3.1 Introduction to high $T_c$ superconductivity

Vigorous research activity has recently been focussed on the properties of oxygen deficient Perovskite structured ceramics which exhibit superconductivity at remarkably high temperatures. These exotic materials have been the subject of intense research by a large number of scientists from a wide range of fields of basic and applied research. Within a short period of two years, the highest known transition temperature has raised from 23.3 K of the transition metal alloy Nb$_3$Ge [1,2] to nearly 125 K in Tl-Ca-Ba-Cu-O. The ground work for this extra-ordinary increase in $T_c$ was done by Bednorz and Muller in 1986 [3] who discovered that multiphase mixtures of BaO, LaO and CuO with nominal composition $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$ is superconducting at around 30 K. The superconducting phase was subsequently identified as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with the highest transition temperature occurring at $x \sim 0.15$ [4]. It was later found that doping with Sr in place of Ba produced higher $T_c$'s of $\sim 36$ K [5]. Shortly thereafter another major breakthrough
was achieved when Wu et al. [6] found superconductivity above the boiling point of liquid nitrogen in multi-phase samples with the nominal compositions \( Y_{1.2}\text{Ba}_{0.3}\text{Cu}_{2}\text{O}_{4-x} \) and \( Y_{0.6}\text{Ba}_{0.4}\text{CuO}_{3-x} \). Several groups identified the single phase compound responsible for superconductivity as \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) [7-9] with \( T_C \) in the 90 K range. Within a short period a number of rare-earth based copper oxide ceramics have been synthesized with \( T_C \) in the 30 K and 90 K ranges. Superconductivity at temperatures above 100 K has been obtained in Bismuth and Thallium based oxide systems \( \text{Bi}-\text{Ca-Sr-Cu-O} (T_C \simeq 110 \text{ K}) \) [10,11] and \( \text{Tl}-\text{Ca-Ba-Cu-O} (T_C \simeq 125 \text{ K}) \) [12] in 1988. These systems do not contain any rare earth which were earlier considered essential for the occurrence of high \( T_C \). All the high \( T_C \) superconducting cuprate systems exhibit certain important common features [23-25] in their properties.

A great deal of work has gone into characterizing the superconducting properties of these materials and into the search for new high \( T_C \) compounds. In spite of the enormous amount of data taking during the last 3-4 years, many important questions still remain unanswered. In particular, the basic mechanisms that are responsible for superconductivity in these systems at such high temperatures are not yet known. In the conventional superconductors the phonons mediate Cooper pairing of electrons which is evidenced
by isotopes effect and many other properties. The near absence or marginality of isotope effect in these materials, especially in Y-Ba-Cu-O (1:2:3) compound [13-15], is puzzling both to experimentalists and theorists alike. The question that is being asked is whether these are phonon mediated BCS superconductors or not. A number of theoretical models ranging from conventional phonon mediated coupling [16,17] to a variety of exotic mechanisms involving plasmons [18,19], charge transfer excitations [20], polarons and bipolarons [21] and a new electronic ground state [22] have been put forward. Despite all the activities a clear picture of the mechanism of the phenomenon is yet to evolve.

All the high $T_c$ superconducting cuprate systems exhibit certain important common features [23-25] in their properties. All of them possess Perovskite type structures. They all have low dimensional characteristics, the two-dimensional Cu-O sheets being common to them. The 1:2:3 compounds have, in addition, one-dimensional Cu-O chains. They crystallize in orthorhombic or tetragonal structures with the former being more common. The Cu-O bonds are highly covalent and the distances are generally in the 1.90 ± 0.50 Å range. The coordination of Cu is essentially square planar.
<table>
<thead>
<tr>
<th>$T_c$</th>
<th>Dimensionality</th>
<th>Normal state</th>
<th>Crystal structure</th>
<th>Cu-coordination</th>
<th>Short Cu-O distance</th>
<th>Oxidation state of Cu as found</th>
</tr>
</thead>
<tbody>
<tr>
<td>90-125 K</td>
<td>2 (Cu-O sheets)</td>
<td>Marginally metallic</td>
<td>Orthorhombic</td>
<td>Square-planar</td>
<td>2+</td>
<td>$1^+, 2^+$</td>
</tr>
<tr>
<td>60-110 K</td>
<td>2 (Cu-O chains)</td>
<td>Marginally metallic</td>
<td>Orthorhombic</td>
<td>Square-planar</td>
<td>1.93</td>
<td>$1^+, 2^+$</td>
</tr>
<tr>
<td>90-100 K</td>
<td>2 (Cu-O sheets)</td>
<td>Marginally metallic</td>
<td>Orthorhombic</td>
<td>Square-planar</td>
<td>1.90±0.05</td>
<td>$1^+, 2^+$</td>
</tr>
<tr>
<td>30-40 K</td>
<td>2 (Cu-O sheets)</td>
<td>Marginally metallic</td>
<td>Orthorhombic</td>
<td>Square-planar</td>
<td>1.90</td>
<td>$1^+, 2^+$</td>
</tr>
</tbody>
</table>

