

**Chapter 2**

Crystal structure and properties of ferrites

2.1 Spinel compounds

2.1.1 Introduction to spinel compounds

The word spinel is derived from Italian *spinella*, diminutive of spine, thorn (from its sharply pointed crystals). Spinel crystallizes in the cubic system, forming octahedral crystals. There are at least 30 oxide minerals included in spinel supergroup. The majority of spinel compounds belong to the space group $Fd\bar{3}m$. The principal member of the group has the formula, AB_2O_4 ; the 'A' represents a divalent metal ion such as magnesium, iron, nickel, manganese and zinc. The quadrivalent lead ion can also occupy this site. The 'B' represents trivalent metal ions such as aluminum, iron, chromium and/or manganese. However, titanium Ti^{4+} and Pb^{2+} etc. may also occupy this site. Solid solutioning is common in this group of minerals meaning that they may contain certain percentages of different ions in any particular specimen [1]. In most oxide structures, the oxygen ions are appreciably larger than the metallic ions and the spinel structure can be approximated by a cubic close packing of O^{2-} ions in which the cations (e.g. Co^{2+} , Fe^{3+}) occupy certain interstices.

The structure of a spinel compound is similar to the highly symmetric structure of diamond. The position of the A ions is nearly identical to the positions occupied by carbon atoms in the diamond structure. This could explain the relatively high hardness and high density typical of this group. The arrangement of the other ions in the structure conforms to the symmetry of the diamond structure. The arrangement of the ions also favors the octahedral crystal structure, which is the predominant crystal form and is in fact the trademark of the spinels. There are well over a hundred compounds with the spinel structure reported to date. Most are oxides, some are sulphides, selenides and tellurides and few are halides. Many different cations may be introduced into the spinel structure and several different charge combinations are possible;

almost any combination that adds up to eight positive charges to balance eight anionic charges [1], for example $\text{Co}^{2+}\text{Fe}_2^{3+}\text{O}_4$, $\text{Mg}_2^{2+}\text{Ti}^{4+}\text{O}_4$, $\text{Li}^{1+}\text{Al}^{3+}\text{Ti}^{4+}\text{O}_4$, $\text{Li}_{0.5}^{1+}\text{Al}_{2.5}^{3+}\text{O}_4$ and $\text{Na}_2^{1+}\text{W}^{6+}\text{O}_4$, etc.

In oxide spinels, the two types of cations do not usually differ greatly in size, because the spinel structure is stable only if the cations are rather medium sized and, in addition, the radii of the different ionic species in the same compound do not differ too much. Similar cation combinations occur in sulphides, e.g. $\text{Zn}^{2+}\text{Al}_2^{3+}\text{S}_4$ and $\text{Cu}_2^{2+}\text{Sn}^{4+}\text{S}_4$. However, in halide spinels e.g. $\text{Li}_2^{1+}\text{Ni}^{3+}\text{F}_4$ and $\text{Li}^{1+}\text{Mn}_2^{3+/4+}\text{F}_4$, cations are limited to charges of +1 and +2, in order to give an overall cation: anion ratio of 3:4.

Most spinels fall into three series determined by a B metal: aluminate series with Al^{3+} (Hercynite, Gahnite, Galaxite); a magnetite series with Fe^{3+} (Magnetite, Magnesio ferrite, Franklinite); a chromite series with Cr^{3+} (Chromite, Magnesio chromite). There is extensive cationic exchange (solid solution) within each series but very little between the series [2]. Spinel is classified on the basis of the distribution of cations in the two principal sites, tetrahedral site (T-) and octahedral site (O-) [3], into three types.

2.1.2 Types of spinel

The spinels are any of a class of minerals of general formulation $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4^{2-}$ which crystallise in the cubic (isometric) crystal system, with the oxide anions arranged in a cubic packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. A and B can be divalent, trivalent, or quadrivalent cations, including magnesium, zinc, iron, manganese, aluminium, chromium, titanium, and silicon. Although the anion is normally oxide, structures are also known for the rest of the chalcogenides. A and B can also be the same metal under different charges, such as the case in Fe_3O_4 (as $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$).

Members of the spinel group include:

- Aluminium spinels:
 - ✓ Spinel – MgAl_2O_4 , after which this class of minerals is named
 - ✓ Gahnite- ZnAl_2O_4

- ✓ Hercynite - FeAl_2O_4
- Iron spinels:
 - ✓ Cuprospinel - CuFe_2O_4
 - ✓ Franklinite - $(\text{Fe}, \text{Mn}, \text{Zn})(\text{Fe}, \text{Mn})_2\text{O}_4$
 - ✓ Jacobsite - MnFe_2O_4
 - ✓ Magnetite - Fe_3O_4
 - ✓ Trevorite - NiFe_2O_4
 - ✓ Ulvöspinel - TiFe_2O_4
 - ✓ Zinc ferrite - $(\text{Zn}, \text{Fe})\text{Fe}_2\text{O}_4$
- Chromium spinels:
 - ✓ Chromite - FeCr_2O_4
 - ✓ Magnesiochromite - MgCr_2O_4
- Others with the spinel structure:
 - ✓ Forsterite - Mg_2SiO_4
 - ✓ Ring woodite - $(\text{Mg}, \text{Fe})_2\text{SiO}_4$, an abundant olivine polymorph within the Earth's mantle from about 520 to 660 km depth, and a rare mineral in meteorites

Cation disorder in multi-site oxides is quantified in terms of an "inversion parameter" (δ). The spinel structure is cubic, with two distinct cation sites characterized by different oxygen coordination (octahedral and tetrahedral). There are twice as many octahedral sites as tetrahedral sites.

Normal spinel:

The cation disorder is defined in terms of a "normal" spinel structure, such as that for ideal MgAl_2O_4 , in which all the Mg resides on sites tetrahedrally coordinated with oxygen, and all the Al resides on sites octahedrally coordinated with oxygen. The inversion parameter is defined relative to this configuration, and is the ratio of the atomic fraction of Al on tetrahedral sites to the atomic fraction of Al on octahedral sites. For a perfect normal spinel, the inversion parameter is 0.0. Normal spinel structures are usually cubic closed-packed oxides with one octahedral and two tetrahedral sites per oxide. The tetrahedral points are smaller than the octahedral points.

B^{3+} ions occupy the octahedral holes because of a charge factor, but can only occupy half of the octahedral holes. A^{2+} ions occupy $1/8^{\text{th}}$ of the tetrahedral holes. This maximises the lattice energy if the ions are similar in size. A common example of a normal spinel is $MgAl_2O_4$.

