CHAPTER 1
INTRODUCTION

1. Nano materials and Nanoscience:

The word ‘nano’ originates from Greek word ‘dwarf’ which is referred to the length scale of billionth of a meter. Thus nanoscience deals with the science of materials and technologies in the range of 1-100 nm. This means, the nanoscience deals with a few hundred to a few thousand atoms or atomic clusters, whereas the microscopic world is made of trillion of atoms or molecules. Presently, the nanoscience and nanotechnology represents the most active discipline all around the world and is considered as the fastest growing technological-revolution the human history has ever seen [1]. The immense interest in the science of materials confined within the atomic scales stems from the fact that these nano materials exhibit fundamentally unique properties with great potential of bringing plethora of next-generation technologies in electronics, computing, optics, biotechnology, medical imaging, medicine, drug delivery, structural materials, automotives, aerospace, food, energy, etc: in almost all walks of life.

Material Science encompasses various disciplines, namely, physics, chemistry and engineering and is truly interdisciplinary in nature. The evolution of material science is always an indicator to man's progress and his urge to improve upon the existing and replace the obsolete with newer and novel materials often results in newer materials and innovations. The emergence of nanoscience and nanotechnology as a leading technology of the 21st century has only accelerated the growth of material science. Today
nanoscience and nanotechnology has become synonymous with material technology. Magnetism and magnetic materials has been playing a seminal role in ones life. The magnetic industry is all set to surpass the semiconductor industry with the proliferation of new gadgets based on magnetic materials and new innovations in the area of nanomagnetism. The realm of modem day magnetism and magnetic materials is always a subject of intense research. Newer devices based on magnetism are hitting the markets. For example, we have spintronic devices, giant magnetoresistance based (GMR) sensors, magnetic random access memories and other novel gadgets based on nanomagnetism. So it is only natural that magnetism and magnetic materials at the nanoregime attracts the attention of researchers’ world wide. Although the research in present day of nanomaterials is based largely on the curiosity of investigating fundamental properties of matter in nanoscale regime, however, the timely attention and efforts are essential for the transformation of these new findings into technologies-products so that the well-assumed technological revolution can became day-light reality. By now, a variety of chemical, biological as well as physical processes have been established for the preparation of different kinds of nanoparticles, systems and the groundbreaking inventions such as scanning tunnelling microscope (STM), atomic force microscope (AFM), etc, together with the conventional high resolution transmission electron microscope (HRTEM) have made the characterization and atomic scale manipulation of nanoscale materials a practical reality.
1.0 The History of Nanoparticles Research:

The existence of nanoscience can be traced back both in the living as well as non-living things existing in nature since billions of years. For instance, living-cells are the glaring examples of multifunctional nano-machines. Similarly, nanomaterials cannot be viewed differently from the colloidal system occurring naturally or made synthetically. Thus, it is difficult to fix a date for origin of nanoscience. However, one of the historically important observations on the size dependent properties of materials came from the great scientist of 19th century, Sir Michael Faraday. On March 11, 1856, he wrote in his diary [2]:

“… and then, put small pieces of gold above the convex surface of a rock crystal and pressed it by hand steadily, rocking it a little. The applied pressure converted the violet or dark colour of the place of contact into a beautiful green; far more beautiful than any I have ever seen in a gold leaf beaten. The effect was perfect”.

Sir Faraday was trying to make bigger pieces of gold from small (colloidal) particles by pressing them together. As one expects from a great scientist, it is not surprising that diary continues with an accurate explanation of this phenomenon of colour change in fine gold particles under pressure,

“… has the pressure converted the; layer of atoms into a continues layer by expansions and welding? I rather think it is. So, it appears that these different layers are all gold only, and own their different appearance not to composition but to physical difference in size”.
Thus, Sir Faraday discovered that the colour or to be more precise, the electronic structure, of material can be size dependent. Probably, this was the first reported observation on the size dependence of fundamental properties of matter.

1.1 Nanotechnology and Nanoscience:

Nanotechnology, termed as the technology of the century and deals with the design, fabrication and application of nanostructures or nanomaterials [3-5]. It also embraces the fundamental understanding of the relationship between the different physical and chemical properties and material dimensions. The technology has a wide range of applications from nanoscale electronics and optics to nanobiological systems and nanomedicine [6-8]. Basically it is a multidisciplinary subject which essentially requires contributions from physicists, chemists, material scientists, engineers, molecular biologists, pharmacologists for the proper development.

The transition from micro particles to nanoparticles can lead to a number of changes in the physical properties. At the nanometre dimensions, a large fraction of the atoms are at or near the surface resulting in a large surface to volume ratio. The increase in the surface to volume ratio leads to increasing dominance of the behaviour of atoms on the surface of the particle over that of those in the interior of the particle. This affects the properties of the particles in Isolation and its interaction with other particles. This is where quantum size affects starts playing its role [9, 10]. At nanolevel, materials exhibit superlative physico-chemical properties when compared to their nanosized counterparts.
With the emergence of nanotechnology in the horizon of research, magnetism at the nanoscale is being probed deeply from a fundamental perspective.

The applications of magnetic spins in solid-state materials have enabled significant advances in current informational and biological technologies including information storage, magnetic sensors, bio separation, and drug delivery [11-13]. Although micron-sized magnetic materials have been utilized for such purposes, researchers are now pursuing further miniaturization of magnetic devices while possessing superior magnetic properties. Magnetic nanoparticles are emerging as a potential candidate for fulfilling such expectations. Being different from their bulk counterparts, they exhibit unique nanoscale magnetic behaviours which are highly dependent on morphological parameters such as size and shape. Such size and shape effects in nanoparticles enable us the possibility to control their properties (e.g. coercivity, $H_c$ and susceptibility, $\chi$) as we desire by synthetically tuning their morphological parameters.

