A new method of AC calorimetry using thermoelectric devices

by Gregory James Pastalan

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Physics
Montana State University

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The field of calorimetry currently uses separate measurement methods for determining the thermal conductivity and heat capacity per unit volume of a material. This thesis describes the construction of a prototypes apparatus which gathers the data necessary to calculate both of these properties of a solid material. The novelty of this apparatus is that it uses thermoelectric devices in both the stimulating and receiving portions of its design for both dc and ac measurements, so that both thermal conductivity and heat capacity can be determined. The two materials studied at room temperature were Triglycine Fluoberyllate (TGFB), a ferroelectric crystal, and Lead. The data gathered from the apparatus were temperature values expressed as complex numbers representing amplitude and phase relative to the thermal input power. The measurements, for no sample and lead sample being measured showed good agreement with the theoretical prediction of the received signal having decreasing amplitude and increasing phase angle with respect to the driving signal over a frequency range of 0.5 to 15.0 Hz. The data from the TGFB sample showed good agreement with predicted behavior over the frequency range 0.5 to 3.0 Hz.

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ABSTRACT

The field of calorimetry currently uses separate measurement methods for determining the thermal conductivity and heat capacity per unit volume of a material. This thesis describes the construction of a prototype apparatus which gathers the data necessary to calculate both of these properties of a solid material. The novelty of this apparatus is that it uses thermoelectric devices in both the stimulating and receiving portions of its design for both dc and ac measurements, so that both thermal conductivity and heat capacity can be determined. The two materials studied at room temperature were Triglycine Fluoberyllate (TGFB), a ferroelectric crystal, and Lead. The data gathered from the apparatus were temperature values expressed as complex numbers representing amplitude and phase relative to the thermal input power. The measurements for no sample and lead sample being measured showed good agreement with the theoretical prediction of the received signal having decreasing amplitude and increasing phase angle with respect to the driving signal over a frequency range of 0.5 to 15.0 Hz. The data from the TGFB sample showed good agreement with predicted behavior over the frequency range 0.5 to 3.0 Hz.

CHAPTER 1

INTRODUCTION

This thesis reports the construction and successful operation of a prototype AC calorimetry apparatus for solid samples which makes use of thermoelectric devices to apply and receive temperature waves. This method allows calculation of thermal diffusivity, thermal conductivity, and specific heat of a solid material from the gathered data.

Definitions and Basic Theory

There are three fundamental thermodynamic properties which need to be defined, specific heat, thermal conductivity, and thermal diffusivity.

The heat capacity of a material at constant volume is defined to be $C_v = (dQ/dT)_v$. As the material is heated at constant volume in a reversible process, dQ is the amount of heat necessary to raise the temperature of the material by dT. When considering the properties of a unit mass of a material, the properties are called specific. Hence the definition of specific heat is the heat capacity at constant volume per unit mass of the material, $c_v = m^{-1} (dQ/dT)_v$.

Thermal conductivity is defined from Fourier's heat conduction law, $dQ/dt = -kA(dT/dx)$. In the rearranged expression $(dQ/dt)/A = J = -k(dT/dx)$, the thermal conductivity k of a material is the constant of proportionality relating the heat flux per unit area to the temperature gradient in the material.

The thermal diffusivity, defined as $\alpha = k/\rho c_v$, is the ratio of thermal conductivity to the product of density of the material and the specific heat at constant volume. More simply, it is the ratio of thermal conductivity to heat capacity per unit volume.

Thermal diffusivity determines how quickly a material responds when a temperature transient is applied to its surface.

To illustrate how the thermal diffusivity α enters into the one-dimensional ac heat flow process, consider a thin slab of thickness dx perpendicular to the heat flow direction x. From the Fouier law, the heat flux entering the left side is $-kA\partial T/\partial x$. The flux entering the right side is $+kA[\partial T/\partial x + (\partial^2 T/\partial x^2)dx]$. The net heat flux input $kAdx\partial^2 T/\partial x^2$ is equal to the heat capacity per unit volume $c_v\rho$ multiplied by the volume Adx of the slab and the rate of temperature change $\partial T/\partial t$, so we obtain the differential equation for time-dependent one-dimensional heat flow,

$$\partial T/\partial t = \alpha\partial^2 T/\partial x^2 \quad (1\text{-}1).$$

Measurement Methods

DC Methods

Since the thermal diffusivity has a known relation to heat capacity and thermal conductivity, knowledge of any two easily yields the third. In the case of heat capacity, there exist two methods for making dc measurements. The first method is to produce joule heating from a current-carrying resistor attached to the sample, then measure the temperature change of the sample by an attached thermometer.