Inverse spinel:

For an ideal "inverse" spinel structure (such as for $MgFe_2O_4$), all of the Mg resides on octahedral sites, and the Fe is distributed equally over the remaining octahedral sites and all of the tetrahedral sites. In this case the inversion parameter would be 1.0. Inverse spinel structures however are slightly different in that one must take into account the crystal field stabilization energies (CFSE) of the transition metals present. Some ions may have a distinct preference on the octahedral site which is dependent on the d-electron count. If the A^{2+} ions have a strong preference for the octahedral site, they will force their way into it and displace half of the B^{3+} ions from the octahedral sites to the tetrahedral sites. If the B^{3+} ions have a low or zero octahedral site stabilization energy (OSSE), then they have no preference and will adopt the tetrahedral site. A common example of an inverse spinel is Fe_3O_4 , if the Fe^{2+} (A^{2+}) ions are d^6 high-spin and the Fe^{3+} (B^{3+}) ions are d^5 high-spin.

Random spinel:

For a "random" spinel structure, the cations are equally distributed over the two sites in ratios proportional to their stoichiometry and the site ratios. A random spinel structure has an inversion parameter of $(2/3)$, or 0.667. 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.

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



where the ions inside the bracket are located in octahedral sites and the ions outside the brackets in tetrahedral sites.

2.2 Chemical composition of spinel ferrite

Complex oxides with the spinel structure often called “spinel” belong to the group of strategic materials which are used in the wide area of modern technologies. They exhibit excellent magnetic, refractory, semi conducting, catalytic and sorption properties. The general chemical formula of ferrites possessing the structure of the mineral spinel, MeAl_2O_4 , is MeFe_2O_4 , where Me represents a divalent metal ion with an ionic radius approximately between 0.6 and 1 Å. In the case of simple ferrites, Me is one of the transition elements Mn, Fe, Co, Ni, Cu and Zn, or Mg and Cd. A combination of these ions is also possible, a mixed ferrite. The symbol Me can represent a combination of ions which have an average valency of two e.g. Li^{1+} and Fe^{3+} in lithium ferrite, $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$. The trivalent iron ions (Fe^{3+}) in MeFe_2O_4 can be completely or partly replaced by another trivalent ion such as Al^{3+} or Cr^{3+} , giving rise to mixed crystals with aluminates and chromites. These compounds are also ferrimagnetic at room temperature if large amount of non-magnetic ions are not present. If the ferric ions are replaced by a tetravalent ion like Ti^{4+} , an equal part of the Fe^{3+} are changed into Fe^{2+} . A great variety of the chemical composition of ferrimagnetic oxide with spinel structure is possible.

2.3 Crystal structure of ferrite

2.3.1 Spinel ferrite

Spinel ferrite crystallizes in the cubic structure. The spinel lattice is composed of a close-packed oxygen anions arrangement in which 32 oxygen ions form the unit cell (the smallest repeating unit in the crystal network). These anions are packed in a face centered cubic (FCC) arrangement leaving two kinds of spaces between anions: tetrahedrally coordinated sites (A), surrounded by four nearest oxygen atoms, and octahedrally coordinated sites (B), surrounded by six nearest neighbor oxygen atoms (Figure 2.1). There are total 64 tetrahedral sites and 32 octahedral sites in the unit cell, of which only 8 tetrahedral sites and 16 octahedral sites are occupied, resulting in a structure that is electrically neutral [4].

Spinel has a general formula $M(Fe_2O_4)$, where M is usually a divalent cation such as manganese (Mn^{2+}), nickel (Ni^{2+}), cobalt (Co^{2+}), zinc (Zn^{2+}), copper (Cu^{2+}), or magnesium (Mg^{2+}). M can also represent the monovalent lithium cation (Li^+) or even vacancies, as long as these absences of positive charge are compensated for by additional trivalent iron cations (Fe^{3+}). The ionic distribution in this kind of structure may be represented by $[M_\delta Fe_{1-\delta}]^A [M_{1-\delta} Fe_{1+\delta}]^B O_4$, where δ is the inversion parameter and $\delta = 0$ and 1 stand for the inverse and normal cases respectively.

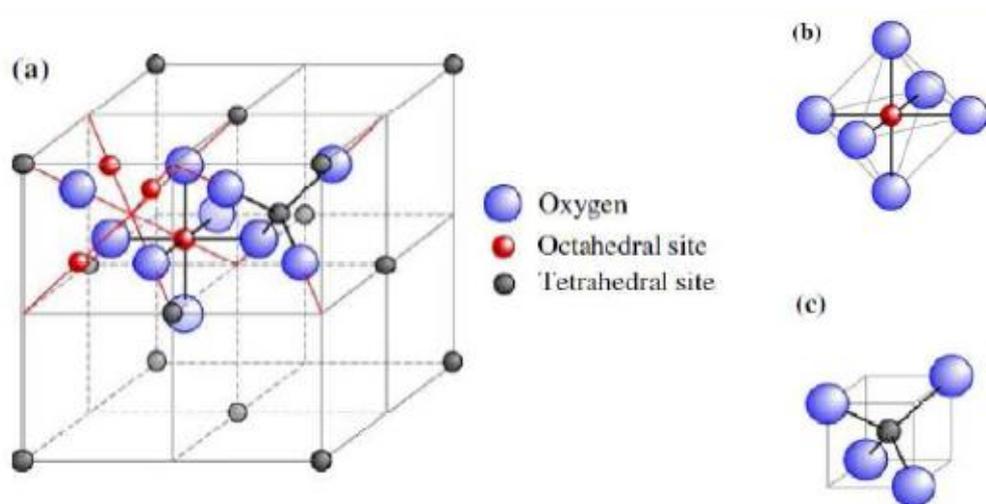


Fig. 2.1: (a) Spinel structure, (b) octahedral interstice (B site: 32 per unit cell, 16 occupied), and (c) tetrahedral interstice (A site: 64 per unit cell, 8 occupied).

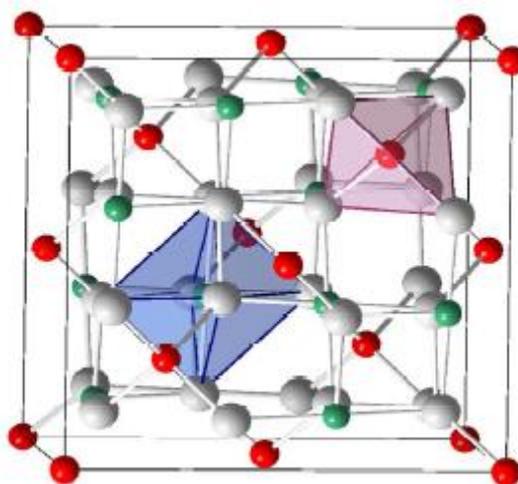


Fig. 2.2: Spinel unit cell structure

Although most spinel ferrites are cubic, there are some exceptions like CuFe_2O_4 that can have tetragonal unit cell symmetry if the sample is slowly cooled from high temperatures. There exists a super exchange interaction between the cations occupied in different interstitial sites through oxygen anion.

