Chapter 1
General Introduction

This chapter introduces the relevance and important aspects concerning the spinel ferrite nano systems, which are selected for the present investigation. It discusses the microstructural and magnetic properties of these systems in detail. It also briefly presents the review of the works carried out in the field of nano spinel ferrites, the objectives of this research and major characterization techniques used in this study.
1.1 Introduction

Nanoparticles are of great scientific interest, because they represent a bridge between bulk materials and molecules and structures at atomic level. A nanoparticle is a quasi-zero-dimensional nano object, in which all characteristic linear dimensions are of the same order of magnitude not more than 100 nm. The discovery of unusual physical and chemical properties of nanomaterials enhanced the interest of researchers in such materials. The unusual properties are manifested as quantum size effects [1, 2]. These effects arise, when the size of the system is commensurable with the de-Broglie wavelengths of the electrons, phonons or excitons propagating in them.

When the size of particles decreases, the fraction of atoms in the surface will be increased, this in turn results in an increase in the fraction of the surface energy in its chemical potential. This will result in the differing of the conditions, such as symmetry of the local environment or coordination number from those of the bulk atoms. Currently, unique physical properties of nanoparticles are under intensive research. Magnetic properties in which the difference between a bulk material and a nanomaterial is especially pronounced, belongs to a special place there.

1.2 Magnetic Nanoparticles

The magnetization per atom and the magnetic anisotropy of nanoparticles were shown to be much greater than those of a bulk specimen, while differences in the Curie ($T_c$) or Neel ($T_N$) temperatures, i.e., the temperatures of spontaneous parallel or antiparallel orientation of spins, between nanoparticle and the
General Introduction

corresponding macroscopic phases reach hundreds of degrees [3, 4]. In addition, magnetic nanomaterials were found to possess a number of unusual properties, like giant magnetoresistance (GMR) [5] and extraordinary Hall effect in metallic systems [6, 7]; large tunnelling magnetoresistance (TMR) in insulating materials [8]; remanence, coercivity and magnetocaloric effect enhancements [9, 10]; glassy behaviour and quantum tunnelling of the magnetization [11]. These properties enable nanomaterials, viable for enormous technological innovations. The generation of new ultra-high density magnetic information storage devices and the industrial technologies, such as magnetic sensors, refrigerant materials and permanent magnets are some of the examples [12, 13]. Besides, magnetic particles and clusters of nanometric size possess an increasing importance in quantum computing, spintronics [14-16] and as diagnostic and therapeutic tools in medicine and other life sciences [17]. Examples of the exciting and broad field of magnetic nanoparticles applications, include drug delivery, contrast agents, magnetic hyperthermia, therapeutic in vivo applications of magnetic carriers and in vitro magnetic separation and purification, molecular biology investigations, immunomagnetic methods in cell biology and cell separation and in pure medical applications [18-20].

The magnetic properties of nanoparticles are determined by many factors, including chemical composition, type and the degree of defectiveness of the crystal lattice, the particle size and shape, morphology and interaction of the particle with the surrounding matrix and the neighbouring particles. By changing the nanoparticle size, shape, composition and structure, one can control the magnetic characteristics of the material to an extent. However, these factors cannot always be controlled during the synthesis of nanoparticles.
Therefore, the systems with same size and chemical composition will exhibit different magnetic properties.

1.2.1 Superparamagnetism

The most important finite size effect in the magnetic nanoparticle is superparamagnetism. Domains, groups of spins all pointing in the same direction and acting cooperatively, are separated by domain walls, which have a characteristic width and energy associated with their formation and existence. The motion of domain walls is a primary means of reversing magnetization. Size reduction in magnetic materials (multi-domain materials), resulting in the formation of single domain particles, also gives rise to the phenomenon of superparamagnetism. Briefly, superparamagnetism occurs, when thermal fluctuations or an applied field can easily move the magnetic moments of the nanoparticle away from the easy axis, the preferred crystallographic axes for the magnetic moment to point along. Each particle behaves like a paramagnetic atom, but with a giant magnetic moment, as there is still a well-defined magnetic order in each nanoparticle [21]. Superparamagnetic materials are intrinsically nonmagnetic, but can be readily magnetized in the presence of an external magnetic field. The critical radii, $r_c$, for different particles differ, based on shape, temperature and crystalline magneto anisotropy.

1.3 Spinel Ferrites

Spinel ferrites are an important group of magnetic materials, with general equation MFe$_2$O$_4$, in which M represents a divalent metal ion, such as Fe$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ or Zn$^{2+}$. A combination of these cations is also possible and in this case, we refer to them as a solid
solution of two ferrites, mixed crystal or in general terms, as a mixed ferrite. They exhibit unique chemical, electrical, mechanical, structural and magnetic properties and have a variety of promising technological applications in high-density recording devices, colour imaging, ferrofluids, high frequency devices and magnetic refrigerators [22].

1.3.1 Crystal Structure

Spinel-type oxides are often denoted by the formula \( \text{AB}_2\text{O}_4 \), where A and B refer to tetrahedral and octahedral sites, respectively, in the fcc oxygen lattice. The stoichiometry can also be written as \((\text{AO})(\text{B}_2\text{O}_3)\). A unit cell of the spinel structure consists of 8 formula units \((8 \times \text{AFe}_2\text{O}_4)\) [23]. The structure can be divided into eight octants with two groups of sublattices sharing the same crystal structure as shown in Figure 1.1. Each formula unit contains four oxygen ions on the body diagonals, while these four oxygen ions also occupy the corners of a tetrahedron as shown in Figure 1.1.

There are two kinds of interstitial sites present, as shown in Figure 1.1 and 1.2. One is the octahedral site (B site) shown in Figure 1.3(a) and the other is tetrahedral (A) site shown in Figure 1.3(b). The \(\text{B}^{3+}\) ions on B sites are surrounded octahedrally by six oxygen ions and the \(\text{A}^{2+}\) ions on A sites are surrounded tetrahedrally by four oxygen ions as shown in Figure 1.3. Out of the 96 internal sites in the unit cell of a spinel structure, there are 32 oxygen \((8 \text{ formula units} \times 4 \text{ oxygen ions})\) anions, 32 octahedral sites and 64 tetrahedral sites. However, only 8 tetrahedral sites are occupied by \(\text{A}^{2+}\) ions, while 16 octahedral sites are occupied by \(\text{B}^{3+}\) ions.
Figure 1.1. The unit cell of \( \text{AB}_2\text{O}_4 \) spinel [24].

Figure 1.2. Adjacent octants of \( \text{AB}_2\text{O}_4 \) spinels with octahedral and tetrahedral sites occupied by the A and B cations [25].

Figure 1.3. The sublattice of ferrites: (a) Octahedra sublattice (b) Tetrahedra sublattice (The larger ball indicates oxygen ions while the smaller ball indicates metal ions) [26].

