Heat Capacity Measurement of YBa$_2$Cu$_3$O$_{7-\delta}$

By

Mahin Bahrami

B.Sc. Simon Fraser University, 1991

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in
THE FACULTY OF GRADUATE STUDIES
PHYSICS

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

October, 1995
© Mahin Bahrami, 1995
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Physics

The University of British Columbia
Vancouver, Canada

Date Oct 16 '95
Abstract

A modified AC method is developed for measuring the specific heat of very small high quality single crystal samples of \( \text{Y}_1\text{B}_2\text{C}_3\text{O}_{6+x} \) (Yttrium Barium Copper Oxide). The system developed combines the original AC calorimetry method introduced by Sullivan et al. and the thermal relaxation method by Bachmann et al. The modification involves the use of a sapphire as substrate to support the crystal, heater and the temperature sensor. A complete thermal analysis of the experimental setup is presented in addition to a detailed experimental procedure for measuring the heat capacity of a small sample. Some experimentation with diamond substrate is performed as well and compared with sapphire. Another feature added to our AC calorimetry setup is a Dewar pressure regulation system. This was to minimize the variations in the liquid bath temperature due to changes in ambient pressure. Our system also allows for multiple sweeps, as bath temperature is monitored, from which the best sweeps corresponding to the most stable temperature interval is chosen for further analysis.

Considering the different mathematical models developed so far for explaining the behavior of the specific heat fluctuation of YBCO, our results seem to support the 3D XY model near the transition temperature of 93.1K. From the heat capacity data our crystal sample showed a transition width, \( \Delta T_c \), of 0.45K, and a superconducting transition jump \( \Delta C_p \), of 6.1mJ/gK.
# Table of Contents

Abstract ........................................................................................................................................ ii

Table of Contents ......................................................................................................................... iii

List of Figures ................................................................................................................................... v

List of Nomenclature ....................................................................................................................... vii

Acknowledgements ......................................................................................................................... ix

Chapter One
Superconductivity

  introduction ................................................................................................................................. 1

Chapter Two
Heat Capacity Measurement Techniques

  2.1) adiabatic method ..................................................................................................................... 9

  2.2) relaxation time method ......................................................................................................... 10

  2.3) AC temperature method ...................................................................................................... 10

Chapter Three
Experimental

  3.1) introduction .......................................................................................................................... 13

  3.2) modified AC calorimetry technique .................................................................................... 13

  3.3) thermal analysis ................................................................................................................... 16

  3.4) implementation of the AC calorimetry technique ............................................................... 24

  3.5) experimental verification of the thermal model .................................................................. 29

  3.6) heat capacity measurement ................................................................................................ 40

  3.7) data collection ..................................................................................................................... 53
Table of Contents

Chapter Four
Theory and Analysis

4.1) introduction .................................................. 63

4.2) thermal fluctuation ........................................... 64

Concluding Remarks .................................................. 69

References .............................................................. 70

Appendix A1 Results of the diamond substrate experiment .................................................. 73

Appendix A2 Problematic behavior of the heat capacity data acquired ..................................... 77
List of Figures

Chapter One

1.1 Unit cell structure of YBCO .......................................................... 4
1.2 Relative distances within planes and chains ...................................... 5
1.3 Resistivity behavior of YBCO ........................................................... 7

Chapter Three

3.1 Equivalent thermodynamic schematic ............................................. 17
3.2 Calculated frequency response of the substrate and sample ................. 19
3.3 Proposed experimental setup .......................................................... 26
3.4 Top view sketch of the low temperature probe ................................... 27
3.5 Side view photograph of the low temperature probe ............................ 29
3.6 Block diagram of the system for AC calorimetry ............................... 31
3.7 Circuit diagram for thermal resistance measurement .......................... 32
3.8 Circuit diagram for frequency response measurement ........................ 34
3.9 Plot of frequency response of the substrate and sample ....................... 36
3.10 Circuit diagram for frequency response measurement ........................ 37
3.11 Plot of frequency response of PAR190 transformer .......................... 38
3.12 Plot of corrected frequency response of the substrate and sample ........ 40
3.13 Circuit diagram for thermal time constant measurement .................... 41
3.14 Plot of thermal decay rate of the copper base .................................. 43
3.15a Plot of thermal time constant of the copper base vs temperature ........ 44
3.15b Plot of thermal resistance vs temperature ..................................... 44
3.16 Circuit diagram for linear temperature sweep ................................... 45
3.17 Plot of the linear temperature sweep .............................................. 46
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.18a</td>
<td>Plot of the variation of DC temperature offset vs temperature</td>
<td>48</td>
</tr>
<tr>
<td>3.18b</td>
<td>Plot of the total temperature offset</td>
<td>48</td>
</tr>
<tr>
<td>3.19</td>
<td>Plot of the thin film resistance vs temperature</td>
<td>49</td>
</tr>
<tr>
<td>3.20</td>
<td>Circuit diagram for heat capacity measurement</td>
<td>51</td>
</tr>
<tr>
<td>3.21a</td>
<td>Plot of the raw thermocouple data vs temperature</td>
<td>53</td>
</tr>
<tr>
<td>3.21b</td>
<td>Plot of the total heat capacity data vs temperature</td>
<td>53</td>
</tr>
<tr>
<td>3.22a</td>
<td>Plot of drifting heat capacity data vs temperature</td>
<td>55</td>
</tr>
<tr>
<td>3.22b</td>
<td>Plot of drifting heat capacity slope vs temperature</td>
<td>55</td>
</tr>
<tr>
<td>3.23a</td>
<td>Plot of the liquid nitrogen bath temperature variation with time</td>
<td>56</td>
</tr>
<tr>
<td>3.23b</td>
<td>Plot of the ambient pressure variation with time</td>
<td>56</td>
</tr>
<tr>
<td>3.24</td>
<td>Block diagram of liquid nitrogen pressure regulation system</td>
<td>57</td>
</tr>
<tr>
<td>3.25a</td>
<td>Plot of pressure regulated heat capacity vs temperature</td>
<td>59</td>
</tr>
<tr>
<td>3.25b</td>
<td>Plot of non-regulated heat capacity vs temperature</td>
<td>59</td>
</tr>
<tr>
<td>3.26a</td>
<td>Plot of the liquid nitrogen bath temperature variation with time</td>
<td>61</td>
</tr>
<tr>
<td>3.26b</td>
<td>Plot of the raw AC signal vs time</td>
<td>61</td>
</tr>
<tr>
<td>3.27a</td>
<td>Plot of the total and the background heat capacity vs temperature</td>
<td>62</td>
</tr>
<tr>
<td>3.27b</td>
<td>Plot of the sample heat capacity vs temperature</td>
<td>62</td>
</tr>
<tr>
<td>3.28a</td>
<td>Plot of the fitted specific heat of sample vs the reduced temperature</td>
<td>68</td>
</tr>
<tr>
<td>3.28b</td>
<td>Plot of the fitted specific heat/temperature curve vs the reduced temperature</td>
<td>68</td>
</tr>
</tbody>
</table>

**Appendices**

- A1.1 Rough sketch of diamond substrate preparation process   73
- A1.2 Rough sketch of evaporated thermocouple on sapphire substrate  74
List of Nomenclature

Chapter one

\( \xi \) coherence length
\( \lambda \) penetration depth
\( T_C \) critical temperature
\( J_C \) critical current
\( \kappa \) \( \lambda/\xi \)
\( \delta \) oxygen deficiency
\( \kappa_{el} \) electronic thermal conductivity
\( \kappa_{lat} \) lattice thermal conductivity

Chapter two

\( C \) heat capacity
\( Q \) heat
\( \Delta T \) change in temperature
\( k \) thermal conductance
\( \tau \) relaxation time
\( P \) power
\( \omega \) coupling frequency

Chapter three

\( C_S \) sample heat capacity
\( C_B \) substrate heat capacity
\( P_0 \) input power
\( R \) thermal resistance between copper block and liquid nitrogen
\( R_B \) thermal resistance between substrate and copper block
\( R_S \) thermal resistance between substrate and sample
\( \tau \) thermal time constant of copper block
\( T_S \) sample temperature
\( T_B \) substrate temperature
\( \omega_B \) coupling frequency of substrate
\( \omega_{SB} \) (non-physical) coupling frequency involving \( C_B \) and \( R_S \)
\( \omega_S \) coupling frequency of sample
$\omega_{\text{th}}$ coupling frequency of thermocouple

$R_{\text{th}}$ Thin Film Heater Resistance, 138 ohms

$R_{\text{sc}}$ Copper/Constantan Thermocouple

$R_n$ General Radio, Type 1432-T Precision Resistor, same value as thermocouple

$R_s$ Series Resistor, 100 Kohms

$R_{\text{bk1}}$ Copper Block Heater Resistor, 125 ohms

$R_{\text{bk2}}$ Copper Block Heater Resistor, 33 ohms

C-G Lake Shore Carbon-Glass Thermometer

$V_{\text{ref}}$ pressure regulator reference volume
Acknowledgement

As a show of appreciation I would like to sincerely thank the individuals who contributed into this thesis and without whom it would have never been realized. To Erwin Klein I wish to extend the warmest thanks for his work in designing the original experiment and his continual efforts in solving the many problems associated.

I would like to thank Jim Carolan, my supervisor, for his assistance and support throughout the experimental progress, particularly during the more difficult times. I would also like to thank Ruixing Liang for providing the experimental crystals.

But most of all I am greatly indebted to Pinder Dosanjh for his kindness and incredible patience with me as I struggled throughout this experiment. I sincerely appreciate his continual guidance and support, both technically and emotionally, without which this work would have not been completed and my sanity may have been lost.