General concepts in magnetism and theory of magnetism in fine particles are briefly discussed in this introduction. The properties of specific nanomaterials: ferrites and nanocomposites are depicted with giving importance to the synthesis techniques and applications. Magnetocaloric effect as the basis of magnetic refrigeration is explained with adequate theory and equations. The objectives undertaken are emphasized along with the motivation.
1.2 Magnetism:

1.2.1 Origin of Magnetism:

A magnetic field is a force field similar to gravitational and electrical fields that is surrounding a source of potential; there is a contoured sphere of influence or field. The origin of the magnetic potential is known as magnetic dipoles. Magnetism essentially results from two electronic motion associated with the atom; the orbital motion of the electron and the spin motion of the electron. For macroscopic purposes these tiny currents due to these motions can be treated as magnetic dipoles. Ordinarily they cancel each other out because of the random orientation of the atoms. But when a magnetic field is applied, a net alignment of these magnetic dipoles occurs and the medium becomes magnetically polarized. [15-17]

The strength of magnetic field which magnetises the material is measured by magnetic field (H) The magnetic moment per unit volume of the magnetised material is measured by magnetisation M. B is termed as the magnetic induction or magnetic flux density inside the magnetised material. The magnetisation M is the sum of the magnetic moments $m_i$ per unit volume

$$M = \sum m_i \quad (1.1)$$

The magnetic properties of magnetic materials are characterised not only by the magnitude and sign of M, but also the way in which M varies with H. The ratio of these two quantities is called magnetic susceptibility

$$\chi = \frac{M}{H} \quad (1.2)$$

The magnetisation M of a material is defined by the relation
Where $\mu_0 = 4\pi \times 10^{-7} \text{Hm}^{-1}$ is the permeability of free space and $B$ and $H$ are measured in Tesla (T) and Am' I respectively. $\mu_r$ is termed as the relative permeability of the material.

Hence from the relations 1.2-1.3, it can be shown that

$$\mu = \mu_0 (1 + \chi)$$

(1.4)

The value of $\mu$ and $\chi$ characterises the magnetic properties of a material. Typical curves of $M$ Vs $H$ called magnetisation curves are characterised by phenomena like saturation magnetisation and hysteresis (figure 1.1). At higher values of $H$, the magnetisation $M$ becomes constant at its saturation value of $M_s$. After saturation, a decrease in $H$ to zero does not reduce $M$ to zero which is termed as hysteresis. $M_r$ is the remanent magnetisation and $H_c$ is the coercive field or coercivity of the material.

![Figure 1.1 Typical Hysteresis Curve](image)
1.2.2 Types of Magnetism:

All materials are affected by a magnetic field. Based on the nature of interaction with the magnetic field, materials can be classified mainly into following five types [15-17]

a. Diamagnetism

b. Paramagnetism

c. Ferromagnetism

d. Antiferromagnetism

e. Ferrimagnetism

Materials in the first two groups are those that exhibit no collective magnetic interactions and are not magnetically ordered. Materials in the last three groups exhibit long range magnetic order below a certain critical temperature. Ferromagnetic and ferrimagnetic materials are usually what we consider as being magnetic. The remaining three are so weakly magnetic that they are usually thought of as "nonmagnetic".

1.2.2. a. Diamagnetism:

Diamagnetism is a fundamental property of all matter although it is usually very weak. It is due to the non-cooperative behaviour 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 orbital shells are filled and there are no unpaired electrons. However, when exposed to a field, a negative magnetisation is produced and thus the susceptibility is negative (figure 1.1).
The diamagnetism of atoms, ions and molecules can be modelled as if the orbits of the electron were current loops. The induced moment is proportional to the current times the area of the loop. Current will depend upon the passage of electron times the charge on the electron $e$ and on the frequency of the orbital motion, which also depends on the charge $e$. Thus susceptibility is directly proportional to $Ze^2\langle r^2 \rangle$ where $r$ is the orbital radius and $Z$, the atomic number By Langevin's theory of diamagnetism the susceptibility is predicted as

$$\chi = \frac{NZe^2}{m_c}\langle r^2 \rangle$$  \hspace{1cm} (1.5)

Where $N$ is the number of atoms per unit volume, $m$ the electron mass, and $c$ is the speed of light. The other characteristic behaviour of diamagnetic material is that the susceptibility is temperature independent figure (1.2).

1.2.2. b. Para magnetism:

In this class of materials, some of the atoms or ions in the material have a non-zero magnetic moment due to unpaired electrons in partially filled
orbitals. Then an applied field modifies the direction of the moments and an 
induced magnetisation parallel to the field appears.

Figure 1.3 Partial alignments of atomic magnets in a para magnet

However the individual magnetic moments do not interact magnetically 
and like diamagnetism the magnetisation is zero when the field is removed. In 
the presence of field, there is now a partial alignment of the atomic magnetic 
moments (figure 1.3) in the direction of the field resulting in a net positive 
magnetisation and positive susceptibility (figure 1.4)

Figure 1.4 Variation of M Vs H and X Vs T in a paramagnetic material
In addition the efficiency of the field in aligning the moments is opposed by the randomizing effects of temperature. These results in a temperature dependent susceptibility (figure 1.4) which is given as the Curie's law developed on the basis of Langevin's theory of paramagnetism. At normal temperature and in moderate fields, the paramagnetic susceptibility is small, but larger than the diamagnetic contribution. Langevin theory of Paramagnetism explains the importance of temperature in governing the magnetic properties. By Classical Langevin model of paramagnetism, the total magnetic moment is given by

\[ M = NmL(x) \quad (1.6) \]

\[ L(x) = Coth(x) - x^{-1} \quad (1.7) \]

\[ x = \frac{mH}{k_B T} \quad (1.8) \]

Where it is the number of atoms each with magnetic moment \( nm \), \( H \) the applied magnetic field \( k_B \) the Boltzmann’s constant, \( T \) is the temperature in degree Kelvin and \( L(x) \) is called the Langevin function.

