CHAPTER 5

Transport and magneto-transport properties of SrFe$_{1-x}$Ti$_x$O$_{3-\delta}$ systems (x = 0 to 0.3)

This chapter describes the results of the transport and magneto-transport studies on SrFe$_{1-x}$Ti$_x$O$_{3-\delta}$ (x = 0 to 0.3) carried out by the standard four probe technique using the dc transport option of PPMS. These systems have defects (vacancies) originating from the oxygen deficiency and site disorder caused by a partial substitution of Ti$^{4+}$ at Fe sites. Large change in resistivity due to charge ordering is observed when lowering the temperature. In all the above systems, semiconducting like decrease in resistivity with increase in temperature is observed. The temperature dependence of resistivity is well described by the three dimensional Variable Range Hopping (3D-VRH) model. Magneto-resistance is measured by applying a field of 80 kOe and the results are discussed.
5.1 Introduction

In ABO₃ perovskite systems the transport properties generally are governed by B-site cation and additionally in oxides, by the stoichiometry of the compound. SrFeO₃₋δ systems have four distinctly different crystallographic phases with respect to oxygen deficiencies. Stoichiometric SrFeO₃ is a metal up to the lowest measurable temperature. Any deviation from stoichiometry transforms the system from a metal to a semiconductor and with further decrease in oxygen stoichiometry, to an insulator.

5.2 Review of earlier work

Transport and magneto-transport in tetragonal SrFeO₃₋δ has been studied by a number of groups. A few of the important results are discussed here. Lebon et al [1, 2] reported transport behavior of three different oxygen deficient single crystals. The resistivity of mainly tetragonal SrFeO₂.₈₅ single crystal (in which 70% tetragonal and 30% orthorhombic phase is present) increases by one order of magnitude at 70 K and around 70 K, a large negative Magnetoresistance (MR) of 90% is observed. The negative MR is attributed to Fe⁴⁺- Fe³⁺ charge and magnetic ordering. Williams et al [3, 4] reported the resistivity and MR in two different oxygen deficient samples, namely, SrFeO₂.₈ and
SrFeO$_{2.71}$. In tetragonal SrFeO$_{2.8}$ system, below 70 K an increase in the resistivity and with the application of 120 kOe field a positive MR of 10% is observed from room temperature down to 80 K. Around 80 K, there is a jump from positive MR to negative MR of 80% and this high value of negative MR persists down to low temperatures. The difference in MR observed in this system in comparison to those of single crystals is attributed to the contribution from transport across the grain boundaries.

In view of the reported sensitivity of MR to the microstructure, a study of transport in the present ball-milled tetragonal samples with and without Ti doping, wherein the microstructure shows the presence of nanograins, could yield interesting results.

5. 3 Transport mechanisms in Oxides

The transport mechanism for the mixed-valence manganites and doped semiconductors is discussed mainly using three different models. They are (i) thermal activation or band gap model, (ii) adiabatic nearest-neighbour hopping model of small polarons or small polaron hopping model (SPH), (iii) Variable-
range hopping (VRH) model. To understand the conduction mechanism in an oxide system, it is imperative to check which of these models describes the observed dependence of resistivity on temperature.

5.3.1 Band gap model
The band gap model has been applied to many semiconductors and insulators in the literature. In this model, a band gap exists between the conduction band and the valence band and if the thermal energy is sufficient to cause thermal excitation of the electrons across the band gap, the electrons excited to the conduction band become available for conduction. If a graph between $\rho$ and $T$, constructed out of the measured $\rho (T)$, is linear, the band gas model holds. However, this simple check yielded a non-linear graph in the present case. Thus, the band gap model is inadequate to explain the conduction process in the systems under investigation.

