CHAPTER 7

EFFECT OF SUPERCONDUCTING TRANSITION ON LATTICE ANHARMONICITY IN HIGH \( T_c \) SUPERCONDUCTORS
7.1 Introduction

Since the discovery of superconductivity in mercury by Kamerling Onnes [1] a host of elements, alloys and compounds were found to exhibit superconductivity at low temperatures. But the limited scope of these conventional superconductors for their low transition temperature \( T_C \) initiated the search for compounds with higher \( T_C \)'s. The discovery of superconductivity at about 35 K in the oxide compound La-Ba-Cu-O [2] was followed by finding several other oxide systems. Y-Ba-Cu-O [3,4], Bi-Sr-Ca-Cu-O [5,6], Tl-Ba-Ca-Cu-O [7,8] and Hg-Ba-Ca-Cu-O [9,10] which have \( T_C \)'s above the boiling point of liquid nitrogen. These came to be known as high-\( T_C \) superconductors. Ever since their discovery, the interesting properties of these materials and the mechanism of superconductivity in them has posed a challenge to the experimentalists as well as to the theoreticians. There have been many models which were proposed to explain various electronic, magnetic and thermal properties of superconductors. For the conventional superconductors the first satisfactory microscopic theory was given by Bardeen, Cooper and Schrieffer (BCS Theory) [11]. They showed that a conduction electron distorts the lattice due to Coulomb interaction and creates a virtual phonon. A second electron with the opposite spin of that of the former one, sees the lattice distortion by absorbing the virtual phonon. Both the electrons develope a weak attractive force through the exchange of the virtual phonon and they form a Cooper pair. These Cooper pairs which are formed due to this electron lattice electron interactions, condense into a state whose ground state energy is much less than the normal ground state energy and is separated from it by a band gap. Even though the BCS theory could explain most of the phenomenon observed in the conventional superconductors, it suggested an
upper limit of 40 K for the $T_c$ of a superconductor. Hence the discovery of high-$T_c$ cuprate superconductors showed the inadequacy of the BCS theory in these materials.

The mechanism responsible for inducing pairing in high-$T_c$ cuprate superconductors continues to be elusive. One of the potential candidates is the electron-phonon interaction which according to one viewpoint [12 — 16] could be effectively large because of the imperfect screening of the coulomb interactions and can thus lead to high $T_c$. Another viewpoint [17 — 21] is based on the formation of bipolarons which can undergo Bose-Einstein condensation to give rise to superconductivity. There is yet another approach [22,23] which rests on the idea that the large effective coupling constant may have its genesis in the high lattice polarization caused by the lattice anharmonicity. The bipolaronic mechanism might also be intimately connected with this viewpoint.

Experimentally there have been a host of activities in recent years to explore the role of phonons in high $T_c$ materials. A softening of the Raman mode at 335 cm$^{-1}$ has been observed [24] at $T_c$ in $YBa_2Cu_3O_{7-\delta}$. Ion channeling studies [25] on $YBa_2Cu_3O_{7-\delta}$ and $ErBa_2Cu_3O_{7-\delta}$ show a phonon anomaly due to the Cu-O atom vibrations. Pulsed neutron diffraction [26] on $Tl_2Ba_2CaCu_2O_8$ and inelastic neutron scattering measurements [27] on $YBa_2Cu_3O_7$ show local structural distortion at $T_c$ in these materials. Polarized EXAFS results [28] show that the relative displacements of the axial oxygen in high $T_c$ materials are not harmonic and change around $T_c$. Cu-$K$ edge polarized EXAFS data [29] for $YBa_2Cu_3O_7$ show an axial oxygen centered lattice instability at $T_c$ suggesting a coupling between superconducting fluctuations and anharmonic phonons. Neutron resonance absorption spectroscopy [30] for Cu in $Bi_2Sr_2CaCu_2O_8$ indicates a rapid decrease in the kinetic energy slightly
above $T_c$ and detailed neutron scattering measurements [31] for selected phonons in $Bi_2Sr_2CaCu_2O_8$ also show considerable anharmonic effects. In our opinion, thermal expansion results should offer more direct evidence of the anharmonic effects and therefore we have studied the temperature variation of the thermal expansion data of $YBa_2Cu_3O_{7-\delta}$ ($\delta = 0.15$) (Y-123) and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ (Bi-2223) over a wide range of temperature both in the normal and superconducting phases. The data of $YBa_2Cu_3O_{7-\delta}$ ($\delta = 0.15$) superconductor have been taken from ref.33. In the case of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ we have performed the thermal expansion measurements using our three terminal capacitance cell. For both the cases we have done the data analysis using our semiclassical model described in Chapter-3. We find that there is indeed an anomaly in the thermal expansion behaviour of Y-123 and Bi-2223 superconductors which begins to show up at a temperature somewhat higher than $T_c$. In the case of Y-123 superconductor we try to attribute this anomaly to a lattice instability induced by polaron formation [32]. Bi-2223 superconductor shows an anomaly in the vibrational contribution to thermal expansion at the superconducting transition temperature and in the superconducting phase the thermal expansion shows the presence of the two dimensional (2D) Gaussian fluctuations near the transition temperature.

