Chapter 2
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2.1 INTRODUCTION

The advances made in the physics and chemistry of solids has led to the recent progress in science and technology. The physics and chemistry of condensed matter draw attention to chemical composition, atomic configuration, electrical and magnetic properties, crystal structure etc. of the solids. It also helps to co-relate the physical and chemical properties of solids and their use in technological applications. Due to the needs of society, material science dealing with the physics and chemistry of solids along with engineering and technology was developed. In the recent years, solid state physics mainly concentrates on crystal structure, chemical and physical
properties of solids. A proper understanding of the nature and properties of solids form the basis for developing new tailor made materials with the desired properties that can be used in many electrical and electronic devices.

Among the magnetic ceramics, magnetic oxides are the most important and rather the only relevant materials from the point of view of their applications. They are being studied over a long period of five to six decades for their basic properties such as structural, magnetic and electrical as well as wide field of applications.

The ferrites by virtue of their structure can accommodate a variety of cations at different sites enabling a wide variation in properties. Further variation in synthetic methods can bring about large changes in extrinsic properties. A majority of them are high resistivity materials making them more suitable for high frequency and low loss applications.

2.2 CRYSTAL STRUCTURE OF SPINEL FERRITE
Ferrite materials have crystalline structure similar to the mineral spinel MgAl$_2$O$_4$, where the divalent ions replaces Mg, trivalent ions replaces Al. Spinel crystallizes in a close packed cubic structure. The unit cell contains eight molecules and may thus be written as M$_8$Fe$_{16}$O$_{32}$. The crystal structure of spinel ferrite is shown in Fig 2.1. The white circles in this figure represent the oxygen ions and the black and hatched circles represent the metal ions. The radius of the oxygen ion is about 1.32 Å, which is much larger than that of metal ions (0.6-0.8 Å) hence the oxygen ions in the lattice touch each other and form a close packed face-centered cubic lattice. In this oxygen lattice the metal ions take interstitial position which can be classified into two groups, one is a group of lattice sites called tetrahedral sites or 8A sites, each of which is surrounded by four oxygen ions as shown by the hatched circles in the Fig. 2.1. The other is a group of sites called octahedral or 16B sites, each of which is surrounded by six oxygen ions as shown by the black circles. These groups are called tetrahedral (A) sites and octahedral [B] sites. From the point of view of valence, it seems reasonable to have M$^{2+}$ ions on A-sites and Fe$^{3+}$ ions on B-sites, because of the number of oxygen
ions which surround A and B sites are in the ratio 2:3. There are
ninety-six interstitial sites in the unit cell size, 64 tetrahedral, 32
octahedral; of these 8 and 16 respectively are occupied by cations.

Wyckoff [1] gives the spinel space group as O_7^+ (Fd3m) and
the ionic positions as

Anion 32b:  \( u, u, u; \frac{1}{4}, u, \frac{1}{4}; \frac{1}{4}, u, \frac{1}{4}; \frac{1}{4}, u, \frac{1}{4} \)

\( u + \frac{1}{4}, u + \frac{1}{4}; u + \frac{1}{4}, u + \frac{1}{4}; u + \frac{1}{4}, u + \frac{1}{4} \)

Cation 16C:  5/8, 5/8, 5/8; 5/8, 7/8, 7/8; 7/8, 5/8, 7/8;

7/8, 7/8, 5/8

Cation 8f:  0, 0, 0; 1/4, 1/4, 1/4;

With the translations, for a face-centered lattice, 0, 0, 0;
0, 1/2, 1/2; 1/2, 0, 1/2; 1/2, 1/2, 0.

Packing of the ions within the lattice is perfect when the oxygen
parameter \( u = 3/8 \). From the data in Table 2.1, it is seen that the
values of ‘u’ do not differ remarkably from the perfect value.

2.3 TYPES OF SPINEL FERRITES

Based on the coulombic energy of charged ions [2, 3] and
their influence in the polarization of anions [4], large divalent ions
favour tetrahedral occupancy and large trivalent ions favour octahedral occupancy. From these considerations it follows that 2-3 spinels favours normal configuration, thus in normal spinel all divalent metal ions occupy tetrahedral A-sites and all trivalent ions occupy octahedral B-sites symbolically normal spinels can be represented as

\[(M)^A [Fe^{3+}M^{2+}]^B O^{2+}_4\]

Example: Zinc ferrites \((Zn)^A [Fe^{2+}]^B O^{2+}_4\)

If half of the Fe\(^{3+}\) ions occupy A-site and remaining half of the Fe\(^{3+}\) ions and all the M\(^{2+}\) ions occupy B-sites, we call this structure as inverse spinel.


In spinel ferrites if the divalent metal ions and trivalent Fe\(^{3+}\) ions are distributed randomly over the tetrahedral and octahedral B-sites, then the spinel ferrite is called random spinel.

Example: Magnesium ferrite

\[(Mg_{0.1}Fe_{0.9})^A [Mg_{0.9}Fe_{1.1}]^B O^{2-}_4\]

A whole range of possible distribution is observed. This can be represented in general terms by

\[(Me_{\delta}^{II} Fe_{1-\delta}^{III})^A [Me_{\delta}^{II} Fe_{1-\delta}^{III}]^B O^{2-}_4.\]
where the ions inside the bracket are located in octahedral sites and the ions outside the brackets in tetrahedral sites. The limiting case, $\delta=1$ is called normal spinel and the other limiting case, when $\delta=0$ is called inverse spinel. For a random distribution $\delta$ can have value in between 0 and 1.