In the ideal spinel lattice, each oxygen ion is enclosed by one cation on tetrahedral (A) site and three cations on octahedral (B) sites, as shown in Figure 1.4. The distance from an oxygen nucleus to its nearest metal ion nucleus [27] is

\[
d_{M-O} = \frac{1}{8}a_0\sqrt{3}
\]

\(a_0\) : lattice parameter of the spinel unit cell
\[ r_A = \frac{1}{8} a_0 \sqrt{3} - r_o \]  
(1.2)

\[ r_B = \frac{1}{4} a_0 - r_o \]  
(1.3)

\( r_A \): The ideal radii of the tetrahedral (A) sites.

\( r_B \): The ideal radii of the octahedral (B) sites.

\( r_o \): The radius of the oxygen anion.

Figure 1.4. Distances between cations in an ideal spinel lattice. The small white spheres indicate the metal ions occupying the B sites, the small black sphere indicates the metal ion occupying the A sites and the big white sphere indicates the oxygen ion [28].

1.3.2 Cation Distribution

Cation distribution of a spinel ferrite is generally represented as \( A_2^+Fe^{3+}_4[Fe^{3+}_8]O_4 \). The value of \( \delta \) is a measure of the inversion of a material and usually depends on the processing conditions of the sample. A normal spinel material has \( \delta = 1 \) and for an inverse spinel, \( \delta = 0 \) [28].

The crystal structure of the inverse spinel structure can be written as \( B(AB)O_4 \). It indicates that the \( B^{3+} \) ions distribute equally among the tetrahedral and the octahedral sites, while \( A^{2+} \) ions occupy the rest of octahedral sites. In an inverse spinel structure of \( AFeO_4 \), the spin moments of all \( Fe^{3+} \) ions, which occupy the octahedral sites are aligned parallel to each other. But, their spin directions are opposite to the spin moments of the \( Fe^{3+} \) ions, which occupy the tetrahedral sites. Therefore, all the magnetic moments of \( Fe^{3+} \) ions are cancelled in
the ferrite. Nevertheless, all $A^{2+}$ ions have their moments aligned parallel to each other and the total moments of these $A^{2+}$ ions represent the net magnetization of the ferrite as shown in Figure 1.5.

![Figure 1.5. Magnetic structure of a ferrimagnetic inverse spinel [29].](image)

The temperature dependence of the distribution is shown to correspond to a Boltzman distribution,

$$\frac{\delta(1+\delta)}{(1-\delta)^2} = \exp\left(-\frac{E}{kT}\right)$$

where $E$ is the activation energy for changing the site. The interesting and useful electrical and magnetic properties of the spinel ferrites are governed by the distribution of the iron and the divalent metal ions among the octahedral and tetrahedral sites of the spinel lattice.

The chemical bonding in spinel ferrites may be taken as purely ionic. Thus, the main part of the lattice energy is contributed by the Coulomb energy and Born repulsive energy. The energy calculations show that the size and valency of the cations and the oxygen parameter of the anions are important factors. Large divalent ions tend to occupy tetrahedral sites, as this is favoured by polarization effects. If the A site ions have a lower valency and the B site ions, a higher valency, the intermediate $O^{2-}$ ions will become polarized towards B sites. Thus, polarization favours normal spinel configuration. From the calculation for the complete lattice made by
Verwey et al., it follows that the inverse structure has the lowest lattice energy for oxygen parameter, $u < 0.379$, whereas the normal structure has the lowest energy, when $u > 0.379$ [30]. However, nonequilibrium cation distributions are possible using novel or nonequilibrium processing routes. A nonequilibrium distribution of cations in the spinel structure can influence the intrinsic magnetic properties of these materials.

1.3.3 Magnetic Properties

Ferromagnetic materials, with the moments of all the ions oriented in the same direction, give rise to high values of magnetic moments, while antiferromagnetic substances, with spins aligned in an antiparallel fashion, show a resultant magnetic moment of value zero. In ferrimagnetic materials, the magnitude of the magnetic moments oriented in either way differ, so that, there always exists a resultant uncompensated magnetic moment. It is for this reason that the magnetic moments of the ferrimagnets are, in general, less than those of ferromagnets. Ferrites exhibit ferrimagnetic behaviour. The nature of ferrimagnetism and hence, the resultant magnetic properties has emanated from the spin-spin interaction of cations available in the sublattices of the ferrite. A wide range of compositions and magnetic properties could be secured by substituting various kinds of cations on different sublattices. The magnetic moments of each sublattice tends to arrange themselves antiferromagnetically, that is antiparallel to each other. The direction of arrangement with respect to each other, being parallel or antiparallel, is determined by so called exchange (coupling or interaction) energy, $E_{ex}$ given by the following expression:
\[ E_{ex} = -2J \overrightarrow{S}_1 \cdot \overrightarrow{S}_2 \cdot \cos \varphi \] (1.5)

where \( \overrightarrow{S}_1 \) and \( \overrightarrow{S}_2 \) are the magnitude of the spin vectors of electron no. 1 and no. 2, respectively and \( \varphi \) is the angle between their spin vectors. The term, \( J \) is the exchange integral, which is defined as

\[ J = \int \Psi_a(1) \Psi_b(2) \Psi_a(2) \Psi_b(1) \left( \frac{1}{a} - \frac{1}{a_2} - \frac{1}{a_4} + \frac{1}{r_{12}} \right) dt \] (1.6)

where \( a \) is the lattice separation, \( a_2 \) is the distance between electron no. 2 and atom no. 1, \( a_4 \) is the distance between electron no 1 and atom no. 2 and \( r_{12} \) is the distance between electrons.

The total energy of a system consisting of two magnetic moments is decreased, if the moments are coupled with each other. Parallel or antiparallel alignment of magnetic moments is a consequence of the sign of the coupling energy. The magnetic moments are arranged antiferromagnetically (antiparallel) to each other, if the exchange energy is positive or vice versa. In the case of ferrites, antiparallel alignment of magnetic moments on different sublattices has been observed. However, a net magnetization (total magnetic moment) results, due to the fact that the magnitude of the total magnetic moments in each sublattice differs from each other. The net magnetic moment can be calculated by the summation of magnetic moments of tetrahedral and octahedral sites [31].

In general, the magnitude of interaction energy between two magnetic ions, \( \text{Me}^I \) and \( \text{Me}^II \) depends upon (a) the distances from these ions to the oxygen ion, represented by the quantities through which the interaction occurs and (b) the angle represented by the term \( \varphi \) as shown in Figure 1.6. An angle of 180° will give rise to great amount of exchange energy and the energy decreases very rapidly with increasing distance.
The various possible configurations of the ion pairs in spinel ferrites, with favourable distances and angles for an effective magnetic interaction, as envisaged by E.W.Gorter, are given in Figure 1.7 [23]. Based on the values of the distance and the angle, it may be concluded that, of the three interactions, the AB interaction is of the greatest magnitude. The two configurations for A-B interaction have small distances (p, q and p, r) and the values of the angle are fairly high. Of the two configurations for the B-B interactions, only the first one will be effective, since in the second configuration, the distance, s is too large for effective interaction. The A-A interaction is the weakest, as the distance r is large and the angle φ is ~ 80°.

