Chapter 2

Spinel ferrites: crystal structure and chemistry
2.1 History of Ferrites

The first type of magnetic material known to man was in the form of lodestone, consisting of the ore magnetite. This is believed to have been discovered in ancient Greece around the time period of 800 BC. The deposits of stones were found in the districts of Magnesia in Asia Minor; hence the mineral’s name became magnetite (Fe₃O₄). Much later, the first application of magnetite was as ‘Lodestones’ used by early navigators to locate magnetic North. A milestone in the history of magnetism was the work done by William Gilbert in 1600. His work “De Magnete” described the magnetic properties of lodestone up to that point in the time.

The term “ferrite” is derived from the Latin word “ferrum”, meaning iron. Ferrites are homogeneous ceramic materials composed of various oxides containing iron oxide as their main constituent [1]. The term “ferrite” means different to different scientists. To metallurgists, ferrite means pure iron. To geologists, ferrites are a group of minerals based on iron oxide. To an electrical engineer, ferrites are a group of materials based on iron oxide, but one that have particular useful properties: magnetic and dielectric. Magnetite or lodestone is a naturally occurring iron oxide that is considered a ferrite by both geologists’ and engineers. Over 2,000 years ago, the Greeks recognized the strange properties of lodestone, and almost 1,000 years ago the Chinese used it to invent the magnetic compass. Dielectric properties mean that even though electromagnetic waves can pass through ferrites, they do not readily conduct electricity. This gives them an advantage over iron, nickel and other transition metals that have magnetic properties (“ferromagnetic”) in many applications because these metals also conduct electricity. Magnetite, i.e., Fe²⁺Fe²⁺O₄ (Fe₃O₄) is a naturally occurring ferrite. The first artificial ferrite was actually made in 1909 by Hilpert. Since the method of producing ferrite involves more chemistry than physics, it was not until 1940 that methods of controlling the ferrite composition were developed.

In 1947, J.L.Snoek published the book, New Developments in Ferromagnetic Materials. Studies done by Snoek and others at Phillips Laboratories in the Netherlands led to magnetic ceramics with strong magnetic properties, high electrical resistivity [2]. At about the same time, in 1948, L.Neel announced his celebrated
theoretical contribution on ferrimagnetism [3]. This dealt with the basic phenomenon of “spin-spin interaction” taking place in the magnetic sublattices in ferrites. The stage was now set for the development of microwave ferrite devices. In 1956, Neel, Bertaut, Forrat and Pauthenet discovered Garnet ferrite class of materials which possess extremely low ferromagnetic line width [4]. Another class of ferrite material that was developed during this time is the hexagonal ferrite with hexagonal structure. In 1959, J.Smit and H.P.J.Wijn published a comprehensive book on ferrite materials entitled Ferrite [5]. With these publications and results, ferrites hold the main position in worldwide research on magnetism, which it retains to recent stage.

2.2 Importance of Ferrites

Ferrites are homogeneous ceramic materials composed of various oxides being Iron oxide (Fe₂O₃) their main constituent. Strictly speaking all substances are magnetic, but only ferromagnetic and ferrimagnetic substances, which are capable of being magnetized by relatively weak field, are referred to as magnetic materials. The simplest class of magnetic material is the elemental magnetic materials; only few like Fe, Co, Ni, Dy and Gd qualify to be in this category. They are best suited for the study of magnetism and magnetic phenomena. Alloys containing magnetic elements, Mn, rare earth elements etc. often show magnetic ordering. Their properties depend a lot on the elements present, and their composition. These alloys have a broad range of applications. The well-studied Alnicos steel is widely used as the basic materials for permanent magnets because of its high coercivity. This ensures that these materials are not magnetically altered by weak field intensities. The other important alloy used in heavy current engineering is Fe-Si alloy because of low eddy current losses. Fe-Al and Fe-Al-Si also fall in this category and are used in the current engineering. Alloys of Fe-Ni, Fe-Co, and Fe-Ni-Mo/Cr/Co/Cr are used as core of inductors and transformers. Apart from these there are many alloys, which can be used as materials for information storage, magneto-mechanical resonators, temperature compensator in magnetic circuits etc.

