1.1 Introduction

The rare-earth perovskites LnTMO$_3$, with Ln a rare-earth element and TM a transition metal have been intensively studied because of large variety of physical phenomena such as superconductivity, ferroelectricity and colossal magnetoresistance, exhibited by them. Out of these interesting materials, colossal magnetoresistive manganites are currently being investigated by a sizable fraction of the condensed matter community and their popularity is reaching levels comparable to that of the high-temperature superconducting cuprates. Mixed valent manganites with the perovskite structure have been studied for almost 50 years. The system offers a degree of chemical flexibility which permits the relation between the structural, electronic and magnetic properties of these oxides to be examined in a systematic way. Research on the manganites has revealed new phenomena such as colossal magnetoresistance (MR) [1] and dense granular magnetoresistance [2] which led to the understanding of various physical concepts such as Zener double exchange (ZDE) [3, 4] and the Jahn-Teller (JT) effect etc. [5, 6]. Early research was motivated by a need to develop insulating ferromagnets with a large magnetization for high-frequency applications. More recent work has been driven by a desire to understand and exploit the large negative magnetoresistance effects which appear near and below the Curie temperature. The manganites also have potential as solid electrolytes, catalysts, sensors and novel electronic materials. Their rich electronic phase diagrams reflect the fine balance of interactions which determine the electronic ground state. These compounds represent the interplay of experiment, theory and application which an important aspect of condensed matter physics research.

1.1.1 CMR effect in Manganites

Materials are known by their intrinsic and extrinsic properties are classified accordingly for different applications. Manganese based oxide materials, known as manganites, possess unique intrinsic property of, change in the electrical resistance under
the application of magnetic field, known as magnetoresistance (MR) which can be expressed as -

\[ MR\% = \frac{\rho_0 - \rho_H}{\rho_0} \times 100 \]

where \( \rho_0 \) and \( \rho_H \) are the resistivities in the absence and presence of magnetic field respectively. The value of magnetoresistance (MR) may be negative and positive depending on the fall or rise in the resistivity with the applied magnetic field.

During last five decades, the following forms of magnetoresistance have been studied having their origin in different physical aspects.

[i] Anisotropic magnetoresistance (AMR)

[ii] Granular and tunneling magnetoresistance (TMR)

[iii] Giant magnetoresistance (GMR)

Large negative MR \( \sim 20 \text{ to } 50\% \) is reported in metallic multilayers [7, 8], hence termed as ‘Giant magnetoresistance’ (GMR). Owing to such a large negative MR, these materials were in application for a quite some time. Though, the search for better magnetoresistive materials never ended and in 1993, the ABO\(_3\) perovskite structured oxide materials of type \((\text{Ln}_{1-x}\text{A}_x)\text{MnO}_3\) (R = trivalent rare-earth cation, A = divalent cation) became the center of attention for research, after the work of Von Helmolt et al. [9] and Charara et al. [10] reporting a huge magnetoresistance. Simultaneously, Jin et al. [1] reported magnetoresistance \( \sim 99\% \) in similar compounds having large value of MR termed as a ‘Colossal Magnetoresistance’ (CMR). The big boost to the research on manganites led to the present explosion of interest in the subject produced by the discovery of the CMR effect. The origin of MR in manganites is quite different than that observed in other forms of MR. CMR effect is an intrinsic property of crystal structure and has its origin in the spin disorder of conduction electron, which can be suppressed by an application of the magnetic field resulting in large magnetoresistance [9, 10]. The discovery of CMR effect in manganites and its relation to various electronic and magnetic properties revived the research interest in similar compounds.
1.1.2 Structure of Manganites

The doped LnAMnO₃ type perovskite structure has cubic unit cell. At the corner, Mn ions are surrounded by octahedral oxygen units known as the MnO₆ octahedra and the R occupying the holes between the octahedra which form the stable skeleton of the structure. The undistorted cubic parent structure is schematically depicted in fig. 1.1.