The inter-ionic distances between the cations (b, c, d, e and f) and between the cation and anion (p, q, r and s) were expressed in terms of atomic positional parameter (u) and lattice constant (a) are given by the following equations [32, 33].
\[ p = a(0.5 - u) \]
\[ q = a(u - 0.125)\sqrt{3} \]
\[ r = a(u - 0.125)\sqrt{5} \]
\[ s = \frac{a}{3}(u + 0.5)\sqrt{3} \]
\[ b = (a/4)\sqrt{2} \]
\[ c = (a/8)\sqrt{11} \]
\[ d = (a/4)\sqrt{3} \]
\[ e = (3a/8)\sqrt{3} \]
\[ f = (a/4)\sqrt{6} \]

(1.7)

Thus, with only A-B interaction predominating, the spins of the A and B site ions in ferrites will be oppositely magnetized sublattices A and B, with a resultant magnetic moment equal to the difference between those of A and B site ions. In general the value of saturation magnetic moment for the B lattice \( (M_B) \) is greater than that of the A lattice \( (M_A) \), so that, the resultant saturation magnetization \( (M_S) \) may be written as \( M_s = |M_B - M_A| \).

### 1.4 A Review of Literature on Spinel Ferrites

In spinel ferrites, the magnetic order depends on the competition between various kinds of superexchange interactions among A and B site cations, i.e., \( J_{AB} \) (A-O-B), \( J_{BB} \) (B-O-B) and \( J_{AA} \) (A-O-A) [33]. Certain amount of site exchange of cations is sufficient to change \( J_{AB} \) and \( J_{BB} \) interactions and has shown drastically different magnetic behaviour in nanoparticle spinel in comparison with the bulk [35, 36]. In most of the reports on nanoparticle spinel, the magnetic order is of long range with collinear spin structure and \( J_{AB} \) is much stronger than \( J_{BB} \). In the case of \( \text{NiFe}_2\text{O}_4 \), Kodama et al. had calculated the \( J_{AB} \) value as \(-36\) in the units of \((^\circ\text{K})\), which is well above the value of \( J_{AA} \) \((-21) \) and \( J_{BB} \) \((-28) \) [37, 38]. Similar observations were reported in the case of Mn-Zn
ferrites [39], Mn ferrite [40], Cu ferrite [41], Cu–Zn ferrite substituted with rare earth ions [42] and Co ferrite [43, 44].

In spinels, a strong surface spin canting effect occurs, when the particle size reduces to nanometre range. Sepelak et al. reported the spin canting effects in the surface of nickel ferrite nanoparticle of 8.6 nm, in which a shell of thickness 1 nm, with disordered spin is responsible for the effect [45]. In a detailed analysis of the relation between the surface roughness and the magnetic behaviour in nickel ferrite nanoparticles, Nathani et al. noted that an increase in surface roughness of nanocrystalline ferrites, results in increased tendency towards non-squaredness of the hysteresis loop, with consequent increase in surface anisotropy and coercivity and decrease in the magnetization value [46]. They established that magnetic anisotropy of nanocrystalline ferrites is governed by surface effects rather than magnetocrystalline anisotropy. The competition between the disordered (canted) surface spins and ordered core spins determines the magnetic ground state and usually exhibits a decrease of magnetization and ordering temperature in spinel nanoparticles [38, 40]. In the case of CoFe₂O₄, a room temperature saturation magnetization value of 80.8 emu/g is observed for bulk samples [47], while the nanoparticles possess only 67.95 emu/g [48]. The reduction in saturation magnetization is attributed to the existence of a “dead” surface layer for each particle, in which magnetic moments do not contribute to the magnetization in the field applied.

The variation in magnetization may occur due to various other reasons also. For example, the antiferromagnetic order of bulk ZnFe₂O₄ below 10 K transforms into ferrimagnetic order even at \( T < 10 \) K, with large magnetic moment by mechanical milling. Such a magnetic enhancement in mechanical milled ZnFe₂O₄ nanoparticle
has been attributed to the exchange of cations among A and B sites [49]. Though magnetic order and magnetization are enhanced, the experimental value of saturation magnetization was found to be well below the expected value, in case of various other mechanical milled spinels. In the case of CdFe$_2$O$_4$, the lower value of experimental finding; 21.7 emu/g at 5 K lower than the expected value; 80 emu/g was attributed to the local spin canting in both A and B sites, even after mechanical milling. [50].

The effect of morphology of ferrite nanoparticles on their magnetic properties is well studied [51, 52]. Son et al. reported that in nanoparticles of Mn and Mn–Zn ferrites, synthesized by a radio frequency induction plasma torch, the truncation of the surfaces lead to surface anisotropy and a resulting variation in Neel temperature [53]. Swaminathan et al. reported that there was a preferential termination of surfaces in polydispersed and monodispersed Ni–Zn ferrite nanoparticles [54]. In polydispersed, faceted nanoparticles both the (100) and (111) terminating faces were observed, while the (111) surfaces dominated in monodispersed particles. In another case, Swaminathan et al. reported the preferential breaking of unlike (A–B) bonds compared to like (B–B) bonds in the (111) terminated surfaces of Ni–Zn ferrites [55]. Also, it was observed that in (111) surfaces, there was an increase in the concentration of Zn in A sites compared to B sites [54, 56]. The preferential breaking of A–B bonds as well as the preferential occupation of Zn cations in A sites, resulted in a reduced A–O–B surface exchange interaction, leading to the origin of triangularly canted spin structure in B-sites of (111) terminated surfaces, like the Yafet and Kittel [57] structure in ferrospinels [58]. Nanoparticle systems with (100) terminated surfaces exhibit uniaxial surface magnetic anisotropy [53]. The morphology of nanoparticles
determines the fraction of (111) and (100) surfaces, which in turn affect the effective anisotropy in the samples. The above mentioned studies by Swaminathan et al. also shown that the morphology of ferrite nanoparticles can cause effects like nonsaturation of magnetic moments even in high applied field, open and irreversible hysteresis curves, smaller values of saturation magnetization and higher values of coercive field [54-56, 58].

The flexibility of the crystal structure, which is particularly pronounced in the spinel ferrite nanoparticles, directly points to the flexibility of magnetic properties [59]. For example, ZnFe$_2$O$_4$ in bulk form shows paramagnetic behaviour, due to its normal spinel structure, with Zn ions incorporated almost exclusively at tetrahedral sites. On the other hand, when ZnFe$_2$O$_4$ is prepared in the form of nanoparticles, it becomes ferrimagnetic, due to a partial migration of Zn ions to the octahedral sites [60, 61]. Zinc is known to play a decisive role in determining the ferrite properties [62]. The redistribution of metal ions over the tetrahedral and octahedral sites in the spinel lattice on incorporation of zinc is responsible for the modification in ferrite properties.

The properties of ferrites are also sensitive to their composition and microstructure, which in turn are dependent on the method of processing. A close review of the literature reveals that electrical properties of zinc doped lithium ferrites were so far studied only on those samples, which were prepared through conventional solid state method, which involves both long and high temperature treatments for the oxides used in the preparation. In zinc doped ferrites, prepared by conventional solid state method, there may be a loss of zinc by evaporation, caused by high sintering temperatures and long time treatments. This results in non-stoichiometric ferrite [63].
Mozaffari et al. reported that the zinc ferrite nanoparticles synthesized after calcination at 350 °C, have a different ionic distribution in comparison with that of bulk zinc ferrite. Also, the results show that by increasing annealing temperature, the ionic distribution of the zinc ferrite nanoparticles tends to that of bulk sample [64].

