Chapter 5

THERMOELECTRIC POWER STUDIES

This chapter deals with the systematic study of thermoelectric power (TEP) on
$\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_{x}\text{Cu}_2\text{O}_y$ ($M = \text{Pr, Ce & Tb}$) samples. The experimental data are analyzed
in view of various theoretical models existing in the literature. TEP measurements on the
well characterized samples were carried out using dc differential technique as described in
chapter II, as a function of temperature in the temperature range 40-300 K. The results
and their analysis are presented in the following pages.

5.1 Background

5.1.1 Thermoelectric power of metals and semiconductors

The TEP ($S$) for a free electron gas in a metal in the classical picture can be written as
[1,2]

$$S = \int_0^T \frac{C_e(T)}{nT} dT$$  \hspace{1cm} (5.1.1)

where $C_e$ ($T$) is the electronic specific heat per unit volume, $n$ is the number of
electrons per unit volume, $e$ is charge of the electron and $T$ the temperature.

For a free electrons in a metal, $C_e$ is given by

$$C_e = \frac{\pi^2 k_B^2 n T}{(2E_F)}$$  \hspace{1cm} (5.1.2)
TEP is given by the equation

\[ S = \frac{\pi^2 k_B^2 T}{2eE_o} \mu V K^{-1} \]  \hspace{1cm} (5.1.3)

where \( C_e \) is the electronic specific heat per unit volume, \( n \) is the number of electrons per unit volume and \( k_B \) is Boltzmann constant. At absolute zero temperature, the lowest possible states will be occupied up to a certain maximum energy \( E_o \).

According to this expression, TEP should be proportional to absolute temperature and dependent on the sign of charge. It should be negative and small in magnitude. In this expression the electron scattering processes are not taken into account.

Mott gave a more general expression needed for the interpretation of the TEP [3] as

\[ S\sigma = \frac{k_B}{e} \int \sigma_E \frac{E - E_F}{kT} \frac{\partial f}{\partial E} dE \] \hspace{1cm} (5.1.4)

and \( \sigma \) is

\[ \sigma = \int \sigma_E \frac{\partial f}{\partial E} dE \] \hspace{1cm} (5.1.5)

where \( f \) is Fermi function and \( \sigma_E \) is energy dependent conductivity.

For metals the current is determined by the electrons with energies in the neighborhood of \( E_F \). So \( S \) can be written as

\[ S = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{d(ln\sigma)}{dE} \right) \bigg|_{E_F} \]

where the differential is the change in the electrical conductivity \( \sigma \) as the Fermi energy \( E_F \) changes evaluated at the actual Fermi surface of the metal \( E_F \), which in turn is sensitive to the Fermi surface area and the mean free path.
The essential difference between metals and semiconductors is that in semiconductors the electrons are usually non-degenerate and they have Maxwellian distribution. Then the specific heat per electron is given by $3k_B/2$. This is much greater than the specific heat of electrons in a metal. Then the eqn. (5.1.1) becomes

$$S = \int_0^T \frac{3k_B}{2cT}dT = -\frac{k_B}{e} \frac{3}{2} \ln T + \text{constant} \quad (5.1.7)$$

According to Heikes [4], if $k_B T$ is greater than the band width then $S$ is given by

$$S = -\frac{k_B}{e} \ln \left( \frac{c}{1-c} \right) \quad (5.1.8)$$

where $c$ is the ratio of number of electrons to the number of sites.

In the case of semiconductors which have a mobility gap at the Fermi surface, TEP (S) is given by

$$S = \frac{k_B}{e} \left[ \frac{E_c - E_F}{k_B T} + A \right] \quad (5.1.9)$$

$E_c - E_F$ is the energy required to excite a carrier to the mobility edge and $A$ is a constant.

In the case of variable range hopping (VRH), the characteristic energy for a hop is given by [3,5,6]

$$W \sim T^{d/(d+1)} \quad (5.1.10)$$

where $d$ is the dimensionality of the hopping, the temperature dependence of conductivity is given by

$$\sigma \sim \exp(-W/T) \sim \exp(-T_0/T)^{1/(d+1)} \quad (5.1.11)$$

and $S$ is given by
So $S$ is proportional to $W^2/T$. The temperature dependence of $S$ can be written as

$$S = \frac{1}{2} \frac{k_B W^2}{e F} \left( \frac{d\ln N}{dE} \right)_{E=E_F}$$  \hspace{1cm} (5.1.12)

So $S$ varies as $T^{1/2}$ for 3D VRH and $T^{1/3}$ for 2D VRH.

For hopping between nearest neighbors $S \to \infty$ as $1/T \to 0$. These equations are valid for spinless particles below Neel temperature in amorphous antiferromagnets. Above the Neel temperature there should be an additional term $(k_B/e)\ln 2$ in TEP, which is frequently observed in amorphous semiconductors in the hopping regime.