Finally, I thank the technical support staff at the UBC physics department, the electronic and the machine shop technicians and especially the STS group for continually repairing our pumping stations as they were being destroyed.
Chapter 1

Superconductivity

1.1 Introduction

Superconductivity was first discovered in 1911, by Kamerlingh-Onnes, who noticed its manifestation in the disappearance of the electrical resistance of mercury at its critical temperature, ~ 4K. Ever since, enthusiastic material scientists have discovered and synthesized over 6000 superconducting compounds. These new compounds have been classified into several groups according to their properties and structure. Of the many groups of superconducting compounds two major classes are the conventional BCS(Bardeen-Cooper-Schrieffer) and the new high temperature non-conventional superconductors. The former group consists of superconductive compounds whose behavior is accurately predicted by the BCS model. Copper-oxides constitute the latter group, with yttrium-barium-copper-oxide, Y$_1$Ba$_2$Cu$_3$O$_7$, or YBCO, the material of interest here, as a member of this family. A brief history and discussion of the properties of this group of superconductors will follow.

Beginning with the discovery of superconductivity in the lanthanum-barium-copper-oxide system, LaBaCuO, in 1986 by Alex Muller and George Bednorz, researchers were led to a new class of materials called High-$T_c$ copper oxides with $T_c$, the critical temperature, as high as 125K. (Recently, there have been reports of superconductivity at 134K in mercury-barium-copper-oxide systems and even higher temperatures, 164K, under quasihydrostatic pressures of 31 GPa.) By replacing lanthanum with yttrium and determining the proper stoichiometry, M. K. Wu and P. W. Chu produced Y$_1$Ba$_2$Cu$_3$O$_{7-8}$, the first material to become a superconductor.
Chapter 1. Superconductivity

above liquid nitrogen temperature. Since then YBCO has become the most extensively studied copper-oxide superconducting compound. Relative to other copper-oxides, this material is considered effectively more homogeneous and thus a more suitable material for fundamental experiments. This is because YBCO can be grown to purity levels higher than any other High-\(T_c\) material in single crystal form. As compared to the conventional superconductors, which obey BCS theory, the exact electron pairing mechanism of YBCO and other copper-oxides is not yet clear. There is some experimental evidence which points to a BCS-like theory. For example, in the superconducting state, the fundamental charge is \(2e\), indicating paired electrons. There seems to exist an anisotropic yet controversial energy gap lying in the range \(3.5 k_B T_c\). Vortex structure has been found, as in any type II superconductor, (defined as superconductors whose value for \(\kappa = \lambda/\xi > 1/\sqrt{2}\) where \(\lambda = \) London penetration depth and \(\xi = \) coherence length) as well as Josephson tunneling. Despite these conventional BCS-like properties, YBCO and other Hi\(T_c\) Cuprates exhibit some unusual properties such as linear dc resistivity in the normal state, unusual behavior of the nuclear relaxation rate in the superconducting state, close proximity of antiferromagnetic phases and of course, extremely

<table>
<thead>
<tr>
<th>(\xi_0) (coherence length)</th>
<th>(\lambda) (penetration depth)</th>
<th>(T_c) (critical temperature)</th>
<th>(J_c) (critical current)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sim 4.8\text{Å} \perp c)</td>
<td>(\sim 1180\text{Å} \perp c)</td>
<td>(\sim 93\text{K})</td>
<td>(\sim 1.3 \times 10^8) A/cm(^2) (\perp c)</td>
</tr>
<tr>
<td>(\sim 10\text{Å} \parallel c)</td>
<td>(\sim 1400\text{Å} \parallel c)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1-1 Characteristic parameters of YBCO crystals.
high values of $T_c$ and short coherence lengths.$^8$ Various characteristic parameters of YBCO and their typical values are listed in Table (1-1).

The layered crystal structure, apparently essential for high temperature superconductivity in YBCO, leads to the large spatial anisotropy (between the a,b plane and the c direction) in the electrical transport properties of YBCO and similar materials. In the case of YBCO, the layers are composed of Cu-O planes separated from each other by planes of barium-oxide and yttrium. YBCO is observed to crystallize to a tetragonal form at high temperatures, converting to an orthorhombic form upon cooling. In the former structure all oxygen atoms assume perovskite-like anion positions, halfway between copper atoms along the cube edges.$^9$

As shown in Fig. (1.1), there are pairs of Cu-O planes, perpendicular to the c-axis, about 3.2 Å apart, separated by a single relatively sparsely occupied yttrium atomic plane. Two such pairs of immediately adjacent Cu-O planes are $> 8.2$ Å distant from each other and are separated by three "isolating" planes. These charge reservoirs consist of one Cu-oxide plane, (composed of chains in the b direction), surrounded by two barium-oxide planes. The copper oxide planes are labeled as Cup-O$_p$ and Cu$_c$-O$_c$, respectively. The relevant distances are sketched and marked in Fig. (1.2). Comparing the interatomic distances in all directions of both Cup-O$_p$ and Cu$_c$-O$_c$, it is evident that the Cu-O planes extend indefinitely in the a-b plane, due to the strongly covalently bonded Cu-O molecules, while the Cu-O chains extend in only the b-axis direction. YBCO's structural phase varies from the tetragonal phase to orthorhombic phase as the oxygen content is increased. The phase transition occurs at 6.4
Figure 1.1 Unit cell structure of YBa$_2$Cu$_3$O$_6$ and YBa$_2$Cu$_3$O$_7$. (Courtesy of Paul R. Schelger)
Cu-O planes

Cu-O chains

Figure (1.2) Actual distances between copper and oxygen atoms in each direction. Note the difference between distances in Cu-O planes and chains.
oxygen per unit cell.\textsuperscript{10} \(T_c\) reaches a maximum when the oxygen content has reached 6.95 and decreases both above and below it.

Efforts to determine the structure of YBCO\(_{7.5}\) with intermediate oxygen content, \((0 \leq \delta \leq 1)\), have reported no new structure, other than O\(_C\) vacancy-ordered structure observed via electron diffraction measurements. Neutron and X-ray diffraction experiments have reported unit cell lengths and positional parameter variations with \(\delta \sim 0.65\).\textsuperscript{11} Evidently, the crystal structure is highly anisotropic, a feature common to many HiT\(_C\) compounds manifesting itself in electrical transport properties which are also highly anisotropic with the high conductivity direction parallel to and due to conduction in the planes. In plane and normal to a-b plane Cu-oxide conductivity measurements demonstrate that for the most part the carriers (holes) are confined to the planes and that interlayer transitions are less favorable. The behavior of the resistivity in the a-b plane, of large, high quality YBCO crystals was measured by Liang et al.\textsuperscript{7} and is shown in Fig. (1.3). It should be emphasized that in the metallic region the carrier concentration is one to two orders of magnitude smaller than those of typical metals, namely \(10^{21}\) to \(10^{22}\) carriers per cubic centimeter.\textsuperscript{12} Thermal conductivity of this material and other cuprates is similar to ordinary metals in that considering the relation \(\kappa = \kappa_{el} + \kappa_{lat}\) where \(\kappa_{el}\) and \(\kappa_{lat}\) are the electronic and the lattice components of the thermal conductivity, respectively, it has been found, though not universally agreed upon, that \(\kappa_{el} \gg \kappa_{lat}\) below the critical temperature.\textsuperscript{13} K.C. Yu et al.\textsuperscript{14} have shown that, this is the effect of a strongly suppressed quasiparticle scattering rate with decreasing temperature in the superconducting state. In
Chapter 1. Superconductivity

Resistivity vs Temperature
(j//ab plane)

Figure (1.3) a-b plane resistivities of a YBCO single crystal, measured by a four-probe technique at 98 Hz. (Courtesy of R. Liang et al.)
addition to these properties, the short coherence length of cuprates tends to increase the significance of fluctuation effects in the neighborhood of $T_c$. Specific heat, a bulk property of crystals and one of the most effective tests for homogeneity of a superconductor, displays these fluctuation effects clearly. A detailed discussion of several methods of measuring specific heat of YBCO as a function of temperature will be presented in the following chapter.
Chapter 2

Heat Capacity Measurement Techniques

2.1 Adiabatic method

In this chapter the various experimental methods used for heat capacity measurements at low temperature will be reviewed. There have been three main techniques developed for measuring heat capacity beginning with the adiabatic method, first used by Nernst in 1909. This method employs a vacuum chamber containing the sample suspended on supports with low thermal conductance. The sample in turn, is equipped with a thermometer and a resistance heater, and the complete assembly is then immersed in a low temperature bath with an exchange gas in the vacuum chamber. Following the cool down of the sample, the exchange gas is pumped out, and a pulse of heat, $Q$, is applied to the heater resulting in a slight temperature rise of the sample, $\Delta T$. The ratio of these two quantities yields the heat capacity, close to the initial temperature:

$$C = \frac{Q}{\Delta T}$$  \hspace{1cm} (2.1)

This process is then repeated to obtain the value of the heat capacity at successively higher temperatures. The main constraint, when applying this method, is the size of the sample which must be large enough, $\sim 10$ grams, to minimize the effects of stray heat leaks and low thermal conductance, $k$, of the supporting wires. If the latter condition is not satisfied the relaxation time method becomes a better technique.
2.2 Relaxation Time Method

This procedure was first introduced by Bachmann et al.\(^6\) in 1973 and utilizes a platform made of sapphire to form the interface between the sample and the thermometer/heater. The leads of the thermocouple are used to suspend the platform from the temperature regulated reference block and to provide a thermal conductance, \(k\), between the platform and the block. The total heat capacity of the sample and platform, \(C\), is determined from the following:

\[
C = \tau k = \tau \frac{P}{\Delta T}
\]  

(2.2)

where \(P\) is the input DC power to the heater, \(\Delta T\) is the temperature difference between the sample and block and \(\tau\) is the relaxation time after the heater current is turned off and the sample is allowed to cool down to \(T_0\), the block temperature. This calculation assumes that there is no thermal resistance between the sample and the platform and that the sample's thermal conductivity, \(k_s\), is infinite. With a finite \(k_s\) the heat capacity can still be obtained without much complication, and in fact this method is applicable even to the point where \(k/k_s \sim 1\). In addition, this method has the advantage of easy signal averaging at a given \(T_0\). Moreover, the only heating needed to be accurately known is the dc heating used for measuring the thermal conductivity \(k\) of the supporting wires which is given by

\[
P = \kappa \Delta T
\]  

(2.3)