### 2.3.1 Mechanism of solid state reaction

The most common method of preparation of inorganic solids is by the reaction of component materials at elevated (high) temperature. If all the components are raw solids, the method is called ceramic method. In one of the constituents is volatile or sensitive to atmosphere, the reaction is carried out in sealed evacuated capsules. Ternary oxides, sulphides, phosphides, etc. have been prepared by this method. Knowledge of the phase diagram is generally helpful in finding the desired composition and conditions for essential synthesis.

Some caution is necessary in deciding the choice of the container. Platinum, silica and alumina containers are generally used for the synthesis of metal oxides, while graphite containers are suitable for sulphides and other chalco-genide. Usually, the
exact composition, firing time, temperature and furnace atmosphere required to produce ferrite. Though ceramic method has some drawback the ceramic techniques have been widely used for solid state synthesis.

Various modifications of ceramic techniques have been employed to overcome some of the limitations. One of these related to decreasing the diffusion path length. In a polycrystalline mixture of reactant, the individual particles are approximately 10 µm size, which represent diffusion distances of roughly 10,000 unit cell. By using freeze-drying, spray-drying, co-precipitation and sol-gel and similar techniques it is possible to bring down the particle size to a few hundred Å.

In spray drying, suitable constituents dissolved in a solvent are sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously leaving behind an intimate mixture of reactants, which on heating at elevated temperatures gives the product. In freeze-drying the reactants in a common solvent are frozen by immersing in liquid nitrogen and the solvent removed at low pressure.
In co-precipitation, amount of required metal cations are co-precipitated from a common medium, usually as hydroxides, carbonates, oxalates or citrates, which are subsequently heated at some temperature to yield the final product.

The sol-gel process involves forming a concentrated sol of the reactant oxides or hydroxides and converging to a reactant oxide or hydroxide and converging to a semi rigid gel by removing the solvent. The solvent is removed by passing fine droplets of the sol through a column of an aliphatic (2-ethyl-1-hexanol). The dehydrated gel is heated at an appropriate temperature to obtain the product [5].

2.4 X-RAY DIFFRACTION

X-ray diffraction technique is well established to scientific and industrial work for the study of crystal structure of material, identification of the initial material and the final products, chemical analysis and phase equilibrium.

X-rays are electromagnetic radiations having the wavelength of the order of 0.5 to 2.5 A.U. X-ray diffraction is one of the most interesting and informative property of X-rays. This phenomenon
is explained as the scattering of X-ray by metal accompanied with variation in intensity in different direction due to the interference effect.

2.4.1 The diffraction of X-ray by a lattice array of atom

An atom is an electrical system capable of being disturbed by external electrical field. The fluctuation of electric field of an impinging electromagnetic wave displaces the electron on an atom for this reason they undergo vibration having the same frequency as the electromagnetic wave (X-ray radiation). These accelerating charge particles are themselves the origin of radiation of this frequency. The electrons of an atom, therefore, absorb and re-emit X-rays, and in accordance the atoms are said to scattered X-ray radiation. When a wave front of X-rays impinges on a set of atom, each atom scatters the X-ray.

A lattice of arrays of atoms can be regarded as an infinite stag of parallel, equally spaced planes. Any rational plane (hkl) of the array can be chosen as the plane in question, and then the whole array can be thought of as a stag of planes parallel to the one. The condition for scattering-phase by one plane of the stag was
established above if two or more are considered (Fig. 2.2), it is evident that the path length from incoming wave front to plane, to scattered wave front is longer in the case of lower plane. The condition is

\[ n\lambda = 2d_{hkl} \sin \theta \]  

(2.1)

where \( d_{hkl} \) is the inter planer distance,

\[ \theta \] glancing angle for scattering in phase is known as Bragg’s law.

### 2.4.2 The diffraction by the whole structure

Any crystal structure can be regarded as several mutually displaced lattice arrays each lattice array can diffract X-ray as it reflecting them from a plane (hkl), provided the glancing angle \( \theta \) is adjusted so that it is one of the discrete solution of glancing angle

\[ \theta = \sin^{-1} \left( \frac{\lambda n}{2d_{hkl}} \right) \]  

(2.2)

When equation 2.2 is satisfied all atoms of lattice array 1 scattered in phase with each other, and all atom of lattice arrays 2 scatter in phase with each other. But the path from the incoming wave front two arrays 2 is no longer than to array 1. This means
that array 2 contributes to the resultant wave scattered by the whole crystal a wave whose phase is behind that scattered by array 1. In conclusion

1. The full crystal structure scattered at the same glancing angle as any of the component lattice arrays.

2. The displacement between the component lattice arrays cause phase difference in their contribution to the net scattered waves.

3. These phase differences tend to reduce their contribution to the intensity from a value which would be obtained if all atoms of the structure scattered in phase.

2.5 MAGNETIC MATERIALS

Magnetic materials may be divided into five main groups, according to their magnetic properties i.e.

1. Diamagnetic (e.g. MgO)

2. Paramagnetic (e.g. Gd$_2$O$_3$)

3. Ferromagnetic (e.g. EuO)

4. Anti-ferromagnetic (e.g. Cr$_2$O$_3$)

5. Ferrimagnetic (e.g. Fe$_3$O$_4$)
It has been observed experimentally that, the complexes of the elements of the first transition series obey the Curie law. The molar magnetic susceptibility is inversely proportional to the absolute temperature.

For complexes, which do not obey Curie law, it has been found that the Curie-Weiss law,

\[ \chi_m = \frac{C}{T - \theta} \]  

satisfies the experimental observations.

Here \( \theta \) is constant and has the dimension of the temperature.

The non-zero value of \( \theta \) indicates that existence of magnetic interactions between discrete molecules in condensed physics or in magnetically dilute systems i.e. paramagnetic and diamagnetic systems. Ferromagnetic, anti-ferromagnetic and ferrimagnetic substances belong to magnetically non-dilute materials.