At small \( x \),

\[ L(x) \approx \frac{x}{3} \quad (1.9) \]

Hence the magnetisation

\[ M = \frac{Nm^2}{3k_B T} \quad (1.10) \]

This results in the inverse temperature dependence of the susceptibility known as the Curie’s law (figure 1.4) given by
\[ \frac{M}{H} = \frac{C}{T} \quad (1.11) \]

Where \( C \) is called the Curie's constant given by

\[ C = \frac{N m^2}{3k_B} \quad (1.12) \]

This equation applies when \( k_B T \ll mH \). At large \( x \), \( L(x) \sim 1 \), and all moments are aligned. This is known as saturation magnetisation, \( M_s = N_m \).

Considering the quantum effects in magnetism, the total magnetic moment is written as

\[ M = N q B J(x) \quad (1.13) \]

\[ B_J(x) = \frac{2J+1}{2J} \coth \left( \frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right) \quad (1.14) \]

\[ x = \frac{gJ \mu_B H}{k_B T} \quad (1.15) \]

The function \( B_J(x) \) is called the Brillouin function. The Brillouin function has two limits with \( j \). When \( j = \frac{1}{2} \),

\[ M = N_m \tanh x \quad (1.16) \]

When, the Brillouin function becomes the Langevin function.

The theory of paramagnetism implies that magnetisation data for a paramagnet fall on a universal curve if plotted as a function of \( H/T \). The temperature dependence of \( X \) in a paramagnetic material gives a straight line with a slope. In real materials deviations from Curie's law are often observed, in particular at low temperature. One of the most usual contributions to these deviations is the Van Vleck's paramagnetism. In metals, conduction electrons
can also give rise to a paramagnetic behaviour called Pauli paramagnetism with a susceptibility that is virtually temperature independent

1.2.2. c. Ferromagnetism:

The atomic magnetic moments in magnetic materials like iron, nickel, cobalt etc. exhibit very strong interactions. The interactions are produced by electronic exchange forces and result in a parallel or antiparallel alignment of atomic moments. The positive exchange interactions in favour a parallel arrangement of magnetic moments in neighbouring atoms. On account of the magnetic interactions, susceptibility instead of becoming infinite at OK as in a paramagnet becomes infinite at a characteristic temperature called the Curie temperature $T_c$. Below this temperature the interactions overcome thermal agitation and a spontaneous magnetisation appears in the presence of an applied magnetic field. The spontaneous magnetisation reaches its maximum value $M_0$ at OK corresponding to parallelism of all the individual moments (figure 1.5).

![Figure 1.5 Alignment of atomic magnets in a ferromagnetic under an applied field H](image-url)
Thus the ferromagnetic materials are found to display a modified
temperature dependence of $\chi$ which is described by the equation

$$\chi = \frac{c}{T - \theta} \quad (1.17)$$

Where $(T)$ is a critical temperature that can be either positive or negative. This
modification is called Curie Weiss Law. In the case of ferromagnetism this
ordering temperature is called the Curie temperature (figure 1.6). This law was
developed on the basis of Weiss Molecular field theory based on the magnetic
Interactions between atomic moments.

![Figure 1.6 Variation of $M$ vs $H$ and $\chi$ vs $T$ in a ferromagnetic material](image)

By Weiss molecular field theory, a molecular field acts in a
ferromagnetic material below its curie temperature as well as in the
paramagnetic phase above $T_c$ and that this molecular field is strong enough to
magnetise the substance even in the absence of an external applied field. To
model this interaction he assumed that the net interaction on a given magnetic
moment is an effective mah'lletic field, a mean field due to all other moments.
However the temperature dependence of $X$ yield a unrealistic large values for
the molecular field and hence the theory was found to have some serious problems. However more accurate theories consider the only nearest neighbour interactions for the magnetic atomic moments and the interactions are not magnetic, but rather due to what is called exchange interaction, which is quantum mechanical in origin. The true physical origin of the exchange coupling was elucidated by Heisenberg. Quantum mechanics provides for an exchange interaction between two atoms based on symmetry, the Pauli's exclusion principle and the coulombic interaction. Heisenberg showed the exchange interaction in a two electron system lead to an exchange energy given by

\[ E_{ex} = -2J_{ex}S_i S_j \]  

(1.18)

between neighbouring spins, \( S_i \) and \( S_j \), \( J_{ex} \) is called the exchange integral. If \( J_{ex} \) is positive, the lower energy configuration is that of lower energy and hence parallel magnetic moments as required for ferromagnetism. If \( J_{ex} \) is negative, antiparallel configuration results.

Two theories of magnetism were used to explain the ferromagnetism in metals: (i) localized moment theory (ii) band theory in the localized moment theory, the valence electrons are attached to the atoms and move about the crystal. The valence electrons contribute a magnetic moment which is localized at the atom. The localized moment theory accounts for the variation of spontaneous magnetisation with temperature in the ferromagnetic phase and explains the Curie Weiss behaviour above the Curie temperature. In the collective electron model or band theory, the electrons responsible for magnetic
effects are ionized from the atoms and are able to move through the crystal. Band theory explains the non integer values of the magnetic moment per atom that are observed in metallic ferromagnets. In real situations neither model can be considered perfectly correct, but rather a good approximation. By far the most successful method currently available for calculating the magnetic properties of solids is density functional theory which includes all the interactions between all the electrons. By this theory it is assumed that the electrons choose the arrangement which will give them the lowest possible total energy. However Density Functional Theory (OFT) calculations are both intensive and difficult as the exact form of the exchange and correlation part of the interelectronic interaction energy is not known.