In the above treatment, contribution to TEP due to diffusion of carriers under the influence of temperature gradient has been considered. It has been assumed that the phonon distribution is in equilibrium whenever any interaction with the electron system is being considered. Its only contribution is to scatter the electrons by electron-phonon interaction, which gives rise to a mean free path for the diffusing electrons. If there is an electric current flowing, momentum will be transferred from the electrons to phonons and this momentum will not be able to be dissipated into the whole phonon system (because the relaxation time of the phonons, with the interaction with other phonons, impurities or boundaries is longer than the relaxation time for electron-phonon interaction) before further electron interaction occurs to increase the momentum still more. Hence these phonons will not be able to come to equilibrium with the rest of the system. Phonon-phonon and phonon-impurity interactions become very small as the temperature is reduced. Some momentum will be transferred from phonons to electrons and
extra carriers will be piled up at the cold end in addition to those coming from diffusion alone with a consequent change in current flow. This is called phonon-drag effect. Its effect is widely observed in TEP of metals and semiconductors as peaks and faster enhancement or decrement in TEP than that for pure diffusion alone. For detailed calculation of phonon-drag contribution one has to take all the scattering mechanisms into consideration.

5.1.2 Thermoelectric power of high $T_c$ superconductors

Several groups have reported the TEP measurements on various cuprate superconducting systems, namely La - [7-10], Y- [7,10,22,37] Bi- [7,13-37] Tl- [7,23,26,38-41] and Hg- [42] based systems. From these measurements, some common features in the temperature and carrier dependence of TEP have emerged. For the overdoped system (high concentration), TEP is negative and small and it varies almost linearly with temperature. For the underdoped system (low carrier concentration), TEP is positive and large and approaches a temperature independent value at high temperatures. For the medium carrier concentrations, TEP first increases with temperature and then shows a broad maxima followed by a decrease.

It is now more or less established that different sign and magnitude of TEP and the $T_c$ values are closely related to the carrier concentration. Presland et al [43] have given quite general relation between $T_c$ and carrier concentration $p$ for several doped cuprate systems. According to Presland, $T_c$ appears to be maximized at $p = 0.16$, falls to zero on the underdoped and overdoped sides at $p = 0.05$ and $p = 0.27$, respectively and is

$$\frac{T_c}{T_{c_{\text{max}}}} = 1 - 82.6(p - 0.16)^2 \quad (5.1.14)$$
Obertelli et al [26] examined the temperature dependent TEP of several high $T_c$ systems Y-123, Bi-2212, Tl-1212, Bi-2223 and Tl-2223 and concluded that a universal correspondence between room temperature TEP vs carrier concentration ($p$) exists. In the overdoped region the variation of TEP with $p$ is found to be linear and in the underdoped region it is logarithmic. Tallon et al [44] obtained a direct relationship between $T_c$ and hole concentration $p$ for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ by investigating the properties of fully oxygen deficient ($S \approx 1.0$) compound for which $p = x/2$. They used these $p$ values to check the previously reported correlation with the room temperature TEP [26] and found that their data follows the Obertelli's universal relation [26]. They parameterized the correlation by the relation

$$
S_{290} = \begin{cases} 
372 e^p(-32.4p) & 0.00 < p < 0.05, \\
992 e^p(-38.1p) & 0.05 < p < 0.155, \\
-139p + 242 & p > 0.155
\end{cases}
$$

There is a discontinuity in $S(290,p)$ in the neighborhood of the superconductor-insulator transition at $p = 0.05$.

According to the conventional Fermi liquid theory, the TEP is expected to be approximately linear in temperature, showing a phonon-drag peak below $\theta_D/2$ and goes to zero as $T$ tends to zero. The TEP of high temperature superconductors in the normal state is temperature independent or weakly dependent on temperature, but the zero temperature extrapolated value is not zero. So, it is believed that the temperature dependence of $S$ can not be explained in the conventional picture.

Several conventional and unconventional approaches have been adopted to explain
the TEP of high $T_c$ superconductors. A brief summary of these models is given below.

In high $T_c$ superconductors, the occurrence of peak in TEP is commonly observed in both polycrystalline samples and within $ab$ plane of single crystals. Cohney et al [45] adopted a phonon-drag model to explain this peak as arising from freeze-out of carrier phonon umklapp process involving holes in the CuO$_2$ layers and optical-mode phonons. Uher and Kaiser et al [8,11] suggested that the peak in the TEP of high temperature superconductors is caused by phonon-drag. However, some groups are not in favor of this phonon-drag peak [12,40,46,47].

Kaiser [48,49] tried to explain the major features of TEP with the metallic diffusion model which is proved to be successful for normal metal systems with the only difference being the anomalously large size of the electron-phonon enhancement effect. Kaiser [48] has performed calculation of the enhancement of TEP due to electron-phonon interaction in the high $T_c$ superconductors using the Eliashberg function calculated by Weber [50] and also inferred the existence of two types of carriers from the observed positive Hall coefficient and negative TEP. Vijayashree et al [12] emphasized the evidence that phonon-drag is not responsible for the peak from the TEP data of YBa$_2$Cu$_{3-x}$Zn$_x$O$_{7-x}$ and the enhancement of TEP is more steep with temperature over linear diffusion TEP than what would be expected for electron-phonon interaction.