### 2.5.1 Diamagnetic materials
These substances do not contain any unpaired electron. A diamagnetic material is distinguished from all the other by the fact that its susceptibility is negative. The diamagnetism offers through deformation of the electric charge distribution when field is applied and it disappears when the field is removed.

2.5.2 **Paramagnetic materials**

The property is associated with metal complexes where spin arbitrary derived magnetic moments co-exist. The materials are also called magnetically dilute systems. In a paramagnetic material the individual ions, atoms or molecules possess magnetic moments. These arise because system contains an odd number of electrons or because an inner electron shell is unfilled. The magnetic susceptibility is positive and the classical explanation of the magnetization observed on applications of strong magnetic field is that, it results from the tendency of the individual moments to align with the field and the opposing tendency of the thermal agitation to destroy this order. There is no interaction between atoms. The substances obey Curie or Curie-Weiss law.
2.5.3  *Ferromagnetic materials*

In ferromagnetic materials, such as metallic iron, cobalt and nickel, the individual moments of the atoms or ions are strongly coupled and are more or less parallel, one to another even in the absence of magnetic field, their results have a very large magnetic moment. In the microscopically demagnetized state, there are very small regions (Weiss domains) within which the moments are all parallel, but there is distribution of directions in which many domain magnetizations point, so that the overall moment is zero. This is even in a single crystal of, say, iron.

2.5.4  *Antiferromagnetic materials*

In antiferromagnetic materials (the transition ions) adjacent metal ions are coupled with their spins anti-parallel. There are always equal numbers of two alignments so that in the absence of magnetic field their is no resultant magnetization.
The maxima on the curve are called Neel point. Below the Neel point, the susceptibility to some extent is temperature dependent, which is one of the criteria of identifying anti-ferromagnetism in compounds.

At the temperature above the Neel point, anti-ferromagnetic materials follow Curie-Weiss law. In fact that, a material follows Curie-Weiss law indicates that there is anti-ferromagnetic coupling to some extent. Anti-ferromagnetic materials become paramagnetic above the transition temperature $T_N$, and susceptibility $\chi$ is given by

$$\chi = \frac{C}{T + \theta} \quad (2.4)$$

where,

$\theta$ - is the asymptotic Curie point.

### 2.5.5 Ferrimagnetic materials

Several oxide magnetic materials have been found to be ferrimagnetic. These oxides possess a net resultant magnetism due to the unequal anti-parallel spin moments. The ions have
opposed the spin arrangement. But unlike anti-ferromagnetic materials they do not cancel each other. Therefore, there is a resultant permanent magnetic moment. The best-known example is iron oxide, Fe$_3$O$_4$, which is also called magnetic iron oxide or ferrous ferrite. In this case, one site contains Fe$^{II}$ and Fe$^{III}$ in equal amounts, while the other site contains only Fe$^{III}$ ions. Fig. 2.3 represents paramagnetism, ferromagnetism and anti-ferromagnetism, ferrimagnetism domains in the presence and absence of magnetic field. Fig. 2.4 shows the variation of $1/\chi$ as a function of temperature T for the different class of materials.

2.6 MAGNETIZATION

The magnetization is a powerful tool to study the different parameters such as domain wall rotation, anisotropy, magnetic hardness or softness of material, magnetic ordering etc. Ferrites exhibit almost all the properties similar to that of ferromagnetic materials. When the magnetic field is applied to the ferromagnetic material, the magnetization may vary from zero to saturation value. This behaviour is expressed by Weiss
[6] by introducing the idea of existence of domains. According to Weiss, though each domain is spontaneously magnetized in the direction of field magnetization may vary from one domain to another domain. In general, specimen consists of many domains, in domain configuration i.e. a function of applied field. The magnetic moment of specimen is a vector sum of magnetic moment of each domain. As a result the magnetization or average magnetic moment per unit volume may have value between zero to saturation.

Studies on magnetic hysteresis of ferrite provide useful information of the magnetic parameter like saturation magnetization (Ms) coercive force (Hc) and Remanance ratio (Mr/Ms). According to the values of these parameters, the ferrites can be classified as soft and hard ferrites. The ferrites with low coresive force are called soft ferrites and ferrites with high Hc are called hard ferrites. Soft ferrites are those material which do not retain permanent magnetism which provide easy magnetic path. Hard ferrites retain permanent magnetism and are difficult to magnetize and demagnetize. According to Neel [7] the coercive force (Hc) is related to saturation
magnetization, internal stress, porosity [8] and anisotropy [9].
The Hysteresis properties are highly sensitive to crystal
structure, heat treatment, chemical composition, porosity and
grain size. A typical hysteresis curve exhibited by ferrite
sample is shown in Fig. 2.5.

Magnetic interactions in ferrites

In spinel ferrites, the metallic ions occupy two
crystallographically different sites namely tetrahedral (A) and
octahedral [B] sites. Among these ions, there exists magnetic
interaction. Three types of magnetic interaction are possible in
the metallic ions through the intermediate oxygen ion by super-
exchange mechanism. These interactions are A-A interaction,
B-B interaction and A-B interaction. Among these interaction
A-B interaction is predominant. It has been established
experimentally that interaction energy are negative and hence
induces antiparallel orientation. Two types of magnetic
interactions are present in oxide spinels via direct exchange
and super-exchange interactions. The sign and strength of
exchange interaction depends upon bond angle and bond
distances involving the two cations and the intermediary anions.

