

Chapter-1

Introduction

General Introduction

Nanoscience and nanotechnology related to the synthesis, characterization, development and utilization of nanostructured materials which are characterized by at least one dimension in the nanometer ($1\text{nm}=10^{-9}\text{m}$) range. Such nanostructured systems constitute a bridge between single molecules and infinite bulk systems. Individual nanostructures involve clusters, nanoparticles, nanocrystals, quantum dots, nanowires and nanotubes, while collections of nanostructures involve arrays, assemblies and super lattices of individual nanostructures. The dimensional range of 1 to 100 nm is referred as the nanoscale and materials at this scale are called nanocrystals or nanomaterials.

The chemical and physical properties of nanomaterials can significantly differ from those of bulk materials of same chemical composition. The uniqueness of the structural characteristics, energetic, response, dynamics and chemistry of nanostructures constitutes the experimental and conceptual background for the field of nanoscience. Suitable control of properties and response of nanostructures can lead to new devices and technologies. The underlying themes of nanoscience and nanotechnology are dual: first, the bottom-up approach of the self assembly of molecular components where each molecular or nanostructured component plugs itself into a superstructure; second, the top-down approach of miniaturization of the components.

The deviation of properties of the nano sized materials from the bulk material properties are due to surface effects which mainly depend upon the ratio of surface area to volume and size of the particles along with the chemical composition and interaction between particles.

The increase in surface to volume ratio, which is a gradual progression as the particle gets smaller, leads to an increasing dominance of the behavior of atoms on the surface of particles over that of those in the interior of particle as these atoms have lower coordination number than the interior atoms. In addition, depending on the geometry, different sites on the surface will be different in local coordination number.

In the last two decades, a class of materials with a nanometer-sized microstructure have been synthesized and studied. These materials are assembled from nanometer-sized building blocks, mostly crystallites. The building blocks may differ in their atomic structure, crystallographic orientation or chemical composition. In cases where the building blocks are crystallites, incoherent or coherent interfaces may be formed between them, depending on the atomic structure, the crystallographic orientation, and the chemical composition of adjacent crystallites. In other words, materials assembled of nanometer-sized building blocks are micro-structurally heterogeneous, consisting of the building blocks (e.g. crystallites) and the regions between adjacent building blocks (e.g. grain boundaries).The inherently heterogeneous structure on a nanometer scale that is crucial for many of their properties and also distinguishes them from glasses, gels etc., that are micro structurally homogeneous .

In recent years, a lot of work has been done on nano crystalline materials because of their unusual properties compared to the properties of bulk materials. Several research groups are involved in the investigations of spinel oxide nano particles because of their potential applications in magnetic devices, microwave technology and high-density magnetic recording media, etc.

Various types of nanoparticle materials such as metal (Fe, Co, Ni), metallic alloys (Fe-Cu) and metallic oxides (CoFe_2O_4 , MnFe_2O_4 and ZnFe_2O_4) are under current research activity. While metal and inter-metallic nanoparticles suffer from stability problems in atmospheric conditions, metallic oxides are highly stable under ambient conditions. Various factors such as, particle size distribution, inter-particle interactions grain and grain boundary structure and meta-stable structure of the system control the properties of nanoparticles. The other fields where nanostructured materials are used include electronics, medical, energy production, energy utilization, transportation and national security.

Magnetite (Fe_3O_4) is the first magnetic material known to man. In the eighteenth century, compound steel magnets were made composed of many magnetized steel strips fastened together, which could lift 28 times their own weight of iron [1]. But its power of attracting iron was certainly known for centuries. The first scientific study of magnetism was made by William Gilbert (1540 - 1603).

Magnetism was probably the first natural force discovered by man but it was only in the last century that a large usage of magnetic materials has been made. Much of the glamour of modern electronics has been centered on the semiconductor (Transistor and IC) industry but many of the devices using these new concepts would not be practical without the accompanying magnetic components. The frequency of application of magnetic materials ranges from DC to the highest ones at which any electronic device can function. The emergence of many new technologies driven by differing requirements, in turn, has lead to a large variety of magnetic materials supplied in many different shapes and sizes [2].

1.1 Types of Magnetic Materials

1.1.1 Ferrites

Ferrites are an important new class of magnetic materials, which are complex magnetic oxides containing ferric oxides like (Fe_2O_3) as their basic magnetic components and are cubic in structure. The most important development in this field was initiated by J.L.Snoek. Ferrites are classified into soft ferrites and hard ferrites depending on the properties like coercivity. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of Switched-Mode Power Supply (SMPS) and RF transformers and inductors.

Early computer memories stored data in the residual magnetic fields of hard ferrite cores, which were assembled into arrays of core memory. Ferrite powders are used in the coatings of magnetic recording tapes. One such type of material is iron (III) oxide. Ferrite particles are also used as a component of radar-absorbing materials or coatings used in stealth aircraft and in the expensive absorption tiles lining the rooms used for electromagnetic compatibility measurements. Most common radio magnets, including those used in loudspeakers, are ferrite magnets. Ferrite magnets have largely displaced alnico magnets in these applications. In entertainment applications like television picture tube, fly back transformers, radio and television antenna, magnetic materials find the vast usage. Because of the low production cost and processing techniques, most of the systems, which were not available to common man, few years back, are now readily available. One of the most amazing results in the application of nano magnetic materials is the so-called pen drive / memory stick and palm top computers which is used for data storage with high reliability.

1.1.2 Orthoferrites

One of the most important magnetic materials is the Orthoferrites or perovskite structure. The formula is $MFeO_3$, where M is usually yttrium or a rare earth material. The structure is orthorhombic rather than cubic. It exhibits weak ferromagnetism due to the canting or non-parallel alignment of the antiferromagnetically coupled ions.

Jonker and Van Santen (1953) found ferromagnetic perovskite of the type $LaCaMnO_3$ or $LaSrCoO_3$. Bertaut and Forrat (1956) determined the structure of the rare earth Orthoferrites and perovskite and it was during that period that the rare earth garnets were accidentally discovered. The practical importance of the Orthoferrites related in their application in the original bubble memory structures. They have since been replaced by anisotropic rare earth garnets.

1.1.3 Chalcogenides

Another magnetic material related to the ferrimagnetic spinels is the Chalcogenides group of the type $CdCr_2S_4$, $CdCr_2Se_4$ or $HgCr_2Se_4$. In this case, the oxygen of the ferrites is replaced by S or Se. These substances are interesting because in addition to being ferromagnetic, they are also semiconducting. It cannot complete as a semiconductor or in a purely magnetic application but in cases in which both properties are needed, there are possibilities of usage.

1.2 Magnetism in materials

1.2.1 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, as shown in Figure 1.1.