The second method requires the sample to reach an elevated equilibrium temperature, usually through contact with a heat reservoir. It is then placed in contact with a heat sink, and the sample-heat-sink system is thermally isolated. The calorimeter (heat sink) can then be observed for change in its temperature or for a phase transition. Two common examples of these methods are the Nernst-Eucken, used in the liquid helium temperature range, and the Method of Mixtures, used for temperatures > 20 K.[1-3]

A common dc method of determining specific heat is through the use of a Differential Thermal Analyzer (DTA). The DTA compares the temperatures of two materials, the sample under study and a thermally inert reference sample as both samples are heated in a furnace at a constant rate. Inside each sample are thermocouple junctions connected by a common wire. When the sample undergoes an enothermic or exothermic reaction heat energy is absorbed or liberated respectively. This results in a temperature difference between the sample and reference yielding a voltage difference between them. Hence as voltage is plotted as a function of time a voltage spike will appear at a temperature where a phase transition occurs.

AC Methods

An important contribution to the development of the theory of AC calorimetry was made by Sullivan and Seidel.[4,5] Heat energy is supplied sinusoidally to one end of a sample, to which the magnitude and phase of the temperature at the opposite end of the sample are compared. The usual boundary condition is that the sample is in contact with a thermal reservoir such that the sample can quickly return to thermal equilibrium once given an energy input.

There are several methods of generating an incident ac temperature wave upon a sample surface. One method uses a chopped laser beam incident on one face of the sample while thermocouples attached along the sample determine temperature as a function of position and time.[6,7]

Another method makes use of thermally conductive films which are deposited on opposite ends of a sample.[8] One face acts as a signal generator while the other acts as a receiver. A third method, which is similar to our method, makes use of a thermoelectric device to generate an ac temperature wave.[9] Santucci and Verdini[9] studied a sample of copper at a pressure of 1 x 10^{-6} mbar, providing it an ac temperature wave from a Melcor FC-06-32-06 TL unit and measuring temperatures along the sample via thermocouples. A United States Patent[10] was granted in 1973 to Stanley and Reich for a method and apparatus for measuring thermal conductivity and thermoelectric properties of solids using thermoelectric devices. Their configuration of sandwiching a sample between two thermoelectric devices is identical to ours. However, the work of Stanley and Reich was limited to applying a dc voltage signal to the driver instead of an ac voltage signal.

CHAPTER 2

EXPERIMENTAL SETUP

The system to be described consists of several components, some of which were built in-house.

The basic idea of this method is to apply an ac temperature wave to a solid and compare the amplitude and phase shift of the transmitted signal to the applied signal. In the low frequency limit, results yield thermal conductivity, while in the high frequency limit, results yield thermal diffusivity from which one finds specific heat if the thermal conductivity is known.