2.7 NEEL’S THEORY

Neel assumed that a ferrimagnetic crystal lattice could be divided into two sublattice such as would be formed by the A (tetrahedral) and B (octahedral) sites in the spinel structure. He supposed the existence in the material of one type of magnetic ion only, of which a fraction $\lambda$ appeared on A site and a fraction $\mu$ on B-sites. Thus,

$$\lambda + \mu = 1 \quad (2.5)$$

The remaining occupied lattice sites were assumed to have only ions of zero magnetic moment. Considering a simple ferrite of the form $MFe_2O_4$, which satisfies Neel’s assumption, the magnetic ions are trivalent ferric $Fe^{3+}$, M is non-magnetic and the formula might be written as,

$$Fe_{2\lambda}M_{(1-2\lambda)}[Fe_{2\mu}M_{2\mu}]O_4 \quad \text{or}$$

$$Fe_{2\lambda}M_{(1-2\lambda)}[Fe_{2\mu}M_{2\mu}]O_4$$

where the bracketed ions are those on the octahedral sites.
Since an A-ion has near neighbours of both A and B types, as has a B-ion, there are several interactions between magnetic ion to be considered and these may be classified as A-A, B-B, A-B and B-A (where A-A refers the interaction of an ion on an A site with its neighbours also on A site, with similar definitions of the other terms). In the Neel theory it is assumed that the A-B, B-A interactions are identical and predominant over A-A, B-B interactions, and are such as to favour the alignment of the magnetic moment of each A-ion more or less anti-parallel with the moment of each B-ion. Thus, for the ferrite considered above, assuming each ferric ion to have a movement of 5 Bohr magneton ($\mu_B$), the moment of the ferrite “molecule” would be $2(\lambda-\mu)5\mu_B$ instead $2(\lambda+\mu)5\mu_B$, which would occur with parallel orientation of all the moments. The Neel theory predicts magnetic moments which may be much smaller than the sum of the moments of the constituent ions. This is experimentally observed. Clearly Neel’s assumption that only one type of magnetic ion is present will rarely be met, but it has been found that the general features of ferrites may be adequately represented on the Neel model, with suitable qualitative modifications.
Neel defined the interactions within the material from the Weiss molecular field viewpoint. The magnetic field action upon an ion is written in the form

\[ H = H_0 + H_m \]  \hspace{1cm} (2.6)

where,

- \( H_0 \) is the externally applied field and
- \( H_m \) is the internal or molecular field which arises due to interactions with other atoms or ions within the material.

When the molecular field concept is applied to a ferrimagnetic material, we have,

\[ H_A = H_{AA} + H_{AB} \]  \hspace{1cm} (2.7)
\[ H_B = H_{BB} + H_{BA} \]  \hspace{1cm} (2.8)

Here, the molecular field \( H_A \) acting on an ion on A-site is represented as the sum of the molecular field \( H_{AA} \) due to neighbouring A-sites, and \( H_{AB} \) due to its neighbours on B-Sites. A similar definition holds for the molecular field \( H_B \), acting on a B-ion. The molecular field components may then be written as,

\[ H_{AA} = \gamma_{AA} M_A, \quad H_{AB} = \gamma_{AB} M_B \]  \hspace{1cm} (2.9)
\[ H_{BB} = \gamma_{BB} M_B, \quad H_{BA} = \gamma_{BA} M_A \]  \hspace{1cm} (2.10)
where, the $\gamma$'s are the appropriate molecular coefficients and $M_A$, $M_B$ are the magnetic moments of the A and B sub-lattices. It may be shown that,

$$\gamma_{BA} = \gamma_{AB}, \text{ but } \gamma_{AA} \neq \gamma_{BB},$$

unless the two sublattices were identical. Neel showed that $\gamma_{AB} < 0$, favouring antiparallel arrangement of $M_A$ and $M_B$, gives rise to ferrimagnetism.

In the presence of an applied field $H_O$, the total magnetic fields acting on each sublattice may be written, using equations (2.3) and (2.6)

$$H_a = H_o + H_A = H_o + \gamma_{AA} M_A + \gamma_{AB} M_B \quad (2.11)$$

$$H_b = H_o + H_B = H_o + \gamma_{BB} M_B + \gamma_{AB} M_A \quad (2.12)$$

2.8 YAFET-KITTEL THEORY

Experimentally it is observed that the saturation magnetization of a ferrite initially increase upto certain value and then decreases rapidly. Neel’s model successfully explains the initial rise in saturation magnetization, but fails to explain the further decrease in it. This discrepancy between observed and
calculated values of saturation magnetization, can be explained by Yafet-Kittel model.

According to Yafet-Kittel model, in spinel ferrites, nonmagnetic substitution in one sub-lattices could lead to non-collinear or canted spin arrangement. It is possible only if A-B magnetic interaction is equal to or smaller than that of A-A and B-B interactions. When non-magnetic ion like Zn$^{2+}$ and Cd$^{2+}$ is substituted in spinel ferrite, the B sub-lattice splits into B$_1$ and B$_2$ with equal magnetic moments with an angle $\theta_{YK}$ with the direction of net magnetization of B sub-lattices at 0K. To calculate the uniform canting angle $\theta_{yk}$ a split sub-lattice model was developed by Yafet-Kittel [10].

Yafet-Kittel model can be understood from Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite system. For pure nickel ferrite (NiFe$_2$O$_4$) the A-B interaction is dominant. As Zn concentration (x) is increased, magnetic moment on A site decreases to zero. The B-B interaction will give rise to anti-ferromagnetic order in B sub-lattice with Zn concentration, and then the intermediate arrangement is expected. At a particular value of (x), the A-A interaction and B-B interaction are comparable. The B-B interaction arranges
magnetic moments on B lattice in anti-parallel direction whereas A-B interaction arranges them in parallel direction on B site. This leads to a canted spin arrangement [11] on B-site. The Yafet-Kittel model splits B sub-lattice into $B_1$ and $B_2$ sub-lattices each making an angle $\theta_{YK}$ with the direction of net magnetization of B sub-lattices. The moment on B site is anti-parallel to moment on A site. The net magnetic moment for the system can be expressed as

$$\mu(x) = M_B \cos \theta_{YK} - M_A$$

(2.13)

where, $M_A$ is magnetic moment on A site,

$M_B$ is magnetic moment on B site.