The magnetic oxides, especially ferrites are the modern day materials with uses in transformer cores, magnetic recording and information storage devices, etc.
Ceramic ferrimagnetic materials composed of mixed oxides of inorganic materials and transition metals, one of which is ferric oxide (Fe$_2$O$_3$) are termed as ferrites. The rapid expansion of technology had been a great motivation for research in the field of ferrites. Apart from technological and experimental research, the developments of theoretical description of magnetic properties of these oxides have made many advances. The outstanding fact about the ferrites is that they combine extremely high electrical resistivity with reasonable good magnetic properties.

Ferrites are useful in the electronics industry due to a combination of two key characteristics:

I. high magnetic permeability, which concentrates the magnetic-flux density, and
II. high electrical resistivity, which limits the amount of electric current flow in the ferrite.

Thus, ferrites exhibit low energy losses are efficient and functional at high frequencies (1MHz to 1GHz). These qualities make ferrites good design devices for the manufacture of small high-frequency electronic components. Some of the more common use of ferrite includes magnetic devices, power transformer and chokes, inductors and tuned transformers, pulse and wide-band transformers, magnetic deflection systems, recording heads, rotating transformers and shield beads. Ferrites are manufactured in several different shapes like toroids, beads, rods, cylinders, blocks and multihole and in different sizes.

### 2.3 Classification of Ferrites

According to the nature of the magnetic properties, Ferrites are usually classified as soft ferrites and hard ferrites which refer to their low or high corecivity of their magnetism, respectively. Soft magnetic materials are used in devices (such as transformer core) that are subjected to alternating magnetic field and in which energy loses must be low. Hard magnetic materials or hard ferrites are utilized in permanent magnets, which has high remanence, corecivity, saturation flux density as well as low initial permeability and high hysteresis energy loss.

- **Soft Ferrites** and its application:
Soft ferrites are ceramic electromagnetic material, dark grey or black in appearance and very hard and brittle. The terms “SOFT” has nothing to do with their physical properties but refers to their magnetic characteristics. Soft ferrite dose not retain significant magnetization. Soft ferrite is the general term to a class of ceramic and electromagnetic materials. From the crystallographic aspect, soft ferrites are inverse spinels and belong to the cubic crystal system. The most important type in terms of output is Mn-Zn ferrite (MnZnFe$_2$O$_4$) and Ni-Zn ferrite (NiZnFe$_2$O$_4$). A soft ferrite’s magnetic properties arise from interactions between metallic ions occupying particular positions relative to the oxygen ions in its spinel crystalline structure. The magnetic domain theory suggests these interactions create magnetic domains, which are microscopic magnetized regions within the material. When no magnetizing force is present, the magnetic domains are random and the net flux contribution is zero even though local domains are fully magnetized. When a magnetizing force is present the magnetic domains align in the direction of the magnetizing force resulting in a large net flux contribution. Soft magnetic materials have high initial permeability and low corecivity (easily magnetized and demagnetized). Low value of corecivity, gives easy movement of domain walls but they are restricted by the structural defects like voids or any nonmagnetic phases, so soft magnetic materials are must be free of such structural defects. They have also high electrical resistivity.

Soft ferrites are used mainly in radio and television engineering, telephony and telegraphy. For example, ferrite coils, shell cores, pot cores, E-cores, cross cores, loading coils etc., of ferrite materials, are used in telephone engineering. The development of modern radio, television and telecommunications engineering would have been impossible in the absence of such ferrite components as U–cores for transformers, yoke rings, intermediate frequency band filters and balancing transformers. They also serve as magnetostriction vibrators in high frequency heating devices and many other electrical apparatus.

- **Hard Ferrite**

In the case of hard ferrites, a strong magnetization remains after a magnetizing field has been removed and residual magnetization is stable even if certain strength of demagnetizing field is applied. These characteristics are valuable in making
permanent magnets. For hard ferrites, however, there is a considerable difference between the $B - H$ curve and the $M - H$ curve, in which $M$ shows the magnetization. Naturally occurring magnetite is a weak hard ferrite. Hard ferrites possess magnetism, which is essentially permanent.