### 7.2 YBa$_2$Cu$_3$O$_{7-\delta}$ Superconductor

#### 7.2.1 Data Fitting and Analysis

The fractional length change data taken from ref.33 are fitted to the eqn.(3.2) with the reference temperature being 20 K and the average lattice displacement $\langle x \rangle_T$ being given by eqn.(3.14) which we reproduce here for the sake of completeness:
where $\gamma_{el}$ is the linear electronic contribution to the average lattice displacement and $e$ is given by the eqn.(3.15). The parameters used were $\gamma_{el}$, $g'$, $g''$, $l'$, $\Theta_D$, $p$ and $\Theta_E$. The fit gives the best results for the average number of phonon modes $p = 3$. Therefore in the final fits we have used only the Debye terms and have removed the Einstein terms from the fitting function. For superconducting Y-123 we find, quite interestingly, that it is not possible to fit the fractional length change data with a single set of parameters. The r.m.s. deviation for the best fit in this case comes out to be as large as 40%. However the data could be fitted separately for $T < T_p$ and $T > T_p$ where $T_p$ is around 110 K as shown in the Fig.7.1. Clearly the fits are very good both below and above $T_p$. In fact the r.m.s. deviations in this case are 5% below $T_p$ and 2.5% above $T_p$. The values of the parameters are given in Table.7.1. The value of $\Theta_D$ has been obtained from the fit below $T_p$ and is kept fixed at the same value for the fitting above $T_p$, while other parameters are varied. The value of $\Theta_D$ obtained from our fit is 418.9 K and it compares quite impressively with the reported value of about 420 K [34,35] in literature. Interestingly enough, for nonsuperconducting $YBa_2Cu_3O_{\delta}$ ($\delta = 0.9$) [33] the data could, however, be fitted to our model for the entire temperature range with a single set of parameters, the r.m.s. deviation being only 9% in this case (see Fig.7.1).

To study the temperature dependence of the thermal expansion coefficient we differentiate eqn.(7.1) with respect to $T$ and plot as a function of $T$. The plot is shown in fig.7.2 which clearly shows that the thermal expansion coefficient $(a)$ has a finite discontinuity at $T_p$ which is what is also expected from fig.7.1.
Fig. 7.1: The fractional length change data of superconducting $YBa_2Cu_3O_{7-\delta}$ ($S = 0.15$) and non-superconducting $YBa_2Cu_3O_{7-\delta}$ ($S = 0.9$) with temperature. The solid lines show the fits to the data.
Fig. 7.2: The coefficient of linear thermal expansion of superconducting \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) \((\delta = 0.15)\) with temperature.
Another feature we would like to mention is that the electronic contribution to the thermal expansion is linear in temperature in both normal and superconducting phases. This might have some correlation with the electronic specific heat behaviour of high $T_c$ superconductors. But as the electronic Griineisen constant is not known for the Y-123 superconducting sample the electronic specific heat could not be calculated.

7.2.2 Discussion

The cubic anharmonicity parameters $g'$ and $g''$ are clearly larger below $T_p$ than above $T_p$ which implies an increase in the asymmetry of the lattice atom-atom potential below $T_p$. The quartic anharmonicity parameter $\lambda$ however shows the most dramatic increase in its value below $T_p$ which indicates a softening of the lattice potential around $T_p$. The enhancement in the cubic and quartic anharmonicities leading to the asymmetry and softening of the lattice might originate in our opinion from the high lattice polarization present in the cuprates. This lattice polarization can give rise to a lattice instability favouring the possibility of polaron formation around $T_p$. This indirectly suggests the bipolaronic mechanism as a possible pairing mechanism in the high $T_c$ superconductors. In a one - electron polaron problem the phonon dynamics is not affected by the polaron formation. But in a many electron system, the polaron formation will give rise to phonon - phonon interactions leading to anharmonic effects which will largely depend on the strength of the polaronic interactions. The polaronic interaction might be of Frohlich type or Holstein type depending on the material. If real anharmonic phonons are present in the system then one should also incorporate in the polaron formation the effect of electron - biphonon interaction which can be written in a mean field-like approximation [36].
Table 7.1: The Debye temperature, anharmonicity parameters and the coefficient of linear electronic term obtained from the fit of the thermal expansion data of superconducting (δ = 0.15) and non-superconducting (δ = 0.9) YBaCuO sample. The value of the Debye temperature inside square brackets is from literature [34,35].

