Chapter 4

Impurity substitution in Bismuth and Thallium cuprates: Suppression of $T_c$
and estimation of pseudogap

4.1 Introduction

In this chapter our attempt will be to understand the effects of impurity substitution at Cu-site of high-$T_c$ cuprates. In high-$T_c$ superconductors, studying the suppression of $T_c$ by impurity substitution at the Cu-site of the CuO$_2$ plane is of considerable importance, because it provides useful information regarding the symmetry of the superconducting order parameter, and also throws light on the recent striking issue of the observation of a normal-state pseudogap in underdoped materials. In fact, studies of suppression of $T_c$ in high-$T_c$ cuprates by intentional substitution of both magnetic (Co, Ni) and non-magnetic (Zn) impurities at copper(Cu) sites have become a leading subject of interest. These impurities essentially cause pair breaking [1, 2, 3] leading to the reduction of $T_c$ while leaving the carrier concentration in the CuO$_2$ plane unaltered. In conventional superconductors it is well known that paramagnetic impurities are much more effective $T_c$ suppressors than non-magnetic ones. Time-reversal -symmetry-breaking perturbations such as paramagnetic scattering have a strong pair-breaking effect for the spin-singlet s-wave cooper pairs [4]. In the case of high-$T_c$ cuprates, things look different. In the YBa$_2$Cu$_3$O$_7$ system, Zn and Ni occupy Cu sites in the CuO$_2$ plane whereas Co and Fe go into the CuO-chain site and decrease carrier density. Zn impurity which is a non-magnetic ion is 3 to 4 times more effective than Ni in depressing $T_c$ [1, 5] and the gradient $dT_c/dz$ turns out to be $-(12 - 13)K/\%$ for Zn and $-(3 - 4)K/\%$ for Ni, where $z$ is the metal impurity concentration per Cu atom. In order to examine the generality of this result in other 123 materials, Gold-
schmidt et al. [2] found that in 1:2:3 Ca-La-Ba-Cu-O system, the depression of $T_c$ by both Zn and Ni substitutions is almost the same where $dT_c/dz \sim -9$ and $-7K/\%$, respectively. On the other hand, in Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) system [6], for all kinds of impurities, $T_c$ is found to decrease with increasing impurity concentration. Here, both non-magnetic Zn as well as magnetic Fe, Co and Ni cause a decrease in $T_c$ without affecting the carrier density. So to clarify the $T_c$ suppression results due to impurity substitution in high-$T_c$ systems, detailed studies are necessary.

The issue of the symmetry of the superconducting order parameter (OP) in high-$T_c$ superconductors has attracted considerable attention in the recent past and has been discussed widely in the high-$T_c$ literature, a large fraction of which reported evidence of a $d_{x^2-y^2}$ OP symmetry [7, 8], and a consensus seems emerging in this direction. But, the striking results relating the pseudogap, as reported in NMR [9, 10, 11], optical conductivity [12, 13], heat capacity [14], transport data [15] and angular resolved photoemission spectroscopy (ARPES) studies [16], are yet to be understood within an unified framework. In other words, there have been no consensus so far regarding the origin of the pseudogap and the issue regarding the role played by the pseudogap to affect the physical characteristics of high-$T_c$ cuprates. Presently what is generally recognized regarding the pseudogap, is that, for underdoped cuprates there occurs some form of correlation above $T_c$ referred to as the pseudogap state, that reduces the electronic entropy, magnetic susceptibility and also has considerable effects on transport properties. Recently ARPES studies [16] have given direct evidence for the presence of a pseudogap in the density of states (DOS) at the Fermi level ($E_F$) above $T_c$. Loram et al. [17] and Williams et al. [11] argued that the normal-state pseudogap starts opening up in the lightly overdoped region and extends back into the underdoped region with a growing magnitude, progressively depleting the DOS near $E_F$. On the other hand, with the disappearance of the pseudogap in the more overdoped region, the DOS remains largely unchanged [18]. J L Tallon [3], from detailed NMR and heat capacity studies shows that the pseudogap and superconductivity are independent and even compete with each other towards low temperatures, an observation strongly confirmed by the absence of an isotope effect in the pseudogap energy and the concurrent presence of the same for the superconducting gap [19]. In contrast, from tunneling spectroscopy studies on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals, Renner et al. [20] suggests that the pseudogap scales with the superconducting gap i.e., the pseudogap has the same origin as the superconducting gap. Although there is a controversy regarding the origin of the pseudogap, it is now well accepted that any theory for the superconducting cuprates will need to account for the pseudogap. With the above background, it is now clear that the
study of the behavior of the pseudogap, how pseudogap evolves as a function of different impurity concentration in different doping regime and its relation to superconductivity will be an important step to elucidate the mechanism for superconductivity in high-$T_c$ cuprates.

