CHAPTER 1
Introduction

It is well known that nanoscience and nanotechnology is the science and technology of ultrafine particles. Particles when reduced to nanometric dimensions display novel and superlative physical, chemical, electrical, optical and magnetic properties with respect to their coarser sized cousins. At these dimensions the surface area becomes very large and the ratio of surface to bulk atoms dictates the properties of the material. Grains, grain size, intergranular interaction, quantum magnetization, quantum tunneling, superparamagnetism are some of the various phenomena exhibited by particles at the nanodimension. So manipulation of properties means the understanding of these phenomena for tailoring the properties. With the emergence of nanotechnology, newer applications of these materials are conceived and are realized as products soon.

At the same time many phenomenon are not clearly understood and exclusive investigations are to be carried out.

Magnetism and magnetic materials is an area where large scope for such an activity exists. Moreover nanomagnetic materials are going to play a dominant role in the day-today life of human beings. The birth of new class of materials like diluted magnetic semiconductors (DMS), spin valve transistors, giant magneto resistive (GMR) materials, ferrofluids, giant magneto caloric materials (GMC), are all indication of these. Thus study on magnetic nanocomposites and nanomagnetic materials assumes significance and is very relevant in understanding various phenomena. This chapter provides an introduction to the various phenomena of nanomagnetism and spells out the motivation of the present work and its objectives.

1. Nanotechnology-An overview

Nanotechnology is known as the technology of the 21st century which deals with the synthesis and study of ultra fine materials and their employment in technology for various applications. It can be defined as the synthesis and engineering at the molecular level for possible device applications where nanoscience deals with the investigations of phenomena and properties exhibited by materials at the nanolevel.
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The demand for smaller materials for high density storage media is the fundamental motivation for the fabrication of nanoscale magnetic materials. The idea of nanoscale molecular device is not entirely new, and has been around since days immemorial. Richard Feynmann, who addressed the issue of quantum mechanical computers once opined “at any rate, it seems that the laws of physics present no barrier to reducing the size of computers until bits are the size of atoms, and quantum behaviour holds dominant sway” – a task, considering the small size that is necessary for realizing such device.

The ultimate motive in nanotechnology is to manipulate and control the individual atoms and thereby, the programmed formation of the superstructures. However, such a definition may be extended to the organization of objects having nanodimension such as molecules/biomacromolecules and other nanoscale matters such as quantum dots, buckyballs (also known as fullerenes) and nanotubes [1,2].

Materials consisting of particles with diameter less than 100 nm have attracted a great deal of recent research attention. Owing to their ultrafineness in size and very high surface area, these particles possess dramatic changes in physical and chemical properties as compared to their bulk counterparts which makes them ideal templates to study the physics at the nanolevel from a fundamental point of view in addition to the vast application potential in versatile fields [3,4].

Nanoparticles behave quite different from their coarser-grained counterparts of the same composition due to the high surface to volume ratio. The more loosely bound surface atoms constitute a significant fraction of the sample and their properties influence its behaviour. For example, the melting point of gold is dramatically reduced when the particle diameter drops below 5nm. Improvements can be made in the mechanical and magnetic properties of materials.

At sufficiently small domain sizes, the particle roughness increases and becomes comparable to the radius of curvature, in the case of a spherical particle. This reduces the strength of the bonding to adjacent atoms and often results in surface atoms with increased reactivity. The abundance of particle edges and corners can create non-equivalent reactive sites on a single particle.

Their magnetic and optical properties will be profoundly modified. Smaller grained magnetic materials exist as single domain because of the energy considerations. Ferro/ferrimagnetism is reduced and below a critical diameter the materials exist as
superparamagnetic. Optical properties are modified because of the quantum size effects on the band structure. Optical energy Bandgap is blue shifted for ultra fine materials. Nano sized gold is green in colour which is a semiconductor while bulk is a noble yellow metal!. We can make junctions with the same materials with different grain sizes due to the modified band structures of these ultra fine particles. This gives scope for a variety of applications in the semiconductor industry.

1.1 Particles at the nanolevel

The physical and chemical properties of materials with their grain size approaching molecular dimensions are of great fundamental interest. Hence they became a hot topic of intensive research. Nanoparticles display novel physical properties resulting from surface effects. The enhancement of the magnetization per atom and decrease in the blocking temperature from the bulk values is induced by the controlled size in a superparamagnetic nanoparticle. There has been a great deal of interest in the optical and magnetic properties of ultra fine particles in recent years.

The optical properties of materials change abruptly when the grain size becomes comparable to the Bohr radius of electron-hole pairs (excitons), quantization effects can be observed due to the quantum confinement of charge carriers in the finite volume of the particles which becomes very large when the size approaches the Bohr radius limits. Interesting and novel optical properties have been observed in the case of gold and silver when their sizes are reduced to nanodimensions.

1.2 Quantum wells, quantum wires and quantum dots

When one of the dimensions in a crystal are made smaller so as to reach the nanoscale (a few nanometer), electrons and holes can be confined in space in along that direction as compared to their motion in a bulk crystal, which is equivalent to the reduction of one of the degree of freedom for the electrons/hole/quasi particles. These states can be termed as quantum well like states.

In quantum wires, two of the dimensions are cut off. Materials could be made into the nanowires in which one of the degrees of freedom is retained for the charge carriers electrons and holes. Hence the diameter of the nanometer is few tens of nanometers. Hence confinement is stronger as there is only one degree of freedom.
In a quantum dot, the crystal is miniaturized in all the three dimensions to a few nanometers. The greatest difference between a quantum dot as compared with a bulk crystal, quantum well and quantum wire is that Coulomb energy contribution to the ground state energy is non zero where as for quantum well and quantum wires, electrons are free and coulomb energy contribution tends to zero. A detailed discussion on the theoretical aspects of these materials is provided in Chapter 2.

1.3 General Methods of Synthesis

Synthesis of nanomaterials and fabrication of nanodevices is one of the major active areas of current interests in nanotechnology. The two major approaches currently being used for the generation of nanoscaled materials, viz. the “top down” ("engineering down") and “bottom up” ("engineering up") methods.

a) Top Down Method

In the top down method, ultra fine particles are prepared from their bulk cousins by a continuous grinding process. This is the traditional way of synthesis of nanoparticles from their bulk counterparts which in turn is synthesized by ceramic techniques. Generally, a “two roll mill” is employed for the reduction of grain size of the powder specimens. Nowadays, high energy ball milling (HEBM) is employed for attrition which can impart high momentum to the milled powders through the high speed rotation and revolution of the vials which helps in obtaining high efficiency in low milling times. Thin films consisting of nanograins could be synthesized from bulk materials by a variety of other techniques like vacuum evaporation, RF sputtering, pulsed laser ablation etc.

b) Bottom Up Process

It is the ideal and the most commonly employed method for the synthesis of nanoparticles. In this method, nanomaterials are grown slowly from the atomic scale mostly by chemical methods in which careful control of the preparation parameters like pH and temperature is utilised to tune the grain size in a favourable way. Chemical co-precipitation and sol-gel techniques are used for the synthesis of ultra fine powder particles. There are several techniques for the growth of ultra fine grains on a substrate by atom by atom deposition. They include physical and chemical methods. For the synthesis
of fine grained thin films, processes like chemical vapor deposition, chemical bath deposition, spray pyrolysis, Sol-gel dip coating are also employed.