<table>
<thead>
<tr>
<th>Sample</th>
<th>YBa$_2$Cu$<em>3$O$</em>{7-d}$ (δ = 0.15)</th>
<th>YBa$_2$Cu$<em>3$O$</em>{7-d}$ (δ = 0.9)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>T &lt; $T_p$</td>
<td>T &gt; $T_p$</td>
</tr>
<tr>
<td>$\Theta_D$ (K)</td>
<td>$418.9 \pm 0.8$ [420.0]</td>
<td>$418.9 \pm 0.8$</td>
</tr>
<tr>
<td>$g'(eV^{-1})$</td>
<td>$(5.32 \pm 0.08) \times 10^{-2}$</td>
<td>$(2.51 \pm 0.06) \times 10^{-2}$</td>
</tr>
<tr>
<td>$g''(eV^{-1})$</td>
<td>$(6.06 \pm 0.06) \times 10^{-3}$</td>
<td>$(1.96 \pm 0.06) \times 10^{-4}$</td>
</tr>
<tr>
<td>$f(eV^{-1})$</td>
<td>$(9.98 \pm 0.06) \times 10^{-4}$</td>
<td>$(1.35 \pm 0.06) \times 10^{-5}$</td>
</tr>
<tr>
<td>$\gamma_d(K^2)$</td>
<td>$(1.37 \pm 0.06) \times 10^{-8}$</td>
<td>$(1.54 \pm 0.06) \times 10^{-8}$</td>
</tr>
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</table>
where $C^\dagger_k(C_k)$ is the creation (annihilation) operator for the electron and $B_q$ is the electron-phonon interaction matrix element. Bussman-Holder and Bishop have combined this interaction with the BCS Hamiltonian to reproduce some of the interesting features of the high $T_c$ superconductors. Morawitz et al. [37] have studied the effect of this non-linear electron-phonon interaction on the normal state properties and the transition temperature of cuprates in the tight binding model.

We would like to emphasize that the non-linear electron-phonon term will contribute a four-phonon interaction to the phonon dynamics in the lowest-order perturbation theory. This might be one of the probable reasons for the dramatic enhancement of the quartic anharmonicity below $T_p$.

We like to point out that we have used the thermal expansion data for polycrystalline YBaCuO for which we do not distinguish among a, b and c axes and therefore the model we have used is an averaged isotropic model. Single crystals of high-$T_c$ cuprates are however known to be highly anisotropic and for these materials one will naturally have to make separate analysis of each crystallographic direction. The parameters $f, g$ etc. in that case are expected to come out different for the three directions exhibiting an anisotropy in the thermal expansion coefficient. Nevertheless, the anomaly at $T > T_c$ observed for polycrystalline YBaCuO in its thermal expansion behaviour and its qualitative nature are expected to remain even for the single crystals of YBaCuO. We try to attribute this anomaly to the polaron formation which can induce a lattice instability and mode softening.
If polarons and bipolarons do form in the high - \( T_c \) cuprates then these materials should show some polaronic effects in their behaviour. Several advocates [17-21] of the polaronic mechanism have addressed themselves to this issue and it is well known that some of the normal state and superconductive properties of high - \( T_c \) cuprates can be explained using polaronic models. For example, if one calculates the transport properties of superconducting cuprates using the polarons and bipolarons as the charge carriers, one can very easily explain the linear - T resistivity behaviour exhibited by these materials [38,21]. Evidence of polaron formation in cuprates has also come, albeit indirectly, from photo-induced conductivity and photo-modulation experiment [39], optical conductivity data [40], \( Cu-K\)-edge EXAFS measurements [29], ion-channeling studies [25] and resonant neutron absorption spectroscopy [30]. Mustre de Leon et al [41] have recently performed an exact diagonalization of an electron-phonon model Hamiltonian for the \( O(4) - Cu - O(4) \) cluster in the 123 compound and have shown that for strong electron-phonon coupling the motion of holes and ions become polaronic leading to a double well structure for the infrared mode as observed in their EXAFS experiment. However these results and also our thermal expansion data analysis which do indicate the formation of polarons in cuprates may or may not have any bearing on the mechanism of high \( T_c \) superconductivity.