The Ni-Ce doping in ZnFe\textsubscript{2}O\textsubscript{4} was studied recently and found that the saturation magnetization will increase with the decrease in particle size. [65]. Zinc ferrite coated thin films are recently reported to be better candidates for photocatalytic applications [66]. The bismuth substitution in zinc ferrite can induce multiferroic nature. Mito et al. reported the enhancement of dielectric property of ZnFe\textsubscript{2}O\textsubscript{4} with the substitution of bismuth [67]. Recently, even some biological methods by the use of bacteria to facilitate the production of magnetic nanomaterials is maturing into a feasible technological asset. Yeary et al. reported the magnetic properties of bio-synthesized zinc ferrite [68]. In the ferrofluids prepared using zinc ferrite nanoparticles, a cation redistribution that enhances the magnetic and magneto-optical responses of the nanoparticles were observed [69].

In case of CoFe\textsubscript{2}O\textsubscript{4}, conductivity was observed to decrease, when the grain size increased from 8 to 92 nm, which was clearly due to the predominant effect of migration of some of the Fe\textsuperscript{3+} ions from octahedral to tetrahedral sites. Also, Neel temperature was found to increase from 709 K for 8 nm to 809 K for the 92 nm particles, because of the change in the cation distribution and it remains almost the same for the higher grain sizes, as there is no further change in the cation distribution [70]. Similar results are observed in the magnetic properties of MnFe\textsubscript{2}O\textsubscript{4} nanoparticles [71].
It is well established that Zn$^{2+}$ ions have a strong preference for tetrahedral (A) sites. This has been advantageously used for incorporating diamagnetic zinc into (Mn,Zn)Fe$_2$O$_4$ and (Ni,Zn)Fe$_2$O$_4$ ferrites, to enhance their magnetization [72]. In the case of Zn$_{1-x}$Ni$_x$Fe$_2$O$_4$ ferrite, it is found that for $x$ greater than 0.5, the tetrahedral and octahedral (B) site Fe moments have collinear arrangement, whereas for $x$ less than 0.5, a noncollinear arrangement of B site Fe moments exists. The Néel temperature of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ spinel ferrite increases significantly from 538 K in the bulk state to 592 K, when the grain size is reduced to 16 nm by milling in a high-energy ball mill [73]. The variation in Neel temperature was explained in account of the increased number of magnetic ions in the A sites, which eventually strengthen the superexchange interaction between A and B sites. Zhu et al. reported the effect of Zn doping on electronic and magnetic properties of NiFe$_2$O$_4$ spinel using first-principles density functional theory within the generalized gradient approximation method [74]. The electronic structure calculations show that the Fe(A)3d states are relatively insensitive to the change of the Zn content and substitution of Ni with Zn, enhances localization of the Fe(B)3d states.

From the viewpoint of fundamental magnetism, much attention has been devoted to understand the effect of nano-scaled confinement and the role of atoms lying at or near to the surface on the spin arrangement within a nanoparticle [75, 76]. More particularly, the reduced coordination and the large number of broken exchange bonds of surface atoms can give rise to surface anisotropy, frustration and spin disorder [77, 37]. Among these effects, one of the most intriguing effects in ferrite nanoparticles is the observation of a unidirectional exchange [78-80], as in re-entrant spin-glasses [81, 82].
and as exchange bias in magnetic multilayer sandwiches [83]. It is usually attributed to the presence of canted spins, either in the bulk for re-entrant spin-glasses or at the interfaces for nanoparticles and magnetic multilayer sandwiches.

The localization of the spin disorder inside a nanoparticle and its influence on the magnetodynamics of such a nanosystem may be quantified by the parameter called the surface pinning parameter [84-86]. Various investigators reported different values of spin canting on nano cobalt ferrite material. There are reports of canting of tetrahedral and octahedral spins of 53° and 47° in cobalt ferrite nano systems prepared from cobalt-iron hydroxide carbonate complex [87]. Ngo et al. had shown that the canting angle of both tetrahedral and octahedral spins will increase from 40° and 26° to 75° and 39°, with the decrease in particle size from 6.2 nm to 3.1 nm [88]. In 2011, Peddis et al. reported a tetrahedral and octahedral canting of 41° and 36° in the cobalt ferrite nanoparticles, with a particle size of 6 nm, synthesized using citric acid [89]. The spin distortions are ousted from the magnetically ordered core to the surface. These distortions are then localized in a thin surface shell, magnetically disordered, in close contact with the magnetically ordered core. An interfacial anisotropy, related to the exchange interaction across the core-shell border, is also entailed to the spatial border between the two magnetic materials (the core and the shell), which have two different kinds of magnetic ordering. Such unidirectional (or rotatable) exchange anisotropy, first discovered by Meiklejohn and Bean at a ferromagnet/antiferromagnet border, is a customary effect for spin-glass films and superlattices [90, 91]. It has been also evidenced in maghemite nanoparticles through isotropic contributions to both linewidths and resonance fields in ferromagnetic resonance experiments [84-86].
In the design of new nanostructured magnetic materials, molecular coating of nanoparticles represents probably the most important step. It is found that the coating of CoFe₂O₄ increases the magnetic anisotropy, arising from the interaction between molecules and surface atoms, which in turn leads to a strong modification of surface magnetic properties is an important obstacle to overcome [92]. It is found that in cobalt ferrite, the higher order anisotropy constant, K₂ dominates the anisotropy energy [93]. Further, the magnetic measurements of cobalt ferrite nanoparticles indicate that the influence of the production process of samples on saturation magnetization, coercivity and magnetostriction, decreases with annealing temperature, becoming almost insensitive for large grains [94]. In 2012, nanocomposite fibers made from polyacrylonitrile (PAN) containing carbon nanotubes (CNTs) and cobalt ferrite nanoparticles were fabricated by electrospinning [95]. These nanocomposite fibers exhibited effective electromagnetic interference shielding and the magnetic characterizations showed that the magnetization property of the nanocomposite can be tailored by adjusting the loading of cobalt ferrite.