2.9 MAGNETIC PROPERTIES

Magnetic properties play important role in the applications of soft magnetic materials. Magnetic properties are dependent upon metallurgical conditions of the material viz.

(A) The size, shape and orientation of grains,

(B) The concentration and distribution of various crystal imperfections and

(C) The state of lattice regarding impurities, residual traces and atomic arrangement in alloys.
All magnetic properties are not depends upon these metallurgical conditions. (However all magnetic properties are dependent upon composition and temperature). Accordingly magnetic properties are divided into two groups; intrinsic or structure-insensitive and extrinsic or structure-sensitive.

Saturation magnetization and Curie temperature are the two prominent structure-insensitive properties. Structure-sensitive properties, on the other hand, are numerous and may be classified further as static or dynamic, according to whether or not the property displays frequency dependence. Induction, permeabilites, hysteresis loop and associated energy loss, coercive force and remanance are structure-sensitive, static properties. Eddy current loss and resonance of spin and domain walls are structure-sensitive dynamic properties.

2.9.1 Intrinsic Properties

A) Saturation Magnetization

The maximum attainable intensity of magnetization per unit volume is known as the saturation magnetization of ferromagnetic material. It is denoted by $M_s(T)$, signifying that it varies as a
function of temperature. As T → 0°K, $M_s(T) → M_0$, which is called absolute saturation magnetization. For each material, $M_0$ is the largest value of $M_s$, because rising temperature generally exerts decreasing effect on $M_s$ as indicated by Bloch’s $T^{3/2}$ law.

The intrinsic nature of saturation magnetization can be verified both theoretically and experimentally. For the theoretical verification, we have

$$M_A = N_0. J.g. \mu_B$$ (Weiss molecular field theory)

which is obtained from the quantum mechanical treatment for paramagnetism, but is valid also for saturation magnetization by virtue of the absolute zero temperature and existence of the intense molecular field in a ferromagnet. On the basis of unit volume, we may rewrite the definition of $M_0$ by switching $N_0$ to $N$,

$$M_0 = N\mu = N_0. J.g. \mu_B$$ (2.14)

where,

$$J = l+s = \text{angular momentum quantum number}$$

$$g = \text{Lande factor} = 1 + \frac{(j^*)^2 + (S^*)^2 - (l^*)^2}{2(j^*)^2}$$

None of the parameters, $N$, $J$ and $g$ in the above expression is structure sensitive. Thus, theoretically we expect saturation
magnetization to be insensitive to the metallurgical condition of the specimen.

This definition of $M_0$ works well for the heavy lanthanide metals e.g. Gd, Tb, Dy, Ho, Er, Tm etc. But for metals like Fe, Co and Ni however there are large differences between theoretical equation and experimental values of $M_0$. Also there is a basic discrepancy that, the observed $J_g$ values in these metals are all nonintegral, instead of integral numbers predicted by the Heisenberg theory of localized spins. This discrepancy is mainly responsible for the iron-group transition metals. Therefore for these metals equation (2.9) is replaced by

$$M_0 = N_{\text{eff}} \mu_B \tag{2.15}$$

where, $n_{\text{eff}}$ is the effective or apparent mean, Bohr magneton per atom.

Experimentally, the independence of saturation magnetization on metallurgical conditions of the specimen can be demonstrated easily. In conducting the saturation measurements, for instance, it is immaterial weather the specimen is a single crystal or polycrystalline nor would the state of internal stresses
affect the result so long as the applied field is sufficiently strong to saturate the material.

The usual experimental procedure for determining $M_s$ is to conduct a saturation measurement under a strong field. Absolute saturation magnetization is determined by conducting a series of saturation measurements at $4.2^\circ K$ (the boiling point of liquid helium at 1 atmospheric pressure) and extrapolating the $M_s$ value to $0^\circ C$. The experimental method for the determination of saturation magnetization has reviewed by McGuire and Flanders [12]. The saturation magnetization can be determined using by using high field hysteresis loop technique [13]. The magnetization is a powerful tool to study the different parameter such as domain wall motion, anisotropy, magnetic hardness or softness of material, magnetic ordering etc.

When the magnetic field is applied to the ferromagnetic material, the magnetization may vary from zero to saturation value. This behaviour is expressed by Weiss [6] by introducing the idea of existence, of domains. According to Weiss, though each domain is spontaneously magnetized in the direction of field, magnetization may vary from one domain to another domain. In
general, specimen consists of many domains. The magnetization moment of specimen is a vector sum of magnetic moment of each domain. As a result, the magnetization or average magnetic moment per unit volume may have value between zero to saturation.

B) The Curie temperature

All ferromagnetic materials exhibit a characteristic temperature known as the Curie temperature $\theta_c$. This is the critical temperature at which thermal energy is just enough to destroy the spontaneous magnetization. Thus, the Curie temperature marks the transition point at which a ferrimagnet is converted into paramagnet upon heating. Recent studies also have revealed that ferromagnetic and ferrimagnetic materials display singularities in their thermodynamic behaviour in the vicinity of $\theta_c$ known as the critical phenomenon.