Out of these two techniques, bottom up process is advantageous for the synthesis of ultra fine powder sample as it provide atom by atom growth thereby reducing the surface imperfections and strain that could be imparted in the milling process and careful control of the preparation conditions could ensure systematic tuning of the grain size and other characteristics of these powder particles. Top down process like PLD and RF sputtering are routinely made use of for thin film fabrication.

1.4 General Synthesis Techniques.
There are a variety of experimental techniques for the synthesis of ultra fine magnetic particles. All these techniques need complete control over the reaction parameters.

The first technique involves the preparation of isolated particles. However ultra fine crystallites having uncontaminated free surfaces followed by a consolidation process either at room or at elevated temperatures. The specific processes used to isolate the nanostructured materials are for example, inert gas condensation, decomposition of starting chemicals and precipitation from the solutions.

1. Chemical vapour deposition (CVD), Physical vapor deposition (PVD) and some electrochemical methods have been used to deposit atoms or molecules of desired materials on suitable substrates. Nanocomposites of these materials could be synthesized in thin film form by consecutive coating of chemically different materials.

2. By introducing defects in a formerly perfect crystal another class of materials could be synthesized. This can be effected by processes like HEBM, and ion irradiation which shatters the bigger crystal.

3. The most efficient method of fine particle synthesis is the chemical co-precipitation from super saturated solutions by careful control of reaction conditions.

4. Another method being employed currently for the synthesis of metal/semi conductor oxides which is the sol-gel process in which the samples are taken in the required molar ratio and it is made into a gel and finally ignited at a higher temperature to yield nanostructured fine particles.
Of these different methods for the synthesis of nanostructured materials, inert gas condensation, physical vapour deposition, High energy ball milling and ion irradiation can be included in the physical methods for the synthesis of materials.

Chemical methods include, chemical vapour deposition, chemical bath deposition, (for thin film fabrication) chemical co-precipitation, sol-gel (for nanoparticle and composite synthesis) etc

Synthesis of metal nanoparticles comes under a separate category as the preparation process is quite tedious with more chances of contamination so that the additional provision should be given to passivate these explodingly reactive surfaces.

1.4.1. Chemical Methods

Chemical methods are the most widely employed technique [5] for the synthesis of nanostructured materials owing to the versatility in design, its economic nature and its capability for tailoring the properties by carefully controlling the grain growth as it offers mixing at the nanolevel. A basic understanding of the principles of crystal chemistry, thermodynamics, phase equilibriums, phase changes and reaction kinetics is necessary to take advantage of several benefits the chemical process offer.

The grain size and size distribution, the physical properties such as crystallinity and crystal structure, and the degree of dispersion can be affected by the reaction kinetics, pH, reaction temperature, concentration of reactions, molarity and its ratio and several other factors. There can be other factors like agglomeration of individual grains that make them unidentifiable from their bulk counter parts. There are chances of getting non stoichiometric undesired components precipitated along with the desired final product because of the slow reaction dynamics and nucleation. Hence other measures like size control, surface modification and capping are to be adopted to modify these processes.

1.4.2 Size control

Control of both grain size and grain size distribution becomes important in the synthesis of nanomaterials. The grain size could be controlled by varying the synthesis parameters like concentration, choice of reactants, temperature, pH etc. Choice of templates with natural pores for the synthesis of nanoparticles is also in use. *Insitu* surface modification using stabilizers such as thiols, phosphates, and polymers prevents further grain growth. [5-10].
1.4.3 Grain size distribution

The control of grain size distribution is quite important in the synthesis of nanoparticles. To narrow the size distribution, exclusion chromatography and capillary zone electrophorosis are employed [10]. These are based on the principle of charge to size ratio is different for different grain sizes. Filtration through molecular sieves of different mesh size is also used for getting the size distribution narrower.

1.4.4 Size quantization effects

Quantization in ultra fine particles originates from the confinement of charge carriers in semiconductors with potential wells of narrow dimensions less than the De-Broglie wavelength of electron and holes. Confinements could be mere electronic, excitonic or polaronic based on the grain size and excitation energy [11]. Under these conditions, the energy bands of electrons and holes becomes close to discrete energy levels as of in atom and thus a semiconductor becomes atom like. In addition to the large change in electronic/optical properties, they also exhibit change in the effective redox potentials of photo-generated carriers.

Size quantization effects on the optical properties of semiconductors are extensively studied [12-16]. In CdS nanocrystals, a blue shift in energy band gap of 1.54 eV is obtained for a particle with radius 1nm. Blue shift is observed for many other semiconductors because of the quantum confinement effects. Trapping of charge carriers is possible for the nanostructured materials [17-22]

1.4.5 Optical Properties

Optical properties of ultra fine particles are profoundly modified by the grain size dependant confinement effects. In the ultra fine regime, due to very small wave function overlapping, the energy levels tends to be discrete and when the grain sizes are reduced to the order of exciton Bohr radius limit of the material, they are near molecule like materials and hence the energy levels tend to be discrete and thus there is confinement of carriers. This will alter the band gap towards the high energy limits which can be as high as 3 eV in a 5Å particle! Thus by manipulating grain sizes, materials with same chemical formulae but different band gaps can be synthesized. The influence of grain size vis a vis quantum confinement have been investigated extensively [23-25]
1.4.6 Nonlinear optical properties

Semiconductor nanoparticles are investigated because of their excellent nonlinear optical properties by many researchers [26-28]. In the linear regime, photoinduced blue shift in absorption edge is observed, which causes transient bleaching in nonlinear regime [29]. Third harmonic generation, and free carrier absorption are also observed in semiconductor nanoparticles especially in CdS nanoclusters [30]. Due to near molecule like energy levels, they show strong Saturable Absorption (SA), Reverse Saturable Absorption (RSA) and multi photon absorption.

1.4.7 Surface modification of nanoparticles

Due to the high surface to volume ratio and these nanoparticles possess surfaces which are explodingly reactive. This makes it necessary that the surface of the nanoparticles should be capped properly to prevent explosive reactions and grain growth. Surface modification can be classified in to three.

