Chapter 5

Magneto-electric transport properties of half doped wide bandwidth manganites (La$_{0.5}$Sr$_{0.5}$MnO$_3$)

This chapter discusses the conduction mechanism in La$_{0.5}$Sr$_{0.5}$MnO$_3$ manganites by analysing the data on the dependence of temperature on electrical resistivity, magnetization and thermoelectric power. The data have fitted to suit various models. The correspondence between the variation of thermoelectric power and magnetoresistance (MR) with temperature has been established.
5.1 Introduction

In the preceding chapters we have discussed the various physical properties of low and medium bandwidth manganites namely GSMO and LCMO, in that, GSMO falls under the family of small bandwidth manganites and LCMO belongs to the class of intermediate bandwidth manganites. Our investigations have found a close correlation between magnetism and thermoelectric power, especially, at low temperatures.

A striking feature of the above investigation is that they display charge ordering wherein the concentration of Mn\(^{3+}/\)Mn\(^{4+}\) is almost unity. However, none of the compositions investigated and described in earlier chapters were pure ferromagnets. We have seen that the transport data can be fitted with modified versions of various models. For instance, the thermoelectric transport in GSMO and LCMO was fitted with a modified Mandal model where Fischer’s spin glass term, \(S^2T^2\) is incorporated. Mott’s polaronic model was found suitable for fitting the high temperature data in the case of GSMO/LCMO samples [1-4].

Substitution of divalent cations at trivalent rare earth sites in REMnO\(_3\) results in the replacement of Mn\(^{3+}\) by Mn\(^{4+}\) which gives rise to mixed-valence manganites with a general formula of the form RE\(_{1-x}\)AE\(_x\)MnO\(_3\) [Where RE is the rare earth element, AE is the divalent cation]. La\(_{1-x}\)Sr\(_x\)MnO\(_3\) is a prototypical double exchange ferromagnet in a range of x concentration \(0.1<x<0.6\) and is a wide bandwidth manganite where the enhanced bandwidth is largely due to the strong overlapping of atomic orbitals. It may be noted that the bandwidth is the width of conduction band formed by the hybridization of manganese e\(_g\) level and oxygen p level [5-6]. As bandwidth increases, magnitude of hopping amplitude for e\(_g\) electrons is also increase, which is favourable for double exchange and hence exhibits
ferromagnetic behaviour. Their Curie temperature $T_C$ and metal to insulator transition temperature are relatively high.

In these class of compounds, valence electrons are more delocalized and are conducive for double exchange phenomenon [7]. From the phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [8-10], it is seen that LSMO has a ferromagnetic metallic ground state at half doping. Though the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ is ideally suited for charge ordering, in practice, they are not. The interplay of delocalization and conduction under an externally applied magnetic field and their transport properties are interesting from a fundamental perspective. $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (coded as LSMO5) is an ideal template for validating various models namely, small polaron hopping model, Zener double exchange polynomial law for explaining conduction process. This is a unique system which is ferromagnetic in nature and the possibility of spin polarised tunnelling exist at low temperature.

LSMO5 is ferromagnetic due to double exchange. There can be a possibility of existence of spin polarised tunnelling at low temperature and having appreciable thermoelectric power. Also there exists close correlation between thermoelectric power and magnetoresistance with respect to temperature. Fitting the thermoelectric power and resistivity data in various temperature regions with appropriate models can reveal the exact mechanisms behind the conduction in this half doped manganites. At the metal to insulator boundary of this half doped manganites, there could be a tendency to form coexisting clusters of FM-AFM phases. With this motivation in mind, $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was prepared and a thorough investigation on its thermoelectric power, resistivity and magnetization was carried out.
5.2 Method of synthesis

La$_{0.5}$Sr$_{0.5}$MnO$_3$ sample was prepared by citrate gel technique. Stoichiometric amounts of La$_2$O$_3$, SrCO$_3$ and MnO$_2$ were mixed in dilute nitric acid and suitable amounts of ethylene glycol and citric acid were added. Then the solution was heated to 80°C. After a few hours the solution gets boiled, frothed, turned dark, ignited and caught fire to give a spongy powder. The resulting black powder was calcined in air at 900°C for 12 hours and then pressed into pellets of cylindrical discs with diameter 12 mm and thickness 2 mm. The pellets were then sintered at 1050°C for 12 hours.