Many efforts were also performed on the study of mixed ferrite, which usually presents a wide choice in its properties and could meet different kinds of need [96]. Cobalt and nickel ferrites are some of the most versatile centrosymmetric magnetic materials [97]. Cobalt ferrite is a kind of hard ferrite, with a high and positive magnetocrystalline anisotropy constant, K₁ (~ +10⁶ erg/cm³) while, nickel ferrite, a kind of soft magnetic ferrite, with a relatively low and negative magnetocrystalline anisotropy constant, K₁ (~ -10⁴ erg/cm³) [98]. So, the magnetocrystalline anisotropy constant, K₁ of the mixed spinel ferrite, Co₀.₀²⁷Ni₀.₉₇₃Fe₂O₄ should be zero theoretically and
consequently, the ferromagnetic resonance line width of the mixed spinel ferrite $\text{Co}_{0.027}\text{Ni}_{0.973}\text{Fe}_2\text{O}_4$ should reach to its minimum \cite{99}, which had been demonstrated experimentally by Sirvetz and Sounders \cite{100}. Thakur et al. had reported the magnetic behavior of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Co}_{0.1}\text{Fe}_{1.9}\text{O}_4$, of size 8-12 nm, synthesized by a co-precipitation method \cite{101}. These measurements show that the sample is superparamagnetic above the blocking temperature, $T_B \sim 253$ K, when an external magnetic field of 20 Oe is applied. A reduction in saturation magnetization was observed in the case of nanoparticles, which may be attributed to the fact that magnetic moments in the surface layers outside the core are in the state of frozen disorder. The material showed superparamagnetic behavior at room temperature.

The electrical properties of ferrites are dependent upon several factors, namely, the method of preparation, the grain size, the chemical composition, etc \cite{102}. The conduction mechanism in ferrites is quite different from that in semiconductors. In ferrites, the temperature dependence of mobility affects the conductivity and the carrier concentration and is almost unaffected by temperature variation \cite{103}. Ferrites behave as inhomogeneous dielectric materials, in which the individual high conducting grains are separated by low conducting layers \cite{104-106}. The conductivity values of $\text{CoFe}_2\text{O}_4$ shows a decreasing trend with the increase in grain size, which against expectations is reported and attributes to the localized lattice defects present in the samples with lower grain size \cite{107}. It has long been known that low resistivity or high conductivity in ferrites is caused in particular, by simultaneous presence of ferrous and ferric ions on equivalent sites \cite{108}. The electrical properties of different spinels, such as manganese ferrite \cite{109}, Mn-Mg ferrites \cite{110}, zinc ferrite \cite{111}, Mn-Zn ferrite \cite{112} and Co-Zn ferrite \cite{113}
have been extensively studied by many investigators. In the A.C. and D.C. conductivity study of Ni-Zn ferrite nanoparticles in wet and dry conditions, Saafan et al. reported that the behaviour of conductivity differs significantly in the two cases showing a noticeable effect, due to humidity [114]. In the aluminium industry, ferrite materials are recently used in the development of inert anodes. Nickel ferrite and its derivatives have been utilized as an inert anode for electrometallurgical applications, particularly for the production of aluminium using the Hall–Heroult process [115]. The DC conductivity is one of the important properties of nickel ferrite as inert anode and can be improved further by using different preparation conditions, like the sintering temperature, dwell time and sintering atmosphere [116, 117]. Balaji et al. studied the substitution of tin in nickel ferrite to improve the electrical and structural properties to make it more suitable for anode materials in molten salt systems [118]. Liu et al. recently showed that the direct current conductivities of the spinel nickel ferrites sintered in nitrogen atmosphere showed a drastic increase compared to those sintered in air, believed to be due to the effects of increased Fe²⁺ ion concentration at octahedral sites and the increase of the relative density [119].

The investigations of optical properties of spinel ferrites, generally orient around two major areas of technological interest. First one is the light absorption properties of ferrites, which can be utilized in different environmentally friendly and sustainable wastewater pollution treatment technology and hydrogen generation. Photocatalytic activities of spinel ferrites, which have a relatively narrow band gap, enable them for such applications [120]. To make full use of solar energy, many attempts have been made to prepare the narrow band gap semiconducting material that utilizes the much
larger visible region. Among those, zinc ferrite (ZnFe₂O₄) is regarded as a promising visible-light photocatalyst, with a band gap of 1.9 eV, which makes it possible to utilize solar energy [121]. In addition to its photochemical stability and low toxicity, ZnFe₂O₄ has been applied to degrade organic pollutants [122]. Cd-Zn ferrite, which has an enhanced optical and photocatalytic property is reported to be a good candidate for such applications [123]. The second important property related to the optical activity of spinel ferrites is the magneto-optical rotations. Cobalt ferrite is known to be a good candidate for magneto-optic recording material [124, 125]. It also shows changes in the magneto-optical rotations by the addition of lanthanide ions, such as Gd, Tb and Dy [126]. Ionic ferrofluids based on nickel ferrite nanoparticles are also reported to exhibit such type of optical activities [127].

Advances in the development of new communication methods and new sources of radiation, particularly optical power sources, such as lasers, had resulted in research oriented towards the protection from exposure to such sources. In this context, the development of optical power limiter has been focused on the design of novel materials showing large nonlinear optical effects upon irradiation with high energy sources. However, the research in this area has not utilized the potentials of spinel ferrites considerably [128]. The investigations in this area mainly concentrated on metal oxide nanoparticles [129] and thus, need a thorough investigation with different spinel ferrites.

1.5 Objectives

A detailed review of the existing literature in spinel ferrites indicates a profound significance of synthesis method on various
physical and chemical properties. The possibility of developing innovative technological applications with these compounds depends on a simple, cost-effective and gentle chemistry synthesis route, which can give consistent results for the wide range of spinel ferrites in ultra fine and homogenous powder form.

The micro-level magnetic properties of spinel ferrites show extensive variations due to its dependence on synthesis method. One such property is the spin orientations in the tetrahedral as well as octahedral sites of these ferrites, which contribute to the overall macro-level magnetic behavior of the systems. These spin orientations are structured by different aspects, such as particle size, cationic distribution, inter-atomic bond lengths and angles and the exchange interaction between the cations. Further, there are reports of both the collinear and noncollinear nature of the spins in these systems. Even in reports of noncollinear spin structure, canting angle values varied significantly. Thus, a detailed investigation on the spin structure, which influences the macro-level magnetic ordering in different spinel ferrites, is vital.

The basic structural factors such as lattice parameter, bond angle, bond length and oxygen parameter will influence the micro-level magnetic properties of the spinel ferrites. The variation in magnetic moments with temperature can be correlated with the variation of these structural factors. However, very few information is available regarding this correlation. Thus, the temperature dependent neutron diffraction of spinel ferrites, which gives magnetic as well as structural details of these nanocrystals is of great relevance.

Recently, nanomaterials have drawn significant attention as optical limiters. The spinel ferrite nanoparticles have a very high shelf life and remarkable thermal stability, which are important
requirements for sustainable use with intense lasers. This physical and chemical stability of ferrites, which is an important attribute for an optical limiter, prompted us to investigate their optical limiting properties. The optical limiting properties of spinel ferrite nanoparticles are not thoroughly studied yet.

This investigation is pursued to address the above mentioned problems in the area of spinel nano ferrite research. NiFe$_2$O$_4$, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, ZnFe$_2$O$_4$, CoFe$_2$O$_4$ and Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ are selected as the representative compounds from different spinel groups of inverse, normal and mixed structure.

