CHAPTER-1

INTRODUCTION
1.1 INTRODUCTION AND HISTORICAL BACKGROUND:

During the last decade, interest has grown in heterogeneous ferromagnetic materials, such as thin film multilayers and cluster alloy compounds which display the so called giant magnetoresistance (GMR). More recently, it has been recognised that some materials specifically 3d transition metal oxides, posses large room temperature magnetoresistivity associated with a paramagnetic-ferromagnetic phase transition. The compounds which have been the focus of the majority of the studies are the magnetic perovskites $R_{1-x}A_xMnO_3$ where $R$ is a trivalent rare earth cation (e.g.-La, Pr, Sm, Nd, etc) and $A$ is a divalent alkaline earth cation (e.g.-Ca, Sr, Ba, Pb etc).

Since after the discovery of superconductivity in lanthanum cuprates, the perovskites materials have received much attention. The existence of metal-insulator transition (MIT) in lanthanum based manganites was established in early 1950’s [1, 2], and was extensively studied thereafter. Transition metal perovskites present a very interesting group of materials because of extremely rich variety of their electrical properties, from a large gap insulator to metal and magnetic properties such as non magnetism to magnetism, antiferromagnetism to ferromagnetism. [3, 4]. These phenomena have been observed in a family of doped manganites.

1.1.1 PEROVSKITES:

Perovskites form the most important class of ferroelectric materials. Manganites crystallize in a ‘perovskite’ structure. They are named after the mineral perovskite $CaTiO_3$ (it was discovered later that $CaTiO_3$ shows only a distorted perovskite structure). The perfect structure follows the formula $ABO_3$, where $A$ is a mono or divalent and $B$ is a tetra or pentavalent metal. As shown in Fig 1.1, the $A$ atoms form the corners of the cubic cells and $B$ atoms are in the centre and the oxygen atoms are situated in the centres of faces. As the $B$ atoms are
enclosed in $O_6$ octahedra, this structure is also regarded as $BO_6$. Many superconducting ceramic materials especially cuprate superconductors also have perovskite type structures.

![Diagram of a typical ABO$_3$ type compound](image)

**Fig 1.1: The structure of a typical ABO$_3$ type compound**

The stability of a perovskite structure depends on the tolerance factor defined by:

$$t = \frac{(r_A + r_O)}{V_2(r_B + r_O)}$$

(1.1)

Where $r_A$, $r_B$, and $r_O$ being the radii of A, B cations and oxygen ions respectively. Perovskite structure is supposed to be stabilized in the range of $0.75 < t \leq 1.0$. However, for an ideal perovskite $t = 1$. For $t < 1$, the cubic structure transforms to the orthorhombic structure which leads to deviation in Mn-O-Mn bond angle from $180^0$ (a case for ideal perovskite). As tolerance factor decreases, the tendency to charge localization increases due to reduction in carrier mobility. The manganites of the type $R_{1-x}A_xMnO_3$ have attracted the attention of the
scientific community due the "colossal magnetoresistance" (CMR) phenomenon exhibited when the ferromagnetic ordering of Mn spins occurs [5, 6].

1.1.2 MAGNETORESISTANCE (MR), GIANT MAGNETORESISTANCE (GMR) AND COLOSSAL MAGNETORESISTANCE (CMR):

Magnetoresistance (MR) is the relative change in the electrical resistivity of a material produced by the application of a magnetic field. It is generally defined as:

\[ MR = \frac{\Delta \rho}{\rho(0)} = \frac{\rho(H) - \rho(0)}{\rho(0)} \]  (1.2)

where \( \rho(H) \) and \( \rho(0) \) are the resistivities at a given temperature in the presence and absence of a magnetic field respectively. MR can be negative or positive. Most metals show a small MR (only a few %). In non-magnetic pure metals and alloys, MR is generally positive and it shows a quadratic dependence on \( H \). MR can be negative in magnetic materials because of the suppression of the spin disorder by the magnetic field.

