Chapter I

INTRODUCTION

The term "Ferrites" has been used to signify semiconducting materials having Fe₂O₃ as a basic constituent, regardless of the crystal structure of the material (1). In a more restricted sense (2), this term applied to materials which have the crystal structure of the mineral 'spinel' and molecular formula MnFe₂O₄ where Mn is a divalent metallic ion.

Ferrites have gained importance because they possess the combined properties of magnetic materials and electric insulators (3). It has been shown by number of workers (Gorter (4), Goodenough (5) and Hlasse (6)) that a variety of substitutional ferrites can be prepared within a fairly large range of saturation magnetisation and Neel temperature values. These materials are also of considerable theoretical interest, as they are ideal for the study of the various types of spin arrangement and exchange interactions. Ferrites are also important in microwave applications (7). To prepare ferrites with specified properties, it is necessary to have the knowledge of the various magnetic and electrical properties such as the saturation magnetisation $4\pi N_s$. 
Neel temperature $T_N$, resistivity $\rho$, dielectric constant $\varepsilon$, permeability $\mu$ etc.

Of the various techniques employed in understanding magnetic properties of ferrites, Mossbauer measurements have played an important role. This technique involves the study of the recoil free scattering from the nucleus. The electrostatic and magnetic interactions between the probe nucleus and the surrounding electrons perturb the nuclear energy levels and the relevant information is obtained by scanning these energy levels. The method provides information about electronic charge density, electric field gradient and magnetic field at the nucleus, which can be related to the extranuclear environment.

Magnetically ordered materials exhibit a hyperfine field spectrum at 0 K. The increase in temperature of the spin system initially introduces collective modes of excitation described by the spin wave modes of frequency of the order of $10^{11}$ rad/sec. This spin wave frequency is larger than the nuclear Zeeman frequency which is of the order of $10^8$ rad/sec. Therefore, the nucleus experiences time independent hyperfine field which is proportional to the average value of spin $\langle S_z \rangle$. As the temperature increases
higher and higher the spin wave approximation becomes increasingly poorer because of the interactions between thermally excited spinwaves. Under such circumstances the molecular field approximation may be used. A single spin experiences Weiss field due to the neighboring spins and the fluctuations in the spin system cause the hyperfine field to be time dependent. As the spin correlation time $T_C$ decreases with temperature and becomes comparable to the nuclear Larmor period, $\omega_N^{-1}$, the line shape undergoes rapid changes. The outer lines get broadened while the inner lines grow in intensity at the cost of the former. This process is often referred as the relaxation spectrum of the system. When the temperature is increased still further $T_C << \omega_N^{-1}$ and there is only one central line which may be split due to quadrupole interactions. In most ferromagnets the relaxation effects have been observed close to $T_C$. But for some of the Zn - substituted mixed ferrites like Ni - Zn, Co - Zn, Li - Zn, relaxed spectra have been observed at the temperatures significantly lower than the transition temperature (8-11). Since in the ordered phase at these temperatures, there is a definite average value of $\langle S_z \rangle$, the nuclear spin should see sharp hyperfine field as the nucleus experiences a static hyperfine field. Hence a normal Zeeman pattern is expected for $T_C >> \omega_N^{-1}$. The existence of relaxation spectra cannot, therefore, be
accounted interns of the critical point spin fluctuations in bulk of the material.

Survey of the literature:

Magnetostriiction measurements\(^{(12)}\) of slowly cooled and quenched (997 K) Copper ferrite samples show transitions around 423 K and 373 K respectively which are attributed to Jahn–Teller type crystal distortions. A similar transition was observed by Yamada et al.\(^{(13)}\) for a quenched (923 K) copper ferrite sample at 363 K which was found to be a cubic to tetragonal transition. This ferrite has also been studied by Evans et al.\(^{(14)}\) using high magnetic fields and they suggest that meta-stable cubic phases may even exist at lower temperatures for slowly cooled sample. But the intensity ratio of the two sites found by Evans et al. was a factor of two off from the x-ray diffraction measurements\(^{(15)}\). No meta-stable transitions of slowly cooled copper ferrite have been reported via Mössbauer study. No Mössbauer measurements exist on zinc substituted copper ferrite with different zinc concentrations except the Mössbauer study of Cu\(_{0.5}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) at 4.2 K by Evans et al.\(^{(14)}\) Hence no information exists about the magnetic properties of this ferrite at different zinc concentrations.
Aim and plan of the present work:

The Mossbauer study of slowly cooled copper ferrite as a function of temperature was undertaken to investigate meta-stable transition at lower temperature, to relate this transition to Jahn-Teller type crystal distortions, and to remove the ambiguity about the intensity ratio of the two sites existed between the earlier Mossbauer study\(^{(14)}\) and the x-ray diffraction measurements.

The Mossbauer studies of copper-zinc ferrite were undertaken at room temperature primarily to investigate magnetic properties of this ferrite at different zinc concentrations as these properties are not known from previous work. In addition to it, there is a correlation between the magnetic relaxation processes and the observed Mossbauer relaxation in zinc-substituted ferrites. So, it was thought that a Mossbauer study of Cu - Zn ferrite system would clarify the explanation of the occurrence of this process in similar systems like Ni - Zn, Co - Zn etc. In order to observe the effect the of temperature on relaxation, the Mossbauer spectra of Cu - Zn ferrites were also taken at 85 K.

The magnetisation measurements of Cu - Zn ferrite up to Neel temperature were made for the following two
reasons. Firstly to determine the Neel temperatures of Cu - Zn ferrites at different concentrations, secondly to gain information about the Yafet-Kittel angles in the system.

Finally to verify the Neel temperatures from the magnetisation measurements, the Neel temperature of $X = 0.4$ sample was also found from Mossbauer studies.