![Figure 1.1 ABO₃ type perovskite structure (simple cubic system)](image)

The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion of MnO₆ octahedra, can produce several lower-symmetry distorted structure, in which the coordination numbers of Ln (and A) cations, Mn cations or both are reduced. Tilting of the MnO₆ octahedra reduces the coordination of an undersized Ln cation from 12 to as low as 8. Conversely, off-centering of an undersized Mn cation within its octahedron allows it to attain a stable bonding pattern. Complex perovskite structures contain two different Mn-site cations. This results in the possibility of ordered and disordered structures. The orthorhombic and tetragonal phases are most commonly observed non-cubic structures for doped manganites. In LnAMnO₃ structure with Pnma space group, there are two nonequivalent oxygen positions, apical (O₁) and equatorial (O₂), which characterize the distortion of MnO₆ octahedra in terms of the Mn-O-Mn bond angles and Mn-O bond lengths.
The transport properties of manganites can be governed by the structure of MnO$_6$ octahedra [11] which can be decided by MnO$_6$ octahedra distortions, Q$_2$ mode in basal plane, lattice distortion, its band width of charge carriers to move freely, difference between the apical (O$_1$) and equatorial (O$_2$) Mn-O bond lengths and Mn-O-Mn bond angles.

1.2 Parameters and effects in manganites

1.2.1 Tolerance Factor (t)

In ABO$_3$ type perovskite structure, octahedral tilting type distortion was first examined by Goldschmidt in 1926 [12]. The mismatch or degree of distortion between the A-O and B-O bond lengths in ABO$_3$ perovskite can be determined using the following equation,

$$ t = \frac{\langle r_A \rangle + r_O}{\sqrt{2} (\langle r_B \rangle + r_O)} = \frac{d(A-O)}{\sqrt{2}d(B-O)} $$
where $<r_A>$, $<r_B>$ and $r_O$ are the average A-site, average B-site cation and anion ionic radii (purely ionic bonding is assumed) respectively. The structure is ideally cubic when $t$ is unity with B-O-B bond angle 180°. $t < 1$ or $t > 1$ makes the system strained and drives it towards the lower symmetry space group, away from its ideal cubic symmetry. Cubic perovskite structure is stabilized for the $t$ values between 0.89 < $t$ < 1, while the structure changes to rhombohedral for 0.96 < $t$ < 1 and orthorhombic for $t$ < 0.96 which sets the critical limit on $<r_A>$ and $<r_B>$ cationic radii. The perovskite structure adjusts to $t < 1$ by a cooperative rotation of the BO$_6$ octahedra around a cubic [001] axis as in tetragonal, a cubic [111] axis as in rhombohedral (R-3c), a cubic [110] axis as in orthorhombic (Pbnm or Pnma) or a cubic [101] axis as in orthorhombic (Imma). These cooperative rotations bend the B-O-B bond angle from 180° to 180° - $\phi$. The application of hydrostatic pressure has the same influence on the physical properties as an increase in the tolerance factor [13], which indicates that, the B-O bond is more compressible than the A-O bond in the paramagnetic phase.

1.2.2 Average A-site Cationic Radius ($<r_A>$)

Average A-site cationic radius, $<r_A>$, can be determined using the following formula,

$$<r_A> = \sum_i x_i r_i$$

where, $r_i$ is the ionic radii of $i^{th}$ cation. The variation of $<r_A>$ at A-site cation in ABO$_3$ perovskite has a similar effect as an external pressure which enhances the B-O-B transfer integral through a change in B-O-B bond angle and a measure of the degree of radial distortion of the BO$_6$ octahedra [14]. There is a linear relationship found between $T_C$ and $<r_A>$, and both of them exhibit inverse correlation with MR [15].

A smaller change in $<r_A>$, gives rise to the structural distortion at B-O-B bond angle up to a large extent and hence bending of B-O-B bond angle which in turn tilts the BO$_6$ octahedra for $t < 1$ and narrowing the $e_g$ electron bandwidth affecting the electronic transport [16].
1.2.3 Size variance ($\sigma_A^2$)

This factor, first introduced by L.M. Rodriguez-Martinez and J.P. Attfield [17] is related to the ionic mismatch due to the doping of divalent alkali and alkaline cations or trivalent rare earth cations at A-site and is quantified as,

$$\sigma_A^2 = \sum x_i r_i^2 - \langle r_A \rangle^2$$

where, $x_i$ is the fractional occupancies of the different $i$ cations of $r_i$ radii. Size variance is attributed to the displacements of the oxygen atoms due to the A site disorder, as shown by the simple model in fig.1.3 [17]. This shows that, $\sigma$ provides a measure of the oxygen displacements $Q$ due to A-site cation size disorder and that $\langle r_A \rangle$ is the complementary measure of displacements due to $\langle r_A \rangle$ being less than the ideal value $r_A^0$.