2.3.2 Garnet structure

The garnets have orthorhombic crystal structure (oxygen polyhedra, surrounding the cations) but with trivalent cations (including rare earth and Fe^{3+}) occupying tetrahedral (d), octahedral (a), or dodecahedral—a 12-sided distorted polyhedral—(c) sites. Specifically, the interaction between tetrahedral and octahedral sites is anti parallel, and the net magnetic moment is anti parallel to the rare earth ions on the c sites. The garnet structure is one of the most complicated crystal structures and it is difficult to draw a two dimensional representation that shows clearly all the ions (160) in the unit cell. For simplicity, only an octant of a garnet structure that shows just the cation positions is shown in Fig. 2.3. The garnet structure is composed of a combination of octahedral (trivalent cation surrounded by six oxygen ions), tetrahedral (trivalent cations surrounded by four oxygen ions), and 12-sided polyhedral - dodecahedral - (trivalent cations surrounded by 8 oxygen atoms) sites, the orientations of which are shown in Fig. 2.4 (a) [5]. The chemical formula for garnets is $3\text{Me}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$ where Me represents the trivalent rare earth ions like nonmagnetic yttrium or a magnetic rare earth such as from lanthanum through ytterbium.

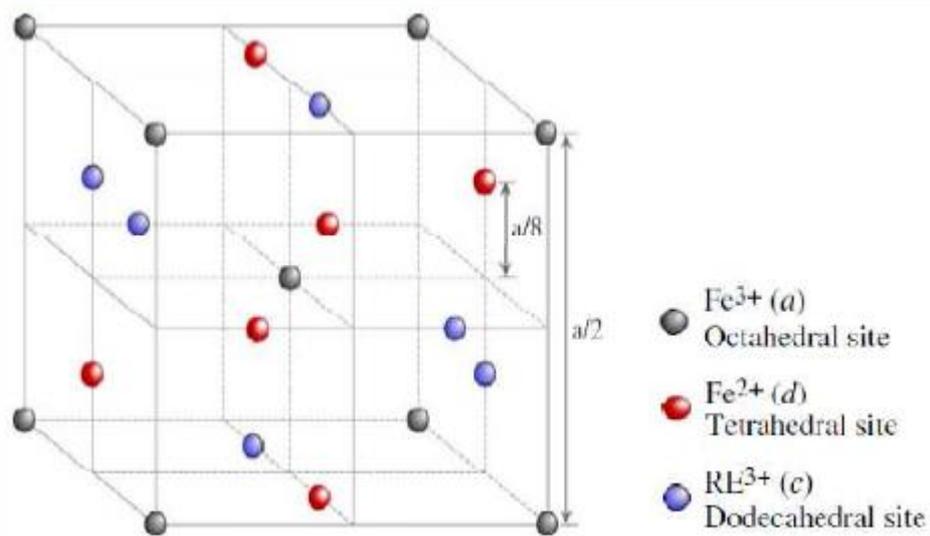


Fig. 2.3: Schematic representation of an 'octant' of a garnet crystal structure (lattice constant 'a') showing cation positions.

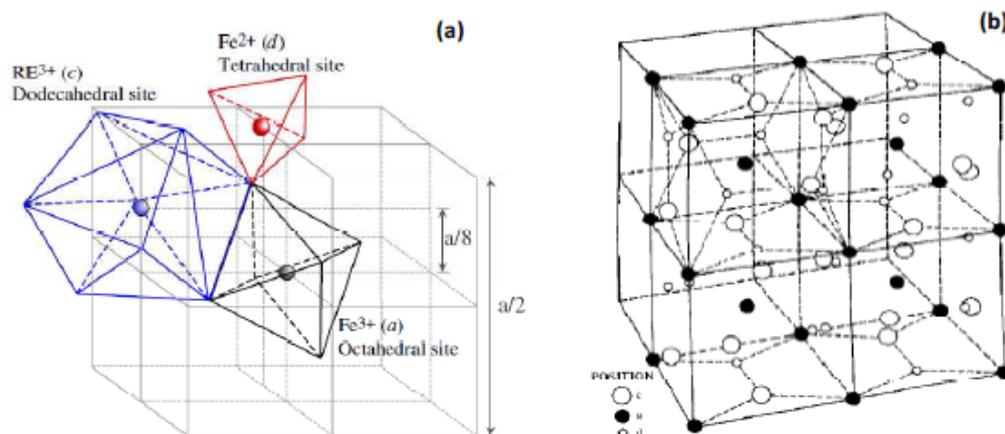


Fig. 2.4: (a) An 'octant' of a garnet crystal structure (b) Unit cell of a rare earth garnet.

Fig. 2.4 (b) shows a unit cell of rare earth garnet. In YIG, the five iron (III) ions occupy two octahedral and three tetrahedral sites, with the yttrium (III) ions coordinated by eight oxygen ions in an irregular cube. The iron ions in the two coordination sites exhibit different spins, resulting in magnetic behavior. By substituting specific sites with rare earth elements, interesting magnetic properties can be obtained. Trivalent iron ions on Tetrahedral (d) and Octahedral (a) are important for magnetic property. These two sites are coupled anti-ferromagnetically [6] and yields a Ferrimagnetic crystal [7].

2.3.3 Ortho ferrite

Rare earth ortho ferrites are classified as ferrites, although they are canted antiferromagnets. The magnetic oxides with perovskite structure, which have been studied by Jonker and Van Santen [8], are an exception in the group of oxides. The perovskite structure is shown schematically in Fig. 2.5. Large divalent or trivalent ions (A) occupy the corners of a cube and small trivalent or tetravalent metal ions (B) occupy the centre of the cube. The oxygen ions are situated centrally on the faces of the cube. The general chemical formula is ABO_3 , where A represents yttrium or a rare earth.

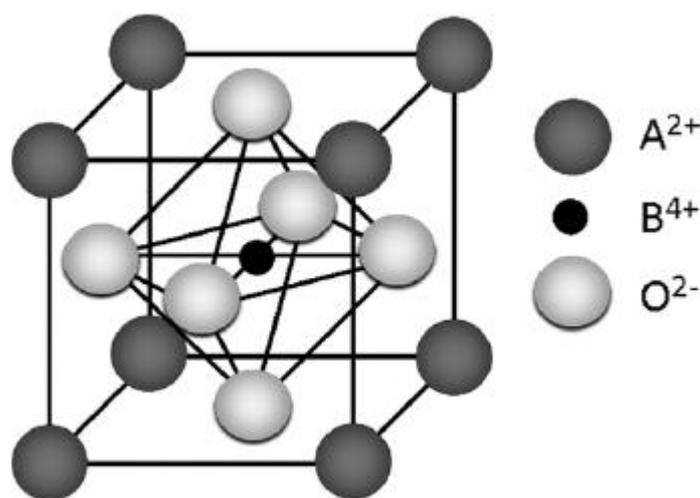


Fig. 2.5: A Perovskite structure of an orthoferrite

The magnetic structure inside of a sublattice is usually collinear ferromagnetic, but the different sub lattices are coupled antiferromagnetically. Due to the different number of magnetic ions in different sublattices, there is a net resulting magnetic moment, giving rise to ferrimagnetism. The nature of the superexchange interaction depends not only on the type of the magnetic ion, but rather strongly on the bond length and bonding angle.

