Chapter 1

Introduction
CHAPTER – 1

1.1 INTRODUCTION

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. Nanomaterials are very important because of their unique electrical, magnetic, optical and other physical properties. The magnetic nanoparticles are interesting as their size is comparable to the size of a magnetic domain which results in two important types of magnetic behaviour namely superparamagnetism and ferromagnetism. The Magnetic nanoparticles have attracted considerable interest in recent years, both at academic as well as technical fronts, because of their potential applications in high frequency transformers, ferrofluids, pigments in paints and ceramics, biomedical applications like drug delivery system, hyperthermia, NEMS/MEMS, high density magnetic recording, sensors, varistors and dye-sensitized solar cells [1-10]. A variation in particle size can also modulate the physical properties even without varying the composition. As the size of the particles decreases below 100 nm, a large fraction of the constituting atoms are found on the surface of the nanocrystals, this induces significant changes in the structure and magnetic properties of the nanophase materials as compared with their bulk counterparts. The increase in surface to volume ratio leads to an increasing dominance of the behaviour of the atoms on the surface of the particles over that of those in the interior of particles which affect both the properties of the particles in isolation and interactive environment with other materials. Large surface area of the magnetic nanoparticles also results in a lot of interaction between the intermixed materials in composition leading to special properties such as increased number density, chemical reactivity and increased chemical/heat resistance. The increase in the interfacial energy due to defects, dislocations and lattice imperfections leads to changes in various physical properties. This makes them quite flexible to tailor the material for specific applications [11-15]. Specially, the domain wall structure encountered in the bulk crystalline ferrites is replaced by a single domain structure characteristic of each particle, thus leading to new phenomena such as superparamagnetism, extra anisotropy contributions and spin canting [16-21]. These materials have created a high interest in
recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties.

1.2 FERRITES

Ferrites are chemical compounds consisting of ceramic materials with Iron (III) oxide (Fe$_3$O$_4$) as their principle component. Ferrites are the ferrimagnetic materials which possess the combined properties of magnetic materials and insulators. They are used to make permanent magnets and ferrite cores for transformers. The high electrical resistance, low eddy current loss and good magnetic properties of these materials make them an ideal for wide range of potential applications such as microwave devices, high-density memory devices, transformer cores, recording heads, magnetic fluids etc. [22-35]. The magnetic and electrical properties of the ferrites materials depend upon their chemical composition, synthesis conditions and crystal structure of the lattice [22]. In terms of the magnetic properties, ferrites are often classified as "soft" and "hard" which refer to their low or high coercivity of their magnetism, respectively. In terms of their magnetic properties, the different ferrites are often classified as "soft" and "hard" which refers to their low or high magnetic coercivity, respectively.

1.2.1 Classification of Ferrites

(i) Soft ferrites

Soft ferrites are ferrimagnetic materials with cubic crystal structure and they are characterized by chemical formula MO·Fe$_2$O$_3$, where M is a transition metal ions like Iron, nickel, manganese or zinc. These ferrites are used in transformer or electromagnetic cores have low coercivity value. The low coercivity means the material's magnetization can easily reverse direction without dissipating much energy (hysteresis losses), while the material's high resistivity prevents eddy currents in the core, another source of energy loss [36]. 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. Soft ferrites are ceramic electromagnetic materials, dark gray
or black in appearance. The most common examples are Mn-Zn ferrite and Ni-Zn ferrites.

(ii) **Hard ferrites**

In contrast permanent ferrite magnets are made of hard ferrites, which have a high coercivity and high remanence after magnetization. These are composed of Iron, Barium or Strontium oxides. In a magnetically saturated state they conduct magnetic flux well and have a high magnetic permeability [37]. This enables these so-called ceramic magnets to store stronger magnetic fields than Iron itself. The main advantage of hard ferrites in that they are of extremely low cost because of their ease of processing and the low cost of the raw materials due to which these materials are most widely used in household products such as refrigerator magnets. The maximum magnetic field $B$ is about 0.35 Tesla and the magnetic field strength $H$ is about 30 to 160 kiloampere turns per meter.

The most common hard ferrites are:

1. Barium ferrite: $\text{BaFe}_{12}\text{O}_{19}$ ($\text{BaO}\cdot6\text{Fe}_2\text{O}_3$), a common material for permanent magnet applications. They are used in subwoofer magnets and as a medium for magnetic recording, on magnetic stripe cards.

2. Strontium ferrite: $\text{SrFe}_{12}\text{O}_{19}$ ($\text{SrO}\cdot6\text{Fe}_2\text{O}_3$), used in micro-wave devices, recording media, telecommunication.

3. Cobalt ferrite ($\text{CoFe}_2\text{O}_4$) used for magnetic recording.

On the basis of the crystal structure, ferrites are classified as spinel, garnet, ortho and hexaferrites. The work described in the thesis is based on the spinel ferrites which have the cubic spinel structure. The spinel ferrites are discussed in details in the following section.

