1.1 INTRODUCTION

Oxides of the transition elements form a large group of compounds possessing different physical properties and in particular different electrical and magnetic properties. Among the magnetic materials, magnetic oxides are the most important and rather the only relevant materials from the point of view of their applications. So they are studied over a long period for their properties and applications.

The first magnetic material used by a mankind was magnetite \((\text{Fe}_3\text{O}_4)\) commonly known as lodestones which is a natural non-metallic magnetic material. The magnetic oxides, which are commonly known as ferrites are ferrimagnetic in structure as originally proposed by Neel (1). Ferrites are magnetic ceramics which are composed of
oxides of iron and metals possessing combined properties of magnetic conductor and electrical insulator.

1.2 Different type of Magnetic materials :-

Depending upon their response to the applied magnetic field and net resultant magnetization, which is usually expressed in terms of magnetization per unit magnetic field (M/H), the magnetic materials are classified as,

1) Diamagnetic
2) Paramagnetic
3) Ferromagnetic
4) Antiferromagnetic
5) Ferrimagnetic

Magnetic materials exhibit different kinds of magnetic ordering depending upon the spin orientation. The magnetic behaviour is caused by the spinning of electrons
of 'd' orbit about their own axis, giving rise to spin magnetic moment. The motion of electrons in the orbit round the nucleus results in orbital magnetic moment. In the case of transition elements, orbital magnetic moments are quenched by the crystalline electric field. The different magnetic behaviours are observed due to different combination of the electron spin coupling.

1. Diamagnetism

In this type of material resultant electron spin on each cation is zero. That is there is no net permanent atomic magnetic moment. However the electron in an orbit rotates in an applied magnetic field so as to oppose the effect of the applied field and the susceptibility is –ve.

2. Paramagnetism

If there is no interaction between the spin of different atoms, paramagnetisms result. Paramagnetic materials have +ve susceptibility. In paramagnetic material the application of the magnetic field tends to align the atomic magnetic
moments in the direction of the field itself so as to produce an overall magnetization in the specimen. At a finite temperature the effect of thermal agitation is towards reducing the alignment to reduce the magnetic moments.

3. Ferromagnetism

Positive interaction between the spins of the different atoms, causing them to align parallel to each other, yields ferromagnetism. In ferromagnetic materials, the interaction between adjacent atomic magnetic moments is very large. So in most of these materials atomic moments are very nearly aligned even at room temperature and beyond.

If the temperature of the ferromagnetic material is above curie temperature (Tc), the alignment between atomic moments will be destroyed. Under these circumstances, the material behaves like a paramagnetic material.
4. Antiferromagnetism

When the spins are equal and antiparallel, due to negative interaction, it results in antiferromagnetism.

Antiferromagnetic materials have strong coupling of antiparallel magnetic dipoles. In antiferromagnetism, Neel suggested the presence of two sublattices. The spins of all the atoms within a sublattice are parallel, but the two sublattices have their atomic spins in opposite directions. The magnetic moment of the two sublattices are equal and opposite and hence resultant magnetic moment of the material is zero.

5. Ferrimagnetism

Due to the presence of both negative and positive interaction, when some spins are antiparallel to other but leaving a resultant moment, then it is known as ferrimagnetism.

Like the ferromagnetic materials, this class of substance also exhibits spontaneous magnetization below a certain temperature. In ferromagnetic materials the spins of
all atoms in two sublattices are oppositely coupled but the net spin in the two sublattices is unequal giving rise to an appreciable net magnetization. The unequal magnetization of the two sublattice may arise due to-

i) The two sublattice A and B are occupied by atoms with identical spins, but the number of atoms in the sublattice are unequal.

ii) The spins of the atoms in the two sublattice are unequal.

iii) Triangular spin configuration.

Ferrites exhibit ferrimagnetic behaviour. Figure(1.1) depicts the spin arrangement in a crystal. Ferromagnetic and ferrimagnetic substances show the paramagnetic behaviour above a certain temperature known as Neel temperature ($T_N$) for antiferromagnetic and ferrimagnetic compounds.

Ferromagnetism occurs in materials which are essentially antiferromagnetic but whose spins can be rotated slightly away from usual orientation.
Ferrites possess ferrimagnetic properties. Smit defined ferrites as the magnetic oxides containing iron oxide as their main component. Ferrites are substances recently developed having high permeability, high coercive force and high B-H product but also they have high specific resistance.

Ferrites have attracted the attention of scientists and technologists due to their interesting and controllable physical properties, which depend upon method of preparation (2), Oxidation states of cation (3), site preference of cations (4) etc.

Snoek and his associates (5) first developed the ferrities. The extensive studies on the development of new ferrites and their applications have been made by number of peoples.

The ferrimagnetic oxides known as ferrites have the general formula $\text{M}^{2+}\text{Fe}_2^{3+}\text{O}_3^2$ or $[\text{M}^{2+}\text{Fe}_2^{3+}\text{O}_4^2]$ Where $\text{M}^{2+}$ stands for divalent metallic ions. The ferrites have spinel structure. The study of structural properties of spinel crystals was carried out by Barth et.al(6) with the help of
X-rays. They found that in case of spinel ferrites it is necessary to assume that the divalent metal ions and trivalent Fe ions interchange positions in crystal. According to Verway et. al. (7) electrical conductivity of ferrites is mainly due to hopping of electrons i.e. the exchange of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions. Further he showed that ferrites with inverse spinel structure are magnetic whereas those with normal spinel are non-magnetic. The a.c. conductivity in ferrities has been explained on the basis of model proposed by Koops (8) and Gellio (9).