Table 3.1: Salient features of high $T_c$ superconductors.
since these materials superconduct in directions parallel to the copper planes, many theorists believe, this unusual planar arrangement contributes significantly to the remarkable electronic properties of these materials. In table 3.1 a summary of the properties of cuprate superconductors is given.

3.2 Thermal properties of high $T_c$ superconductors

Eventhough there has been frantic experimental activity since the discovery of high $T_c$ superconductors, only relatively few measurements of the thermal properties such as specific heat, thermal conductivity etc., of these materials have been reported. Such measurements are of fundamental importance in understanding many basic features of the phenomenon. For example, specific heat measurements can provide a direct means for verifying BCS and BCS like theories. On the other hand, since heat is conducted both by charge carriers and phonons, a measurement of the thermal conductivity can yield information not only about the spectra of electrons and phonons but also about the interaction between them.

Specific heat measurements are mainly centered around finding solution to two problems. First, to verify
whether at low temperatures there is a contribution to specific heat that varies linearly with temperature. Experimental data on high $T_c$ superconductors indicate that in these materials the electronic specific heat is very small and that existence of a linear term is not certain. Secondly, one can check whether there is a jump in specific heat at $T_c$ and if it exists, to verify whether it is in agreement with the expectations of the BCS theory.

For a conventional superconductor, BCS theory, predicts a jump in specific heat at the transition temperature $T_c$ given by,

$$\Delta C_p = \alpha \gamma T_c$$

where $\alpha$ is a constant and $\gamma$ is the electronic heat capacity coefficient in the normal state. The value of $\gamma$ is 1.43 for weak coupling superconductors and can be as large as 2.5 for strong coupling superconductors. In the high $T_c$ superconductors the determination of $\Delta C_p$ is hampered due to several reasons. First of all, since the $T_c$ of these materials is high the specific heat jump is only a few per cent of the lattice contribution. Another difficulty is due to the inhomogeneities in the sample which tend to wash out the specific
heat jump. Also, since the fraction of the superconducting phase in the sample is not known with any degree of certainty, it is difficult to deduce $\Delta C_p$ for a fully superconducting sample from the measured jump. Finally, since the critical field $H_{c2}$ of these materials is very large, it is almost impossible to drive the material to normal state by the application of a magnetic field to determine from the low temperature specific heat measurements.

Inderhees et al. [26] have reported measurement of the jump in specific heat $\Delta C_p$ associated with the superconducting transition in YBa$_2$Cu$_3$O$_{7-\delta}$. They found that with decreasing temperature, $C_p$ exhibits a step like increase to a maximum at 90 K corresponding to the completion of the transition. The measured $\Delta C_p$ is 6.2 mJ/gm and the ratio $\Delta C_p / \gamma T_c = 1.23$ is close to the value of 1.43 of the weak coupling BCS model. They did not find any critical behaviour (a logarithmic peak in $T_c$) such as might be expected from a breakdown of the Ginzburg criterion in these materials.

Nevitt et al. [27] have measured the specific heat of a single phase sample of YBa$_2$Cu$_3$O$_{7-\delta}$ revealing a discontinuity at $T_c$. Magnetic susceptibility measurements suggest that $\Delta C_p / \gamma T_c$ is close to the weak coupling BCS value of 1.43.
The data of Junod et al. [28] on the specific heat jump in different pellets of YBa$_2$Cu$_3$O$_{7-\delta}$ having different densities illustrate the effect of sample quality on the nature of the specific heat jump. Sample which has the highest Meissner fraction of 70% shows the largest jump in $\Delta C_p/T_c = 57$ mJ mole$^{-1}K^{-2}$. Fossheim et al. [29] who made high resolution specific heat measurements on single crystal of YBCO reports a value of about 30 to 40 mJ mole$^{-1}K^{-2}$. There have also been some reports of specific heat measurements on Bi and T based superconductors [30,31]. The behaviour of $C_p$ is similar to that of YBCO system except that the peaks are not as pronounced as in the YBCO system.

