Chapter 4

RESISTIVITY STUDIES

This chapter deals with the resistivity studies on $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_y$ ($M = \text{Pr, Ce} \& \text{Tb}$) samples as a function of temperature. The systematic resistivity measurements on these samples were carried out by the standard four probe method as a function of temperature in the temperature range 8-300 K using a closed cycle He-refrigerator. The results obtained are presented below.

4.1 Results

Fig.4.1 shows the temperature dependence of resistivity for various members of the Pr-doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (Bi-2212) system. In the normal state, the samples for $0 < x < 0.55$ are characterized by linear temperature dependence of resistivity of the form

$$\rho = \rho_o + \alpha T$$  \hspace{1cm} (4.1.1)

where $\rho_o$ and $\alpha = (\frac{d\rho}{dT})$ are the residual resistivity and the metallicity of the material respectively. In the normal state, the temperature derivative of resistivity is positive. The sample with $x = 0.6$ shows semiconducting behavior throughout the temperature range of measurement. The room temperature resistivity ($\rho_{300}$), residual resistivity ($\rho_o$), metallicity ($\alpha$), superconducting onset temperature $T_c$(onset), the zero resistivity temperature $T_c$(zero) and the temperature at which $d\rho/dT$ is maximum $T_c$, are given in Table-4.1. A linear increase in $\rho_{300}$ and $\rho_o$ is observed with increasing Pr-content ($x$)
Fig. 4.1 Plot of resistivity vs. temperature for Bi$_2$Sr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ samples.
Table 4.1

Various physical parameters obtained for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_y$
(M = Pr, Ce and Tb) systems

<table>
<thead>
<tr>
<th>sample</th>
<th>$\rho_{300}$ (m$\Omega$ cm)</th>
<th>$P_o$ (m$\Omega$ cm)</th>
<th>$a$ (µ$m$ cm$K^{-1}$)</th>
<th>$T_c$(zero) (K)</th>
<th>$T_c$(onset) (K)</th>
<th>$T_c$ (K)</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pr-doped</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.56</td>
<td>0.14</td>
<td>4.7</td>
<td>78</td>
<td>86</td>
<td>82</td>
<td>0.20</td>
</tr>
<tr>
<td>0.1</td>
<td>2.84</td>
<td>0.81</td>
<td>6.7</td>
<td>77</td>
<td>93</td>
<td>89</td>
<td>0.18</td>
</tr>
<tr>
<td>0.2</td>
<td>4.20</td>
<td>1.09</td>
<td>10.3</td>
<td>75</td>
<td>93</td>
<td>87</td>
<td>0.13</td>
</tr>
<tr>
<td>0.3</td>
<td>5.08</td>
<td>1.94</td>
<td>10.3</td>
<td>61</td>
<td>92</td>
<td>80</td>
<td>0.12</td>
</tr>
<tr>
<td>0.4</td>
<td>5.68</td>
<td>2.87</td>
<td>9.4</td>
<td>37</td>
<td>87</td>
<td>64</td>
<td>0.10</td>
</tr>
<tr>
<td>0.45</td>
<td>6.62</td>
<td>4.23</td>
<td>8.2</td>
<td>20</td>
<td>58</td>
<td>42</td>
<td>0.08</td>
</tr>
<tr>
<td>0.5</td>
<td>9.49</td>
<td>7.00</td>
<td>8.3</td>
<td>-</td>
<td>52</td>
<td>29</td>
<td>0.07</td>
</tr>
<tr>
<td>0.55</td>
<td>10.90</td>
<td>8.56</td>
<td>7.9</td>
<td>-</td>
<td>54</td>
<td>31</td>
<td>0.07</td>
</tr>
<tr>
<td>0.6</td>
<td>32.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Ce-doped</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>3.01</td>
<td>1.25</td>
<td><strong>5.9</strong></td>
<td>69</td>
<td>87</td>
<td>78</td>
<td>0.12</td>
</tr>
<tr>
<td>0.1</td>
<td>3.89</td>
<td>1.48</td>
<td><strong>8.0</strong></td>
<td>67</td>
<td>85</td>
<td>77</td>
<td>0.12</td>
</tr>
<tr>
<td>0.15</td>
<td>16.6</td>
<td>14.39</td>
<td>7.4</td>
<td>20</td>
<td>88</td>
<td>65</td>
<td>0.10</td>
</tr>
<tr>
<td>0.2</td>
<td>19.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>54</td>
<td>30</td>
<td>0.07</td>
</tr>
<tr>
<td>0.3</td>
<td>72.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>75.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Tb-doped</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>3.16</td>
<td>1.14</td>
<td>6.8</td>
<td><strong>63</strong></td>
<td><strong>98</strong></td>
<td>92</td>
<td>0.16</td>
</tr>
<tr>
<td>0.1</td>
<td>3.22</td>
<td>0.96</td>
<td>7.6</td>
<td>60</td>
<td><strong>98</strong></td>
<td>92</td>
<td>0.16</td>
</tr>
<tr>
<td>0.15</td>
<td>5.87</td>
<td>3.13</td>
<td>9.3</td>
<td>54</td>
<td>98</td>
<td>89</td>
<td>0.14</td>
</tr>
<tr>
<td>0.2</td>
<td>9.27</td>
<td>6.13</td>
<td>10.7</td>
<td>30</td>
<td>98</td>
<td>83</td>
<td>0.13</td>
</tr>
<tr>
<td>0.3</td>
<td>16.85</td>
<td>12.56</td>
<td>14.6</td>
<td>-</td>
<td>86</td>
<td>61</td>
<td>0.10</td>
</tr>
<tr>
<td>0.4</td>
<td>11.25</td>
<td>5.37</td>
<td>19.8</td>
<td>-</td>
<td>84</td>
<td>33</td>
<td>0.07</td>
</tr>
<tr>
<td>0.5</td>
<td>160.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>271.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
upto \( x = 0.55 \). With increase in Pr-content \((x)\), the superconducting transition width is found to increase. The Metal-Insulator (MI) transition \( i.e., \) the change in the sign of the temperature coefficient of resistivity is observed for room temperature resistivity value \( \approx 2 \times 10^{-2} \Omega \text{ cm} \). With increasing Pr-content, there is no significant change in \( T_c(\text{zero}) \) for \( x \leq 0.2 \); while for \( 0.3 < x < 0.55 \) the decrease is rather fast. The \( T_c(\text{onset}) \) increases with increasing \( x \) upto \( x < 0.2 \) and for \( x > 0.3 \) it decreases. \( T_c(\text{zero}) \) is observed for samples with \( x < 0.45 \) whereas only \( T_c(\text{onset}) \) is seen for \( x < 0.55 \). The sample with \( x = 0.6 \) shows semiconducting behavior.