- The primary aim is to synthesize these ferrites within a particle size range below 10 nm, through a poly vinyl alcohol (PVA) assisted sol-gel route. This method has the advantage of simple preparation, cost-effective and gentle chemistry route, resulting in ultra fine and homogeneous powder.
- Detailed investigations of the distribution of cations within tetrahedral as well as octahedral sites of these nanoparticles to be carried out using Mossbauer spectroscopy and neutron diffraction methods.
- The possibility of structural changes, chemical and coordination differences of iron in the nanocrystalline environment and micro level spin orientations and magnetic moments in these materials are also to be investigated using Mossbauer spectroscopy and neutron diffraction, to get an accurate picture of the microstructure.
- The magnetization behaviour of these materials are to be investigated using the vibrating sample magnetometer (VSM), to find out how the micro level magnetic orientations add up to give the magnetic behaviour of these materials.
• To get a more precise idea about the size dependence of magnetic properties and micro structure, investigations in samples with same composition and different particle sizes are compared.

• A comparative study of the optical limiting properties of these five different spinel ferrite systems using the Z-scan technique is one of the important objectives of this study.

1.6 Synthesis of Nano Spinel Ferrites through Sol-gel Method

Several techniques have already been used to produce NiFe₂O₄ nanoparticles, including hydrothermal reactions [130], co-precipitation [131], combustion synthesis [132], thermal decomposition [133], sol-gel method [134], microwave processing [135], electrospinning [136], reverse micelle technique [137], plasma deposition method [138], radio frequency thermal plasma torch technique [139], pulsed wire discharge [140], sonochemical synthesis [141], high-energy milling [142] and electrophoretic deposition [143]. In a comparative study of various synthesis methods for the synthesis of nano spinel ferrites, Kumar et al. reported that sol–gel synthesis is the effective one in providing smaller average crystallite size and little variation in crystallite size over the range of temperatures studied [144]. Further, among the synthesis methods, such as co-precipitation, citrate–gel method, oxalate precursor method and sol-gel method, a higher saturation magnetization was observed in Ni-Zn ferrite, synthesized through sol-gel method.

The sol-gel process is a wet-chemical technique, widely used in the field of materials science and ceramic engineering. It has the advantage of good stoichiometric control and the production of ultra
fine particles with a narrow size distribution in a relatively short processing time at lower temperatures [145]. This method is used primarily for the fabrication of typical metal oxide materials, starting from a chemical solution, which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Generally, the precursors will be metal alkoxides, metal nitrates or metal chlorides. The precursors undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centres with oxo (M-O-M) or hydroxo (M-OH-M) bridges, thereby generating metal-oxo or metal-hydroxo polymers in solution. Thus, the sol evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase, whose morphologies range from discrete particles to continuous polymer networks [146].

We can chemically modify the precursors, which consist of a metal or metalloid element surrounded by various ligands, using certain chelating agents. The nature of chelating agent greatly aids in the formation of a cross-linked gel, which may result in the control of properties of the nanostructured material formed in the process. In a sol-gel process, where a chelating agent is used, the functional group of the chelating agent forms a chelate with cations, resulting in a sol. During the sol formation process, the chelating agent acts to distribute the cations atomistically throughout the polymeric structure and prevent cation segregation and thereby precipitation. Heating the sol to moderate temperature causes a condensation reaction via dehydration with the concurrent formation of water. As most of the excess water is removed, the sol turns into a gel and extremely high viscosity polymeric resins are formed. The gel can be either cross-linked or non-cross-linked, depending on the
stoichiometry of the ratios of reactants. Calcination of the gel in air or other gases causes breakdown of the gel. While the chemical bonding of the cations to the polymeric chains is destroyed during pyrolysis, the high viscosity of the gel causes low cation mobility, which prevents the different mixed cations from segregation. Therefore, it is assumed during the calcination that there is little segregation of the various cations that remain trapped in the char. Subsequently, the cations are oxidized to form crystallites of mixed cation oxides.

1.7 Important Characterization Techniques Used

This section deals with the details of the experimental set up and the basic operation principles of various structural and physical characterizations of the materials prepared.

1.7.1 Phase and Crystallite Size Analysis

Phase formation of as burnt and calcined ferrite powder samples were studied by the powder X-ray diffraction performed on a PANanalytical X’pert Pro X-ray diffractometer. In the powder, grains have random orientations. With random orientations, it is expected that most of the atomic planes lie parallel to the surface in some of the grains. Thus, scanning through different angles would be associated with different atomic spacing. A powdered sample is packed on a sample stage, so that it can be irradiated by the X-ray.

To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube and rotated the sample through different Bragg’s angles. The goniometer keeps track of the angle (θ) and the detector records the detected X-rays in units of counts/sec and sends this information to the computer. The operating parameters were; 40 kV and 35 mA with the Cu target, a
step size of 0.02° and a count time of 4 s per step. After scan of the sample, the X-ray intensity (counts/s) was plotted against the angle, 2θ. The angle 2θ for each diffraction peak was then converted to d-spacing, using the Bragg’s law;

\[ n\lambda = 2d \sin \theta \]  

(1.8)

where \( \lambda \) is the wavelength of X-ray and \( n \) is the order of diffraction.

The identification of different phases was carried out by Hanawalt method using Philips X’pert high score software. The powder pattern is characterized by a set of line position, 2θ and a set of relative line intensities, \( I \). But the angular positions of the lines depend on the wavelength used and a more fundamental quantity is the spacing, \( d \) of the lattice planes forming each line. Each pattern is described by listing the \( d \) and \( I \) values of its diffraction lines. Each substance is characterized by the \( d \) values of its 3 strongest lines. The \( d \) values together with the relative intensities are sufficient to characterize the pattern of an unknown crystal structure [147].

The crystallite sizes of as burnt and calcined powder samples were determined from X-ray line broadening, using the Scherrer’s equation [147] as follows:

\[ t = \frac{0.9 \lambda}{B \cos \theta} \]  

(1.9)

where, \( t \) is the crystallite size, \( \lambda \) is the wavelength of the radiation, \( \theta \) is the Bragg’s angle and \( B \) is the full width at half maximum (FWHM). Line broadening due to instrument was subtracted from the peak width before calculating the crystallite size using the following formula:

\[ B^2 = B_{\text{meas}}^2 - B_{\text{equip}}^2 \]  

(1.10)
where, $B_{\text{meas}}$ is the measured FWHM from peak, $B_{\text{equip}}$ is the instrumental broadening [Standard Si sample was used, whose $B$ value was 0.09821 at $2\theta = 29^\circ$, with $(hkl)$ value (111)].

Lattice parameters were determined using the following relationship for cubic spinel structure:

$$a^2 = \frac{\lambda^2 (h^2 + k^2 + l^2)}{4 \sin^2 \theta}$$  \hspace{1cm} \text{(1.11)}$$

where, $a$ is the lattice parameter, $\lambda$ is the wavelength of the radiation, $\theta$ is the Bragg’s angle and $(hkl)$ is Miller indices.

1.7.2 Magnetization

Various magnetometers have been devised to study magnetic materials. VSM is one among the instruments that are used relatively widespread for magnetic measurements. A vibrating sample magnetometer (VSM) operates on Faraday’s Law of Induction, which tells us that a changing magnetic field will produce an electric field. If a sample of any material is placed in a uniform magnetic field, created between the poles of an electromagnet, a dipole moment will be induced. If the sample vibrates with sinusoidal motion, a sinusoidal electrical signal can be induced in suitably placed pick-up coils. The signal has the same frequency of vibration and its amplitude will be proportional to the magnetic moment, amplitude and relative position with respect to the pick-up coils system.