### 1.2.2 Spinel Ferrite

Ferrites are a class of spinel, which have FCC structure with the molecular formula $\text{AB}_2\text{O}_4$, where A and B are divalent and trivalent ions respectively. This structure consist of a cubic closed packed cage of Oxygen ions with the metallic ions occupying the tetrahedral A and octahedral B interstitial site. Fig. 1.1 shows two of the eight octants of
the cubic unit cell structure of the spinel ferrite showing the tetrahedral, octahedral and Oxygen sites. There are 64 tetrahedral and 32 octahedral sites in the unit cell of which only 8 tetrahedral and 16 octahedral sites are occupied by the metal ions. All Fe$^{2+}$ and half of the Fe$^{3+}$ metal ions occupy octahedral sites and remaining Fe$^{3+}$ metal ions occupy tetrahedral sites. Electron spins of Fe$^{3+}$ ions in octahedral interstices are aligned antiparallel to those in tetrahedral interstices, and hence no net magnetization is observed from these ions. The Fe$^{2+}$ ions align their spins parallel to Fe$^{3+}$ ions in adjacent octahedral sites leading to a net magnetization. Hence, Fe$_3$O$_4$ exhibits ferrimagnetisms.

The general formula representing the spinel ferrites is given as [38, 39].

$$\left[\text{Me}^{2+}_x\text{Fe}^{3+}_{1-x}\right] \left[\text{Me}^{3+}_{1-x}\text{Fe}^{3+}_{x}\right] \text{O}_4$$

Where, Me is a divalent metal ions such as Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ etc. and x is the degree of inversion. The magnetic structure of the spinel ferrite depends upon the magnetic ions residing on the interstitial A and B sites and relative strength of inter and intra sub lattice interaction.

**Figure 1.1:** A unit cell of spinel structure with the tetrahedral and octahedral types of interstitial sites.
Depending on the site occupancy of divalent and trivalent ions in the spinel structure, it is further classified as normal spinel, inverse spinel and mixed spinel [40, 41]. In normal spinel, the divalent ions occupy one-eighth of tetrahedral sites and trivalent ions occupy one-half of octahedral sites. When divalent and one half of the trivalent ions have exchanged their positions, then they are called the inverse spinel (Table 1.1) and the mixed spinel ferrites are the one in which divalent ions are present both in tetrahedral and octahedral sites. The inverse spinel and the normal spinel structure are considered as two extreme cases, since X-rays and neutron diffraction show that intermediate structure do really exist [42, 43]. Hence it is a common practice to describe spinel structure in terms of a parameter denoted by \( \lambda \) which is defined as the fraction of B ions in the tetrahedral sites. The value of \( \lambda \) ranges from zero for those having normal spinel structure to 0.5 for inverse spinel structure. With the help of this parameter, one can easily express cation distribution and type of structure by just a number.

**Table 1.1** Cation distribution and net moment per molecule of some typical ferrites.

<table>
<thead>
<tr>
<th>Ferrite Type</th>
<th>Structure</th>
<th>Tetrahedral (A) sites</th>
<th>Octahedral (B) sites</th>
<th>Net moment (( \mu_B ) per molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe(_2)O(_4)</td>
<td>Inverse</td>
<td>( \text{Fe}^{3+} ) 5 ( \rightarrow )</td>
<td>( \text{Ni}^{2+} ) 2 ( \leftarrow )</td>
<td>( \text{Fe}^{3+} ) 5 ( \leftarrow )</td>
</tr>
<tr>
<td>ZnFe(_2)O(_4)</td>
<td>Normal</td>
<td>( \text{Zn}^{2+} ) 0</td>
<td>( \text{Fe}^{3+} ) 5 ( \leftarrow )</td>
<td>( \text{Fe}^{3+} ) 5 ( \rightarrow )</td>
</tr>
<tr>
<td>MgFe(_2)O(_4)</td>
<td>Inverse</td>
<td>( \text{Mg}^{2+} ) 0</td>
<td>( \text{Fe}^{3+} ) 4.5 ( \rightarrow )</td>
<td>( \text{Mg}^{2+} ) 0</td>
</tr>
<tr>
<td>Ni(<em>{0.9})Zn(</em>{0.1})Fe(_2)O(_4)</td>
<td>Mixed</td>
<td>( \text{Fe}^{3+} ) 4.5 ( \rightarrow )</td>
<td>( \text{Ni}^{2+} ) 1.8 ( \leftarrow )</td>
<td>( \text{Fe}^{3+} ) 4.5 ( \leftarrow )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
1.3 THEORY OF MAGNETIC DOMAINS

Ferromagnetic materials get their magnetic properties not only due to magnetic moments carried out by their atoms but also because of the materials is made up of small regions known as magnetic domains each separated by domain wall. In each domain, all of the atomic dipoles are coupled together in a preferential direction. This alignment develops as the material develops its crystalline structure during solidification from the molten state. A domain wall is an interface separating magnetic domains as shown in figure 1.2. It is a transition between different magnetic moments and usually undergoes an angular displacement of 90° or 180°. Although they actually look like a very sharp change in magnetic moment orientation, when looked at in more detail there is actually a very gradual reorientation of individual moments across a finite distance. The energy of a domain wall is simply the difference between the magnetic moments before and after the domain wall was created. The width of domain wall varies due to two opposing energies that created it; these are the magnetocrystalline anisotropy energy and the exchange energy, both of these tends to be as be in a more favorable energetic state. The anisotropy energy is lowest when the individual magnetic moments are aligned with the crystal lattice axes thus reducing the width of the domain wall, whereas the exchange energy is reduced when the magnetic moments are aligned parallel to each other and thus makes the wall thicker, due to the repulsion between them (where anti-parallel alignment would bring them closer – working to reduce the wall thickness). In the end equilibrium is reached between the two and the domain wall's width is set as such.