5.3 Results and Discussions

5.3.1 Structural studies using XRD

The crystal structure of the sample was determined using X-ray diffraction. The X-ray powder diffraction pattern of LSMO5 is shown in figure 5.1.a.

![Figure 5.1: (a) XRD pattern for La$_{0.5}$Sr$_{0.5}$MnO$_3$. (b) Rietveld refinement performed on La$_{0.5}$Sr$_{0.5}$MnO$_3$.](image)

From the diffraction pattern, it is evident that La$_{0.5}$Sr$_{0.5}$MnO$_3$ is single phasic with orthorhombically distorted perovskite structure belonging to the space group R3c. The average particle size estimated from XRD data using Scherrer’s formula is 25nm. The XRD data have been analysed by refining the experimental data using a standard Rietveld refinement technique.
Refined lattice parameters determined at room temperature are $a = 5.455 \, \text{Å}$, $b = 5.524 \, \text{Å}$, $c = 7.714 \, \text{Å}$ which are consistent with earlier reports [11-13]. The Rietveld refined pattern of XRD is also shown in figure 5.1.b.

5.3.2 Electrical and magnetoresistive properties

Resistivity measurements by usual standard four probe techniques in the temperature range of 5K-300K for different magnetic fields are shown in figure 5.2. A giant MR can be noticed from the figure. The external field when applied aligns the spins favourably thereby reducing the scattering of charge carriers during hopping which results in the decrease of resistivity.

![Figure 5.2: Temperature dependence of resistivity measured under 0T, 1T, 5T, and 8T magnetic fields.](image)

The metal to insulator transition temperature $T_{\text{im}}$ is taken as the maxima of $d\rho/dT$ versus temperature curve which is found to be 120 K at 0T. When the temperature is further lowered from $T_{\text{im}}$, a second transition is observed at $T<50$ K with a broad resistive minimum in the temperature range of 30 K-40 K. Hence the sample exists in three different states at different temperatures. To explore different scattering mechanisms involved, we analysed resistivity data by dividing the entire temperature range (5 K-300 K) into three different temperature regimes: (i) temperature above $T_{\text{im}}$ ($T>T_{\text{im}}$), (ii) metallic regime $50K<T<T_{\text{im}}$ and (iii) low temperature weak metallic regime $T<50K$. 

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5.3.2.1 Conduction mechanism in insulating region (T>T_{im})

Above T_{im}, the semi covalent bond between Mn-O-Mn becomes covalent and the Jahn - Teller distortion is prominent so that the charge carriers are trapped which gives rise to polarons [14-16]. Hence above T_{im}, the resistivity shows a polaronic like behaviour. This can be explained by small polaron hopping model equation,

$$\rho = AT e^{E_{A}/kT},$$  \hspace{1cm} (5.1)

where T is absolute temperature, E_{A} is activation energy and A is constant [17-21]. The graph between log (\rho/T) and 1/T shown in figure (5.3) is a straight line. This straight line indicates that the exact conduction mechanism in the temperature regime T>T_{im} for this particular composition is due to polarons.

![Figure 5.3: Plots of log (\rho/T) vs 1/T for La_{0.5}Sr_{0.5}MnO_{3} under 0T, 1T, 5T, and 8T magnetic fields.](image)

5.3.2.2 Conduction mechanism at metallic region (50K<T<T_{im})

In the metallic region, thermal frustration of spins rises with increasing temperature and hence the increasing resistivity. The conduction in metallic ferromagnetic region (50K<T<T_{im}) is assumed to be due to electron magnon
interaction in double exchange and hence resistivity data are well fitted according to Zener double exchange polynomial law.

\[
\rho = \rho_0 + \rho_2 T^2 + \rho_{4.5} T^{4.5}
\]  

(5.2)

where \( \rho_0 \) is temperature independent resistivity term due to domain and grain boundary, \( \rho_2 T^2 \) due to electron-electron scattering and the last term \( \rho_{4.5} T^{4.5} \) is due to electron magnon scattering in the double exchange theory [21]. The fitted parameters are shown in table 5.1. From the fitted values it is found that the value for magnon scattering term \( \rho_{4.5} T^{4.5} \) decreases with applied field suggesting the suppression of magnetic fluctuations with the applied magnetic field. Significant decrease in value of \( \rho_0 \) with applied field indicates the influence of magnetic field on the magnetic domains where the size of domain boundary reduces with increasing field and there by diminishing \( \rho_0 \). Also the shift in the transition temperature \( T_{\text{im}} \) to high temperature with the application of fields indicates the growth of FM region by suppressing the formation of polarons and spin disorder scattering.