5.3.2 VRH Mechanism
VRH theory was originally developed to explain the transport in doped semiconductors where electrons are localized by potential fluctuations associated with the dopant. According to the VRH model, if the electron
is not deeply trapped it can hop from one site to another site with the assistance of a phonon [5-10]. At low temperatures if the electron does not have enough energy to hop to the nearest neighboring site, but it is possible to hop further to find a site with a smaller potential difference. Since the hopping range is variable, it is called variable range hopping. According to this model, the resistivity varies as

5.3.3 Adiabatic nearest-neighbour hopping model of small polarons

If the electrons are deeply trapped as small polarons, the thermal energy is not sufficient to overcome the deep potential well (deeply trapped electrons) to hop out of its site. In this situation, the hopping is possible through a multiphonon assisted process. The electron is activated to an intermediate state which is a localized state with a higher energy. Then from the thermal energy acquired due to the second phonon the electron hops out from the intermediate state to its nearest-neighbour site or further sites. Hopping to nearest-neighbour site is considered as multiphonon assisted nearest-neighbour hopping. The hopping to the non-nearest-neighbour site is termed as variable-range hopping of small polarons, because the carrier in both the initial and final states is localized as small polarons [11-16].

If the conduction occurs via the SPH process, a plot of log \((\rho/T)\) against \(1/T\) should be linear. In the present system, this graph yielded a
nonlinear curve. This permits us to conclude that the SPH model cannot account for the conduction process.

5.4 Resistivity and Magnetoresistance of Tetragonal SrFeO$_{3-\delta}$

Resistivity of tetragonal SrFeO$_{3-\delta}$ (T0) sample is measured from 300 K to 5 K using standard four probe method. Figure 5.1 shows the resistivity as a function of temperature in the above temperature range. The shape of the curve is typical of a semiconductor/insulator in that the resistivity monotonously decreases with increasing temperature (T). Since the voltage across the sample T0 at 2 K was well within the compliance voltage of the constant current source, resistivity could be measured over the complete temperature range. Zero-field resistivity data show hysteresis between cooling and warming cycles at T \( \approx \) T$_{N}$. Hysteresis in resistivity between cooling and warming is reported in the literature [1, 2, 17-19] and is attributed to the coexistence of antiferromagnetic and paramagnetic domains. Around 70 K (\( \sim \) T$_{N}$ of the tetragonal phase) a large change in slope with a sudden increase in resistivity by at least an order of magnitude is observed, indicating the inter-relationship between the magnetic and transport properties. On further cooling, the increase in resistivity exhibits a power-law behavior. On heating, the sample shows a hysteresis around the T$_{N}$. The hysteresis starts at 72 K and closes at 45 K.
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Figure 5.1. Resistivity of Tetragonal SrFeO\textsubscript{3-δ} system measured while cooling and warming in zero magnetic field.

Figure 5.2. Resistivity of Tetragonal SrFeO\textsubscript{3-δ} system measured while cooling and warming in the presence of 80 kOe field.
Figure 5.2 depicts the temperature variation of resistivity, measured in the presence of 80 kOe magnetic field during both cooling and warming cycles. The overall shape of the resistivity curve is very similar to that observed in the zero field case. The measured resistivity at the lowest temperature is smaller than the zero field and also temperature range over which the hysteresis observed between the cooling and warming cycles is small in comparison to the zero field case.

The magnetoresistance (MR) is the fractional change in resistivity ($\rho$) on the application of external magnetic field and is defined as $\text{MR} = \frac{[\rho(H) - \rho(0)]}{\rho(0)}$. To measure MR in these materials, $\rho(H)$ is measured both while cooling and warming in the presence of a field of 80 kOe.

A comparative assessment of the temperature variation of zero-field resistivity $\rho(0)$ and the 80 kOe resistivity $\rho(H)$ is carried out in Figure 5.3 for the warming cycles. It is clear from the figure that $\rho(H)$ shows a decrease in comparison to the $\rho(0)$ as a function of temperature, indicating negative MR. With increasing temperature, MR decreases indicating decreasing trend in magnetic interactions, possibly by a hopping electron. The tetragonal phase transition is clearly visible in both cases as a slope change, with a slightly reduced temperature for the 80 kOe curve. The calculated MR is shown in Figure 5.4. MR is negative.
in the entire temperature range with a maximum of -15.2% at 76 K, which is close to the $T_N$ of the sample. The maximum MR close to $T_N$ is due to the enhanced spin fluctuations. Even though signatures of cubic and orthorhombic minor phases are observed in the low field magnetization data of T0, no such signatures are noticed either in the resistivity or MR of this sample, indicating that the trace

Figure 5.3. Resistivity of Tetragonal SrFeO$_{3-\delta}$ system measured in the warming cycle at $H = 0$ and $H = 80$ kOe.
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phases, if present, are essentially of no consequence. The relatively smaller MR (compared to those reported in the literature) in the present case could be due to the presence of nanograins (seen in microstructure).