In an external magnetic field, the directions of the magnetization of domains are forced to align with the field or domains with favorable magnetization direction grow in size at the cost of domains with unfavorable directions. Both mechanisms increase the net magnetization of the bulk material. These both mechanisms increase the net magnetization of the bulk material. At infinite magnetic field strength, all dipoles are aligned with the magnetic field and the system has reached to its saturation magnetization. When the field is removed, the magnetization tends to relax into its original state with randomly oriented domains. However, in order to reach this equilibrium state, the system may have to pass unfavorable states that can keep it away
from actually reaching equilibrium. When all of the domains are aligned, the material is said to be magnetically saturated as shown in Fig. 1.3. When a material is magnetically saturated, no additional amount of external magnetization force will cause an increase in its internal level of magnetization.

Figure 1.2: Domain wall and domain wall energy [44].

Figure 1.3: Magnetized and unmagnetized materials
1.4 HYSTERESIS LOOP AND MAGNETIC PARAMETERS

All the ferrites generally show hysteresis behaviour like ferromagnetic materials. A hysteresis loop shows the relationship between the induced magnetic flux density B and the magnetizing force H. The lag between the inductions with respect to as the B-H curve or M-H curve, where M is the induced magnetic moment. A typical hysteresis loop is shown in Fig. 1.4. The loop is generated by measuring the magnetic flux of a magnetic material while the applied magnetic field is varied from +ve to –ve value. A material which has never been magnetized will follow the dotted line as the applied magnetic field increased. The dotted line shows that magnetic flux is stronger when the applied magnetic field is greater. At point “a” the maximum number of domains are aligned in the same direction and further increase in the magnetic field will produce very little or sometimes no increase in the magnetic flux. The material has reached the position which is called saturation magnetization. When applied field approaches to zero, the sample starts to demagnetize and the loop moves from point “a” to “b”.

The point “b” shows that even in the absence of external magnetic field, the material retains some magnetic moment. This is called retentivity. As the applied field is reversed, the curve moves from point “b” to “c” and the magnetic flux reduce to zero. This point is called coercivity. Due to this –ve applied field, the domains flipped so that the net magnetic flux become zero.

When again the magnetic field is increased in reverse direction, the material again moves toward the saturation magnetization but in –ve direction and reaches to “d”. After removing the applied field H, the curve moves from point “d” to “e”. The increase in the +ve direction will bring the magnetic flux to zero. It is noted that the curve is not passing through the origin because of remanence. It reaches to point “f” and then loop is completed. The area under include in the hysteresis loop is a measure of magnetic losses. So it provides information about the magnetic materials, which can be useful in the selection of the materials for the specific purpose [45].
1.5 MAGNETIC DOMAINS AT VARIOUS LENGTH SCALES.

In multidomain particles, the nucleation of domain walls takes place when the sample is placed in the magnetic field and the whole process is time dependent [43]. Single domain nanoparticles can be characterized by their large total magnetic supermoment, which exhibits a paramagnetic like behavior above a characteristic temperature threshold named blocking temperature. This particular temperature, in contraposition with the Tc, is extremely dependent on the experimental observational time-window and this characteristic gives place to a complex theoretical frame with especial experimental features [46].

Figure 1.4: Hysteresis loop of a magnetic material.
In a multidomain magnetic material, multiple magnetic domains exist as a result of the balance between the exchange interaction energy that favors the parallel alignment of neighboring atomic moments and the magnetostatic interaction energy that tries to break them into smaller domains oriented antiparallel to each other. The domain size is determined by the relative counterbalance between both energies. With decreasing size of the magnetic system, there is a critical value below which the magnetostatic energy no longer allows for the breaking of the system into smaller domains and so the system is composed of a single domain, as illustrated in Fig. 1.5. Typical values for $r_c$ are of the order of tens of nanometers. For single domain particles, the magnetization procedure is realized by coherent rotation of all inside spins and hence larger coercivities. On the other hand, superparamagnetic particles relax by Neel process and Brownian process thus having no coercivity and coercivity. The superparamagnetic phenomenon is discussed in detail in the following section.
1.6 SUPERPARAMAGNETISM

Superparamagnetism (SPM) is a phenomenon by virtue of which ferro/ferri-magnetic materials exhibit a behavior similar to paramagnetism even below the Curie (T$_C$) or the Neel temperature (T$_N$) [47, 48]. This is a small length-scale phenomenon, where the energy required to change the direction of the magnetic moment of a particle is comparable to the ambient thermal energy. At this point, the rate at which the particles will randomly reverse their direction becomes significant. If we consider ferro-magnetic or ferri-magnetic particles, a decrease in particle size implies that the energy barrier for magnetization reversal may become so low that it can overcome by the independent SP particles leaving no coercivity (H$_C$) or retentivity while studying the sample to magnetization cycles.

Normally, coupling forces in ferromagnetic materials cause the magnetic moments of the neighboring atoms to align, resulting in very large internal magnetic field. This is what distinguishes ferromagnetic materials from paramagnetic materials. At temperatures above the Curie temperature for ferromagnetic materials or the Neel temperature for antiferromagnetic materials, the thermal energy is sufficient to overcome the coupling forces, causing the atomic magnetic moments to fluctuate randomly. Because there is no longer any magnetic order, the internal magnetic field no longer exists and the material exhibits paramagnetic behavior. If the material is non-homogeneous, one can observe a mixture of ferromagnetic and paramagnetic clusters of atoms at the same temperature.