The most important of these permanent magnetic materials in practical use are barium ferrite (BaO. $6\text{Fe}_2\text{O}_3$) and strontium ferrite (SrO. $6\text{Fe}_2\text{O}_3$). Since they have a larger coercive force than metallic magnetic materials, it is possible to design very thin magnets. Compared with soft magnetic ferrite, hard magnetic ferrite is weak in structural sensitivity, and is relatively little influenced by impurities and by firing conditions. Two classes of hard magnets, comprising oriented (anisotropic) and non-oriented (isotropic) ferrites, are distinguished.

Hard ferrites as permanent magnets play an important role in many electromechanical and electronic devices used in domestic and professional appliances. Magnetic resonance imaging used, as a medical diagnostic tool is an example of professional appliance where large amounts of permanent magnets are used. Apart from the many domestic and professional appliances, information technology, automotive and aerospace systems are significant users of permanent magnets, in particular actuators and motion systems. The most common types of magnets applied at present are alnico type magnets, hard ferrite magnets and rare-earth based magnets (SmCo, NdFeB).

- **Structural Classification of Ferrites**

  However, in most of the research work done on ferrites, scientists classify the ferrites according to their crystal structure. Hence technically speaking, we have four important classes of ferrites: (i) spinel
  (ii) garnet
  (iii) hexaferrite and
  (iv) orthoferrite.
Table 2.1 Different types of ferrites with their structures, general formulae and examples

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>General Formula</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>Cubic</td>
<td>$A^{II}\text{Fe}_2\text{O}_4$</td>
<td>$A^{II}$ - Mn, Zn, Ni, Mg, Co etc.</td>
</tr>
<tr>
<td>Garnet</td>
<td>Cubic</td>
<td>$\text{Ln}^{III}_3\text{Fe}<em>5\text{O}</em>{12}$</td>
<td>$\text{Ln}^{III}$ - Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Lu</td>
</tr>
<tr>
<td>Magnetopluhmite</td>
<td>Hexagonal</td>
<td>$\text{A}^{II}\text{Fe}<em>{12}\text{O}</em>{19}$</td>
<td>$\text{A}^{II}$ - Ba, Sr</td>
</tr>
<tr>
<td>Orthoferrites</td>
<td>Pervoskite</td>
<td>$\text{Ln}^{III}\text{FeO}_3$</td>
<td>$\text{Ln}^{III}$ – same as garnets</td>
</tr>
</tbody>
</table>

- **Spinel Ferrites**:

  The spinel is by far the most widely used ferrite, so much so that the term is almost synonymous with the word “ferrite”. The spinel structure is derived from the mineral spinel (MgAl$_2$O$_4$ or MgO.Al$_2$O$_3$), that crystallizes in the cubic system. This crystal structure was first determined by Bragg [6] and by Nishikawa [7]. Analogous to the mineral spinel, the magnetic spinel has the general formula MeO.Fe$_2$O$_3$ or MeFe$_2$O$_4$ where Me is the divalent metal ion. The detailed description of spinel structure has been discussed in next subsection.

- **Garnet Ferrites**:

  These are the ferrites that can accommodate large trivalent rare earth ions with large magnetic moments. Garnet ferrites have the structure of the silicate mineral garnet. Magnetic garnets crystallize in the dodecahedral or 12-sided structure related to the mineral garnet. The general formula is Me$_3$Fe$_5$O$_{12}$. It is to be noted that in this case all the metal ions are trivalent in contrast to the other two classes. In the important magnetic garnets, Me is usually Yttrium (Y) or one of the rare earth ions. The crystal structure and the unit cell dimensions of the rare earth iron garnets were first reported by Bertaut and Forrat [4], then by Geller and Gilleo [8] and Gilleo and Geller [9,10].
The garnet structure is particularly stable because all the sites are occupied by cations. This contributes to the high stability of this compound.

- **Hexagonal Ferrites**:

  This class of magnetic oxides has magnetoplumbite structure [11] which comes from the mineral of the same name. The so-called hexagonal ferrites have the formula MeFe$_{12}$O$_{19}$, where Me is usually Ba, Sr or Pb. The symmetry of the magnetoplumbite structure is hexagonal. Thus, it has a major preferred axis called the c-axis and a minor axis called a-axis. The preferred direction is used to good advantage as a permanent magnet material. Most of these compounds are ferrimagnetic but some are antiferromagnetic. They were first developed by Went et al [11], Fahlenbrach and Heister [12]. The best known compounds in this class are BaFe$_{12}$O$_{19}$, SrFe$_{12}$O$_{19}$ and PbFe$_{12}$O$_{19}$. Further studies in the ternary system BaO – FeO – Fe$_2$O$_3$ have led to the discovery of many other compounds having related hexagonal structures [13]. The complex crystal structures of these compounds were established by Braun [14].