Figure 1.3 Model for local oxygen displacements in ABO$_3$ perovskites. A fragment of ideal cubic structure with A cations of radii $r_A^0$ is shown schematically in (a) and as spherical ions in (b) Cation size disorder in (c) gives rise to random oxygen displacements $Q = \sigma$ and a reduction in the A site radius in (d) leads to ordered oxygen displacements $Q = r_A^0 - r_A$.
The structural disorder creates local oxygen displacement resulting into bond angle fluctuations and bond length variations leading to carrier localization due to the Jahn-Teller distortion of BO$_6$ octahedra thereby affecting the electrical transport, $T_P$ and $T_C$ in manganites. The analogous effect of increasing $\sigma^2$ have been extensively investigated for Ln$_{0.7}$A$_{0.3}$MnO$_3$ [Ln = La$^{3+}$, Pr$^{3+}$, Sm$^{3+}$, Pm$^{3+}$ and Nd$^{3+}$ and A = Ca, Sr and Ba] at fixed carrier concentration $x = 0.3$ and $\langle r_A \rangle$ which shows the linear reduction in $T_P$ with $\sigma^2$ [18].

1.2.4 Zener Double Exchange (ZDE) Mechanism

Most of the early reported theoretical work on manganites was focused on the qualitative aspects of the experimentally discovered relation between transport and magnetic properties, namely the increase in conductivity upon the polarization of the spins. Not much work was devoted to the magnitude of the magnetoresistance effect itself. The formation of coexisting clusters of competing phases was not included in the early considerations.

The states of manganites were assumed to be uniform and double exchange (DE) was proposed by Zener in 1951, in terms of his theory of indirect magnetic exchange between 3d atoms wherein ferromagnetic interactions are favored when the magnetic atoms are fairly well separated and conduction electrons are present. The theory was applied to the manganese perovskites with the aim of explaining the strong correlation between conductivity and ferromagnetism [19]. Starting from the insulating antiferromagnetic LaMnO$_3$ end member where electrons are localized on the atomic orbitals, Zener showed how the system should gradually become more ferromagnetic upon hole doping (introduction of Mn$^{4+}$). He considered the problem of the exchange between Mn$^{3+}$ and Mn$^{4+}$ ions via an oxygen ion and introduced the concept of simultaneous transfer of an electron from the Mn$^{3+}$ to the oxygen and from the oxygen to the neighboring Mn$^{4+}$ [fig. 1.4].
1.2.5 Carrier Density

Doping determines the carrier concentration and sign of the charge carriers (i.e. positively charged holes or negatively charged electrons) in the Ln$_{1-x}$A$_x$MnO$_3$ (Ln = Rare earth cation, A = divalent or trivalent smaller cation) mixed valent manganites. Carrier density decides the fluctuated valence of the transition metal cations i.e. Mn$^{3+}$/Mn$^{4+}$ in manganites which is responsible for the ferromagnetic Zener Double Exchange (ZDE) [20]. At a fixed amount of doping, perovskite compounds exhibit very rich phase diagram as a function of temperature, magnetic field, external and internal chemical pressure, etc. which in turn governs their physical properties.

![Double Exchange Diagram](image)

**Figure 1.4** (a) Sketch of the Double Exchange mechanism which involves two Mn ions and one O ion. (b) The mobility of $e_g$ - electrons improves if the localized spins are polarized. (c) Spin-canted state which appears as the interpolation between ferromagnetic (FM) and antiferromagnetic (AFM) states in some mean field approximations.
1.2.6 Jahn - Teller (JT) Distortion

The discovery of high-temperature superconductivity in the copper oxides and of colossal magnetoresistance (CMR) in the manganese oxides with perovskite structure has reawakened interest in dynamic, cooperative Jahn-Teller (J-T) deformations in solids, particularly where they occur at a cross-over from localized to itinerant electronic behavior. Whereas electrons in a partially filled cation shell are localized in a transition metal compound. High site symmetry at the cation may leave the localized electron manifold orbitally degenerate. In this case, the cation becomes a JT ion. With localized d\textsuperscript{n} configuration, a cubic crystalline field quenches the orbital angular momentum of a twofold orbital degeneracy leaving behind orbital angular momentum at a threefold orbital degeneracy. An appropriate local JT site deformation to lower symmetry removes the orbital degeneracy at a JT cation, the deformation may be static or dynamic.