The reciprocity theorem is used in the design and the theoretical analysis of the detection coil system with vibration along the $z$ axis, so that only the $z$ component of the vector moment is detected [148, 149].

The magnetic measurements of this thesis work were carried out using vibrating sample magnetometer in a Physical Property Measurement System (PPMS) of Quantum Design, at UGC-DAE
Consortium for Scientific research, Indore, India. For the magnetic measurements in the PPMS, the samples are fixed to a quartz sample holder using low magnetic Brown Tape. The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization was measured in different applied magnetic fields. Hysteresis loops were recorded at different temperatures in the low temperature phases of the system. In the temperature dependent ZFC magnetization, the sample was cooled to lowest temperature in the absence of field, then the field was applied at the lowest temperature and the data were recorded on re-heating the sample. In the FC measurements, the sample was cooled in the applied field to lowest temperature and the data were recorded on re-heating the sample, keeping the field applied.

### 1.7.3 Mossbauer Spectroscopy

$^{57}$Fe Mossbauer spectroscopy, one of the main nuclear spectroscopic techniques, have been employed in this thesis to investigate the local structures and the role they play in controlling the properties of sol-gel prepared nanoscale ferrites. It provides the quantitative microstructural information on both ionic and spin configuration within the ferrite nanoparticles. $^{57}$Fe Mossbauer spectroscopy, as a nuclear probe technique, is very well suited for the investigation of the local symmetry, the magnetic state and the charge state of iron ions in Fe-containing materials. This local sensitivity is due to the interactions of $^{57}$Fe nuclei with their neighbourhood.

In ferrite materials, which are the main subject of this thesis, Mossbauer spectra are often dominated by magnetic interactions. The splitting of the characteristic six-line spectra reveals the local magnetic fields (H) at the positions of the Mossbauer nuclei. At room
temperature and at lower temperatures, these fields often are of the order of 50 T [150]. Quadrupolar interaction (QS) of the Mössbauer nuclei reflects local symmetry. Here, the symmetry of the charge distribution is experienced through the electric field gradients set up the charges surrounding the nuclei. In the case of ferric ions, this interaction is dominated by the distribution of ionic charges in the lattice. On the other hand, the isomer shift (IS) reflects the electron density at the nuclei. This interaction causes a marked dependence on the position of the Mössbauer transition on the charge state of the Mössbauer ion and to a lesser extent, on the geometry of its coordination. Because of its great sensitivity to the magnetic fluctuations, $^{57}$Fe Mössbauer spectroscopy was found to be a suitable technique for the detection of superparamagnetism. Such magnetic fluctuations can however, complicate the analysis of spectra by a collapse of the magnetic hyperfine field, far below the Néel temperature and give rise to relaxation line broadening and even down to very low temperatures to unresolved hyperfine field distributions [151].

The Mössbauer spectra were recorded at UGC-DAE Consortium for Scientific research, Indore, India using a conventional constant acceleration Mössbauer spectrometer, with $^{57}$Fe in an Rh matrix as the Mössbauer source at room temperature and low temperature, with and without 5 T field. Least squares fitting were performed using the WINNORMOS-SITE program.

The spectra consist of distribution of hyperfine interaction, which was fitted using Voigt profile. Populations of iron cations on various sublattices provided by a complex oxide were calculated from the relative intensities of corresponding sextets. In the case of spinel ferrites, the degree of inversion, $\delta$, characterizing the distribution of
cations over the two nonequivalent cation sublattices [tetrahedral (A) and octahedral (B)] of the spinel structure was calculated from the Mossbauer subspectral intensities $I_A/I_B = f_A/f_B \times \delta/(2-\delta)$, assuming that the ratio of the recoilless fractions is $f_B/f_A = 1$ at low temperatures [152].

1.7.4 Neutron Diffraction

Neutron diffraction, similar to X-ray diffraction, is a crystallographic method for the determination of atomic structure of a material. However, neutron diffraction is a very expensive technique, as it requires a neutron source. A sample to be examined is placed in a beam of thermal or cold neutrons and the diffraction intensity pattern of the sample gives information about the structure of the material. Upon impinging on a crystalline sample, neutrons will scatter under a limited number of well-defined angles according to the Bragg law that describes X-ray diffraction. Neutron diffraction is a more powerful technique to solve the structure of materials having light atoms, especially hydrogen in hydrides, hydrates and organic moieties and oxides materials.

The interaction of neutrons with matter is different from X-rays. Neutrons interact directly with the nucleus of the atom rather than the electron cloud surrounding each atom, which happens as in the case of X-ray. Hence, the contribution of each isotope to the diffraction intensity is different; for example, hydrogen and deuterium contribute differently. The scattering length varies with isotope rather than linearly with atomic number. Thus, even in the presence of large Z atoms, the light (low Z) atoms contribute strongly to the diffraction intensity. The high resolution data of neutron diffraction helps to obtain very precise values for the atomic positions.
in the structure. Although neutrons are uncharged, they carry a spin and therefore interact with magnetic moments, including those arising from the electron cloud around an atom. Therefore, neutron diffraction can reveal the magnetic structure of a material. As magnetic scattering is caused by the much larger electron cloud around the tiny nucleus, it does require an atomic form factor. Therefore, towards higher angles, the intensity of the magnetic contribution to the diffraction peaks will dwindle.

Neutron diffraction study has been carried out at different temperatures from 20 K to 300 K, in the scattering angle range of $8^\circ$ to $137^\circ$, using a PSD based medium resolution powder diffractometer at the Dhruva reactor, Bhabha Atomic Research Centre, India. The wavelength of the incident neutrons is 1.249 Å. A closed cycle refrigerator is used to go to lower temperature. Structural and magnetic analysis were carried out by Rietveld method [153] using FULLPROF program in the WINPLOTER [154] suite.

A powder diffraction pattern can be recorded in numerical ring variable. Then, the experimental powder diffraction pattern is usually given as two arrays $\{T_\nu, y_\nu\}_{\nu=1,\ldots,n}$. In the case of data that have been manipulated or normalized in some way, the three arrays $\{T_\nu, y_\nu, \sigma_\nu\}_{\nu=1,\ldots,n}$, where $\sigma_\nu$ is the standard deviation of the profile intensity, are needed in order to properly weight the residuals in the least squares procedure. The profile can be modeled using the calculated counts, $y_\nu$ at the $i$th step by summing the contribution from neighboring Bragg reflections plus the background:

$$y_{c,i} = \sum_\phi S_\phi \sum_h I_{\phi,h} \Omega(\nu_i - T_{\phi,h}) + b_i \quad (1.12)$$