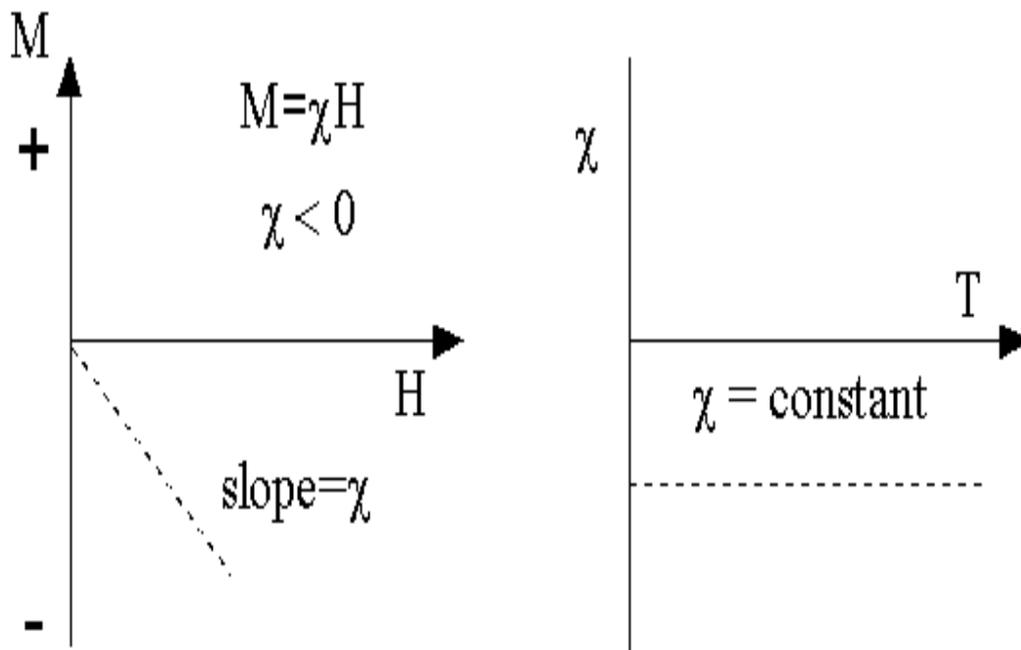


Figure 1.1: Negative and small susceptibility

1.2.2 Paramagnetism

In 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 orbital. 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 a partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility as shown in Figure 1.2.

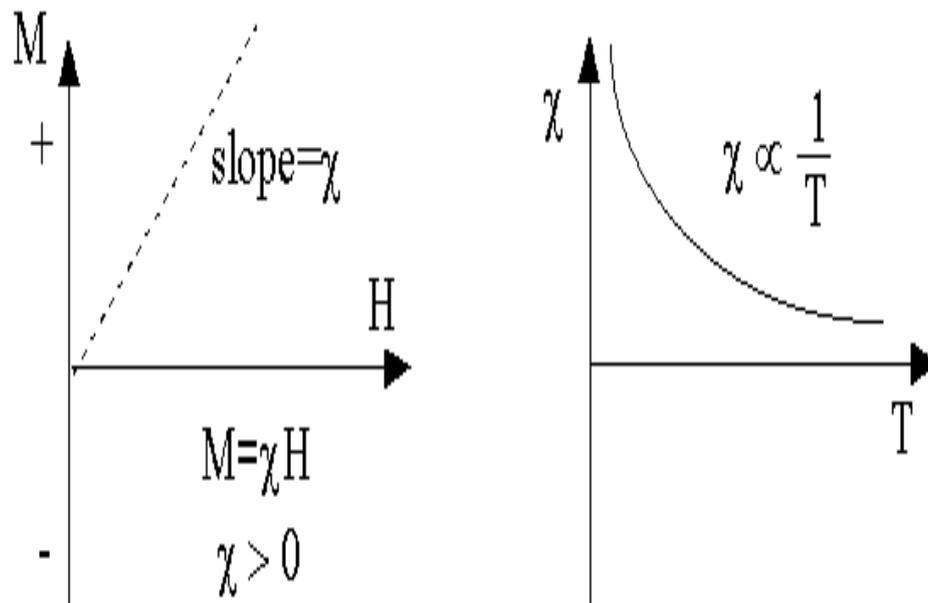


Figure 1.2: Positive and small susceptibility

1.2.3 Ferromagnetism

According to Weiss theory, ferromagnetism is caused by a powerful molecular field, which aligns the atomic moments. In modern language we say that “exchange forces” causes the spins to be parallel, as shown in Figure 1.3. Ferromagnetic materials exhibit parallel alignment of moments resulting in large net magnetization even in the absence of a magnetic field. The elements Fe, Ni, and Co and many of their alloys are typical ferromagnetic materials. Two distinct characteristics of ferromagnetic materials are their (1) spontaneous magnetization and (2) the existence of magnetic ordering temperature.

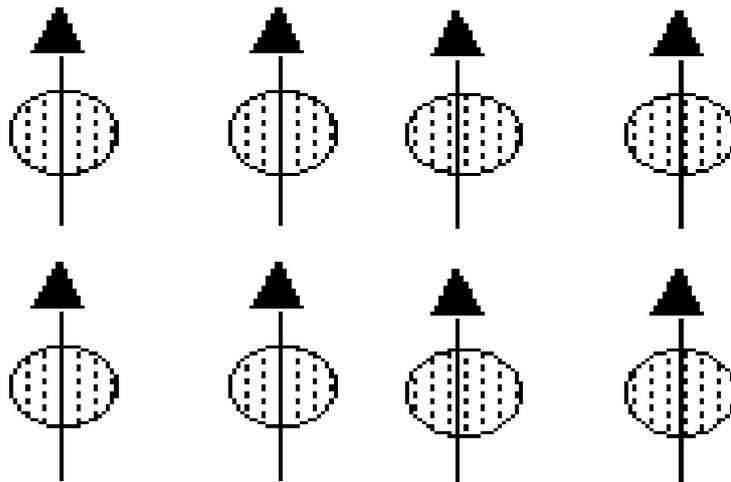


Figure 1.3 Atoms have parallel-aligned magnetic moments

1.2.4 Antiferromagnetism

Antiferromagnetic substances have small positive susceptibility at all temperatures, but their susceptibilities vary in a particular way with temperature. When the spins are antiparallel, due to negative interaction, it results in Antiferromagnetism, as shown in Figure 1.4.