In fact all transport properties of high-$T_c$ superconductors including the thermopower ($S$) most notably, exhibit a systematic dependence on hole concentration. The thermopower is a simple but highly sensitive tool to detect any changes in the electronic transport mechanism due to small variations of carrier density or disorder in the CuO$_2$ plane. For example, in YBa$_2$Cu$_3$O$_7$ [21], YBa$_2$Cu$_4$O$_{8}$ [21], and La$_{2-x}$Sr$_x$CuO$_4$ [22] systems, thermopower decreases systematically with the doping of Zn and Ni and a clear indication of the normal-state gap opening and its suppression with Zn doping have been reflected in the temperature dependence of the thermopower of the underdoped samples. Measurements of thermopower are equally valid on sintered or ceramic samples as the thermopower of untextured polycrystalline samples is just the $a-b$ plane thermopower.

The above observations have prompted the following investigations on polycrystalline Co-doped Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ (Bi-2212) and Tl$_2$Ba$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ (Tl-2212) systems. The compositions studied are $x = 0, 0.2, 0.3, 0.4, 0.5$ and $y = 0.00, 0.02, 0.04, 0.06, 0.08$ for Bi-2212 system and $x = 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3$ and $y = 0.00, 0.02, 0.04, 0.06$ for Tl-2212 system.

The investigations consist of five distinct parts:

(a) Measurement of resistivity in the temperature range $15K<T<300K$ and analysis of $T_c$-suppression data within the unitary pair-breaking formalism due to Abrikosov & Gorkov.

(b) Measurement of thermopower (TEP) in the temperature range $310K$ down to $T_c$ and to study the effect of Co-substitution on TEP compared to other doping at Cu site in other high-$T_c$ systems.

(c) Scaling of thermopower of the underdoped Bi-2212 and Tl-2212 samples and to examine whether the thermopower of underdoped cuprates has a single functional form.

(d) Estimation of the pseudogap magnitude within a "fermi level density of states suppression" picture and to correlate this with the characteristic temperature $T^*$ obtained.
from thermopower measurement

(e) Calculation of susceptibility considering the DOS-suppression effects of the pseudo-gap

It may be mentioned here that the carrier concentration for the samples is changed by substitution of yttrium (Y) at Ca sites. This procedure of changing carrier concentration does not affect the CuO₂ plane responsible for superconductivity. Whereas a change of the carrier concentration by oxygenation procedure might directly affect the CuO₂ plane by leaving traces of inherent impurities during sample preparation. These impurities are not accounted for while studying the $T_c$ suppression by impurity substitution and hence, the samples prepared by Y-substitution procedure are better suited for the purpose of studying $T_c$-suppression as discussed in this chapter.

4.2 Effect of Co-doping on resistivity

4.2.1 Bi-2212

The effect of Co-doping on the temperature dependence of the resistivity ($\rho$) and superconducting transition temperature of Bi₂Sr₂Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ system is shown in Fig 4.1 for two batches of samples with $x$=0.0 and 0.3. Both the conductivity and $T_c$ are observed to decrease with increasing Co concentration. The midpoint of the superconducting transition in the $\rho$ vs $T$ plot is defined as $T_c$ here. $T_c$ determined in this way is very close to the temperature at which $d\rho/dT$ is maximum. For $x$ = 0, all the samples are metallic (i.e., $d\rho/dT$ is positive) and superconducting. The $\rho$ vs $T$ of Co-riched samples shows a small upturn or semiconducting-like behavior for higher Y-content samples. The $x$ dependence of $T_c$ for the $y = 0$ samples is similar to that reported in the literature [23, 24]. The variation of $T_c$ as a function of $y$ is shown in Fig 4.2 for samples with different $x$. From the figure, it is clear that $T_c$ decreases linearly with Co doping. The slope of $T_c$ vs $y$ curves, i.e., the rate of $T_c$ suppression with Co doping, increases with increasing Y content. This suggests that the $T_c$ suppression is stronger in the underdoped regime. Similar nature of $T_c$ suppression was observed for La-214 and (Y,Ca)-123 systems by Tallon et al. [25]. According to them the more rapid suppression of $T_c$ in the underdoped region is due to the appearance of a pseudogap.
Fig. 4.1 Temperature dependence of the electrical resistivities ($\rho$) of \( \text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_{1-y}\text{Co}_y\text{O}_8 \) for various Co doping. (a) \( x = 0.0 \), (b) \( x = 0.30 \).

Fig. 4.2 The suppression of $T_c$ for \( \text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_{1-y}\text{Co}_y\text{O}_8 \) as a function of Co concentration ($y$) for various $Y$ contents ($x$)
4.2.2 Tl-2212