1. Deposition of metals on the nanoparticles

Metals are deposited on synthesized nanoparticles by variety of techniques. By this the selectivity and efficiency of a photoelectrochemical reaction could be greatly enhanced by surface modification of these nanoparticles. Gold and platinum are the commonly used surface modifying metals because of their very low reactivity at the surface. Platinisation could be done by the direct photoreduction of PtCl$_6$ on the nanoparticles [31,32] or by stirring the nanoparticles by platinum colloids [33-35]. Gold layer coating could be done by employing similar techniques. Mostly this is meant for the improvement of the photocatalytic properties of the synthesized nanoparticles in addition to the protection provided by the noble metal layer to the surface.

2. Capping with organic/inorganic molecules

Nanoparticles could be capped most effectively using insitu capping of organic/inorganic materials on the surface of each and every particles. Thiols have been extensively used for capping the materials [36-37]. Nowadays polymers like PVPA, Polypyrrole etc have been used for the capping of materials [38-44] which provides surface passivation and modifies the electronic and optical properties because of the
presence of a thin capping layer which provides necessary electric field to act as confinement potential.

3. Surface modification with sensitizing dyes

By the surface modification of materials using sensitizing dyes, the optical response could be tuned to the low energy regime. While surface modification using metals and organic molecules provides improved catalytic/dielectric properties, this enhances optical properties of the materials in general [45-47]. The process of charge injection from the excited state into the conduction band of the semiconductor has been studied with respect to the photoresponse of large band gap semiconductor which has applications in imaging science and solar energy conversion. Erythrosine B, Eosin, Rose Bangal, Rhodamines, methlene Blue etc have been used for the surface modification.

Since the focus of this thesis is nanomagnetism and nanomagnetic materials, some of the very relevant aspects of magnetism and magnetic materials will be discussed in the ensuing sections.

1.5 Nano magnetic materials

The emergence of nanotechnology has given rise to a new class of materials called nanomagnetic materials and this is as important as semiconducting materials. Magnetic nanomaterials are important both from the fundamental as well as application point of view. From a fundamental point of view, nanomaterials, especially, magnetic nanomaterials exhibit superlative properties with respect to their, structural, magnetic, electrical, optical and magneto-optical properties as compared to their coarser sized cousins. For example magnetic materials at reduced dimensions exhibits quantum magnetization, single domain characteristics, superparamagnetism, and spin polarized tunneling. These quantum mechanical phenomenon are wisely exploited to increase the density of bit storage, make spintronics a reality, make CMR sensors for data accessing etc. A more detailed discussion of the anomaly in exhibited properties for ultra fine articles is provided in Chapter 2.

Magnetism and magnetic materials find applications in almost all realms of human life. They play a vital role in making life more sophisticated and humane. The most important use of magnets in the home is the electric motors. All electric motors use
electromagnets. These motors run refrigerators, vacuum cleaners, washing machines, compact disc players, blenders, drills, race cars etc. Audiotape and videotape players have electromagnets called heads that record and read information on tapes covered with tiny magnetic particles. Magnets in speakers transform the signal into a sound by making the speakers vibrate. An electromagnet called a deflection yoke in TV picture tubes helps form images on a screen. [48-54].

The magnets used in the industry and business are mostly electromagnetically powered devices, such as cranes, cutters, fax machines, computers etc. Generators in power plants rely on magnets like the ones found in electric motors to produce electricity. Transformers are devices that use electromagnetics to change high-voltage electricity to low-voltage electricity needed in homes and businesses. In transportation, systems that use electromagnetics are trains, subways, trolleys, monorails, escalators, elevators etc. Scientists and engineers have developed trains that use electromagnetism to float it above the track by the principle of magnetic levitation. It eliminates friction thereby attaining higher speeds over ordinary trains.

Another important magnetic material category which attracted recent research interest are dilute magnetic semiconductors. They are potential materials for magneto-optical devices. Ferromagnetic semiconductors are obtained by doping magnetic impurities into host semiconductors with out forming islands of magnetisation. They are key materials for spin electronics (spintronics) in which the correlation between the charge and spin of electron is used to bring about spin dependent electronic functionality such as GMR and spin field effect transistor [49]. Among such materials reported so far GaAs has a Tc of about 100K.

Magnetic nanocomposites find a host of other applications because of their remarkable properties. They are used as magnetic recording media, colour imaging, ferrofluids, catalysts etc. Magnetic nanocomposite consisting of iron oxide embedded in polymer matrices are found to be behaving like transparent magnets with remarkable electrical and optical properties. Flexible magnets or rubber ferrite magnets find applications in many devices because of their easy mouldability and microwave absorbing properties [55-56].
To understand the physics that dictates various properties of magnetic nanomaterials, it is necessary to have a look into the basic concepts and theories regarding the origin of magnetism in a material from the classical as well as quantum approach.

1.6 Physical origin of Magnetism

To understand the anomalous magnetic behaviours exhibited by these magnetic fine particles, it is necessary to understand the basic theories of magnetism. It is recognized that the magnetic behaviour of atoms, molecules and solids is related to the orbital and spin motion of the electrons. The magnetic dipole moment associated with an electron describing a circular orbit is related to the angular momentum of the electron as:

\[ \mu = \frac{e}{2m} \]  

(Angular momentum).  

All the known magnetic materials can be classified into the following classes depending on their electronic configurations and properties.

1) Diamagnetic
2) Paramagnetic
3) Ferromagnetic
4) Antiferromagnetic
5) Ferrimagnetic

If an atom or ion contains only paired electrons, the total magnetic moment is practically zero as a result of the nullifying effect of the added orbital and spin angular moments. Such materials for which the permeability is less than unity and the magnetic susceptibility is negative are called diamagnets. If the atom or ion contains one or more unpaired electrons and thus possesses a permanent magnetic moment, the material can be either paramagnetic or ferromagnetic. If there is no interaction between the adjacent magnetic moments and, thus, they can interact independently with an external magnetic field, the materials are ideal paramagnets, for which the permeability is slightly greater than unity and the susceptibility has a slight positive value and varies inversely with the absolute temperature. If a strong interaction between adjacent magnetic moments tends to
align them parallel to one another, the materials are called ferromagnetic, for which the susceptibility values are very large, positive and the magnetic induction is approximately equal to the magnetization produced in the material. Above a certain critical temperature, called the Curie temperature or Curie-Point \( (T_C) \), ferromagnetic materials become paramagnetic and follow the so-called Curie Weiss Law:

\[
\chi = \frac{C}{T - \theta}
\]

Where \( C \) and \( \theta \) are the Curie and Weiss constants respectively.

Under certain circumstances, the interaction between neighbouring magnetic moments may lead to an antiparallel alignment resulting in a vanishing resultant moment at zero Kelvin; such materials are called antiferromagnetic. Above a certain temperature called the Neel Temperature or Neel Point \( (T_N) \), antiferromagnetic materials become paramagnetic and follow the Curie -Weiss type relation:

\[
\chi = \frac{C}{T + \theta_n}
\]

Where \( \theta_n \) is a constant.