1.2.2.d. Antiferromagnetism:

In an antiferromagnet, exchange coupling between neighbouring moments that causes the moments to align in an anti parallel fashion: the exact opposite of a ferromagnet (figure 1.7). In terms of Heisenberg Hamiltonian interaction, the exchange integral \( J_{\text{ex}} \) is negative. This antiparallel alignment causes the system to have small positive susceptibility, because an applied field tends to align the spins and this induced alignment is larger than the diamagnetism of the electron orbitals. Similar to ferromagnetic materials, the exchange energy can be defeated at high temperature and then the system becomes paramagnet.
The thermal variation of the reciprocal susceptibility of an antiferromagnetic material measured exhibit a minimum at a critical temperature termed as Neel temperature (figure 1.8). When temperature is reduced down to below $T_N$, the susceptibility decreases as the thermal agitation which works against the antiferromagnetic order of the moment decreases. At higher temperatures the thermal agitation overcomes interaction effects and one observes again a thermal variation of the susceptibility similar to that of a paramagnet. For temperatures greater than $T_N$, the susceptibility of antiferromagnetic substance follows Curie -Weiss law with a negative $\gamma$. An antiferromagnetic material can be viewed microscopically consisting of two sublattices A and B and an antiparallel interaction occur between these lattices. These equal and opposite interaction compensate each other in nearly zero magnetisation of the antiferromagnetic material. Many antiferromagnetic systems are known, usually ionic compounds such as metallic oxides, sulphides, chlorides etc.
1.2.2. e. Ferrimagnetism:

Ferrimagnetism characterises a material which microscopically, is antiferromagnetic like, but in which the magnetisation of the two sublattices are not the same. The two sub lattices no longer compensate each other exactly. A finite difference remains to leave a net magnetisation (figure 1.9). This spontaneous magnetisation is defeated by the thermal energy above a critical temperature called the Curie temperature and then the system is paramagnetic. The variation of magnetisation with applied field and susceptibility with temperature is shown in figure (1.10).

At high temperatures, Curie Weiss behaviour is seen with \(1/\chi\) linear with \(T\). near the Curie temperature, \(1/\chi\) versus \(T\) is curved. A large number of
ferrimagnets are known: ferrites are a major class. Ferrimagnetism in ferrites based on Neel's sublattice model are dealt in detail in the proceeding sections.

![Diagram](image)

Figure 1.10  Variation of $M$ Vs $H$ and $1/\chi$ Vs $T$ in a ferrimagnetic material

1.2.3 Magnetic Interactions:

The different types of magnetic interactions which allow the magnetic moments in solids to communicate with each other to produce a long range order are described here[15].

1.2.3.a. Magnetic dipolar interaction:

Each magnetic moment of the substance is subjected to a magnetic dipolar interaction with the other moments. The magnetic dipole interactions between two magnetic dipoles separated by a distance $r$ have an energy equivalence given by

$$E = \frac{\mu_o}{4\pi r} \left[ m_1 m_2 \frac{3}{r^3} (m_1 \cdot r)(m_2 \cdot r) \right]$$

(1.19)

The dipolar interaction is much weaker than the exchange interaction among near neighbour moments, become dominant only at large distances. The magnetic dipolar interactions are found to be too weak to account for the ordering of most magnetic materials with higher ordering temperatures.
1.2.3. b. Exchange Interactions:

Exchange interaction is the main phenomenon governing the long range magnetic order in ferro, antiferro and ferromagnetic materials. It is of quantum mechanical origin and electrostatic in nature. It is very strong, but acts between neighbouring spin moments only and falls off very rapidly with distance. The interaction between two atoms having spins Si and Sj was shown by Heisenberg as in equation 1.18. The major exchange interactions are direct exchange, indirect exchange or superexchange, RKKY interaction and double exchange [15].

1.2.3. b. 1. Direct Exchange:

In direct exchange interactions, the interaction between neighbouring magnetic proceeds directly without the help of an intermediatory. Often direct exchange is not found to be an important mechanism in controlling the magnetic properties because there is insufficient direct overlap between the neighbouring magnetic orbitals. Hence direct interactions are not found to be effective in rare earth metals and transition metals.

1.2.3. b. 2. Indirect Exchange or Super Exchange interactions in ionic solids:

Indirect exchange or super exchange interactions between non neighbouring magnetic ions is mediated by a nonmagnetic ion which is placed in between the magnetic ions in the case of ionic solids. Super exchange interactions involve the oxygen orbitals as well as metal atom (in ferrites) and it is a second order process derived from second order perturbation theory.
Super exchange interactions could occur in ferromagnetic materials but less common than the usual antiferromagnetic or ferromagnetic super exchange.

1.2.3. b. 3. Indirect Exchange in metals-RKKY interactions:

In metals, the exchange interactions between magnetic ions can be mediated by the conduction electrons. A localized spin magnetic moment polarizes the conduction electrons and this polarization in turn couples to a neighbouring localized magnetic moment a distance r away. The interaction is called RKKY interaction after Ruderman, Kittel, Kasuya and Yosida. The interaction is long range and has an oscillatory dependence on the separation between the magnetic moments. The resulting interaction can be either ferro or antiferromagnetic depending on the separation between the ions.