Fig. 4.3 displays the temperature dependence of the electrical resistivity ($\rho$) of Tl$_2$Ba$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ system for four batches of samples with $x=0.0$, 0.1, 0.2 and 0.3. Similar to the Bi-2212 system, both the conductivity and $T_c$ decreases with increasing Co concentration. Also for $x=0.0$ to 0.1, all the Co-doped samples are found to be metallic but for higher Y-content samples, it is found that Co substitution introduces a semiconducting-like resistivity behavior in Co-riched samples. The $x$ dependence of $T_c$ for different Co-doped samples is shown in Fig 4.4a. The $T_c$ vs $x$ behavior for the cobalt-free
(i.e. $y=0$) samples are similar to that for Poddar et al. [26], $T_c$ remains almost constant up to 10% yttrium concentration and then starts to decrease sharply with increasing yttrium content. Only difference is that the rate of decrease i.e. $dT_c/dx$ beyond $x=0.1$ in our sample is $\sim 1.7$ times higher than that for the samples of Poddar et al. [26]. We think this discrepancy lies in the difference in oxygen intake during sintering due to the different synthesis conditions of the two groups. It may be noted that with increasing Co concentration the $T_c$ vs $x$ curve shifts smoothly to the lower yttrium concentration region without showing any plateau or a local minimum of $T_c$.

![Graph](image-url)

Fig 4.4 (a) The suppression of $T_c$ as a function of Y concentration ($x$) for various Co contents ($y$) and (b) plot of $T_c/T_{co}$ as a function of Co concentration ($y$) for various Y contents ($x$) for $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_{1-x}\text{Co}_y\text{O}_{28}$

The variation of $T_c$ with Co doping for different $x$ is shown in Fig 4.4b. Here $T_c$ at different $x$ are scaled to its value at zero Co doping i.e. $T_{co}$. Similar to Bi-2212 system, here also $T_c$ decreases linearly with Co doping. Also with increasing yttrium concentration (i.e. decreasing $p$), the slope $dT_c/dy$ increases.
4.3 Analysis of $T_c$ suppression data

Here we discuss the results of $T_c$ suppression for both Bi-2212 and Tl-2212 systems within the framework of Abrikosov- Gorkov (AG) pair-breaking theory [27]. It has been shown earlier [28, 29] that depending on the symmetry of the superconducting order parameter, the pair-breaking rate or the variation of the experimentally measured $T_c$ would be different. This is due to the fact that a pairing state of reduced symmetry is unstable to impurity scattering to a very high degree, i.e., depression of $T_c$ is significantly stronger for a superconductor with $d$-wave symmetry than for a superconductor with pure $s$-wave symmetry.

Within the AG formalism, pair breaking rate is inversely proportional to the DOS at the fermi level denoted by $N(E_F)$. Experimental data are fitted to the AG relation using $N(E_F)$ as a fitting parameter and its values are thereby found out corresponding to each doping. The AG relation is given by

$$-\ln \left( \frac{T_c}{T_c^0} \right) = \psi\left[ \frac{1}{2} \right] + \frac{\Gamma}{2\pi k_B T_c} \psi\left[ \frac{1}{2} \right], \quad (4.1)$$

where $T_c^0$, as mentioned earlier, is the value of $T_c$ at $y = 0$, i.e., without any impurity scattering centre in the sample. Here $\psi[z]$ represents the digamma function for argument $z$ and $\Gamma = n_i/\pi N(E_F)$ is the pair-breaking scattering rate for unitary scattering. The quantity $N(E_F)$ is the DOS at fermi level (in units of $eV^{-1} A^2$) and $n_i = \alpha y/abc$ is the density of impurity scatterers per unit volume where $\alpha$ is the number of CuO$_2$ planes per formula unit and $a, b, c$ are lattice constants. A justification for using the AG equation for the short coherence length cuprate superconductors can be found in references [3, 14].

In Figs 4.5a and 4.5b, solid and dashed lines are fitted curves using equation (4.1) for both the Bi-2212 and Tl-2212 samples. Matching of the fitted lines with the experimental data are quite good, as seen in figures. In the curve fitting process, $N(E_F)$ is taken as a fitting parameter and its values are found out by a least square fitting of $T_c$ versus $y$ data. Fitted $N(E_F)$ values corresponding to different doping levels (different $x$) are listed in Table-I. It may be noted here that the typical r.m.s deviation in the least square fitting of data is of the order of 1-2K which reaffirms the visual excellence of data fitting curves presented in Figs 4.5a and 4.5b.
Fig 4.5 Plot of $T_c$ as a function of Co concentration for various Y contents ($x$). Figure (a) corresponds to Bi-2212 and (b) corresponds to Tl-2212 samples. In both the panels, the symbols represent experimentally measured $T_c$ values and lines (solid and dashes) represent fitted curves using AG equation (4.1)

From table I, it is seen that $N(E_F)$ shows a progressive depletion towards underdoping which could imply the opening up of a gap of growing magnitude. As a consequence, pair breaking rate increases as one goes towards the underdoped region. This is consistent with our result that $T_c$ suppression is stronger in the underdoped region.
### Table-I