2.3.4 Hexagonal ferrite

The regular barium hexaferrite has the crystal structure of the mineral magnetoplumbite, as shown in Fig. 2.6. It belongs to the group of hexagonal ferrite of the so-called M-type. The crystallographic unit cell corresponds to the space group $P6_3/mmc$ and contains two molecules of the chemical composition

$\text{BaFe}_{12}\text{O}_{19}$. The dimensions of the unit cell are approximately $a = b = 6\text{\AA}$ and $c = 23\text{\AA}$.

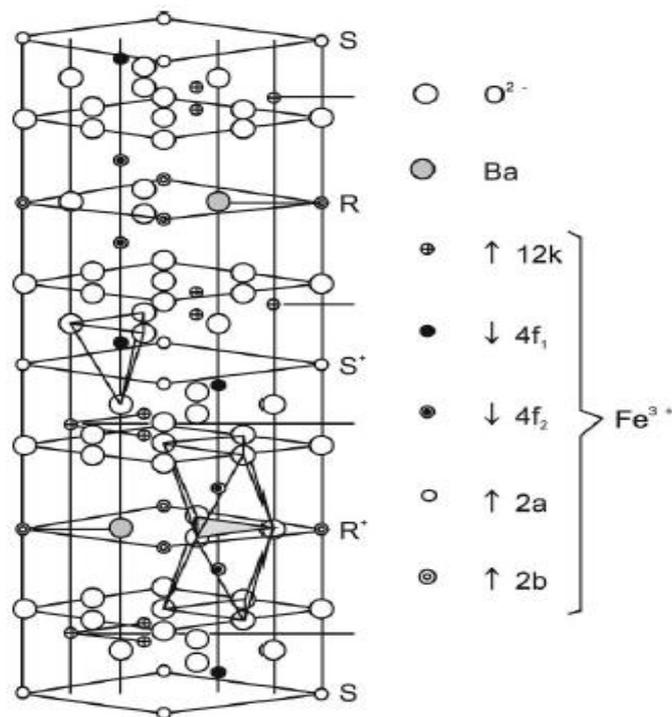


Fig. 2.6: Unit cell of barium hexaferrite based on two cells of $\text{BaFe}_{12}\text{O}_{19}$.

The basic structure of the unit cell is built up by ten layers of oxygen ions which are formed by a close packing of cubic or hexagonal stacked layers alternately. One O²⁻ ion is replaced by barium in every fifth layer (Fig. 2.6).

The crystal structure of M-type barium can be divided into several blocks. The structure of M-type barium ferrite is symbolically described as RSR^*S^* , where R is a one-layer block with composition $\text{Ba}^{2+}\text{Fe}_3^{3+}\text{O}_3^{2-}$ and S is a four O²⁻ layers block with composition $\text{Fe}_9^{3+}\text{O}_{16}^{2-}$, where the asterisk means that the corresponding block has been turned 180° around the hexagonal c-axis. All the metal ions are arranged in the interstices of oxygen atom. There are five Fe sites: two ions have tetrahedral surroundings (4f₁), and one Fe ion is located in a trigonal bipyramid (2b) with five-fold coordination [9] three octahedral positions (2a, 4f₁ and 12k) are occupied by one, two and six Fe ions, respectively, as shown in Fig. 2.7.

According to Fig. 2.7, it can also be seen that Fe^{3+} ions with up-spin are distributed on the 2a, 2b and 12k sites and the ions with down-spin are located on the $4f_1$ and $4f_2$ sites. Due to antiparallel spin direction of ions, the magnetic moment can be expressed as following:

$$M=12k+2a+2b+4f_1+4f_2 \quad (2.1)$$

According to Eq. (2.1), the more Fe^{3+} ions with up-spin exist, the larger magnetization will be. But, the excessive displacements of Fe ions will destroy the matching distribution of Fe ions between A site (tetrahedral positions) and B site (octahedral positions), which will weaken the super exchange interactions.

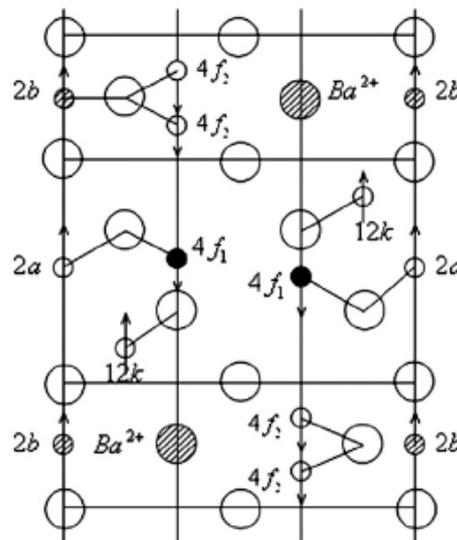


Fig. 2.7: The magnetic structure of Barium hexaferrite.

2.4 Cation distribution in spinel ferrite

2.4.1 Ionic radius

Since the tetrahedral site is the smaller, one might expect that the smaller ions will prefer to occupy the tetrahedral sites. Trivalent ions are usually smaller than the divalent ions and this favours the inverse structure.

2.4.2 Electronic configuration

Certain ions have special preference for a certain environment. For example, Zn^{2+} and Cd^{2+} show a marked preference for tetrahedral sites where their $4s, p$ or $5s, p$ electrons respectively can form a covalent bond with the six

$2p$ electrons of the oxygen ion. This produces four bonds oriented towards the corner of a tetrahedron. A marked preference of Ni^{2+} , Co^{2+} and Cr^{3+} for octahedral environment is due to favorable fit of the charge distribution of these ions in the crystal field at an octahedral site [10].

2.4.3 Electrostatic energy

The electrostatic energy is gained when the ions are brought close together to form the spinel cubic lattice from infinity. In the normal spinel, the cation with the smallest positive charge is surrounded by four oxygen atoms while the cation with the higher positive charge by six oxygen atoms, being electrostatically more favorable. In the spinels the inverse structure is electrostatically more favorable and has the lowest energy when the oxygen parameter value (u) is smaller than the normal value ($u = 0.379$) while normal spinel has the lowest energy when ' u ' is larger than the normal [10].

2.5 Magnetic properties

Magnetic material exhibits different kind of magnetic ordering depending upon spin orientation. The magnetic behaviour is caused by spinning of electrons of 'd' orbital about their own axis gives rise to spin magnetic moments. The motion of electron in the orbit around the nucleus results in orbital magnetic moments. In case of transition element, this orbital magnetic moments get quenched by crystalline electrical field. The different magnetic behaviour observed is due to different contribution of electron spin.

2.5.1 Classification of magnetic properties

On the basis of electron spin magnetism is classified in number of classes as diamagnetism, paramagnetism, ferromagnetism, anti-ferromagnetism and ferrimagnetism.