All the measurements indicate that a finite jump in specific heat, though very small, is associated with the superconducting transition in all the high $T_c$ materials. There is however no general agreement on the magnitude of $\Delta C_p$ which may mainly be due to sample inhomogeneities. It is also not clear whether there is any fluctuation contribution to specific heat around $T_c$.

It has not yet been answered conclusively whether the electron-phonon interaction produces the high transition temperatures in these materials. In this regard thermal
conductivity measurements are an indispensable tool. The thermal conductivity is a particularly useful transport coefficient in that it can probe scattering processes in both the normal and superconducting states. Thermal conductivity of superconducting materials usually undergoes anomalous changes at the transition point. It either decreases or increases below $T_c$, depending on the nature of the heat carriers and their interactions. There have been reports of measurements of thermal conductivity of many of the high $T_c$ superconductors such as La-Sr-Cu-O [32], Y-Ba-Cu-O [33-36], Er-Ba-Cu-O [37], Sm-Ba-Cu-O [38], Gd-Ba-Cu-O [39], Bi-Sr-Ca-Cu-O [40,41] and Tl-Ba-Sr-Cu-O [42].

The interpretation of thermal conductivity data on these materials is rendered difficult due to the following reasons:

i) The normal state electrical resistivity of these materials is of the order of a few milliohm-cm which implies that the phononic contribution may be the dominant mode of heat transport.

ii) The thermal conductivity of these samples should be anisotropic, but since most of the measurements are made on sintered polycrystalline pellets, one actually measures...
the value averaged over all possible orientations of the individual grains. Also the average grain size in different pellets can be different and the grain size and existence of pores can impose serious limitations on the mean free path of phonons at low temperatures.

iii) Oxygen stoichiometry plays an important role on the superconducting properties of these materials. For a given oxygen stoichiometry, the distribution of oxygen atoms do play an important role in defect scattering.

iv) Magnetic excitations which are likely to be present in some of the superconductors can play a part in scattering phonons and even in the transport of heat.

In spite of the complications mentioned above, thermal conductivity measurements on high $T_c$ superconductors have revealed a uniformity in behaviour. In all the high $T_c$ materials the thermal conductivity shows an increase below $T_c$ and exhibits a bump like behaviour at a temperature below $T_c$. In the case of La-Sr-Cu-O, this effect is very weak and shows only a hint of a small upturn in the thermal conductivity curve close to $T_c$ [32]. This general behaviour is explained on the basis of strong electron-phonon interaction in these materials which causes a reduction in the phonon mean free
path in the normal state. When the material becomes superconducting, the scattering of phonons by electrons are reduced and hence the thermal conductivity increases with decreasing temperature. Ultimately the scattering of phonons by defects, grain boundaries etc., come into play and the conductivity starts decreasing on a further reduction of temperature.

In order to understand the thermal properties of the high \( T_c \) superconductors better, we have carried out photoacoustic measurements on YBCO and Bi-Ca-Sr-Cu-O samples. In this chapter the details of the measurements done on YBCO samples and the results obtained are given.

3.3 Preparation and characterization of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) samples

The ceramic oxide superconductors are all granular superconductors prepared by sintering the component oxides at high temperatures. Due to their multicomponent nature one usually ends up with a multi-phase bulk containing the required superconducting phase plus other parasitic phases and unreacted oxides. Control of processing conditions during synthesis is very important and has a direct impact on the particle size, stoichiometry, intergrowth of unwanted phases and the stability of the superconducting phase. All these parameters eventually decide the quality of the end
product in terms of basic characteristics like the transition temperature ($T_c$), critical current density ($J_c$) and other properties such as Meissner effect and upper critical field.

