K-edge (0.58 eV) is rather surprising, neither characteristic of ionic situation nor covalent character. This indicates that copper is found in a screen type of potential as in the case of metal probably which is connected intricately with magnetic interactions.
REFERENCES