SPM occurs when the magnetic material is composed of very small crystallites in the size range of 1-10 nm. It is a size-dependent phenomenon as the magnetic anisotropy energy which keeps a particle magnetized in a specific direction is proportional to the volume of a particle [49, 50]. In this case, even at the temperatures, the thermal energy is not sufficient to overcome the coupling forces between neighboring atoms but it is sufficient to change the direction of magnetization of the entire crystallite. The resulting fluctuations in the direction of magnetization cause the magnetic field average to zero. Thus the ferro/ferri-magnetic materials behave in a manner similar to paramagnetism except that the magnetic moment of the entire crystallite tends to align with the magnetic
field instead of each individual atom being independently influenced by an external magnetic field in paramagnetic materials.

1.6.1 Magnetic relaxations in superparamagnetic size particles

When placed in an external magnetic field, the magnetic moments of SP size particles align in the direction of applied magnetic field via magnetic moment and particle rotation. In superparamagnetic particles when the gradient field is removed, the randomization of aligned spins is governed by Brownian motion and Néel rotation. Brownian motion and Néel rotation are magnetic relaxation mechanisms due to particle and spin rotation respectively. Brownian relaxation is achieved via bulk rotation of the particles dispersed in a fluid. On removal of applied magnetic field these particles completely relax back with the help of thermal energy available at ambient temperature. For superparamagnetic particles anisotropic energy (KV) is always less then thermal energy (kT).

1.7 MAGNETIC ANISOTROPY

The term magnetic anisotropy is used to portray the directional dependence of magnetic properties in magnetic materials. This dependency arises when internal energy of the material is associated directionally to the spontaneous magnetization of the magnetic material. It results in the generation of easy and hard axis of magnetization. The overall magnetization of these kind of magnetic systems tend to lie in one direction. The main cause of this directionality dependence arises due to spin-orbit interaction and dipolar coupling of magnetic moments. The main consequences of spin-orbit coupling are the intrinsic anisotropy [51], surface anisotropy [52], and magnetostriction [53], while the shape anisotropy comes from a dipolar contribution [54]. These anisotropy energies ranges from $10^{-3} - 10^{6}$ erg/cc which is equivalent to $10^{-8} – 10^{-3}$ eV per atom. The magnitude varies due to symmetry aspects in magnetic structure and extent of coupling [54]. In bulk magnetic materials, the contribution from magnetocrystalline anisotropy and magnetostatic interactions dominate on other terms. On the other side, when the size is confined to a space of few nanometers, the dominance of surface and shape anisotropy is observed, though contribution from other terms exist in the nanostructures. A magnetic
material is said to have this kind of anisotropy when it gets magnetized in certain directions easily as compared to others. These directions are related to the principal axes of the lattice structure of crystal. The combination of spin-orbit coupling and crystal symmetry of the lattice gives rise to this effect, also known as crystal magnetic anisotropy [55].

1.8 INTERACTIONS BETWEEN MAGNETIC NANOPARTICLES

In ultra fine particles different kinds of magnetic interparticle interactions exist and the interaction strength varies with the volume concentration [54]. The different types of magnetic interactions which can be important in allowing the magnetic moments in a solid to interact with each other are explained in the following:

(i) Dipole – dipole interaction:

Two magnetic dipoles $\mu_1$ and $\mu_2$ separated by a distance $r$ will have a potential energy

$$E = \frac{\mu}{4\pi r^3} \left[ \mu_1 \mu_2 \frac{3}{2} (\mu_1 \cdot r) (\mu_2 \cdot r) \right]$$  \hspace{1cm} (1.1)

This interaction is long-range and anisotropic in nature. From Fig. 1.6, it is seen that the strength of this interaction depends between their separation and their degree of mutual alignment. One can easily estimate the order of magnitude of dipolar effect for two moments each of $\mu_1 \approx \mu_2 \approx 1 \mu B$ separated by $r \approx 0.1$ nm that turns out to be $\mu^2/4\pi r^3 \approx 10^{-23}$, which is equivalent to about 1 K in temperature. Therefore dipolar interaction is much too weak to account for the ordering of most magnetic materials, since most of the magnetic materials order at much higher temperature.

(ii) Exchange interaction: The exchange interaction is actually an effect that arises from the interplay of electromagnetism with quantum mechanics. This interaction lies at the heart of the phenomenon of long-range magnetic order.
(iii) **Tunneling exchange interaction:** Another kind of interaction in fine particle system is tunneling exchange interaction where nanoparticles are only few nanometers apart from each other [56].

(v) **Superexchange interactions:** When the matrix is insulating, superexchange interaction can exist depending on the structure and the nature of the matrix and the bonding at the particle matrix interface. Exchange interactions are short ranged in insulating magnetic materials, but if the bonding is favorable, superexchange interactions may extend over large distances.

(iv) **RKKY interaction.** In nanoparticle assembly where the matrix and particles are both metallic, RKKY (Rudermann-Kittel-Kasuya- and Yosida) interaction occurs and depends on $d$, where $d$ is the distance between particles similar to dipolar interaction [57].

(v) **Superexchange interactions:** When the matrix is insulating, superexchange interaction can exist depending on the structure, the bonding at the particle matrix interface and the nature of the matrix and Exchange interactions are short ranged in insulating magnetic materials, but if the bonding is favorable, superexchange interactions may extend over large distances.