The Curie temperature varies on a wide range from the lowest values like $19^0K$ for Ho and $19.5^0$ K for Er to the highest value of $1400^0K (1127^0C)$ for Co. To detect the reason for this wide
range, we need to express $\theta_C$ in terms of basic physical parameters as

$$\theta_C = z J_{ex} J (J +1) 3k$$  \hspace{1cm} (2.16)

where,

$J_{ex}$ is the exchange integral,

$J$ is the total angular quantum number of atom and

$Z$ is the co-ordination number

This expression should be applicable to the Lanthanide metals, for which Heisenberg model of localized electrons is effective and theoretical value of $J$ is substantiated by experiments. Thus, we may use equation (2.11) to evaluate $J_{ex}$. The deduced values of $J_{ex}$ along with other, pertinent data are given in Table 2.2. As can be seen, $\theta_C$ is closely related to $J_{ex}$, not to $J (J+1)$, for the lanthanides. No analysis of this sort can be made for the iron-group metals because of the inapplicability of equation (2.11).

In the quantum-mechanical treatment of the Langevin-type paramagnetism, we have,

$$M (T) = NJ_g \mu_B B_J(a)$$  \hspace{1cm} (2.17)

where $B_J (a)$ is the Brillouin function
\[ a = J_g \mu_B \mu_0 \frac{H}{kT} \quad (2.18) \]

\( N \) is the number of magnetic atoms per unit volume. For a specific system with fixed \( J \) and \( g \), a study of \( M(T) \) shows that, the existence of molecular field will induce a spontaneous magnetization to the saturation value \( M_S(T) \) in a material that would otherwise be paramagnetic. Moreover the value of \( M_S(T) \) will increase steadily with decreasing temperature from \( \theta_C \).

For a quantitative examination of temperature dependence of saturation magnetization in connection with \( \theta_C \), let’s combine equation (2.9) and (2.11) to obtain another expression for \( \theta_C \),

\[ \theta_C = \mu_0 (J + 1)g \mu_B \lambda M_0 / 3k \quad (2.19) \]

We have from Weiss theory

\[ \frac{M_S(T)}{M_0} = B_J(a) \quad (2.20) \]

This \( \frac{M_S(T)}{M_0} \) may be determined as a function of the reduced temperature \( T/\theta_C \). The plot of \( \frac{M_S(T)}{M_0} \) versus \( T/\theta_C \) indicates that results are best fit with \( J = 1/2 \) for Fe, Lo, Ni. Unfortunately none of these metals have \( J = \frac{1}{2} \). Thus the knowledge of ferromagnetism is still inadequate.
2.9.2  *Structure-sensitive properties*

2.9.2.1  *Static properties*

The following magnetic properties are static in nature

a)  *Induction or Magnetic induction*

If the performance of a magnetic component or device depends on the magnetization of the ferromagnetic material involved, induction, rather than magnetization is used to assess the performance. This is so because the definition of induction,

\[ B = \mu_0 (H + M) \]  \hspace{1cm} (2.21)

has made it inherently structure-sensitive static property through the \( \mu_0, H \) term; and therefore induction is more useful than magnetization in practice.

b)  *Permeabilities*

The magnetic permeability (\( \mu \)) is defined as ratio of magnetic induction (\( B \)) to magnetic field (\( H \)) or strength of applied field. The following four permeabilites are particularly important.

- Initial permeability, (\( \mu_i \)): The limiting value approached by normal permeability when \( H \) is reduced to zero.
• Maximum permeability, \( \mu_{\text{Max}} \): the largest value of normal permeability obtained from a (B-H) curve.

• Intermediate permeability, \( \mu_{\delta} \) is equal to \( B_{\delta}/H_{\delta} \), where \( H_{\delta} \) is an alternating field in addition to a constant biasing field and \( B_{\delta} \) is the alternating induction caused by \( H_{\delta} \).

• Differential permeability \( \mu_{d} \) is equal to \( dB/dH \) and is simply the slope of B-H curve at each point.

In a perfect lattice, since the surface energy density of domain walls is the independent of position of the wall, the displacement of a domain wall will not cause any change in the surface energy density. This means that the displaced wall do not return to its original position when the field is withdrawn. In other words, if the crystal were completely free from defect an internal traces, the moment could not be stopped. Thereby, leading to an infinite initial permeability, this suggests that the initial permeability is strongly dependent on structural condition of the specimen. The initial permeability determinations can be carried out using LCR-Q meter in the range from room temperature to 800K at 1KHz from low field inductance measurement of foils with toridal cores using the formula,
\begin{equation}
L = 0.0046 N^2 h \mu_i \log_{10} (d_2/d_1)
\end{equation}

(2.22)

where, \( d_2 \) is the outer diameter,

\( d_1 \) is the inner diameter,

\( L \) is inductance in micro-Henry,

\( h \) is the height in inches and

\( \mu_i \) is initial permeability.

C) **Hysteresis loop and energy loss**

The word hysteresis has its origin in the Greek word ‘hysterein’ which means “to lag behind”. In the B-H curve B lags behind H and thus the closed B-H curve is called hysteresis loop. This loop appears in the four-quadrant as shown in Fig. 2.5.

In the B-H plot, the area enclosed by hysteresis loop represents an energy given by

\[ W_b = \oint H \cdot dB \]

This magnetic energy is converted into heat, which dissipates into the lattice immediately upon generation and it is permanently lost. Thus \( W_b \) is called the hysteresis loss in units of Joules per m\(^3\) per cycle. With soft magnetic materials hysteresis loss is very undesirable, not only because it wastes energy, but
also because a heat involved could create further problems in the application of the material.