1.2.4 Magnetic Domains:

Weiss first proposed that a ferromagnet contains a number of small regions called domains. Ferromagnetic domains are small regions in ferromagnetic materials within which all the magnetic dipoles are aligned parallel to each other (figure 1.11). When a ferromagnetic material is in its demagnetised state, the magnetisation averages to zero. The process of magnetisation causes all
The domains to orient in the same direction. Domains are separated by domain walls. The formation of domains allows a ferromagnetic materials to minimize its total magnetic energy. The main contribution to the magnetic energy are magneto static energy, magneto crystalline energy and magnetostrictive energy which influence the shape and size of the domains. The magnetisation and hysteresis occurring in a ferromagnetic material can be suitably explained by domain theory [16, 18].
In the initial demagnetised state, the domains are arranged that the magnetisation averages to zero. When the field is applied, the domain whose magnetisation is nearest to the field direction starts to grow at the expense of other domains. The growth occurs by domain wall motion is provided by the external magnetic field. Eventually the applied field is sufficient to eliminate all domain walls from the sample leaving a single domain, with its magnetisation pointing along the easy axis oriented closely to the external magnetic field. Further increase in magnetisation can occur only by rotating the magnetic dipoles from the easy axis of magnetisation into the direction of the applied field. In crystals with large magnetocrystalline anisotropy, large fields can be required to reach saturation magnetisation. So we will now discuss the magnetocrystalline anisotropy associated with magnetic materials.

1.2.5 Magnetic Anisotropy:

Magnetic anisotropy generally refers to the dependence of magnetic properties on the direction in which they are measured. The magnitude and type of magnetic anisotropy affect properties such as magnetisation and hysteresis curves in magnetic materials. The important and common sources of magnetic anisotropy, magneto crystalline anisotropy, shape anisotropy, surface anisotropy along with induced magnetic anisotropy are discussed here [15].

1.2.5. a.Magnetocrystalline Anisotropy:

Magneto crystalline anisotropy is the tendency of the magnetisation to align itself along a preferred crystallographic direction. For example, body centred cubic Fe has the (100) direction as its easy axis. In nickel, which is a
face centred cubic, the easy axis is (111). It is observed that the final value of the spontaneous magnetisation is the same, no matter which axis the field is applied along, but the field required to reach that value is distinctly different in each case. The physical origin of magnetocrystalline anisotropy is the spin orbit coupling resulting in orientation of the spins relative to the crystal lattice in a minimum energy direction, the so called easy direction of magnetisation.

\[
E = \frac{\mu_0}{4\pi r} (\alpha_1 \alpha_1 + \alpha_2 \alpha_2 + \alpha_3 \alpha_3) + k_1 \alpha_1 \alpha_1 \alpha_2 \alpha_2
\]

**Figure 1.13** Anisotropy of magnetisation in Fe

Aligning the spins in any other direction leads to an increase in energy, the anisotropy energy \( E_k \). For a cubic crystal \( E_k \) is related to two anisotropy constants \( K_J \) and \( K_i \) by

\[
E = \frac{\mu_0}{4\pi r} (\alpha_1 \alpha_1 + \alpha_2 \alpha_2 + \alpha_3 \alpha_3) + k_1 \alpha_1 \alpha_1 \alpha_2 \alpha_2
\]

(1.20)
where \(a_1, a_2\) and \(a_j\) are the direction cosines of the magnetisation vector relative to the crystallographic axis. In all materials the anisotropy decreases with increasing temperature and near \(T_c\), there is no preferred orientation for domain magnetisation.

1.2.5. b. Shape Anisotropy:

In a nonspherical piece of material it is easier to induce a magnetisation along the long direction than along the short direction. This is so because the demagnetising field is less along a short direction, because the induced poles at the surface are farther apart. For a spherical sample there is no spherical anisotropy. The magnetostatic energy density can be written as

\[
E = \frac{1}{2} \mu_0 N_d M^2
\]

(1.21)

where \(N_d\) is the tensor and represents the demagnetised factor (which is calculated from the ratio of the axis). M is the saturation magnetisation of the sample. For example the shape anisotropy energy of a uniform magnetised ellipsoid is

\[
E = \frac{1}{2} \mu_0 V (N_x M_x^2 + N_y M_y^2 + N_z M_z^2)
\]

(1.22)

Where the tensors satisfied the relation: \(N_x + N_y + N_z = 1\)

1.2.5. c. Surface Anisotropy:

In small magnetic nanoparticles, a major source of anisotropy results from surface effects. The surface anisotropy is caused by the breaking of the symmetry and their reduction of the nearest neighbour coordination. The protective shell or ligand molecules which cover the small particles play an
important role as well leading to a change of the electronic environment on the particle surface.

1.2.5. d. Induced Magnetic Anisotropy

Induced magnetic anisotropy is not intrinsic to the material, but is produced by treatment such as annealing which has directional characteristics. Both the magnitude of the anisotropy and the easy axis can be altered by appropriate treatments. Techniques such as casting, rolling or wire drawing are used to induce anisotropy in polycrystalline alloys.

1.3 Magnetism in ultrafine nanoparticles:

Nanomagnetism Ultrafine magnetic particles with nanometric dimensions are found to exhibit novel properties compared with their conventional coarse grained counterparts. Magnetic nanoparticles are dominated by unique features like single domain nature, superparamagnetism and sometimes by unusual phenomena like spin glass and frustration. The variation of coercivity in ultrafine particles is also an interesting phenomenon. The unusual behaviour exhibited by nanoparticles is mainly due to two major reasons, finite size effects and surface effects. We will briefly deal with these special features of ultra fine nanoparticles one by one.

1.3. a Single Domain Particles:

In a large body there could be a minimum domain size below which the energy cost of domain formation exceeds the benefits from decreasing magnetostatic energy. This implies that a single particle of size comparable to the minimum domain size would not break up into domains. Qualitatively it is
observed that if a particle is smaller than about 100 nm, a domain wall simply can't fit inside it, resulting in single domain particles. A single domain particle has high magnetostatic energy, but no domain wall energy, whereas a multidomain particle has lower magnetostatic energy but higher domain wall energy. Before application of an external field, the magnetisation of a single domain particle lies along an easy direction which is determined by the shape and magnetocrystalline anisotropies. When an external field is applied in the opposite direction, the particle is unable to respond by domain wall motion and instead the magnetisation must rotate through the hard direction, to the new easy direction [16, 19, and 20].