2.3 AC Temperature Method

The technique used for the specific heat measurements in this thesis is based on the AC
temperature method. The principle of AC calorimetry, first introduced by Sullivan and Seidel\textsuperscript{17} in 1968, is to heat the sample periodically and detect the amplitude of the temperature oscillations. The experimental setup is identical to the relaxation time method described above. The difference lies in the method of heating which is oscillatory in this case and its period, 1/f, must be much longer than the internal thermal relaxation times of the sample, thermometer and the heater, $\tau_{\text{int}}$, and much shorter than the sample to bath thermal relaxation time, $\tau_{\text{ext}}$. Having satisfied these conditions as well as the requirement for high sample thermal conductivity, the specific heat can be determined from the temperature oscillation amplitude, $\Delta T_{AC}$, by the following relation:

$$C = \frac{P_{AC}}{\omega \Delta T_{AC}}$$

(2.4)

where $P_{AC}$ is the input power to the heater and $\omega = 2\pi f$. In the case of low sample thermal conductivity the analysis becomes more complicated but to the lowest order the above relation may be corrected to:

$$C = \frac{P_{AC}}{\omega \Delta T_{AC}} \left[ 1 + \frac{1}{\omega \tau_{\text{ext}}^2} + \omega \tau_{\text{int}}^2 + \frac{2k_b}{3k_s} \right]^{1/2}$$

(2.3)

where $k_b$ is the sample to block thermal conductance and $k_s$ is the sample thermal conductance.\textsuperscript{17} This method is not favorable when high absolute accuracy is needed or samples with low thermal conductivity are studied. Instead, it is most suitable when high relative accuracy is required to detect small changes in the specific heat while measuring phase transitions. In addition, a continuous readout of $C$, as various parameters such as temperature
or magnetic field are varied, is possible. While the traditional adiabatic method needs large samples, ~1 gram, the AC method is most advantageous with small samples of the the order of 1 mg.

The experiment performed and described in this thesis is based on the AC calorimetry technique because the crystals under investigation have large thermal conductivity and small masses.
Chapter 3

Experimental

3.1 Introduction

After obtaining high purity YBCO single crystals, the growth process of which is reported elsewhere by R. Liang et al., a modified AC calorimetry method was decided upon as the best method for measuring the heat capacity close to the transition temperature because of the samples' small mass. In this chapter we will first discuss the modified AC technique designed to meet specific measurement criteria. Then a complete mathematical model analysis of the experimental system will follow along with the predicted results. Next, the procedure for building the experiment will be presented in detail followed by the first characterization measurements to verify the validity of the mathematical model predictions. The remaining sections explain the process of further characterization and heat capacity measurement of the sample.

3.2 Modified AC Calorimetry Technique

To begin with the experimental design process let us consider the design setup of some earlier AC calorimetry techniques. First we discuss the work by Sullivan and Seidel. Their general experimental layout consisted of a resistance thermometer and a wire resistance heater mounted on the sample. An appropriate link from the sample to a reference temperature bath was maintained by a copper wire. The heat capacity measurements were obtained by passing an alternating current at $\omega/2$ through the wire heater and detecting the voltage variation developed across the thermometer at the frequency $\omega$. Bachmann et al. designed a different
type of a calorimeter utilizing a silicon chip bolometer as sample holder, temperature sensor and sample heater. The bolometer, insulating at low temperatures, was doped on one side and cut, forming two resistance elements, one to be used as a resistance thermometer, the other as a source of Joule heat. The sample was mounted on the back or the insulating side of the bolometer. Their apparatus was capable of measuring very small samples (1-500 mg), and applicable to a number of different experimental methods such as the AC calorimetry and the thermal relaxation method. A more recent variation of the AC temperature technique is reported by Inderhees\textsuperscript{18}. Her method involves the use of an external quartz lamp as a heater as opposed to a wire resistance. This is to avoid the addition of heat capacity to the background due to wires for heating. However, we conclude that a better alternative is a thin film heater evaporated on the sapphire substrate. The advantage is that the total heat applied to the system is more accurately known this way as opposed to the light source method where the total heat reaching the system can only be estimated. Also an evaporated film maintains better coupling to the substrate, in principle, than a glued wire resistance. Inderhees' temperature oscillation detection procedure utilized the conventional copper/constantan thermocouple with one junction glued to the sample (also acting as the support for the sample) and the reference junction placed in thermal contact with the reference temperature bath. Clearly, her heating and temperature measurement techniques eliminate the need for a supportive substrate thereby minimizing background heat capacity.

In our experimental design since it is necessary to allow easy removal and replacement of the crystal to accommodate for subsequent measurements of doped or oxygenated samples and background measurements, a sapphire substrate will be used to support the sample, the
temperature sensor and the thin film heater. A copper/constantan thermocouple similar to Inderhees' will be employed as our temperature sensor and a copper block as our reference temperature. The thermal analysis of this setup will be discussed in the next section.
3.3 Thermal Analysis

The system shown in Fig. (3.1) depicts the thermal paths of the substrate, the sample and the copper block and the following equations describe the net power into the sapphire substrate and the YBCO crystal sample, respectively,

\[ C_B \frac{\partial T_B}{\partial t} = P_{in} - P_{out} \]
\[ = P_{in} - \frac{1}{R_B} [T_B - T_0] - \frac{1}{R_S} [T_B - T_S] \]  
(3.1)

\[ C_S \frac{\partial T_S}{\partial t} = \frac{1}{R_S} [T_B - T_S] \]  
(3.2)

The parameters in the equations are defined in the same figure. Rewriting in terms of the various characteristic frequencies the following two equations are arrived at:

\[ \frac{\partial T_B}{\partial t} = \frac{P_{in}}{C_B} - \omega_B [T_B - T_0] - \omega_{SB} [T_B - T_S] \]  
(3.3)

\[ \frac{\partial T_S}{\partial t} = \omega_S [T_B - T_S] \]  
(3.4)

where 

\[ \omega_B = \frac{1}{R_B C_B}, \ \omega_S = \frac{1}{R_S C_S}, \ \omega_{SB} = \frac{1}{R_S C_B} = \omega_S \frac{C_S}{C_B} \]

and \( \omega = \) frequency of the input power. The temperature of the substrate, the sample and the input power are assumed to have the following forms, respectively,

\[ \bar{T}_B = T_{AC} + T_{DC} \]
\[ = T_S e^{i\omega t} + \bar{T}_B \]  
(3.5)

\[ \bar{T}_S = T_S e^{i\omega t} + \bar{T}_S \]  
(3.6)

\[ \bar{P} = P_0 e^{i\omega t} + \bar{P} \]  
(3.7)
Figure (3.1) Equivalent thermodynamic schematic of the AC calorimetry setup.
and the average temperature of the sample and the substrate are assumed equal and given by:

\[ T_s = T_B = R_B \bar{P} \quad (3.8) \]

Using these equations to solve the first order differential heat equations above and setting \( T_0 \) to zero, for simplicity, the following relation for the substrate temperature is obtained.

\[ T_B = \frac{P_0}{C_B} \left[ \frac{\omega_s^2 + \omega^2}{\left( \omega_s^2 + \omega \omega_s^2 + \omega_s^2 \omega_B^2 \right) + \omega^2 \left( \omega_s \omega_B + \omega_s^2 + \omega_s^2 \right)^2} \right] \quad (3.9) \]

The magnitude of this equation corresponds to the physical measured quantity, temperature, therefore, the final form of substrate and the sample temperatures are calculated to be:

\[ |T_B| = \frac{P_0}{C_B} \left[ \frac{\omega_s^2 + \omega^2}{\left( \omega_s^2 + \omega \omega_s^2 + \omega_s^2 \omega_B^2 \right) + \omega^2 \left( \omega_s \omega_B + \omega_s^2 + \omega_s^2 \right)^2} \right] \quad (3.10) \]

\[ |T_s| = |T_B| \left[ \frac{\omega_s}{\omega_s^2 + \omega^2} \right]^2 \quad (3.11) \]

Fig. (3.2) displays the behavior of equation (3.10). Clearly, the latter set of equations are functions of \( \omega \), where \( \omega \) is the frequency of the input power, and if the various frequency and heat capacity extreme values are approached, some interesting and useful limits and relationships are obtained. Upon expansion of the denominator in equation (3.10) we arrive at the following relationship:
Calculated Temperature Oscillations vs Frequency

Figure (3.2) Calculated amplitude of the substrate temperature oscillations as a function of frequency of the input power.
\[ |T_B| = \frac{P_0 \left( \omega_s^2 + \omega^2 \right)}{C_B A^{1/2}} \]  \hspace{1cm} (3.12)

where \( A = \omega^6 + \omega^4 \left( 2\omega_s^2 + 2\omega_s \omega_{sb} + \left( \omega_B + \omega_{SB} \right)^2 \right) + \omega^2 \left( \omega_s^4 \omega_{SB} + \omega^4 + 2\omega_s^3 \omega_{SB} + 2\omega_s^2 \omega_B \left( \omega_B + \omega_{SB} \right) + \omega_s^4 \omega_B^2 \right) \)

Considering the operating frequency's lower limit, all \( \omega \) dependent terms tend to zero in the above equation and the following temperature limit is arrived at.

\[ |T_B| \rightarrow \frac{P_0 \omega_s^2}{C_B \omega_{SB}^2} = \frac{P_0}{C_B \omega_B} = R_B P_0 = \bar{T} \]  \hspace{1cm} (3.13)

\[ |T_S| \rightarrow |T_B| \]

Intuitively, at the lower end of the frequency spectrum all components should be coupled and all temperatures should be equal and proportional to the DC input power. This is correctly predicted by the above equation where the temperature depends only on the rms value of the input power and the thermal resistance between the substrate and the copper base. The sample heat capacity becomes irrelevant. Applying the operating frequency's upper limit to equation (3.12), and considering only the highest order operating frequency terms of the denominator, the following approximation is derived.

\[ |T_B| \rightarrow \frac{P_0 \left( \omega_s^2 + \omega^2 \right)}{C_B \left( \omega_B \right)^{1/2}} \sim \frac{P_0}{C_B \omega_B} \]  \hspace{1cm} (3.14)

\[ |T_S| \rightarrow \frac{P_0 \omega_s^2}{C_B \omega^2} \]