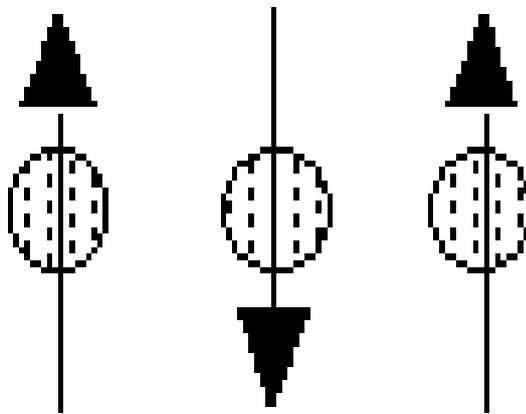


Figure 1.4: Atoms have mixed parallel and anti-parallel aligned magnetic moments

1.2.5 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 in Figure 1.5.

The magnetic structure is composed of two magnetic sub lattices (called A and B) separated by oxygen's. 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 antiparallel alignment of spins between the A and B sub lattice.

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, ferromagnets 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, which provided the theoretical framework for understanding ferrimagnetism.

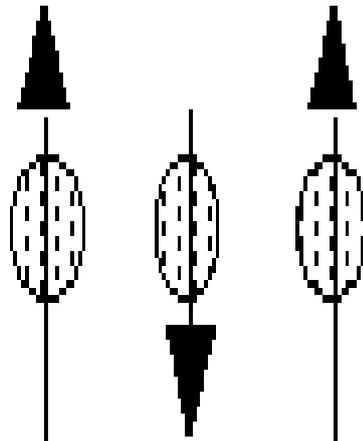


Figure 1.5: Atoms have anti-parallel aligned magnetic moments

1.2.6 Origin of Ferrimagnetism

In many ionic crystals, as in the majority of oxides, the exchange energy 'J' between the spins of the neighboring metal ions is found to be negative, so that antiparallel alignment gives the lowest energy [3]. In these substances, however, the metal ions are more or less separated by the negatively charged ions, which, like the inert gases, have a closed shell configuration in the ground state. For example, the electron structure of the O^{II} ions is like that of neon ($2s^2 2p^6$). The distance between the metal ions is usually much too great for a direct exchange interaction to be possible, since the extent of overlapping of the wave functions (orbital) decreases exponentially with distance. Various magnetic interaction mechanisms have therefore proposed in which the interlying anion plays an essential part (super exchange). In the ground state with the inert gas configuration the ion is inert and can produce no spin coupling. The surrounding ions will, however, disturb this state somewhat, so that the extra electrons will for a small part of the time belong to the neighboring ions. In quantum mechanics this is expressed by the principle of the superposition of states. That is say the state O^{II} and (for a small amount) the state O^I and possibly that the neutral O atom. In reality a whole variety of excited state will be mixed together, but we shall consider only those, which can be of use in explaining magnetic interaction. The electron separated from the oxygen will return to one of the surrounding metal ions from which it originally came (M_1 from Figure 1.6).

Within these metal ions there exists a strong exchange interaction between the spins. The electron can only be there if its spin has a given orientation with respect to the resultant spin moment of the ion, and that depends upon the orbit in which the electron in this excited state chooses to move.

Where this (according to Anderson) is the 3d orbit, the spin will be parallel to the resultant moment if the shell was less than half occupied (five or less 3d electrons); otherwise it must occupy an orbit with antiparallel spin. The electron under consideration has come from a 2p oxygen orbit since this has the highest energy.

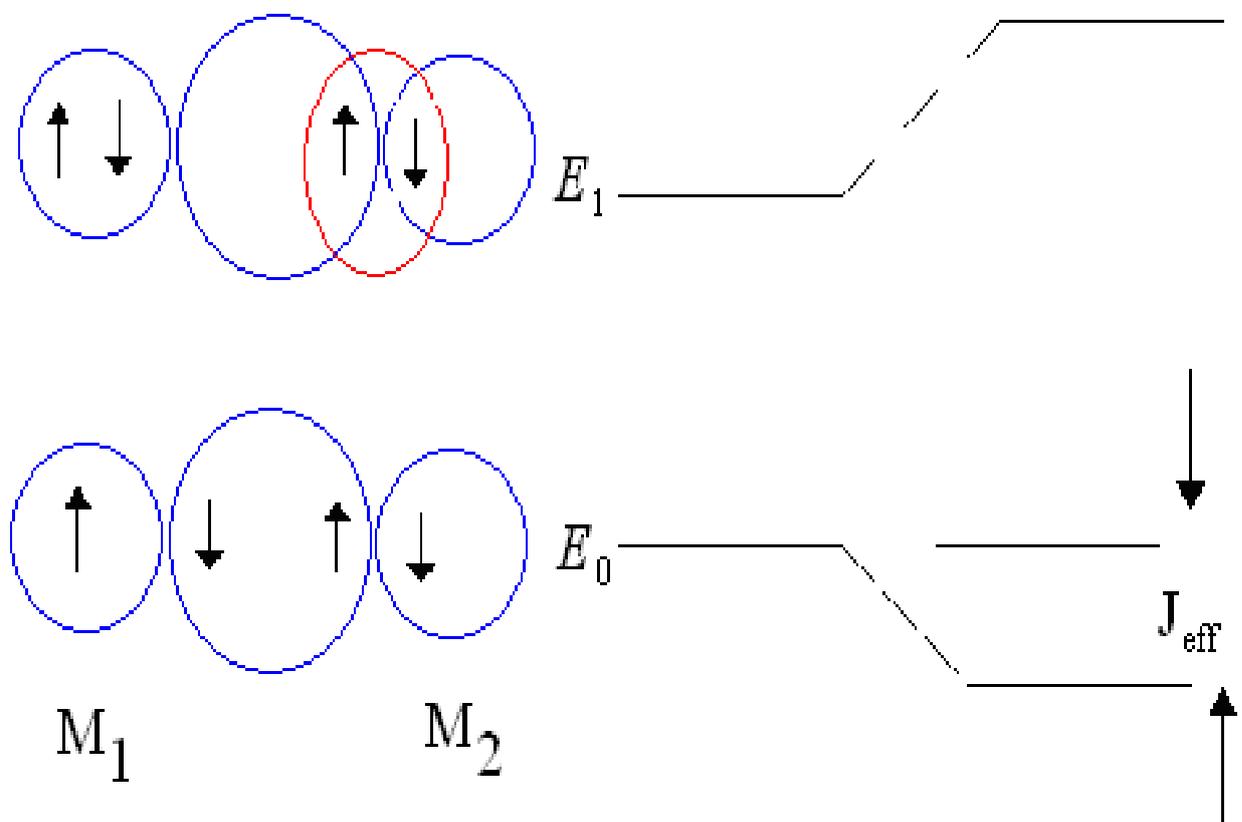


Figure 1.6: Ground state and excited state if two metal ions, M_1 and M_2 , with an oxygen ion between them

According to the Pauli principle, an orbit can contain two electrons with opposite spins. The remaining, now unpaired, electron can interact with another metal ion. There are also many other possibilities, but this excited state will certainly be intermingled to a small extent. According to Anderson the second electron interacts with one of the metal ion electrons as in the covalent bond or hydrogen molecular bond, in which the two associated electrons constantly jump to and fro between the ions concerned and continually exchange (antiparallel) spins. The latter will now only take place to a more limited extent, since the spins at the position of the ions are not free to orient themselves. In that case the energy gain will therefore only be half as large.