In general, the most reliable method for the determination of the hysteresis loss is to obtain the loop experimentally and measure $W_b$ from the loop area graphically.

d) Coercive force and coercivity

Hysteresis loop (Fig. 2.5) shows a characteristic field known as the coercive force $H_c$ and a characteristic induction known as remanence, $B_r$. Coercivity often is used as the most important single criterion for determining whether a ferromagnetic material is soft or hard. The Materials with $H_c$ values less than 400 A-m$^{-1}$ (5 Oe) are definitely considered as soft magnetic material and those with $H_c$ values greater 8000 A-m$^{-1}$ (100 Oe) are labeled as hard magnetic materials. For materials showing coercivity value between 400-8000 Am$^{-1}$, other criteria, such as the energy product $B_rH_c$ must be considered to establish a clear classification. Keeping coercivity at a minimum is a primary goal in a preparation of soft magnetic material. The lowest coercivity ever
recorded is approximately $0.4\text{Am}^{-1}$ (0.005 $O_e$) in supermumetal (73% Ni, 20% Fe, 5% Cu and 2% Cr or Mo).

e) Remanance or retentivity

During the cycle of magnetization $B_r$ (Fig. 2.5) is the amount induction remained ever after the field $H$ is made zero. This characteristic induction is known as remanance or retentivity.

2.9.2.2 Dynamic properties

The following magnetic properties are of dynamic nature.

a) Eddy current and associated energy losses

This property is of great importance in the application of soft magnetic metals and alloys. When an alternating field is applied to magnetize a ferromagnetic body, an electromagnetic force (emf) is setup in the body. If the material is also a good conductor, as with metal and alloys, the induced emf is produced appreciable amount of currents in different regions, these currents are known as the eddy currents and their occurrence gives rise to energy loss ($W_e$) through Joule (resistance heating). Thus, in a.c. application,
metallic ferromagnet suffers the hysteresis as well as the eddy current losses.

Also, $W_e$ increases with frequency according to the second power law. Hence, the eddy current loss becomes even more burdensome than the hysteresis loss at intermediate and high frequencies.

b) **Motion and resonance of domain walls**

The resonance of Bloch walls is prominent phenomena detected in ferrites at high frequency. It plays an important role in the application of soft magnetic materials. It is found that, the eddy-current power loss is proportional to the square of the velocity of the domain walls. Thus to minimize the loss, we must try to keep the wall velocity at the lowest possible value. On the other hand, some applications of ferrites at microwave frequency involve the resonance of domain walls. Again the dynamic behaviour of domain walls plays an essential role in the magnetic performance of ferrites.
2.10 ELECTRICAL PROPERTIES

The range of published values of the resistivity of ferrite is wide from about $10^{-4} \, \Omega m$ to $10^9 \, \Omega m$ at room temperature [14-18]. As the electrical conductivity of soft ferrites is low compared to those of the magnetic materials. This factor is responsible for the wide use of ferrites in microwave frequencies.

The resistivity of soft ferrites is of the order of $10^6 \, \Omega m$ like semiconductor. The conductivity is due to the presence of Fe$^{3+}$ and Me$^{2+}$ (Me = Ni, Co etc.) ions. The presence of Fe$^{3+}$ results in n type behaviour and of Me$^{2+}$ in P type behaviour. The conductivity arises due to the mobility of the extra electron from (Fe$^{3+}$) or the positive hole (Me$^{2+}$) through the crystal lattice. The moment is described by the hopping mechanism, in which the charge carriers jump from one ionic site to the next. On this basis, the semiconducting behaviour of nickel and cobalt ferrite has been successfully treated by Jonker [19] and Elwell et. al. [20] respectively. If the material has to be conducting, lattice must contain the same cations in at least two different valence state. In spinel, since distance between two A site cations is larger than the distance between adjacent B site cations and as tetrahedral and
octahedral sites are not energetically equivalent, conductivity is mostly due to the electron exchange between B site cation. For example in Fe$_3$O$_4$ though the conductivity is due to hopping of electron from Fe$^{2+}$ to Fe$^{3+}$ ion at B site, in this mechanism initial and final states are equivalent,

$$\text{Fe}^{2+} + \text{Fe}^{3+} \leftrightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$$

therefore unbindered electron transfer process can takes place.

According to Verwey [21], the conductivity of high resistivity oxides can be increased by the addition of small amount of impurities to the structure. The substitution of cations of the low valence state gives rise to p type of conduction while the substitution of cations of high valence state to n type of conduction [22]. The presence of Fe$^{2+}$ ions is sometimes desirable [23] as it reduces magnetostriction and resistivity.

*It has also been shown that conduction mechanism in spinel can be explained on the basis of small polaron hopping mechanism [23-27]. The small polaron are trapped carriers which exhibits thermally activated phonon assisted hopping from one site to other. In the case of low mobility oxides the charge carriers remains in the vicinity of the particular atomic site over an interval longer than*
typical vibrational period, an atoms in the vicinity of the excess charge have sufficient time to assume new equilibrium position consistent with presence of added charge. The atomic displacement generally produces a potential well for the excess carriers, if this carriers induced potential well is sufficiently deep, the carrier occupies a bound state as it is unable to move without alteration of the position of the surrounding atoms. This unit comprising of trapped carriers and its induced lattice deformation is the polarons and since it is confined to a small region it is termed as small polaron.

The temperature dependence of electrical conductivity is given by the relationship,

\[ \rho = \rho_0 e^{[-E_g/kT]} \]  \hspace{1cm} (2.23)

where,

k is Boltzmann constant,

\( E_g \) activation energy of conduction,

\( \rho_0 \) is a constant which is the energy required for the hopping of the electron for hole.

The value of drift mobility (\( \mu_0 \)) is obtained from the value of conductivity (\( \sigma \)) and number of charge carriers (n) by the equation
\[ \sigma = e(n)(\mu_D) \quad (2.24) \]

where, \( \mu_D \) is called the drift mobility.

The value of \( n \) can be calculated from Seebeck coefficient measurement. The Seebeck coefficient \( \theta \) and the number of charge carriers is related by the equation

\[ \theta = \frac{K}{e} \left[ \ln \left( \frac{N}{n} \right) + \frac{a}{k} \right] \quad (2.25) \]

where,

\[ \theta \] is Seebeck voltage per degree,

\[ N \] is the concentration of lattice site available for the charge carriers of concentration \( n \),

\[ a, k \] are the constants related to the transport of K.E.