Large magnetoresistance, referred to as Giant magnetoresistance (GMR) was first observed on the application of magnetic field to atomically engineered magnetic super lattices (e.g.-Fe/Cr) [7] and in magnetic semiconductors. Besides some of the bimetallic or multi-metallic layers, comprising of ferromagnetic and antiferromagnetic or nonmagnetic metals, GMR is also found in ferromagnetic granules dispersed in paramagnetic metal films. The discovery of negative GMR in rare-earth manganites \( R_{1-x}A_xMnO_3 \) with the perovskite structure has attracted wide attention.

GMR has found applications for these materials in device applications such as (i) magnetic recording (memory storage), (ii) actuators and (iii) sensors. The first observation concerning GMR was made in respect of Fe/Cr multilayers [8] with thin Cr layers; prepared by molecular beam epitaxy (MBE).
For Cr layers of 9 angstroms thickness, the resistivity was found to drop by almost a factor of 2 in a magnetic field of 2 Tesla at 4.2 K as shown in Fig. 1.2, giving a negative GMR of about 50 percent. Another term 'Colossal Magnetoresistance' (CMR) is often used to describe the extremely strong influence of the magnetic field. The CMR is defined as

$$\Delta \rho/\rho (H) = \{\rho (H)-\rho (0)\}/\rho (0)$$  \hspace{1cm} (1.3)

\[p(B)/p(0)\]

**Fig. 1.2** Variation of resistivity of multilayers [(001) Fe 30 angstroms/ (001) Cr 9 angstroms]60 as a function of the magnetic field at 4.2K. The specimen is a super lattice of 60 bilayers in which the current flows along the (110) direction and the magnetic field is applied in the layer plane (001) along the current direction. At the magnetic field $B_s$ (in the saturated state; $B_s = 2T$) the resistivity drops to almost half its zero field value.

The CMR reaches its maximum (in access of $10^6$ percent) at 110 K with the magnetic field at 6 Tesla as shown in Fig. 1.3. The peak occurs just below the Curie temperature. For films thicker than 2000 angstroms, the MR is
reduced by orders of magnitude. The presence of grain boundaries leading to lattice strain is detrimental to achieve large MR. The MR improves further on heat treatment.

The two most striking features of the GMR-CMR effects in manganites are as under;

(i) Firstly, the MR peak can be shifted to occur at room temperature by adjusting the processing parameters.

(ii) Secondly, the resistivity can be manipulated by magnetic field to change by orders of magnitude.

The magnetic and transport properties of these samples are determined by several factors such as the percentage of the divalent ions, the ionic radii of the metal ions and the method used in the preparation of samples etc [10, 11]. These properties have traditionally been examined within the framework of the "Double-Exchange" (DE) mechanism proposed by Zener[12] which considers the magnetic coupling between Mn$^{3+}$ and Mn$^{4+}$ changing due to doping level in the perovskite or its oxygen stoichiometry. In both cases the result is a distortion of the pervoskite structure that has direct influence not only on the Mn-O distance but also on the angle of the Mn$^{3+}$-O-Mn$^{4+}$ bond. It has also been observed that the ferromagnetic coupling and the metal-insulator transition temperature are very sensitive to the change of these parameters. Although some researchers [13, 14] believe that the DE model is very rough and could not explain alone very large resistivity of the insulating phase for $T>T_c$, it still remains the main and essential theoretical mechanism used to explain the anomalous phenomena. There are a lot of possibilities of technological applications of these materials due to their interesting properties mentioned above. In view of this fact many new experiments are being performed and new
materials with similar properties searched for a precise understanding of the origin and mechanism of these effects.

Fig .1.3 Variation of magnetoresistance of a thin film of La-Ca-Mn-O as a function of temperature. The MR peaks at 110K in a magnetic field of 6T. [After S. Jin, et al.[9], Appl. Phys. Lett., 67, 557, (1995)]

1.2 THEORETICAL MODELS:

The basis for the theoretical understanding of Mn oxides is usually the concept of the double exchange (DE) [12] that considers the exchange of electron between neighbouring Mn$^{3+}$ and Mn$^{4+}$ sites with strong on-site Hund’s coupling. Attempts based on mean field treatments of a Kondo lattice model for DE [15] and a Hubbard-Kondo lattice model [16] have been made to account for the
transport properties of Mn oxides. However, the sharp change in the resistivity and the CMR near $T_C$ were not reproduced successfully in these reports. Perturbative calculations carried out by Millis et al [13, 17] showed that DE alone could not explain the experimental data of Mn oxides and suggested that a strong Jahn-Teller distortion should be responsible for the transport properties. Later on it was suggested that the localization effect [18, 19] in the double exchange model based upon non-perturbative treatments might be able to account for the novel properties of manganites.