Zhang et al [51] suggested that there are two kinds of carriers; localized carriers giving the constant part of TEP, and mobile carriers contributing to the diffusion part of the TEP which is proportional to the temperature

$$S = S_1 + S_2 = A + BT$$ (5.1.16)
This is based on the assumption that the contribution of the phonon-drag is small above $T_c$.

Another model is based on the assumption that high $T_c$ superconductors have strongly correlated electrons. According to Chaiken and Beni [52]

$$S_1 = -(k_B/e)ln(2(1-p)/p) \quad (5.1.17)$$

for the constant part of the TEP [$S_1$ in eqn.(5.1.16)], which represents the contribution from the relatively localized carriers. $p$ is the hole concentration per Cu ion.

Some groups, from photoemission spectroscopy studies reported the evidence of existence of two bands in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ [53,54]. Though it is possible to explain the sign change of $S$ in a single-band model, many authors have adopted two band models to explain the experimental results. These models generally adopt the picture that the holes are in CuO$_2$ layers and electrons in Cu-0 chains in $\text{YBa}_2\text{Cu}_3\text{O}_y$ system or in Bi-0 or Tl-O layers in Bi- and Tl-based systems, respectively. Such two band models are consistent with the band structure calculations.

Allen et al [55] from the band structure calculations for Tl$_2$Ba$_2$CuO$_6$ (Tl-2201) suggested that the transport is dominated by a wide Cu-0 band with a possible contribution from the smaller Tl-O band. The transport properties of $\text{YBa}_2\text{Cu}_3\text{O}_y$ were also examined and it was concluded that YBCO does have a charge carrier in the Cu-0 chains analogous to the Tl-0 layer.

Wang et al [56] have proposed a two-carrier model in analogy to the two band model, concerning the O 2$p$ holes and Cu 3$d_{\sigma^2 - \pi^2}$ electrons and explained qualitatively the change
from +ve to -ve value of S. According to them, in parent insulators Cu $3d_{x^2-r^2}$ electrons are strongly localized and TEP is determined by O 2p holes. With increase in doping, Cu $3d_{x^2-r^2}$ electrons may become delocalized, so that they may contribute to conduction. In the overdoped region, Cu $3d_{x^2-r^2}$ electrons may play an important role in the transport mechanism and result in the -ve TEP.

Kubo et al [39] proposed a two-dimensional tight binding model of Cu-0 plane assuming next nearest-neighbor interactions. The single band showed both electron like and hole-like character depending on the geometry of the band. The model showed that in the areas of half filling, there can be a negative TEP and a positive Hall coefficient. In the nearest neighbor tight binding models, Seeback coefficient changes its sign at half filling. In his calculations, as the next-nearest neighbor interaction is turned on, this sign change occurs on either side of half filling (depending on the limiting case) by as much as 0.2 holes, which is very close to the experimentally observed value for various high $T_c$ superconductors [26].

Fisher et al [57-60] used narrow band model which assumes the existence of a very narrow band in the band to explain the normal state transport properties structure near $E_F$. Tsidilovski and Tsidilovski [61] also used a phenomenological narrow band model which assumes the existence of narrow peak in the density of states near Fermi level.

Newns et al [62] explained the temperature and doping dependence of TEP of high $T_c$ superconductors in view of a saddle point (SP) in logarithmic density of states singularity (van Hove singularity (VHS)). The universal relationship between the TEP and $T_c$ can be explained in view of this model. As the Fermi level, controlled by doping, is swept through the SP, the density of states (DOS) at the Fermi level goes through a
maximum and so does $T_c$ ($T_c$ maximum) and the TEP zero corresponds to the Fermi level lying at the SP. As mentioned earlier, certain other anomalous properties of high $T_c$ superconductors, such as marginal Fermi liquid behavior [63], specific heat jump [64] and isotope shift [65-67] have also been explained in terms of VHS.

Tallon et al [17] from the Zn substitution studies in Y-123 reported that a strong enhancement in the S(T) is related with a smooth opening of energy gap in the normal state spectrum. The energy gap called normal state gap (NS), pseudogap or spin gap is observed from NMR [68,69] and heat capacity [70] measurements. In sufficiently underdoped samples this gap opens at a temperature $T_g$ well above $T_c$. They showed that this gap is responsible for the p-dependent variation of TEP [26]. They showed that Zn substitution suppresses both the NS and the superconducting order parameter and, at an intermediate concentration, the former survives while the latter does not. This picture is consistent with the van Hove singularity picture [62] and phonon-drag picture [71] of TEP.