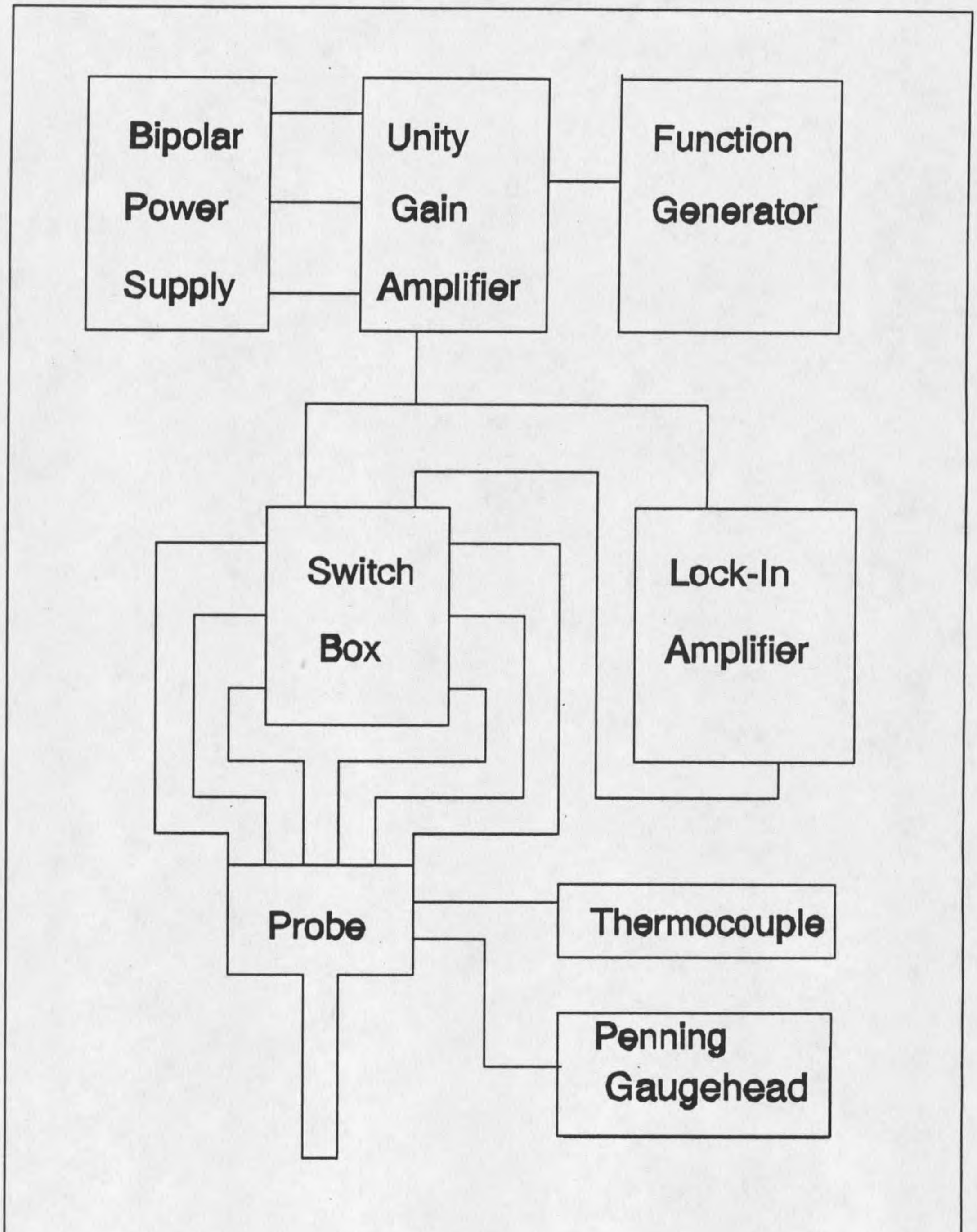
A description of the overall system will be given first, followed by a more detailed description of the critical components.

The system makes use of a pair of thermoelectric devices, which sandwich the solid sample between them. One device is used in an active role, as a driver, while the second device is used in a passive mode, as a receiver. The driver converts an applied ac voltage into a temperature wave, which propagates through the solid under study. The receiver, on the opposite side of the solid, accepts the temperature wave and converts this signal into an ac voltage. The thermoelectric elements used are produced by MELCOR[11] and employ the Peltier[3] and Seebeck[3] effects in their operation.

Through use of a lock-in amplifier the in-phase and quadrature components of the ac voltage from the receiver are compared with the ac voltage applied to the driver. The lock-in amplifier is necessary because the amplitude of the receiver output signals is very small.