In mixed valent manganites, the electronic properties are intimately related to the lattice. Many of the interesting phenomena exhibited by them involve a complex interplay between the spin, charge and orbital degrees of freedom, accompanied with subtle displacements in the crystal lattice. In the perovskite manganites Ln\textsubscript{1-x}A\textsubscript{x}MnO\textsubscript{3}, the Mn\textsuperscript{3+} ion has a d\textsuperscript{4} configuration. In octahedral symmetry, the d level splits into three t\textsubscript{2g} and two e\textsubscript{g} orbitals. The Mn\textsuperscript{3+} ion has high-spin configuration, with three electrons occupying the three t\textsubscript{2g} orbitals and one electron occupying the doubly degenerate e\textsubscript{g} orbitals as t\textsubscript{2g}\textsuperscript{3}e\textsubscript{g}\textsuperscript{1}. According to the Jahn-Teller (JT) theorem, the structure will distort thereby removing the degeneracy of the e\textsubscript{g} orbitals. In solids, the orbital degree of freedom of the Mn\textsuperscript{3+} ion often shows long range ordering associated with the cooperative JT effect. It is observed for the most extensively studied compounds throughout the LnAMnO\textsubscript{3} series, i.e. LaMnO\textsubscript{3}, that below a transition temperature T\textsubscript{JT}, the 3d\textsubscript{3x}\textsuperscript{2} and 3d\textsubscript{3y}\textsuperscript{2} orbitals are ordered in the ab plane in an alternating fashion [fig. 1.5]. Fig. 1.6 shows the energy band structure affected by the JT effect.
There are two types of distortions associated with the JT effect: $Q_2$ and $Q_3$. The $Q_3$ is a tetragonal distortion which results in an elongation or contraction of the MnO$_6$ octahedron corresponding to the filled $3z^2 - r^2$ orbital or $x^2 - y^2$ orbital, respectively [Fig. 1.7 (a) and (b) respectively]. The $Q_2$ is an orthorhombic distortion [Fig. 1.7 (c)] obtained by a certain superposition of the $3z^2 - r^2$ and $x^2 - y^2$ orbitals [21, 22].
Figure 1.7  (a) and (b) The Q₃ distortion with oxygen displacements corresponding to the filled $3z^2 - r^2$ and $x^2 - y^2$ orbitals, respectively  (c) The Q₂ distortion which stabilizes a certain superposition of $3z^2 - r^2$ and $x^2 - y^2$ orbitals

The oxygen framework is described in Pbnm [space group No. 62] symmetry by two oxygen positions: the O₁ position situated on the mirror plane and attributed to the out-of-plane oxygens; the O₂ position attributed to the in-plane oxygens [see fig. 1.8 (a)]. The rotations of the octahedra are reflected in the deviation from 180° of the Mn-O-Mn tilting angle. The JT effect in LnMnO₃ is dominated by the Q₂ distortion with alternating long (l) and short (s) Mn-O₂ bond lengths in the ab plane and a medium out of plane Mn-O₁ (m) bond length as shown in fig. 1.8 (b). The medium bond length m deviates from the average bond length, such that $m < (l + s)/2$, indicating that the JT distortion is not of a pure Q₂ type. A contribution of the Q₃ distortion is also present.
1.3 Microstructure

Since the discovery of CMR effect in manganites, the interest in the microstructural studies on these materials in relation to their electrical and magnetic properties has grown exponentially. The physical behaviour of material is directly related to the crystal structure as well as its microstructure. An interrelated structural, transport, magnetotransport and magnetic properties of manganites are strongly governed by the grain morphology and grain boundary nature [23 - 25].

The structure and properties of grain boundaries depend on how the material was prepared and on the subsequent thermal history. It has also been observed that, as the sintering temperature decreases, the width of transition broadens which suggests that, at low sintering temperatures, grains are loosely connected, which in turn directly affect the $T_C$ and $T_P$ of the material. Lowering of sintering temperature reduces the metallic transition temperature and hence the concomitant increase in resistivity. Hence, it should be expected that, the physical properties of the systems can be governed by the nature and
number of grain boundaries and will directly affect the transport and magnetotransport of material. It is well known that, the lattice structure of the grain surface is often distorted. This may cause a structural relaxation from the surface to the core of the grain. Since the surface plays a dominant role as the particle size decreases, the internal structure of the grains may be more influenced by the surface for manganite system.