For some materials, the antiferromagnetic alignment may lead to a non-vanishing resultant magnetic moment. These materials are called Ferrimagnetic and become paramagnetic above the ferrimagnetic Neel Temperature \( (T_{fn}) \).

### 1.7 Ferro magnetic Domains

To explain the appearance of a large magnetization in a Ferro magnet on the application of even a small magnetic field, Weiss introduced the concept of “domains”. A ferromagnetic sample of macroscopic dimensions contains a number of small regions called domains. Within each domain, spontaneous magnetization exists, whose value depends on the temperature. The vector sum of magnetizations of the individual domains gives the overall spontaneous magnetization of the sample. ‘domain walls’, called the Bloch Walls, separate the different domains. The volume of the domains is critically of the order of \( 10^{-8} \) to \( 10^{-12}\) m\(^3\).
1.8 The Two-sub lattice Model

A simple antiferromagnet consists of two interpenetrating sub-lattices such that the atomic or ionic spins on one sub-lattice are aligned antiparallel to those on the other and the net magnetization is zero at the absolute zero of temperature. Ferrimagnetic materials are those, which exhibit spontaneous magnetization due to antiparallel alignment between two magnetic sub lattices. The principal reasons for the non-vanishing magnetization are:

a) The two sub lattices are occupied by different types and number of magnetic ions

b) The two sub-lattices correspond to two different crystallographic sites, which may be occupied either by the same type or different types and number of magnetic ions

1.9 Ferrites:

The most important ferromagnetic material known is magnetite which corresponds to the chemical formulae Fe₃O₄ or more specifically, Fe²⁺Fe³⁺O₄. When one replaces the divalent ferrous ion by another divalent metal such as Mn, Co, Ni, Cu, Mg, Zn, or Cd, one obtains a ferrite of the general composition Me²⁺Fe³⁺O₄, where Me²⁺ is the divalent metal ion. In mixed ferrites, a mixture of ions replaces the Fe²⁺ ion.

1.10.8 The structure of ferrites

The physical properties of ferrites are intimately related to the structure of these solids. They belong to the large class of compounds, which have the spinel structure. The oxygen ions with a radius of 1.32 Å, forms to be a good approximation for a close-packed cubic structure. The unit cell contains 32 oxygen ions, 16 Fe³⁺ ions, and 8 divalent metal ions. The total of 24 metal ions, ranging in radius between 0.4 and 1Å, are in eight tetrahedral interstices surrounded by four O²⁻ ions and sixteen octahedral interstices, surrounded by six O²⁻ ions. The distribution of metal ions is very important for an understanding of the magnetic properties of these materials: the following distributions may occur.

1) In the ‘normal’ spinel structure of a ferrite, eight divalent metal ions occupy tetrahedral positions: the sixteen trivalent iron ions occupy octahedral positions Me²⁺[Fe³⁺]O₄. The brackets around the Fe³⁺ ions indicate that they occupy the octahedral sites.
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2) In the ‘inverse’ spinel structure of a ferrite, the divalent Me\(^{2+}\) ions occupy octahedral sites: the Fe\(^{3+}\) ions are distributed equally over the tetrahedral and octahedral sites. The arrangement may thus be represented by Fe\(^{3+}\) [Me\(^{2+}\)Fe\(^{3+}\)]O\(_4\).

3) In the intermediate case we have arrangement of the type;
Fe\(_x^{3+}\) Me\(_{1-x}^{2+}\) [Me\(_x^{2+}\)Fe\(_{2-x}^{3+}\)]O\(_4\).

In the mixed ferrites obtained from normal and inverse spinels, it may become necessary to consider as many as 10 molecular field constants. However, in practice, consideration of only three molecular field constants is often sufficient, especially when the dominant interaction is that between the A and B sub lattices [58]. When interactions become comparable in magnitude, canting of spins, becomes energetically favourable.

\[\text{Fig. 1a Exchange interactions as per "Two sub lattice model"}\]

1.10.b Crystal Structure of Spinel ferrites

Ferrites having the spinel structure have the general formula MFe\(_2\)O\(_4\) where M is a divalent metal. They resemble the structure of the naturally occurring mineral MgAl\(_2\)O\(_4\). The oxygen anions have an fcc arrangement accommodating the smaller positive ions in the interstices. The available spaces are of two kinds. One is called tetrahedral or A site, because it is located at the centre of a tetrahedron whose corners are occupied by oxygen ions. The other is called octahedral or B sites, because the oxygen ions around it occupy the corners of an octahedron. In the mineral spinel Mg ion occupy the A site, known as tetrahedral site because it has four nearest oxygen neighbours. The B
site ions have six nearest oxygen ions (and the site is termed octahedral site) and the site is occupied by the Al ions.

The crystal structure is best described by subdividing the unit cell into 8 octants with edge $a/2$ as shown in Fig. 1.2. The location of oxygen ions and metal ions in every octant can be easily described. The oxygen ions are arranged in identical manner in all octants. Each octant contains four oxygen ions in the body diagonal and they lie at the corners of a tetrahedron. Positions of metal ions are different in the two octants sharing a face. In the case of octants sharing only an edge the location is the same. Hence a complete picture of the location of metal ions is obtained if position of ions is drawn in two adjacent octants is also shown in Fig 1.1b.

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**Fig. 1.2.b** Crystal structure of a cubic ferrite
The distribution of metal ions is very important for an understanding of magnetic properties of these materials. Not all available sites are occupied by metal ions. Only one fourth of the A sites and one half of the B sites are occupied. In the case of mineral spinel, Mg\(^{2+}\) ions are in the A site and Al\(^{3+}\) ions are in B sites. Such an arrangement is called normal spinel structure in which the divalent ions are on B sites and trivalent ions are on the A sites. ZnFe\(_2\)O\(_4\) is a normal spinel in the micron regime. The structure in which divalent ions are in the A sites and trivalent ions are equally distributed between A and B sites, is called an inverse spinel structure. CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) ferrites have inverse structure and they are all ferrimagnetics.

### 1.11 Superparamagnetism

A particle of ferromagnetic material below a critical particle size would consist of a single magnetic domain. For a spherical sample, this size limit is around 100Å. The treatment of the thermal equilibrium magnetization properties of an assembly of isotropic single domain particles is analogous to the Langevin treatment of atomic Paramagnetism. It differs only in that the moment \(\mu\) we are dealing with is not that of a single atom, but rather of a single domain ferro/ferrimagnetic particle, which may contain more than \(10^5\) atoms ferromagnetically coupled with exchange forces.

Since one of the central themes of this thesis is magnetic fluids, a brief insight into the various aspects of magnetic fluids will be provided in the subsequent subsections.