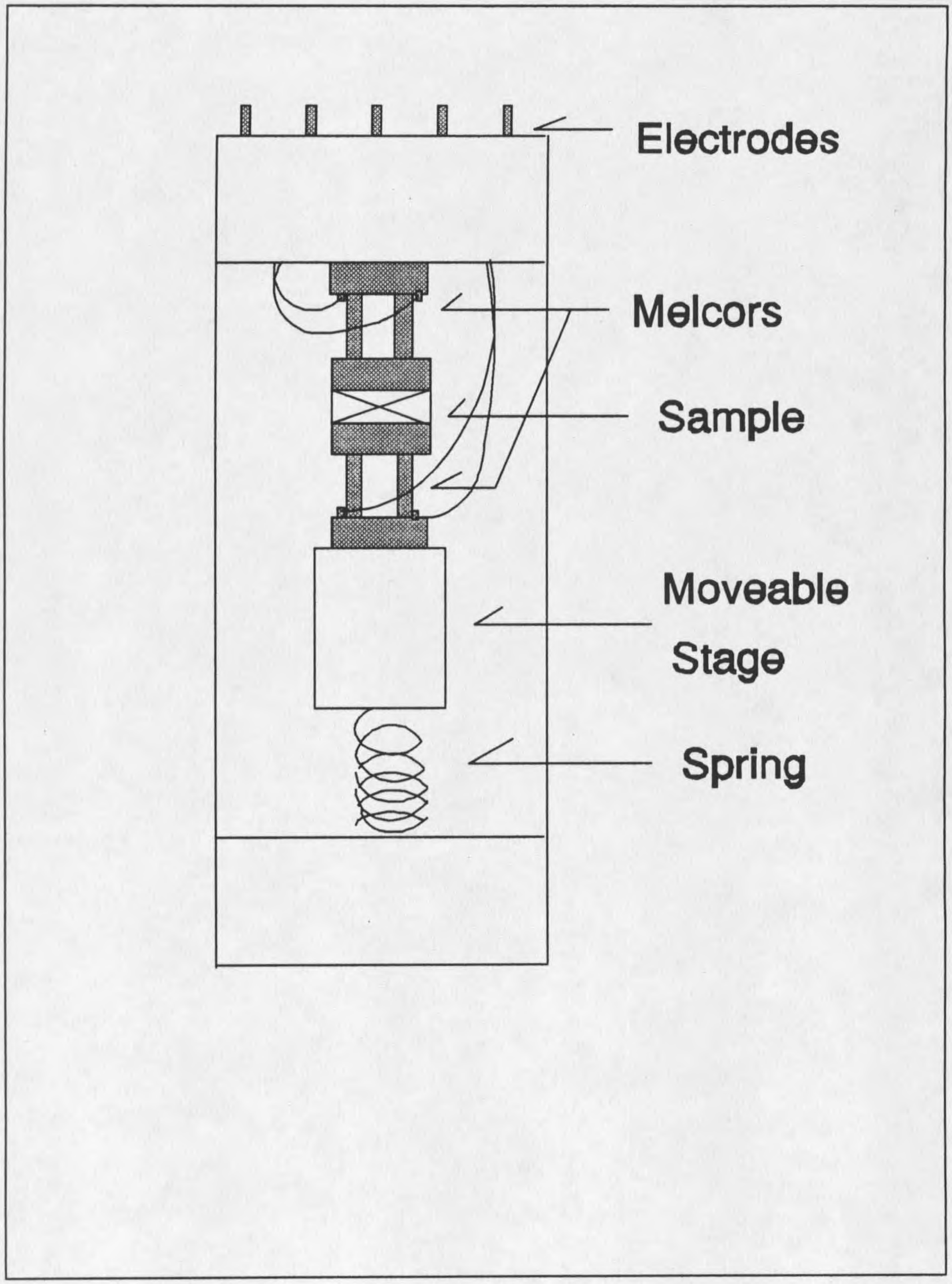
The system can be divided into two parts, the probe and the external equipment, as seen in Figure 1. At the bottom of the probe is attached the copper slug which contains the thermoelectric elements and the samples.

The copper slug, shown in Figure 2, consists of a cylindrical copper mass which acts as a thermal reservoir upon which three pairs of Melcor devices are aligned parallel to the cylinder axis and spaced 120 degrees apart. The three Melcor pairs are arranged with one mounted on a fixed surface, while the second is mounted to a retractable block which is attached by a compression spring to the bottom of the copper slug. This design allows for the easy insertion and removal of solid samples.[12] A copper can attached by three screws to the bottom of the slug acts as a thermal shield covering the copper slug. The copper slug is connected to a thin-wall stainless steel tube, 1.47 m long and 2.5 cm diameter, by a Teflon cylinder which acts as an insulating mating surface. The tube length is determined by the dimensions of the dewar.



Overall System Schematic

Figure 1



Copper Slug

Figure 2

The tube houses coaxial cable connections between the slug and the top flange.

These internal coaxial cables are connected to external coaxial cables by floating BNC connectors. Floating connectors are necessary since the driver and receiver signals must be isolated in order to avoid ground loop problems. The tube also contains leads to a chromel-alumel thermocouple which is attached to the copper slug in order to monitor the ambient temperature of the system.

The probe is connected electrically to a switch box which connects to any one of the three Melcor pairs at a given time. The switch box is divided into driver and receiver channels. The driver channel is connected to a unity gain amplifier which acts to impedance match the Hewlett-Packard 3325B Synthesizer/Function Generator to the low-impedance Melcor device. The output of the unity gain amplifier is also connected to the Reference Signal port of the EG&G 5204 Lock-In Amplifier. The receiver channel of the switch box is connected to the Signal-In port of the lock-in amplifier. The unity gain amplifier[13] and switch box were constructed in-house.

The probe is inserted into the dewar which is capable of achieving internal temperatures over the range +4 K to +375 K. The range of temperatures used in this project were +25°C to +80°C.

Critical Components of the System

The three critical components of the system are the thermoelectric elements, the Lock-In Amplifier and the thermocouple based mean temperature monitoring system.