In the manganites, a deviation of $T_C$ and $T_P$ has been attributed to the effect of the surface strain-induced grain-boundary effects [26, 27]. The deviation from ideal oxygen stoichiometry does not generally show such a strong variation of $T_C$ and $T_P$ as explained by Rivas et al [26]. Huang et al [28] pointed out that, there occur antiferromagnetic insulating regions near the grain boundaries. Such regions do not modify the transition temperature, but can make the electrical transition shift to a low temperature [29]. Magnetoresistive properties of manganites can be tailored by the grain morphology specifically grain boundaries in polycrystalline bulk, thin films, nanomanganites and devices. For polycrystalline manganites with charge ordering, the grain-boundary contribution results in a small Coulomb barrier of electrostatic origin. This can cause low temperature insulating state.

1.4 Transport and Magnetotransport

Doping of divalent ions like $\text{Ca}^{+2}$, $\text{Sr}^{+2}$ or $\text{Ba}^{+2}$ etc at Ln site in $\text{LnMnO}_3$ insulator results in to interesting behavior in $\text{Ln}_{1-X}\text{A}_X\text{MnO}_3$ ($\text{A} = \text{divalent ion}$) which has been explained on the generation of $\text{Mn}^{+4}$ state in the compound with the interplay between $\text{Mn}^{+3}$ and $\text{Mn}^{+4}$ due to the electron hopping from one site to another leading to electronic transport in them. Doped manganites exhibit two types of transitions. One is electrical transition from insulator to metal transition ($T_P$) accompanied with magnetic transition from paramagnetic to ferromagnetic transition ($T_C$). At room temperature, most of the manganites are in paramagnetic - semiconducting or insulating (PMI) state and with decreasing temperature, they show signs of increase in electrical resistivity but when cooled below $T_C$, insulator-metal (I-M) transition occurs in the vicinity of paramagnetic to ferromagnetic transition. In the case of half doped manganites, at low temperature, below $T_P$ one can observe an increase in the resistivity along with decrease in
magnetization at temperature $T_N$ known as Neel’s temperature. In the $T < T_N$, there is a real space ordering of all Mn$^{3+}$ and Mn$^{4+}$ ions which causes the increment of resistivity and reduction in magnetization in this low temperature region. The doped manganites, with doping level $x = 1/3$ demonstrate very interesting behaviour, as we decrease the temperature, compound exhibits a transition from high temperature PMI state to a low temperature ferromagnetic metallic (FMM) state.

When magnetic field is applied to the materials, the resistivity decreases sharply, particularly in the region of the insulator-metal transition $\sim T_P$. The decrease in resistivity can be almost 100% and, hence, the use of the term colossal while referring to the magnetoresistance in these materials. There are various parameters such as doped compound, average ionic radius, size variance, grain morphology, heat treatment, etc. which can directly affect the transport and magnetotransport properties.

To explain the resistivity in semiconducting or insulating region, there are several models proposed -

1. Nearest neighborhood hopping or the activation beyond the mobility edge [30], given by
   \[ \rho = \rho_0 \exp\left(\frac{E_a}{kT}\right) \]

2. Adiabatic nearest neighbor hopping model of small polaron conduction [31, 32],
   \[ \rho = AT \exp\left(\frac{E_a}{kT}\right) \]

3. Schklovskii - Efros (SE) type of Variable Range Hopping with a soft gap due to the modification of the density of states by the Coulomb interaction [33],
   \[ \rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{2}} \]

4. Variable Range Hopping (VRH) of the Mott type for uncorrelated carriers [34 - 36], given by
   \[ \rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{2+d}} \] where $d$ is the dimensionality and this becomes,
\[ \rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{4}} \] for three dimensional systems

In doped manganites the size disorder increases with doping level \( x \) which generates random spin and Coulombic potential fluctuations. Hence, the carriers experience some potential difference beyond the Mn - O distances to hop at farther distances and hence conduct through the Mott’s type of Variable Range Hopping. The \( T_0 \) occurring in the VRH relation can be related to the carrier localization length by the expression,

\[ kT_0 = \frac{18}{L^3 N(E)} \]

where \( k \) is the Boltzmann constant, \( L \) is the carrier localization length and \( N(E) \) is the density of states [37] the values of the localization length should be comparable to Mn - O distances for the VRH type of conduction [37].