Fig.4.2 shows the temperature dependence of resistivity for various members of the Ce-doped series. The superconducting samples with \( 0 < x < 0.15 \) are characterized by linear temperature dependence of resistivity in the normal state with positive temperature derivative of resistivity \((\alpha)\). The sample with \( x = 0.2 \) shows weak semiconducting behavior and superconducting onset temperature around 54 K. Samples with \( x = 0.3 \) and \( x \approx 0.4 \) show semiconducting behavior throughout the temperature range. The values of \( \rho_{300}, \rho_{0}, \alpha, T_c(\text{onset}), T_c \text{ and } T_c(\text{zero}) \) are listed in Table-4.1. Slow increase in \( \rho_{300} \) and \( \rho_{0} \) with increasing Ce concentration \((x)\) upto \( x = 0.1 \) is observed. The increase is sharp as we go towards the higher dopant concentrations. \( T_c(\text{onset}) \) is more or less constant and \( T_c(\text{zero}) \) decreases with increase in \( x \). The pronounced change in the normal state resistivity and its temperature dependence is accompanied by the drastic decrease in \( T_c \) as \( x \) increases from 0.1 to 0.2. This means that upto 10\% of Ce substitution, the dopant can be accommodated without seriously affecting the superconducting matrix. With increase in \( x \), the transition width is also found to increase. For Ce-substitution between 10-20\% of Ca, the \( T_c \) depression rate is very fast in comparison to other rare-earth substitutions. In this system also MI transition is observed around the normal state resistivity value of \( 2 \times 10^{-2} \Omega \text{ cm} \).
Fig. 4.2 Plot of resistivity vs. temperature for Bi$_2$Sr$_2$Ca$_{1-x}$Ce$_x$Cu$_2$O$_y$ samples.
Fig. 4.3 shows the resistivity variation as a function of temperature for various samples of Tb-doped series with 0<x<0.6. Samples with x<0.4 are superconducting and characterized by linear temperature dependence of resistivity in the normal state [Eqn.(4.1.1)]. Samples with x = 0.5 and 0.6 are semiconducting. The room temperature resistivity $\rho_{300}$, $\rho_{0}$, $T_c$(onset), $T_c$(zero) and $T_c$ are given in Table-4.1. The $\rho_{300}$ and $\rho_{0}$ values are found to increase with increase in dopant concentration except for the sample with x = 0.4. The increase in $\rho_{300}$ is sharp for x > 0.4. The $\alpha$ value increases with increasing x value. The MI transition is observed when $\rho_{300} \approx 2 \times 10^{-2}\Omega\text{cm}$. $T_c$(zero) decreases with the increase in dopant concentration. Initially $T_c$(onset) increases when x is increased from 0 to 0.05 and then it attains a constant value for 0.05<x<0.2. Only $T_c$(onset) could be observed for sample with x = 0.4. From the $T_c$ vs x plot, it can be seen that $T_c$ initially increases marginally with x, reaching a maximum value at around x = 0.1 and then it decreases rapidly for higher dopant content [Fig.4.4]. The transition broadening takes place with increase in x value. The MI transition is observed at around x = 0.5.

4.2 Analysis of the resistivity data of the superconducting samples

The observed increase in $\rho_{300}$ and $\rho_{0}$ can be attributed to the impurity scattering due to the introduction of dopant ion into the lattice. Similar kind of changes are reported in other rare-earth doped systems [1].

The transition broadening is observed in all the three series of samples with increase in x value. The transition broadening may indicate the presence of secondary phases, but XRD patterns do not indicate the presence of any secondary phases. Rare-earth substitution in Bi-2212 system is expected to reduce the hole concentration and raise
Fig. 4.3 Plot of resistivity vs. temperature for Bi$_2$Sr$_2$Ca$_{1-x}$Tb$_x$Cu$_2$O$_y$ samples.
Fig. 4.4 Plot of $T_c$ vs. $x$ for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_y$ ($M = \text{Pr, Ce & Tb}$) samples
the oxygen content [2]. From STS studies, Samanta et al [3] found extra oxygen intercalated in the redox Bi-0 layers. The observed transition broadening may be due to the intercalated oxygen between the Bi-0 layers. Chen et al [4] in the Pr-doped Bi-2212 system attributed this transition broadening to the existence of two phases with different modulation periods. From the electron diffraction studies, they found two modulated structures, one with a long period and other with short period. They have attributed the short-period phase to a Pr-poor phase which possess high $T_c$, and the long period phase to a Pr-rich phase having low $T_c$. The increase in transition width suggest the intergrowth of these two phases in grains. At higher concentrations, the long period phase governs the transport. This kind of model was used to explain the Pr-doping effects in YBa$_2$Cu$_3$O$_{7-\delta}$ [Y-123] also [5-6].

Superconducting phase diagrams for several high $T_c$ oxides [7-10] show that $T_c$ increases with increase in carrier concentration, passes through a maximum and then falls steeply to zero when the carrier concentration reaches a critical value. So, the changes in $T_c$ values can be explained in terms of change in carrier concentration. The increase in dopant content leads to a decrease in carrier concentration. Optimum carrier concentration (for which maximum $T_c$ is expected) is achieved as the dopant content increases, leading to an increase in $T_c$(onset).

Presland et al [10] have found that the phase diagram for several doped cuprate systems is well described by the parabola

$$\frac{T_c}{T_c(max)} = 1 - 82.6(p - 0.16)^2$$

(4.2.1)

For Bi-2212 system $T_c$ (max) = 92 K is taken to calculate the $p$ value for the superconducting samples. The estimated $p$ values are given in Table-4.1. The initial increase
in $T_c$ with increase in dopant content indicates that undoped sample is slightly in the overdoped region.

The $T_c$ depression rate is faster in the case of Ce-doped series compared to the other two series [Fig. 4.4] of samples. In other studies on rare-earth doped Bi-2212, the critical concentration $x_{cr}$ at which $T_c(zero)$ goes to zero is reported to be generally between 0.4 and 0.6 [11-21]. In the present study, the critical concentration of Ce is about half that of other trivalent rare-earth dopant [22-24]. From this we can infer that Ce-exists predominantly in +4 valence state. The faster decrease observed in the c-lattice parameter of Ce-doped Bi-2212 also supports this conclusion.