### 7.3 \( \text{Ba}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y \) Superconductor

The \( \text{Ba}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y \) (Bi-2223) Superconductor was prepared and characterized by Seshu Bai et al. [42]. The susceptibility measurements gave the normal to superconducting transition temperature \( T_C = (107 \pm 1) \text{K} \) (see Fig. 7.3). From the
Fig. 7.3: Variation of ac susceptibility as a function of temperature of $Bi_{1.6}Pb_{0.4}Sr_2Cu_2Cu_3O_y$ superconductor.
original sample made by Seshu Bai et al. [42] we have cut a rectangular piece of dimensions \((2 \times 3 \times 3) \text{ mm}^3\) and performed the thermal expansion measurements on it. Fig. 7.4 shows the temperature dependence of the fractional length change \(\Delta L(T)/L(T_0) = 293.0 \text{ K}\) and the Fig.7.5 gives the \(a(T)\) data obtained from the numerical three point differentiation of \(\Delta L(T)/L(T_0)\) with respect to temperature. Even though the \(\Delta L(T)/L(T_0)\) data does not show any observable change at \(T_c\), the \(a(T)\) data gives a slope change.

7.3.1 Results and Discussion

As in Y-123 superconductor we have tried to fit the \(AL/L\) data of Bi-2223 superconductor to the theoretical expression given by eqns.(3.2) and (7.1), separately in the temperature range above \(T_C\) (normal region) and below \(T_C\) (superconducting region). The \(AL/L\) data in the normal region \((110K < T < 300K)\) is fitted to eqn.(3.2) with \(\gamma, g', g'', l', \Theta_D, p\) and \(\Theta_E\) as parameters. The fit gives the best results for \(p = 3\). Hence in the final fits we have used only the Debye terms. Interestingly the \(AL/L\) data in the superconducting region \((80K < T < 106K)\) could not be fitted to the eqn.(3.2) and (7.1). This may be because of our experimental temperature range in the superconducting phase is very near to \(T_C\) \((108 \text{ K})\). In this temperature range strong fluctuations in the superconducting order parameter are expected due to the short coherence length of the superconductor. Experimentally the effects of fluctuations are also observed in the specific heat \([43-47]\), in the conductivity \([48,49]\), in the dc-susceptibility \([50]\) and on the resistivity \([48,51,52]\) of the high temperature superconductors. Also it has been observed experimentally that the linear in temperature term in the low temperature specific heat data of Bi-2223
Fig. 7.4: Temperature variation of measured fractional length change data of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ superconductor.
superconductor is either absent or very small [53-55]. Therefore following the specific heat data analysis of Braun et al. [56] near the superconducting transition temperature $T_C$ we can write a theoretical expression for $\alpha(T)$ as,

$$\alpha(T) = \gamma_{BCS} e^{-1.5T_c/T} + \gamma_{GFL} \left| \frac{T - T_c}{T_c} \right|^{-1} + \frac{3g}{4\epsilon^2 a(T_0)} \left[ \epsilon' - 2G \times \epsilon \times \epsilon' - 3F \times \epsilon^2 \times \epsilon' \right]$$  \hspace{1cm} (7.3)

The first term comes from the mean field contribution by taking the BCS weak coupling limit to $a$ where $\gamma_{BCS}$ is a constant. The second term comes from the 2D Gaussian fluctuation contribution to $a$ with $\gamma_{GFL}$ being a constant. The third term comes from the analytical differentiation of eqn.(3.14) with respect to the temperature and $G = (15g^2/16\epsilon^3) - (8/\epsilon^3)$. $F = (35/16)[(15g^2f/4\epsilon^5) + (3f^2/\epsilon^4)]$.

But as we could not write an analytical expression for $AL/L$ from the theoretical expression of $\alpha$ given by the above eqn.(7.3), we decided to fit our experimental data.