- **Ortho Ferrites**:

  Apart from the hexagonal, spinel and garnet ferrites, the next important structure is the orthoferrite or perovskite structure. The formula is RFeO$_3$ where R is usually Yttrium or a rare earth ion. These are also cubic ferrites but having a slightly distorted perovskite structure. Perovskite structure is the name given to the atomic arrangement of the oxides having the formula RMO$_3$ e.g., BaTiO$_3$, PbTiO$_3$ etc. This structure is often acquired by a material, which have a complicated molecular arrangement consistent with cubic symmetry. The structure is orthorhombic rather than cubic. The canting or non-parallel alignment of the antiferromagnetically coupled ions leads to weak ferromagnetism in the perovskite structured materials. These compounds have the structure formed by the superposition of a canted spin antiferromagnetic sublattice M and sublattice R that is magnetically ordered at low temperature and is paramagnetic at higher temperature. The rare earth iron perovskites are also known as “Orthoferrite” [15]. They were first studied by Forestier and Guillot.
– Guillain [16] and then by Pauthenet and Blum [17]. They observed that these rare earth iron perovskites have a parasitic ferromagnetic moment at room temperature and the curie points are about 700 °K. Real progress in the magnetic properties was achieved with the successful growth of perovskite single crystals [18] and the structure determination of GdFeO$_3$ [19, 20]. The crystal structure of GdFeO$_3$ and YFeO$_3$ has been of single crystals were measured by Bozorth et al [21, 22], Bozorth and Kramer [23] and Treves [24], and the magnetic structure was established with neutron diffraction by Koehler and Wollan [25]. Mössbauer studies were reported by Eibschutz et al [26]. The practical importance of the orthoferrites rested in their applications in the original bubble memory structures.

Considering the crystal structure and magnetic ordering, out of the four types of ferrites mentioned above the simplest ferrite is the spinel type and form a major class. The Spinel and Garnet are soft ferrites whereas Magnetoplumbite and the Orthoferrites are hard ferrites.

### 2.4 Crystal structure and Chemistry of spinel Ferrites

- **Spinel structure:**

  The spinel crystal structure is the most well-known, diverse and useful example of uncompensated antiferromagnetism. The spinel structure is named after the mineral spinel (MgAl$_2$O$_4$) and can be represented as M$'$ M$''$$_2$ X$_4$ , where X represents oxygen or one chalcogenic bivalent anion (S$^{2-}$, Se$^{2-}$, Te$^{2-}$)and M$'$ and M$''$ are metallic ions. The valences have to fulfill the electroneutrality requirements. Due to large electronegativity of Oxygen, the ionic type of bonds prevails in almost all oxide spinels. The crystallographic structure is formed by a nearly closed packed face centred cubic (fcc) array of anions with two inequivalent sites for cations. These differ in oxygen coordination; four oxygen ions surround tetrahedral cationic sites and octahedral sites by six oxygen ions. These are also called A and B sites, respectively. In a cubic unit cell, 64 tetrahedral sites and 32 octahedral sites are present. Of which only 8 and 16 respectively are occupied by metal ions. The crystal structure is best described by subdividing the unit cell into eight octants, with edge $\frac{1}{2}$ a (‘a’ is edge of the unit cell) as shown in Fig.2.1. The location of oxygen ions and metal ions in every
octant then can be easily described and accordingly the geometry of the occupied interstitial sites is shown in Fig. 2.2, where the primitive cell contains two formula units is shown [5].