5.4 Resistivity and Magnetoresistance of Ti doped SrFeO$_3$-$\delta$

Resistivity and magnetoresistance of 10%, 20% and 30% of Ti doped SrFeO$_3$-$\delta$ (T1, T2 and T3) are measured by the four probe method on PPMS. Figure 5.5 shows $\rho$ (H=0) of T1 measured in both cooling and warming cycles. There is a sharp increase in resistivity close to 74 K and unlike in T0, $\rho$(H=0) could be measured only down to 55 K, which lies above the magnetic ordering temperature of T1 (50 K). The $\rho$(H=0) at 55 K is $4.2 \times 10^4$ $\Omega$-cm, which is much higher in comparison to T0. The hysteresis between the cooling and warming cycles is also much smaller.
in comparison to T0. Figure 5.6(a) shows $\rho$ (H =80 kOe) of T1 measured in both cooling and warming cycles. MR as a function of temperature is shown in Figure 5.6(b). It is interesting to note that from RT to 105 K the MR is positive with a maximum value of 11 % close to RT. The MR decreases continuously with decrease in temperature and at 105 K MR changes sign and becomes negative with further decrease in temperature the negative MR increases and close to 58 K reaches a maximum of 4.3%. The positive MR observed in similar systems is, in general attributed to the opening of the gap.

Figure 5.5. Resistivity of SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$ system measured in zero field while cooling and warming.
Figure 5.6(a) Resistivity of SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$ system while cooling with zero and 80 kOe field.

Figure 5.6 (b) Temperature dependence of MR of T1 at H = 80 kOe.
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The resistivity $\rho$ (H=0) increases more sharply at a higher temperature of 140 K and the resistivity could be measured only up to 104 K, reaching a maximum value of $2.3 \times 10^5$ $\Omega$-cm. No hysteresis is observed between the cooling and warming cycles. The figure 5.8 shows the cooling and warming $\rho$ (H = 80 kOe) data of T2 system. Field has a very little effect on the resistivity of this sample, as the sample is in the paramagnetic

Figure 5.7. Resistivity of SrFe$_{0.8}$Ti$_{0.2}$O$_{3-\delta}$ system measured in zero field while cooling and warming.
state throughout the measurement temperature range. The lowest temperature up to which $\rho(H = 80 \text{ kOe})$ could be measured and the value of resistivity at this temperature match well with those of zero field measurement. The calculated MR for the T2 is shown in figure 5.9. A small positive MR of 0.9% is observed close to RT. MR decreases continuously with decrease in $T$. The sign of MR changes at 160 K and with further lowering of temperature, negative MR increases and reaches a maximum value of -1.1% at 105 K.

Figure 6.8 Resistivity of SrFe$_{0.8}$Ti$_{0.2}$O$_{3-\delta}$ (T2) at $H = 80 \text{ kOe}$.
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Figure 5.9  Temperature dependence of MR in SrFe\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3-\delta} at 80 kOe field.

Figure 5.10  Resistivity of SrFe\textsubscript{0.7}Ti\textsubscript{0.3}O\textsubscript{3-\delta} in zero field.
Figure 5.10 shows $\rho(H = 0)$ of T3 measured in cooling and warming cycles. Similar to T2 sample, no hysteresis is observed between the cooling and warming cycles. A sharp increase in $\rho$ is seen for $T < 190$ K. The resistivity value reaches the maximum compliance value at $T = 161$ K and hence $\rho(T)$ could not be measured below this temperature. $\rho(H = 80$ kOe, $T)$ of T3 is shown in figure 5.11. Similar to the zero field data, no hysteresis is observed in this case also and the resistivity could not be measured below 164 K.