The following procedure has been adopted for the preparation $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples for the present studies. Appropriate amounts of $\text{Y}_2\text{O}_3$, $\text{BaCO}_3$ and $\text{CuO}$ (99.9%) are thoroughly mixed and ground with an agate mortar and pestle and the mixture is heated in an alumina crucible at 950°C for 24 hours in air. The process is repeated with intermediate grindings and treated in a stream of pure oxygen at 900°C for 24 hours. The powder is then cooled to room temperature at a rate of 12 °C/hr. and is ground again. The powder is then pressed into pellets of 10 mm diameter using a pressure of 20 MPa applied for 10 min. Finally, the pellets are heated to 930°C for 24 hrs. in flowing oxygen and slowly cooled to room temperature at the same cooling rate.

In order to characterize the samples electrical resistivity and magnetic susceptibility measurements have been carried out. Fig.3.1 shows the resistivity curve measured using four probe method. The measuring current is kept at 10 mA. The room temperature resistivity is $3.4\times10^{-3}$ ohm cm and decreases almost linearly as the
Fig. 3.1: Resistance as a function of temperature in YBa$_2$Cu$_3$O$_7$. 
The temperature is lowered. The onset of the superconducting transition takes place at \( T_\text{c} \approx 105 \text{ K} \) and the transition is complete at 93 K. In fig. 3.2 the d.c. magnetic susceptibility of the sample is plotted against temperature. The curve clearly shows the flux expulsion (Meissner effect) associated with the superconducting transition.

### 3.4.1 Amplitude and phase measurements

The amplitude and phase of the PA signal have been measured as a function of temperature on bulk YBa\(_2\)Cu\(_3\)O\(_7\) samples in the range 85-300 K. The experimental set up described in chapter 2 has been used for these measurements. The measurements have been carried out on two superconducting samples (samples I and II) and a non-superconducting sample of the same composition. Sample II has a slightly lower critical temperature resistivity, but has almost the same \( T_\text{c} \) as that of sample I. Pellets having thickness 1 mm and diameter 1 cm have been used for the measurements. The samples are thermally thick at the experimental chopping frequency of 21 Hz. White light with the infrared filtered out is used for optical excitation of the samples. Measurements have been carried out during both heating and cooling cycles. The results are discussed in section 3.5.
temperature is lowered. The onset of the superconducting transition takes place at \( \approx 105 \text{ K} \) and the transition is complete at 93 K. In fig.3.2 the d.c. magnetic susceptibility of the sample is plotted against temperature. The curve clearly shows the flux expulsion (Meissner effect) associated with the superconducting transition.

3.4 Photoacoustic measurements on YBa\(_2\)Cu\(_3\)O\(_7\)

3.4.1 Amplitude and phase measurements

The amplitude and phase of the PA signal have been measured as a function of temperature on bulk YBa\(_2\)Cu\(_3\)O\(_7\) samples in the range 85-300 K. The experimental set up described in chapter 2 has been used for these measurements. The measurements have been carried out on two superconducting samples (samples I and II) and a non-superconducting sample of the same composition. Sample II has a slightly higher room temperature resistivity, but has almost the same \( T_c \) as that of sample I. Pellets having thickness 1 mm and diameter 10 mm have been used for the measurements. The samples are thermally thick at the experimental chopping frequency of 21 Hz. White light with the infrared filtered off is used for optical excitation of the samples. Measurements have been carried out during both heating and cooling cycles. The results are discussed in section 3.5.
3.4.2 Thermal diffusivity measurements

Thermal diffusivity of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples have been measured in the temperature range 85-300 K using photoacoustic technique. This has been done by measuring the amplitude of the PA signal as a function of the chopping frequency. One of the parameters which determine the amplitude of the PA signal is the thermal diffusion length $\mu$ given by,

$$\mu = \left[ \frac{\alpha}{\pi f} \right]^\frac{1}{2} \quad (3.2)$$

where $\alpha$ is the thermal diffusivity of the sample and $f$ is the chopping frequency. In the thermally thick regime ($\mu < l$ where $l$ is the thickness of the sample) the PA signal is independent of the thermal properties of the backing material on which the sample is mounted, whereas in the thermally thin regime ($\mu > l$) the PA signal gets modified by the thermal properties of the backing material as well. For an appropriate sample thickness, one can obtain a crossover from the thermally thin regime to the thermally thick regime by increasing the chopping frequency. The amplitude versus chopping frequency plot hence shows a change in slope at the characteristic frequency $f_c$ at which the crossover takes place. The characteristic frequency $f_c$ is related to the thermal diffusivity of the sample as follows.
The Rosencwaig and Gersho theory shows that the complex expression for the pressure variations $Q$ inside a photoacoustic cell can be written as,