Recently, Tallon et al [22] reported TEP measurements on different sets of Y-123 compounds in which the interplanar coupling between the superconducting CuO$_2$ planes in RBa$_2$Cu$_3$O$_{7-\delta}$ is controlled by changing the size of the rare-earth (R) and by changing the oxygen deficiency in the chains while keeping the hole concentration on the planes fixed at optimum doping by means of Ca substitution at R site. From the insensitivity of $T_c$ to interlayer coupling and the absence of peak in the density of states determined by Y-NMR, they concluded that the doping dependence of TEP and the density of states are inconsistent with the VHS model.

Trodhal [71] has recently explained the temperature and doping dependence of TEP within the conventional Fermi liquid picture itself. According to him, the anomalous
behavior is a manifestation of the strong scattering of phonons by electrons, which is already inferred from thermal conductivity data [72] that the acoustic phonons remain scattered predominantly by electrons up to room temperature. Trodhal has included a large phonon-drag contribution to the negative diffusion TEP for an electron gas. The cumulative TEP decreases linearly with temperature. The net TEP is set to zero below the superconducting transition temperature of 90 K, which is the value it would have in the absence of superconductivity.

From the brief summary it can be concluded that the TEP of high $T_c$ superconductors still lacks a satisfactory explanation.

5.2 Results

The temperature variation of TEP (S) for Bi$_2$Sr$_2$Ca$_{1-x}$M$_x$Cu$_2$O$_y$ (M = Pr, Ce & Tb) are shown in Fig.5.1-5.3. There are some common characteristic features in the S vs. T plots of the three series of samples. For all the three series of samples, the room temperature TEP (S300) is positive and its magnitude increases with increase in x. For the superconducting samples S is small and S vs. T plots show a broad maxima in the normal state. In the temperature range above the maxima, S decreases almost linearly as the temperature increases. The S maxima shifts towards high temperatures as x increases. In the temperature range below the maxima. S decreases rapidly and goes to zero at the $T_c$. Superconducting samples in all the three series show the room temperature TEP value < 11μV/K.

Fig.5.4 shows room temperature TEP (S300) and room temperature resistivity ($\rho_{300}$) as a function of x for all the three series of samples. Their variations with x are similar. Sharp change in TEP and resistivity are occurring at the same concentration except
Fig. 5.1 Temperature dependence of S for Bi$_2$Sr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ samples.
Fig. 5.2 Temperature dependence of $S$ for Bi$_2$Sr$_2$Ca$_{1-x}$Ce$_x$Cu$_2$O$_y$ samples
Fig. 5.3 Temperature dependence of $S$ for Bi$_2$Sr$_2$Ca$_{1-x}$Tb$_x$Cu$_2$O$_y$ samples
Fig. 5.4 The variation of room temperature resistivity ($\rho_{300}$) and thermoelectric power ($S_{300}$) with $x$ 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
in the case of Pr-doped sample. From the TEP measurements the Metal-Insulator (MI) transition is found to occur at the same doping level as found from the resistivity studies. This indicates that the same carriers are responsible for resistivity and TEP properties.

The TEP value of the undoped sample is small \( S_{300} = 0.19 \) \( \mu V/K \) and positive throughout the measured temperature range. There are several reports on TEP measurements on Bi-2212 system. Mandal et al [34], Munakanta et al [33] and Rao et al [23] reported negative TEP value for the Bi-2212 sample in the temperature range of \( T_c \) to 300 K. Wang et al [36] reported negative \( S_{300} \) value and positive \( S \) in the temperature range \( T_c \) to 196 K. Mandrus et al [32] reported a positive TEP value for the Bi-2212 single crystal with \( T_c = 80 \) K.

The \( S_{300} \) value of \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y \) (Bi-2212) reported by Obertelli et al [26] for polycrystalline sample (with \( T_c = 92 \) K, the maximum for Bi-2212 phase and the corresponding optimum carrier concentration according to eqn. (5.1.14) is \( p = 0.16 \)) is \( \approx 2 \mu V/K \). A comparison of the TEP value of our polycrystalline sample of \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y \) [with \( T_c = 82 \) K] shows that our sample is slightly in the overdoped region with \( p = 0.20 \). The overdoping is reduced when the small amount of dopants (Pr, Ce and Tb) are substituted at Ca site as indicated by the initial increase in \( T_c \) and TEP value of the doped samples.

Fig.5.5 shows \( S_{300} \) vs. hole concentration \( p \) (calculated from Presland's equation as mentioned in chapter IV)) and Obertelli's universal curve for the superconducting samples (0.07<\( p <0.20 \)). The figure shows that the experimental points follow the universal curve at higher carrier concentrations (\( p > 0.12 \)) and at lower carrier concentrations the present experimental data is below the universal curve.
Fig. 5.5 Plot of room temperature thermoelectric power ($S_{300}$) vs. carrier concentration ($p$).
TEP of the semiconducting samples is high ≈ 30-40 \( \mu \text{V/K} \) except in the case of Pr-doped Bi-2212 sample with \( x = 0.6 \), which has TEP ≈ 8 \( \mu \text{V/K} \). The plot of S versus T for the semiconducting sample in the Pr-doped series with \( x = 0.6 \) shows a slow increase in S with T in the temperature range 40-200 K and a sharp increase in the temperature range 200-300 K. This type of temperature dependence of S is similar to what has been reported in La-system [9] and in amorphous semiconductors in the hopping regime [3,5]. In the case of other semiconducting samples i.e., in Ce-doped (\( x = 0.4 \) and 0.5) and Tb-doped (\( x = 0.5 \)) Bi-2212 series, S is almost constant around room temperature and as we go to the low temperatures a smooth decrease in S is observed. For the Tb-doped (\( x = 0.6 \)) Bi-2212 sample, S decreases continuously with the decrease in temperature.