1.9 **FERROFLUID**

Ferrofluids were first developed and classified in the 1960s by Stephen Pappell at NASA as a method for controlling fluids in space [58]. NASA initially used them as rotating shaft seals in satellites and they are now serving the same purpose in a wide variety of machines, ranging from centrifuges to computer hard disk drives [59-61]. In South Africa, a company is utilizing ferrofluids in the separation of metals from ores or even separation of diamonds from beach sand by taking advantage of a density change that appears in the fluid under application of a magnetic field [62]. Ferrofluid is a stable colloidal dispersion of surfactant coated single domain ferro/ferri-magnetic particles in a suitable carrier liquid [63, 64]. The particles are typically of the order of 2-20nm in diameter and are in a permanent state of magnetization, i.e., they behave as magnetic dipoles even in the absence of an applied magnetic field. The liquid carrier can be a polar
or nonpolar. True magnetic fluids are homogenous throughout their volume and stable over longer time even in high intense magnetic field. It is a balance phenomenon of various attractive and repulsive forces. The number density of particle is \( \sim 10^{23} / \text{m}^3 \). The nanoparticles are coated with adsorbed surfactant layers to prevent particle agglomeration due to the Vander Waals force and dipole-dipole interactions among them even when strong magnetic field gradient (VM) is applied to the ferrofluid. The surfactant must be matched to the carrier type and must overcome the attractive Vander Waals and magnetic forces between the particles. The colloid and thermal stabilities, crucial to many applications, are greatly influenced by the choice of the surfactant. A typical ferrofluid is a two phase (solid & liquid) and three component system. Each of the constituent should be compatible and present in appropriate compositions. This is first primary requirement for a stable ferrofluid. These three primary constituents of magnetic liquids are discussed below:

(i) 5 – 10 % are the superparamagnetic nanoparticles particles made from materials such as iron oxide or mixed iron oxides of type \( [\text{M}^{2+}_{x} \text{Fe}^{3+}_{1-x}] [\text{Me}^{3+}_{x} \text{Fe}^{2+}_{1-x}] \) where \( \text{M} = \text{Ni, Co, Mn, Zn, Fe, Cd, Me = Fe, Gd, Er, Sm, La} \) [65] etc. Magnetic particles to be dispersed should be of approximately superparamagnetic size limit. The size of magnetic particles should be small enough to be suitably dispersed in a carrier liquid, but not too small so that their magnetic properties may disappear. Particles having size in the range 2-10 nm are suitable for stable ferrofluid.

(ii) 10 % is the surfactant e.g., oleic acid, tetramethyl ammonium hydroxide (TMAH), and sodium oleate, etc. The surfactants make layer around the nano-magnetic particles and prevent the agglomeration among them to maintain the consistency of the colloidal suspension. The surfactant should have an anchor polar group (head) that has a high affinity for the particle surface, as well as a flexible tail of proper length. The surfactant should also be chemically stable in the environment in which it is to be used. It must prevent particles from aggregation.

(iii) 80–85 % is the carrier liquids in which the surfactant coated particles are suspended. It can be polar or nonpolar. The selection of host liquids depends on the type of applications and should be chosen with lesser chemical reactivity. Carrier liquid plays a dominant role in deciding the suitability of magnetic fluid for different applications.
Carrier liquid should be so chosen as to cater the need of specific application. Commonly used carrier liquids are water, hydrocarbon ester, mineral and vacuum oil, silicon oil, etc. In general, the carrier liquid must have following characteristics. It should be magnetically passive and chemically stable. Its vapour pressure, viscosity and other physical properties must be chosen according to the type of application. It should be compatible with the surfactant. Ferrofluids are stable against gravitational and high intense magnetic field gradient. Brownian motion of particles caused by the thermal agitation at room temperature compensates the gravitational and magnetic forces. Surfactant layer of nearly 2 nm thickness coated on particles surface prevents agglomeration and coagulation by keeping magnetic particles at a distance to overcome the forces of attraction caused by Van der Waals forces and magnetic interaction. Fig. 1.6 shows the various constituents of magnetic fluids and the role of surfactant chain length in maintaining stability of the colloidal dispersion of magnetic nanoparticles.

Ferrofluid is one such nanoscale material which has been extensively used in microfluidic devices. The devices based on these are changing with spectacular pace. The particles are sufficiently small so that the ferrofluid retains its liquid characteristics even in the presence of a high magnetic field and substantial magnetic forces can be induced which results in fluid motion.

![Figure 1.6: Figure showing various constituents of magnetic fluids.](image-url)
1.9.1. General stability aspects of ferrofluids.

The stability of these colloids is an important issue which can be considered in a physicochemical view. The important energy terms per particle in this regard can be written as follows [66, 67]: Thermal energy = kT, Magnetic energy = \( \mu_0 HV \), Gravitational energy = \( \Delta \rho V g L \), where k is Boltzmann’s constant, T is temperature, \( \mu_0 \) is permeability of free space, V is the particle volume and L is the elevation in gravitational field.