![Figure 5.11 Resistivity of SrFe$_{0.7}$Ti$_{0.3}$O$_{3-\delta}$ (T3) at H = 80 kOe.](image)

The calculated MR is shown in figure 5.12. MR is negative in the entire temperature range. At room temperature there is not much change in
MR and negative MR increases continuously with the decrease in temperature and finally at 164 K reaches 9%.

![Figure 5.12 Change in MR with 8T field of SrFe$_{0.7}$Ti$_{0.3}$O$_{3-\delta}$.](chart)

In all the Ti doped samples, the resistivity could be measured only in the paramagnetic region and this explains the small magnitude of MR.

### 5.5 3D Variable Range Hopping and Data Analysis

The most notable aspect of the transport properties is the observation of 11% positive MR at room temperature and positive MR
from RT to 104 K for T1. MR has a small positive value at RT for T2 and remains positive up to 160 K. It is obvious that the increase in resistivity on the application of a magnetic field is related to either the opening up of the gap between the bands or due to the increased scattering of electrons. $\rho(H=0, T)$ and magnetization data point to localized electron spin moments in all the samples giving rise to a semiconducting behavior. Such antiferromagnetic-insulators are classified as Mott insulators where a metal-insulator (M-I) transition could occur due to electron-electron correlation. Anderson pointed out that the disorder in a solid could introduce random potential energy in the lattice which ultimately leads to a localization of the electron wave function.

At low temperatures, Anderson localization occurs in many disordered metals, semiconductors and perovskite type oxides. The most striking examples of this category are high $T_c$ superconductors and colossal magnetoresistance oxides like La(SrMn)O$_3$. In these materials, conduction mechanism is governed by ‘variable range hopping’ (VRH), where the hopping energy ($W$) varies with a temperature [20-24]. The resistivity in the present system of SrFe$_{(1-x)}$Ti$_x$O$_{3-\delta}$ [25-27] is analyzed in terms of ‘variable range hopping’, a mechanism where the electron hops between localized antiferromagnetic states. Such hopping mechanism can be described using the following equation
where the dimensionality of the hopping is 3, $T_0$ is a characteristic temperature related to the density of states at the $E_F$. In materials undergoing VRH, the plot of $\ln \rho$ vs $T^{1/4}$ appears as a straight line. The localization length $\lambda'$, calculated from the relation

\begin{equation}
\lambda' \end{equation}

indicates the extent to which the 3d orbitals of the metal atom overlap with the oxygen 2p orbitals.

Figure 5.13(a) Resistivity of $T_0$ along with the fit (straight line passing through the data points) based on the three-dimensional variable range model.
Figure 5.13(b) Resistivity of T1 along with the fit (straight line passing through the data points) based on the three-dimensional variable range model.

Figure 5.13(c) Resistivity of T2 showing fit to variable range hopping model
Figure 5.13(d) Resistivity of T3 along with the fit (straight line passing through the data points) based on the three-dimensional variable range model.

Figure 5.13(a), 5.13 (b) shows the fits to the resistivity data of T0 in the temperature range 130-270 K and to $\rho(H = 0, T)$ for T1 from 185 K to 300 K. The values of $T_0$ and $\Omega$ calculated from Eqs. (5.1) and (5.2) for different samples are tabulated in Table 5.1. For temperatures lower than 130 K, $\rho( H = 0, T)$ for T0 did not fit to either $d=3$ or 2, indicating a mechanism of conduction that is more complex than variable range hopping. This is understandable considering the disproportionateness of varying valence states of Fe at low temperatures and their arrangement in the crystal lattice.
In a solid with a high degree of disorder, a large network of varying potential barriers hampers the mobility of the electron and in such cases, the electron percolates through the network in a set of varied jumps than a single jump, assisted by the phonons to reach the final