$p, N(E_F)$ and $\Gamma_c$ values for Bi-2212 and Tl-2212 samples

<table>
<thead>
<tr>
<th>Material</th>
<th>$x$</th>
<th>$p$</th>
<th>$N(E_F)$ ($/\text{eV}-\text{Å}^3$)</th>
<th>$\Gamma_c$ values (in meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>From curve fitting</td>
</tr>
<tr>
<td>Bi2212</td>
<td>0.0</td>
<td>0 225</td>
<td>0.0805</td>
<td>5.90</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.160</td>
<td>0.0435</td>
<td>6.77</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.135</td>
<td>0.0250</td>
<td>6.98</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.110</td>
<td>0.0191</td>
<td>6.09</td>
</tr>
<tr>
<td>Tl2212</td>
<td>0.0</td>
<td>0.17</td>
<td>0.0820</td>
<td>8.31</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.13</td>
<td>0.0625</td>
<td>8.13</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.102</td>
<td>0.0556</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.09</td>
<td>0.0503</td>
<td>4.23</td>
</tr>
</tbody>
</table>

Plotting the ratio $|d\Gamma_c/dy|$ (obtained by numerical differentiation of the $T_c$ versus $y$ data) as a function of $y$, we observe that with increasing $y$, the slope $|d\Gamma_c/dy|$ increases monotonically for small $y$ and then registers a steep rise before falling sharply to zero at some value of $y$ denoted as the critical value of the impurity concentration $y_c$. One representative plot of $|d\Gamma_c/dy|$ vs $y$ for Bi-2212 samples is given in Fig 4.6. Values of $y_c$ are different for different doping levels of the samples. For overdoping, $y_c$ is considerably large and decreases progressively but rapidly towards underdoping. Noting the values of $y_c$ from each curve, one could calculate the corresponding critical values of the pair breaking scattering rate as $\Gamma_c = \alpha y_c/\sqrt{\pi N(E_F)abc}$ which are listed in Table-I. The AG relation used here (in equation (1)) is valid for the weak coupling $d$-wave superconductors for which the critical scattering rate (at which $T_c$ reduces to zero) is evaluated [30] to be $\Gamma_c = 0.88k_BT_c$. Values of $\Gamma_c$, calculated by this empirical relationship, are also presented in Table-I which are within 1-2% of the values obtained by data analysis. This correspondence could serve as a crosscheck for the correctness of the data fitting procedure and could also signify the validity of the AG relation used for data fitting.
Fig 4.6  Modulus of the slope of different fitted curves, as in Fig. 4.5 for Bi-2212 samples, are plotted against Co concentration (y). The slope is found numerically and has the dimension of Kelvin per percent of Co concentration.

4.4 Effect of Co doping on thermopower

The thermopower \(S\) for Bi-2212 samples for different \(x\) and \(y\) are plotted against temperature in Fig 4.7. For the \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\) \((x = 0\) and \(y = 0)\) sample, \(S\) is negative from 310K down to \(T_c\), and decreases linearly with increasing \(T\). \(S\) increases systematically with increasing impurity \((y)\) concentration but remains mostly negative and maintains its linear dependence on \(T\) up to the highest doping level of Co. The following clear characteristics are observed in the \(S\) vs \(T\) curve with increasing Y doping \((x)\): (1) \(S\) changes from negative to positive and becomes nonlinear in \(T\), (2) a broad peak appears and this peak shifts towards higher temperatures, (3) a small anomaly appears slightly above the peak in the \(S\) versus \(T\) curve for \(x \geq 0.3\) samples (clearly depicted in Fig 4.8). The small, negative and linear \(T\)-dependence of \(S\) in the overdoped regime is consistent with the metallic nature of
Fig 4.7 Temperature dependence of the thermopower ($S$) of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ samples for various Co concentration ($y$) (a) $x = 0$ (b) $x = 0.20$ (c) $x = 0.30$ (d) $x = 0.40$ (e) $x = 0.50$
the resistivity

The thermopower $S$ for Tl-2212 samples with different $x$ and $y$ are plotted against temperature in Fig 4.9. It is found that $S$ for sample with $x = 0$ and $y = 0$ is positive and nearly zero at room temperature, increases linearly with decreasing temperature, shows a peak slightly above $T_c$ and then falls sharply to zero at $T_c$. Similar type of $S - T$ behavior is maintained up to the highest doping level of Co. On increasing Y concentration, $S$ remains positive but a broad peak appears in the $S$-$T$ curve which shifts towards higher temperatures.

![Fig 4.8](image.png)

**Fig 4.8** Temperature dependence of the thermopower for the underdoped Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_8$ samples with $x = 0.30, 0.40, 0.42, 0.44$ and $0.46$. For $x = 0.30$ sample, $S$ has been shifted upward by $85 \mu V/K$. The arrows indicate the appearance of a weak anomaly due to the opening of the noraml-state gap.