**Fig.2.1** Eight octants of unit cell of spinel ferrite. The location of metal ions in four shaded and unshaded octants are identical

**Fig.2.2** The geometry of the occupied interstitial sites in Spinel structure

Tetrahedral (A)  Octahedral (B)
The symmetry of the structure is cubic and belongs to the space group $\text{Oh}^7 (\text{Fd}^3\text{m})$. A small displacement defined by a single parameter $u$ of the anions, from their ideal position is allowed along the corresponding body diagonal which enables a better matching of anion positions to the relative radii of A and B cations. For the ideal closed packed anion lattice, $u = 3/8$, but in real situations it is more than $3/8$. The local symmetry of the cation sites is cubic in the case of tetrahedral (A) site and trigonal in the case of octahedral (B) site, the trigonal axis being one of the body diagonals. The trigonal symmetry is due to both the configurations of neighbouring cations and the distortion of the anion octahedron if $u \neq 3/8$. Each of the body diagonals belongs to just one of the B cations in the primitive cell. On the other hand the local symmetry of the A positions remain cubic even if $u \neq 3/8$. When considering the aspects for which the local symmetry is irrelevant, all the A positions may be treated as belonging to one sublattice 13 (tetrahedral or A), and all the B positions may be unified to form another sublattice (octahedral or B).

Both translational and local symmetries corresponding to the $\text{Oh}^7$ space group strictly apply only if each sublattice contains only one kind of cations, i.e. if all M’ ions in $\text{M’ M”}_2 \text{X}_4$ are in tetrahedral and all M” ions are in octahedral positions. The spinel is then called normal spinel. We also have so called inverse spinel structure in which half the cations M” are in A positions and the rest, together with the M’ ions, are randomly distributed among the positions. There are many examples of intermediate cases between a normal and an inverse spinel where a fraction of M’ and M” ions are inverted, that is M’ occupies B positions and M” occupies A positions. They are termed as partially inverse spinels. Therefore, in order to characterize the spinel structure fully, a further parameter is needed describing the degree of inversion. The formula may be explicitly written as,

$$\left(\text{M’}_{1-\delta} \text{M”}_\delta\right) \left[\text{M’}_\delta \text{M”}_{2-\delta}\right] \text{X}_4,$$

where $\delta$ is known as inversion parameter, and is equal to zero in case of normal spinel spinel and one in case of inverse spinel. As a part of convention, the cations at tetrahedral (A) sites are written in parentheses and those at octahedral (B) sites in square brackets.
The electroneutrality leads to three basic types, according to the cation valency combinations. These are,

\[ M^{n+} M'^{n'+} O_4: \text{(2-3 spinel)}, \text{e.g. NiFe}_2O_4, \text{CuFe}_2O_4 \]
\[ M^{n'+} M'^{n+} O_4: \text{(4-2 spinel)}, \text{e.g. GeFe}_2O_4, \text{TiFe}_2O_4 \]
\[ M^{6+} M'^{1+} O_4: \text{(6-1 spinel)}, \text{e.g. MoLi}_2O_4, \text{WAg}_2O_4 \]

It is found that practically any cation with radius within the limits 0.4 to 1Å may be incorporated into the spinel structure and most of them can occur in both octahedral and tetrahedral positions. The smallest cations with valency \( \geq 4 \), however, are found in the tetrahedral coordination only, while the monovalent cations occurring mainly in 6-1 spinels are confined to the octahedral sites. Besides the geometrical factors, the distributions of cations among A and B positions is influenced by many other factors.

The interstices available for cations in the spinel structure have radii,

\[ R_{tetra} = (u - 0.25) a (1.73) - r (O^2) \]
\[ R_{octa} = (0.625 - u) a - r (O^2) \]