The magnetisation curve for a single domain particle can be calculated using Stoner-Wohlfarth Model [15]. The coherent domain rotation concept is considered here. Consider a single domain magnetic field $H$ which is applied at an angle $\theta$ to the easy axis of uniaxial anisotropy. If the magnetisation of the particle then lies at an angle $\theta$ to the magnetic field direction, the energy density of the system

$$E = k \sin^2(\theta - \phi) - \mu_0 H M \cos \phi$$  \hspace{1cm} (1.23)

The energy can be minimized to find the direction of the magnetisation at any given value of the applied magnetic field. Analytic calculations are possible for this model for $e = 0$ to $e = 12$. This model demonstrates how the anisotropies present in a system can lead to hysteresis.
1.3. b Variation of coercivity with particle size in fine particles:

As the particle size is reduced, it is typically found that the coercivity increases goes through a maximum and then tend toward zero. In multidomain particles, magnetisation changes by domain wall motion. The size dependence of coercivity is experimentally found to be given by [16]

\[ H_c = a + \frac{b}{D} \]  \hspace{1cm} (1.24)

where \( a \) and \( b \) are constants and \( D \) is the particle diameter.

Below a critical particle size \( D_c \), the particles become single domain and in this range the coercivity reaches a maximum. The particles with size \( D_c \) and smaller change their magnetisation with by spin rotation. As the particle size decreases below \( D_c \) the coercivity decreases, because of thermal effects according to

\[ H_c = g - \frac{h}{D^{3/2}} \]  \hspace{1cm} (1.25)

where \( g \) and \( h \) are constants.

![Figure 1.14 Variation of coercivity with particle size](image)
Below a critical diameter $D_s$ the coercivity is zero, because of thermal effects, which are now strong enough to spontaneously demagnetise a previously saturated assembly of particles. Such particles are called superparamagnetic and the phenomenon, superparamagnetism.

### 1.3. c Superparamagnetism:

If single domain particles become small enough that, $KV$ (where $K$ is the magnetic anisotropy), constant and $V$ the volume of the particle) would become so small that the thermal energy fluctuations could overcome the anisotropy forces and spontaneously reverse the magnetisation of a particle from one easy direction to the other even in the absence of an applied field. As a result of the competition between anisotropy and thermal energies, assemblies of small particles show behaviour similar to paramagnetic materials, but with much larger magnetic moment. This moment is the moment of the particle and is equal to $m=MV$. It can be quite large thousands of Bohr Magnetons. An applied field would tend to align this giant moment, but $k_BT$ would fight the alignment just as it does in paramagnet. Thus this phenomenon is called superparamagnetism [14]. If the anisotropy is zero or very weak, one would expect that the total moment could point in any direction. Hence Langevin Function can be used to define magnetization $M = N_m L(x)$ where $L(x) = \coth(x) - \frac{1}{x}$ as given in equation 1.6 and 1.7. The two distinct features for superparamagnetic systems are (i) magnetisation curves measured at different temperatures superimpose, when $M$ is plotted as a function of $\frac{H}{T}$. There is no
hysteresis: both remanence and Coercivity are zero. The anisotropy energy $K_V$ represents an energy barrier to the total spin reorientation hence the probability for jumping thin barrier is proportional to the Boltzmann factor $\exp(-\frac{kV}{k_B T})$.

At high temperature, the moments on the particles are able to fluctuate rapidly. The relaxation time $\tau$ of the moment of a particle is given by

$$\tau = \tau_o \exp(\frac{kV}{k_B T})$$  \hspace{1cm} (1.26)

where $\tau_o$ is typically 10.9 s. These fluctuations slow down ($\tau$ increases) as the sample is cooled and the system appears static when $\tau$ becomes much larger than the measuring time of the particular laboratory experimental technique.

The typical experiment with a magnetometer takes 10 to 100 seconds. Using $\tau$=100s and $\tau$=10·9 s, we can obtain the critical volume as

$$V_{cr} = \frac{25k_B T}{k}$$ (1.27)

A particle with volume less than this act superparamagnetically on the 100s experimental time scale. The equation can be rearranged to yield

$$T_B = \frac{kV}{25k_B}$$ (1.28)

$T_B$ is called the blocking temperature. Below $T_B$, the free movement of the magnetic moment is blocked by the anisotropy. Above $T_B$ the system appears Superparamagnetic. The blocking temperature can be easily measured FC-ZFC measurements using a SQUID/magnetometer.

**1.3. d Frustration:**

Consider a lattice in which only nearest antiferromagnetic interactions operate. On the square lattice it is possible to satisfy the requirement that
nearest neighbour spins must be antiparallel. However on a triangular lattice, if two adjacent spins are placed parallel, naturally there is a dilemma for the third spin. The system cannot achieve a state that entirely satisfies its microscopic state, but does possess a multiplicity of equally unsatisfied states, hence under aggravation. Aggravated systems hence show metastability, hysteresis effects and time dependent relaxation towards equilibrium. In some systems, geometry of the lattice can disturb the ordering of the spins [13].

1.3. e Spin glass:

Spin glass can be considered as a random yet co-operative freezing of spins at a well defined temperature $T_f$ or $T$, below which metastable frozen state appears without usual magnetic long range ordering. This behaviour is normally exhibited in a non magnetic lattice populated within a dilute random distribution of magnetic atoms. The phase transition at the freezing temperature (glass transition) shows a transition to a disordered state which is distinctly different from the high temperature disordered state. The distribution of distances between moments in a random site spin glass leads to competing interaction of RKKY type and therefore the sign depends on the distance between the ions [21, 22].