Where these states are admixed and then cause a reduction in energy, it means that an effective coupling has arisen between the spin moments of the two metal ions. For instance, if the moments had been parallel there would have been no intermingling and hence no reduction of energy. This reduction of energy occurs because, owing to the intermingling of excited states, the total charge distribution can adapt itself with more economy of energy to the potential occurring in the lattice. Accordingly we can again speak of an effective exchange energy J . In this case we may therefore expect positive exchange energy for the d^1 to d^4 configuration and negative exchange energy for d^5 to d^9 .

1.3 Classification of Ferrites

Ferrites are of classified into different types such as spinel, garnets and hexagonal ferrites. Among these ferrites, spinel ferrites are of importance due to its extensive applications and interesting characteristics.

1.3.1 Spinel Ferrites

1.3.1.1 Crystal structure arrangement

In the magnetic ceramics, the various crystal structures start with the arrangement of the oxygen ions. Let us consider a layer of these oxygen ions closely packed so that the lines connecting their centers form a network of equilateral triangles. The next layer of oxygen ions is also closely packed so that their centers lie directly over the centers of the equilateral triangles of the first layer. Now the third layer can be arranged in two different ways. First, it can repeat the positions of the first layer in which we call it a hexagonal close-packed structure in a type 'ababab' arrangement. This leads to a structure that has a unique crystal axis that we find in some ferrites. Second, the oxygen ions can be so placed that their centers lie directly over the centers of the equilateral triangles adjacent to the ones used for the hexagonal close-packed structure. The fourth layer would then repeat the first so that the pattern would be 'abcabcabc'. This gives rise to crystal structure called cubic-close packed. The spinel ferrites are an example of this class. The type of crystal structure preferred is determined by the size and the charge of the metal ions that will balance the charge of the oxygen ions and the relative amounts of these ions, some oxides such as yttrium oxide (Y_2O_3) may form more than one class depending on the ratio of Y_2O_3 or Fe_2O_3 . Thus $Y_2O_3.Fe_2O_3$ and $3Y_2O_3.5Fe_2O_3$ have different crystal structure.

The crystal structure is frequently related to the ultimate application. Cubic crystal structure has many equivalent crystal directions and so will be useful when it is advantageous to avoid preferred directions.

1.3.1.2 Ionic charge balance

The spinel lattice is composed of a close packed oxygen arrangement in which 32 oxygen ions form a unit cell that is the smallest repeating unit in the crystal network. Between the layers of oxygen ions, if we simply visualize as spheres, there are interstices that may accommodate the metal ions. Now, the interstices are not all the same: some which we call A sites are surrounded by or coordinated with four nearest neighboring oxygen ions whose lines connecting their centers form tetrahedron. Thus A sites are called tetrahedral sites. The other type of site (B sites) coordinated by six nearest neighbor oxygen ions whose center connecting lines describe octahedron. The B sites are called octahedral sites. In the unit cell of 32 oxygen ions there are 64 tetrahedral sites and 32 octahedral sites. If all of these were filled with metal ions, either of +2 or +3 valences, the positive charge would be very much greater than the negative charge and so the structure would not be electrically neutral. It turns out that of the 64 tetrahedral sites, only eight are occupied and out of 32 octahedral sites, only 16 are occupied. The general spinel structure is shown in Figure 1.7.

If, as in the mineral spinel the tetrahedral sites are occupied by divalent ions and the octahedral sites are occupied by their trivalent ions, the total positive charge would be $8 \times (+2) = 16$ plus $16 \times (+3) = +48$ or a total of +64 which is needed to balance the $32 \times (-2) = -64$ for the oxygen ions. There would be then eight formula units of $MO \cdot Fe_2O_3$ or MFe_2O_4 in a unit cell. A spinel unit cell contains two types of subcells. The two types of subcells alternate in a three-dimensional array so that each fully repeating unit cell requires eight subcells.