Equation (3.14) predicts the sample and substrate temperature behavior on the other end of the
spectrum as unequal. In fact the sample temperature decreases as the square of the input frequency and has a linear dependency on the sample coupling frequency. The behavior is sensible since at higher frequencies the sample should decouple from the substrate and follow a different temperature curve. In addition, since the sample is essentially decoupled from the substrate, the temperature limit should approach that of a system without a sample, derived later. An important aspect of these derivations is that at the lower limit no approximations were necessary and in the upper limit the approximations made did not require the knowledge of the non-physical frequency term, $\omega_{SB}$. The mathematical results seem to coincide with our expectations, however, neither of these regions are suitable for heat capacity measurements. In the first case the input frequency dependency is lost, and in the second case the sample and substrate temperatures are not equal. Let us consider equation (3.12) in the intermediate frequency range, i.e. $\omega_B << \omega << \omega_S$, and derive the temperatures of the sapphire and the sample in that region.

\[
|T_B| \equiv \frac{P_0}{C_B} \frac{\omega^2}{\left(\omega_B^2 + \omega_0^2 + \omega_{SB}^2\right)^2 + \omega^2 \omega_0^4 \left(1 + \frac{C_S}{C_B}\right)^2} \quad \text{since } \omega << \omega_S
\]

\[
\equiv \frac{P_0}{C_B} \frac{\omega^2}{\omega_B^2 \omega_0^2 + \omega_0^4 \left(1 + \frac{C_S}{C_B}\right)^2} \quad \text{since } \omega_B << \omega_S << \omega^4
\]

\[
\equiv \frac{P_0}{C_B} \frac{1}{\omega^2 \left(1 + \frac{C_S}{C_B}\right)^2} \quad \text{since } \omega_B \omega_0^2 << \omega^4
\]
\[ |T_B| = \frac{P_0}{\omega (C_B + C_S)} \]  

(3.15)

And finally,

\[ |T_s| = |T_B| \left| \frac{\omega_s}{\left(\omega_s^2 + \omega^2\right)^{1/2}} \right| \sim |T_B| \quad \text{since } \omega^2 \ll \omega_s^2 \]

Clearly, this is the appropriate region of operation since the crystal is still coupled to the substrate, hence both are at equal temperatures, and they form a simple relation with the input frequency and the total heat capacities of the sample and substrate. All three regions are displayed in Fig. (3.2) where the intermediate region corresponds to the linear section between the substrate coupling frequency and sample coupling frequency. Next we shall derive a similar temperature equation describing the system without a sample.

We start with a simple differential equation involving only the heat capacity of the substrate and its coupling frequency and proceed as such.

Using equations (3.3) and (3.5),

\[ \frac{\partial T_B}{\partial t} = i\omega T_B = \frac{P_m}{C_B} T_B - \omega_B \left[ T_B - T_0 \right] \]

we let \( T_0 = 0 \) since it is arbitrary.

\[ T_B = \frac{P_m}{C_B (i\omega + \omega_B)} \]

The real part of the temperature is:

\[ |T_B| = \frac{P_0}{C_B \left[ \omega^2 + \omega_B^2 \right]^{1/2}} \]  

(3.16)

This curve is also indicated in the same graph and represents the behavior of the system without a crystal. As intuitively expected, the system without a crystal has a lower heat capacity value, therefore, the effective substrate to base coupling frequency should be higher, as evident in Fig. (3.2). As stated before, at higher operating frequencies, the crystal will decouple from the substrate and the frequency response will approach that of the system without a crystal. The difference between the two curves, at the operating frequency, is
Chapter 3. Experimental

proportional to the sample heat capacity.

To summarize, the equation of interest, (3.15), is rewritten in terms of the substrate temperature oscillations which is the quantity to be measured.

\[ C_S + C_B = \frac{P_0}{\omega \Delta T_B} \]
\[ \omega_B \langle \omega \times \omega_S \rangle \]

(3.17)

where \( C_S \) = sample heat capacity
\( C_B \) = substrate heat capacity
\( P_0 \) = input power
\( T_B \) = substrate temperature
\( \omega_S \) = sample to substrate coupling frequency
\( \omega \) = operating frequency
\( \omega_B \) = base to substrate coupling frequency

In the above relation the optimum operating frequency is half way between the coupling frequencies of the sample and the substrate which are as far apart as possible. This is to facilitate the decoupling of the substrate from the copper block while maintaining the coupling between the sample and the substrate. Assuming that the input power and the operating frequency are constant, the total heat capacity is simply inversely proportional to the AC temperature oscillations which can be readily measured, provided that the relevant parameters of the system are known. The remaining sections describe, in detail, the implementation of the experimental setup for determining the total (including the sample) and the background heat capacity via the AC calorimetry technique.
3.4 Implementation of the AC Calorimetry Technique

The experimental setup, as illustrated in Fig.(3.3) excluding wires and adhesives, consists of a copper block base which is our temperature reference, carbon glass thermometer, sapphire substrate, thermocouple and YBCO sample. Beginning with the substrate, a thin film of nichrome (800Å) and gold pads (700Å) are evaporated on the sapphire (0.1mm), forming the heater on the substrate. A thin layer of chromium (1500Å) is used as the interface between the gold and the sapphire to allow good bonding to the substrate. Sapphire forms a stronger bond with chromium than with gold thereby minimizing the possibility of the gold contacts peeling off. To measure the temperature oscillations a copper/constantan thermocouple is used. The wires (copper: #50, constantan: 0.002” diameter) are first tinned with indium. The tinned sections (5 mm) are then placed in a vice and flattened under a pressure of 5000 psi. The flattened sections are placed atop one another and soldered together using a low temperature soldering iron. The thermocouple is then attached to the sapphire substrate with GE varnish. A heavy mass, 40 gram brass piece, is placed on top to squeeze out any bubbles which may have formed within the varnish interface, insuring good coupling between the thermocouple and the substrate. The sample is mounted on the substrate in a similar fashion. Silver epoxy (EPO-TEK, type 410-E) is used to bond thin copper wires (#50) to the heater gold pads with much care taken to lessen background heat capacity by applying as little epoxy as possible. Before the substrate is mounted on the copper block the thermometer (LakeShore carbon glass) is glued on a copper housing with silver paint (High Purity, type JBS-711), which is then mounted on top of the copper block using a brass screw and silver paint to form a good thermal contact. To mount the substrate two nylon threads (0.009” diameter, 10 mm length) are used to support it on the block as well as to form a
consistent thermal resistance, roughly 1000 K/W, between the block and the substrate. The adhesive used is a very dilute drop of GE varnish applied to the thread forming a thin veneer at the interface between the substrate and the nylon thread. Because the nylon threads act as heat sinks relative to the heater, the section of the substrate in contact with the heat sink has large temperature gradients in all three directions, especially in the direction perpendicular to the surface of the substrate. Due to the finite thermal conductivity of the sample these gradients would appear across the sample as well. As seen from the Fig. (3.3), the sample is placed furthest from the nylon threads, represented by the thermal resistance, to minimize the effects of these temperature gradients on the sample.

After the varnish has completely dried the wire connections can be made. The two sets of thermocouple and the thin film heater wires are soldered, with indium, to two sets of thicker copper wires (#36). The joints on the copper block are electrically isolated from ground by small paper contact pads which are mounted on top of the copper block with GE varnish, shown in Fig. (3.4). The thermocouple joint on the pad serves as the reference point for the joint placed on the substrate. The thermometer and the thin film heater wires run along the side of the probe to the electrical connectors at the top of the probe while the thermocouple wires are fed through a metal rod in the center of the probe and connected directly to the PAR190 transformer. This is to avoid creating metal to metal junctions in the path of the thermocouple wire which would introduce stray voltages since the junctions would inevitably be at different temperatures.

The thermocouple wires are tested for stray thermal-emf voltages produced by inhomogeneity and impurities in the wire. The test is performed by immersing 15 cm sections
Figure (3.3) Measurement setup for AC calorimetry.
Figure (3.4) Top view sketch of the low temperature probe. 

- a. copper base
- b. carbon glass thermometer
- c. isolating paper pads
- d. thermocouple wires
- e. sapphire substrate
- f. YBCO crystal
- g. nichrome heater

To electrical connectors at other end of probe.
of thermocouple wire in a bath of liquid nitrogen and monitoring voltage changes across the wire ends. The sections of wire are in effect acting as thermocouples. A perfectly homogeneous wire would register no change but of course there is always some inhomogeneity and defects in wires which accounts for the stray voltage produced. After scanning a 5 meter piece of wire a small section of 1 meter corresponding to the most homogeneous section was selected as the thermocouple wire to be used in the experiment.

As shown in Fig.(3.5), the copper block is equipped with two coil heaters (#34) of different lengths (resistances, 125 ohms and 33 ohms) which are connected to the Keithley current source and the Lake Shore temperature controller, respectively. Their purpose is to set the temperature of the block and the substrate to any desired value or to vary it linearly. GE varnish is used as the adhesive to bond the heaters to the block.

To avoid any breakage of wires and electrical shorts, all wires along the side of the block are further wrapped with Teflon tape. The electrical feedthroughs at the top of the probe are sealed using 5 Minute Epoxy (Devcon). The probe assembly is then enclosed in a brass casing and sealed with indium. Using a diffusion pump the probe is evacuated down to about $10^{-6}$ Torr and cooled to liquid nitrogen temperature. To insure an efficient pumping process, all adhesives used above must be allowed to dry completely to avoid outgasing during pumping and more importantly, to avoid the formation of bubbles in the varnish which would expand during cool down and cause an increase in the thermal resistance between the copper block and the substrate. The same applies to the varnish between the sample and the sapphire substrate. To check for breaks in the wires or shorts to the probe body, the resistances of the relevant components are recorded both before immersion into liquid nitrogen and again after cool down.
Figure (3.5) Side view photograph of the low temperature probe.
3.5 Experimental Verification of the Thermal Model

Before the actual heat capacity measurements can be taken we must first verify the mathematical model. This is done by a set of measurements which involve the frequency response of the thermocouple and the thermal resistance between the copper block and the substrate. The measured frequency response should be close to Fig. (3.2) with the sample coupling frequency much higher than the substrate coupling frequency. The thermal resistance should be high enough to avoid total absorbance of the AC power from thin film heater by the copper block. In addition, since the substrate heat capacity is known we can calculate the cutoff frequency of the copper base using the measured thermal resistance and verify the value with the measured frequency response. By measuring the sample and substrate coupling frequencies we can then decide on a proper operating frequency somewhere in between. After the relevant parameters are measured we may then proceed with the actual heat capacity run.