### 1.12 Magnetic Fluids

A homogeneous fluid with magnetic characteristics has been the dream of researchers and scientists for quite sometime which remained unfulfilled as efforts for producing a liquid out of a solid by melting the metallic magnets became impractical because all the magnetic materials have a property of loosing their magnetic properties if heated above a certain temperature called the Curie temperature. These particles have melting point much greater than the Curie temperature, twice as that of the value of its Curie temperature. This makes the process of producing magnetic fluids by melting, a non-viable one.

The dream of producing a liquid that possess strong magnetic properties was not realized until the early 1960s, when Stephen Papell of National Aeronautics and Space Administration (NASA) developed a colloidal system. Papell’s fluid consists of finely divided particles of magnetite suspended in kerosene. To keep the particles from
clumping together, Papell added oleic acid, an organic substance that served as surfactant or dispersing agent [59].

This kerosene-based fluid had a high evaporation rate and was not suitable for industrial applications. After a few years of NASA funded magnetic colloid research at AVCO, Ferrofluid Corporation was founded by Rosensweig and Moskowitz, to commercialise this technology. Magnetic fluids are of great interest, since they possess the properties of a fluid and act as a ferromagnetic material. [60]

1.13 Components of a Magnetic Fluid

The unique combination of fluidity and the capability of interacting with a magnetic field is achieved in magnetic fluids because of their composition. Three components are required to synthesize a magnetic fluid namely, a liquid base (or in other words, a carrier liquid), single domain magnetic particles of a colloidal size and a stabilizer to prevent colloid particles from aggregating. Each of these components must satisfy certain requirements [61].

(a) Base Fluid

A carrier liquid is chosen to conform to its field of application. Thus for lubrication and sealing systems, mineral oils and silicon organic bases are used. For medical applications, water is used as base fluid. Liquid bases need to be of low evaporation, non toxic, resistant to corrosive media, insoluble in specified media and so on [61]

(b) Single Domain Magnetic Particles

Ferromagnetic particles in colloidal dispersion make the fluid act like a ferromagnetic material. They may be cobalt, iron, nickel or one of their magnetic compounds or alloys. The most usual material is magnetite. Typically magnetic fluids contain $10^{20}$ particles per litre [59,61].

The size of the particles must be sufficiently small, for preventing agglomeration and precipitation. The thermal motion of the particles ensures the stability of magnetic fluid and this thermal motion increases with decreasing particle size. At the same time the particles must not be too small, since at sizes less than 1-2 nm, their magnetic properties disappear [61].
(c) Surfactant (Stabilizer)

The surfactant must prevent particles from aggregating. To this end long chain molecules are used with functional groups OOH, H₂OH, H₂NH₂ and so on. A stabilizer is chosen so that its molecules interact with magnetic particles, via bonds of functional group, to form a tightly bonded monomolecular layer around the particles [59,61].

1.14 What is a Ferrofluid?

Ferrofluids are stable colloidal suspension of single domain magnetic particles in a base fluid, which is magnetically passive. The number density of the particle in a typical ferrofluid is of the order of 10²³ particles per m³. The particles are so small in nature and the size of the particles is of the order of 100 Å [59,61,62].

To synthesize ferrofluids, at least two components, mono domain magnetic particles and a suitable carrier liquid are required. Since randomising Brownian energy may not be enough to counteract attraction owing to van-der-Waal and dipole-dipole forces, aggregation and sedimentation are prevented by providing suitable repulsive forces either by Coulomb repulsion or by steric repulsion. In the former case particles are either positively charged or negatively charged and the fluid is called ‘ionic ferrofluid’, while in the later case each particle is coated with an appropriate surfactant and resulting ferrofluid is classified as ‘surfacted’ ferrofluid. The ionic fluid requires a polar medium like water as base fluid; the surfacted fluid can use any carrier liquid like oil, water and hydrocarbons [62].

The choice of the carrier liquid depends on the application. For a surfactated ferrofluid, selection of surfactant is crucial for its stability. A surfactant molecule consists of a polar head and a tail of hydrocarbon chain. An example is oleic acid

\[
\text{CH}_3(\text{CH}_2)_\gamma \text{CH}-\text{CH(\text{CH}_2)}_\gamma \text{OH}
\]
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The anchor polar group is adsorbed on the particle while the chain performs thermal movement in the carrier. When a second particle with a similar chain approaches closely, the movement of the chains is restricted and results in steric repulsion.

![Image of magnetic particles suspended in a carrier liquid.]

Figure 1.3 Magnetic particles suspended in a carrier liquid.

Rosenweig gives a simplified estimate for the entropic effect for the short chains

\[
E_s = \frac{2}{3} \pi N k_B T \left( \delta - \frac{x}{2} \right)^2 \left( \frac{1.5D + 2\delta + x/2}{\delta} \right)
\]

1.4

where \( N \) is number of molecules per unit area, \( \delta \) is the thickness of the stabilized layer, \( x \) is the distance between two surfaces, and \( D \) is the diameter of the particle. The equation is useful to calculate \( \delta \) which gives a reasonable barrier of \( 25k_B T \) to prevent agglomeration [62, 59].

1.15 Physics of Ferrofluids

Many of the properties of the ferrofluids can only be well understood by studying the physical laws governing the behaviour of these special fluids. So a brief discussion of major physical laws governing their special properties becomes relevant here. This section mainly consists of three parts, namely, Modified Bernoulli's equation, Kinematics of ferrofluids and Brownian motion of the particles in a ferrofluid.
1.15.1 Stability criteria for the magnetite based ferrofluids

Stability against settling of the suspended particles is achieved if the ratio of thermal energy to magnetic energy is greater than 1, ie,

\[
\frac{k_B T}{\mu_0 MH V} \geq 1
\]

where \( M \) is the magnetisation, \( H \) is the applied magnetic field and \( V \) the volume of the particles. Assuming the particles to be spherical, the diameter of individual particles is given by

\[
d \leq \left( \frac{6 k_B T}{\pi \mu_0 MH} \right)^{1/3}
\]

so that with a permanent magnet having a magnetic field of \( 8 \times 10^4 \) A/m, we can separate the aggregates to have an average particle diameter around 80 Å.

Stability against individual particle agglomeration is achieved if the thermal energy becomes at least equal to the dipole-dipole energy:

\[
\frac{\mu_0 M^2 V}{24} \leq k_B T
\]

and for magnetite particles the magnetization \( M = 4.46 \times 10^5 \) A/m, giving the maximum size limit for an agglomeration less ferrofluid as 100 Å.

1.15.2 Modified Bernoulli’s Equation

The equation presented by the Swiss mathematician Daniel Bernoulli in his Hydrodynamica of 1738, is one of the most useful relations in ordinary fluid mechanics. This equation relates the pressure, the velocity and the elevation of a fluid in a gravitational field. Bernoulli showed that the sum of the three forms of energy; pressure energy, kinetic energy and gravitational energy inherent in the flow remains constant, provided, the effects of friction are negligible [59].