Thermoelectric Elements

The thermoelectric elements used in this apparatus are manufactured by the MELCOR Corporation and will be referred to hereafter as the Melcors. These devices consist of two ceramic slabs which are composed of alumina (Al_2O_3) separated by eight semiconductor pillars (Bi_2Te_3) oriented orthogonal to the ceramic slabs as seen in Figure 3. The Peltier[3] effect takes place at the soldered junctions joining the pillars to the slabs. As shown in Figure 4 the semiconductor pillars are doped to be alternately n and p type.

The solder junction joining the n and p type materials is non-rectifing so that current flow is not impeded when an external voltage is applied.[11] As depicted in Figure 4, the negative thermal gradient and hence the flow of heat is in the same direction as the majority carrier flow in both types of semiconductor. This is the Peltier[3] effect which, for the applied voltage polarity shown, transports heat energy via the majority charge carriers from the upper slab to the lower slab. This mode of operation is denoted the "cooling" mode. Joule heating is produced in the semiconductor, so the net cooling provided by the upper slab is that produced thermoelectrically, less the joule heat flow to the upper slab. When the applied voltage polarity is reversed, the net heat available at the upper slab includes contributions from both joule heating and thermoelectric heating. Hence this operation mode is denoted as the "heating" mode.[11]

The Peltier effect can be expressed mathematically[14]

$$j^q = \Pi j \quad (2\text{-}1)$$

where j^q is the thermal current while j is the electric current and the constant of proportionality Π, is the Peltier coefficient. The Peltier coefficient is related to the thermoelectric power by the relation[14] ,

$$\Pi = QT \quad (2\text{-}2)$$

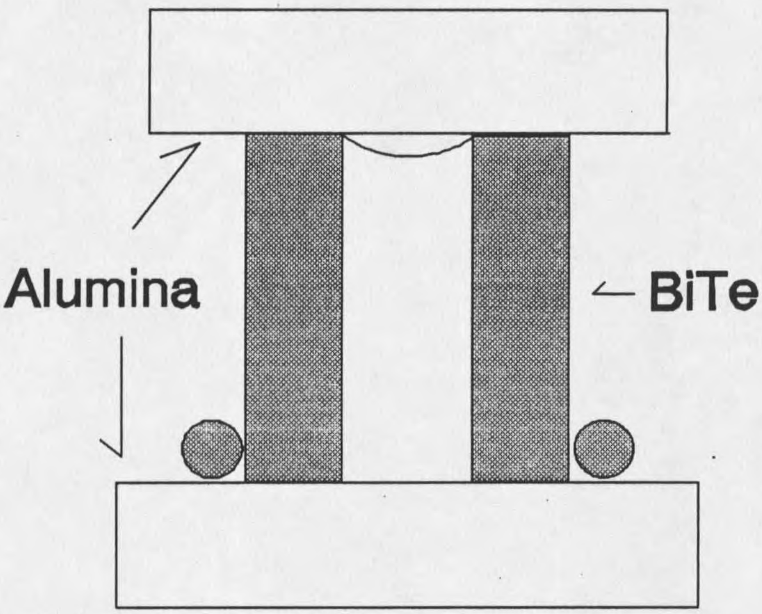
with Q being the thermoelectric power or Seebeck coefficient, and T is temperature. The Seebeck coefficient is the constant of proportionality between the temperature gradient in the material and the resulting emf.

$$V = -\int \xi \cdot dl = Q\Delta T \quad (2\text{-}3)$$

Since the Melcors make use of both n and p type Bi_2Te_3, the best results that could be found were $|Q_n - Q_p| = (0.63K/mV)^{-1}$, which is discussed in chapter three. Likewise expression (2-2) becomes $|\Pi_n - \Pi_p| = |Q_n - Q_p|T$, so at T = 300K the expression becomes $|\Pi_n - \Pi_p| = 0.476V$.