It has been pointed out [21] that the appearance of the broad peak in the $S$-$T$ curve with increasing $x$ (decreasing carrier density) is due to the opening of a gap in the normal-state termed as the *pseudogap*. The rapid decrease of $S$ below this peak is also due to the opening of this gap. In the Zn-substituted YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$ samples, this
Fig 4.9  Temperature dependence of the thermopower ($S$) of Tl$_2$Ba$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ samples for various Co concentration ($y$) (a) $x = 0.0$ (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.20$, (e) $x = 0.25$ and (f) $x = 0.30$. 
broad peak is suppressed considerably and the thermopower is enhanced at low temperatures well below the peak [21]. The disorder introduced in the CuO$_2$ plane by the random distribution of Zn ions suppresses the gap. The temperature, at which $S$ of Zn-doped samples deviates from the undoped one, has been assigned as the gap-opening temperature. In the La$_{2-x}$Sr$_x$CuO$_4$ system too, thermopower decreases considerably with Zn and Ni doping [22]. This behavior is seen in the underdoped as well as in the highly overdoped region. Sera et al. [22] proposed that $S$ consists of two parts: a $T$-linear part and an anomalous part. The linear term is usual and ascribed to electron diffusion in metals while the anomalous term is due to the spin-fluctuations or spin correlation. They suggested that the decrease of $S$ by Zn substitution is due to the decrease of the anomalous spin fluctuation term. However, the thermopower of both Bi-2212 and Tl-2212 systems show a different kind of behavior with Co doping. $S$ is observed to increase monotonically with Co concentration up to the highest value of $y$ and shows a broad peak for optimum and underdoped samples. Also, any enhancement of $S$ below the peak is not seen in the Co-substituted samples as observed in Zn-doped YBa$_2$Cu$_3$O$_7$ [21]. Except for a small shift in the peak towards the higher temperature, the nature of the $T$ dependence of $S$ for the Co-doped samples is similar to that for undoped samples. The above unusual behavior of $S$ with Co doping can not be ascribed to a decrease in the carrier density. Maeda et al. [6] measured the Hall coefficient of Zn-, Ni-, Co- and Fe-doped Bi-2212 and did not observe any decrease in the carrier density. In fact, their results show a small decrease in the Hall coefficient for Fe-doped samples as compared to the undoped one. The room temperature Hall coefficient for Bi-2212 ($x = 0.4$) and Tl-2212 ($x = 0.05$) samples for different Co concentrations have been measured and it is observed that $R_H$ does not depend on the impurity concentration. Thus the increase of $S$ with Co doping must have a different origin.

In Fig. 4.8, the temperature dependence of $S$ for Bi-2212 underdoped samples ($x \geq 0.3$) with $y = 0$ are shown. Above the peak, thermopower shows a small anomaly below a characteristic temperature ($T^*$). This feature was reproduced in several measurements. As has already been discussed, the broad peak in $S$ arises due to the opening of the normal-state gap. The temperature $T^*$ below which $S$ shows anomaly is assigned to the gap opening temperature. A deviation from the linear resistivity [31, 32] behavior below a certain temperature and a small anomaly in the thermopower [32] close to this temperature has been observed for oxygen deficient Bi-2212 samples. It has been suggested that the normal-state gap opens below this temperature [31, 32]. The gap opening temperatures $T^*$ are 179, 196, 203, 230 and 258 K, respectively, for our samples with $x = 0.3, 0.4, 0.42, 0.44$ and...
0.46. These temperatures ($T^*$) are comparable with those reported by others for samples with similar $T_c$ and doping level [13, 31, 32, 33]

Due to the complicated temperature dependence of thermopower in high-$T_c$ superconductors, it is difficult to determine the normal-state parameters related to electron transport in these systems. Several theoretical models have been proposed to explain the temperature dependence of $S$ but at this moment it is hard to judge which one is best to describe the thermopower of high-$T_c$ materials. Nevertheless, efforts have been made to find whether any correlation between the thermopower and other physical parameters such as carrier density, $T_c$, etc. exists [34, 35, 36]. With the variation of carrier level, a strong dependence of $T_c$ on room-temperature thermopower ($S_{300}$) similar to that of $T_c$ vs carrier density has been observed in different systems. To observe whether the Co-doped Bi-2212 and Tl-2212 samples show a similar behavior we have plotted $S_{300}$ as a function of $T_c$ and Co concentration in Figs 4 10 and 4 11. Fig 4 10 shows that for a given $Y$ concentration,

![Graph](image)

Fig 4 10 The variation of $T_c$ with room-temperature thermopower ($S_{300}$) for various $Y$ content ($x$). Figure (a) corresponds to Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ and (b) corresponds to Tl$_2$Ba$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ samples.
\( T_c \) decreases linearly with \( S_{300} \). This behavior is quite different from that of parabolic dependence of \( T_c \) on \( S_{300} \) in oxygen deficient systems [34] where \( T_c \) is suppressed due to the decrease of carrier density. Thus the effects of \( T_c \) suppression on normal-state thermopower due to the disorder in the CuO\(_2\) plane and due to changes in carrier density are different in nature. It is clear from Fig 4.11 that \( S_{300} \) increases linearly with Co concentration for