5.3 Analysis of the experimental data of the superconducting samples

The temperature and carrier concentration dependence of S in the present systems are similar to that reported in other high \( T_c \) systems and having the common characteristics mentioned earlier. A detailed analysis of the experimental data in view of various two-band models and a phenomenological narrow band model proposed for high \( T_c \) superconductors is undertaken. The band structures and formulas proposed in these models are different. Thus, it is essential to ascertain which model is more suitable for describing the TEP behavior of high \( T_c \) superconductors. A brief description of each model and its applicability to the experimental data is discussed in the following pages.

5.3.1 Two band model with linear T term

The temperature dependence of S of high \( T_c \) systems resemble that observed in mixed valent heavy Fermion systems [73]. In heavy Fermion system \( \text{CeNi}_x \), the TEP variations were analyzed using an expression (assuming Lorenzian resonance near the Fermi level)
where \( a_T \) is the normal band contribution. It is essentially different from the two band models which fits the temperature dependence of \( S \) with the usual formula, with electrons and holes having different mobilities.

Present data also fits well to the eqn.(5.3.4) (Fig.5.6-5.8). Mandal \textit{et al} [34] and Keshri \textit{et al} [40] also got good fittings for Bi\(_2\)Sr\(_2\)Ca\(_{1-x}\)Y\(_x\)Cu\(_2O\(_y\)\) and Tl\(_2\)Ba\(_2\)Ca\(_1-x\)Y\(_x\)Cu\(_2O\(_y\)\) systems respectively. The fitting parameter \( A \), \( B \) and \( \alpha \) and the estimated values of \( E_o - E_F \) and \( \gamma \) are given in Table-5.1.
Fig. 5.6 Best fit curves (solid lines) for Bi$_2$Sr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ samples corresponding to Eqn. (5.3.4)
Fig. 5.7 Best fit curves (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_y$ samples corresponding to Eqn.(5.3.4)
Fig. 5.8 Best fit curves (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Tb}_x\text{Cu}_2\text{O}_y$ wimples corresponding to Eqn.(5.3.4)
Table-5.1

Best fit parameters $A$, $B$, $\alpha$ of eqn.(5.3.4) and the estimated values $E_o - E_F$ & $\gamma$ 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

<table>
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<th>$x$</th>
<th>$A$ (foV)</th>
<th>$B$ (K)</th>
<th>$\alpha$ ($\mu$ V/K$^2$)</th>
<th>$E_o - E_F$ (K)</th>
<th>$\gamma$ (K)</th>
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For all the three series of samples in the present study, no systematic variation of $\alpha$ with $x$ is observed. $E_o-E_F$ and $\theta$ values increase with increase in dopant concentration (x). It is expected that with the increasing carrier (hole) density the Fermi level should go down relative to the top of the band. But $(E_o-E_F)$ increases with $x$. This is in contradiction to the expected result. Moreover, there is no evidence of the existence of the assumed band structure in high $T_c$ systems.

5.3.2 Nagaosa-Lee model

Using gauge-field theory for a uniform RVB [75] state, Nagaosa-Lee [76] proposed that, for superconducting cuprates TEP can be expressed as

$$S = S_F + S_B$$

(5.3.5)

where $S_F$ and $S_B$ estimated using Fermi and Maxwellian states are

$$S_B = \frac{k_B}{e} \left[ 1 - \ln \left( \frac{2\pi p}{mk_BT} \right) \right]$$

(5.3.6)

and

$$S_F = -\left( \frac{k_B}{e} \right) \frac{k_BT}{E_F}$$

(5.3.7)

Here $p$ denotes the concentration of holes on $\text{CuO}_2$ sheet per $[\text{Cu-O}]$ and $m$ is the mass of the Bosonic carrier. In order to fit the experimental data, $m$ and $E_F$ were regarded as fitting parameters. However, those fitted curves were not in reasonable agreement with experimental data. Ikegawa et al [77] slightly modified this model by introducing an additional parameter $F$ and fitted for the $(\text{EuCe})_4(\text{BaEu})_4\text{Cu}_6\text{O}_{14}$ and $\text{Nd}_{1.4}\text{Ce}_{0.2}\text{Sr}_{0.4}\text{Cu}_{1-x}\text{Zn}_x\text{O}_y$ systems using the equation for $S$ given by
where $F$, $G$ and $H$ are the fitting parameters. From this model, the value of $G(\approx m^{-1})$ and $H(\approx E_F)$ are expected to be of the order of exchange energy $J (\approx 1000 \, K)$.