1.2.1 DOUBLE EXCHANGE INTERACTION:

The magnetic and electronic properties have traditionally been examined within the framework of the double exchange model that considers the magnetic coupling between $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ resulting from the motion of an electron between the two partially filled d shells with strong on-site Hund’s coupling.

All unpaired electrons within each atom or ion strive to attain the configuration of a lowered energy state in which, according to Hund’s rule, all spins are parallel to one another. Since the conduction electrons carry along their own spins unchanged as they move from atom to atom, they are able to move within an environment of parallel spins only if the spins of all the incomplete d-shells point in the same direction. This indirect coupling via the conduction electrons will therefore lower the energy of the system when the spins of the d-shells are all parallel. This model also assumed that the direct coupling between incomplete d-shells always tends to align their spins antiparallel. It was thereby predicted that ferromagnetism would never occur in the absence of conduction electrons.

The pure $\text{LaMnO}_3$ shows the semiconducting property. When some of the $\text{La}^{3+}$ ions are replaced by divalent ions like $\text{Ca}^{2+}$ ions, it is necessary that a
corresponding number of Mn$^{3+}$ ions be replaced by Mn$^{4+}$ ions to preserve the charge neutrality.

Then, if we define $\Psi_1$ and $\Psi_2$ as follows

$$\Psi_1: \text{Mn}^{3+}O^2\text{Mn}^{4+}$$
$$\Psi_2: \text{Mn}^{4+}O^2\text{Mn}^{3+}$$

Since $\Psi_1$ and $\Psi_2$ are degenerate functions, more exact waveforms will be obtained by taking the linear combinations.

$$\Psi_+ = \Psi_1 + \Psi_2 \quad ; \quad \Psi_- = \Psi_1 - \Psi_2 \quad (1.4)$$

The energy difference of these two linear combinations is represented by $2\varepsilon$; $\varepsilon$ being the exchange energy, given explicitly by

$$\varepsilon = \int \Psi_1^*(H - \varepsilon_0)\Psi_2 \, dt \quad (1.5)$$

where $H$ is the Hamiltonian of the whole system and $\varepsilon_0$ is the energy associated with the initial states $\Psi_1$ and $\Psi_2$. The above integral known commonly as the exchange integral extends over the coordinates and the spins of all the electrons. The integral (1.5) is non vanishing only if spins of the two d-shells are parallel. The lowest energy of the system thus corresponds to a parallel alignment of electron spins in Mn$^{3+}$ and Mn$^{4+}$. It can be concluded that the lining up of the spins adjacent to incomplete d-shells of the Mn ions will be accompanied by an increase in the rate of migration of Mn$^{4+}$ ions and hence by an increase in the electrical conductivity. Further, it should be realized that a stationary state is represented neither by $\Psi_1$ nor by $\Psi_2$ but by either of the two linear combinations as shown in (1.4).
Depending upon the sign of the exchange integral (1.5), the double exchange raises the energy associated with $\Psi^+$ and lowers the energy associated with $\Psi^-$ or vice-versa. Thus the energy of one of these two stationary states is lowered by the double exchange, which takes place when the d-shell spins are parallel. However, at low temperatures, regardless of the sign of the exchange integral, the energy of the system will be lowered by a parallel alignment of spins. The rate at which electron jumps from a Mn$^{3+}$ ion across an intervening O$^{2-}$ ion to an adjacent Mn$^{4+}$ ion is given by the frequency;

$$v = \frac{2 \varepsilon}{h}$$

The diffusion coefficient for the Mn$^{4+}$ ion is thus given by

$$D = a^2 \frac{\varepsilon}{h} \quad (1.6)$$

where 'a' is the lattice parameter. From Einstein relation

$$\sigma = ne^2 D/kT$$

where $\sigma =$ electrical conductivity

$D =$ diffusion coefficient

$n =$ no. of ions (Mn$^{4+}$) per unit volume

Electrical conductivity can be written as

$$\sigma = xe^2 \varepsilon /ahkT \quad (1.7)$$

Here x is that fraction of Mn ions which have 4+ charges.