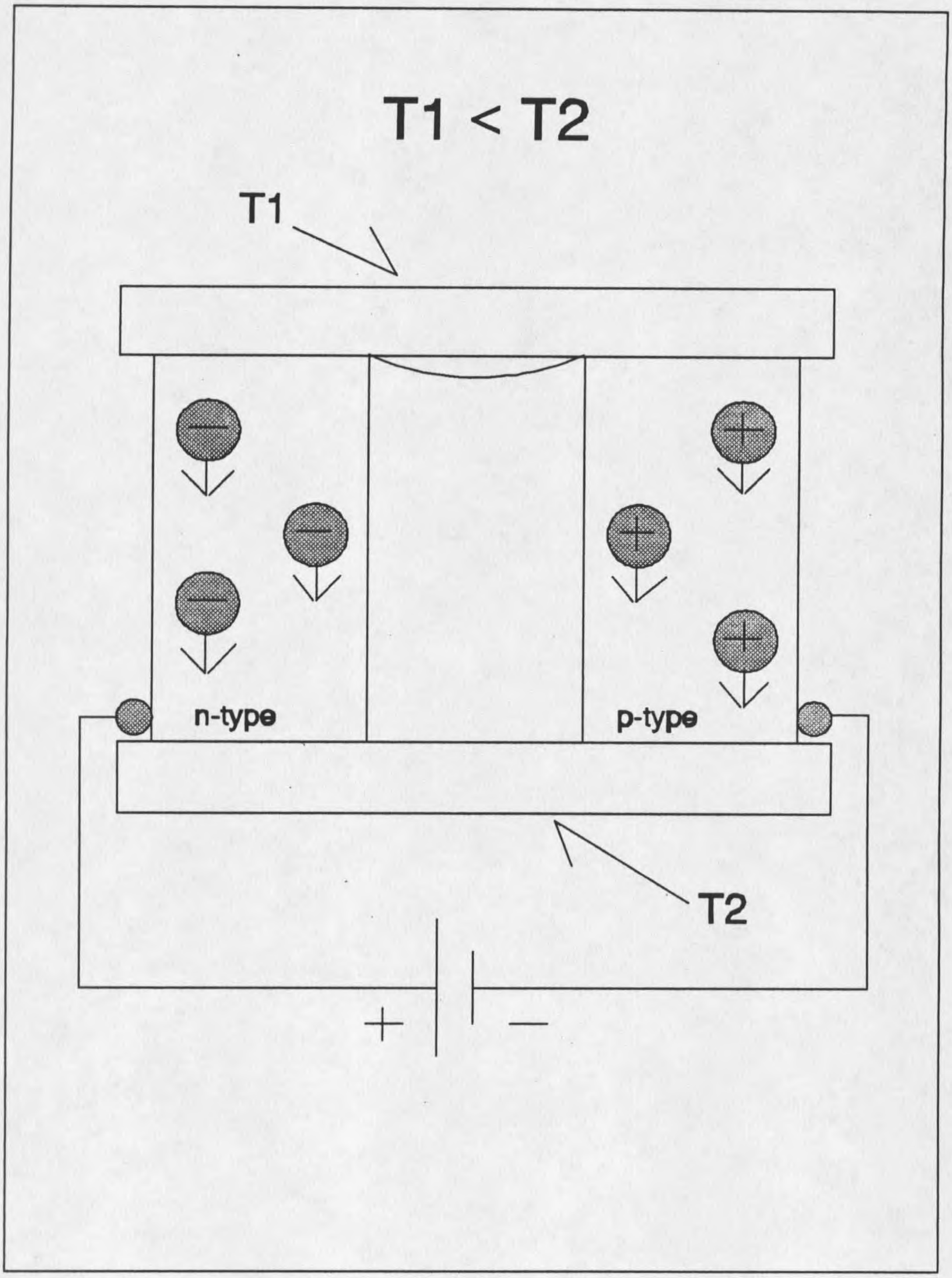
If an ac current flows in the Melcor, the heating and cooling cycles alternate with the same frequency as the applied ac voltage. This describes the action of the driver Melcor in the apparatus.

The receiver Melcor acts passively as a thermal transducer, receiving the temperature waves from the sample sandwiched between the two Melcors. Since the receiver Melcor is bounded on top by the sample and beneath by the copper slug a temperature gradient is created between the two alumina slabs. Because of this thermal gradient an electrical potential is developed due to the Seebeck effect.[3] In the case where the temperature gradient is constant the receiver Melcor will yield a dc voltage. When the temperature gradient is alternating the receiver Melcor yields an ac voltage response.