Using the $p$ value calculated from Presland’s relation [43] (chapter IV), the experimental data is fitted to eqn. (5.3.8) (Fig. 5.9-5.11). The fitting parameters obtained for the superconducting samples are given in Table-5.2. For all the three series of samples the value of $F$ increases and the value of $G$ and $H$ decreases with increasing $x$. As expected from the theory, $H$ is of the order of $J$. But $G$ values are large. Wang et al [36], Mandal et al [34] and Keshri et al [40] also obtained high values of $G$ for higher carrier concentration samples of the $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_y$, $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ systems, respectively. Though, good fittings were obtained for this model, the parameter $G$ obtained from the fittings is unreasonably large, which cannot have any physical basis. The large $H$ value and small $F$ value indicates that Boson contribution turns out to be negligible, which is unreasonable.

5.3.3 Two band model of Xin et al

Xin et al [41] have used the two band model to analyze the temperature dependence of TEP of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$. For the case of a system which contains both electrons and holes, $S$ can be written as [2]

$$ S = \frac{(S^+ \sigma^+ + S^- \sigma^-)}{\sigma} \tag{5.3.9} $$

where $\sigma = \sigma^+ + \sigma^-$ is the sum of the electrical conductivities by holes ($\sigma^+$) and by electrons ($\sigma^-$) and $S^+$ and $S^-$ are the TEP values due to holes and electrons respectively. In the case of high $T_c$ superconductors, it is assumed that one band which is formed by
Fig.5.9 Best fit curves (solid lines) for Bi$_2$Sr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ samples corresponding to Eqn.(5.3.8)
Fig. 5.10 Best fit curves (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_y$ samples corresponding to Eqn.(5.3.8)
Fig. 5.11 Best fit curves (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Tb}_x\text{Cu}_2\text{O}_y$ samples corresponding to Eqn.(5.3.8)
Table-5.2

Best fit parameters $F$, $G$ and $H$ of eqn.(5.3.8) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_y$ (M = Pr, Ce & Tb) samples

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>P</th>
<th>F</th>
<th>$G(\text{K})$</th>
<th>$H(\text{K})$</th>
</tr>
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<tbody>
<tr>
<td><strong>Pr-doped</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.20</td>
<td>0.0146</td>
<td>8.50 $\times 10^{30}$</td>
<td>6792.6</td>
</tr>
<tr>
<td>0.2</td>
<td>0.13</td>
<td>0.0281</td>
<td>4.20 $\times 10^{16}$</td>
<td>5615.8</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.10</td>
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<td>1.12 $\times 10^7$</td>
<td>2679.0</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.07</td>
<td>0.1274</td>
<td>2.00 $\times 10^5$</td>
<td>1904.8</td>
<td></td>
</tr>
<tr>
<td><strong>Ce-doped</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.12</td>
<td>0.0305</td>
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<td>6005.0</td>
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<tr>
<td>0.15</td>
<td>0.10</td>
<td>0.0657</td>
<td>4.99 $\times 10^7$</td>
<td>1764.4</td>
<td></td>
</tr>
<tr>
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<td>0.07</td>
<td>0.1323</td>
<td>8.88 $\times 10^4$</td>
<td>1424.1</td>
<td></td>
</tr>
<tr>
<td><strong>Tb-doped</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.16</td>
<td>0.0259</td>
<td>1.01 $\times 10^{18}$</td>
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</tr>
<tr>
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<td>2.50 $\times 10^9$</td>
<td>2416.7</td>
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</tr>
<tr>
<td>0.4</td>
<td>0.07</td>
<td>0.1575</td>
<td>1.52 $\times 10^4$</td>
<td>970.9</td>
<td></td>
</tr>
</tbody>
</table>
Cu-0 planes contribute to holes and another formed by Bi-0 layers contribute to electrons. \( CT' \) is proportional to \( 1/T \) because Cu-0 layers are metallic and \( \sigma^- \) is proportional to \( \exp(E_c/kT) \). The following equation is used by Xin et al [41] for Tl-based and by Awana et al [27, 30] for Bi-based high \( T_c \) superconductors

\[
5 = AT + (B\lambda + CT)\exp(-\lambda/T)
\]  

(5.3.10)

A, B, C and A are constants for a particular sample. The fits of the above equation to the TEP data are shown in Fig.5.12-5.14. Parameters estimated from the fittings are given in Table-5.3. The estimated values of the energy gap \( (E_g = E_c/k_B \) where \( E_c = \lambda/k_B \) of the semiconducting band of Bi-0 layers are listed in Table-5.3. The \( E_g \) value increases with increase in x. These \( E_g \) values are consistent with the room temperature energy gap values in a wide range 0-0.3 eV obtained from scanning-tunneling spectroscopy studies on Bi-2212 system [78-80]. This gap depends on the extent of intercalation of excess oxygen in the Bi-0 layers. In the absence of excess oxygen the gap approaches zero. We have attributed as pointed out earlier the transition broadening with dopant content observed in the resistivity vs. T plots is due to the excess oxygen intercalated in the Bi-0 layers. The increasing \( E_g \) values can, therefore, be correlated to the \( T_c \) depression as the dopant content is increased. We did not observe any systematic variation in A parameter value, which represents contribution from mobile holes does not vary systematically with the dopant content.