(i) Stability in a magnetic field gradient. When magnetic field is applied particles are attracted to the higher-intensity regions of a magnetic field, while thermal motion counteracts the force of field and provides statistical motions that allow particles to move all portions of fluid. The magnetic energy \( \mu_0 MHV \) represents the reversible work in removing a magnetized particle from a point in the fluid, where the field is H, to a point in the fluid that is outside the field:

\[
W = -\int_{H}^{0} (\mu_0 M \frac{dH}{ds} V) ds \approx \mu_0 MHV
\]  

(1.2)

When some part of the fluid is located in a field-free region, then stability against segregation is favored by a high ratio of the thermal energy to the magnetic energy:

\[
\frac{\text{Thermal energy}}{\text{Magnetic energy}} = \frac{kT}{MHV \mu_0} \geq 1
\]  

(1.3)

By assuming spherical sized particle of diameter d, the above expression for maximum particle size becomes.

\[
d \leq \left( \frac{kT}{MHV \mu_0} \right)^{3/2}
\]  

(1.4)

Under normal conditions, the value of d is \( \sim 10 \) nm for having a stable dispersion in field gradient [57].

(ii) Stability against gravitational sedimentation. The relative influence of gravity to the magnetism can be understood by taking ratio of respective energies.
Under normal conditions, the ratio is near to 0.047 which indicates its lesser contribution in making the fluid unstable, as compared to gradient effects produced by magnetic field.

(iii) **Stability against agglomerative behavior.** A typical magnetic fluid consists of 10^{16} /mL where the particle collisions are very frequent. The energy required to separate a pair of dipole-dipole pair particles of diameter, \( d \) with surface to surface distance, \( s \) can be written

\[
E_{dd} = \frac{1}{12} \mu_0 M^2 V
\]

as But thermal energy is available to disrupt these agglomerates with the effectiveness of disruption governed by the ratio.

\[
\frac{\text{thermal energy}}{\text{dipole-dipole interaction}} = \frac{24 kT}{\mu_0 M^2 V}
\]

The ratio needs to be greater than unity for stability of dispersion which limits the particle size given by

\[
d \leq \left( 144 \frac{kT}{\pi \mu_0 M^2} \right)^{1/3}
\]

For magnetite particles at room temperature, the value of \( d \) is close to 10 nm [66].

### 1.9.2. Surface adsorption and steric stabilization

Apart from above physical factors, attractive Vander Waals interactions also prevails. To prevent the particles coming close to each other, they are coated with long chain molecules. The polar groups of adsorbed species associate onto the particle surface either physically/chemically with tails are chosen similar to surrounding fluid matrix. The chemical compatibility surfactant and carrier medium is basic requirement to while dispersing particles of ferrofluid [68].
In case of ionic ferrofluids the stability is maintained by an ionic surfactant, say TMAH with water as carrier medium. The particles are provided with electrical charges to keep away from each other. These ionic surfactant species adhere similar to the surface of magnetite particles, creating a net repulsion between the particles and stabilizing the colloid. In such magnetic fluids, particles usually acquire electrical charges due to:
1. Ions leaving the surface of particles,
2. Adsorption of ions formed by the liquid, e.g. H\(^{+}\) and OH\(^{-}\) in water,
3. Adsorption of ions formed by substances when dissolved in liquid e.g., fatty acid, phosphate etc.

![Image](image.png)

**Figure 1.7:** Schematic of a charge stabilized ionic ferrofluid.

The electric repulsion between charged particles is the Coulomb repulsion, which is controlled by the screening action of the surrounding counter ions in liquid. In colloidal science, the layer containing electrical charges is called “double layer” as shown in Fig. 1.7. The Coulomb repulsion is effective only when particles are close; hence, the double layer gets overlap. This results into a repulsive force and its strength depends on the size of the particles, concentrations of ions in liquid and the surface potential (usually 10 – 100 mV). Both surfacted and ionic ferrofluids are stable and the overall stability can be calculated theoretically while assuming certain physical parameters. The net interaction curve is an algebraic sum of Van der Waals attractive energy, attractive magnetic energy...
and steric repulsion energy whose decisive role are shown in Fig. 1.8 [69]. It is seen that the net potential energy curve presents an energy barrier of more than 20kT. Since the energy barrier exceeds the average thermal energy by twenty times and hence rate of agglomeration will be negligible.

\[ \delta = 2 \text{ nm} \]
\[ \delta = 0.5 \text{ nm} \]

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Figure 1.8: Potential energy versus surface–to-surface separation of sterically protected colloidal magnetite particles (d= 10nm, N= 10\textsuperscript{18} molecule, \( \delta \) is length of the tail).

1.9.3. Preparation of ferrofluids

There are several chemical method available for the synthesis of stable ferrofluid viz., sol-gel processing, hot spraying, evaporation condensation, matrix isolation, laser induce vapor phase reactions and aerosols amongst them coprecipitation is most convenient one to follow [70–76]. Generally spinel ferrites can be prepared from an aqueous solution containing ferric ions and the other divalent metal ions using an alkaline solution. There are two basic steps in creating a stable ferrofluid: synthesis of the magnetic solid and suspension of these superparamagnetic particles in carrier liquid with the aid of suitable surfactant. The magnetic particles must lie in superparamagnetic size range of the order
of 10 nm. Ammonia solution is also employed occasionally to co-precipitate the magnetic nanoparticles. The surfactant used in this synthesis is oleic acid. The hydroxide (OH\textsuperscript{-}) ions of surfactant in solution tend to bind to the iron sites on the magnetite particles, creating a net negative charge on each particle. This charged shell raises the energy required for the particles to agglomerate, stabilizing the suspension. A schematic diagram to highlight important steps used for the preparation of ferrofluid is shown in Fig. 1.9. In the present thesis the developed nano-particles of Ni-Zn, Mn\textsubscript{0.5}Zn\textsubscript{0.5}Gd\textsubscript{2}Fe\textsubscript{2-x}O\textsubscript{4} and Mn\textsubscript{0.5}Zn\textsubscript{0.5}Sm\textsubscript{2}Fe\textsubscript{2-x}O\textsubscript{4} were used for ferrofluid preparation.