Fig. (3.6) illustrates a general outline of the experimental equipment employed and their interconnections. The list of the devices is provided in the same figure. Only the relevant equipment is used to measure each specific parameter.

### 3.5.1 Thermal Resistance Measurement

The electronic schematic for measuring the thermal resistance between the substrate and the copper block base is shown above. With the copper base set to an initial temperature, $T_0$, current is passed through the thin film heater in discrete steps and the temperature difference between the substrate and base is monitored via the thermocouple and recorded. The ratio of this value to the input power, calculated from the input current, yields the thermal resistance which depends on the interfacing materials used, that is, the nylon threads and varnish, and in turn determines the decoupling frequency of the copper block base. The nylon threads happen to provide a thermal resistance of about 1000 K/W, increasing slightly with temperature. This is convenient since, with the sapphire substrate heat capacity, $C_B = 1.05$ J/gK, the cutoff frequency of the copper base, $\omega_B$ is determined theoretically from $\omega_B = 1/(C_BR_B) \sim 0.1$ Hz which, as we will see later, sets a reasonable lower limit on the operating frequency. However, this value depends on the mass of the substrate which is kept to a minimum to decrease the background heat capacity. If the thermal resistance is not within 500 K/W of the expected
value the varnish interface was likely not dried thoroughly before cool down and will have to be re-applied at room temperature. It should be noted that each cool down of the probe results in an effective increase in the thermal resistance due to thermal stresses on the varnish, hence, it is important to monitor this parameter before continuing with the experiment.
3.5.2 Frequency Response of Thermocouple

In the current and the proceeding sections we shall elaborate on the procedure for frequency response measurements, including the corrections involved and compare the results with the mathematical predictions.

The thermocouple coupling frequency, $\omega_d$, is determined by the thickness of the varnish used for mounting the thermocouple to the substrate as well as the smoothness of the interface, i.e. existence of bubbles, which are eliminated by pressing the surfaces together while the varnish is drying. Ideally the cutoff frequency of the thermocouple should be infinite to insure that it does not lie in the operating region and reduce the output signal strength. Of course an infinite value is unattainable in practice and the highest frequency reached, after experimenting with three different techniques for mounting the thermocouple on the sapphire substrate, is $\sim 42$ Hz. The above circuit diagram is used to measure these parameters. As shown in Fig. (3.8), the lockin amplifier applies a reference voltage, 1V rms, across the thin film heater scanning the frequency between 0.01-1000 Hz. An important note
is that since the thermocouple is thermally activated the output is proportional to the input power, i.e. the thermocouple responds at twice the frequency of the input voltage. This signal is relayed to the lockin amplifier through the PAR190 transformer. The frequency response of the thermocouple varies only slightly with temperature, therefore, the copper block temperature was allowed to remain at 77K during the frequency scan. Figure (3.9) illustrates the results. From the figure it is obvious that the transformer is lossy at lower frequencies. In order to correct for the loss we must measure the transformer signal as explained in the following section and then normalize the raw frequency response to the transformer signal.
Figure (3.9) Thermocouple frequency response. Note the loss in amplitude due to transformer loss at lower frequencies.
3.5.3 Frequency Response of a PAR190 Transformer

The above circuit is designed to measure the transformer frequency response. It is important to normalize the frequency response of the thermocouple to the transformer signal since the transformer exhibits a loss at lower frequencies. The transformer frequency response is obtained by placing a precision resistor with the same resistance as the thermocouple in parallel with the transformer forming a high pass filter and scanning the frequency of a constant amplitude signal from the lockin amplifier. The input signal, 1V rms, is varied from 0.01 to 1000 Hz and the transformer response is normalized to a signal at 53 Hz where the filter has negligible loss. An odd normalizing frequency is chosen to insure no 60 Hz harmonic pickup. Since the thermocouple signal is very small, ~ 500 nanovolts, a relatively large resistor, $R_s$, is placed in series to cut down the signal across the normalization resistor, $R_n$, and to represent the thermocouple behavior more closely. Fig. (3.11) displays the frequency response of the transformer with $R_n = 8$ ohms.
Figure (3.11) Frequency response of a Par190 transformer with normalization resistor equal to 8 ohms.
3.5.4 Corrected Thermocouple Frequency Response

Fig.(3.12) illustrates the corrected frequency response of the thermocouple with and without the crystal mounted on the substrate and outlines the characteristic frequencies. The correction is done by dividing the raw thermocouple frequency response Fig.(3.9) by the transformer frequency response Fig.(3.11). The operating frequency is selected at approximately half way between these two frequencies. Comparing the experimental response with the calculated response, Fig.(3.2), a noticeable discrepancy exists at the lower frequencies. The upper curve, corresponding to the measurement without crystal, is higher because $R_{th}$, the thermal resistance between the sapphire and the copper block, has increased. This is an unavoidable result of stress on the varnish and the nylon thread between the sapphire and the block, as the probe is warmed up to remove the crystal and cooled down again. Other than this difference the experimental and the theoretical curves agree quite well and we may conclude that the theory has been verified experimentally. From the measured data 1 Hertz is decided as the operating frequency since it lies one order of magnitude from both substrate and sample coupling frequencies, 0.1 Hertz and 10 Hertz, respectively. Once a satisfactory frequency response is obtained and an operating frequency is decided upon the next set of parameters characterizing the system may be measured.
Chapter 3. Experimental

Measured AC Temperature Amplitude Variation vs Frequency

Figure (3.12) Corrected frequency response of a typical copper/constantan thermocouple pressed on sapphire substrate using varnish. The coupling frequencies of the substrate and the thermocouple are indicated.
3.6 Heat Capacity Measurement

With the operating frequency chosen we must next decide on the type of temperature sweep. Choosing the discrete temperature sweep initially which implies setting a specific temperature on the DRC and allowing the system to reach equilibrium we attempted to measure the heat capacity. Unfortunately, we encountered some problems with this method, namely, the long time required to reach equilibrium and more important, the lack of stability of the DRC temperature controller. Therefore, it was decided to set up a linear sweep using a programmable current source to avoid the long equilibrium time and eliminate the need for constant temperature stability. However, when using a linear sweep we must correct for the sweep rate and any other time constants in the system.

3.6.1 Thermal Time Constant of Copper Block

To obtain a linear temperature sweep, two characteristic parameters must be taken into account; the thermal time constant of the copper block and the thermal resistance between the block and the liquid nitrogen bath, in the relevant temperature range. As seen from the schematic above, the DRC temperature controller is used to set the starting temperature of the
copper block to 120K, via $R_{bk2}$, and the current source supplies a decrementing current beginning at 80mA. The relaxation time between each current setting is 20,000 seconds, allowing sufficient time for the copper block to reach equilibrium temperature. Fig. (3.14) illustrates a sample graph of the results. The time constants are then calculated at each temperature step as follows:

$$\tau = -(T - T_{\text{equ}}) \frac{\partial \tau}{\partial T}$$

where $T_{\text{equ}}$ is the equilibrium temperature. The behavior with respect to temperature is plotted in Fig. (3.15a). From the input power, which is calculated from $P = I^2 R$ where $I$ is the input current and $R$ is the thin film heater resistance, and the temperature difference between the block and the nitrogen bath, the thermal resistance between the two is easily calculated and plotted in Fig. (3.15b); note the linear relationship.

Since particles in the vacuum space provide a thermal path from the copper block to the nitrogen bath, the thermal resistance inversely depends on the probe pressure. This quantity may differ at each vacuum state reached after each pump down. The accuracy of the thermal resistance and the time constant at any given time is quite significant for obtaining a linear temperature sweep, therefore, it is important that the probe pressure remain relatively constant during the experiment and also not differ significantly from the previous pump down.
Temperature Decay of the Copper Block

Figure (3.14) Thermal decay rate of the copper base at various equilibrium temperatures.
Thermal Time Constant of Copper Block vs Temperature

Figure (3.15a) Thermal time constant of copper base at various equilibrium temperatures. Fitted to a straight line as a first approximation.

Thermal Resistance of Copper Base vs Temperature

Figure (3.15b) Thermal resistance between the copper base and liquid nitrogen bath as a function of temperature.

3.6.2 Linear Temperature Sweep and Temperature Response of Thin Film Heater

The next step is to use the characteristic parameters of the copper block, to obtain a linear temperature sweep. This is done by correcting the input power at each temperature by an amount proportional to the thermal time constant and the thermal resistance of the copper block, measured in the previous section. The sweep rate is normally set to 1 mK/s with a variation of 0.1 mK/s which is relatively linear over the experimental temperature range of 80 K to 120 K. The thermal time constant of the copper block, $\tau$, and the thermal resistance between the copper block and liquid nitrogen, $R$, are calculated from the graphs, at each temperature. Using the following equation,

$$P = \frac{(T - T_0 + \tau \Delta T/\Delta t)}{R}$$

where $T$ is the current temperature of copper block, $T_0$ is the liquid nitrogen bath temperature, and $\Delta T/\Delta t$ is the desired sweep rate, the input power to copper block heater, $P$, to maintain the
Figure (3.17) Linear temperature sweep of the copper block, 1 mK/s, obtained by accounting for the copper block's finite thermal time constant and thermal resistance.
sweep rate is calculated. From this value the necessary input current, \( I = \sqrt{\frac{P}{R_{bk1}}} \) is readily calculated and applied to the copper block heater, \( R_{bk1} \). Fig.(3.17) illustrates the results of the temperature scan as a function of time.