The electron transport mechanism and the cause of resistivity in the conducting region have been understood by fitting the resistivity data to a general Zener-Double Exchange polynomial law,

\[ \rho = \rho_0 + \rho_2 T^2 + \rho_n T^n \]

where \( \rho_0 \) is the residual resistivity, \( \rho_2 \) is the resistivity contributed by an electron-electron and electron-phonon scattering mechanism, \( n \) is a higher order term (\( n = 2.5, 3, 4.5 \) and 7.5) and \( \rho_n \) is the corresponding resistivity coefficient [38 - 43]. In this law, \( n = 2.5 \) and 3 correspond to the one magnon scattering process whereas \( n = 54.5 \) and 7.5 correspond to two magnon scattering phenomena.

1.5 Types of MR

Two types of MR are observed depending upon the temperature range the field required to observe them. One is the, intrinsic MR governed by the intrinsic properties of the materials, \( e_g \) spins, requires relatively large magnetic field (> 1T) and is exhibited around metal to insulator transition. The cause for intrinsic MR can be explained on the
basis of zener double exchange (ZDE) mechanism. Second is the extrinsic MR generally achieved below the metal to insulator transition temperature can be governed by the external parameters like, synthesis route used, sintering temperature, time and environment, grain morphology, grain boundary density and nature etc. This component of MR at low temperature requires relatively low field ($\leq 1$T). This can be explained on the basis of intergranular spin polarized tunneling or spin dependent scattering phenomena [2, 44].

1.6 Magnetic Behavior

The magnetic properties of the manganites are governed by exchange interactions between the Mn ion spins. These interactions are relatively large between two Mn spins separated by an oxygen atom and are controlled by the overlap between the Mn d-orbitals and O p-orbitals. The corresponding super exchange interaction depends on the orbital configuration following the rules of Goodenough [45]. Generally, for Mn$^{4+}$-O-Mn$^{3+}$, the interaction is antiferromagnetic (AFM), whereas in the divalent doped LaMnO$_3$ manganite, both ferromagnetic and antiferromagnetic interactions coexist for Mn$^{3+}$-O-Mn$^{4+}$ configuration [3]. The LaMnO$_3$ end member is AFM, with ferromagnetic planes having alternating magnetic spins while the other end member CaMnO$_3$ is AFM with each Mn$^{4+}$ surrounded by the six closest neighbors having opposite spins. Other doping levels result in to different types of AFM orderings but in the doping range of $x \approx 0.3$, the samples are FM. Goodenough has explained the magnetic structures for different doping levels in terms of different types of bonding, where some bonds are FM and others are AFM or paramagnetic (PM) [45]. This is determined by the relative orientation of occupied and unoccupied orbitals of the Mn-O-Mn pairs. Around the FM Curie temperature, $T_C$, the materials also undergo an insulator-metal transition. Metallicity below $T_C$ occurs because only those electrons possessing ferromagnetically aligned spins are involved in the conduction process. When magnetic field is applied to these materials, the resistivity decreases appreciably, particularly in the region of the $T_C$.  

Introduction to CMR Manganites
1.7 Charge and Orbital Ordering (CO and OO)

Charge Ordering (CO) refers to the ordering of the metal ions in different oxidation states in specific lattice sites of a mixed valent material. Such ordering generally localizes the electrons in the material, making it insulating or semiconducting due to the charge localization which in turn restricts the electron hoping from one cation site to another. Charge-ordering is not a new phenomenon in metal oxides. One of the earliest examples of charge-ordering in inorganic solids is that of Fe₃O₄ (magnetite), which undergoes a disorder-order transition, popularly known as the Verwey transition, at 120 K [46]. The study of charge-ordering phenomena in doped rare earth manganites with the general formula, Ln₃₋ₓAₓMnO₃ (Ln = rare earth, A = alkaline earth) has recently attracted much attention because of the discovery of colossal magnetoresistance and other interesting properties exhibited by these materials [47, 48]. Charge-ordering had been reported by Wollan and Koehler [49] and later by Jirak et al. [50] and is associated with novel properties which are useful in understanding the electronic behavior of compounds studied.