Jayaram et.al. [19] explained the observed gradual decrease in $T_c$ as a function of normal state resistivity (in the range 3-12m$\Omega$ cm) in the Gd-doped Bi-2212 samples on the basis of a theoretical model derived for 2D conventional superconductors considering the disorder effects [25]. The $T_c$ depression rate observed in the present series of samples with the normal state resistivity in the range 3-12m$\Omega$ cm does not permit the analysis on the lines adopted by Jayaram et al [19].

The rare-earth substitution at Y-site in Y-123 have been well studied. The $\text{PrBa}_2\text{Cu}_3\text{O}_7$ compound is the only isostuctural member of the series of $\text{RBa}_2\text{Cu}_3\text{O}_7$ compounds, which is non-metallic and non-superconducting [26]. Several reasons have been proposed for the suppression of superconductivity by the Pr-substitution in $\text{RBa}_2\text{Cu}_3\text{O}_7$ [27] i.e., hole filling effect, pair breaking effect via exchange scattering of mobile holes by Pr-magnetic moments and hole localization effect. The origin of $T_c$ suppression in Y-123 by Pr-substitution still remains a subject of controversy.
The magnetic property measurements [28] suggested that Pr\textsuperscript{+4} ion in Pr-doped Y-123 system fills the holes in the conduction band. The recovery of superconductivity by partial substitution of Ca in PrBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} is interpreted as a verification of this view (29). However, electron energy loss spectroscopy (EELS) study [30] indicates that the total hole concentration is uneffect\textsuperscript{ed} by Pr. Optical measurements [30,31] such as x-ray photoemission spectroscopy suggest that Pr exists as a +3 ion and localizes the holes. The localization of holes is attributed to the hybridization of Pr-4/\textsuperscript{f} states with the Cu3d-O2p states in the CuO\textsubscript{2} planes [32,33]. From the studies like Hall effect and muon spin relaxation measurements [34], it is apparent that substitution of Pr at Y-site reduces the mobile hole concentration while the total hole concentration does not change.

It is well known for conventional superconductors that magnetic impurities have dramatic effects on \(T_c\). Abrikosov and Gorkov (AG) developed a theory to explain the suppression of \(T_c\) due to magnetic impurity [35]. According to AG theory, the magnetic impurity interacts with the spins of the electrons in the Cooper pairs, making the spin states of the electrons change, which leads to the breaking of Cooper pairs and in turn suppression in \(T_c\). The AG interactions deal with the exchange interaction between the magnetic impurity (of spin S) and a conduction electron (of spin s) given by \(H_{ex} = -JSs\) where J is the exchange integral, which characterizes the strength and the sign of the interaction. The theory predicts a decrease in \(T_c\) with x given by a universal relation

\[
\ln(T_c/T_{co}) = \Psi(1/2) - \Psi(1/2 + 0.14T_{co}x/x_{cr}T_c) \tag{4.2.2}
\]

or

\[
T_c/T_{co} = f(x/x_{cr}) \tag{4.2.3}
\]

where x is the impurity concentration, \(T_c\) is the superconducting transition temperature of the sample with impurity concentration x. \(x_{cr}\) corresponds to the concentration
for $T_c = 0$ (complete suppression of superconductivity) and $\gamma$ is digamma function.

For small values of $x$

$$T_c \approx T_{co} - \left[ \frac{\pi^2}{4k_B} N(E_F)J^2(g - 1)^2J(J + 1) \right] x$$  \hspace{1cm} (4.2.4)

$N(E_F)$ is the density of states at the Fermi level. $g$ and $J$ are, Lande $g$ factor and total angular momentum for the Hund's rules ground state of impurity ion respectively. According to this formula, $T_c$ depression should follow approximately the de Gennes factor ($G = (g-1)^2 J(J+1)$) and $T_c$ is expected to decrease linearly with $x$ at low carrier concentrations and at a critical concentrations $x_{cr}$, superconductivity completely vanishes. Substituting the slopes of the $T_c$ vs $x$ plot in the following equation one can calculate $x_{cr}$

$$x_{cr} = \frac{-\pi^2e^{-r}}{(dT_c/dx)} \left[ \frac{T_{co}}{8} \right]$$  \hspace{1cm} (4.2.5)

where $r = -0.5772$ is the Euler's constant.

It is seen that strong magnetic ions like Gd are not affecting the $T_c$, whereas Pr affects the $T_c$ drastically. This result is not in accordance with the theory.

Zhao et al [36] suggested that the observed deviations from AG pair-breaking theory may be explained by taking into account the correlations between the spins of the impurity and their ordering. In the AG pair breaking theory, there are two basic assumptions. First, the magnetic impurities are distributed randomly. Secondly, the spins of the magnetic impurity do not show any correlation (such as magnetic order). These assumptions can be satisfied in conventional superconductors because $x_{cr}$ is low. In the case of high $T_c$ materials, $x_{cr}$ is high; inter impurity interaction may arise. The spins of the magnetic impurity may have some correlation and this will weaken the effect of pair breaking. The inhomogeneous distribution of the dopant ion may weaken the effect of pair-breaking.
Considering the above factors, the deviation from the $T_c$ vs $x$ plot may be qualitatively explained.

Neumeier et al [37] from their studies on Pr doped Y-123 system, (Y partially replaced by Ca), suggested an empirical relation which incorporates the hole filling (or localization) of mobile holes in the CuO$_2$ planes and superconducting electron pair breaking via exchange scattering of mobile holes in the CuO$_2$ planes by Pr-magnetic moments [37,38]. Both these effects are assumed to involve hybridization of Pr 4f with O 2p states [39]. Hybridization could generate an appreciable exchange interaction between the Pr magnetic moments and the spins of the mobile holes in the CuO$_2$ planes. This results in a depression of $T_c$ with paramagnetic impurity concentration that is linear in the low concentration regime [40,41].