Two other parameters which must be measured and accounted for when measuring the heat capacity are the change in the DC offset temperature and the variation in the thin film heater resistance, \( R_{thb} \), as the temperature is swept. The first quantity originates from the AC input power applied to the thin film heater causing an effective DC temperature difference between the substrate and the copper block. Because the DC temperature offset is not constant with temperature, it must be corrected for when calculating the heat capacity. To measure this parameter the input power is applied at 53Hz, which is much higher than the cutoff frequency of the thermocouple to insure AC decoupling, and the Keithley 182 nanometer is used to detect the thermocouple voltage. Fig.(3.18a) displays the variation of the DC temperature offset; i.e. the temperature difference between the substrate and the copper block, with temperature. Ideally, this quantity should be constant at all temperatures but, as observed, the offset decreases with temperature, varying about 200 mK in the temperature range. This variation indicates a temperature dependent temperature gradient on the copper block top surface where the thermometer and the thermocouple are located. Nevertheless, an appropriate correction will be made to the final measurement. In Fig.(3.18b) the AC temperature offset is shown superimposed on top of the DC temperature offset. The amplitude of the former is frequency dependant and diminishes at higher values; i.e. the thermocouple can not track the input and decouples from the substrate at higher frequencies. The second parameter of interest is the
Figure (3.18a) Variation of the DC temperature offset which is the temperature difference between the substrate and the copper block, with temperature.

Total Temperature Offset

Figure (3.18b) Total temperature offset as measured by the thermocouple on the substrate which is composed of the AC temperature offset superimposed on the DC temperature offset relative to the copper base.
Figure (3.19)  Slight variation of the thin film resistance with temperature measured via the 4 probe method.
thin film resistance which is simply measured with the Lock-In Amplifier by applying the 4-probe method. The result is plotted at each temperature and shown in Fig(3.19). The peculiar jumps apparent in the graph are due to the finite resolution of the voltmeter. The value of the thin film resistance is used to calculate the input power. Because the variation in this parameter is relatively small, ~ 0.26% in the temperature range, a constant value 113.5 ohms at 100K is assumed over the entire range.

Having obtained a satisfactory linear temperature sweep, DC offset and the thin film resistance variation with temperature, the system is now ready for heat capacity measurement. It should be emphasized that it is possible to measure the DC offset during the heat capacity measurement using an extra thermocouple placed on the crystal. However, this method increases the background heat capacity, therefore, the DC offset is assumed constant during any cool down and measured immediately prior to the heat capacity.
Figure (3.20)  Circuit diagram for measuring the heat capacity while maintaining a linear temperature sweep.  

- a. Keithley 220 Programmable Current Source
- b. Keithley 182 Programmable Voltmeter
- c. DRC 91C Temperature Controller
- d. C-G = Carbon-Glass thermometer
- e. Stanford Research Systems SR850 Lock-In Amplifier

$R_{\text{source}} = \text{source resistance, } 50 \text{ ohms}$

$R_{\text{th}} = \text{Thin Film Heater Resistance, } 138 \text{ ohms}$

$R_{\text{fe}} = \text{Copper/Constantan thermocouple}$

$R_{\text{bl1}} = \text{copper block heater resistor, } 125 \text{ ohms}$

$R_{\text{bl2}} = \text{copper block heater resistor, } 33 \text{ ohms}$

3.6.3 Acquisition of Raw Heat Capacity Data

The circuit setup for the actual heat capacity measurement is identical to the previous setup except that the thermocouple voltage is monitored rather than the voltage drop across the thin film heater. With the appropriate parameters known the temperature of the copper block is linearly swept while a constant amplitude, oscillatory power is applied to the thin film heater on the substrate. The width of the crystal phase transition, $\sim 300 \text{ mK}$, dictates the required AC amplitude to be detected by the thermocouple. To obtain at least 10 points in that region the AC amplitude must be no more than 30 mK. For the reasons discussed earlier, the operating thermal frequency is chosen to be about 1 Hertz and the electrical frequency of the input power is half of that value. During the experimental runs a sliding average of 30 consecutive points, obtained during a time interval of 30 seconds, are recorded as the temperature of the probe is swept at the rate of 1 mK/s. Assuming the internal thermal time constant of the substrate is very short, the temperature of the crystal and the substrate may be considered equal. The
quantity of interest is the AC temperature variations, relative to the copper base, which is monitored by the thermocouple mounted on the substrate. The PAR190 transformer (10:1000) relays the detected raw thermocouple voltage to the lock-in amplifier. All instruments are IEEE interfaced to the GPIB card of the IBM PC-AT which is used to control the temperature sweep and to record the data. Following data acquisition the raw data is then properly shifted and corrected for the various time constants and converted to heat capacity.

Before evaluating the temperature oscillation data several sources of systematic temperature shifts inherent to the experimental setup must be taken into account. The first of these is due to the lock-in amplifier's output time constant which was set to 1 second. This means the temperature readings obtained from the LIA corresponds to the time 1 second earlier, therefore, all data must be shifted back in time. The second temperature correction is due to the finite time constant between the base and the sapphire plate. Of course this is just the inverse of the coupling frequency \( \omega_B \) and is used to shift data back in time. The equivalent shifts reflected in temperature are only of the order of a few milliKelvins. However, the major source of systematic error is the DC temperature offset between the substrate and the copper base discussed earlier, which is of the order of 500 mK. This is corrected for by fitting a straight line to the DC offset data and adding an appropriate value to each temperature reading in the raw data set. This correction may also be made after evaluating the raw data since the AC signal is independent of the DC offset temperature shift.

Following the corrections, the data which corresponds to the AC temperature oscillations is converted to heat capacity using equation (3.17), assuming a constant input power and operating frequency. The sweeps are then grouped within a 50 mK interval.
Figure (3.21a) Thermocouple output as a function of a linear temperature sweep.

Heat Capacity variation with Temperature

Figure (3.21b) Derived heat capacity from thermocouple output above at constant input power and frequency. Data shown includes background heat capacity.
This is to increase the signal to noise ratio. Fig. (3.21) displays the raw data and the evaluated and corrected heat capacity data as a function of temperature.

3.7 Data Collection

Up to this point the heat capacity results produced were based on one sweep only. However, there seemed to be no reason not to sweep more than once and obtain a set of overlapping data which could be averaged out and produce heat capacity results based on accumulated statistics. Therefore, we performed 15 temperature sweeps, and, after the necessary corrections were made, the heat capacity was evaluated and is shown in Fig. (3.22). The results clearly indicated a systematic drift in the data set, the source of which had to be investigated. The details of the investigation to determine the source are presented in appendix B, however, the final solution will be discussed here.

After varying different parameters and observing the effect on the heat capacity data, it was found that the variations in the ambient pressure, shown in Fig. (3.23), were causing changes in the liquid nitrogen bath temperature, \( \sim 77K \). This in turn was affecting the thermocouple voltage. The solution was to control the Dewar pressure to within 0.05% with a membrane based pressure regulator.

3.7.1 Membrane Based Pressure Regulator

In order to regulate the liquid nitrogen bath temperature a membrane based pressure regulator was installed to regulate the bath's vapor pressure. Fig.(3.24) is a schematic of the system setup. A volume of 1 liter of nitrogen gas at a constant reference pressure is setup around a latex membrane through which the liquid nitrogen vapor travels. The volume of constant pressure is connected through lines to a much larger volume of nitrogen gas, 20 liters,
Figure (3.22a) Drift in heat capacity clearly apparent after fifteen sweeps.

Figure (3.22b) Ratio of heat capacity to temperature exposes the systematic drift more clearly.
Liquid Nitrogen Bath Temperature
as measured by CG thermometer

Figure (3.23a) Relative variations of liquid nitrogen bath temperature with time. Measured with carbon-glass thermometer. (Nov. 4 - Nov. 9 1994)

Temporal Ambient Pressure Variations

Figure (3.23b) Independent measure of ambient pressure variation with time. (Courtesy of Environment Canada) (Nov. 4 - Nov. 9 1994)
Figure (3.24) Block diagram of liquid nitrogen pressure regulation system. a. small constant pressure chamber. b. pressure sensitive membrane. c. connecting flanges d. connection lines. e. constant temperature water vessel. f. copper tubing to circulate water. g. large constant pressure chamber. h. water temperature regulator.
\( V_{\text{ref}} \), the pressure of which is regulated by placing it in a vessel of water which in turn is temperature regulated. This is done by wrapping a coil of copper tubing around \( V_{\text{ref}} \). Temperature regulated water flows through the tubing maintaining a constant water temperature around \( V_{\text{ref}} \). The water vessel is covered to minimize heat loss. Ideally the gas pressure should remain constant at a pressure slightly (~ 3 psi) above ambient pressure. Also \( V_{\text{ref}} \) should be as large as possible to minimize fluctuation effects. Once the constant reference pressure is established a line is connected from the top of the Dewar to the membrane tube opening. Except for this connection the Dewar and the probe are otherwise sealed to ensure proper pressure regulation. Any increase in liquid nitrogen pressure in the Dewar relative to the ideally constant reference pressure around the membrane would cause it to expand, thereby releasing the excess pressure. Any decrease in pressure would cause the membrane to close, allowing the Dewar pressure to build up. This method turned out to be a very sensitive and an effective way to control the temperature of the liquid nitrogen bath to within a few tens of millikelvin and to minimize drifts in signal measurements, as described earlier.

### 3.7.2 Pressure Regulated Heat Capacity Data Set

Fig. (3.25) illustrates the result of 15 sweeps of the pressure regulated heat capacity experiment and the non-regulated heat capacity results for comparison. Clearly the drift problem has been solved and the experimental setup is ready for the final heat capacity measurement. At this point we decided to include direct liquid nitrogen bath temperature measurement during the sweeps as a useful parameter for indicating which sweeps correspond to the most constant bath temperature interval. The complete experiment, was performed with
Heat Capacity Measurement
(with pressure regulation)

Figure (3.25a) Measure of heat capacity presented in the form C/T. Result of 15 temperature sweeps with dewar pressure regulation.