The Bernoulli’s equation is
Hydrodynamically magnetic fluids follow the Bernoulli’s equation, modified by adding a term, which takes the magnetic properties into consideration. The pressure energy, potential energy and magnetic energy are constant along the streamline flow. It is expressed by the modified Bernoulli’s equation,

\[ P + \frac{1}{2} \rho v^2 + \rho gh = \text{const.} \]

Where \( P \) is the pressure energy, \( \rho \) is the mass per unit volume, \( \mu_0 \) is the permeability of free space, \( M \) is the magnetization and \( H \) is the magnetizing field. From this equation it is clear that in the absence of magnetic field, the magnetic fluid acts like other liquids, but in magnetic field an additional force appears and affects the fluid. [59,63].

![Fig. 1.4 Various interaction energies those are significant in the prevention of particle agglomeration.](image)

1.15.3 Kinematics of ferrofluids

The kinetic theory of matter suggests that sufficiently fine particles of matter can remain suspended indefinitely in a liquid even though the particle density is much higher.
than that of the liquid. This is due to the continuous collisions of the particles with molecules of liquid, which are in thermal motion. When many particles are present in the same volume of the liquid, agglomeration may take place, creating a heavy particle, since the ratio of the thermal energy (kT) to the gravitational energy (ρgh) is reduced.

The forces of attraction that affects the particles in a ferrofluid are magnetic force and Van der Waal's force. Due to the extremely small size of the particles, the magnetic force is very weak. But Van der Waal's force of attraction arises between the dipoles, which are created by the fluctuations in electronic structure. According to Fritz London, the energy needed to overcome the Van der Waal's force is inversely proportional to the sixth power of the centre-to-centre separation of the particles. Hence to overcome this force, the particle must be kept well apart. In preparing ferrofluids the necessary separation can be achieved by coating each particle with a molecular film that acts as an elastic cushion. [59].

1.15.4 Brownian Motion of Particles

The problem of agglomeration of the particles in a ferrofluid due to Van der Waal's force is overcome by the coating of the surfactant layer on each particle. But to avoid the gravitational settling of the particles, the gravitational energy must be exactly balance the viscous force of the base fluid. For that, there is a maximum limit for the size of the suspended particles. Then only there is a stability of the fluid by means of the vigorous non-uniform zigzag motion of the particles inside the base fluid. This is called the 'Brownian motion' of the particles. [59]

For balancing the viscous force, which acts upward must at least be equal to the gravitational force.

\[
\text{Viscous force} = \text{gravitational force}
\]

\[
6\pi \eta a v = mg
\]

Where \(mg\) is the weight of the particle, which acts in downward direction.

\[
6\pi \eta a v = \frac{4}{3} \pi a^3 \rho g
\]
Here \( p \) is the density of the particle, \( \eta \) is the co-efficient of viscosity, \( 'a' \) is the radius of the particle. Substituting the typical values, assuming the number density is of the order of \( 10^{23} \) per \( m^3 \), we get the particle size maximum of 100Å [59].

1.15.5 Physical Properties of Ferrofluids

- The size of the particles in the ferrofluid is of the order of 100Å. They are single domain particles and exhibits superparamagnetism.
- The number density of the ferrofluids is of the order of \( 10^{23} \) per \( m^3 \). It is comparable with the number of molecules in air at STP (ie; \( 2.7 \times 10^{23}/m^3 \)).
- Physical properties of the ferrofluids like specific gravity, viscosity, magnetization, dielectric constant etc. are modified with the application of a magnetic field.
- Depending on the choice of the surfactant and base fluid, density of ferrofluid varies with the density of water to twice its value.
- Magnetic fluids have zero remanance and coercivity.
- They spike under the influence of a magnetic field.
- Cluster Formation:

  In the absence of magnetic field, the particles are well dispersed. When a weak field is applied, particle tends to form tiny clusters elongated parallel to the field. These are called micro clusters. Further increase in the magnetic field results in a growth of clusters, and forms the so-called macro clusters. Under the influence of strong magnetic fields, well elongated macro clusters repel each other, thus forming an ordered arrangement. This cluster formation leads to the remarkable magneto-optical properties such as dichroism and birefringence. [64-68].

1.16 Optical Properties of Ferrofluids

Magnetite based ferrofluids are black and practically opaque; however thin layers exhibit the magnetic field effect both on isotropic optical properties such as extinction and anisotropic optical properties such as birefringence, dichroism etc, when they are exposed to its effect. For high concentration fluids, a difference in refractive indices of the ordinary and extraordinary rays attains \( 5 \times 10^{-3} \) and dichroism amounts to \( 4 \times 10^{-3} \). That
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is, the magnetic fluid displays the pronounced properties of an optically single axis crystal in an external field.

1.17 Synthesis of magnetic Nanoparticles.

Generally the magnetic nanocomposites are prepared by the following techniques.

a. Ceramic Method

It is the physical mixing of reactants in the appropriate molar ratio in an acetone-mixing medium. By the heat treatment of the above mixture at a high temperature, highly crystalline ferrite particle of micron scale is formed.

b. Co precipitation Method.

In Cold co-precipitation method the precursor materials are taken in the appropriate molar ratio in aqueous medium maintaining an appropriate pH and temperature. In aqueous medium the reactants are in ionized form, and thus the ferrites formed are in the nanoscale. [69-76]

c. Sol-Gel synthesis

In sol-gel technique, the precursor materials are completely dissolved in a suitable solvent and the solution is allowed to react at low temperature until a gel is formed. The gel is then heated at a higher temperature to obtain the desired final product. Mainly oxides are synthesized by this technique.

1.18 High energy ball milling

High energy Ball Milling is a method for the synthesis of nanograins out of bulk by the top-down approach. Here due to the very high rotation and revolution, the momentum imparted is very high as compared to the conventional low energy milling techniques.

The properties of the nanophase materials synthesized by high energy ball milling are dependant on the ball milling conditions. Among the key parameters characterising the process, the impact speed of the balls is of the most important one in determining the rate of energy transfer. The deformation is by the impact of a body on a target material can be characterized by a dimension less number called “Best number” (B.N)
where \( \rho \) and \( Y_d \) are the density and dynamical field strength of the target material. Here \( V \) is the impact velocity of the body. B.N values below \( 10^{-5} \) correspond to the deformation in the elastic range whereas for \( B.N > 10^{-4} \) plastic deformation prevails.

In the plastic deformation range, a correlation can be established between the relative impact velocity \( V \) of a sphere with the target material and the indentation radius ‘\( a \)’ assuming normal impact and the hardness of the material of the sphere greater than that of the target. With ball mass \( m \) and ball radius \( R \),

\[
V^2 = \frac{4.5\pi mY a^4}{2R} \tag{1.13}
\]

Momentum of the balls in each grinding, means the correlated impulsive force “\( F \)” is key parameter in the plastic deformation produced by the high-energy ball milling. This momentum is correlated to the impulsive load

\( F = mV/t \) where the ball-vial contact time. Such load \( F \) determines the mechanical energy transfer to the grains during grinding. ‘\( F \)’ can be varied by adjusting the rpm and duration of the milling. The transferred energy to the vial is a factor that determines the particle size distribution.