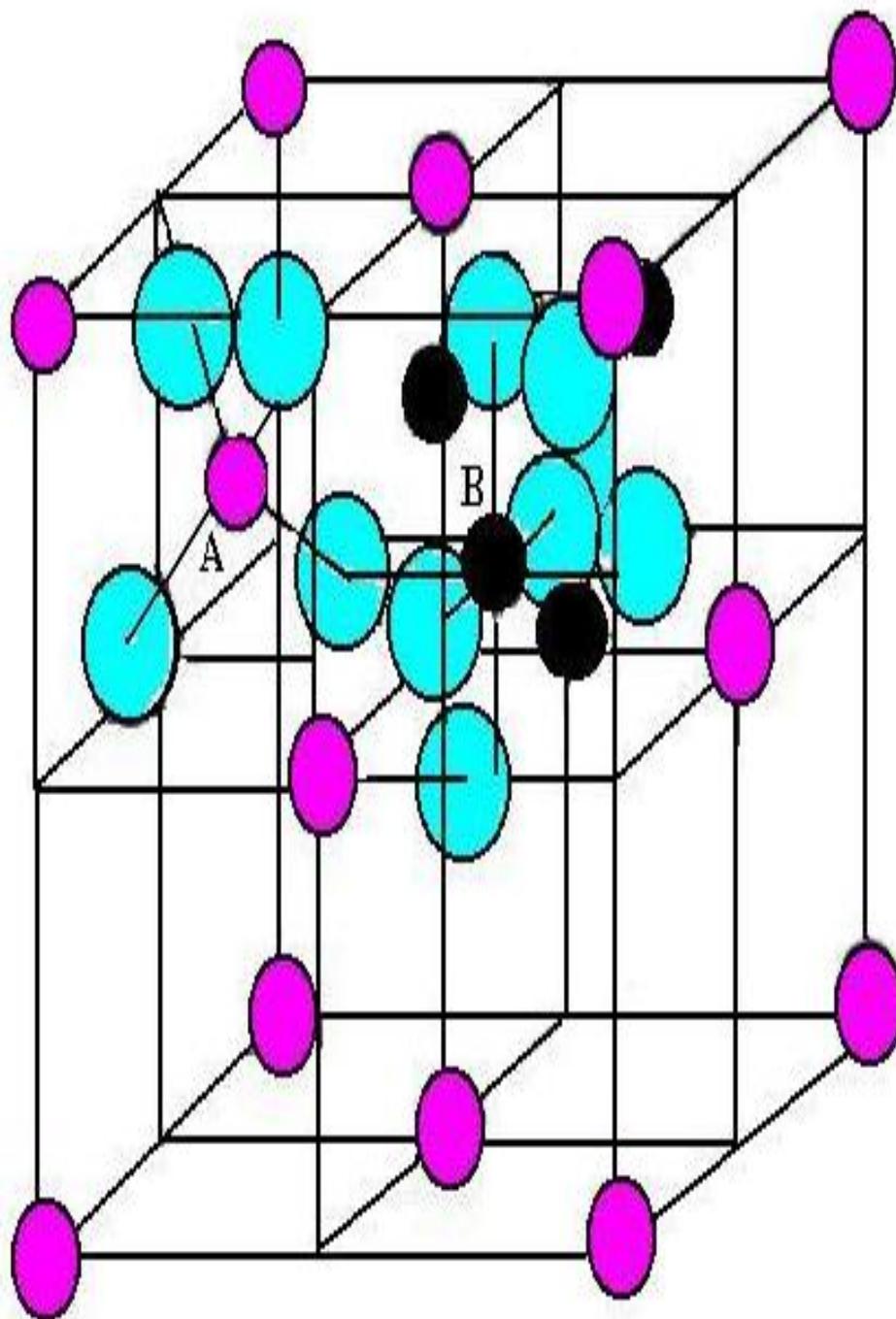


Figure 1.7: General Spinel Structure

1.3.1.3 Spinel Chemistry

The spinel is by far the most widely used ferrite, so much so that the term is almost synonymous with word “ferrite”. The spinel structure is derived from the mineral spinel, (MgAl_2O_4 or $\text{MgO}\cdot\text{Al}_2\text{O}_3$) whose structure was elucidated by Bragg (1915).

Analogous to the mineral spinel, magnetic spinels have the general formula $\text{MO}\cdot\text{Fe}_2\text{O}_3$ or MFe_2O_4 where M is the divalent metal ions. The trivalent Al is usually replaced by Fe^{3+} or by Fe^{3+} in combination with the other trivalent ions. Although the majority of ferrites contain iron oxide as the name might imply, there are some ferrites base on Cr^{2+} , Mn^{2+} , and other elements. Although Mn and Cr are not ferromagnetic elements, in combination with other elements such as oxygen and different metal ions, they can behave as magnetic ions. In the magnetic spinels, the divalent Mg^{++} can be replaced by Mn^{2+} , Ni^{2+} , Cu^{2+} , Co^{2+} , Fe^{2+} , Zn^{2+} , or more often, combinations of these. The presence of Fe^{3+} , Fe^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} can be used to provide the unpaired electron spins and therefore part of the magnetic moment of a spinel. Other divalent ions such as Mg^{2+} or Zn^{2+} (or monovalent Li^{1+}) are not paramagnetic but used to disproportionate the Fe^{3+} ions on the crystal lattice sites to provide or increase the magnetic moment.

1.3.1.4 Oxygen Parameter (u)

In any octant four oxygen ions form a tetrahedron. All the oxygen ions are tetrahedrally surrounded by four cations of which three are from B site and one from A site. Therefore, in tetrahedral sites, only metal ion with radius less than or equal to $0.30A^0$ and in octahedral site only ion with radius less than or equal to $0.55A^0$ can be occupied. In order to occupy cations like Mn^{2+} , Ni^{2+} , Cu^{2+} , Co^{2+} , Zn^{2+} , the lattice has to be expanded. The difference in the expansion of octahedral and tetrahedral sites is characterized by a parameter called oxygen parameter (u).

In ideal spinel tetrahedral and octahedral sites are enlarged in the same ratio and accordingly the distance between tetrahedral site (0, 0, 0) and oxygen site is $3/8$ and hence oxygen parameter is $3/8 = 0.375$ so that, In many cases the close packing of oxygen ions is deformed due to the presence of metal ions of different size in these inter sites.

The oxygen ion then moves along the body diagonal. However, the incorporation of divalent metal ions in tetrahedral sites reduces a large expansion of tetrahedral sites, leading to large value of u than the ideal value. The tetrahedral sites are expanded by an equal displacement of the four oxygen ions outwards along the body diagonal of the cube, still occupying the corners of an expanded regular tetrahedron. The four oxygen ions of the octahedral sites are shifted in such a way that the oxygen tetrahedron shrinks by the same amount as that the first expands. The oxygen ions move along the arrow as shown in Figure 1.8.

The radii of ions in both the sites are given by the expression

$$R_A = (u - 1/4) a - R_O \quad (1.1)$$

$$R_B = (5/8 - u) a - R_O \quad (1.2)$$

Where

a is lattice constant,

R_O is radius of oxygen ion (1.32 \AA)