Heat Capacity Measurement
(without pressure regulation)

Figure (3.25b) Measure of heat capacity presented in the form C/T. Result of 15 temperature sweeps without dewar pressure regulation.
the sample mounted on the substrate and again without the sample, to obtain the background (substrate, wires, etc...) heat capacity. As before the temperature was swept at 1 mK/s, sampled once every second and averaged over a 30 second time interval. We attempted a longer temperature range, 80 to 120 K, however, only 4 sweeps were possible due to computer memory space limitations. Therefore, from the bath temperature data set, Fig. (3.26a), the best AC signal sweeps, Fig (3.26b), were selected and evaluated. The total (sample and background) heat capacity as well as the background is shown in Fig.(3.27a). The background is fitted to a third order polynomial and subtracted from the data containing sample and background signal, to obtain the specific heat of the crystal as a function of temperature, Fig. (3.27b), i.e.

\[ C_{\text{sample}} = C_{\text{total}} - C_{\text{background}} \]

\[ = C_{\text{total}} - (a_0 + a_1 T + a_2 T^2 + a_3 T^3) \]

where

\[ a_0 = 0.9687 \, \text{mJ/K}, \quad a_1 = -0.0374 \, \text{mJ/K}^2, \quad a_2 = 5.482 \times 10^{-4} \, \text{mJ/K}^3, \quad a_3 = -1.1656 \times 10^{-6} \, \text{mJ/K}^4. \]

The specific heat of the sample can be decomposed into its various components which include the background phonon term, the fluctuation term and the electronic term, respectively:

\[ C_{\text{sample}} = C_{\text{ph}} + C_{\text{fl}} + C_{\text{el}} \]

There are a number of mathematical models developed by researchers attempting to describe the behavior of the heat capacity of YBCO close to the transition temperature. In the next chapter we shall review these models and apply an appropriate mathematical representation to our data.
Liquid Nitrogen Bath Temperature variation with Time

Figure (3.26a) Temporal variations of the liquid nitrogen bath temperature in a pressure regulated Dewar.

AC Signal Vs Time

Figure (3.26b) Raw AC signal as measured by the copper/constantan thermocouple on the substrate. Only the first two sweeps up to 20 hours corresponding LN temperature are selected.
Figure (3.27a) Total specific heat, including sample and background, as measured using the modified AC calorimetry system. Background measurement is also shown above.

Specific Heat of YBCO
(background subtracted)

Figure (3.27b) Total specific heat of YBCO sample after subtraction of background heat capacity including contributions from substrate, wires, heater, etc...
4.1 Introduction

In this section the theoretical derivation of mean-field specific heat, by the phenomenological Ginzburg-Landau approach, will be presented followed by a discussion of fluctuation contribution to specific heat. These fluctuations will be discussed in terms of several possible models which may be used to fit the experimental data. Central to the formalism of GL theory is the difference in free energy of the superconducting state, relative to the normal state, expanded and expressed in terms of an order parameter, $\Psi$, which is zero above the critical temperature and non-zero below. The square of this complex value corresponds to the density of superconducting electrons. The relative GL free energy, including gradients and field terms is given by,

$$\Delta f = \alpha_0 t |\Psi|^2 + \frac{\beta}{2} |\Psi|^4 + \sum_i \frac{1}{2m_i} \left( -i \hbar \nabla_i - \frac{e^*}{c} A_i \right) |\Psi|^2 + \frac{H^2}{8\pi}$$

(4.1)

where $\alpha_0$ and $\beta$ are constants, $t$ is the reduced temperature, $(T - T_c)/T_c$, $m$ is the effective mass, $e^*$ is the effective charge, $2e$, $H$ is the magnetic field, and $A$ is the vector potential. In the absence of a magnetic field while assuming a spatially uniform wave function, the free energy is simply minimized with respect to the order parameter. In the two regions the results are:
\[ \Psi_0 = 0 \quad T > T_c \quad (4.2a) \]
\[ \Psi_0 = \left( -\frac{\alpha}{\beta} t \right)^\frac{1}{2} \quad T < T_c \quad (4.2b) \]
\[ \Delta f = -\frac{\alpha_0^2 t^2}{2\beta} = -\frac{H_c^2}{8\pi} \quad T < T_c \quad (4.3) \]

where \( H_c^2 = \frac{4\pi}{\beta(T_c)} (T_c - T)^2 \left( \frac{\partial \alpha}{\partial T} \right)_{T_c}^2 \)

Using the mean free energy density difference given in equation (4.3), the specific heat discontinuity is calculated to be:

\[ \Delta C_{\text{MF}}(T) = -VT \frac{\partial^2 (\Delta f)}{\partial T^2} \]
\[ = \frac{VT \alpha_0^2}{T_c^2 \beta} \]
\[ = \frac{VT}{4\pi} \left[ \left( \frac{\partial H_c}{\partial T} \right)^2 + H_c \frac{\partial^2 H_c}{\partial T^2} \right] \quad (4.4) \]

Note the linear temperature behavior. At \( T_c \) this continuity is predicted to be of the order

\[ \Delta C_{\text{MF}}(T_c) = \frac{VT_c}{4\pi} \left( \frac{\partial H_c}{\partial T} \right)_{T_c}^2 \quad (4.5) \]

### 4.2 Thermal Fluctuations

Experimental observations of the specific heat transition of standard superconductors as compared to other systems such as YBCO and the superfluid transition of \(^4\)He, have shown contrasting results. In the former case the sharp transition is modeled quite accurately by mean-field theory whereas the latter displays divergences which are not modeled satisfactorily.
by the standard mean-field theory and corrections have to be made. Briefly, the divergence near \( T_c \) is due to fluctuations in \( \Psi \), of thermal energy \( k_B T \), around the equilibrium value \( \Psi \). In other terms, close to the transition region the superconducting electron density exhibits spatial variations of length scale, \( \xi \), the GL coherence length and since this effect translates into increase in entropy of the system, the specific heat is, therefore, affected as well. These variations are calculated from the free energy density in a volume which depends on \( \xi \), i.e.

\[
f_{\text{fl}} \propto \frac{k_B T_c}{\xi^d(T)}
\]

where \( d \) indicates the dimensionality and from which the fluctuation contribution to the heat capacity is found to be:

\[
C_{\text{fl}} \propto \left[ V T \frac{\partial^2 f_{\text{fl}}}{\partial T^2} = VT \frac{\partial^2 \left( \frac{k_B T}{\xi^d(T)} \right)}{\partial T^2} \right]
\]

\[
\propto \frac{k_B}{\xi^d(T)} \left| \eta \right|^{-2\nu + \delta}
\]

Evidently, from the inverse relation between the heat capacity fluctuation and the coherence length, these variations would be easier to detect in materials with short coherence lengths such as YBCO. Now if these fluctuations remain small relative to the equilibrium value of the order parameter they can be considered as Gaussian fluctuations and treated as corrections to mean-field theory. This state occurs in the temperature region just outside of the critical region, quantized by GL as

\[
t \gg t_g = \frac{1}{32\pi^2} \left( \frac{k_B}{\Delta C_{\text{MF}}} \frac{\pi \xi^2}{\eta} \right)^2
\]
Within the critical region the fluctuations in the order parameter approach the amplitude of the equilibrium value of $\Psi$, $\Psi_0$, and mean-field theory breaks down. Gaussian approximations are no longer applicable and a model for the critical behaviour is necessary. Two models describing critical behaviour of specific heat near $T_c$ are logarithmic behaviour and 3D XY critical behaviour. Experimental data fittings of YBCO performed by various groups tended to support the Gaussian approximation in the past,\textsuperscript{19-21} but recent progress in obtaining data has shifted this trend towards the critical behaviour model, 3D XY in particular.\textsuperscript{22-29} This is related to the short coherence length of this material whose accessible critical region has been estimated to extend as much as 10 K above and below $T_c$. Since the superfluid transition in liquid $^4$He is fully explained by this model and from the growing evidence that YBCO exhibits similar critical fluctuations, they may be considered as belonging to the same universality class.

The 3D XY model is represented by:

$$C_{\text{sample}} = C_{\text{ph}} + C_{\text{el}} + C_{\text{fl}}$$

$$C_{\text{ph}} + C_{\text{el}} = bt + c$$

$$C_{\text{fl}} = C_0 - A^+ t^{\kappa_\text{fl}} \quad (t > 0)$$

$$C_{\text{fl}} = C_0 - A^- t^{\kappa_\text{fl}} \quad (t < 0)$$

$$R = \frac{A^+}{A^-}$$

where $t = (T - T_c)/T_c$ is the reduced temperature and $C_0$ is the maximum $C$ at $t = 0$. The amplitude ratio $R$ is a universal quantity, whose measured value in liquid $^4$He is 1.058 +/- 0.004.\textsuperscript{30} Figure (3.28) shows the specific heat of our sample. The solid line is a fit assuming the above form for the different components. The value of $T_c$ was chosen as 93.1 K
corresponding to the temperature at which the specific heat has the greatest slope. The value of \( \alpha \) and \( C_0 + c \) were fixed and a least square fit performed. Table 4-1 compares our values to that of Overend et al.\(^{28} \) who measured a similar sample and fit their data to the 3D XY model. Here we are only concerned with the relative measurements and do not compare the absolute values of the fitted parameters.