In doped manganites, the charge-ordered phases are novel manifestations arising from the interaction between the charge carriers and the phonons where in the Jahn Teller distortions play a significant role. Charge ordering arises because the carriers are localized into specific sites below a certain temperature known as charge ordering temperature, T_{CO}, giving rise to long-range order throughout the crystal structure. Although, charge ordering would be expected to be favoured when doping level x = 0.5, due to the presence of equal proportions of the Mn³⁺ and Mn⁴⁺ states, it is found in various compositions in the doping range 0.3 < x < 0.75, depending on the Ln and A ions. In the charge-ordered (CO) state, the Mn³⁺ and Mn⁴⁺ ions are regularly arranged in the ab plane with the associated ordering of the dₓ²−ᵧ² and dₓ²−ᵧ² orbitals [51] as shown in fig. 1.9. Charge ordering also competes with double exchange, and promotes insulating behaviour and antiferromagnetism. Furthermore, the Mn³⁺ (e₉) orbitals (3dₓ²) and the associated lattice distortions (long Mn - O bonds) also develop long-range order, giving rise to orbital ordering, which is responsible for the anisotropy of the electron-transfer interaction. This gives rise to complex spin-orbital coupled state. The orbital-ordering is
coupled with Jahn Teller distortion. Charge-ordering competes with double-exchange, giving rise to an unusual range of properties which are sensitive to factors such as the size of the A-site cations, internal and external pressure, chemical melting of CO state by doping and melting of CO state by application of magnetic field.

At low temperatures, the rare earth manganites are antiferromagnetically ordered with CE- or A-type ordering, but only the former occurs in the charge-ordered materials where the $e_g$ electrons are localized. The CE-type spin ordering is characterized by the ordering of Mn$^{3+}$ and Mn$^{4+}$ ions alternately. The spin ordering in the ab plane is somewhat complex and it stacks antiferromagnetically along the c axis. In the A-type spin ordering, the spins order ferromagnetically in the ab plane (with the moments pointing towards the a-axis) and these planes stacked antiferromagnetically along the c axis. In fig 1.10, CE and A-type AFM ordering in half-doped manganites ($x = 0.5$) can be seen clearly. Orbital ordering can occur in both A- and CE-type AFM ordering, but they differ in detail. The CE-type AFM state is attained on cooling a ferromagnetic state or a charge-ordered paramagnetic state. Fig. 1.11 depicts the three dimensional views of A-, C- and F-type charge and orbital ordering.
Two distinct types of charge-orderings can be delineated. In one, a ferromagnetic metallic (FMM) state transforms to the charge-ordered (CO) state on cooling the material. In the other, the CO state is found in the paramagnetic ground state and there is no ferromagnetism down to the lowest temperatures. Magnetic field transforms the CO state to the FMM state, when the average radius of the A-site cations is sufficiently large.
Fig. 1.12 shows the schematic diagram of different charge ordering behaviors of Ln$_{0.5}$A$_{0.5}$MnO$_3$ depending on $<r_A>$. Accompanying with these all factors, cooperative Jahn Teller effect induces additional effects such as lattice distortion and electron localization in the charge-ordered state. Fig. 1.13 reveals the effect of charge ordering on structural, transport and magnetic properties of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ compound, which is a ferromagnetic metal with a $T_C \sim 250$K and transforms to an insulating CO state around 150 K [51]. The FMM – CO transition is accompanied by spin and orbital ordering, and the CO insulator is antiferromagnetic (CE type). At the low temperature, around $T_{CO}$, compound shows a sign of structural transition which can be observed from the changes in structural parameters as well as resistivity increases due to charge ordering, which localize electrons and suppress the ZDE and the value of magnetization also decreases due to CE – type antiferromagnetic ordering. Application of a magnetic field destroys the CO state, and the material becomes metallic. The transition is first order showing hysteresis and is associated with changes in unit cell parameters.

Figure 1.12 Schematic diagram of charge ordered state of Ln$_{0.5}$A$_{0.5}$MnO$_3$ depending on $<r_A>$, Key: FMM, ferromagnetic metal; PMI, paramagnetic insulator; AFMI, antiferromagnetic insulator; CO, charge-ordered state.
1.8 Applications of CMR materials

Magnetoresistance (MR) is important in many technological applications, such as magnetic data storage, read-write heads, magnetic-bolometric sensors, Magnetic tunnel junction (MTJ) and magnetoresistive random access memory (MRAM). The discovery of colossal magnetoresistance has launched a new scientific event mainly aimed at understanding and improving their magnetoresistance properties. On the other hand, manganites are opening up vast and exciting possibilities for basic condensed matter physics. The delicate interplay between different sources of energy, such as the kinetic and electro-static energies of the mobile carriers and their coupling to the lattice, and strong coupling between spin, charge, and lattice degrees of freedom, leads to a wide range of striking physical phenomena. These interactions can be tuned by simply modifying the chemical composition. These materials provide a unique opportunity to study the physics of complex systems in which electrons, spins and phonons are strongly
coupled, and in particular, to elucidate the interplay between local structural deformations and macroscopic transport, magnetic and optical properties.