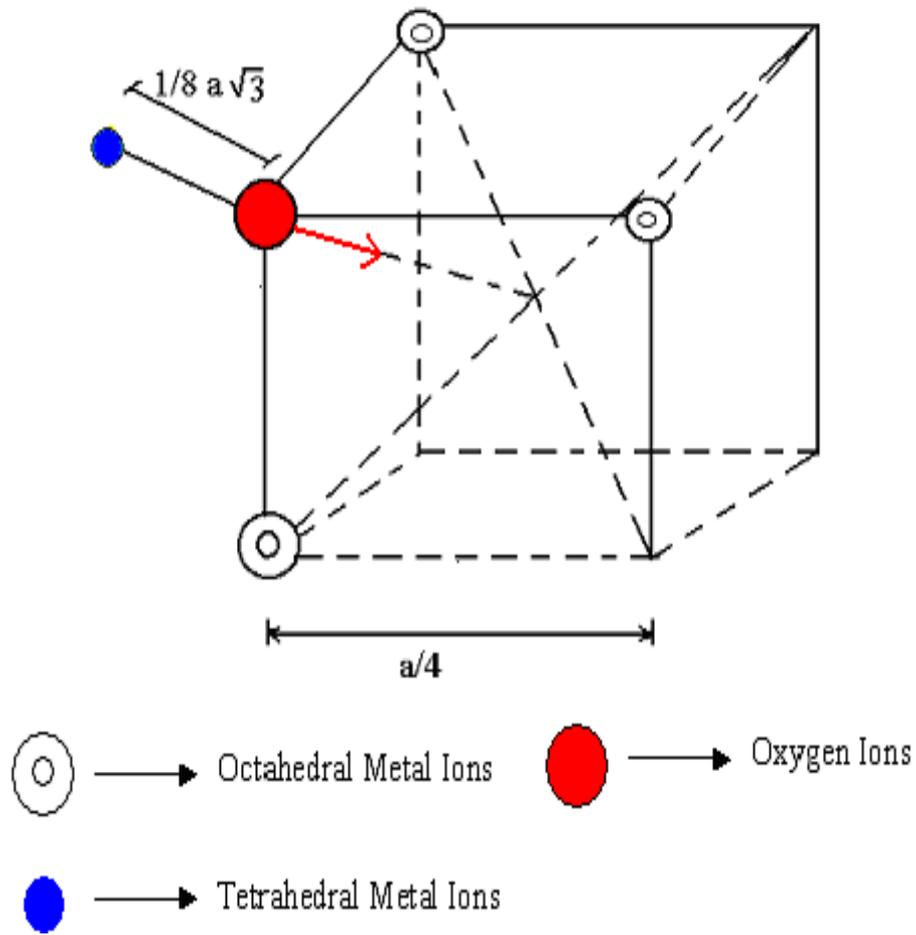


Figure 1.8: Movement of oxygen ion in the lattice

1.3.1.5 Unit Cell Dimensions

The dimensions of the unit cell are given in Angstrom Units, which are equivalent to 10^{-8} cm. If we assume that the ions are perfect spheres and we pack them into a unit cell of measured (X-ray diffraction) dimensions, we find certain discrepancies that show that the packing is not ideal. The positions of the ions in the spinel lattice are not perfectly regular (as the packing of the hard spheres) and some distortion does occur.

The tetrahedral sites are often too small for the metal ions so that the oxygen ions move slightly to accommodate them. The oxygen ions connected with the octahedral sites move in such a way as to shrink the size of the octahedral cell by the same amount as the tetrahedral site expands. The movement of the tetrahedral is reflected in a quantity called the oxygen parameter, which is the distance between the oxygen ion and the face of the cube edge along the cube diagonal of the spinel subcell. This distance is theoretically equal to $3/8a_0$. The eight octants in a unit cell is shown in Figure 1.9. Unit cell lengths of some spinel Ferrites as found in literature are given in Table 1.1.

In a unit cell of spinel lattice, eight tetrahedral and sixteen octahedral sites are occupied by metal ions or by one tetrahedral and two octahedral for each formula unit. In the case of Zinc ferrite, the tetrahedral sites are occupied by Zn^{2+} ions, which being Non-paramagnetic (having no unpaired electronic spins) produces no anti-ferromagnetic orientation of the ions on the octahedral sites that are occupied in Fe^{3+} ions. The Fe^{3+} (B-B) interactions are so weak as to be unimportant. Therefore, Zinc ferrite is not ferrimagnetic. This type of arrangement is called a Normal spinel structure.

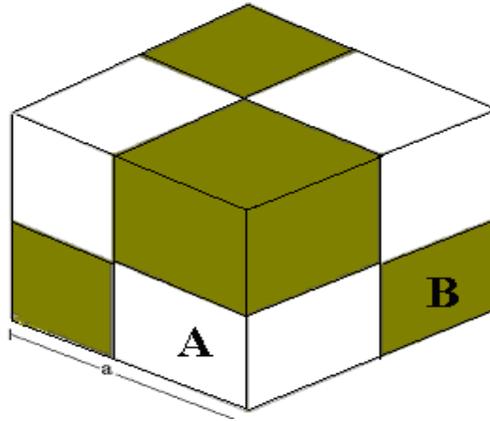


Figure 1.9: The eight octants in the unit cell

Table 1.1: Unit cell lengths of some spinel Ferrites

Ferrites	Unit cell length (Å)
Zinc Ferrite ($\text{Zn Fe}_2\text{O}_4$)	8.44
Manganese Ferrite ($\text{Mn Fe}_2\text{O}_4$)	8.51
Ferrous Ferrite ($\text{Zn Fe}_2\text{O}_4$)	8.39
Cobalt Ferrite ($\text{Co Fe}_2\text{O}_4$)	8.38
Nickel Ferrite ($\text{Ni Fe}_2\text{O}_4$)	8.34
Magnesium Ferrite ($\text{Mg Fe}_2\text{O}_4$)	8.36

There are analogous of inverse spinels in magnetic ferrites. Let us consider the case of nickel ferrite in which eight units of NiFe_2O_4 go into a unit cell of the spinel structure. The ferric ions preferentially fill the tetrahedral sites, but there is room only for only half of them (eight).

The remaining eight go on the octahedral sites as do the eight Ni^{2+} ions. The antiferromagnetic interaction orients these eight Fe^{3+} moments and eight-nickel moments antiparallel to eight Fe^{3+} moments on the tetrahedral sites. The Fe^{3+} ion moments will just cancel, but the moments on the nickel ions give rise to an uncompensated moment or magnetization. This type of ferrite is called an inverse spinel structure.

Random spinels are those in which both divalent and trivalent ions occupy tetrahedral (A) and octahedral [B] sites randomly.

1.3.1.6 Magnetic ordering

With regard to the strength of the interactions between moments on the various sites, the negative interaction or the exchange force between the moments of the two metal ions on different sites depends on the distance between these ions and the oxygen ions that link them and also on the angle between the three ions. The interaction is greater for an angle of 180° and also where the interatomic distances are the shortest. The Figure 1.10 shows, the interatomic distances and the angle between the ions for the different types of interactions.