Infante et al [42] discussed the $T_c$ suppression in LaCaBaCu$_3$O$_{7-\delta}$ (the results obtained for this system are quantitatively similar to $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system) in view of a percolation model. According to this model, $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system contains two kinds of unit cells: Y- containing and Pr-containing. The unit cells with Y have itinerant electrons and those with Pr have localized electrons. The connectivity between these cells determines the conduction. The important conductivity is within the planes and the relevant geometry is square planar array. The site percolation threshold is then the relevant parameter in the connectivity problem. This value is 0.59 for square planar array [43]. That means for $x<0.41$, the unit cells containing Y are connected and the system resembles $YBa_2Cu_3O_{7-\delta}$; while for $x>0.59$ the unit cells containing Pr are connected so that the system resembles $PrBa_2Cu_3O_{7-\delta}$. In the region close to $0.41<x<0.59$, there is no percolation of either of the unit cells and in effect a mixed phase behavior is
expected. The region in which Y unit cells are connected is the metallic region. Superconductivity appears in this region only. The superconductivity transition is expected to be sharp in the region for $x<0.4$. The nature of the resistivity changes for the $x>0.4$ samples, which are at the border line of MI transition, is consistent with the nature of resistivity changes associated with the connectedness transition in other percolating systems of thin film superconductors [44]. The classical percolation threshold may not hold good for the superconductivity transition because of constraints on the size due to coherence length. This model is dependent only on the geometry and therefore explains the resistivity behavior of the both $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and $LaCaBa_2Cu_3O_{7-\delta}$ systems. The relevance of the percolation model in the MI transition in 3D perovskite oxides has been discussed by Ganguly [45]. In various $La_{1-x}Sr_xBO_3$ systems ($B = Co, V$ and $Mn$), metallization appears at a value of $x = 0.25$ and $0.3$ which is approximately equal to the site percolation threshold ($\sim 0.3$) of cubic system.

In the present $Bi_{2}Sr_{2}Ca_{1-x}M_xCu_2O_y$ system, the MI transition is observed around $x = 0.6$ for $M = Pr$, around $x = 0.2$ for $M = Ce$ and around $x = 0.4$ for $M = Tb$. This transition can not be explained in view of percolation model because this model depends only on the geometry of the system and MI transition is expected to occur at the same dopant concentration ($x$) in all the three systems.

$T_c$ vs $x$ plot for the present systems show that Ce suppresses the $T_c$ faster than the other two rare-earth ions. The $T_c$ depression rates of Pr and Tb doped $Bi-2212$ systems are similar. The difference in the suppression rates at higher dopant concentrations ($x$), may be ascribed to the difference in ionic radii of the two rare-earth ions. The $T_c$ suppression rate in the present system has no correlation with the magnetic nature of the dopant ion. According to the AG theory, the $T_c$ suppression rate should vary linearly
with the concentration of the dopant ion at lower concentrations, which is not observed in the present system. The $T_c$ depression rate should be more for strong magnetic ion. In our case $\text{Ce}^{+4}$ ion which is non-magnetic shows a faster depression. The disorder introduced by the dopant ion may leads to Anderson localization [46], thereby depressing the $T_c$. Still the faster $T_c$ depression in the case of Ce-doped series is difficult to explain.

The $T_c$ suppression in the present system can be explained by hole filling mechanism. It is well established that the transition temperature in high $T_c$ superconductors is highly sensitive to the hole concentration in $\text{CuO}_2$ planes [7,8]. The $T_c$ suppression in the present system could be due to the extra electrons introduced by the substitution of trivalent rare-earth ion at Ca site which fills the $\text{Cu}_3d - \text{O}_2p$ band. From the faster depression rate of $T_c$ in the case of Ce doped Bi-2212 system, it can be inferred that Ce predominantly exist in +4 valence state. The faster decrease in the c-lattice parameter in the case of Ce doped Bi-2212 also supports this conclusion. Moreover, the closed shell of $\text{Ce}^{+4}$ precludes the possibility of any pair breaking interaction. From the $T_c$ depression rate and the decrease in c-lattice parameter, it can be concluded that Pr and Tb ions predominantly exist in the +3 valence state in the Bi-2212 system. The $T_c$ suppression in the case of non-magnetic Y at the Ca-site follows the same trend as that of Pr and Tb. From the dc susceptibility studies [47] on Pr and Gd in Bi-2212, it has been pointed out that there is no interaction between rare-earth ion magnetic moments via $\text{Cu}_3d-\text{O}_2p$ orbitals. This indicates that magnetization of the rare-earth ion has no additional effect on $T_c$ suppression.
4.2.1 Theoretical models on T-linear resistivity of superconducting samples

The resistivity varies linearly with T in the normal state of the present superconducting samples.

The resistivity data reported in the literature show that, high $T_c$ superconductors are generally characterized by linear temperature dependence of resistivity in the normal state over a wide temperature range [48-50]. The resistivity of La-system is linear in the temperature range, $T_c$ to 1000 K. The linearity extends upto $\approx 600$ K in Y-123 system. The residual resistivity is very small. There are a number of theoretical interpretations [51-55] proposed to explain the T-linear resistivity; ranging from electron-phonon interaction picture to van Hove singularity picture. A brief description about some of these models is given in the following pages.

The linear temperature dependence of resistivity has been interpreted in view of standard Bloch-Gruneisen [BG] transport theory based on the electron-phonon interaction [56,57]. Taking the scattering of electrons by the lattice vibrations into account, the temperature dependence of phonon-limited resistivity is given by the following BG formula

$$\rho(T) = \left(\frac{T}{\theta_D}\right)^5 \int_0^{T/\theta_D} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}$$ (4.2.6)

Here, $\theta_D$ is an effective 'transport' Debye temperature. At high temperatures ($T \gg \theta_D$), resistivity is approximately linear in T down to $T \approx \theta_D/4$, and crosses over to a higher power of T (usually $T^5$) at $T \ll \theta_D$. The observed T-linear resistivity at high temperatures observed in superconductors may be explained in view of phonon-limited resistivity and at low temperatures the sample goes to superconducting state and $\rho(T)$ is zero. In order to make the crossover to $T^8$ dependence invisible, $T_c$ should be comparable to or higher than the cross over temperature of $\approx \theta_D/4$. 
Based on the observed linearity, Gurvitch et al. [50] derived an upper-bound estimate for electron-phonon coupling constant $\lambda_{e-ph}$ (for Y-123 $\lambda_{e-ph}=0.3$) and concluded that high $T_c$s must be non-phonon in nature.

The BG formula can give a reasonable fit to the $\rho(T)$ curve in the case of YBa$_2$Cu$_3$O$_7$ and Bi$_2$Sr$_2$CaCu$_2$O$_y$, which have their $T_c$ in the 90 K range. However, for Bi$_2$Sr$_2$CuO$_y$, which has a much lower $T_c$, Martin et al. [58] have demonstrated that force-fitting the Bloch-Gruneisen formula to the observed $\rho(T)$, linear in $T$ down to $\approx$ 10 K would demand $\theta_D \approx 35$ K, which is probably lower than a physically reasonable lower limit.