1) Diamagnetism

Diamagnetism is a fundamental property of all matter, although it is usually very weak. It is due to the non-cooperative behavior of orbiting electrons when exposed to an applied magnetic field. Diamagnetic substances are composed of atoms which have no net magnetic moments (i.e., all the orbital shells are filled and there are no unpaired electrons). However, when exposed to a field, a negative magnetization is produced and thus the susceptibility is negative. If we plot M vs H , we see (Fig. 2.8):

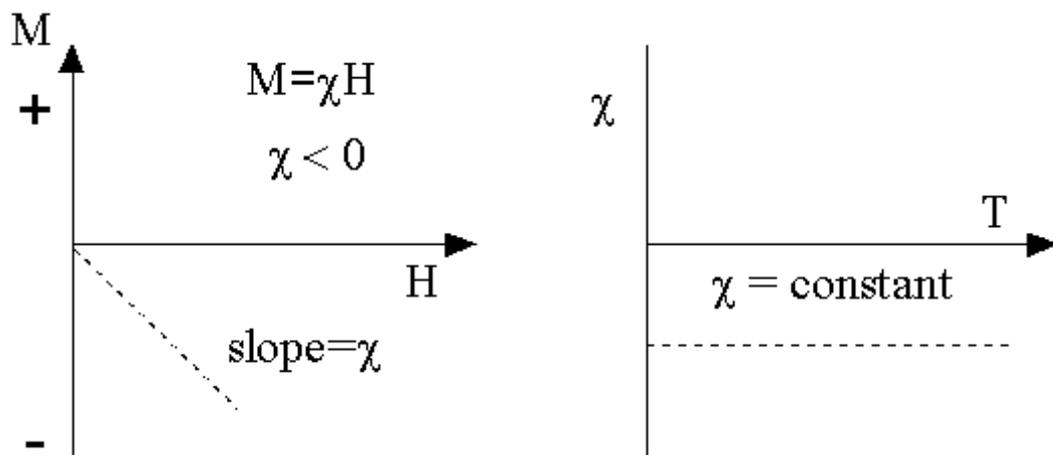


Fig. 2.8: M-H plot of diamagnetic material

When the field is zero the magnetization is zero. The other characteristic behavior of diamagnetic materials is that the susceptibility is temperature independent.

2) Paramagnetism:

This class of materials, some of the atoms or ions in the material have a net magnetic moment due to unpaired electrons in partially filled orbitals. One of the most important atoms with unpaired electrons is iron. However, the individual magnetic moments do not interact magnetically, and like diamagnetism, the magnetization is zero when the field is removed. In the presence of a field, there is now a partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility.

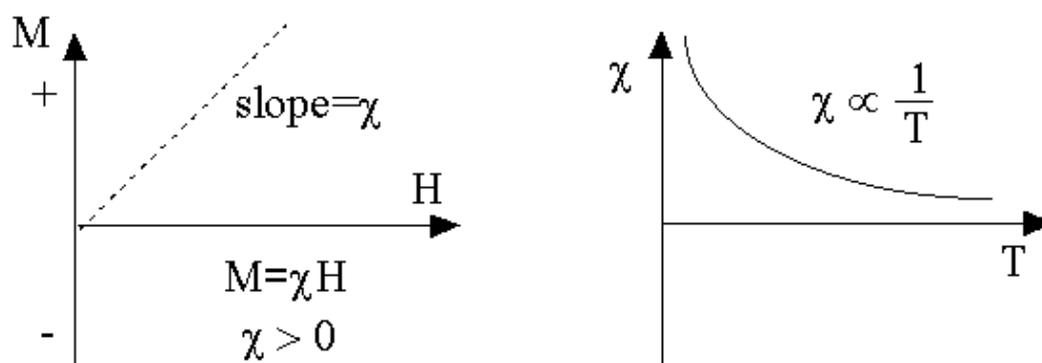


Fig. 2.9:M-H plot of paramagnetic material

In addition, the efficiency of the field in aligning the moments is opposed by the randomizing effects of temperature. This results in a temperature dependent susceptibility, known as the Curie Law. At normal temperatures and in moderate fields, the paramagnetic susceptibility is small (but larger than the diamagnetic contribution). Unless the temperature is very low ($\ll 100$ K) or the field is very high paramagnetic susceptibility is independent of the applied field. Under these conditions, paramagnetic susceptibility is proportional to the total iron content.

3) Ferromagnetism

Unlike paramagnetic materials, the atomic moments in these materials exhibit very strong interactions. These interactions are produced by electronic exchange forces and result in a parallel or antiparallel alignment of atomic moments. Exchange forces are very large, equivalent to a field on the order of 1000 Tesla, or approximately a 100 million times the strength of the earth's field. The exchange force is a quantum mechanical phenomenon due to the relative orientation of the spins of two electron. Ferromagnetic materials exhibit parallel alignment of moments resulting in large net magnetization even in the absence of a magnetic field.

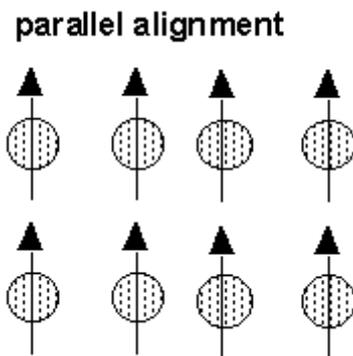


Fig. 2.10: Spin alignment in ferromagnetic material

Two distinct characteristics of ferromagnetic materials are their

- (1) spontaneous magnetization and the existence of
- (2) magnetic ordering temperature

Spontaneous Magnetization

The spontaneous magnetization is the net magnetization that exists inside a uniformly magnetized microscopic volume in the absence of a field. The magnitude of this magnetization, at 0 K, is dependent on the spin magnetic moments of electrons. A related term is the saturation magnetization which we can measure in the laboratory. The saturation magnetization is the maximum induced magnetic moment that can be obtained in a magnetic field (H_{sat}); beyond this field no further increase in magnetization occurs. The difference between spontaneous magnetization and the saturation magnetization has to do with magnetic domains (more about domains later). Saturation magnetization is an intrinsic property, independent of particle size but dependent on temperature. There is a big difference between paramagnetic and ferromagnetic susceptibility. As compared to paramagnetic materials, the magnetization in ferromagnetic materials is saturated in moderate magnetic fields and at high (room-temperature) temperatures:

4) Ferrimagnetism

In ionic compounds, such as oxides, more complex forms of magnetic ordering can occur as a result of the crystal structure. One type of magnetic ordering is called ferrimagnetism. A simple representation of the magnetic spins

in a ferrimagnetic oxide is shown here. The magnetic structure is composed of two magnetic sub lattices (called A and B) separated by oxygens. The exchange interactions are mediated by the oxygen anions. When this happens, the interactions are called indirect or super exchange interactions. The strongest super exchange interactions result in an anti parallel alignment of spins between the A and B sublattice. In ferrimagnets, the magnetic moments of the A and B sub lattices are not equal and result in a net magnetic moment. Ferrimagnetism is therefore similar to ferromagnetism. It exhibits all the hallmarks of ferromagnetic behavior- spontaneous magnetization, Curie temperatures, hysteresis, and remanence. However, ferro- and ferrimagnets have very different magnetic ordering. Magnetite is a well-known ferrimagnetic material. Indeed, magnetite was considered a ferromagnet until Néel in the 1940's, provided the theoretical framework for understanding ferrimagnetism.