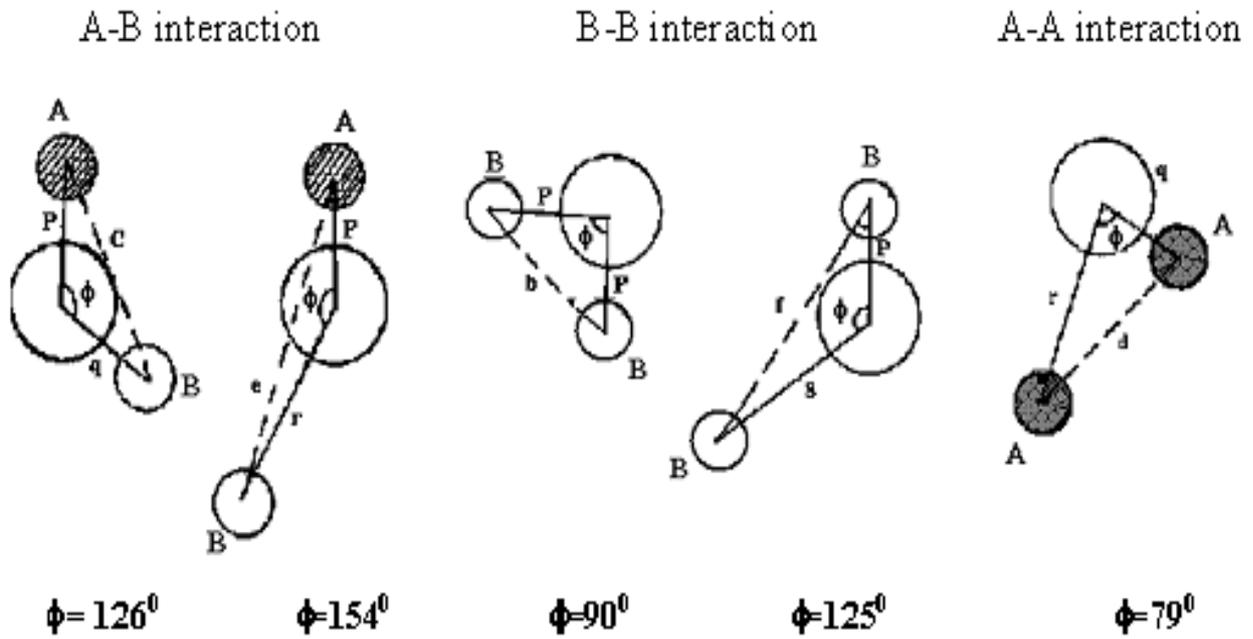


Figure 1.10: Possible arrangements for super exchange interaction in the spinel structure

In the A-A and B-B cases, the angles are too small or the distance between the metal ions and the oxygen ions are too large. The best combinations of the distances and angles are found in A-B interactions. For an undistorted spinel, A-O-B angles are about 125° and 154° . The B-O-B angles are 90° and 125° but in the later, one of the B-O distances is large. In the A-A case the angle is about 80° . Therefore, the interaction between moments on the A and B sites is strongest. The B-B interaction is much weaker and the most unfavorable situation occurs in A-A interaction. By examining the interactions involving the major contributor or the A-B interaction that orients the unpaired spins of these ions antiparallel, Neel (1948) was able to explain the ferrimagnetism of ferrites. The interaction between the tetrahedral and octahedral sites is shown in the Figure 1.10.

An individual A site is interacted with a single B site, but each A site is linked to four such units and each B site is linked to six such units. Thus, to be consistent throughout the crystal, all A sites and all B sites act as unified blocks and are coupled antiparallel as blocks.

1.3.2 Hexagonal Ferrites

This class of magnetic oxide is called a “magnetoplumbite”. The symmetry of the spinel crystal structure is cubic, that for the magnetoplumbite is hexagonal. Thus, it has a major preferred axis called the ‘c’ axis and a minor axis called the ‘a’ axis. The preferred direction is used to good advantage as a permanent magnetic material. The oxygen ions are closely packed as they are in the spinel structure but there are oxygen layers, which now include the Ba^{2+} , Sr^{2+} or Pb^{2+} ions, which have about the same ionic radii as the oxygen ions and therefore can replace them in the lattice. Hexagonal ferrites are ferrimagnetic in nature.

1.3.3 Magnetic Rare Earth Garnets

Garnets are the class of ferrimagnetic oxides. Magnetic garnets crystallize in the dodecahedral or 12-sided structure related to the mineral garnet. The general formula is $3M_2O_3 \cdot 5Fe_5O_{12}$ or $M_3Fe_5O_{12}$. Note that in this case, the metal ions are all trivalent in contrast to the other two classes. In the magnetic garnets of importance, M is usually yttrium (Y) or one of the rare earth ions. Even though yttrium is not a rare earth, it behaves as one and therefore included in the designation “rare earth” garnets. The ions, La^{2+} , Ce^{2+} , Pr^{2+} and Nd^{2+} are too large to form simple garnets but may form solid solutions with other rare earth garnets.

In garnets, there are three different types of sites. These are tetrahedral (a) octahedral (b) and dodecahedral (c) sites. The unsubstituted garnets having only trivalent ions are very stoichiometric so that preparation problems are simplified compared to spinels. The rare earth ions are large so that they occupy the large dodecahedral sites.

There are 16 octahedral, 24 tetrahedral and 16 dodecahedral sites in a unit cell containing 8 formula units. The moments of the Fe^{3+} ions on the octahedral sites are antiferromagnetically coupled to the moments of the Fe^{3+} ions on the tetrahedral sites. The moments of the Fe^{3+} ions on the dodecahedral sites are coupled to the tetrahedral sites similarly and as previously mentioned may contribute to the magnetization of that sublattice. In the absence of the rare earth ions contribution are in the most important of the series, $3\text{Y}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ and all the moments are due to the Fe^{3+} ions.

1.4 Cation Distribution

Spinel ferrites have the general molecular formula $(\text{A}^{2+}) [\text{B}_2^{3+}] \text{O}_4^{2-}$ where A^{2+} and B^{3+} are the divalent and trivalent cations occupying tetrahedral (A) and octahedral [B] interstitial positions of the fcc lattice formed by O^{2-} ions. The magnetic properties of these ions depend on the type of cations and their distribution among the two interstitial positions. The cation distribution and the resulting magnetic properties are found to be different and quite interesting in some nanocrystalline spinel ferrites when compared to those of their bulk counterparts [4-11].

The most important consideration would appear to be the relative size of the ions compared to the size of the lattice site. The divalent ions are generally larger than the trivalent (because the larger charge produces greater electrostatic attraction and so pulls the outer orbit inward). Therefore, it would be reasonable that the trivalent ions such as Fe^{3+} would go into the tetrahedral sites and the divalent ions would go into the octahedral sites.

1.5 Applications

Magnetic materials can be categorized in several different manners (Figure 1.11). First, they can be classified by market:

1. Consumer – radio, television, video recorder, small motors, transformers.
2. Heavy industrial – Generators, large motors, large transformers.
3. Light industrial – circuit components, power supplies.
4. Specially and Custom – aircraft, microwave devices, recording heads.

Still another form of categorizing is by function and this may be, for our purpose, the best way

1. Mechanical – lifting, separation, suspending.
2. Shielding.
3. Electromechanical transducers – motors, speakers, vibrators, relays, ultrasonic generators.
4. Mechanico – electric transducers – electrical generators, phonograph needles.
5. Voltage and current multipliers – Transformers.
6. Impedance matching.
7. Inductor in LC circuit.
8. Filter to remove any unwanted frequencies – wide band transformer, channel filter, EMI (electromagnetic Interference) suppression.
9. Output choke – remove A.C component from D.C.
10. Magnetic head – write or read data on tape or disk.
11. Microwave devices.