Although BG formula with cutoff at $T_c$ seems to give a reasonable fit in a few individual cases, the electron-phonon scattering alone does not seem to give a coherent account of $\rho(T)$ in all high $T_c$ cuprates. If phonons were the only excitations coupled to electrons in any significant way, electron pairing at such high temperatures would probably not take place. The crossover of temperature dependence of resistivity from $T$ to $T^2$ is reported in La-system [59] and Tl-2201 [60,61] systems. The $T^2$ dependence of $\rho$ can not be interpreted in terms of classical BG picture. To account for this cross over, the scattering mechanisms of electronic origin are discussed by a number of authors. In an ordinary Fermi liquid, the electron-electron scattering gives a $T^2$ dependence of the resistivity.

Moriya et al. [62] calculated the temperature dependence of resistivity by assuming that the electrons are scattered by 2D antiferromagnetic (AF) spin fluctuations and explained the linear temperature dependence of resistivity. They also obtained a $T^2$ dependence at low temperatures in nearly AF regime, which is characteristic of Fermi
liquids. The relevant temperature scale for the crossover is set by the width of the spin fluctuation spectrum.

**Ihle et al.** [63] calculated resistivity based on the two-band (Emery) model. They assumed that the oxygen holes are scattered by Cu spin fluctuations, and explained the cross over from a quadratic to linear T-dependence.

Anderson and Zhou [51] tried to explain the resistivity variation in view of RVB theory. The essence of this theory is that the strong electron-electron correlations lead to the separation of charge and spin degrees of freedom. The low energy excitations consists of charged Boson solitons (holons) and neutral Fermion solitons (spinons) with a pseudo fermi surface. From the particle statistics, the scattering rate of holons by spinons is inferred to be proportional to T. In the gauge field theory for a uniform RVB state Nagaosa and Lee [64] explained various physical quantities as a sum of the contribution from Bosons and Fermions. Due to the local constraint, motion of Bosons must be accompanied by a counterflow of Fermions. The resistivity is therefore given by \( \rho \approx \rho_B \approx \left( \frac{m_B}{x} \right) T \), where \( m_B \) and \( x \) are the mass and the density of Bosons.

The marginal Fermi liquid theory by Varma et al [54] relates the T-linear relaxation rate of quasi-particles together with other experimentally observed anomalous normal state properties, to their specific form of polarization function.

Lee and Read [52] and Viroszek and Ruvalds [65] proposed that the temperature dependence of resistivity can be explained in view of 'nested Fermi liquid' model. According to this model, the flatness of the cylindrical Fermi surface and the amount of nesting determines the properties. According to their theory, the \( T^2 \) and \( T \) dependences of
can be attributed to electron-electron scattering and the linear temperature variation is mostly as a result of nesting.

For high temperature superconductors, it was suggested that a [52,66,67] two dimensional Fermi surface topology leads to a logarithmic divergence in density of states (DOS) (a van Hove singularity). Here the characteristic temperature for the crossover from $T^2$ to $T$-behavior of resistivity is set by the van Hove energy scale.

Gasumyant et al [68] have given a narrow band model which can provide simultaneous quantitative description of temperature dependence of resistivity $\rho(T)$, thermoelectric power $S(T)$ and Hall coefficient $R(T)$. They assumed the existence of a narrow peak in the density of states and obtained expressions for $\rho(T)$, $S(T)$ and $R(T)$ in terms of three phenomenological parameters. The first parameter is the degree of band filling $F$, which is equal to the ratio of the number of electrons to the total number of states in the band. The second parameter is the total effective band width $W_D$ and the third is the conduction band width $W_\sigma$ which gives the main contribution to the electrical conduction process.

\[
\rho = \frac{1}{<\sigma>} \frac{1 + e^{-2\mu^*} + 2e^{-\mu^*}\cosh(C/T*)}{e^{-\mu^*}\sinh(C/T*)} \tag{4.2.7}
\]

where

\[
\mu^* = \ln \frac{\sinh(F/T^*)}{\sinh((1-F)/T^*)}
\]

\[
T^* = k_BT/W_D, C = W_\sigma/W_D, F = n/N
\]

For $W<k_BT$, at high temperatures this expression reduces to
where

\[ \rho = \frac{2k_B T}{k_\sigma} \left( 1 + \frac{5}{12} W_\sigma^* \right)^2 \]  \hspace{1cm} (4.2.8)

\[ k_\sigma = \int_0^W \sigma(E) dE \]  \hspace{1cm} (4.2.9)

which can explain the linear temperature dependence of resistivity of high $T_c$ materials in the normal state.

### 4.3 Conduction mechanism in insulating samples

#### 4.3.1 Theory

From the studies of charge transport in the insulating phase, we can get the information about electronic correlation and the density of states [69]. Now it is well established that the charge transport in insulating samples related to high temperature superconductors is due to localized carriers [19,23,25]. The activated nature of the conductivity is attributed to hopping rather than excitation of carriers across an energy gap in a semiconductor. At low temperatures the conductivity of this sample rapidly decreases with decreasing temperature and the activation energy for hopping decreases with decreasing temperature. In many systems, the temperature dependence of resistivity is described by Mott’s variable range hopping (VRH) [69]

\[ \rho = \rho_0 e^{\exp(T_0/T)^m} \]

where \( m = (n+1)/(n+D+1) \) where $D$ is the dimensionality of the hopping process and $n$ describes the energy dependence of the density of states $N(E_F)$ near the Fermi energy, which behaves like
\[ N(E_F) \approx |E - E_F|^n \quad (4.3.2) \]

For energy independent density of states \( n = 0 \), which is the case of Mott's variable range hopping. For Mott's case \( m \) is 1/3 for two dimensions (2D) and 1/4 for three dimensions (3D) respectively [69,70]. Schklovskii and Efros [71] assumed that for low carrier concentrations electrons interact via the unscreened coulomb potential, which leads to a gap in \( N(E_F) \) that is pinned at \( E_F \). According to them \( n = 1 \) and \( n = 2 \) for two and three dimensions respectively. This leads to the same exponent \( m = 1/2 \) for both two and three dimensions.