The Curie temperature $T_C$ is approximately given as

$$kT_C \approx \varepsilon \quad (1.8)$$

From (1.7) and (1.8)
This relation correlates the conductivity ($\sigma$) and Curie temperature ($T_C$) for manganites.

**1.2.2 JAHN-TELLER EFFECT:**

Jahn-Teller theorem [20] states that, "For a nonlinear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy.

In the Jahn-Teller effect, a distortion of the oxygen octahedron surrounding the B- site cation splits the energy levels of a 3d ion such as Mn, thus lowering the energy. The distorted structures are frequently orthorhombic.
Divalent cations which can occupy the body-centered A-site including calcium, barium, strontium and lead; trivalent cations include yttrium, lanthanum, praseodymium, neodymium and some other rare-earths (La).

Besides manganese, many perovskite structures form with aluminium, gallium or another 3d element such as chromium, iron, cobalt or nickel on the B sites. The rare-earth orthoferrits LaFeO₃ are one example of a series of perovskite structure oxides. There are many others. Any of the trivalent 3d cations can be substituted partially for manganese.

The Jahn-Teller polaron can form in a solid when the Jahn-Teller stabilization energy $\delta_{JT}$ is comparable with the conduction electron bandwidth $W$. Unlike the dielectric polaron where a charge polarization decorates the carriers and a local isotropic distortion increases their effective mass, the Jahn-Teller polaron carries with it, an anisotropic local distortion which removes the degeneracy of the electronic ground state.

In manganese oxides where apical O-atoms move towards the Mn-ion, the energy of $d_z^2$ becomes higher than that of $d_x^2 - y^2$ and the degeneracy is lifted as shown in Fig 1.4. This is called Jahn-Teller effect and is represented by the following Hamiltonian for a single octahedron.

$$H_{JT} = -g (T_x Q_2 + T_z Q_3)$$

where $(Q_2, Q_3)$ are the coordinates for the displacement of O-atoms surrounding the transition metal atoms and $g$ is the coupling constant. $T_x, T_z$ are the x and z component of orbital pseudo spins. When a crystal is considered, $(Q_2, Q_3)$ should be generalized to $(Q_{i2}, Q_{i3})$ (where 'i' is site index) which is represented as the sum of the phonon coordinates and the uniform component $(u_2, u_3)$. Here $(u_2, u_3)$ describes the crystal distortion as a whole. In La$_{1-x}$A$_x$MnO$_3$ the electrically active orbitals are the Mn $d_x^2 - y^2$ and $d_z^2$ orbitals (as shown in Fig. 1.4). The Hund’s rule coupling is believed to be very strong relative to the
d-d hopping and the spin orbit coupling. So, the spins of all of the d-electrons on a given site must be parallel. Three of the d-electrons go into the tightly bound core ($d_{xy}, d_{xz}, d_{yz}$ orbitals, Fig. 1.4 forming a core spin $S_i^3$ of magnitude $3/2$), to which the outer shell electron which may hop from site to site) is aligned by the Hund’s rule coupling. The Hamiltonian containing this Physics is:

$$H_{d-cx} = \sum t^{\alpha\beta}_{ij} d^{+}_{i\alpha} d^{+}_{j\beta} - J_H \sum S^3_i d^{+}_{i\alpha} \zeta_{\alpha\beta} d_{i\beta}$$  \hspace{1cm} (1.10)$$

Here $d^{+}_{i\alpha}$ creates an electron in an outer shell orbital state $\alpha$, $b=x^2-y^2$ or $z^2$ and spin $\alpha$, $J_H$ is the Hund’s rule coupling connecting the core spin to the outer shell electrons. $t^{\alpha\beta}_{ij}$ is the transfer integral which depends on the direction of the bond $ij$ and also on the pair of the two orbitals $\alpha, \beta=(x^2-y^2)$ or $z^2$.