Temperature dependent resistivity data in the temperature range \( 50K < T < T_{\text{im}} \) with varying fields fitted to equation (5.2) are shown in figure (5.4).

<table>
<thead>
<tr>
<th>Field</th>
<th>( \rho_0 ) (( \Omega \text{ cm} ))</th>
<th>( \rho_2 ) (( \Omega \text{ cm} /K^2 ))</th>
<th>( \rho_{4.5} ) (( \Omega \text{ cm} /K^{4.5} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>2.12</td>
<td>2.76E-5</td>
<td>-8.50E-11</td>
</tr>
<tr>
<td>1T</td>
<td>1.68</td>
<td>3.86E-5</td>
<td>-8.40E-11</td>
</tr>
<tr>
<td>5T</td>
<td>1.27</td>
<td>3.19E-5</td>
<td>-7.06E-11</td>
</tr>
<tr>
<td>8T</td>
<td>1.04</td>
<td>2.63E-5</td>
<td>-5.34E-11</td>
</tr>
</tbody>
</table>
5.3.2.3 Conduction mechanism at weak metallic region (T<50K)

A distinct resistive minimum is observed in the zero field resistivity data in the temperature range of 30-40 K. In zero field, at very low temperature, the neighbouring grains are aligned randomly so that the charge carriers in them have opposite spins. Hence there exists an energy gap between the charge carriers of the neighbouring antiferromagnetically coupled grains. As temperature increases they get enough thermal energy so as to jump the barrier. Thus the resistivity is decreased with increasing temperature. When the temperature corresponding to the minimum resistivity is reached, it superposes the metallic onset resistivity and follows a metallic behaviour. The observed resistive minimum in the zero field resistivity data is not so profound when external fields are applied. This can be due to the inter grain transport phenomenon [16]. When external fields are applied, the adjacent grains are aligned favourably so that the energy gap reduces as a result of which the resistivity minimum reduces with increasing applied field [22].
Kalyana lakshmi et. al have explained the distinct low temperature minimum observed in the electrical resistivity data of La$_{1-x}$Na$_x$MnO$_3$ by introducing the effect of weak localization in addition to electron-electron and electron magnon scattering in the resistivity equation (5.2) [23]. Earlier Zhang et. al has explained this kind of upturn of resistivity in bilayer manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ by incorporating $T^{1/2}$ term (term corresponding to weak localization) in the conventional resistivity equation of ferromagnetic phase [24]. Later Y.S. Reddy et. al also showed that the low temperature upturn of resistivity is directly proportional to weak localization term, $T^{1/2}$ [25]. By introducing a $T^{1/2}$ term in the resistivity equation of ferromagnetic phase, the low temperature minimum observed in the resistivity data is successfully fitted to equation (5.3).

$$\rho = \rho_0 + \rho_{1/2} T^{1/2} + \rho_2 T^2 + \rho_{4.5} T^{4.5} \quad (5.3)$$

Square root temperature dependence of resistivity indicates the appearance of a weak non metallic behaviour for T< 50K in zero field and from the fitted parameters, this dependence is found to be decreasing with
the application of a magnetic field. It can be due to decrease in magnetic domain boundary with the application of magnetic field.

Table 5.2: Fitted parameters in the temperature variation of resistivity according to the equation (5.3).