In eqn.(4.3.1) \( \rho_o \) and \( T_o \) are model dependent parameters. \( T_o \) depends on the density of states and \( \beta \), which is the inverse of localization length (fall of length of the wave function of a localized state) near the Fermi level and density of states [72-74]. The relation is given by

\[
T_o = \frac{16\alpha^3}{k_B N(E_F)} \quad \text{for} \quad 3D \quad (4.3.3)
\]

\[
T_o = \frac{27}{4\pi \alpha^2 k_B N(E_F)} \quad \text{for} \quad 2D \quad (4.3.4)
\]

For Shklovskii-Efros case

\[
T_o \approx \frac{2.8e^2\alpha}{4\pi \varepsilon_0 k_B} \quad (4.3.5)
\]

where \( k_B \) and \( e \) are Boltzmann constant and static dielectric constant respectively. The pre-exponential factor in eqn.(4.3.1) depends on \( T, \alpha \) and \( N(E_F) \). Different groups have given different expressions for \( \rho_o \) [75-77]. According to Mott
Ortuno-Pollak [78] have assumed that $N(E_F)$ depends on energy exponentially and obtained the expression given below

$$\rho = \left( \frac{10}{\nu e^2} \right) \left( \frac{k_B T \beta}{N(E_F)} \right)^{1/2} \quad (4.3.6)$$

where $\nu$ is the phonon frequency, $e$ is the electronic charge, $k_B$ is Boltzmann’s constant, $a^{-1}$ (a) is the localization length and $N(E_F)$ is the density of states at the Fermi level.

At any temperature, transition probability for the occurrence of a hop to a state at a distance $R$ from the initial state separated by an energy $W$, is given by [79]

$$P \approx \exp[-2\alpha R - (W/k_B T)] \quad (4.3.8)$$

The term $\exp(-2\alpha R)$ denotes the probability of finding an electron at distance $R$ from its initial site [80]. $\alpha$ is the inverse of localization length [a]. The hop distance ($R$) varies with temperature as

$$R = [(3a/2\pi)N(E_F)k_BT]^{1/4} \quad (4.3.9)$$

The second term $\exp(-W/k_B T)$ arises due to the phonon assistance required by the electron in overcoming the energy barrier $W$, where $W$ is the hopping energy given by [76]

$$W = 3/4\pi R^3 N(E_F) \quad (4.3.10)$$
The probability $p$ decreases with decrease in temperature because of the second term in eqn.(4.3.8) as a result electron prefers to hop to sites with lower $W$ value. $R$ and $W$ values are such that at any temperature, the most dominant hops contribute to the conductivity and are related by eqn.(4.3.10).

At high temperatures, the electrons acquire sufficient energy to hop to the neighboring sites at small hopping distance, $R$ with large activation energy, $W$. The temperature dependence of resistivity is given by the eqn.(4.3.1) with $m = 1$.

4.3.2 Discussion

The values of resistivity of the present systems under study at room temperature and 10 K are listed in Table-4.2. The room temperature resistivity is between $10^{-1}$ and $10^{-2}$ $\Omega$ cm, and at low temperatures its value is between $10^{-1}$ and $3 \Omega$ cm.

At low temperatures the resistivity variation with temperature could be fitted to eqn.(4.3.1). Almost all the insulating phases of high $T_c$ materials are reported to exhibit VRH [21,23,81-102]. The temperature range over which VRH is operative is different for different materials. Some groups reported that it is operative over a wide temperature range, room temperature to around 20 K, while the others observed it only at low temperatures. Surprisingly, Ponnambalam et al [96] observed VRH over a large temperature range (100-900 K).

Fig.4.5 and 4.6 show the $\ln \rho$ vs $T^{-m}$ plots for various semiconducting samples for $m = 1/3$ and 1/4 (other values of exponents like $m = 1/2$ etc were also tried). Both
Table-4.2

The resistivity value at room temperature 300 K ($\rho_{300}$) and low temperature at 10 K ($\rho_{10}$)

<table>
<thead>
<tr>
<th>sample</th>
<th>($\rho_{300}$) (mΩ cm)</th>
<th>($\rho_{10}$) (mil cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr-doped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>32.3</td>
<td>50.5</td>
</tr>
<tr>
<td>Ce-doped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>72.2</td>
<td>314.0</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>75.2</td>
<td>1132.0</td>
</tr>
<tr>
<td>Tb-doped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>160.6</td>
<td>479.7</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>271.1</td>
<td>2470.8</td>
</tr>
</tbody>
</table>
Fig. 4.5 Plot of \(\ln \rho\) vs. \(T^{-1/3}\) for various semiconducting samples
Fig. 4.6 Plot of lnρ vs. $T^{-1/4}$ for various semiconducting samples
the plots appear linear over a wide range of temperature. The exponent can be calculated independently from the slope of log-log plot (expected values of slopes are -2/3 for 2D and -3/4 for 3D) of \( d(\ln \rho)/d(1/T) \) vs. \( 1/T \) plot. Due to the scattering of derivative points, it is difficult to make a distinction between the two slopes, unless the temperature range extends over at least one order of magnitude. In the Gd doped Bi-2212 samples, Jayaram et al. [19] reported that their resistivity data in the semiconducting samples fits well to eqn.(4.3.1) for \( m = 1/3 \) (2D VRH) over a wide normal state resistivity range (0.012 < \( \rho < 0.1 \Omega \) cm). For O.K \( \rho < 1 \Omega \) cm, they found equally good fittings for \( m = 1/3 \) and \( m = 1/4 \) in the high temperature range. The \( T_o \) values calculated from the slopes of \( \ln \rho \) vs \( T^{-m} \) and the derived parameters are not affected much by the choice of \( m \). The equation with \( m = 1/4 \) is, therefore, used for the following discussion. It is also not possible to distinguish the difference between the \( T^{-1/4} \) and \( T^{-1} \) dependence of \( \ln \rho \) near the room temperature region. Fig.4.7 shows the \( \ln \rho \) vs \( T^{-1} \) plots for various samples. \( T_o \) and \( \rho_o \) values calculated from these plots are given in Table-4.3.

The slope of \( \ln \rho \) vs \( T^{-1/4} \) plot increases with increase in \( x \). This implies that the material becomes more and more disordered with increasing dopant content. Increase in disorder permits the electron to hop to the site located close by the initial state. The disorder tends to localize a state resulting in the formation of a small polaron [103]. If the carrier is confined to a single site it is called small polaron.