![Diagram](image)

**Figure 1.9:** Flow Chart showing basic procedure used for development of stable ferrofluids.

### 1.9.4 Properties of ferrofluids

Ferrofluid can be considered as homogeneous liquid and by applying external magnetic field. We can collect ferrofluids as homogeneous aggregates [77]. When exposed to a magnetic field, the fluid exhibits very large variations in viscosity and thus are sensitive
to magnetic field but do not have permanent magnetization leaving zero remanence and coercivity after removal of the magnetic field across them. The behavior of the particles and fluid is such that large variations in viscosity can occur and be controlled very rapidly, transitioning from a light viscous fluid to a thick consistency in a few milliseconds [78].

Unique Properties of ferrofluids are
- Stick to magnets
- Take on 3-dimensional shape on applying a magnetic Field
- Change density in proportion to applied magnetic field strength

(i) Magnetic properties.

Each small particle suspended in a carrier liquid is thermally agitated permanent magnet. Ferrofluids are liquids with a susceptibility of roughly 1, not as high as many ferromagnets but still order of magnitudes higher than that of paramagnets. In the absence of a magnetic field, the magnetic moments of the particles are randomly distributed and the fluid has no net magnetization. The ferromagnetic colloidal particles in the ferrofluids form chainlike aggregates in quiescent conditions. For 'strong' magnetic fields, 'low' concentrations and 'moderate' temperatures, these chains are expected to be oriented parallel to the field direction. When a magnetic field is applied to a ferrofluid, the magnetic moments of the particles orient along the field lines almost instantly. The magnetization of the ferrofluid responds immediately to the changes in the applied magnetic field and when the applied field is removed, the moments randomize quickly. In a gradient field the whole fluid responds as a homogeneous magnetic liquid, which moves to the region of highest flux. This means that ferrofluids can be precisely positioned and controlled by an external magnetic field. The forces holding the magnetic fluid in place are proportional to the gradient of the external field and the magnetization value of the fluid. This means that the retention force of a ferrofluid can be adjusted by changing either the magnetization of the fluid or the magnetic field in the region.
(ii) Ferrofluid bearing

Ferrofluids have a very good property of making very low friction bearings around the poles of permanent magnet with co-efficient of friction equal to 0.0008. Fluid bearings are that bearings which supports their load solely on a thin layer of liquid or gas. Hydrostatic bearing are extremely pressurized fluid bearings, where the fluid is usually oil, water or air and the pressurization is done by a pump. Hydrodynamic bearing rely on the high speed of the shaft resting on the fluid to pressurize the fluid in a wedge between the faces.

Fluid bearing are frequently used in high load, high speed or high precision applications where ordinary ball bearing would have short life or cause high noise and vibration. They are also used increasingly to reduce cost [79]. This property of ferrofluid has been used in the design and development of new generation devices like power converting devices, converting wind and mechanical power into electrical power and sensors like vibration and temperature sensors etc.

(iii) Rheological properties

The rheological property of fluids plays an important role for many technological applications. In case of magnetic fluids it is important to determine how rheological properties of magnetic fluids are modified by external magnetic field. Rheological properties become more complicated when the fluid is a mixture of several liquids. A magnetic fluid usually exhibits Newtonian behavior in the absence of a magnetic field where shear stress is dependent on shear rate while in the presence of a field its viscosity is modified. The field induced viscosity can be explained on the hydrodynamical model developed by Shliomis [61]. In this model a fluid particle is assumed to possess an intrinsic angular momentum [80]. Application of homogenous magnetic field on magnetic fluids increases with the viscosity of the magnetic fluid. The effect of an external magnetic field on the viscosity of a dilute suspension of magnetic particles was studied theoretically and experimentally by many workers [63-65].

1.9.5 Applications of Ferrofluids
The magnetic properties of ferrofluids make them attractive for varieties of applications where the combination of liquid state and magnetic properties is essential. An important property of concentrated ferrofluids is that they are strongly attracted by permanent magnets, while their liquid character is preserved. The attraction can be strong enough to overcome the force of gravity. Many applications of ferrofluids are based on this property. For example, ferrofluids are widely used as lubricant in airtight seals of rotary shafts etc [81-82]. A magnetic field gradient keeps ferrofluid in place, even in case of pressure differences between the two separated compartments. Today, many computer hard disk drives contain a ferrofluid-sealed shaft. Ferrofluids are also used to improve heat dissipation in loudspeaker coils, enabling higher output power [83-87]. The ferrofluid have many applications in various field is also shown in Fig. 1.10

![Application areas of ferrofluids](image)

**Figure 1.10:** Application areas of ferrofluids

(i) **Material recycling:** Ferrofluid has a unique property in that applying a magnetic field to the ferrofluid can increase its apparent density. This physical characteristic creates the ability to separate objects of different density through floatation or sinking. Ferrofluids have been used for years in material separation processes in the mining industries, although with limited economic advantage. Ferrofluidics has been working with material recycling and mining industry leaders to commercialize this application. To enhance the economic viability of these processes.
(ii) **Electrical transformers:** Ferrofluidics Corporation has been working in partnership with a major manufacturer of electrical power equipment, to develop ferrofluid for liquid-filled transformer applications. Ferrofluids have been shown to provide both thermal and dielectric benefits to transformers. Ferrofluid can be utilized to improve cooling by enhancing fluid circulation within transformer windings. Ferrofluid can also be applied to increase transformer capacity to withstand lightning impulses, while also minimizing the effect of moisture on typical insulating fluids. The benefits of ferrofluid may be utilized to design smaller, more efficient new transformers, or to extend the life or loading capability of existing units.