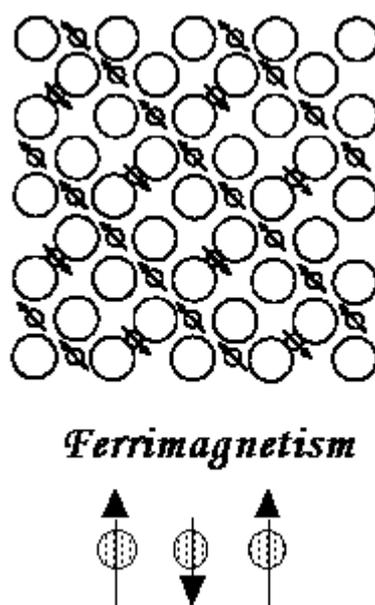


Fig. 2.11: Spin alignment in ferrimagnetic materials

2.5.2 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 [11] 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 (M_s) coercive force (H_C) and remanence ratio (M_r/M_s). According to the values of these parameters, the ferrites can be classified as soft and hard ferrites. The ferrites with low coercive force are called soft ferrites and ferrites with high H_c 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 [12] the coercive force (H_C) is related to saturation magnetization, internal stress, porosity [13] and anisotropy [14]. The Hysteresis properties are highly sensitive to crystal structure, heat treatment, chemical composition, porosity and grain size.

2.5.3 Hysteresis

The lag or delay of a magnetic material known commonly as magnetic hysteresis, relates to the magnetisation properties of a material by which it firstly becomes magnetised and then de-magnetised. The magnetic flux generated by an electromagnetic coil is the amount of magnetic field or lines of force produced within a given area and that it is more commonly called "Flux Density". Given the symbol B with the unit of flux density being the Tesla, T.

The magnetic strength of an electromagnet depends upon the number of turns of the coil, the current flowing through the coil or the type of core

material being used, and if we increase either the current or the number of turns we can increase the magnetic field strength, symbol H .

The relative permeability, symbol μ_r was defined as the product of the absolute permeability μ and the permeability of free space μ_0 (a vacuum) and this was given as a constant. However, the relationship between the flux density, B and the magnetic field strength, H can be defined by the fact that the relative permeability, μ_r is not a constant but a function of the magnetic field intensity thereby giving magnetic flux density as: $B = \mu H$. Then the magnetic flux density in the material will be increased by a larger factor as a result of its relative permeability for the material compared to the magnetic flux density in vacuum, $\mu_0 H$ and for an air-cored coil this relationship is given as:

$$B = \Phi/A \text{ and } \mu_0 = B/H$$

So for ferromagnetic materials the ratio of flux density to field strength (B/H) is not constant but varies with flux density. However, for air cored coils or any non-magnetic medium core such as woods or plastics, this ratio can be considered as a constant and this constant is known as μ_0 , the permeability of free space, ($\mu_0 = 4.\pi.10^{-7}$ H/m).

The magnetic hysteresis loop (Fig. 2.12), shows the behavior of a ferromagnetic core graphically as the relationship between B and H is non-linear. Starting with an unmagnetised core both B and H will be at zero, point 0 on the magnetisation curve.

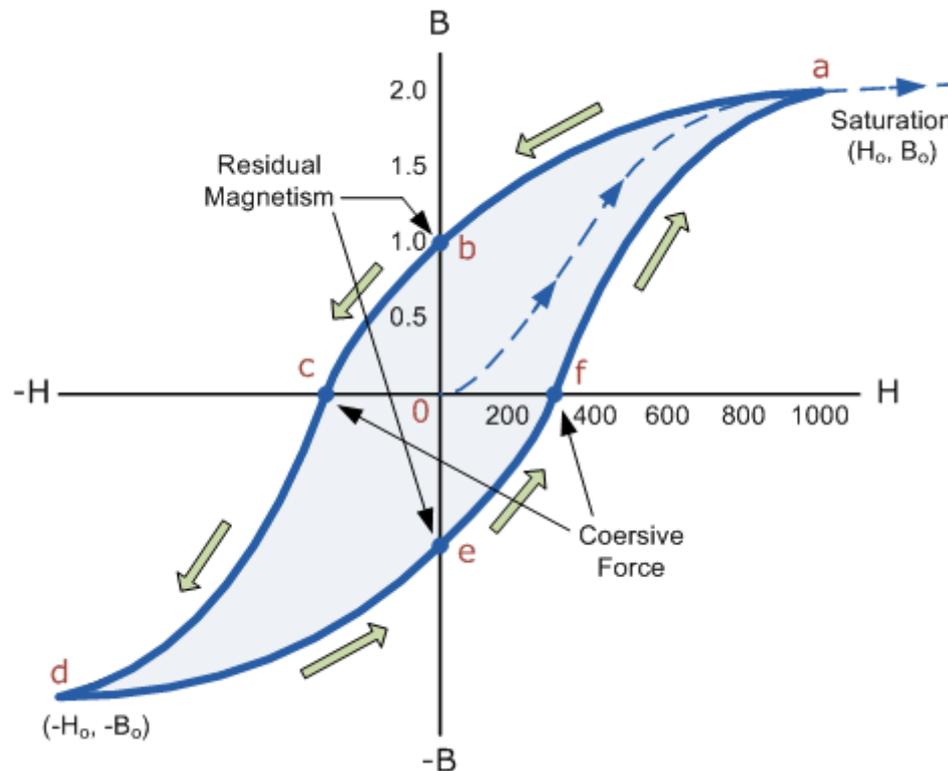


Fig. 2.12: Magnetic hysteresis loop

If the magnetisation current, i is increased in a positive direction to some value the magnetic field strength H increases linearly with i and the flux density B will also increase as shown by the curve from point 0 to point a as it heads towards saturation. Now if the magnetising current in the coil is reduced to zero the magnetic field around the core reduces to zero but the magnetic flux does not reach zero due to the residual magnetism present within the core and this is shown on the curve from point a to point b. To reduce the flux density at point b to zero we need to reverse the current flowing through the coil. The magnetising force which must be applied to null the residual flux density is called a "Coercive Force". This coercive force reverses the magnetic field rearranging the molecular magnets until the core becomes unmagnetised at point c. An increase in the reverse current causes the core to be magnetised in the opposite direction and increasing this magnetisation current will cause the core to reach saturation but in the opposite direction, point d on the curve which is symmetrical to point b. If the magnetising current is reduced again to zero the residual magnetism present in the core will be equal to the previous value but in reverse at point e.