<table>
<thead>
<tr>
<th></th>
<th>( T_c ) (K)</th>
<th>( C_0 + c ) (mJ/gK)</th>
<th>( b^+ ) (mJ/gK)</th>
<th>( b^- ) (mJ/gK)</th>
<th>( A^+ ) (mJ/gK)</th>
<th>( A^- ) (mJ/gK)</th>
<th>( R )</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBC</td>
<td>93.10K +/- 0.05</td>
<td>410</td>
<td>234.6 +/- 3.5</td>
<td>246.4 +/- 7.9</td>
<td>204.8 +/- 0.6</td>
<td>199.1 +/- 0.6</td>
<td>1.028</td>
<td>-0.01</td>
</tr>
<tr>
<td>Overand</td>
<td>92.00K +/- 0.05</td>
<td>238</td>
<td>189 +/- 0.04</td>
<td>59.37 +/- 0.04</td>
<td>55.51 +/- 0.04</td>
<td>1.0695 +/- 0.01</td>
<td>-0.013</td>
<td>+/- 0.002</td>
</tr>
</tbody>
</table>

**Table 4-1** Fitted parameters of our crystal and that of Overand et al.

From the above table it is clear that the errors in the fitted parameters, \( b^+ \), \( b^- \), \( A^+ \), and \( A^- \) are relatively large, although these parameters produced the lowest \( \chi^2 \) value possible using the 3D XY model. The error problem, we believe, is associated with the large noise factor in the data set, as apparent in Fig. (3.28). However, comparing the amplitude ratio, \( R \), and the exponent \( \alpha \) with that of \(^4\text{He}\), we can state with confidence that the specific heat of YBCO near its transition temperature is well represented by the 3D XY model. Further heat capacity measurements of similar crystals utilizing the experimental setup described in this thesis, with better signal to noise ratio, are in progress presently and are expected to confirm the above model.
**Total Specific Heat of Sample vs Temperature**

![Graph](image)

**Figure (3.28a)** Total specific heat of YBCO sample. Solid line is a fit assuming a 3D XY model representing the transition behavior. Inset illustrates transition region where the jump in the specific heat is measured to be 6.2 mJ/gK.

**Fluctuations in Specific Heat of Sample**

![Graph](image)

**Figure (3.28b)** Specific heat/temperature vs reduced temperature. Solid line is a fit assuming a 3D XY model representing the transition behavior. Inset gives data points within the transition region and its width, 0.45K.
Concluding Remarks

To summarize our discussion in this thesis, we have presented a detailed outline of our modified AC calorimetry technique used for measuring the specific heat of a very small YBCO crystal sample. The outline included a mathematical analysis of the setup and a step by step procedure for measuring each parameter leading up to the actual heat capacity measurement. The modifications, as compared to previous setups by other researchers, were the use of a sapphire substrate as support for sample, heater and thermocouple and the addition of a Dewar pressure control system to stabilize the liquid nitrogen bath temperature. Our system also allows for long range sweeps, ideal for measuring the background phonon contribution to the heat capacity dominant at higher temperatures far from $T_c$. The data presented here was the result of the measurement of one pure YBCO crystal sample, however, some candidates for future measurements are doped samples such as nickel, cobalt and zinc doped YBCO. Data from the latter sample would also give a measure of the background phonon contribution in pure YBCO. The sample measured showed a superconducting transition temperature, $T_c$, of 93.1K. The transition width, $\Delta T_c$, was measured to be $\sim$0.45K, a little higher than expected and the specific heat jump $\Delta C_p$, was 6.1mJ/gK, a little lower than our previous samples.
References


APPENDIX A1

Diamond Substrate

One of the inherent problems present in the measurement technique described, is the large background heat capacity which must be subtracted from the total heat capacity. The constraints on the substrate size are that it must be large enough to support the heater, the crystal and the thermocouple with adequate clearance between the components and it must be small enough such that its heat capacity does not completely override the crystal heat capacity, therefore, the specific heat of the substrate must be as low as possible. Because of these constraints a diamond substrate was chosen as a possible candidate. The present section describes the attempted preparation of such a substrate and the results of the heat capacity experiment performed. To begin, a thin wafer of crystalline diamond (Dimonex), $3 \times 6 \times 1$ mm, was cleaned in an ultrasonic bath of acetone, rinsed with distilled water and repeated in an alcohol bath. A layer of Apiezon 100 wax, dissolved in trichloroethylene, was spread on a glass slide and the wafer was carefully placed on the wax and gently pressed. Top half of the wafer was covered with the same material as shown in Fig(A1.1) and allowed to dry overnight. A solution of aqua regia, hydrochloric acid and nitric acid solution with 1:1 concentration, was prepared and used to etch away the top gold layer, 3000 Å. To remove the second layer, platinum at 2000 Å, and the final layer, titanium at 1000 Å, a dilute solution of hydrochloric acid, $3 \text{ ml HCL : 15 ml H}_2\text{O}$, was prepared and heated to 80° C. The wax covered substrate was then immersed in the hot acid for 30 hours. Upon obtaining infinite resistance across the plane of the substrate, the wax was washed off with trichloroethylene and
the process was repeated on the reverse side as shown in Fig.(A1.1b). The problem of forming a heater on the substrate was solved by utilizing the existing metals, titanium and platinum as the heater and the gold layer as wire connection pads. This was achieved by first pasting two thin copper wires (#38) on the gold layer using silver paste as shown in Fig.(A1.1c). The area to be etched was exposed and the rest, including the contacts and wires, were covered with wax as before and allowed to dry overnight. An ohmmeter was used to monitor the heater resistance as the metals were etched away in a solution of hot hydrochloric acid and water, 1:1 concentration, at 70° C. A resistance of about 37 ohms was reached after which etching was stopped and trichloroethylene was used to wash off the wax followed by an ultrasonic bath of alcohol to completely remove all acids and residues. Using silver epoxy two copper wires (#38) were mounted on the gold pads and allowed to dry for 48 hours. A conventional copper/constantan thermocouple was also mounted on the substrate with varnish and the measurement sequence, as explained in chapter 3, was performed with the heat capacity obtained satisfactorily. The background heat capacity, using a diamond substrate, was about 1.5 times less than the corresponding value using a sapphire substrate.

---

**Figure (A1.1)** a. Diamond substrate partly covered with wax on thermocouple side. b. Heater side mostly covered with wax. c. Heater side masked with wax to be etched in acid.

[Diagram of Diamond Substrate with Wax]
Sapphire Substrate

Sapphire, AlO₃, with its diamond like structure, does not readily bond to most elements which means coupling problems between components on the substrate and itself are to be expected and dealt with. In order to increase the surface area and the coupling, sand blasting the surface of the sapphire was attempted unsuccessfully, resulting in breakage. Sandpaper was of no avail either since the surface was much too hard and small for the sanding to have any effect. Another method attempted to improve the coupling was evaporation of the thermocouple directly on the substrate. Beginning with a clean sapphire substrate of dimensions 4 × 8 × 1 mm (cleaned thoroughly with trichloroethylene in distiller), 800Å of pure chromium was evaporated on half of the bottom surface followed by copper, 2000Å, and finally 2250Å of constantan, evaporated through an L shaped mask shown below. Silver epoxy was used as the adhesive to attach the thermocouple wires, copper (#50) and constantan (0.009" diameter), to the appropriate evaporated metal surfaces. Comparing the contribution to the total heat capacity due to the various metals evaporated on the substrate

![Figure (A1.2) Evaporated thermocouple on sapphire substrate.](image)

- Chromium
- Copper
- Constantan
- Silver Epoxy
and the silver epoxy used to attach the wires as well as the wires themselves, it was found that the heat capacity of the epoxy used was 2 to 3 orders of magnitude larger than the rest of the addenda which placed a restriction on the amount of epoxy used. In addition, the effective length of the heater and thermocouple wires was frequency dependant and given by:

\[ L = \frac{K}{C \rho \omega A} \]

where \( K \) is the thermal resistance of the wire, \( C \) is the heat capacity of the wire, \( \rho \) is the density of the wire, \( A \) is the cross sectional area of the wire and \( \omega \) is the thermal frequency.
APPENDIX A2

Problematic Behavior of the Heat Capacity Data Acquired

Analyzing the preliminary heat capacity data set closely, occasional but definite shifts of about 1.5% were observed which seemed to indicate an unknown systematic error in the experimental setup. These shifts were more noticeable in data sets of long duration, of the order of 50 hours. Several hypotheses as to the possible cause of this behavior were considered. What follows is the experimental tests of the hypotheses and the obtained results.

Hypothesis 1. Temporal variations in room temperature may affect the temperature of the crystal and hence variations in its heat capacity. A simple copper/constantan thermocouple was made with one joint immersed in ice-water, (triple point of water being used as reference), and the other attached to a wooden wall close to the probe. The voltage was monitored by Keithley 182 voltmeter.

Hypothesis 2. Temporal line voltage variation may affect the instruments' sensitivities, resulting in false readings and data recordings. The main line voltage feeding all of the electronic instruments used during the experiment was monitored using the HP voltmeter. The experiment was rerun while both room temperature and line voltage were monitored independently. From the curves obtained there was no apparent correlation between variations in these parameters and heat capacity drifts.

Hypothesis 3. Any large variation in the output of the Lock-in Amplifier would vary the thin film heater input power which in turn affects the heat capacity calculation. A resistive voltage divider was set up to resemble the thin film heater and a second LIA was used for measuring
the voltage across one resistor for comparison with the first LIA. Since both LIA's were being referenced by the same source, any variation in the source would appear on the detecting side of both LIA. Again, after a monitoring period of about 48 hours the results showed no correlation with the heat capacity drifts.

**Hypothesis 4.** Temporal resistivity variations in the thin film resistor would influence the input power which in turn affects the heat capacity. Normally this quantity is measured prior to the actual heat capacity measurement, therefore, variations during the temperature sweeps would not be detected. Using a second LIA the voltage across the thin film resistance was monitored during the experiment. After 15 sweeps from 85K to 95K, during a 42 hour time interval, the results show a linear slope and a variation of 0.06%. Since we were looking for variations of the order 1.5% it was concluded that the thin film resistor is not the source of the problem.

**Hypothesis 5.** Pressure dependency of the heat capacity setup should be considered. A brass flange was placed on top of the dewar, sealing the nitrogen gas inside, with a 5psi pressure release valve. This setup only raised the dewar pressure relative to 1 atmosphere but did not eliminate atmospheric pressure fluctuations. The shifting problem was still present under the pressurized environment.

**Hypothesis 6.** Temporal fluctuations in the ambient pressure was considered to be a possible source of the drift. Therefore, controlling the dewar pressure may eliminate the variations in the heat capacity data set. Because these variations are of the order 1.5% the pressure regulation must be as low as 0.2 psi to obtain meaningful results. A pressure regulator, based on mechanical motion of a piston exposing a gas relief slit, was built and installed. The inability to maintain smooth piston motion and adequate sealing between piston and cylinder
walls, simultaneously, resulted in abandoning that specific regulator design in favor of a membrane based pressure regulator.