<table>
<thead>
<tr>
<th>Field</th>
<th>$\rho_0$ ($\Omega\text{ cm}$)</th>
<th>$\rho_{1/2}$ ($\Omega\text{ cm}/K^{1/2}$)</th>
<th>$\rho_2$ ($\Omega\text{ cm}/K^2$)</th>
<th>$\rho_{4.5}$ ($\Omega\text{ cm}/K^{4.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>2.64</td>
<td>-0.07</td>
<td>4.17E-6</td>
<td>-1.31E-9</td>
</tr>
<tr>
<td>1T</td>
<td>2.04</td>
<td>-0.054</td>
<td>4.16E-5</td>
<td>-5.95E-10</td>
</tr>
<tr>
<td>5T</td>
<td>1.58</td>
<td>-0.053</td>
<td>7.30E-5</td>
<td>-6.75E-10</td>
</tr>
<tr>
<td>8T</td>
<td>1.28</td>
<td>-0.04</td>
<td>4.02E-5</td>
<td>-3.17E-10</td>
</tr>
</tbody>
</table>

Figure 5.6: Variation of MR with applied magnetic field at different temperatures.

The variation of MR with magnetic field at different temperatures is shown in figure (5.6). From the figure (5.6), it is clear that a kink can be seen near 0.2T in low temperatures, especially, at 5K. Above and below this field, MR varies linearly with magnetic field. This indicates the co-existence of
ferromagnetism with another phase which is weakly conducting [26]. In the region below this kink (H<0.2T), MR has contributions from spin polarized inter grain tunnelling while ferromagnetic contributions are more prevalent in the region above the kink (H>0.2T). The magnetic field corresponding to this kink is termed as Low Field Magneto Resistance (LFMR). Hwang et al. has reported that this LFMR in polycrystalline materials is due to the spin polarised transport across the grain boundaries [27]. Absence of such a kink in MR variation with field at high temperature indicates that this spin polarised tunnelling is absent at higher temperatures. As temperature increases, thermal energy increases and thus antiferromagnetically aligned grains acquire sufficient energy to overcome the barrier. Spin tunnelling is not present in the high temperature region where it behaves metallic. Also the Low Field Magneto Resistance in 5K is close to 1/3, which is the universal value of all ferromagnetic manganites.

To separate out the contribution of MR from spin polarized transport, a phenomenological model suggested by Raychaudhari et.al was used to analyse experimental MR data [28]. The contribution of inter grain tunnelling in the low temperature can be observed directly from the fitting of magnetic field dependence of $\Delta \rho / \rho$ to the relation

$$MR = -A \int_0^H f(k)dk - JH - KH^3 \quad (5.4),$$

where $f(k)$ gives the contribution from spin polarised tunnelling which is expressed as

$$f(k) = A \exp(-Bk^2) + Ck^2 \exp(-Dk^2) \quad (5.5)$$

Where A, B, C, D, J and K are adjustable fitting parameters. To fit equation (5.4), we have followed the same method as used by Raychaudhari et al [28]. The experimental MR data and simulated curves using equation (5.4) at
various temperatures are shown in figure (5.7). To fit equation (5.4) to these curves, equation (5.4) is differentiated with respect to $H$ and substituting equation (5.5) in equation (5.4) we get,

$$d(MR)/dH = A \exp(-BH^2) + CH^2 \exp(-DH^2) - JH - KH^3$$  \hspace{1cm} (5.6)

The experimental curves were differentiated and fitted to equation (5.6) to find the best fit parameters. Figure (5.8.a) shows the differentiated curve and best fit function at 5K and figure (5.8.b) shows the experimental MR-H curve at 5K along with simulated curves using equation (5.4). It is found that there is an excellent fit for all temperatures up to 300 K where the spin polarized tunnelling contribution is absent. Hence the MR due to spin polarised tunnelling drops rapidly with temperature. Thus the low temperature minimum observed can be due to both spin polarised tunnelling and weak localization effect.
Figure 5.8: (a) The differentiated curve and best fit function at 5K with $A=-3.486$, $B=35.16$, $C=-0.0125$, $D=6.12$, $J=0.47 \times 10^{-2}$ and $K=-0.23 \times 10^{-6}$ (b) The experimental MR-H curves (dots) and the fitted curves (lines) using equation (5.4) at 5K.