Again reversing the magnetising current flowing through the coil this time into a positive direction will cause the magnetic flux to reach zero, point f on the curve and as before increasing the magnetisation current further in a positive direction will cause the core to reach saturation at point a. Then the B-H curve follows the path of a-b-c-d-e-f-a as the magnetising current flowing through the coil alternates between a positive and negative value such as the cycle of an AC voltage. This path is called a magnetic hysteresis loop.

The effect of magnetic hysteresis shows that the magnetisation process of a ferromagnetic core and therefore the flux density depends on which part of the curve the ferromagnetic core is magnetised on as this depends upon the circuit's past history giving the core a form of "memory". Then ferromagnetic materials have memory because they remain magnetised after the external magnetic field has been removed. However, soft ferromagnetic materials such as iron or silicon steel have very narrow magnetic hysteresis loops resulting in very small amounts of residual magnetism making them ideal for use in relays, solenoids and transformers as they can be easily magnetised and demagnetised. Since a coercive force must be applied to overcome this residual magnetism, work must be done in closing the hysteresis loop with the energy being used being dissipated as heat in the magnetic material. This heat is known as hysteresis loss, the amount of loss depends on the material's value of coercive force. By adding additives to the iron metal such as silicon, materials with a very small coercive force can be made that have a very narrow hysteresis loop. Materials with narrow hysteresis loops are easily magnetised and demagnetised and known as soft magnetic materials.

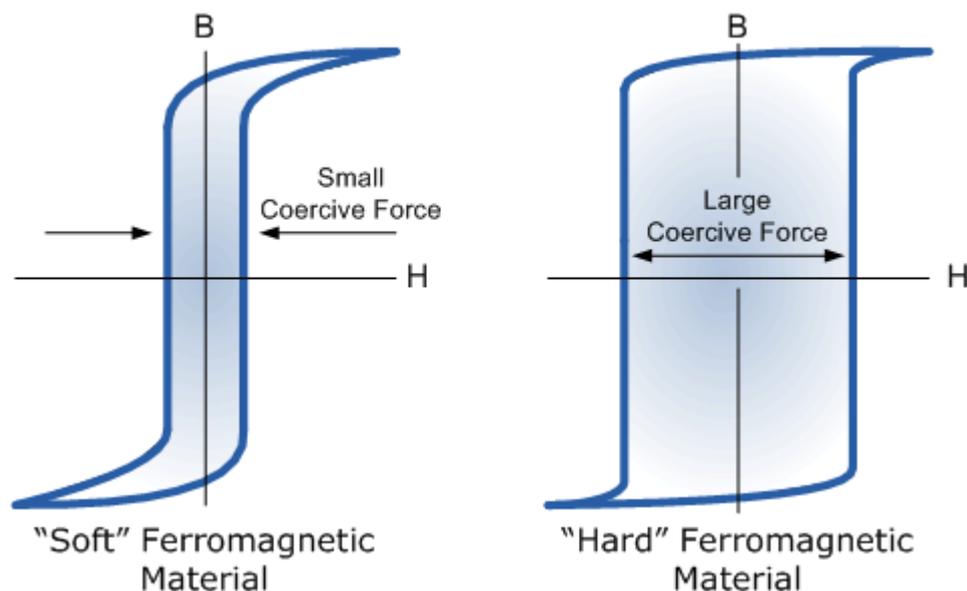


Fig. 2.13:Hysteresis loops of soft and hard magnetic material

Magnetic hysteresis results in the dissipation of wasted energy in the form of heat with the energy wasted being in proportion to the area of the magnetic hysteresis loop. Hysteresis losses will always be a problem in AC transformers where the current is constantly changing direction and thus the magnetic poles in the core will cause losses because they constantly reverse direction. Rotating coils in DC machines will also incur hysteresis losses as they are alternately passing north the south magnetic poles. The shape of the hysteresis loop depends upon the nature of the iron or steel used and in the case of iron which is subjected to massive reversals of magnetism, for example transformer cores, it is important that the B-H hysteresis loop is as small as possible.

2.5.4 Exchange interactions

Magnetism in transition metal oxides is observed to be rather complex than that of individual isolated atoms because of the presence of coupling of atomic moments. This coupling of moments is responsible for cooperative nature of magnetism in transition metal oxides. The statistical correlation for electrons of like spin, with each surrounded by a void due to local depletion of parallel spin electrons, is called exchange. There exist three types of magnetic interactions direct exchange, double exchange and super-exchange.

2.5.4.1 Direct exchange interaction

When the individual moments are located close enough to allow sufficient overlap of their wave functions, the direct exchange can occur. In such conditions minimum Coulomb's interactions will be experienced when electrons are located between the nuclei. The electrons in such a condition should have opposite spins which results in anti-ferromagnetism. While ferromagnetism is observed when the moments are arranged parallel to each other, which is possible only when the electrons are located far from one another. Such a magnetic dipole-dipole interaction would be too small by a factor at least 10^3 to explain the observed Curie temperatures. The interaction can be explained on the basis of an exchange force, which is quantum mechanical in origin; according to Heisenberg. The exchange energy E_{ex} between two atoms having spins S_i and S_j is given simply by

$$\begin{aligned} E_{ex} &= -2J_{ex} S_i \cdot S_j \\ &= -2J_{ex} S_i S_j \cos\theta \end{aligned} \quad (2.2)$$

Where J_{ex} is called exchange integral which occurs in the calculation of the exchange effect and it is a measure of the extent to which the electronic charge distributions of the two atoms concerned overlap one another, and θ is the angle between the spins. If J_{ex} has a positive value then the exchange energy E_{ex} is minimum when electron spins are parallel i.e., $\theta = 0$ (ferromagnetism). If J_{ex} has negative value, then E_{ex} is minimum when electron spins are anti-parallel; i.e., $\theta = 180^\circ$ (antiferromagnetism).

2.5.4.2 Super-exchange interaction

The oxide ion has a very small interaction magnitude with metallic ions in its ground state because of a completely filled 2p orbital. The super exchange interaction has been proposed for the case in which there is a mechanism of excitation from this ground state as the interaction can only take place in the excited state with the metallic ion. The possible excitation mechanism involves the temporary transfer of one oxide 2p electron to a neighboring metal ion. Qualitatively we can describe the superexchange interaction by considering the

following example of ferric ions in an oxide (Fig 2.5). We go from a ground state of these ferric ions in which the five $3d$ electrons according to Hund's rule are all aligned parallel to each other. The six $2p$ electrons of the oxygen ion form three pairs. The spin of electrons in each of these pairs is paired and they reside in a dumb-bell shape p -orbital. In an excited state the electron from the nearby oxide ion leaves the p -orbital and becomes (temporarily) part of Fe^{3+} ion, which becomes Fe^{2+} on gaining Néel electron. The transfer process in which we have one Fe^{3+} ion on one side of the oxygen and another Fe^{3+} ion on the other side is given as shown in (Figure 2.14).