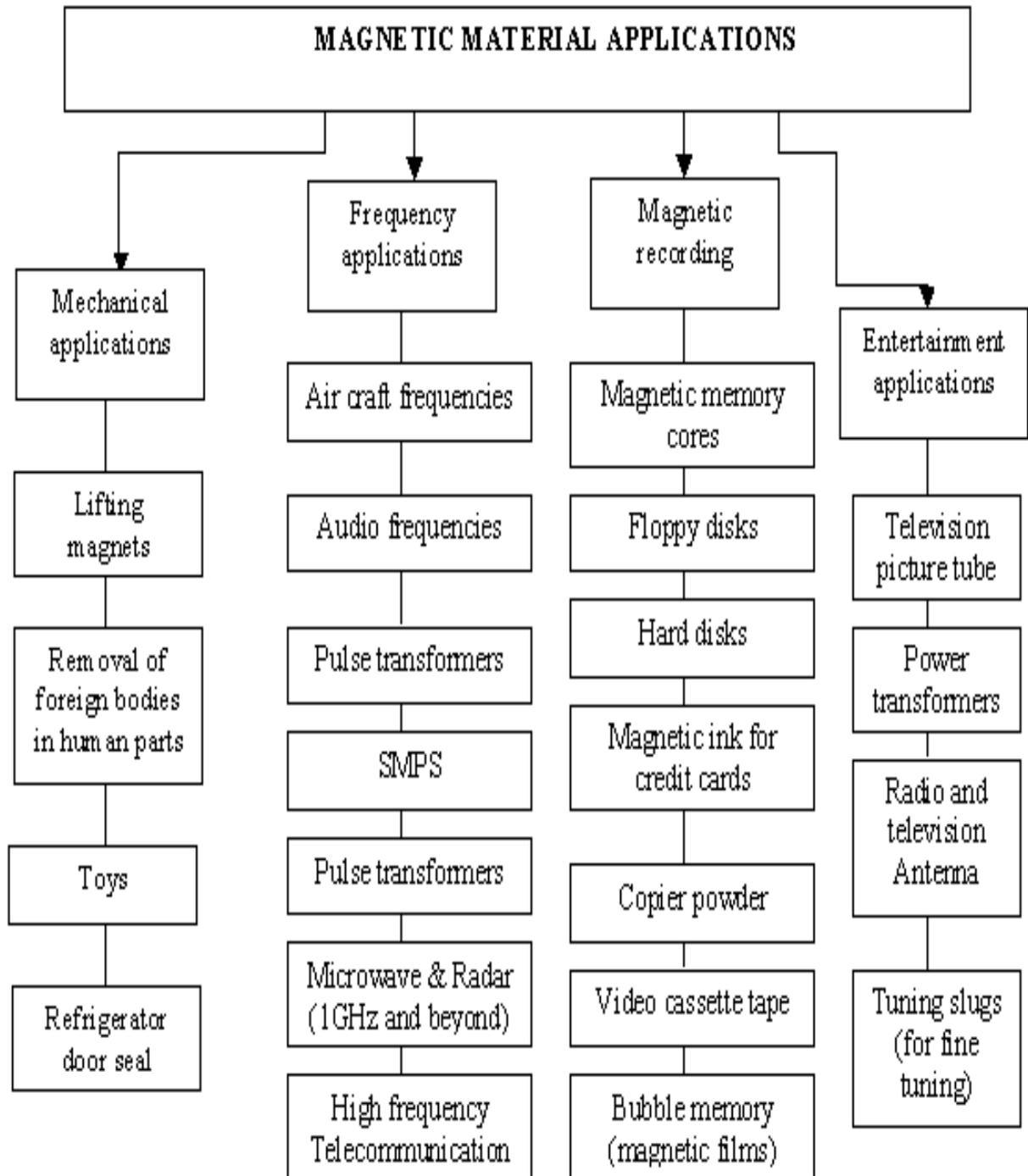


Figure 1.11: Applications of magnetic materials

1.6 Motivation for present work

Ferrites are well-known magnetic compounds that have been studied for potential application in microwave devices and as magnetic recording media. Ferrites in general have important applications in day-to-day life, and its usage ranges from making a building big automobiles. The manufacturing process of ferrite materials is very cheap and has occupied a prominent place in the market with its exciting and reliable applications.

Its properties can be varied according to the type of preparation conditions. Among the several ferrites cobalt ferrite and nickel ferrite have tremendous applications because of their high resistivity and low eddy current losses.

Cobalt ferrite, CoFe_2O_4 , is basically inverse spinel. The cation distribution can be given as $(\text{Co}_{0.1} \text{Fe}_{0.9}) [\text{Co}_{0.9} \text{Fe}_{1.1}] \text{O}_4$. The degree of inversion depends on the thermal history. Cobalt ferrite is well known hard – magnetic material, which has been studied due to its high coercivity (5400 Oe) and moderate saturation magnetization (80 emu/g) as well as remarkable chemical stability and mechanical hardness [12]. Aluminium substituted cobalt ferrite is a soft ferrite with a low magnetic coercivity and high resistance and, thus it is also an excellent core material for power transformers in electric and telecommunication applications [13].

Nickel ferrite, NiFe_2O_4 is an inverse spinel in which the tetrahedral sites (A) are occupied by Fe^{3+} ions and octahedral sites [B] by Fe^{3+} and Ni^{2+} ions [14, 15]. These materials are largely used in electric and electronic devices and in catalysis. Spinel NiFe_2O_4 , combine a wide range of useful magnetic properties with relatively low electrical conductivity. Unlike magnetic materials and alloys, they display low eddy current loss in alternating current applications and they are particularly useful in the radio frequency range [16, 17].

Substitution of divalent, trivalent and tetravalent ions in Cobalt ferrite and Nickel ferrite has been studied by many researchers [18 - 27]. Substitution of non-magnetic ions like Zn^{2+} , Cd^{2+} etc give rise to interesting magnetic structural properties like spin glass behavior, canting arrangements and so on. Therefore to see the effect of non-magnetic Al^{3+} ions at Fe site in Cobalt ferrite and Nickel ferrite, the structural and magnetic properties were carried out.

In the literature study of structural, electrical and magnetic properties of Aluminium substituted Cobalt ferrite and Nickel ferrite are already available. But these studies were not carried on the samples like $CoFe_2O_4$, $CoFe_{1.8}Al_{0.2}O_4$, $CoFe_{1.6}Al_{0.4}O_4$, $CoFe_{1.4}Al_{0.6}O_4$, $CoFe_{1.2}Al_{0.8}O_4$, $CoFeAlO_4$, $NiFe_2O_4$, $NiFe_{1.8}Al_{0.2}O_4$, $NiFe_{1.6}Al_{0.4}O_4$, $NiFe_{1.4}Al_{0.6}O_4$, $NiFe_{1.2}Al_{0.8}O_4$, $NiFeAlO_4$, prepared by sol-gel auto-ignition method nor it has been studied by VSM and Mössbauer and the data for these kinds of ferrites is not available.

Keeping in view of the importance of nano size ferrites in technological applications, light has been focused on the systematic investigation of the structural and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$ and $Cu_{1-x}Zn_xFe_2O_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) by Oxalate based precursor method.

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