Though this model works well for Bi [27,30] and Tl [41] systems and reasonable energy gaps are obtained, but still it is unsatisfactory because many experiments have demonstrated that the Bi-0 and Tl-O layers or Cu-0 chains are insulating. It is unlikely that universalities observed in various physical parameters can be attributed to different bands, because universality rovers a wide variety of physical systems.
Fig. 5.12 Best fit curves (solid lines) for Bi$_2$Sr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ samples corresponding to Eqn. (5.3.10)
Fig. 5.13 Best fit curves (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{3-x}\text{Ce}_x\text{Cu}_2\text{O}_y$ samples corresponding to Eqn. (5.3.10)
Fig. 5.14  **Best fit curves** (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Tb}_x\text{Cu}_2\text{O}_8$ samples corresponding to Eqn. (5.3.10)
Table-5.3

Best fit parameters $A$, $B$, $C$ and $A$ of eqn.(5.3.10) and corresponding $E_\text{g}$ values for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_y$ ($\text{M} = \text{Pr, Ce, Tb}$) samples

<table>
<thead>
<tr>
<th>$x$</th>
<th>$A$ (µV/K)</th>
<th>$B$ (µV/K)</th>
<th>$C$ (µV/K)</th>
<th>$A$ (K)</th>
<th>$E_\text{g}$ (eV)</th>
</tr>
</thead>
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<td>Pr-doped</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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</tr>
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<td>-0.0417</td>
<td>244</td>
<td>0.0420</td>
</tr>
<tr>
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<td>-0.0547</td>
<td>-0.0422</td>
<td>450</td>
<td>0.0774</td>
</tr>
<tr>
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<td>0.0774</td>
<td>-0.1124</td>
<td>-0.0257</td>
<td>484</td>
<td>0.0552</td>
</tr>
<tr>
<td>Ce-doped</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
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<td>-0.0003</td>
<td>-0.0978</td>
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<td>0.0057</td>
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<tr>
<td>0.15</td>
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<td>-0.2576</td>
<td>71</td>
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<td>-0.1125</td>
<td>-0.1756</td>
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<td>0.0433</td>
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<tr>
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<td>0.1</td>
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<td>-0.0244</td>
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<td>0.4</td>
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<td>-0.3954</td>
<td>0.2582</td>
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<td>0.1075</td>
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</tbody>
</table>
5.3.4 Phenomenological narrow band model

From the positron-annihilation [81,82], photoemission [83,84] and the transmission spectroscopy [85] studies, the existence of narrow band in the HTSC systems is inferred. Gasumyant et al [16] used the approach of Kazmin et al [86] and proposed a band spectrum model which supposes the existence of a narrow peak in the electron density of states (DOS) close to the Fermi level to explain the behavior of all the transport coefficients; resistivity \( \rho(T) \), TEP \( S(T) \) and the Hall coefficient \( R_H(T) \) in the normal state of \( \text{Y-123} \) system as a function of oxygen content and different cation substitutions. They have estimated quantitatively some band spectrum parameters which characterize the band width and the band filling degree.

According to Gasumyant et al [16], if the Fermi level \( E_F \) is located in the (DOS) peak, the narrowness of this peak determines the transport properties whatever may be the nature and origin of the peak. This peak can either be a single narrow band or a sharp DOS peak on wide band. If the DOS inside the peak is significantly greater than the outside, the normal state electron transport will also be determined by the structure and the properties of this peak. The van Hove singularity near Fermi level can be the most probable reason for this peak [62]. As mentioned earlier, many properties of HTSC such as marginal Fermi liquid behavior [63], specific heat jump [64], isotope shift [65-67] and transport coefficients could be explained satisfactorily in van Hove singularity picture. The transport coefficient analysis by Gasumyant et al [16] also supports this picture. Whatever may be the origin of the peak, the term "narrow band" is used for this narrow peak in density of states whose width \( W \) is comparable to \( k_B T \).

This model includes three phenomenological parameters. One \( F \), is the degree of band filling with electrons, which is the ratio of number of electrons to the total number of
states in the band. The sign and value of TEP depends on this parameter. In the high
temperature limit \((k_B T > W)\), where \(W\) is the bandwidth, \(k_B\) is Boltzmann constant
\[
S = \frac{k_B}{e} \ln \frac{F}{1 - F}
\]  
(5.3.11)

\(S = 0\) at \(F = 1/2\), \(S > 0\) at \(F > 1/2\) and \(S < 0\) for \(F < 1/2\).