The one Fe^{3+} ion now becomes a Fe^{2+} ion. The unpaired electron of the oxygen p orbital which was directed toward the Fe^{3+} ions now can interact with the Fe^{3+} ion present on the opposite side.

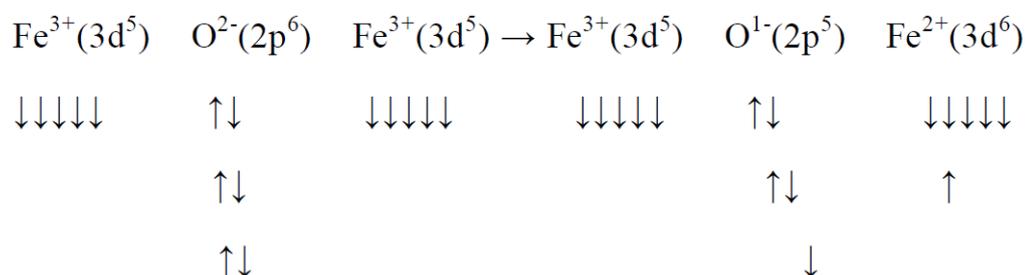


Fig.2.14. Super-exchange Interactions [15]

The overall coupling between the cations depends on a combination of direct exchange, excitation and intra-atomic (Hund's Rule) coupling, and is known as super exchange. If the $3d$ orbital of the metal ions are less than half full, the super exchange should favour a positive interaction; for $3d$ shells which are half filled or more than half filled, e.g. Fe^{3+} ion, a negative interaction with anti-parallel spin is probable. It is generally assumed that this super exchange interaction diminishes rapidly as the distance between the ions increases. The dumbbell shape of the $2p$ orbital makes it reasonable to assume that the interaction for a given ionic separation is greatest when the metal oxygen-metal angle is 180° and is least when this angle is 90° . Thus in a spinel lattice the A interaction is relatively strong, the A - A interaction is relatively weak and the B - B interaction is probably intermediate [15].

2.5.5 Magnetic anisotropy

In most magnetic materials, to varying degree, the magnetization tends to align itself along one of the main crystal directions. That direction is called the easy direction of magnetization. All ferromagnetic and ferrimagnetic materials possess, to a lesser or greater degree, a crystal direction or a set of directions in which the magnetization prefers to be oriented [16].

This magnetic anisotropy can have various causes. The most important in magnetic materials are the shape and magneto crystalline anisotropies. Shape anisotropy is associated with the geometrical shape of a magnetized body, and refers to the preference that the polarization in a long body is for the direction of the major axis. The magneto crystalline anisotropy is associated with the crystal symmetry of the material. There are three situations that give rise to this anisotropy as an intrinsic crystal property. The first and most important one is that in which the atoms possess an electron-orbital moment in addition to an electron-spin moment. In such a situation the spin direction may be coupled to the crystal axis. This arises through the coupling between spin and orbital moments and the interaction between the charge distribution over the orbit and the electrostatic field of the surrounding atoms. There will then be one or more axes or surfaces along which magnetization requires relatively little work. The crystal will then be preferentially magnetized along such an easy axis or plane. The second situation is encountered in non-cubic crystal lattices. In these crystals the magneto-static interaction between the atomic moments is also anisotropic, which may give rise to easy directions or planes of magnetization. The third possibility of crystal anisotropy is found in the directional ordering of atoms as described by Néel [12]. This typically involves solid solutions of atoms of two kinds, A and B, linked by the atomic bonds *A-A*, *A-B* and *B-B*. In the presence of a strong external magnetic field the internal energy of these bonds may be to some extent direction-dependent. Given a sufficient degree of atomic diffusion-as a result of raising the temperature, for example-a certain ordering can be brought about in the distribution of the bonds; in this way it is possible to "bake" the direction of this field into the material as the easy axis of

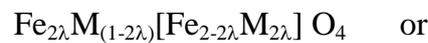
magnetization. In addition to these sources of magnet to crystalline anisotropy mechanical stresses may contribute through the magneto-elastic (magnetostrictive) properties of the crystal. This contribution, however, is considered to be negligible in hard magnetic materials [16].

2.6 Neel's theory

Neither ferromagnetism nor antiferromagnetism could explain the magnetic behavior of ferrite Material. If the situation is assumed as ferromagnetic, one Fe^{++} and the two Fe^{+++} ions per molecule were lined up parallel to one another would give $14 \mu_B$ per molecule but the experimental value comes around $4.2 \mu_B$. To explain this observed behavior Neel assumed that a ferrimagnetic crystal lattice could be divided into two sub lattice such as would be formed by the A (tetrahedral) and B (octahedral) sites in the spinel structure [12]. He supposed the existence in the material of one type of magnetic ion only, of which a fraction λ appeared on A site and a fraction μ on B-sites. Thus,

$$\lambda + \mu = 1 \quad 2.3$$

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,



Where the bracketed ions are those on the octahedral sites.

Since an A- ion has near neighbors 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 neighbors 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 favor the alignment of the magnetic moment of each A- on 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 moment of $5\mu_B$ magneton (μ_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 view point. The magnetic field action upon an ion is written in the form

$$H = H_0 + H_m \quad 2.4$$

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,

$$H_A = H_{AA} + H_{AB} \quad 2.5$$

$$H_B = H_{BB} + H_{BA} \quad 2.6$$

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,

$$H_{AA} = \gamma_{AA} M_A, \quad H_{AB} = \gamma_{AB} M_B \quad 2.7$$

$$H_{BB} = \gamma_{BB} M_B, \quad H_{BA} = \gamma_{BA} M_A \quad 2.8$$

where, the γ '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 sub lattices were identical. Neel showed that $\gamma_{AB} < 0$, favouring anti parallel arrangement of M_A and M_B , gives rise to ferrimagnetism.

In the presence of an applied field H_0 , the total magnetic fields acting on each sub lattice may be written, using equations (2.5) and (2.8)

$$H_a = H_0 + H_A = H_0 + \gamma_{AA} M_A + \gamma_{AB} M_B \quad 2.9$$

$$H_b = H_0 + H_B = H_0 + \gamma_{BB} M_B + \gamma_{AB} M_A \quad 2.10$$

2.7 Yafet-Kittel theory

Experimentally it is observed that the saturation magnetization of a ferrite initially increases up to 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-lattice 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 θ_{YK} with the direction of net magnetization of B sub-lattices at 0K. To calculate the uniform canting angle θ_{yk} a split sub-lattice model was developed by Yafet-Kittel.

Yafet-Kittel model can be understood from $Ni_{1-x}Zn_xFe_2O_4$ ferrite system. For pure nickel ferrite ($NiFe_2O_4$) 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 on B-site. The Yafet-Kittel model splits B sub-lattice into B_1 and B_2 sub-lattices each making an angle θ_{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

$$\mu_{(x)} = M_B \cos \theta_{YK} - M_A \quad 2.11$$

Where M_A is magnetic moment on A site, M_B is magnetic moment on B site.

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