The competing interaction leads to frustration leading a multi-degenerate ground state which also shows a co-operative freezing transition. As a spin glass is cooled from high temperature, the independent spins slow down and build up into locally correlated unit known as clusters. As the temperature cools to $T_f (T_g)$, the fluctuation in the clusters progressively slow down. The
interactions between spins become longer range so that each spin becomes more aware of spin in a progressively gray regions amend it. At T_r, the system finds one of its ground states and freezes. Below T_r the ground state appears to be glassy possessing metastability and slow relaxation behaviour. A wide range of relaxation times is also observed below T_r, showing that some free spins of small superparamagnetic clusters are still there. The co-operative spin freezing in spin glasses is still not yet fully understood.

1.3. f Finite Size Effects and Surface effects:

The nanoparticles are found to exhibit anomalous magnetic properties like enhancement in Curie temperature, change in coercivity, strong decrease in saturation magnetisation etc. These properties are explained on the basis of finite size effect and surface effect. By finite size scaling theory the different magnetic characteristics like T_c, H_c, and M_s etc can be assumed to be varying as a function of particle size and the variations can be theoretically modelled through equations. For example the finite scaling theory predicts a shift in transition temperature from that of a bulk should depend on the size of the system in the following manner

\[ \frac{T_c(\alpha) - T_c(D)}{T_c(\alpha)} = \left( \frac{D}{D_b} \right)^{-\gamma} \]  

(1.29)

Where T_c(\alpha) is the bulk curie temperature, T_c(D) is the curie temperature as a function of particle size D and n the initial exponent of the correlation length. In order to study finite scaling effect, the samples of different sizes should have same microstructure [22,23].
Like all the magnetic properties $T_c$ can also be affected by surface effect at the nanoregime. For nanoparticles a significant fraction of atoms is on the surface and it is reasonable to expect their magnetic interaction to be different from the core atoms and hence a different average of the magnetic properties results. Early models postulated the presence of a so called dead magnetic layer induced by the demagnetisation of the surface spins, which causes a reduction in $M_s$ because of its paramagnetic response. In more recent works devoted to the study of different ferrimagnetic oxides: YFe$_2$O$_3$, NiFe$_2$O$_4$, CoFe$_2$O$_4$, CuFe$_2$O$_4$, in the form of nanometric particles, a random spin canting at the surface, caused by competing antiferromagnetic interactions, was observed [24]. The origin of this noncollinear arrangement of the spins is attributed to the surface effects occurring in magnetic nanoparticle surfaces.

1.4 Ferrites:

Ferrites are one of the most significant magnetic materials which have been extensively used in modern electron technologies. Nanoparticles of spinel ferrites are of practical interest for a wide range of applications like high density magnetic information storage, magnetic resonance imaging, targeted drug delivery etc. Nanosized ferrites are revisited because they serve as ideal templates for fundamental research in ferrimagnetism at the nanolevel. They also offer immense possibilities of tailoring its various properties for applications [25, 26].
1.4. a Structure of Ferrites:

Ferrites are mixed metal oxides with iron (III) oxides as their main component. Ferrites crystallize in three crystal types [27-29].

1. Spin type with cubic crystal structure and general formula $M_2F_2O_4$

   Where $M = \text{Fe, Mn, Mg, Ni, Zn, Cd, Co, Cu, Al or a mixture of these.}$

2. Garnet type with cubic crystal structure and general formula $\text{LnFe}_2\text{O}_{12}$

   where Ln = Y, Srn, Eu, Od, lb, Dy, Ho, Er, Ti. or Lu.

3. Magnetoplumbite type with hexagonal crystal structure and general formula $M_2\text{Fe}_2O_4$ where $M = \text{Ba or Sr.}$

Spinel ferrites are the simplest of these three groups. A detailed picture of the spinel ferrites are shown below.

![Figure 1.15 Unit cell of spinel structure](image-url)
Spinel ferrites crystallize into the spinel structure, which is named after the mineral spinel, MgAlO$_4$. The spinel structure is determined primarily by the oxygen ion lattice (figure 1.15). The oxygen anions are packed in a face centred cubic arrangement such that there are two kinds of interstitial space between the anions-tetrahedrally co-ordinated A sites (figure 1.16) and octahedrally coordinated B sites (figure 1.17). There are eight formula units of MFe$_2$O$_4$ in a unit cell. Thus in a unit cell of 32 oxygen anions, there are 64 tetrahedral sites and 32 octahedral sites. It turns out that of the 64 tetrahedral sites only 8 are occupied and out of 32 octahedral sites, only 16 are occupied.

Factors like ionic radii of the cations, preference of ions to specific sites,
Madelung energy. Crystal field effects determine the distribution of cations in Spinels ferrites. The interesting and useful magnetic and electrical properties of the spinel are governed by the distribution of the iron and the divalent metal ions among the octahedral and tetrahedral sites of the spinel lattice. The general cation distribution is can be represented as \( \text{Me}^{2+}\text{Fe}^{3+}_{\delta}\text{Fe}^{3+}_{1-\delta}\left[\text{Me}^{2+}_{\delta}\text{Fe}^{3+}_{1+\delta}\right]O_{\text{4}} \) where the cations inside brackets are located in octahedral sites and the other outside brackets in tetrahedral sites. For \( \delta=1 \), the ferrite form the normal spinel while for \( \delta=0 \), it is called inverse spinel. For random distribution \( \text{ZnFe}_{2}0_{4} \) and \( \text{CdFe}_{2}0_{4} \) are normal spinels with all the divalent metal cation distributed in the tetrahedral sites. In inverse spinels like \( \text{NiFe}_{2}0_{4} \) and \( \text{CoFe}_{2}0_{4} \), the metallic cation occupies the octahedral sites only with ferric ions equally distributed in the two sites [29, 30].