\[ \text{Fig 4.11 The dependence of room temperature thermopower (} S_{300} \text{) on Co concentration for various Y content (} x \text{). (a) Bi}_2\text{Sr}_2\text{Ca}_{1-x}Y_x(\text{Cu}_{1-y}\text{Co}_y)_2\text{O}_8 \text{ and (b) Tl}_2\text{Ba}_2\text{Ca}_{1-x}Y_x(\text{Cu}_{1-y}\text{Co}_y)_2\text{O}_8 \text{ samples}} \]

samples with \( x < 0.50 \) for Bi-2212 system and for the whole range of Y concentration for Tl-2212 system. In Bi-2212 system, for \( x = 0.5 \) sample, a strong deviation from linear behavior is observed. It may be mentioned that the \( x = 0.5 \) doping is close to the metal-to-insulator transition in this system. This suggests that the influence of Co substitution on \( S \) is different in the metallic and in the insulating regimes.
4.5 A single functional form for thermopower of underdoped cuprates

The various normal-state transport parameters of high-$T_c$ superconductors can be scaled to universal master curves. Uchida [37] showed that the in-plane resistivity of YBa$_2$Cu$_3$O$_{7-\delta}$ deviates from linear behavior below a characteristic temperature $T_p^*$ well above the $T_c$ and observed that all the $\rho_{ab}$ vs. $T$ plots for underdoped samples including HgBa$_2$Ca$_2$Cu$_3$O$_{6+y}$ fall into a single curve by scaling $T/T_p^*$ and $\rho_{ab}(T)/\rho_{ab}(T_p^*)$. Hwang et al. [38] found that the Hall coefficient $R_H(T)$ of La$_{2-x}$Sr$_x$CuO$_4$ can be scaled to a universal functional form $R_H(T) = R_H^0 + R_H f(T/T_H^*)$. $R_H(T)$ is temperature dependent below a characteristic temperature $T_H^*$ and becomes $T$ independent ($R_H^0$) above $T_H^*$. The temperature $T_H^*$ is found close to the characteristic temperatures where the susceptibility and the NMR relaxation rate show peaks. As in the other cases, $T_H^*$ is also found to increase with the depletion of carrier density. For Y-123 system, similar type of scaling behavior for the Hall coefficient is confirmed by Chen et al. [39]. They observed that the characteristic temperatures $T_p^*$ and $T_H^*$ are close to each other. So far the scaling was done on materials with finite $T_c$ and the physical properties considered are mainly resistivity and Hall coefficient. Mandal et al. [35] established a scaling of thermopower for the nonsuperconducting Bi-2212 and Tl-2212 samples. They observed that the $S$ vs $T$ plots for the nonsuperconducting samples fall into a single curve by scaling $S(T)/S^*$ and $T/T^*$ as in the case of resistivity. Here, $T^*$ is the temperature where $S$ shows its maximum value $S^*$. Similar scaling behavior for $S$ has also been reported recently by Cooper and Loram [36] for La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$ systems. They observed that the temperature ($T_\chi^*$) where $\chi$ shows maximum is approximately two times higher than $T^*$. To investigate whether similar type of scaling is also applicable for Co-doped samples, $S/S^*$ vs. $T/T^*$ for both Bi-2212 and Tl-2212 samples are plotted in Fig.4.12. It is clear that all the $S$ vs. $T$ plots for superconducting as well as nonsuperconducting samples of Figs 4.7 & 4.9 which show broad peaks can be scaled to a single curve. For some superconducting samples, the low temperature data deviate and are not plotted in this figure. This is due to the high superconducting onset temperature which is closer to the peak as compared to other samples.

It has been observed [37] that the opening of the pseudogap strongly modify the temperature dependence of in-plane resistivity below $T_p^*$, $\rho_{ab}$ remains linear above $T_p^*$ but follows $T^{2.5}$ dependence below $T_p^*$. This behavior is universal for any underdoped cuprates. This suggests that the resistivity for all the underdoped cuprates can be scaled into a single universal curve after subtracting the residual resistivity [37]. Now the question arises.
whether similar types of universal scaling do also exist for other transport coefficients. For this the thermopower data for La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) (Ref. [36]) and YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) (Ref. [36]) systems are plotted in Fig. 4.12. One can see that all the curves for different systems fall into a single curve. For the La$_{2-x}$Sr$_x$CuO$_4$ system, the small deviation may be due to the scattering of experimental data [36]. Thus as in the case of resistivity and Hall coefficient, one can scale thermopower also into a single universal curve of the form $S/S^* = f(T/T^*)$. As $S$ is zero at $T = 0$, the function $f(T/T^*)$ should also vanish at $T = 0$.