The variation of magnetoresistance with temperature for an applied field of 8T is shown in figure (5.9). A maximum MR percentage of about 64% at around 50K was observed. Two slope changes are seen in MR variation with temperature. This can be explained on the basis of two different mechanisms such as intrinsic and extrinsic [23]. Slope change observed near ferromagnetic non metallic transition can be explained on the basis of an extrinsic inter grain effect. As grain size is very small, large grain boundaries are present. Hence in the presence of field, probability of spin polarisation through inter grain tunnelling is high thereby increasing MR percentage in this region. The other slope change is observed near $T_{im}$ which can be explained on the basis of intrinsic grain effect. In manganites, especially for nano sized ones, there are ferromagnetic metallic regions and antiferromagnetic insulating regions. As temperature increases from $T_{im}$, volume fraction of the AFM insulating region increases, which enhances spin fluctuations within the volume of grains. Hence near $T_{im}$ when external fields are applied these fluctuations are suppressed so that the electron suffers less scattering by local spins. Thus the sharp drop of MR near $T_{im}$ is due to this intrinsic grain effect.
Magneto-electric...

Figure 5.9: Variation of percentage of MR with temperature using a magnetic field of 8T

5.3.3 Magnetization studies

Temperature dependent zero field cooling (ZFC) and field cooling (FC) magnetization measured in different applied magnetic fields of 25, 50 and 200 Oe is shown in figure (5.10). A sharp paramagnetic to ferromagnetic transition is observed at T_C~320K. The transition temperature is taken as the maximum of dM/dT versus temperature curves. This transition is due to the double exchange between neighbouring Mn^{3+} and Mn^{4+} through oxygen, which causes the hopping of electrons from half-filled e_g orbital of Mn^{3+} to empty e_g orbital of Mn^{4+} via 2p_σ orbital of oxygen. However the transition region is relatively wide and also ZFC magnetisation is found to be decreasing at very low temperatures. Earlier Wang et.al explained the wide transition observed in La_{0.5}Sr_{0.5}MnO_3 nanoparticle compact by the weaker magnetic exchange coupling near the grain boundary with respect to that of intra grain [29]. As LSMO5 has equal number of Mn^{3+} and Mn^{4+}, the antiferromagnetic (AFM) Mn^{3+}-O-Mn^{3+} interactions tend to compete with ferromagnetic (FM) Mn^{3+}-O-Mn^{4+} interactions resulting in the evolution of magnetic frustration.

ZFC and FC magnetizations as a function of temperature in magnetic fields of 50 Oe, and 25 Oe are shown in figures (5.10.b) and 161
(5.10.c). It is observed that irreversibility between FC and ZFC is more significant for an applied field of 25 Oe. When the field is higher, FC and ZFC components come closer to each other and hence irreversibility decreases. Also the transition temperatures with applied field are shifted to lower temperatures. This shift in transition and thermo magnetic irreversibility is the most important characteristic of spin clusters which can be due to competing magnetic interactions [30]. Thus the thermo magnetic irreversibility below $T_C$ as well as the magnetization drop can be due to the formation of cluster glass state [31].

![Figure 5.10: Magnetization measurements under ZFC and FC conditions in a magnetic field of (a) 200 Oe, (b) 50 Oe and (c) 25 Oe.](image)

The M-H loops of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ measured at 5K and 300K are represented in figure (5.11). The magnetization at 5 K shows a hysteresis with unsaturated magnetic moment of 69emu/g at 70 kOe. M H at 300K shows linear increase of magnetization which is attributed to the co-existence of FM clusters in the AFM matrix. The increase in magnetization is due to the dominant behaviour of FM component in the system. The
absence of saturation magnetization is in accordance with the existence of antiferromagnetic order. In the MR studies, it is realized that the existence of two linear variations with respect to LFMR indicates the coexistence of FM-AFM phases. This co-existence of FM-AFM phases were further confirmed from magnetization studies.