$$Q = q e^{-i\gamma}$$  \hspace{1cm} (3.3)

where $q$ is the amplitude of the PA signal and $\gamma$ is the phase shift between $Q$ and the excitation. Eq. (3.3) can be written as the product of two terms $A$ and $B$ such that $A$ depends on the modulation frequency $f$, and $B$ is independent of $f$ as given by,

$$B = \frac{P_0 \gamma W_a l^2}{2 l' T_0 K} \frac{\sqrt{\alpha'}}{\sqrt{\alpha}}$$  \hspace{1cm} (3.4)

and

$$A = \left(1 + g \frac{d^+ + d^-}{d^+ - d^-} \right) \left( \frac{d^+ + d^-}{d^+ - d^-} + g \right) \frac{1}{(\sigma^{-1})^2}$$  \hspace{1cm} (3.5)

where

$$d^+ = e^{(\sigma^{-1})}$$

$$d^- = e^{-(\sigma^{-1})}$$

$$\sigma^{-} = (1+i) \sqrt{\pi f/\alpha}$$  \hspace{1cm} (3.6)

and $g$, the ratio between the effusivities of the backing material ($e''$) and the sample ($e$), is given by,

$$g = \frac{e''}{e} = \frac{K''}{K} \frac{\sqrt{\alpha}}{\sqrt{\alpha'}}$$  \hspace{1cm} (3.7)
In the above expressions, \( l \), \( K \) and \( \alpha \) are the thickness, thermal conductivity and thermal diffusivity respectively. Unprimed quantities refer to sample parameters, singly primed quantities refer to gas parameters and doubly primed ones to the backing material. \( T_0 \) and \( P_0 \) are the static temperature and pressure of the gas respectively. \( \gamma \) is the ratio of specific heats of the gas and \( \omega_a \) is the absorbed light. The effusivity of the gas in the cell is neglected compared to the effusivity of the sample. The term \( A \) depends on the modulation frequency through the product \( \sigma l \) which can be written as,

\[
\sigma l = (1+i) \sqrt{\pi f/f_c} \tag{3.8}
\]

where the characteristic frequency \( f_c \) is defined by,

\[
f_c = \frac{\alpha}{l^2} \tag{3.9}
\]

Charpentier et al. [43] have demonstrated the dependence of \( A \) on the modulation frequency for different values of \( g \). When \( f > f_c \), the variation of \( A \) is independent of \( \alpha \) and \( A \) decreases as \( f^{-1} \). When \( f < f_c \), the variation of \( A \) depends both on \( \alpha \) and the ratio of effusivities, \( g \). Thus it is possible to determine \( f_c \) by measuring the amplitude of the
PA signal as a function of \( f \). However, if \( g = 1 \), (same effusivity for sample and backing) the variation of the amplitude is the same for all frequencies and the determination of \( f_c \) becomes impossible. Once \( f_c \) is determined, thermal diffusivity can be obtained from eq. (3.9) as,

\[
\alpha = f_c^2
\]  

Pellets of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) samples have been thinned down to approximately 0.2 mm by hand lapping and polishing of both faces to avoid surface effects if any. A thick aluminium disc has been used as the backing material on which the sample is mounted using silver epoxy to ensure good thermal contact between the sample and the backing material. The temperature of the sample is kept constant within \( \pm 0.5^\circ\text{C} \) during measurements. Thermal diffusivity is determined at various temperatures by measuring the amplitude of the PA signal as a function of the chopping frequency and determining \( f_c \) at each temperature.