Thermoelectric Device

Figure 3



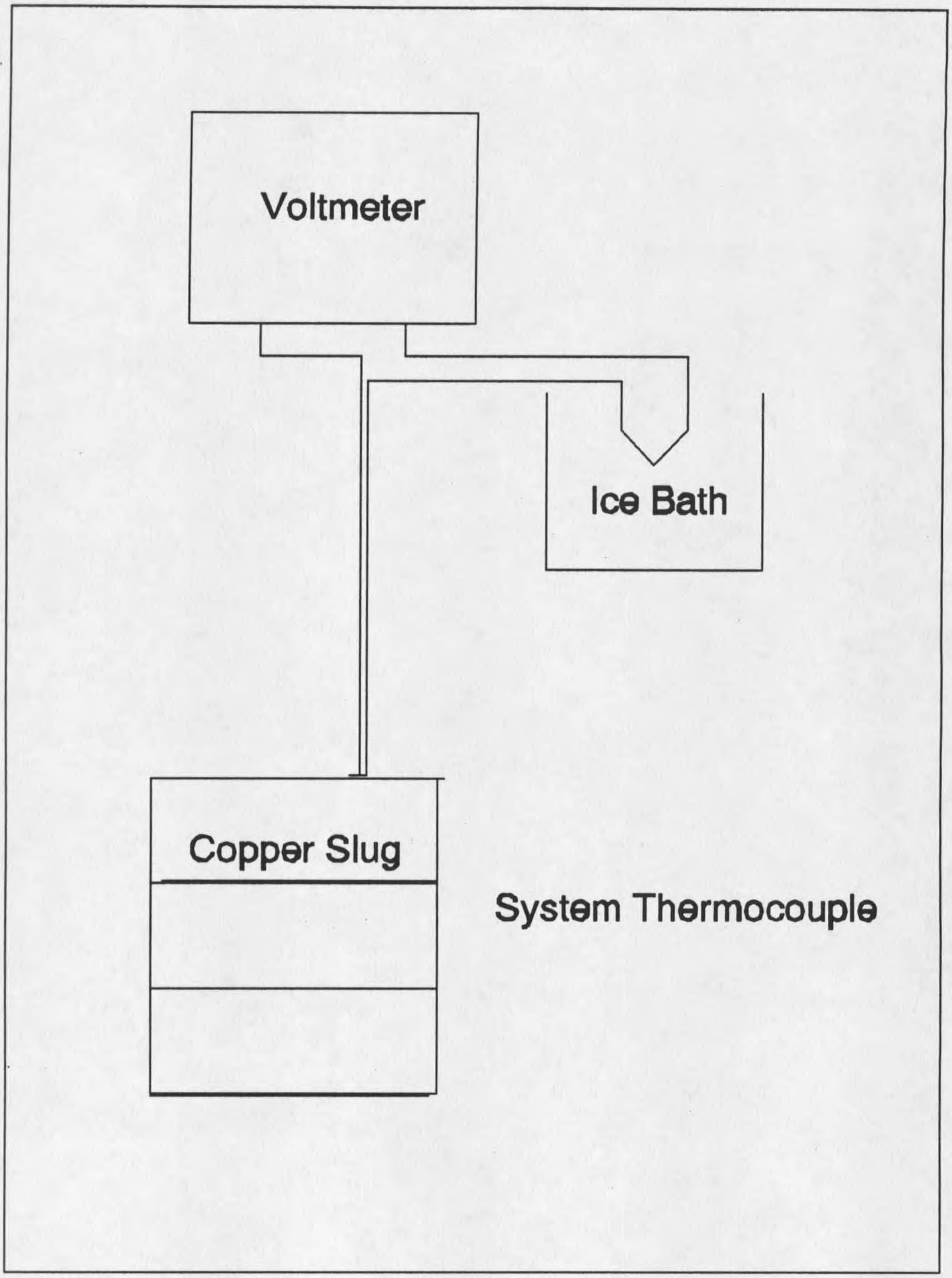
Peltier Effect

Figure 4

Thermocouple Based Mean Temperature Monitoring System

The temperature of the copper slug is continuously monitored by use of a thermocouple attached to its top as shown in Figure 5.

The thermocouple consists of two wires, a chromel-alumel combination, which are soldered together at both ends with a break in one of the wires where terminals of a voltmeter are attached on either side of the break. One soldered end is attached to the copper slug while the other is immersed in an insulated ice bath held at 0°C. Much like the Melcors, the thermocouple makes use of the Seebeck effect.[3] Since the two ends are held at different temperatures an emf is established in the conductors. The value of the thermocouple voltage is then converted through use of a conversion table into a temperature.



System Thermocouple

Figure 5

Lock-In Amplifier

The lock-in amplifier is the heart of the signal receiving system. It amplifies and measures the receiver signal, and compares the phases of the driver voltage and receiver signal, as shown in Figure 6.

The input reference signal is taken directly from the function generator and provided to the reference circuits. The reference circuits then deliver two output signals, the first with phase φ_2, the second with phase $\varphi_2+90°$, to the in-phase and quadrature mixers respectively. The two mixers are also fed the input signal of phase φ_1.