In the normal region the theoretical expression for $\alpha$ obtained by taking the differentiation of $AL/L$ using for $(x)_T$ the expression given in eqn.(7.1) with respect to temperature is,

$$\alpha(T) = \gamma_{\alpha}T + \frac{3g}{4\epsilon^2 a(T_0)} \left[ \epsilon' - 2G \times \epsilon \times \epsilon' - 3F \times \epsilon^2 \times \epsilon' \right]$$  \hspace{1cm} (7.4)

We fit our experimental $\alpha(T)$ data in the temperature range above $T_C$ with $\gamma_{\alpha}, \gamma', \gamma'', \gamma'$, $\Theta_D$ as parameters and the best fit reproduces the parameter values obtained from the previous fitting of the $(AL/L)$ data. In Fig.7.5 we show the fit of our data as a solid line against the experimental data points. Interestingly we find that
the data fits perfectly well up to $T = 123.5$ K and then starts deviating. Following the same analogy as in Y-123 superconductor case we term this temperature as $T_p$ which is above $T_C$ where the anomaly in the thermal expansion starts in the case of Bi-2223 superconductor. The r.m.s. deviation for the best fit in the temperature range $T > T_p$ came out to be 0.9%.

We have fitted the data in the superconducting region to eqn.(7.3) taking $\gamma_{BCS}, \gamma_{GFL}, g''', \Theta_D$ as parameters. Fig.7.5 shows the fit as a solid line to the experimental data points and the fit is good up to about 105 K and the r.m.s. deviation is only 0.8%. This is in conformity with the observations of Braun et.al. [56] in the analysis of specific heat data. They have also seen that the mean field and the 2D Gaussian fluctuation contributions are unable to fit the specific heat data inside a window of $(T_c \pm 5)K$. This has been attributed to the presence of the critical fluctuations which could be setting in inside this window. The data fitting of our experimental $\alpha$ in the superconducting region has been done by keeping the value of $\Theta_D$ fixed to the value obtained from the fit in the temperature region above $T_C$. The parameters obtained from the best fits in both the normal and the superconducting region are given in Table-7.2. The value of $\Theta_L$, obtained from our fit is 286.6 K which compares quite impressively with the reported value of about 280 K given in literature [53].

From Table-7.1 one can see that the behaviour of the anharmonicity parameters above and below $T_C$ is similar to the behaviour seen in the case of Y-123 superconductor. The value of the cubic anharmonicity parameter $g'$ is clearly larger below $T_C$ than that of above $T_C$. There is a dramatic increase in the quartic anharmonicity parameter /' below $T_C$, by almost three orders of magnitude in coming from normal to superconducting phase. This indicates softening of the lattice modes
Fig.7.5: The coefficient of linear thermal expansion data of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ superconductor. The solid lines show the fits to eqn.(7.3) in the superconducting phase and to eqn.(7.4) in the normal phase.
Fig. 7.6: Temperature variation of vibrational contribution ($\alpha_{ph}$) to the thermal expansion coefficient data of $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ superconductor calculated using the parameters obtained from the fit.
Table 7.2: Debye temperature, anharmonicity parameters and the electronic terms obtained from the fit of the thermal expansion data of the Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_y$ superconductor in the superconducting and the normal states. The value of $\Theta_B$ given inside the square brackets is from literature [53].
around $T_c$, which may be due to high lattice polarization present in the Bi-2223 superconductor. In Fig. 7.6 we have plotted the vibrational contribution to the thermal expansion coefficient $\alpha_{ph}$, calculated using the anharmonic parameters and $\Theta_D$ obtained from the fits, below and above $T_c$. There is indeed a jump in $\alpha_{ph}$ at $T_c$ indicating the occurrence of lattice instability at $T_c$. This anomaly in $\alpha_{ph}$ is coming from only the anharmonic contributions to the lattice potential as $\Theta_D$ is same in both the superconducting and the normal phases.

7.4 Conclusion

The thermal expansion analysis in both Y-123 and Bi-2223 superconductors showed similar type of behaviour in the anharmonic terms in the lattice potential across the superconducting phase transition. The values of Debye temperatures obtained from the fits are 418.9 K and 286.6 K for Y-123 and Bi-2223 superconductors respectively. They agree impressively with the values given in the literature obtained from the specific heat measurements. In both the superconductors the cubic anharmonicity terms have increased below $T_c$ implying an increase in the asymmetry of the lattice atom-atom potential in the superconducting phase. Also the quartic anharmonicity parameters have increased tremendously below $T_c$ indicating the softening of the lattice potential and favouring a lattice instability around $T_c$. This agrees well with the other experimental findings using the Raman Spectroscopy [24], ion-channelling [25], inelastic neutron scattering [27] etc. The vibrational contribution to $\alpha$ showed an anomaly in both the superconductors around $T_c$. 
References