3.5 Results and discussion

Fig. 3.3 shows the measured photoacoustic phase change relative to the room temperature value as a function of temperature in sample I. Results are shown only in the
Fig. 3.3: Temperature variation of the photoacoustic phase in YBa$_2$Cu$_3$O$_7$ (sample I) between 85 K and 120 K.
Fig. 3.4: Temperature variation of the photoacoustic phase in YBa$_2$Cu$_3$O$_7$. (sample II) between 85 K and 120 K.
temperature range 80-120 K because in the higher temperature region the phase has a smooth variation which is not of much interest. The corresponding phase variation observed in sample II is shown in Fig. 3.4. The figures show that the photoacoustic phase undergoes a clear anomalous change near Tc. A step-like decrease in the Tc is evident in both samples although the change in Tc is less pronounced in sample II. It may also be noticed that the minimum in Tc occurs at two different temperatures during cooling and heating cycles indicating remarkable temperature hysteresis in phase variations. In Fig. 3.5 the temperature variation of the amplitude of the PA signal (with the change 80-120 K for samples I and II) is plotted. As is evident from this figure, the amplitude increases as the temperature is lowered. Repeated runs lead to the same results for the non-superconducting sample of the same composition but a transition in samples I and II. Measurements have also been carried out on a non-superconducting sample of the same composition but a transition in samples I and II. The non-superconducting sample does not show any anomaly either in phase or in amplitude anywhere in the range 80-300 K.

Fig. 3.5: Temperature variation of the photoacoustic amplitude in YBa$_2$Cu$_3$O$_7$ (samples I and II) between 85 K and 120 K.
temperature range 80-120 K because in the higher temperature region the phase has a smooth variation which is not of much interest. The corresponding phase variation observed in sample II is shown in fig.3.4. These figures show that photoacoustic phase undergoes a clear anomalous change near $T_c$. A step like decrease in phase near $T_c$ is evident in both the samples although the change is less pronounced in sample II. It may also be noticed that the minimum in phase occurs at two different temperatures during cooling and heating cycles indicating remarkable temperature hysteresis in phase variations. In fig.3.5 the temperature variation of the amplitude of the PA signal is plotted in the range 80-120 K for samples I and II. As is evident from this figure, the amplitude does not show any appreciable anomaly near the superconducting transition region. The amplitude increases as the temperature is lowered. Repeated runs lead to the same result.

Measurements have also been carried out on a non-superconducting sample of the same composition to check whether it is the superconducting transition itself that leads to the anomalous changes in phase in samples I and II. The non-superconducting sample does not show any anomaly either in phase or in amplitude anywhere in the range 80-300 K.
An interesting aspect of the above results is that only the PA phase undergoes anomalous changes near $T_C$ without the amplitude showing any significant anomaly. According to R-G theory, for an optically opaque and thermally thick sample, in which the optical absorption length $l_P$ is very much less than the thermal diffusion length $\mu$, the amplitude $I_{PA}$ of the PA signal varies as,

$$I_{PA} \propto C_P^{-\frac{1}{2}} K^{-\frac{1}{2}}$$

(3.11)

where $C_P$ and $K$ are the specific heat and thermal conductivity of the sample respectively. Reports on measurements of thermal conductivity [33-36] and specific heat [26,27] of YBa$_2$Cu$_3$O$_7$ show that the thermal conductivity increases below $T_C$ while the specific heat decreases with temperature. This nearly opposite behaviour exhibited by $K$ and $C_P$ reduces their overall effect on the PA amplitude. This, however, does not fully explain the near absence of the contribution of thermal conductivity on the amplitude. One possible reason is that the assumption made earlier that the optical absorption length $l_P$ is very much less than the thermal diffusion length $\mu$ may not strictly be valid. Optical absorption in YBa$_2$Cu$_3$O$_7$ is centered mainly in the green region of the spectrum whereas in the present measurements a substantial amount of
light falls in the other regions of the spectrum including infrared despite the IR filter. For these wavelengths the optical absorption coefficients may not be large enough to hold the above assumption true and for a sample in which \( |\beta| > \mu \) we have,

\[
I_{PA} \propto \frac{1}{C_p}
\]  

Eq. (3.12) does not contain thermal conductivity. Therefore, it is reasonable to assume that the effect of thermal conductivity on the amplitude of the PA signal will be substantially reduced for values of \( |\beta| \) of the order of \( \mu \). The lamp-monochromator combination is found to be incapable of giving enough monochromatic light intensity to give rise to detectable PA signal in these materials. The increase in the signal amplitude as the temperature falls is due to the corresponding decrease in the specific heat of the sample. However, the small jump in specific heat as reported by other workers [26,27] is not reflected in the amplitude. One cannot expect such minute variations to be reflected in the PA amplitude which is governed by a number of other parameters as well.