Verway, De-Boer and Van Santen (10) carried out X-ray studies on number of oxides having the spinel structure and concluded that Co, Mn, Ni and Cu ferrites, which are magnetic have an inverted spinel structure, whereas Zn and Cd ferrites which are non-magnetic have a normal spinel structure.

Ferrites are classified as soft and hard ferrites. Considering the molecular field theory, Neel gives fundamental theory of ferrimagnetism by introducing the concept of magnetic sublattice as tetrahedral (A) sublattice
and octahedral sublattice (B). Yafet and Kittel (11) extended Neel’s theory by postulating a triangular or canted arrangement of the sublattice when the antiferromagnetic exchange interactions between sublattice are comparable.

1.3 Application of Ferrites:

Ferrites have novel combined electronic and magnetic properties. The most important thing about them is their high resistivity [from $10^{-3}$ $\Omega$cm (e.g. Fe$^{2+}$Fe$^{3+}_2$O$_4^{-2}$) to $10^{11}$ $\Omega$cm (e.g. single crystal YIG.)] and wide useful range of magnetization permeability and coercivity. These properties made them the most useful materials in science and technology. The properties like permeability and magnetic loss factor of material are of prime importance. In development of materials one aims at the best compromise between a high permeability and a low loss level. This can be achieved by suitable chemical composition, method of preparation and processing techniques. Thus the materials of a vast range of promising properties have been
developed and ferrites have become very useful in every walk of life in the modern world. Ferrites are widely used as core materials in transformers and in antenna of radio receivers as well as transmitters. They are used in ultrasonic generators, modulators, phase-shifters and isolators (12). Some ferrites exhibit a typical rectangular hysteresis loop property. This rectangular hysteresis property and suitable coercivity are important factors to use ferrites in memory (13) and recording devices for digital information (14). Ferrites with small coercive force are used in magnetic amplifiers. Some hard ferrites are used in sound systems and in micromotors.

Ferrites with sharp and definite curie temperature are used as sensors for temperature controls. The position and rotational angle sensors have also been designed using ferrites. Radio waves absorbing paints containing ferrites have been developed to render an aircraft or submarine invisible to radar. The precipitation of ferrite precurs is used to scavenge pollutant materials such as mercury from waste streams. Pollutants can be magnetically separated.
Thus ferrites play important role in controlling pollution. The ferrites have been used as electrodes due to their high corrosion resistance and the appropriate conductivity. Ferrites are widely used in radio and television circuits. The large consumption of soft ferrites is in television where half a kilogram is used for each set in the form of deflector and Yoke. High frequency applications of soft ferrites include a large number of microwave components such as circulators, isolators, gyrators, phase-shifters, YIG tuned filters, switches and substrates for microwave integrated circuits. Some ferrites are used in switch mode power supplies. Thus ferrites have covered a vast area of applications.

1.4 Literature Survey and aim of present investigation:

The spinel ferrites with non-magnetic substitution on tetrahedral (A) and octahedral (B) sites have been the subject of many investigations (15-21). Large number of research reports (22-27) are available in literature on \( \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Co}^{2+} \) substituted mixed spinel ferrites. The literature
survey shows that Mn$^{2+}$ ferrites possess an about 80% normal spinel structure (28) and is considered to be collinear ferrimagnet and the degree of inversion depends upon the heat treatment (29). The addition of tetravalent ions like Ti$^{4+}$, Si$^{4+}$, Ge$^{4+}$ influences the electrical and magnetic properties of the system (30-32).

Very few workers have concentrated on the study of electrical and magnetic properties of tetravalent Ti$^{4+}$, Ge$^{4+}$ ion substitution (33,34) in different ferrites. Recently to increase the resistivity and to develop the desired microstructure, tetravalent ions like Ti, Si and Sn are substituted in mixed ferrites. It is observed that the resistivity increases with increase in Si$^{4+}$ in Ni-Cd ferrites (35).

The addition of tetravalent ions like Ti, Si, Sn in Co-Cd mixed ferrites have been studied to understand the role of these ions on the physical properties of ferrites (36). Cation distribution in Si$^{4+}$ substituted CuFe$_2$O$_4$ ferrite systems has been studied by some workers (37). Also
cation distribution of $\text{Si}^{4+}$ substituted in $\text{CoFe}_2\text{O}_4$ ferrite system is recently studied by some workers (38).

The survey of the field of ferrites reveals that no systematic investigation has been carried out to study the effect of the substitution of non-magnetic $\text{Si}^{4+}$ ions in $\text{Mn}^{2+}$ ferrite.

Therefore in the present investigation it is decided to study the effect of the substitution of non-magnetic tetravalent $\text{Si}^{4+}$ ions on the structural, electrical and magnetic properties of the $\text{MnFe}_2\text{O}_4$ and $\text{MnFeCrO}_4$ ferrite systems.
Figure 1.1:- The low temperature ordering of neighbouring magnetic dipole and the consequent behavior of spontaneous magnetization and susceptibility for
a) paramagnetic, b) antiferromagnetic, c) ferromagnetic, d) ferrimagnetic
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