Figure 5.11: Magnetic hysteresis loops of La_{0.5}Sr_{0.5}MnO_3 measured at 5 K and 300 K

5.3.4 Thermoelectric power studies

The variation of thermoelectric power with temperature in the temperature range of 5K-300K is shown in figure (5.12). It is found that the value of thermoelectric power changes from positive to negative with increasing temperature. This change of sign in the thermoelectric power, S may be attributed to the orbital degeneracy of the e_g band [32]. Earlier Asamitsu et al has explained that this sign change in the thermo power is due to orbital degree of freedom of the e_g carriers [33]. S changes its sign from negative to positive with the increase of the spin polarization. From MR, it is found that spin polarised transport is present. The presence of spin polarised transport indicates that the degree of spin polarisation is high [28]. The spin degree of freedom is lost due to the full spin polarization of the e_g electrons and hence that only the orbital degree of freedom survives in the
ferromagnetic ground state. The positive $S$ at low temperature is accredited to the holes which are excited from valence band to the impurity band. At high temperatures, electrons in the valence band are excited into the conduction band. As these electrons have high mobility within the conduction band, $S$ is negative. Thus coexistence of two types of charge carriers is confirmed.

![Figure 5.12: Temperature dependence of thermoelectric power from 5 K – 300 K.](image)

In $S$ versus $T$ plot, two peaks are observed, one at the high temperature region ($\sim T_{im}$) and the other at the low temperature region (10-30K). Existence of peak at the high temperature region is generally common in all manganites which corresponds to metal to insulator transition. Prior reports showed that phonon drag and magnon drag contributions are present in the low temperature region [34]. Thus the low temperature peak found in the ferromagnetic metallic part may be due to the effect of electron – magnon interaction and electron - phonon interaction. Considering this phonon drag and magnon drag, the more general equation for the thermoelectric power is [23, 34 -35]:

$$S = S_0 + S_{3/2}T^{3/2} + S_3T^3 + S_4T^4$$  \hspace{1cm} (5.7)
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Where $S_0$ is a constant which accounts the low temperature variation of thermoelectric power, $S_{3/2} T^{3/2}$ is attributed to the magnon drag contribution, $S_3 T^3$ and $S_4 T^4$ are respectively accredited to the phonon drag and spin wave contribution.

From the section 5.3.2.3, the low temperature resistivity data fitting need a $T^{1/2}$ term (corresponds to weak localization effect). Hence we incorporate the contribution of thermoelectric power from a $T^{1/2}$ term. Besides this, K.H Fischer’s Kondo term, $S_2 T^2$ corresponding to magnetically frustrated state and a term, $S_1 T$, with opposite sign which lead to a change of sign of TEP at a characteristic temperature are additionally needed for fitting [1]. Hence these contributions are also considered in the conventional equation (5.7) so as to make it suitable to account the entire metallic part of thermoelectric power.

Similar to the electrical resistivity, the equation of thermoelectric power data is modified as:

$$S = S_0 + S_{1/2} T^{1/2} + S_1 T + S_{3/2} T^{3/2} + S_2 T^2 + S_3 T^3 + S_4 T^4 \quad (5.8)$$

Figure 5.13: Variation of $S$ with $1/T$ at (a) $T<T_{im}$ (b) $T>T_{im}$. The solid line gives the best fit to equations (5.8) and (5.9).
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Thermoelectric power data are well fitted with equation (5.8) and this is shown in fig (5.13.a). The corresponding fitting parameters are included in table 5.3.

Table 5.3: The best fit parameters of the experimental TEP data.

<table>
<thead>
<tr>
<th>S₀</th>
<th>S₁/2</th>
<th>S₁</th>
<th>S₃/2</th>
<th>S₂</th>
<th>S₃</th>
<th>S₄</th>
<th>Eₛ</th>
<th>Eₓ</th>
<th>α'</th>
</tr>
</thead>
<tbody>
<tr>
<td>(µV/K)</td>
<td>(µV/K³/2)</td>
<td>(µV/K²)</td>
<td>(µV/K⁵/2)</td>
<td>(µV/K⁴)</td>
<td>(µV/K³)</td>
<td>me</td>
<td>meV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-8.12</td>
<td>7.01</td>
<td>-1.26</td>
<td>0.127</td>
<td>-</td>
<td>9.55E</td>
<td>-</td>
<td>4.0</td>
<td>39.2</td>
<td>-0.37</td>
</tr>
<tr>
<td>0.014</td>
<td>-5</td>
<td>2.58E</td>
<td>97</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the insulating region, the thermoelectric power data are fitted excellently with Mott’s well known equation based on polaron hopping [36],

\[ S = \frac{k_B}{e} \left[ \frac{E_s}{k_BT} + \alpha' \right] \]  