The vector $h (= H, or = H+k)$ labels the Bragg reflections, the subscript, $\phi$ labels the phase and vary from 1 up to the number of
phases existing in the model. In FullProf, the term, phase is
synonymous of a same procedure for calculating the integrated
intensities, $I_{\phi h}$. This includes the usual meaning of a phase and also
the case of the magnetic contribution to scattering (treated usually as
a different phase) coming from a single crystallographic phase in the
sample. The general expression of the integrated intensity is:

$$I_{\phi h} = \{LAPCF^2\}_{\phi h}$$

(1.13)

For simplicity, we will drop the $\phi$-index. Sometimes we will refer
to the whole arrays $\{y_i\}$ and $\{y_{ci}\}$ as $y_{obs}$ and $y_{calc}$ respectively. The
meaning of the different terms appearing in (1.12) and (1.13) is the
following:

- $S_{\phi}$ is the scale factor of the phase $\phi$
- $L_{h}$ contains the Lorentz polarization and multiplicity
  factors
- $F_{h}$ is the structure factor
- $A_{h}$ is the absorption correction
- $P_{h}$ is the preferred orientation function
- $\Omega$ is the reflection profile function that models both
  instrumental and sample effects
- $C_{h}$ includes special corrections (non linearity,
  efficiencies, special absorption corrections, extinctions, etc.)
- $b_{i}$ is the background intensity

The Rietveld method consist of refining a crystal (and/or
magnetic) structure by minimizing the weighted squared difference
between the observed $\{y_i\}_{i=1..n}$ and the calculated (1.12) pattern
$\{y_{ci}(\alpha)\}_{i=1..n}$ against the parameter vector, $\alpha = (\alpha_1, \alpha_2, \alpha_3, .. \alpha_p)$. The
function minimized in the Rietveld method is:

$$\chi^2 = \Sigma_{i=1}^{n} w_i \{y_i - y_{ci}(\alpha)\}^2$$

(1.14)
with $w_i = \frac{1}{\sigma_i^2}$, being $\sigma_i^2$ the variance of the “observation” $y_i$.

The quantity of agreement between observed and calculated profiles is measured by a set of conventional factors. In FullProf, two sets of indices are calculated, according to the meaning of the integer $n$ in the first set, $n$ is the total number of points used in the refinement ($n = \text{NTPS-NEXC} = \text{total number of points in the pattern minus total number of excluded points}$). In the second set, only those points, where there is Bragg contributions are taken into account. The definition of the indices is as follows:

Profile Factor:

$$R_p = 100 \frac{\sum_{i=1}^{n} |y_i - y_{ei}|}{\sum_{i=1}^{n} y_i} \quad (1.15)$$

Weighted Profile Factor:

$$R_{wp} = 100 \left[ \frac{\sum_{i=1}^{n} w_i |y_i - y_{ei}|^2}{\sum_{i=1}^{n} w_i \sigma_i^2} \right]^{1/2} \quad (1.16)$$

Expected Weighted Profile Factor:

$$R_{exp} = 100 \left[ \frac{n-p}{\sum_i w_i \sigma_i^2} \right]^{1/2} \quad (1.17)$$

Goodness of fit indicator:

$$S = \frac{R_{wp}}{R_{exp}} \quad (1.18)$$

Bragg Factor:

$$R_B = 100 \frac{\sum_h |l_{obs,h} - l_{calc,h}|}{\sum_h |l_{obs,h}|} \quad (1.19)$$

Crystallographic R-Factor:

$$R_F = 100 \frac{\sum_h |F_{obs,h} - F_{calc,h}|}{\sum_h |F_{obs,h}|} \quad (1.20)$$

where $n-p$ is the number of degrees of freedom. The meaning of $n$ has been given and $p$ is the number of refined parameters.
The experimental points within the excluded regions are always excluded from the calculation of all agreement factors. Conventional Rietveld R-Factors: \( cR_p, cR_{wp} \) are calculated as above, but using background-corrected counts. In the denominators, the quantity \( y_i \) is changed to \( y_i - b_i \). The magnetic R-factor is defined as the Bragg \( R_B \)-factor, but is applied to magnetic intensities.

The observed integrated intensity, \( I_{\text{obs,h}} \) is in fact calculated from the Rietveld formula:

\[
I'_{\text{obs,h}} = I_{\text{calc,h}} \sum_i \frac{Q(T_c - T_h)(y_i - b_i)}{(y_{c,i} - b_i)}
\]  

(1.26)

This formula is equivalent to a proportional sharing of the integrated intensity of a cluster between its components, according to the actual model. Then, if the model contains a strictly zero integrated intensity for the reflection, \( h(I_{\text{calc,h}} = 0) \) the observed integrated intensity is also zeroed: \( I'_{\text{obs,h}} = 0 \), even if it is obvious that \( I'_{\text{obs,h}} \) is non zero from the experimental pattern. This has a consequence that the reflections with \( I_{\text{calc,h}} = 0 \) do not contribute to the Bragg R-factor.

### 1.7.5 Z-scan Technique

Z-scan is a very commonly used experimental configuration to investigate the nonlinear optical properties of various materials. This is proposed as a technique with complete theory by Sheik Bahea et al. in 1990 [155, 156]. The technique is very simple and has a good sensitivity. The experimental setup is given in Figure 1.8.
A single Gaussian laser beam in tight focus geometry is used in this method. The transmittance of a nonlinear medium through a finite aperture in the far field, as a function of the sample position, \( Z \) is measured with respect to the focal plane and this is called the \( Z \)-scan curve. Starting scan from the far field (negative \( Z \)), the beam irradiance is low and negligible nonlinear refraction occurs. Hence the transmittance \( (D2/D1) \) remains relatively constant. As the sample is brought closer to the focus, the beam irradiance increases, leading to self-lensing in the sample. A negative self-lensing prior to focus will tend to collimate the beam, causing a beam narrowing at the aperture, which results in an increase in the measured transmittance. As the scan in \( Z \) continues and the sample passes the focal plane to the right (positive \( Z \)), the same self-defocussing increases the beam divergence, leading to the beam broadening at the aperture and thus, decrease the transmittance. This suggests that there is null, as the sample crosses the focal plane. A prefocal transmittance (peak), followed by a post-focal transmittance (valley), is the \( Z \)-scan signature of a negative refractive nonlinearity. Positive nonlinear refraction gives rise to an opposite valley-peak configuration. The multiphoton absorption suppresses the peak and enhances the valley, while
saturation absorption produces the opposite effect. The removal of the aperture completely eliminates the effect and the Z-scan is sensitive to nonlinear absorption, which is termed as open aperture Z-scan. Closed aperture Z-scan measurements gives information about the nonlinear phase variations and hence, the resulting focusing and defocusing of the transmitted beam. Using open aperture Z-scan, nonlinear absorption coefficients can be extracted. Large nonlinearities in materials are commonly associated with a resonant transition that may be of single or multiphoton nature. The nonlinear absorption of such materials is manifested in the open aperture Z-scan measurements. For example, if nonlinear absorption like two photon absorption (TPA) is present, it is manifested in the measurements as a transmission minimum at the focal point. The coefficients of nonlinear absorption can be easily calculated from such transmittance curves. The aperture in front of detector, D2 is not necessary in induced absorption measurements, because we need to collect the entire transmitted beam. This is the reason why it is called open aperture Z-scan.

References


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