1.2.3 ELECTRONIC LOCALIZATION EFFECT:

The manganites are modelled as systems with both DE off diagonal disorder and non-magnetic diagonal disorder [18, 19] with the help of scaling theory and assuming a mean field distribution for the spin orientation, the localization length of electron can be evaluated as a function of magnetization. The resistivity in the variable range hopping (VRH) regime is calculated as a function of temperature for different values of applied magnetic field. In the manganites, two features apart from the known spin disorder might be important for the electronic localization. The substitution of $R^{3+}$ with Ca, Ba, and Sr may lead to a local potential fluctuation. A rough estimate [21] shows that this potential fluctuation may be comparable with the width of the $e_g$ band. The other feature is the lattice distortion around $A^{2+}$ and $R^{3+}$ due to their different
ionic sizes. These two effects give rise to a rather strong nonmagnetic electron-impurity scattering potential. Based on the above mentioned considerations a Hamiltonian was proposed to describe the transport behaviour of the $e_g$ electrons in manganites.

\[
H_{e_g} = -\sum_{ij} t_{ij} d_i^+ d_j + \sum_i \varepsilon_i d_i^+ d_i
\]  \hspace{1cm} (1.11)

Here the first term is the effective DE Hamiltonian in which

\[
t_{ij} = t\{\cos(\theta_i/2)\cos(\theta_j/2) + \sin(\theta_i/2)\sin(\theta_j/2)\exp[i(\Phi_i - \Phi_j)]\}
\]  \hspace{1cm} (1.12)

where 't' is the hopping integral in the absence of Hund’s coupling and the polar angles $(\Phi_i, \Phi_j)$ characterize the orientation of the local spin $S_i$.

1.2.4 TOLERANCE FACTOR:

The “tolerance factor” being a geometrical factor, plays an important role in manganites and related materials. There are two characteristic distortions that influence the perovskite structure (ABO$_3$) of manganites. One of these distortions results from the cooperative tilting of MnO$_6$ octahedra. This distortion is a consequence of the mismatch of the ionic radii. The Goldschmidt tolerance factor, 't' is defined as [22].

\[
t = (r_A + r_O)/\sqrt{2} (r_B + r_O)
\]
where \( r_A, r_O \) and \( r_B \) represent the ionic radii of rare-earth ion, oxygen and Mn respectively. It is a measure of distortion from the cubic symmetry.

The tolerance factors for some of the manganites are given in table below:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>Tolerance factor (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>LaMnO(_3)</td>
<td>0.889</td>
</tr>
<tr>
<td>2.</td>
<td>PrMnO(_3)</td>
<td>0.868</td>
</tr>
<tr>
<td>3.</td>
<td>NdMnO(_3)</td>
<td>0.864</td>
</tr>
<tr>
<td>4.</td>
<td>SmMnO(_3)</td>
<td>0.858</td>
</tr>
</tbody>
</table>

In the parent compound LaMnO\(_3\), the Mn ions occupy the B site and are surrounded by oxygen octahedral that shares corners to form a three dimensional network. The La ion occupies the A site between these octahedral. In several perovskites, the overlap between the B site d orbital and the oxygen p orbital forms the electronically active band and this overlap can be strongly influenced by the internal pressure by the A-site substitution with ions of different radii. Mainly the effect of decreasing \( <r_A> \) is to decrease the Mn-O-Mn bond angle reducing thereby the matrix element ‘b’ which describes the electron hopping between Mn sites. As discussed above, the tolerance factor is a
simple characterization of the size mismatch that occurs when the A ions are too small to fill the space in the three dimensional network of MnO₆ octahedra. For a perfect size match (t=1), the Mn-O-Mn bond angle (θ) would be 180°. For t< 1, rather than giving a simple contraction of bond lengths, the octahedral tilts and relates to reduce the excess space around the A-site resulting in θ<180°. The apparent decrease in ‘b’ with decreasing <rₐ> originates from the decrease in θ. The band width W of e₉ electrons, which affects the transition temperature (T_c) is controlled by both the Mn-O bond length and the bond angle θ of the Mn-O-Mn. The fine tuning of W and T_c can be obtained by appropriate selection of the size of rare-earth ion. This affects the bond angle θ and not the bond length due to the local disorder in the lattice. The application of external hydrostatic pressure compresses bond length and opens up θ, enhancing the bandwidth W.