They have used the rectangular approximation for \(N(E)\) and \(\sigma(E)\) because of the
narrowness of the band. The second parameter is the total effective bandwidth \(W_D\) and
the third is \(W_\sigma\), effective width of an energy interval of the electrons which gives main
contribution to the electrical conduction process.

According to the present model \(S\) is given by

\[
S = \frac{-k_B}{e} \left\{ \frac{W_\sigma}{\sinh(W_\sigma)} \left[ e^{-\mu^*} + \cosh W_\sigma^* - \frac{1}{W_\sigma^*} \right] \right. \\
\left. \times (\cosh \mu + \cosh W_\sigma^*) \ln \frac{e^{\mu^*} + e^{W_\sigma^*}}{e^{\mu^*} + e^{-W_\sigma^*}} \right\} - \mu^*
\]  
(5.3.12)

\[
\mu^* = \mu/k_B T = \ln \frac{\sinh(FW_D^*)}{\sinh[(1 - F)W_D^*]}
\]  
(5.3.13)

where \(\mu\) is the chemical potential, \(W_D^* = W_D/2k_B T\) and \(W_\sigma^* = W_\sigma/2k_B T\).

Gasumyant et al [16] fitted their TEP data on \(Y-123\) system to the above equation
and calculated the band structure parameters. To analyze the TEP data of their
\(Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y\) system [35], they have used the same model with an additional
assumption that the band is asymmetric. To take band asymmetry into account, the
asymmetry parameter \(b\) is introduced between the \(N(E)\) and \(\sigma(E)\) rectangles centers.
The above expression is still valid, if \(\mu\) is replaced by \(\mu - bW_D^*\). The same approach is used
to explain the temperature dependence of TEP for the present systems under study. The best fits of the present to the eqn.(5.3.12) are shown in Fig.5.15-5.17. The estimated band spectrum parameters are listed in Table-5.4. The variation of these parameters with x is similar to those observed in Y-123 and Nd-doped Bi-2212 system. With increase in x, F value increases. This variation is non-linear. The increase in x leads to an increase in number of electrons (which should be linear) but also decreases the total number of states in the band. So, F is expected to be non-linear.

The total effective band width increases with increase in x. The increase observed in $W_\sigma$ is small compared to that in $W_D$. The ratio of $W_\sigma/W_D$ decreases as x changes from 0 to 0.5. The value of $W_D$ obtained for the present samples are close to the values obtained in $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ system. With increase in x, disorder in the system increases which leads to Anderson localization, i.e., broadening of the band ($W_D$ value increase) and the relative reduction in energy interval shared by the delocalized states ($W_\sigma/W_D$ decrease) occurs. On the other hand, the increase in effective band width causes a decrease in $N(E_F)$ value which in turn causes the decrease in $T_c$.

5.4 Analysis of the data of the Semiconducting samples

The TEP variation with temperature for semiconducting samples, which have mobility gap at the Fermi level, is given by the eqn.(5.1.8). According to this equation, S should decrease with increase in temperature. Contrary to this, in the present samples S increases with increase in temperature. From the resistivity data, it is observed that the conduction in these samples at low temperatures is governed by variable range hopping (VRH). The expression for TEP in the VRH regime is given by the eqn.(5.1.12). Fig.5.18 and 5.19 show the S vs $T^{-m}$ plots for various semiconducting samples for m = 1/3 and 1/2. Both the plots appear linear over a wide range of temperature. For the present
Fig. 5.15 Best fit curves (solid lines) for Bi$_2$Sr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ samples corresponding to Eqn.(5.3.12)
Fig. 5.16 Best fit curves (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_y$ samples corresponding to Eqn. (5.3.12)
Fig. 5.17 Best fit curves (solid lines) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Tb}_x\text{Cu}_2\text{O}_y$ samples corresponding to Eqn. (5.3.12)
Table-5.4

Best fit parameters $W_D$, $W_o$ and $F$ of eqn. (5.3.12) and the corresponding $W_o/W_D$ values for Bi$_2$Sr$_2$Ca$_{1-x}$M$_x$Cu$_2$O$_y$ (M = Pr, Ce & Tb) system

<table>
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<tr>
<th>x</th>
<th>$W_D$ (meV)</th>
<th>$W_o$ (meV)</th>
<th>F</th>
<th>$W_o/W_D$</th>
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</thead>
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<td></td>
<td></td>
</tr>
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<td>28</td>
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<td><strong>0.39</strong></td>
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<td>0.532</td>
<td>0.34</td>
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<tr>
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<td></td>
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<td></td>
<td></td>
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Fig. 5.18 Plot of $S$ vs. $T^{1/3}$ for various semiconducting samples.
Fig. 5.19 *Plot of $S$ vs. $T^{1/2}$* for various semiconducting samples
series of samples it is hard to distinguish the difference between $T^{1/3}$ or $T^{1/2}$ dependence of $S$ (i.e., whether the hopping is in 3D or in 2D). From the resistivity data also, it is not possible to distinguish whether the hopping is in 3D or in 2D.
5.5 References


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