Chemically synthesized nanomaterials if subjected to a high energy ball milling will enhance its shape anisotropy. Magnetic particles exhibit superparamagnetism below its critical size. At these submicroscopic scales, the material exists strictly as single domains. Magnetic, dielectric, and the conductive properties highly depend on the particle size. At this particular size scale novel properties are exhibited mainly dependant on their surface to volume ratio and magnetic interaction.

### 1.19 Magnetic Nanocomposites

Nanocomposites are composite materials containing a phase with one or more average dimension smaller than 100nm, like multiplayer or monolayer films, nanograinened
metals, etc [77]. The improved magnetic properties of such materials can be accounted as follows.

Reduction in the size of materials causes long-range magnetic order to be replaced by some other magnetic state. It is a consequence of the increased uncertainty in momentum and energy of electrons in the ordered region. The uncertainty in momentum is given by:

\[ \Delta P = \frac{\hbar}{d} \]  \hspace{1cm} 1.14

Where ‘d’ is the uncertainty in the position of the electron, which is determined by the particle dimension. This results in an uncertainty in energy. When this energy uncertainty equals the magnetic ordering energy, the long-range order is no more energetically favourable. The gross magnetic behaviour becomes either paramagnetic or superparamagnetic as the sizes of the magnetic species are well reduced.

Ease in control of the magnetic behaviour of these composite materials by controlling the processing parameters present great possibilities for the atomic engineering of materials with specific magnetic properties. They are potentially important to the magnetic recording industry for high-density information storage and in the refrigeration industry for their potential for enhancing the efficiency of magnetic refrigeration cycles.

As already mentioned, when the size becomes smaller and smaller, properties of materials become different from that of their bulk counterparts. The discovery of nanoscopic materials has opened up new vistas in the frontier areas of material science and technology. The recent advances in nanotechnology has made it possible to devise newer materials with novel chemical, magnetic and electrical properties [69,78].

Particles possessing nanometric dimensions, lying in the range 1-10 nm are found to be exhibiting superior physical properties with respect to their coarser sized cousins. The properties of nanostructured materials are determined by the complex interplay among the building blocks and the interfaces between them.

Single nanosized magnetic particles are mono-domains and one expects that in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Magnetic nano-composites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration [69,70,79-80]. Multilayers and other types of materials containing
nanocomposites are found to exhibit properties like GMR and magnetocaloric effect. A research team led by Ron Ziolo [70] developed a composite material consisting of 5 to 10-nm magnetic iron-oxide particles lodged in a polymer matrix. This nanocomposite material consists of tiny magnetic particles dispersed in a lightweight, insulating polymer solid. They serve as transparent magnets and can be converted into magnetic fluids. Other than serving as a lossless transformer, the nanomagnets could act as miniature switches or sensors in smart materials, or as a form of microwave shielding. These materials are expected to have novel acoustic, thermal, and optical properties. Besides these the magnetic nanocomposites can find applications in medical diagnostics, digital information storage, leak free sealing and detection and sensing devices [69,70,78-79]

1.20 Different schemes of preparation of magnetic nanocomposites

There are different schemes available for the synthesis of magnetic nanoparticles/ nanocomposites. Some of the important methods of preparation will be discussed here.

a) Inert gas evaporation

In the inert gas evaporation method [11,69] a metal is evaporated in an inert atmosphere at a reduced pressure and then condensed in the gas phase to form metal clusters or nanocrystals. These could be collected on the cold finger and can be oxidised to fine ceramic powder which can be scrapped off. If a bicomponent composite is to be synthesized two different metals are to be evaporated.

b) Solution chemical route

In the solution chemical route [11,69], molecular mixing is accomplished by aqueous solution of suitable precursors. The solution mixture is aerosolised and rapidly spray dried to get extremely fine mixture of salts. These precursor powders are reduced with hydrogen and then reacted with CO in a fluidized bed reactor to yield nanophase metal carbide powder. Nanocomposites with impressive properties can be prepared by dispersing nanoparticles either inside the larger grains of a second ceramic or in between the grains.

c) Rapid thermal decomposition of precursors in solution (RTDS)
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Rapid thermal decomposition of precursors in solution (RTDS) method is yet another synthesis scheme which can be used to make nanophase powders of NiO and Ni(OH)$_2$. The RTDS process applies a high temperature and pressure to a rapidly flowing solution containing dissolved precursors to synthesize ultra fine particles.

\textit{d) Sol-gel method}

Recently sol-gel method is gaining popularity and can be made use of for the dispersion of small metal, metal oxides or alloy particles in non-metallic matrixes. In this method, precursor materials are dissolved in a suitable solvent and a wet gel is made by slow heating process and finally the gel is ignited at a high temperature to yield the required nanoparticles/alloys [81-82].

\textit{e) Ion exchange method}

Another important method used for the preparation of magnetic nanocomposite is the ion exchange method [70,75-76].

In this method the nanoscopic magnetic components are dispersed in the nonmagnetic matrix of the ion exchange resin. Here in the present study the ion exchange method [83] will be employed to prepare magnetic nanocomposites containing dispersions of iron oxide in a nonmagnetic matrix. Therefore the details are discussed in more detail in the next section.

1.21 Preparation of nanocomposites by ion exchange method.

Nanometer sized $\gamma$-Fe$_2$O$_3$ particles were embedded in a polymer matrix by the method of ion exchange followed by reduction. The method adopted here is a modification of the preparation scheme reported by Ziolo et al [70]. The polymer matrix employed is a cross linked polymer of sulphonated polystyrene and divinyl benzene, which have exchangeable H$^+$ ion containing SO$_3$H$^+$ groups. The detailed synthesis technique employed and schematic of a polystyrene structure is given in Chapter 3 (Fig.3.1)

1.22 Some Applications of magnetic nanocomposites

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Nanocomposites promise to be the wave of the future having major implications in industry and technology. A number of companies all over the world, particularly in Japan, have been utilizing their application potential in versatile fields. Nano Dyne, a U.S.-based company, has started utilizing their properties to employ them in cutting tools and wear-resistant devices. Nanocomposite-based superlattice structures become promising candidates for the next generation of information storage devices. The nanocomposites, which are superparamagnetic, will in general by theory could provide the same refrigerocaloric effect at a given field which is given by a natural paramagnet, but the operation temperature will be much higher so that they can be employed as magnetic refrigerant materials at the same temperature they need only a small applied magnetic field. Polymer-based nanocomposites can be employed used as a dielectric layer in electronic packaging applications.