Coming to the nanolevel a disordered cation distribution compared with the bulk has been observed in a number of ferrite systems. An inversion of degree of 60% (chapter 3) was reported in Manganese ferrite compared with 20% inversion in bulk. Also in Nickel ferrite and cobalt ferrite nanoparticles \( \text{Ni}^{2+}/\text{Co}^{2+} \) ions were experimentally observed in the tetrahedral sites. Most interesting is the cation distribution found in nanoparticles of zinc ferrite, where zinc ions with the highest preference for tetrahedral sites is found in the octahedral sites also. All these redistribution of cations lead to unexpected properties in these ferrites at the nanoregime [31-34].
1.4. b Magnetic Properties of Ferrites:

As the name suggests, ferrites exhibit a ferrimagnetic ordering. Neel explained the spontaneous magnetisation of these ferrites on the basis of Heisenberg's exchange forces. In ferrites three kinds of magnetic interactions are possible between, magnetic ions, which are occupied in the two crystallographically distinct lattice sites. These interactions are possible through the intermediate $\text{Fe}^{2+}$ ions by superexchange mechanism. The three possible interactions are A-A interaction, B-B interaction and A-B interaction [29, 30].

It has been established experimentally that these interaction energies are negative for ferrites and hence induce an antiparallel interaction. The strength in interaction between moments on various sites depends on the distances between the metal ions and the oxygen anions that links them and also on the angle between the three ions. The interaction is greatest for an angle of $180^0$ and also where the interatomic distances are shortest. In A-A and B-B cases, the angles are too small or the distances between the metal ions and oxygen ions are too large. For an undistorted spinel, the A-O-B angles are about $125^\circ$ and $154^\circ$. The B-O-B angles are $90^\circ$ and $125^\circ$. In the A-A interaction the angle is about $80^\circ$. Therefore, the interaction between moments on the A and B sites is strongest. The B-B interaction is much weaker and most unfavourable situation occurs in A-A interaction. Thus with A-O-B interaction predominating the spins will be oppositely magnetised in the sublattices A and
with a resultant magnetic moment equal to the difference between those of A and B site ions.

In developing his theory of ferrimagnetism, Neel postulated two separate Sublattice magnetisation corresponding to the two sublattices. In general, the value of saturation magnetisation based on Neel's two sublattice model is that the resultant saturation magnetisation is may be written as $M_s = |M_B - M_A|$. The variation of magnetisation with temperature in ferrites depends on the magnitude of sublattice magnetisations at O K and the ratios of the magnitudes of exchange interactions between the sublattices. There can be deviations in the net magnetisation which can be attributed to several factors:

(i) The cation distribution on various sites may not be as perfect as predicted.

(ii) The orbital moment may not be quenched.

(iii) The direction of the spins may not be antiparallel in the interactions. They may be canteded. Ferrites exhibit hysteresis phenomenon during the magnetisation cycle (figure 1.1). The shape of the loops varies with respect to individual ferrites.

When the particle size is reduced to a few tens of nanometers, ferrite materials exhibit high coercive field, high Curie temperature and low saturation Magnetisation as compared to their corresponding bulk values. These phenomenon have been explained on the basis of finite size scaling effects and
Surface effects occurring in the nanoregime. In addition to this, the presence of a different cation distribution in the nano regime leading to different type of interactions play a significant role in deciding the magnetic properties.

1.4. c Electrical properties of ferrites:

Ferrites can be clubbed along with the class of somewhere between semiconductors and insulators. Spinel ferrites have high electrical resistivities and low eddy currents and dielectric losses. This is a major advantage over ferromagnetic materials. In ferrites, the temperature dependence of mobility of electrons affects the conductivity and the carrier concentration is almost unaffected by temperature variation. The charge carriers in ferrites are localized at the magnetic atoms. In ferrites the cations are surrounded by close packed oxygen anions and on can be treated as isolated from each other. There will be little direct overlap of the anion charge clouds or orbitals. Alternatively the electrons associated with particular ions cations will remain isolated and hence a localized electron model is more appropriate in the case of ferrites rather than the collective electron band model. The main conductivity mechanism in ferrites is attributed to electrons hopping between Fe$^{3+}$/Fe$^{2+}$ in octahedral sites. Resistivity in ferrites is very sensitive to preparation techniques, stiochiometry, sintering condition, microstructure etc.

The measurement of electrical properties as a function of frequency and analysis by complex dielectric spectroscopy allow a separation of contribution of grains, grain boundaries and electrode polarization. The electrical studies provide important information on the behaviour of localized electric charge
carriers, which give rise to a better understanding the dielectric polarization. It is to be of notice that electrical properties in ferrites are affected by the distribution of cations in the sites, by non magnetic and magnetic substitutions, by the amount of Fe$^{2+}$ present, sintering conditions, grain size and grain growth effects [30]. In the case of nanostuctured ferrites the electrical behaviour is found to be quite interesting on account of the large number of interfaces formed at the boundaries of the nanocrystallites. As in the case of magnetic properties an unexpected cation distribution has a direct influence on the electrical properties of ferrites at the nanoregime.

1.5 Aim of the present work:

The aim of the present work is to study the influence of high valency cation like cobalt on the physical properties of mixed Nickel zinc ferrites. This inturn would give the understanding of site occupancy of substituted cobalt ions and its influence on mixed ferrites. Study of nickel zinc ferrites with cobalt substitution is very limited and no work had been reported with cobalt substitution in mixed nickel zinc ferrites. It is aimed to understand whether the substitutions of cations enter into A or B sites of the lattice of Ni-Zn mixed ferrites and there by resulting the changes in the properties of the mixed Ni-Zn ferrites. The formula of the materials is Ni$_{0.95-x}$Zn$_{0.05}$Co$_x$Fe$_2$O$_4$ and Zn$_{0.95-x}$Ni$_{0.05}$Co$_x$Fe$_2$O$_4$ where x varies from 0.01 to 0.06. It is proposed and expected to obtain the new basic knowledge of cation distribution in sites and the influence of this distribution on structural, magnetic, dielectric and electrical properties.
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