Assuming the value of \( N(E_F) \) [\( \approx 10^{23} \)] as reported in the literature for Bi-system [104], the localization length (\( a \)) value is calculated for various samples of the present systems using the eqn.(4.3.3) [Table-4.4]. With increase in \( x \), \( T_o \) value increases and the localization length decreases. The value of \( a \) is too high for the sample near the metal-insulator transition. As the MI transition approaches from the insulator side, the
Fig. 4.7 Plot of $\ln \rho$ vs. $T^{-1}$ for various semiconducting samples
Table-4.3

The parameters obtained from $\frac{1}{T} - \ln \rho$ fit for high temperature data

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_o$ (K)</th>
<th>$\rho_o$ (mil cm)</th>
<th>Range of Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr-doped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>23.0</td>
<td>29.8</td>
<td>95-300K</td>
</tr>
<tr>
<td>Ce-doped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>130.4</td>
<td>46.9</td>
<td>170-300K</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>116.1</td>
<td>51.1</td>
<td>100-300K</td>
</tr>
<tr>
<td>Tb-doped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>121.9</td>
<td>107.8</td>
<td>200-300K</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>223.1</td>
<td>131.6</td>
<td>190-300K</td>
</tr>
</tbody>
</table>
Table-4.4

The parameters obtained from $T^{-1/4}\ln\phi$ fit

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_o$ (K)</th>
<th>$P_o$ (mΩ cm)</th>
<th>$\alpha$ (Å)</th>
<th>$\nu$</th>
<th>Range of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr-doped</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>23</td>
<td>18.8</td>
<td>52.6</td>
<td>$5.6 \times 10^{11}$</td>
<td>28-300K</td>
</tr>
<tr>
<td>Ce-doped</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>2946</td>
<td>12.8</td>
<td>10.4</td>
<td>$1.8 \times 10^{12}$</td>
<td>38-270K</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>16943</td>
<td>4.4</td>
<td>5.8</td>
<td>$7.1 \times 10^{12}$</td>
<td>38-270K</td>
</tr>
<tr>
<td>Tb-doped</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>1760</td>
<td>35.0</td>
<td>12.3</td>
<td>$6.2 \times 10^{11}$</td>
<td>64-270K</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>15693</td>
<td>67.2</td>
<td>6.0</td>
<td>$4.6 \times 10^9$</td>
<td>54-130K</td>
</tr>
<tr>
<td></td>
<td>76259</td>
<td>23.1</td>
<td>3.5</td>
<td>$1.8 \times 10^{12}$</td>
<td>140-300K</td>
</tr>
</tbody>
</table>
The \( T_o \) value decreases and goes to zero, \textit{i.e.,} localization \textbf{length} diverges, which indicates that carriers are delocalized. The phonon \textbf{frequencies} are estimated using eqn.(4.3.7) and the values are in the range \( 10^{11} - 10^{12} \) Hz which is within the expected limits (Table-4.4) [69,76].

The values of the hopping distance R and the hopping energy W calculated using eqn.(4.3.9) and (4.3.10) for different temperatures between 10 and 300 K are shown in Table-4.5-4.9. Hop distance R decreases with increase in x. The hopping energy W increases systematically with increasing x, because more energy is needed to cross the barrier with increase in disorder.

For a given dopant content, \( T_o \) and a are constants at different temperatures. R decreases and W increases with increase in temperature. Thermal energy decreases at low temperatures and the charge transport is governed by the carriers hopping between states with lower energy and larger distance. Variation of R and W as a function of temperature for various semiconducting samples are given in Fig.4.8.

The increasing slope of \( \ln \rho \) vs \( T^{-1/\beta} \) curve with x implies increase in \( T_o \). The disorder in the material increases with the increase in x value, which implies that \( T_o \) is a measure of disorder in the material.\textit{,} The \( T_o \) value in the case of Ce and Tb doped samples is high compared to Pr doped samples for the same dopant level. This may be due to the lower degree of disorder introduced in the Pr-doped \textbf{Bi-2212} system when compared to Ce and Tb doped Bi-2212 systems. The Tb-doped sample with x = 0.6 shows a double slope behavior in the \( \ln \rho \) vs \( T^{-1/\beta} \) plot, which may be due to the multiphonon assisted hopping [103,105] which operates when \( W > k_B T \).
Table-4.5

Estimated values of \( R \) and \( W \) at various temperatures for \( \text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Pr}_{0.6}\text{Cu}_2\text{O}_y \) sample

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( a=52.6\text{Å} )</th>
<th>( R(\text{Å}) )</th>
<th>( W ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>26.85</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>22.58</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>17.96</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>15.10</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>13.64</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>12.70</td>
<td>2.07</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>12.01</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>11.47</td>
<td>2.81</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.6

Estimated values of R and W at various temperatures for $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.7}\text{Ce}_{0.3}\text{Cu}_2\text{O}_y$ sample

<table>
<thead>
<tr>
<th>T(K)</th>
<th>R(Å)</th>
<th>W (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>17.90</td>
<td>0.74</td>
</tr>
<tr>
<td>20</td>
<td>15.05</td>
<td>1.24</td>
</tr>
<tr>
<td>50</td>
<td>11.97</td>
<td>2.47</td>
</tr>
<tr>
<td>100</td>
<td>10.07</td>
<td>4.16</td>
</tr>
<tr>
<td>150</td>
<td>9.10</td>
<td>5.64</td>
</tr>
<tr>
<td>200</td>
<td>8.47</td>
<td>7.00</td>
</tr>
<tr>
<td>250</td>
<td>8.01</td>
<td>8.27</td>
</tr>
<tr>
<td>300</td>
<td>7.65</td>
<td>9.49</td>
</tr>
</tbody>
</table>
Table 4.7

Estimated values of $R$ and $W$ at various temperatures for $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.6}\text{Ce}_{0.4}\text{Cu}_2\text{O}_y$ sample

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$R$ (Å)</th>
<th>$W$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>15.48</td>
<td>1.15</td>
</tr>
<tr>
<td>20</td>
<td>13.01</td>
<td>1.93</td>
</tr>
<tr>
<td>50</td>
<td>10.35</td>
<td>3.83</td>
</tr>
<tr>
<td>100</td>
<td>8.70</td>
<td>6.44</td>
</tr>
<tr>
<td>150</td>
<td>7.86</td>
<td>8.73</td>
</tr>
<tr>
<td>200</td>
<td>7.32</td>
<td>10.84</td>
</tr>
<tr>
<td>250</td>
<td>6.92</td>
<td>12.81</td>
</tr>
<tr>
<td>300</td>
<td>6.61</td>
<td>14.69</td>
</tr>
</tbody>
</table>
Table-4.8