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field (kOe)</th>
<th>Range (K)</th>
<th>T0 (K)</th>
<th>$l$ (Å) localization length</th>
<th>R (Å)</th>
<th>W (mev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>0</td>
<td>142-300</td>
<td>5.65×10³</td>
<td>2.09</td>
<td>5.7</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>142-300</td>
<td>6.79×10³</td>
<td>1.97</td>
<td>5.6</td>
<td>37.8</td>
</tr>
<tr>
<td>T1</td>
<td>0</td>
<td>78-299</td>
<td>9.81×10⁶</td>
<td>0.81</td>
<td>4.5</td>
<td>72.8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>86-192</td>
<td>1.01×10⁷</td>
<td>0.80</td>
<td>4.5</td>
<td>72.8</td>
</tr>
<tr>
<td>T2</td>
<td>0</td>
<td>111-299</td>
<td>1.46×10⁸</td>
<td>0.33</td>
<td>3.6</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>103-299</td>
<td>1.44×10⁸</td>
<td>0.33</td>
<td>3.6</td>
<td>142</td>
</tr>
<tr>
<td>T3</td>
<td>0</td>
<td>160-300</td>
<td>4.10×10⁸</td>
<td>0.23</td>
<td>3.2</td>
<td>202</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>165-300</td>
<td>3.91×10⁸</td>
<td>0.24</td>
<td>3.2</td>
<td>202</td>
</tr>
</tbody>
</table>

Table 5.1 Calculated values of $T_0$, $l$, $R$, and $W$ at 300 K for Sample T0, T1, T2 and T3 at 0 and 80 kOe.
state. The energy needed \( (W) \) is gained from the phonons and the electron attains its final state through the indirect hops assisted by the two levels of phonon energy. The necessary energy for a hop can be calculated using the relation,

\[
W = 3/[4\pi R^3N(E_F)]
\]  - (5.3)

where \( R \) is the hopping distance in Å calculated from

\[
R = (3/(2\pi N(E_F)kT))^{1/4}
\]  - (5.4)

The calculated values of \( T_0 \), \( R \) and \( W \) (\( R&W \) at RT) using Eqs. (5.1)- (5.4) for all the samples at \( H=0 \) and \( H=80 \) kOe are given in Table 5.1. A constant value for density of states at the Fermi level, \( N(E_F) \), \( 3.6 \times 10^{22} \text{ eV}^{-1}\text{cm}^{-3} \), estimated for the parent compound [28] is taken for all the doped samples as well. From the table, it can be noted that increasing magnetic field causes an increase in \( T_0 \), which, in turn, for the samples \( T_0 \) and \( T_1 \) causes a decrease in the localization length \( \rho \) while the field has practically no effect on \( T_0 \) and \( T_1 \) in the samples \( T_2 \) and \( T_3 \).

It is known that the spatial extension and the orbital overlap could decide the overall increase or decrease of resistance depending on which one is greater. A comparison between the localization lengths \( \rho \) of measured data at \( H = 0 \) and \( H = 80 \) kOe indicates that the value of \( \rho \) at \( 80 \) kOe is smaller than that calculated for \( H = 0 \) (Table 5.1). A decrease
in localization length directly affects the overlap integral resulting in the shrinkage of orbital overlap causing an increase of the resistance with field. On the other hand, with Ti doping the differences in the values of $T_{0}$ and $T_{1}$ are marginal influencing the overall magnetoresistance, which is very small.

5.6 Conclusion

$\rho(\text{H}=\text{0}, \text{T}), \rho(\text{H}=\text{80} \text{ kOe, T})$ is measured in both cooling and warming cycles for T0, T1, T2 and T3 samples. The resistivity of the samples increase with increase in doping which can be understood due to the increase in disorder and also with the decrease in the overlap between the metal and oxygen orbitals. MR is negative and the maximum MR is found to be close to the $T_{N}$ of the undoped sample. The small MR in this case may be due to the increase in resistivity arising due to the nanograin boundaries. All the Ti doped samples show completely insulating behaviour much above the magnetic ordering temperature, hence the field has a very little role to play in changing the resistivity. VRH mechanism seems to explain the transport in the temperature range of 150 – 300 K.
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