- **Crystal field splitting of energy levels and John-Teller Effect:**

With respect to the magnetic properties, the interest is primarily in transition metal ions particularly those of 3d\(^n\) group. The outer d-electrons of these ions may be regarded as practically localized in almost all oxide spinels so that the crystal (or ligand) field theory applies. This theory says that the low lying energy levels are decisive for the magnetic behaviour. The origin of the ligand field splitting of levels is attributed to both the electrostatic crystal field and the covalency between the cation and the surrounding anions (ligands). Both these effects contribute to the stabilization of cations in the given surrounding. Crystal or ligand field stabilization energy = lowering of the ground level with respect to the ground level of the free ion. In an octahedral environment, the five d orbitals on a transition metal atom are no longer
degenerate but split into two groups, the \( t_{2g} \) group of lower energy and the \( e_g \) group of higher energy as shown in Fig. 2.3. If possible, electrons occupy orbitals singly, according to Hund’s rule of maximum multiplicity. For \( d^4 \) to \( d^7 \) atoms or ions, two possible configurations occur, giving low spin and high spin states; these are shown for a \( d^7 \) ion in Fig. 2.4. In these, the increased energy, \( \Delta \), required to place an electron in an \( e_g \) orbital, and hence maximize the multiplicity, has to be balanced against the repulsive energy or pairing, \( P \), which arises when two electrons occupy the same \( t_{2g} \) orbital. The magnitude of \( \Delta \) depends upon the ligand or anion to which the metal ion is bonded: for weak field anions (ligands), \( \Delta \) is small and the high spin state configuration occurs, and vice versa for strong field ligands. For magnitude of \( \Delta \), generally \( \Delta(5d) > \Delta(4d) > \Delta(3d) \). Consequently the high spin behaviour is rarely observed in the 4d and 5d series.

**Fig. 2.3** Crystal field splitting of Energy level and spin states in octahedral coordination.
In many transition metal compounds, the metal coordination is distorted octahedral and the distortions are such that the two axial bonds are either shorter than or longer than the other four bonds. The John-Teller effect \([27, 28]\) is responsible for these distortions in \(d^9\), \(d^7\) (low-spin) and \(d^4\) (high spin) ions. Consider the \(d^9\) ion Cu\(^{2+}\) whose configuration is \((t_{2g})^6 (e_g)^3\). One of the \(e_g\) orbitals contains two electrons and the other contains one. The singly occupied orbital can be either \(d_{z^2}\) or \(d_{x^2-y^2}\) and in a free ion situation both would have the same energy. However, since the metal coordination is octahedral the \(e_g\) levels, with one doubly and one singly occupied orbitals, are no longer degenerate. The \(e_g\) orbitals are high energy orbitals (relative to \(t_{2g}\)) since they point directly towards the surrounding ligands and the doubly occupied orbital will experience stronger repulsions and hence have somewhat higher energy than the singly occupied orbital. This has the effect of lengthening of the metal-ligand bonds in the directions of the doubly occupied orbital, e.g. if the \(d_{z^2}\) orbital is doubly occupied, the two metal-ligand bonds along the \(z\) axis will be longer than the other four metal-ligand bonds. The energy level diagram for this latter situation is shown in Fig.2.5. Lengthening of the metal-ligand bond along the \(z\)-axis leads to a lowering of the \(d_{z^2}\) orbital. The distorted structure is stabilized by an amount \((\frac{1}{2})\delta_2\) relative to the regular octahedral arrangement and, hence, the distorted structure becomes the observed, ground state.

In the oxide spinels, the cooperative Jahn-Teller effect is frequently encountered. The necessary condition for this to appear is the presence of transition
metal ions which have an orbitally degenerate electronic ground state. The interaction between the degenerate states and the lattice vibrations leads to an effective coupling between electronic states on different cations. When this coupling is sufficiently strong and the concentration of active cations exceeds a certain critical value, the electronic states order and simultaneous a structural phase transition from cubic to lower symmetry appears. Thus, Jahn-Teller effect refers to the condition in which a crystal lattice is distorted from the cubic to tetragonal configuration as a consequence of the possession of some 3d orbitals of fewer electrons than other orbitals. This condition results in an electrostatic imbalance that has the effect of repelling some oxygen anions more than others.

In effect, these anions are pushed further away, thus producing the change from cubic to tetragonal symmetry. The phase with lower symmetry is stable only below a critical temperature. In the B-site, there are two ions, namely Mn$^{3+}$ and Cu$^{2+}$ both having doubly degenerate ground state of $e_g$ type, which exhibit the Jahn-Teller effect. The corresponding distortion is always tetragonal with $c/a > 1$. The CuFe$_2$O$_4$ having the degree of inversion, $0.06 < \delta < 0.24$ exhibits Jahn-Teller effect with $c/a$ ratio $\sim 1.06$ [29].