(5.9)

where \( k_B \) is the Boltzmann constant, \( e \) is the electronic charge, \( E_s \) is the activation energy obtained from thermoelectric power data and \( \alpha' \) is a constant of proportionality between the heat transfer and the kinetic energy of electron. \( \alpha' < 1 \) implies the existence of small polarons, while for \( \alpha' > 2 \) suggests that the conduction involves large polarons [37-38]. From the slope of \( S \) versus \( 1/T \) plot, activation energy \( E_s \) and from the y intercept, the constant \( \alpha' \) is obtained. The value of \( \alpha' \) obtained from the equation (5.9) is found to be less than one. This strongly supports the small polaron conduction mechanism in the high temperature region. Figure (5.13.b) shows the best fit curve of \( S \) versus \( 1/T \) plot and the corresponding fitting parameters are given in table 5.3. By using Mott’s equation for resistivity and TEP, activation energy from resistivity plots (\( E_p \)) for zero field and
activation energy from TEP plots ($E_a$) are calculated. The difference between these activation energies termed as polaron hopping energy ($W_{hi} = E_p - E_a$) is found to be 35.1 meV. The huge difference in the values of activation energy is the indication towards the applicability of small polaron hopping (SPH) model in the insulator region. Thus high temperature thermoelectric power and resistivity studies indicate that small polaron hopping as the conducting mechanism.

5.4 Conclusions

The transport properties of strontium doped lanthanum manganite La$_{0.5}$Sr$_{0.5}$MnO$_3$ prepared by citrate gel method has been studied in detail. The XRD pattern of the sample showed a single phase homogeneous orthorhombically distorted perovskite structure in the space group R3c. The FC-ZFC magnetization studies revealed that in accordance with a metal to insulator transition there is a sharp ferromagnetic to paramagnetic transition indicating the role of double exchange. Due to the equal ratio of Mn$^{3+}$ and Mn$^{4+}$, magnetic frustration occurs. Temperature dependent resistivity data measured under varying fields showed that the exact conduction mechanism in the high temperature region is due to polarons and the variation of low temperature electrical resistivity was explained using the combined effect of weak localization and magnon scattering. Resistivity minimum observed below 50 K and metal to insulator transition temperature was found to have strong dependence on the applied magnetic field. This resistivity minimum observed in the ferromagnetic- non-metallic regime shows a $T^{1/2}$ dependence, consistent with weak localization effects, and is explained by inter grain spin- polarized tunnelling through grain boundaries. The contribution of inter grain tunnelling in the low temperature minimum was confirmed by modelling experimental MR data. The shift in the metal to insulator transition peak of resistivity under the application of external field is
probably due to suppression of spin fluctuations. These results were correlated with the results from thermoelectric power measurements. The change of sign in the thermoelectric power is attributed to the orbital degeneracy of the $e_g$ band. Large values of thermoelectric power were not observed in LSMO$_5$ because of the absence of charge ordering.

References

Chapter 6

A study on the magnetic properties of Gd-Sr based low bandwidth manganites in their bulk and thin film forms

This chapter deals with the magnetic properties of both bulk and thin film forms of charge ordered Gd-Sr manganites belonging to the series Gd$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.3, 0.5, 0.6$). In the case of bulk, it is found that the Gd moments order anti parallel to the manganese spins giving rise to a ferrimagnetic behaviour. A spin glass transition due to the competing ferromagnetic (FM) and antiferromagnetic (AFM) phases of manganese is observed at around 42K. Bulk form of Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ exhibits magnetization reversal for applied fields of 25 Oe and 50 Oe at very low temperatures. In the two dimensional thin film forms of Gd$_{1-x}$Sr$_x$MnO$_3$, coercivity is different when compared to their bulk counterparts, moreover, the spin reversal and magnetic behaviour exhibited by thin films are at variance with respect to their bulk. An overview of structural and compositional analysis of films will be presented. Surface morphology of the films was examined from SEM and AFM images.

The work discussed in this chapter has been reported in: Journal of Magnetism and Magnetic Materials 398, 174–182 (2016).
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