### 2.11 DIELECTRIC PROPERTIES

Ferrites have vast applications from microwave to radio frequencies. The low conductivity of ferrite causes them for its use in microwave applications. They exhibit high resistivity and dielectric properties. The dielectric properties of ferrites are dependent upon several factors including the method of
preparation, chemical composition and grain structure or size. When a ferrite is sintered under slightly reducing condition, the valence state changes, the individual cation found in the sample leads to high conductivity and when such a material is cooled in an oxygen atmosphere, it is possible to form films of high resistivity over the constituent grain. Such ferrites in which the individual grains are separated by either air gaps or low conducting layers behave as inhomogeneous dielectric material. This aroused considerable interest in the low frequency range \((10^2 \text{ Hz} - 10^5 \text{ Hz})\) dielectric behaviour of ferrite. Among the many workers involved in this type of studies, the prominent ones are Koops [28] Moltgen [29], Kamiyoshi [30], Iwauchi et. al. [31], Rezlescu [33,34] and Josyolu [35].

The polycrystalline ferrites have high dielectric constant of the order of a few thousands at low frequencies, following to a very low value of only 10-20 at microwave frequencies. The a.c. resistivity decreases with increase in temperature like d.c. resistivity, whereas dielectric constant increases with increase in temperature. According to Rabkin and Novikova [36] the process of dielectric polarization in ferrite takes place through a
mechanism similar to conduction process. Koops [28] gave a phenomenological theory of dispersion based on the Maxwell-Wagner interfacial polarization model for inhomogeneous dielectric structure.

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Table 2.1
Crystallographic data for some spinel ferrites.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>u (Å)</th>
<th>Cell side, a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>0.381</td>
<td>8.33 (8)</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>0.385</td>
<td>8.42 (9)</td>
</tr>
<tr>
<td>MgFe$_2$O$_4$</td>
<td>0.381</td>
<td>8.36 (10)</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>0.381</td>
<td>8.35</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>0.384</td>
<td>8.51 (11)</td>
</tr>
<tr>
<td>Mg$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>0.384</td>
<td>8.45</td>
</tr>
<tr>
<td>MnFe$<em>{1.5}$Cr$</em>{0.5}$O$_4$</td>
<td>0.387</td>
<td>8.49</td>
</tr>
<tr>
<td>MnFeCrO$_4$</td>
<td>0.388</td>
<td>8.46</td>
</tr>
<tr>
<td>MnFeFe$<em>{0.5}$Cr$</em>{1.5}$O$_4$</td>
<td>0.389</td>
<td>8.45</td>
</tr>
<tr>
<td>NiFeGaO$_4$</td>
<td>0.388</td>
<td>8.30 (8)</td>
</tr>
<tr>
<td>NiGa$_2$O$_4$</td>
<td>0.387</td>
<td>8.25 (8)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>0.379</td>
<td>8.39 (12)</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>0.387</td>
<td>8.09 (13)</td>
</tr>
<tr>
<td>NiFeAlO$_4$</td>
<td>0.386</td>
<td>8.20 (8)</td>
</tr>
</tbody>
</table>
Table 2.2
An analysis of the Curie temperature of ferromagnetic lanthanides

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Tm</th>
<th>Er</th>
<th>Ho</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_C (^0\text{K})$</td>
<td>292.7</td>
<td>220</td>
<td>88</td>
<td>32</td>
<td>19.5</td>
<td>19</td>
</tr>
<tr>
<td>$J$</td>
<td>3.5</td>
<td>6</td>
<td>7.5</td>
<td>6</td>
<td>7.5</td>
<td>8</td>
</tr>
<tr>
<td>$J (J+1)$</td>
<td>15.75</td>
<td>42</td>
<td>63.75</td>
<td>42</td>
<td>63.75</td>
<td>2</td>
</tr>
<tr>
<td>$J_{ex} \times 10^{23} (J)$</td>
<td>6.42</td>
<td>1.81</td>
<td>0.477</td>
<td>0.262</td>
<td>0.106</td>
<td>0.091</td>
</tr>
</tbody>
</table>
Fig. 2.1 Crystal structure of spinel ferrite.
Fig. 2.2 X-ray diffraction from lattice point
<table>
<thead>
<tr>
<th>Type of Magnetism</th>
<th>Susceptibility</th>
<th>Atomic / Magnetic Behaviour</th>
<th>Example / Susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>Small &amp; negative.</td>
<td>Atoms have no magnetic moment</td>
<td>Au $-2.74 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu $-0.77 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image" alt="Magnetic Moment Diagram" /></td>
<td></td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>Small &amp; positive.</td>
<td>Atoms have randomly oriented magnetic moments</td>
<td>β-Sn $0.19 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt $21.04 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn $66.10 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image" alt="Magnetic Moment Diagram" /></td>
<td></td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>Large &amp; positive,</td>
<td>Atoms have parallel aligned magnetic moments</td>
<td>Fe ~100,000</td>
</tr>
<tr>
<td></td>
<td>function of applied field, microstructure dependent.</td>
<td><img src="image" alt="Magnetic Moment Diagram" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anti-ferromagnetism</td>
<td>Small &amp; positive.</td>
<td>Atoms have mixed parallel and anti-parallel aligned magnetic moments</td>
<td>Cr $3.6 \times 10^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image" alt="Magnetic Moment Diagram" /></td>
<td></td>
</tr>
</tbody>
</table>
**Fig. 2.3** Different types of magnetic behaviour.
Fig. 2.4- Variation of a $1/\chi$ as a function of a temperature in the paramagnetic region.