Fig. 4.12 The thermopower for Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_{8}$ samples of figure 4.7 with $0.20 \leq x \leq 0.60$ and Tl$_2$Ba$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_{8}$ of figure 4.9 with $0.0 \leq x \leq 0.3$, are plotted rescaled as $S/S^*$ vs. $T/T^*$. The symbols are for present work. The $S$ for all the samples are not plotted in this figure to avoid overlapping among themselves. The scaling behavior for La$_{2-x}$Sr$_x$Cu$_2$O$_4$ (Ref. 36) and YBa$_2$Cu$_3$O$_7$ (Ref. 36) systems are also shown in this figure.
4.6 Estimation of the pseudogap and its correlation with $T^*$

From table-I we observe that the DOS at fermi level $N(E_F)$ shows a progressive depletion towards underdoping which may imply the opening up of a gap of growing magnitude. Assuming that the depletion in $N(E_F)$ is caused by a pseudogap $E_g$ [16], a DOS is being calculated within the "DOS-suppression picture" using the normal-state quasiparticle dispersion given as [11, 14]

$$E_k = [\epsilon_k^2 + E_g(k)^2]^{1/2}, \quad (4.2)$$

where $\epsilon_k$ represents the tight binding band energy for which we consider a realistic band structure obtained by a six parameter tight-binding fit to the ARPES data on Bi2212 [40]. Here $E_g(k) = (E_g/2)|\eta_k|$ with $E_g$ being the pseudogap magnitude and $\eta_k = \cos k_x a - \cos k_y a$ ($a$ is the in-plane lattice constant of a square lattice) is the $d_{x^2-y^2}$ symmetry factor associated with the pseudogap [16]. Appearance of $E_g$ in the quasiparticle dispersion effectively causes suppression of the DOS at the fermi level. In this analysis, $E_g$ is estimated at a fixed doping level by fitting its value such that the DOS calculated within this "DOS-suppression picture" matches $N(E_F)$ found out previously from the data analysis (see table-I).

A plot of scaled $E_g$ and $T_{co}$ as a function of carrier concentration ($p$), for both Bi-2212 and Tl-2212 samples, are given in Figs 4.13 and 4.14. Here, $E_g$ at different $p$ are scaled to its value at optimal doping $p = 0.16$, that is $\bar{E}_g = E_g(p) / E_g(p = 0.16)$. $T_{co}$ values obtained in experimental measurements are also scaled similarly $\bar{T}_{co} = T_{co}(p) / T_{co}(p = 0.16)$. Solid lines in the main figure follow the universal parabolic $T_c-p$ relation and the dashed lines are power law fit to the $\bar{E}_g$ data. It may be noted that the pseudogap magnitude $E_g$ shows a sharp rise towards underdoping which is seen to vary as a power of inverse doping ($1/p$).

Insets of Figs.4.13 & 4.14 show that $T^*$ grows towards underdoping. Substitution of Co at the Cu-site increases $T^*$. More or less similar results are found for Bi- and Tl-systems. An empirical relation $T^* = \frac{c}{p^n}$ yields values of $c$ and $n$ in the range 37-51, 0.58-0.70 and 37-46, 0.55-0.69 for Bi- and Tl-systems respectively. Comparing these values with those of HgBa$_2$CuO$_{4.4}$ where $c = 60$ and $n = 0.54$ (chapter 3), one can state that in general $T^*$ varies as $\frac{1}{p^n}$ with $n$ in the range 0.54-0.70. In Zn-substituted YBa$_2$Cu$_3$O$_{7.8}$ system, this $T^*$ enhancement is absent [21]. As mentioned earlier in this chapter, the Co-substitution does
not alter the carrier concentration of the system. Thus the increase in $T^*$ is not due to any carrier reduction and could find interpretation within a preformed pair model introduced by Emery et al. [41] where $T^*$ is identified with the building up of AF correlation in the system and substitution of magnetic ion (Co) might lead to the building up of the AF correlation at a higher temperature. So the quantity $T^*$ can be thought of as an energy scale related to the pseudogap $E_g$. Both $T^*$ and $E_g$ grow as $\frac{1}{p}$ with different values of $n$. This similarity between $T^*$ and $E_g$ is noteworthy and affirms the idea that $T^*$ is an energy scale related to $E_g$. It is important to note that $E_g$ values towards overdoping do not fall

![Diagram of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ cuprate](image)

Fig. 4.13. Phase diagram of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ cuprate. Solid triangles are scaled $T_{co}$ values corresponding to different carrier concentration ($p$). Solid line is a parabolic fit to these data. Open squares are scaled values of the pseudogap magnitude ($E_g$) as estimated within the DOS suppression picture. Dashed line is a power law fit to $E_g$ data. [Inset: Symbols represent values of $T^*$, as estimated by thermoelectric power measurement, as a function of $p$ for various Co content ($y$). $p$ values of cobalt free samples are used as the carrier concentration remains unaffected by Co substitution. Solid and dashed lines are power law fit to the data.]
to zero, but show monotonic decrease or remain nearly flat implying existence of $E_g$ even in the overdoped cuprates. This feature is visible in both the main figure as well as in the $T^*$ data presented in the inset.