(iii) **Mechanical engineering:** One of the most interesting engineering applications of MR fluid is the construction of smart and controllable MR dampers (Fig. 1.11). The assembly is filled with MR fluid where the piston head with magnetic field acts as an efficient damper. The main asset of a MR based damper is the controllability of the system, which can be adjusted in order to provide the desired level of damping by simply changing the magnetic induction to protect the device. These MR dampers are mainly used in the vibration suppression of mechanical components like clutches, brakes, seat suspension, car suspensions, and industrial vibration suppression, for stabilizing buildings and bridges during earthquakes [88-91].

![Ferrofluid damper](image)

**Figure 1.11:** Ferrofluid damper.

(iv)**Sensors and switches:** The unique properties of magnetic fluid makes it a feasible technology for some sensor and switch applications. The use of ferrofluid may enhance the motion sensitivity in some sensing applications. Fig. 1.12 shows ferrofluid based
temperature sensing device. The device is based on the Charles law \( V \propto T \) (at constant \( P \)). Hence in this ferrofluid makes the separation of air to atmosphere. Thermal expansion of air in the bath ‘A’ leads to move frictionless bearing (coefficient of friction 0.0008). The expansion of air is monitored as a function of temperature raised. This device has sensitivity of 2.5 mK.

![Diagram showing the various parts of the temperature sensor device](image)

**Figure 1.12:** Diagram showing the various parts of the temperature sensor device [80].

(v) **Spacecraft propulsion:** Ferrofluids can be made to self-assemble nanometer-scale needle-like sharp tips under the influence of a magnetic field. When they reach a critical thinness, the needles begin emitting jets that might be used in the future as a thruster mechanism to propel small satellites such as CubeSats.

(vi) **Optics:** MR fluid based polishing method has proven to be highly precise to prepare less contaminated optical lenses. These fluids are also being used for new generation devices like MEMS or lab on chips [92, 93].
(vii) **Analytical instrumentation:** Ferrofluids have numerous optical applications because of their refractive properties; that is, each grain, a micromagnet, reflects light. These applications include measuring specific viscosity of a liquid placed between a polarizer and an analyzer, illuminated by a helium–neon laser.

(viii) **Heat transfer:** An external magnetic field imposed on a ferrofluid with varying susceptibility (e.g., because of a temperature gradient) results in a non-uniform magnetic body force, which leads to a form of heat transfer called thermomagnetic convection. This form of heat transfer can be useful when conventional convection heat transfer is inadequate; e.g., in miniature microscale devices or under reduced gravity conditions. Special magnetic nanofluids with tunable thermal conductivity to viscosity ratio can be used as multifunctional ‘smart materials’ that can remove heat and also arrest vibrations (damper). Such fluids may find applications in microfluidic devices and microelectromechanical systems (MEMS).

(ix) **Medical applications:** Almost all applications in medicine exploit the extreme relative size difference between magnetic nanoparticles and living cells. These are further classified as fellow.

- targeted magnetic hyperthermia.
- as contrast agent in magnetic resonance imaging (MRI).
- magnetic separation of cells
- magnetic drug targeting

### 1.10 AIMS AND OBJECTIVES OF THE PRESENT WORK

After a detailed survey in the area of spinel ferrites it was found that study of these materials will be of high technological importance. Keeping in view, the importance of spinel ferrites, the present work has been carried out with the following aims and objectives:

1. To synthesize the nano size ferrite particles of \( \text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) (\( x = 0.5, 0.75, 0.9 \)), \( \text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4 \) (\( x = 0.1, 0.3, 0.5 \)), \( \text{Gd}^{3+} \) ions doped \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Gd}_{x}\text{Fe}_{2-x}\text{O}_4 \) (\( x = 0.1, 0.2, 0.3, 0.4 \)) and \( \text{Sm}^{3+} \) ions \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Sm}_{x}\text{Fe}_{2-x}\text{O}_4 \) (\( x = 0.0, 0.1, 0.3, 0.5 \)) ferrite nanoparticles by chemical coprecipitation method.
2. Characterization of developed nano ferrite particles to know their physical, properties viz. crystallinity, stress/strain, particle shape/size by various analytic techniques like XRD, FTIR, SEM/EDS, TEM.

3. Study of magnetic properties viz. magnetization values, coercivity, retentivity, blocking temperature, free spin concentration, g-values, line width, line intensity relaxation time by VSM, EPR and AC suseceptometer.

4. To study the effect of composition on structural, magnetic and electrical properties of developed spinel ferrite materials.

5. To develop ferrofluids using synthesized superparamagnetic ferrite particles.

6. To explore the possibilities of heat transfer application of synthesized ferrofluids.
REFERENCES