1.2.5 PHASE DIAGRAMS:

The properties of the perovskite manganites such as Laₐ₋ₓCaₓMnO₃ and La₁₋ₓSrₓMnO₃ depend on the concentration of dopants x, and the temperature. Depending on the doping level (x) and the temperature, these systems present different phases of conduction and complicated magnetic phase transitions. The changes in the electronic and magnetic properties of the manganites with the change in composition have been worked out in several systems. On the basis of these measurements typical phase diagrams for Ca and Sr doped systems of
LaMnO₃ are shown in Fig. 1.6(a) and 1.6(b). The material is always paramagnetic above the transition temperature. The undoped compound (x=0) is insulating and a layered antiferromagnet. On the nominal doping with divalent alkaline elements like Ca, Sr, Ba (x<0.2) complex structures are observed and under certain conditions the material can be a metallic ferromagnet. As the amount of doping increased, the material becomes ferromagnetic below the Curie temperature. The ferromagnetic coupling is strongest at x = 0.3-0.4, the point at which the Curie temperature reaches its maximum value. At low doping (x<0.2) the material behaves like a semiconductor, showing an increase in resistivity as the temperature is lowered.
For increased doping, however, there is a tendency towards metallic conductivity, as observed for La$_{0.67}$Sr$_{0.33}$MnO$_3$ in the paramagnetic phase. In the high doping region (x>0.5) an insulating and antiferromagnetic charge ordered state is formed.
The transition from the paramagnetic to the ferromagnetic state is also accompanied by a sudden reduction in the resistivity. Such a drop is well known in other ferromagnetic metallic systems and is caused by the transition from a state with spin disorder to one with ordered spin. Disorder causes charge carriers with different spin orientations to scatter from each other, increasing the resistivity. The same loss of resistivity should be observed in an applied magnetic field; since this aligns the electrons spins and also prevents the scattering caused by spin disorder.

Since three of the electrons in the 3d orbital of the manganese ions form a triplet state at a lower energy. These electrons are treated as localized electrons that remain bound to the ion, and because their spin point in the same direction, they have an overall magnetic moment of 3/2. While the electrons in the highest energy level are shared with the oxygen ions, forming an energy band that extends through out the solid. The motion of charge carriers through this energy band and hence the conductivity of the material is largely controlled by the width of the band. This is determined by the overlapping of the manganese and oxygen orbitals, which in turn depends on the geometrical arrangement of the ions. A large overlap creates wide band. For a given distance between manganese and oxygen ions, the overlap is largest when the Mn-O-Mn bond angle is 180°. Such an arrangement is found in an ideal perovskite structure in which manganese and six oxygen ions form a regular octahedron. But if the lanthanum is replaced with a smaller ion, the octahedron distorts and the bond angle becomes smaller. This decreases the overlap between the orbitals and narrows the energy band. Materials with narrow energy bands also show weaker ferromagnetic coupling, leading to a lower Curie temperature.

The alignment of electron spins modifies the effective bandwidth of manganites. It is easier for electrons to hop between Mn³⁺/Mn⁴⁺ sites when the localized moments in neighbouring ions are aligned. Thus the effective
bandwidth and the conductivity increases when the material becomes magnetically ordered below the Curie temperature. The ferromagnetic coupling in these materials is therefore transmitted via mobile carriers. When charge carriers are not free to move, the system is insulating and the interaction between the localized electrons induce antiferromagnetic order below the Ne'el temperature.

Electrical, magnetic and other measurements on $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ systems have revealed certain unusual features with respect to charge carriers in these oxides. For example, the manganites exhibit very high resistivity particularly at low temperatures ($<100 \text{ K}$) [21]. The values of resistivity are considerably higher than Mott's maximum value of resistivity [23], the resistivity reaching a value of $10^3$-$10^4$ ohm-cm in the so called metallic state.

The resistivity in the ferromagnetic regime of manganites has been investigated by a number of workers. Just below $T_C$, it varies rapidly with temperature. For $T < 0.5 \ T_C$, the variation is less rapid and is different from what is generally seen in a metallic ferromagnet. In general, for $T < 0.2T_C$, $T^2$ dependence seems to make the major contribution.
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