1.23 Motivation for the present study

Having brought out the importance of nanomagnetic materials and its applications, it is imperative that the motivation for the present investigation is spelled out. From the foregone discussions it can be seen that any study in materials science requires preparation of pristine as well as single phasic compounds. The approach of synthesizing newer compounds and its characterization at various points of preparation using various analytical techniques is advantageous in extracting useful Physics.

The history of materials synthesis and reaction condition plays a vital role as far as the interpretation of the results is concerned and hence it is mandatory that the materials under investigation are prepared by the researcher himself/herself. Thus in this investigation, emphasis was laid in synthesizing pure nanomagnetic materials by adopting ingenious techniques.

This is an investigation in the realm of nanomagnetic materials and ferrofluids and hence pure materials are to be prepared in the ultrafine regime. It has already been mentioned in the earlier sections of this chapter that magnetism presents an indomitable challenge to physicists and chemists in explaining and understanding various phenomena like quantum magnetization, quantum tunneling, spin polarized tunneling, and superparamagnetism. In order to understand various phenomena occurring at the nanolevel, appropriate templates are necessary. While choosing such templates, the researcher has to keep in mind the various surface phenomena occurring at the
nanodimensions. This means that synthesized particles are to be protected by appropriate 
passivation techniques to prevent oxidation. Thus preparation of self protected 
nanoparticles is a viable solution and this can be achieved by incorporating ferrites like 
maghemite and magnetite in matrixes like sulphonated polystyrene. The method of ion 
exchange can be utilized to incorporate maghemite. Under normal circumstances, 
incorporation of magnetic materials in matrixes like sulphonated polystyrene using strong 
ion exchange resin results in weakly magnetic composites. In order to have better 
magnetic characteristics, cycling of magnetic materials (ion/nickel/cobalt cycling) can be 
employed. The insitu incorporation of magnetic materials in matrixes relies on the pore 
size offered by the polymer matrix. The nanopores inside the matrixes limit nucleation 
and growth and thus aid the synthesis of self protected nanocomposites. These studies not 
only provide templates for studying magnetism at the nanolevel, but also help to 
synthesize composites for magneto caloric application and in magneto-optical devices. 
This is a major motive of the present study.

It is known that a transparent magnetic material does not exist in nature and 
hence alternate techniques are to be employed to realize it. With the advent of 
nanotechnology, phenomenon like grain size dependant quantum confinement and 
alloying induced quantum confinement can be successfully employed to induce 
transparency in magnetic materials. This is important from a fundamental point of view. 
Thus preparation of a transparent magnetic composite using sulphonated polystyrene by 
size reduction is another motive of the present investigation.

In composites containing maghemite and sulphonated polystyrene, though 
magnetisation can be manipulated by cycling process, another important performance 
characteristic of a magnetic material is coercivity and this also need to be tuned. ‘Cobalt’ 
is an ideal dopant because of its large magneto-crystalline anisotropy. It can be 
incorporated inside the lattice of maghemite-sulphonated polystyrene nanocomposites. 
Incorporation of cobalt in the maghemite lattice not only modifies coercivity but also 
alters the optical band gap. So modification of saturation magnetization, coercivity and 
optical band gap is possible by the synthesis of cobalt containing maghemite-polystyrene 
nanocomposites.

3d transition metals like Co, Fe, and Ni are magnetic materials that are employed 
extensively for various applications. Studying the finite size effects on the magnetic 
properties assumes significance since various novel phenomena are expected to occur at
reduced dimensions. However, usual synthesis of these particles at the ultra fine regime results in nonmagnetic metal oxides immediately after synthesis because of their large surface area. Hence it was thought that nanocomposites containing cobalt/iron/nickel can be synthesized using sulphonated polystyrene. An ingenious method of synthesis was conceived where in, a reducing agent like NaBH₄ is utilized to arrive at passivated and self protected metal nanoparticles. This is another motive of the present work.

Ferrofluids are commercially important materials which can be employed for a number of engineering applications. Since the individual particles in a ferrofluid are typical of the order of 100Å or less and are self protected using a surfactant, they serve as ideal templates to study magnetism and non-interacting magnetic systems. Phenomena like quantum size effects, excitonic confinement and wave function overlapping and its influence on the optical properties of ferrofluids, alloying induced quantum confinement and enhanced optical transparency can also be studied by using ferrofluid templates. All these phenomena can be studied by synthesizing magnetite and nickel doped magnetite ferrofluids by using oleic acid as surfactant and kerosene as the carrier liquid. The synthesis and characterization of magnetite based ferrofluids is another mandate of this thesis.

Thin films made of ferrofluid (ferrofluidic thin film) display interesting magneto-optical properties like zero field birefringence, field induced birefringence, field induced dichroism, and Faraday rotation. These measurements enable us to extract very useful information like anisotropy constant, rotary diffusion coefficient, and magneto-optical diameter. Since facility for the evaluation of these properties does not exist in the department of Physics, setting up of a full fledged magneto-optics laboratory with vibration isolation table and optical bread board and all its accessories is another task which will be undertaken as part of the investigation. Using this set-up, field induced transmission, measurement of dichroism, birefringence, and Faraday rotation in various ferrofluid systems could be carried out.

It is known from literature that capped silver/gold nanoparticles exhibit useful optical limiting properties. However they are not stable and lack good shelf life. Hence it was thought that ferrofluid with oleic acid coating can be a useful optical limiter. So studies relating to non-optical properties of ferrofluids are also envisaged as a part of this investigation and this forms yet another motive for the present investigation.
A correlation of these properties is always handy in understanding the fundamental properties in the nanolevel and also in proposing new applications in the field of nanophase materials and ferrofluids. So the objective of present investigation can be enlisted as follows.

**Objectives of the present work:**

- Synthesis of ultra fine maghemite inside natural pores of polystyrene
- Optimization of the reaction conditions
- Tuning of optical parameters by manipulating grain size to the Bohr radius limit
- Insitu doping of cobalt with a view to enhancing the coercivity of the samples
- Correlation of the results
- Synthesis of self protected elementary magnetic metal nanoparticles inside polymer pores
- Optimization of reaction conditions
- Evaluation of structural and magnetic properties of the synthesized metal nanocomposites
- Synthesis of magnetite and doped magnetite ferrofluids by direct precipitation technique
- Optimization of reaction parameters for fine tuning the grain size
- Evaluation of their structural, magnetic, and dielectric properties
- Analysis of the magnetic field dependence of dielectric studies
- Setting up of magneto-optical laboratory for measurements
- Magneto-optical characterization of the synthesized ferrofluid samples
- Investigation on the effect of attrition on the magneto-optical signals
- Evaluation of the magneto-optic diameter, anisotropy etc from magneto-optic data
- Correlation of the results obtained from the magneto-optical measurements
- Study of their absorptive nonlinearities by closed aperture z scan technique
- Analysis of the results obtained

**References**

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