The R-G theory does not account for the anomalous change observed in the photoacoustic phase during the
superconducting transition. The decrease in phase may be due to a decrease in the excited electron relaxation time when the material undergoes the transition. A faster relaxation of the optically excited levels leads to a decrease in the photoacoustic phase. This faster relaxation may be due to the creation of additional electron traps when the material changes phase. A quantitative explanation of the above observations, we believe, would evolve along with other experimental observations in the near future.

The nearly opposite behaviours of thermal conductivity and specific heat produce pronounced variations in the thermal diffusivity of YBa$_2$Cu$_3$O$_7$. Fig.3.6 shows the amplitude of the PA signal as a function of chopping frequency at various temperatures. The frequency at which the slope of the curve changes is the characteristic frequency $f_c$ from which the thermal diffusivity $\alpha$ can be determined using the relation $\alpha = f_c l^2$. In fig.3.7 the thermal diffusivity of YBa$_2$Cu$_3$O$_7$ is plotted as a function of temperature. As is evident from the figure, there is a sharp increase in thermal diffusivity below $T_c$ associated with the superconducting transition. Data have been recorded during cooling and heating cycles. The points follow the same curve during both the cycles.
Fig. 3.6: Log-log plots of variation of the PA amplitude with chopping frequency in YBa$_2$Cu$_3$O$_7$ at different temperatures.
When a metal becomes superconducting, electrons form Cooper pairs which cannot carry entropy and so do not contribute to thermal conductivity. Unpaired electrons in a superconductor can however transport heat but as the temperature decreases below $T_c$, the number of such electrons decreases exponentially. The electronic thermal conductivity of a superconductor therefore falls rapidly below $T_c$ from the other hand, since unpaired electrons no longer contribute, phonons can become the dominant carriers of heat below $T_c$, which increases the phononic contribution to thermal conductivity. The net temperature dependence of the thermal conductivity below $T_c$ will therefore be the result of both the electronic and phononic contributions to the superconductor.

The thermal diffusivity $\alpha$ can be written as

$$\alpha = K/\rho c$$

where $K$, $\rho$ and $c$ are the thermal conductivity, density and specific heat of the sample respectively. Substituting for $K$ given by

$$K_{ph} = \frac{1}{3} c_p \rho \nu T$$

Fig. 3.7: Temperature variation of the thermal diffusivity of YBa$_2$Cu$_3$O$_7$. The inset clearly shows the small anomaly in $\alpha$ near $T_c$. 
When a metal becomes superconducting, electrons form Cooper pairs which cannot carry entropy and so do not contribute to thermal conductivity. Unpaired electrons in a superconductor can however transport heat but as the temperature decreases below $T_c$, the number of such electrons decreases exponentially. The electronic thermal conductivity of a superconductor therefore falls rapidly below $T_c$. On the other hand since the paired electrons no longer scatter phonons there can be an increase in phonon mean free path below $T_c$ which increases the phononic contribution to thermal conductivity. The net temperature dependence of thermal conductivity below $T_c$ will depend upon whether the electronic or phononic contribution dominates in the superconductor.

The thermal diffusivity $\alpha$ can be written as,

$$\alpha = \frac{K}{\rho c_p}$$

(3.13)

where $K$, $\rho$ and $c_p$ are the thermal conductivity, density and specific heat of the sample respectively. Substituting for $K$, the phononic contribution to thermal conductivity $K_{\text{ph}}$ given by [44,45],

$$K_{\text{ph}} = \frac{1}{3} c_p \rho \overline{V} \overline{I}$$

(3.14)
where \( \overline{V} \) is the average sound velocity and \( \overline{l} \) is the phonon mean free path, we get,

\[
\alpha = \frac{1}{3} \overline{V} \overline{l}
\]  
(3.15)

Eq. (3.15) shows that the sudden increase in \( \alpha \) below \( T_C \) is the result of an increase in \( \overline{l} \) which is caused by a drastic reduction in phonon carrier scattering. As the charge carriers begin to form superconducting pairs one can expect this effect. This also suggests that the major contribution to heat conduction in these materials is due to phonons.

Another feature that can be noticed in fig.3.7 is a small anomalous decrease in \( \alpha \) and near \( T_C \). This, we think, is a consequence of the jump in heat capacity at \( T_C \) [26,27].

In conclusion, the observed increase in thermal diffusivity below \( T_C \) is an indication of the close coupling of the charge carriers and phonon excitations in 1:2:3 superconductors.
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