The in-phase mixer multiplies the input signal by the reference signal, namely

$S_o\cos(\omega t+\phi_1) \times R_o\cos(\omega t+\phi_2) = (1/2)S_oR_o[\cos(2\omega t+\phi_1+\phi_2) + \cos(\phi_1-\phi_2)]$. The low-pass filter located between the in-phase mixer and output filters out the $\cos(2\omega t+\phi_1+\phi_2)$ signal thus yielding $(1/2)S_oR_o\cos(\phi_1-\phi_2)$ as the output. Likewise the action of the quadrature mixer is,

$$S_o\cos(\omega t+\phi_1)R_o\cos(\omega t+\phi_2+90°) = (S_oR_o/2)[\cos(2\omega t+\phi_1+\phi_2+90°) + \\ + \cos(\phi_1-\phi_2-90°)]$$

and its low-pass filter eliminates the $\cos(2\omega t+\phi_1+\phi_2+90°)$ signal, yielding $(1/2)S_oR_o\cos(\phi_1-\phi_2-90°) = (1/2)S_oR_o\sin(\phi_1-\phi_2)$.

When $(\varphi_1-\varphi_2)=0°$ the in-phase output is maximum while the quadrature output is zeroed, hence the input and reference signals are in phase. When $(\varphi_1-\varphi_2)=90°$, the in-phase output is zeroed while the quadrature output is maximum, hence the input and reference signals are in quadrature or 90° out of phase.

In the case when $0° < (\varphi_1 - \varphi_2) < 90°$, the responces of both the in-phase and quadrature outputs will be non-zero.

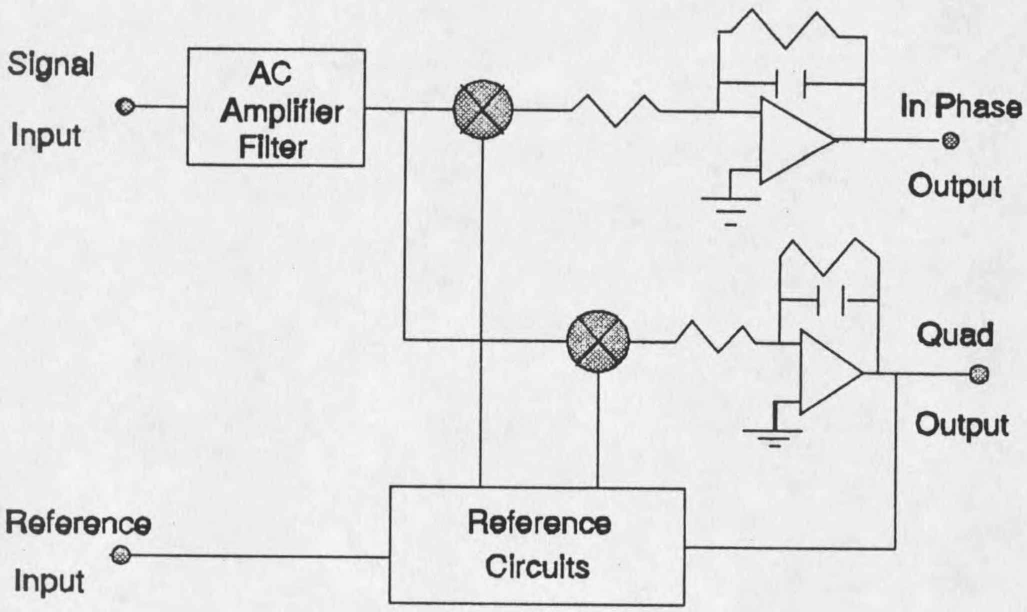


Figure 6 Two Phase Lock-In Amplifier

Two Phase Lock-In Amplifier

Figure 6

CHAPTER 3

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of three areas, the first being system calibration, followed by the dc thermal measurements, and finally ac thermal measurements.

The system calibration included three areas, the Seebeck response of the Melcors, the electrical resistance of the coaxial cables connecting the driver and receiver Melcors to the switch box, and finally the phase calibration of the lock-in amplifier.

The dc thermal measurements consisted of the Melcors being in place on the copper slug and dc voltage signals applied to the driver Melcors and receiving the resulting dc receiver Melcor signals.

The ac thermal measurements were identical to the dc thermal measurements except that ac voltage signals are applied to the driver Melcors and the resulting ac reciever signals are gathered.

System Calibration

Seebeck Response

The thermocouple calibration consisted of two steps. The first involved placing the Melcor device in a known thermal gradient where its voltage response was measured.
This process yielded the Seebeck response for the thermoelectric element. Each Melcor was sandwiched between