Estimated values of R and W at various temperatures for Bi_2Sr_2Ca_{0.5}Tb_{0.5}Cu_2O_y sample

<table>
<thead>
<tr>
<th>T (K)</th>
<th>R (meV)</th>
<th>W (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>18.69</td>
<td>0.65</td>
</tr>
<tr>
<td>20</td>
<td>15.71</td>
<td>1.09</td>
</tr>
<tr>
<td>50</td>
<td>12.50</td>
<td>2.18</td>
</tr>
<tr>
<td>100</td>
<td>10.51</td>
<td>3.66</td>
</tr>
<tr>
<td>150</td>
<td>9.50</td>
<td>4.96</td>
</tr>
<tr>
<td>200</td>
<td>8.84</td>
<td>6.15</td>
</tr>
<tr>
<td>250</td>
<td>8.36</td>
<td>7.27</td>
</tr>
<tr>
<td>300</td>
<td>7.99</td>
<td>8.34</td>
</tr>
</tbody>
</table>
Table-4.9

Estimated values of R and W at various temperatures for Bi$_2$Sr$_2$Ca$_{0.4}$Tb$_{0.6}$Cu$_2$O$_y$ sample

<table>
<thead>
<tr>
<th>T (K)</th>
<th>R (Å)</th>
<th>W (meV)</th>
<th>R (Å)</th>
<th>W (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>15.57</td>
<td>1.12</td>
<td>13.65</td>
<td>1.67</td>
</tr>
<tr>
<td>20</td>
<td>13.10</td>
<td>1.89</td>
<td>11.48</td>
<td>2.81</td>
</tr>
<tr>
<td>50</td>
<td>10.41</td>
<td>3.76</td>
<td>9.13</td>
<td>5.58</td>
</tr>
<tr>
<td>100</td>
<td>8.76</td>
<td>6.32</td>
<td>7.68</td>
<td>9.39</td>
</tr>
<tr>
<td>150</td>
<td>7.91</td>
<td>8.57</td>
<td>6.94</td>
<td>12.72</td>
</tr>
<tr>
<td>200</td>
<td>7.36</td>
<td>10.63</td>
<td>6.46</td>
<td>15.78</td>
</tr>
<tr>
<td>250</td>
<td>6.96</td>
<td>12.57</td>
<td>6.11</td>
<td>18.66</td>
</tr>
<tr>
<td>300</td>
<td>6.65</td>
<td>14.41</td>
<td>5.83</td>
<td>21.39</td>
</tr>
</tbody>
</table>
Fig. 4.8 Variation of hopping distance (R) and hopping energy (W) as a function of temperature
Quitmann et al. [102] have analyzed the resistivity data of the insulating samples of Bi$_2$Sr$_2$Ca$_x$Y$_{1-x}$Cu$_2$O$_y$ using generalized hopping approach based on connectivity criterion. For a given Ca concentration, they have plotted $\ln \rho$ vs. $T^{-m}$ with values of $m$ between 0.15 to 0.6. They have taken the value of $m$ which gives a straight line over a large temperature range and calculated the exponent as a function of Ca concentration. They found different values of $m$ for samples with different Ca concentrations i.e., value of $m = 0.5$ for Bi$_2$Sr$_2$YCu$_2$O$_y$ sample and $m = 0.2$ for Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_y$ sample which is closer to MI transition. They argue that depending on the carrier concentration of the sample, very different values of $m$ and therefore dimensionality can be obtained. The observed variation in $m$ with Ca concentration explains the disagreement in the literature about the exponent in the hopping conduction for the Bi$_2$Sr$_2$Ca$_x$R$_{1-x}$Cu$_2$O$_y$ system and with it the disagreement about the dimensionality. They found that insulating samples with Y content not too far from the critical concentration $x = 0.43 \pm 0.02$ show metallic conduction at high temperatures and hopping conduction at low temperatures. These two regions are separated by a shallow minimum ($\rho_{\text{min}}$). This kind of behavior has been reported in other systems also [9]. This shows the coexistence of delocalized states and localized states separated by a disorder induced mobility edge. From ultraviolet-photoemission spectroscopy studies, they observed a shift in the Fermi level to lower energies and the development of new states at Fermi level. From these experimental observations they concluded that the MI transition is probably of Anderson type [46]. They used a narrow band model to explain qualitatively the MI transition and crossover from insulating to metallic resistivity and the linear resistivity in the normal state for the metallic samples.

In the present set of samples, the insulating compositions available are not very much
away from the MI transition. So, it is not possible to determine the change in exponent value as a function of Ca concentration. Any crossover from hopping conduction to metallic conduction in the insulating samples and a shallow minimum in resistivity could not be observed in the temperature range studied. In the present samples, \( \rho_{min} \) may occur at higher temperatures.

A comparison of the results obtained on the three series of samples shows that

1. In all the three series of samples, the room temperature resistivity increases and \( T_c \) decreases with increase in the dopant concentration. The MI transition is observed between 10-20 \( \text{m}\Omega \text{cm} \) in all the three series of samples.

2. MI transition is observed around \( x = 0.6 \) in Pr-doped system, around \( x = 0.2 \) in Ce-doped system and around \( x = 0.4 \) in Tb-doped system. The \( T_c \) depression is faster in Ce-doped Bi-2212 system compared to the other rare-earth substitutions. From this it is inferred that Ce exists in +4 valence state. The faster decrease in the c-lattice parameter also confirms this conclusion.

3. The \( T_c \) of present systems is sensitive to the hole concentration in CuO\(_2\) planes. Rare-earth ion with +3 or +4 valence states substituted in the place of Ca ion (valence state +2) fills the holes and thereby reduces the \( T_c \).

4. The resistivity variation in semiconducting samples can be explained in terms of VRH. It is not possible to determine the exponent unambiguously. Using \( N(E_F) \approx 10^{23} \) value, the localization length is estimated. For the sample which is closer to the MI transition, the estimated value of localization length is large, because as MI transition is approached, the \( T_o \) value approaches zero and localization length diverges. For higher dopant concentrations the localization length is small. The hopping distance (R) and hopping energy (\( \lambda \)) were estimated at different temperatures and they obey Anderson localization conditions.
4.4 References