Based on the properties of CMR materials discussed above, few applications of CMR materials are listed below-

1. Magnetic field sensors
   (a) Using the CMR effect in a film
   (b) Using a spin valve structure
   (c) as a microwave CMR sensor.

2. Electric field effect devices
   (a) Using a SrTiO₃ gate
   (b) Using a ferroelectric gate.

3. Bolometric uncooled infrared (IR) sensors using the metal \{insulator transition at the Curie temperature.

4. Low temperature hybrid HTS-CMR devices
   (a) Flux focused magnetic transducers
   (b) Spin polarized quasi-particle injection devices.

The industrial requirements for a magnetic sensor can be summarized as follows.

1. Operation at room temperature and up to 100 K above room temperature.

2. At least a 20% response at a field of 100 Gauss.

3. Temperature independent CMR values over 350 - 50 K.

4. Acceptable noise values.

5. Retention of magneto-transport properties in patterned films at dimensions approaching sub-1000Å scales. (The current thinking is that oxide-based CMR sensors will have maximum impact only on memory systems approaching densities of 100 Gb/cm²)
1.9 Motivation of the present work

During the course of this thesis work, I have synthesized, nearly half doped and half doped manganites using conventional SSR method and detailed study of the temperature dependent ND measurements have been carried out. The present work is mainly aimed at understanding the charge ordering and its related phenomena which still remain unclear hence need detailed understanding in the context of manganites. For this purpose, the system selected is half doped manganites having large size disorder and ND and magnetization measurements are the tools employed. Magnetization measurements were carried out to throw light on the magnetic nature of the presently studied manganites and also to correlate them with the ND results taken at various temperatures. The manganite systems investigated during the present work are La$_{0.7-x}$Tb$_x$Ca$_{0.3}$Sr$_{2x}$MnO$_3$ (LTCSMO) ($x = 0.125$), La$_{0.375}$Tb$_{0.125}$Ca$_{0.5}$MnO$_3$ (LTCMO) and La$_{0.375}$Tb$_{0.125}$Sr$_{0.5}$MnO$_3$ (LTSMO). The earlier studies on the La$_{0.7-x}$Tb$_x$Ca$_{0.3}$Sr$_{2x}$MnO$_3$ ($x = 0.05 \leq x \leq 0.1$) system by our group member [D.S. Rana, Ph.D. Thesis, 2005, Saurashtra University] has revealed several interesting results on the transport, magnetotransport and magnetic properties of this system. It was necessary to understand the structure - property correlation in these samples and to study the dependence of transport, magnetotransport and magnetic properties on the variation in structural parameters such as bond length and bond angle variations, estimated using ND study. The detailed magnetization measurements were carried out on the Tb$^{3+}$ and Ca$^{2+}$ and / or Sr$^{2+}$ doped LaMnO$_3$ polycrystalline bulk manganites reveal an interesting results and strong similarity with the magnetic properties derived from ND measurements. Effect of size variance on the transport and magnetoresistive properties in bulk and nanoscale single phasic polycrystalline La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) and Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ (NSMO) manganites having equal $\langle r_A \rangle \sim 1.2$ Å, sintered at various temperatures have been studied. The interplay between the intrinsic and extrinsic MR behavior and its dependence to the grain growth mechanism is very well studied in mixed valent manganites.

Keeping in mind the above mentioned aspects of various structural, microstructural, transport, magnetotransport and magnetic properties of manganites and their dependence on the synthesis parameters, structure, microstructure, size variance,
carrier concentration, during the course of present work, detailed studies on \( \text{La}_{0.7-x}\text{Tb}_x\text{Ca}_{0.3}\text{Sr}_{2x}\text{MnO}_3 \) \((x = 0.125)\), \( \text{La}_{0.375}\text{Tb}_{0.125}\text{Ca}_x\text{MnO}_3 \) (LTCMO) \( \text{La}_{0.375}\text{Tb}_{0.125}\text{Sr}_x\text{MnO}_3 \) (LTSMO) \( x = 0.5 \) manganites have been carried out. In addition, the effect of grain size and grain morphology on various properties of nanostructured \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) (LCMO) and \( \text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) (NSMO) manganites synthesized by Sol-Gel route have been carried out.
References


[42] M.B. Salamon and M. Jaime, Rev. Mod. Phys. 73, 583 (2001)