In a recent experiment, Demsar et al. [42] studied the gap-structure in YBCO single crystals employing real-time measurements of the quasiparticle relaxation dynamics. They found a $T$-independent pseudogap is dominant in the underdoped samples and even

![Graph]

**Fig 4.14** Phase diagram of Tl$_2$Ba$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ cuprate. Solid triangles are scaled $T_{co}$ values corresponding to different carrier concentration ($p$). Solid line is a parabolic fit to these data. Open squares are scaled values of the pseudogap magnitude ($E_g$) as estimated within the DOS suppression picture. Dashed line is a power law fit to $E_g$ data. [Inset: Symbols represent values of $T^*$, as estimated by thermoelectric power measurement, as a function of $p$ for various Co content ($y$). $p$ values of cobalt free samples are used here as the carrier concentration remains unaffected by Co substitution. Solid and dashed lines are power law fit to the data.]
persists in the overdoped state with its magnitude being inversely proportional to doping. These results confirm with the conclusions drawn in this section regarding the estimated pseudogap magnitude at different dopings. This is also consistent with our earlier experimental observations in case of Hg-cuprates (see chapter 3, section 3.6).

4.7 Susceptibility $\chi$

With the assumption, that quasiparticles are well defined in the vicinity of the fermi surface, susceptibility can be written involving DOS as

$$\chi = 2\mu_B^2 \int_{-\infty}^{\infty} \left[-\frac{\delta f(E)}{\delta E}\right] N(E) \, dE \quad (4.3)$$

where $N(E)$ is the DOS at energy $E$ and $f(E) = (e^{\beta E} + 1)^{-1}$ is the fermi distribution function. Susceptibility $\chi$ becomes temperature dependent through the fermi function $f(E)$. Using the quasiparticle dispersion as in equation (4.2), we calculate $\chi$ for different carrier concentrations (different $E_g$). A plot of $\chi/\mu_B^2$ as a function of $T$ for Bi-2212 is given in Fig 4.15. The quantity $\chi/\mu_B^2$ has the dimension of DOS denoted by $N(E)$ in equation (4.3). In each curve in the plot, towards low temperature $\chi$ falls off rapidly and tends to zero in the limit $T \to 0$. With increasing temperature, $\chi$ increases slowly, peaks at a temperature ($T_{\chi}$) and then decreases slowly towards its high-$T$ saturation. Occurrence of the broad peak in $\chi$ at high $T$ (above the corresponding experimentally measured $T_c$) is due to the presence of $E_g$ in the quasiparticle energy and is not observable in case of a normal metal. As one goes towards reduced doping level, $E_g$ increases, the value of $T_{\chi}$ gets shifted towards higher temperatures and the peak becomes more and more broader. In the inset of Fig 4.15, the experimental data [43] of $\chi$ versus $T$ for Bi-2212 system is included which shows the feature that $\chi$ has a broad peak above $T_c$ and the peak position shifts towards higher $T$ with underdoping. This consistency of the earlier experimental data with that calculated using the quasiparticle dispersion in equation (4.2) lends some support to the physical picture that the existence of $E_g$ affects the in-plane ($\text{CuO}_2$-plane) charge transport by suppressing the quasiparticle DOS at the fermi level.

It may be noted here that Williams et al [11, 44] previously analysed NMR data on different HTLS materials within a DOS suppression picture considering a normal state pseudogap of $d$-wave symmetry. Also, Loram et al [45] found that the normal-state heat capacity and magnetic susceptibility data could be analysed in terms of a $d$-wave pseudo-
gap. Thus, although experimental data [43] apparently signify the DOS suppression role of $E_g$, further systematic studies of different transport properties on layered cuprates are needed to elucidate the role played by $E_g$ on DOS as well as on other physical characteristics of cuprate superconductors.

Fig 4.15 Susceptibility for Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$(Cu$_{1-y}$Co$_y$)$_2$O$_8$ cuprate, as calculated using equation (4.3), is plotted as a function of temperature for three different values of $x$ mentioned in the figure. The temperature at which susceptibility has a broad peak, is marked by an arrow and the corresponding value is written [Inset: Experimental susceptibility data for the same system as a function of temperature for various Y content ($x$) as noted in the figure. These data are taken from Ref 43].
4.8 Conclusion

Although a clear understanding of the nature of the pseudogap is still lacking, the above results together with the existing data in the literature point to a resolution concerning impurity substitution on the CuO$_2$ planes. In contrast to the conventional low-$T_c$ superconductors, in high-$T_c$ systems, the rate of suppression of $T_c$ due to impurity scattering solely depends on $p$ (carrier concentration) and not on the type of impurities. The depression of $T_c$ with in-plane impurity substitution can be understood in terms of unitary scattering with a $d$-wave order parameter together with the pseudogap-induced depression in the DOS. The analogous $p$ dependence of $T^*$ and $E_g$ suggests that $T^*$ is not just a temperature at which the normal-state pseudogap opens but an energy scale related to the pseudogap. Substitution of Co at Cu site increases $T^*$. Since the carrier concentration of the system does not alter with Co doping, it is suggested that the increase in $T^*$ with Co doping can be interpreted within a preformed pair model introduced by Emery et al. [41]. Another important point is that the pseudogap magnitude $E_g$ does not identically fall to zero towards overdoping but exists in this region.

References