- **Chemistry of Ferrites:**

  The oxide spinels are commonly prepared at elevated temperatures by a direct solid-state reaction between the simple oxides. The relevant temperature range is about 800ºC to 1500ºC, depending on the type of cations. The thermodynamic stability of spinels compared to the constituent oxides is given by Gibbs free energy of formation ($\Delta G$) for the reaction,
  
  $$M'O + M''_2O_3 \rightarrow M'M''_2O_4$$

  The largest contribution to the crystal energy in oxide spinels comes from the Coulomb energy of the charged ions (Madelung energy),
  
  $$E_c = (-e^2 / a) A_M$$

  Where, $e$ is the charge of electron, $a$ is the lattice parameter and $A_M$ the Madelung constant. The Madelung constant, $A_M$ can be expressed as a function of the mean electric charge $q_A$ of the cations in tetrahedral positions and of the oxygen parameter $u$. With increasing $A_M$ the stability of the spinel increases. Therefore,
owing to its dependence on $q_A$, the Coulomb energy generally plays an important role in the equilibrium distribution of cations among tetrahedral and octahedral positions, even though in some cases other energy contributions may become important.

According to the formula, $(M'_1 - \delta M''_2) [M'_2 M''_1 - \delta] O_4$, oxide spinels may have various degrees of inversion. If the energy difference between two limiting cases $\delta = 1$ and $\delta = 0$ is not very large, we expect the distribution of cations to be random at high temperatures due to the prevailing influence of entropy term $-TS$ in the free energy. When the temperature is lowered, the spinel tends to be more or less normal or inverse depending on the sign and amount of energy corresponding to the interchange of cations $M', M''$ in different sublattices. The equilibrium distribution will be given by the requirement that the Gibbs free energy is minimum, i.e.

$$\frac{dG}{d\delta} = \left( \frac{dH}{d\delta} - T \frac{dS}{d\delta} \right) = 0$$

If one restricts to configurational entropy of cations and assumes total randomization in both sublattices, $S$ may be approximated by,

$$S = Nk \left[ - \delta \ln \delta + 2 (\delta - 1) - (\delta + 1) \ln (\delta + 1) \right]$$

Defining further $\Delta P = \frac{dH}{d\delta}$, we find,

$$\delta \frac{(1+\delta)}{(1-\delta)}^2 = \exp \left( - \frac{\Delta P}{RT} \right)$$

this determines the equilibrium value of $\delta$ at temperature $T$. Generally, $\Delta P$ depends on $\delta$ and frequently a linear expression $\Delta P = H_0 + H_1 \delta$ is used to describe the experimental results. Here, $H_0$ and $H_0 + H_1$ may be interpreted as energies connected with interchange of ions $M', M''$ from different sublattices in the case completely normal and inverse distribution, respectively.

When $\Delta P < 5$ kCal/mol, a partially inverted spinel is usually observed. Otherwise, the energy difference between the normal and inverse structures is sufficient for the spinel to attain either normal or inverse structure. Once again the main contributions to $\Delta P$ come from Madelung energy, Born repulsion energy and further from polarization and ligand field effects. On the basis of systematic studies of cation distribution in various spinels it has been recognized that some regularities exist in them pointing to the possibility to connect the distribution to individual site preference of cations. In such a case, the energy $\Delta P$ can be expressed as a difference $\Delta P = P(M') - P(M'')$, of individual preference energies $P$ of cations $M'$ and $M''$. Once $P(M')$ and $P(M'')$ are known for all relevant cations, the distribution of ions in
arbitrary spinel could be predicted. The values of \( P(M) \) for different spinels are shown in Fig.2.5

![Graph showing cation site preference energy for various transition metal ions](image)

**Fig.2.5** Cation site preference energy for various transition metal ions

Chemistry, crystal structure and microstructure determine the engineering material characteristics of ferrites. Many desirable combinations of chemical ingredients and basic structure cannot be obtained because some ions are incompatible with certain crystal structures despite the best efforts of materials scientists. Microstructure includes the size and number of voids, size of grains, and presence of grain boundary phases, grain shape and orientation.

In essence, microstructure is the architecture of the materials that is, how the various phases and crystalline are put together, their particular patterns and arrangements, and how these are joined. Ferrite microstructures are extremely sensitive to processing because the pre-reaction and grinding of raw materials, forming technique employed, sintering time and temperature and cooling conditions influence crystal composition and size, and also the size and volume of pores.
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