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THERMAL EXPANSION MEASUREMENTS
ON SAPHIRE AND RUBIDIUM IODIDE
BELOW 20°K

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THERMAL EXPANSION MEASUREMENTS ON SAPPHIRE AND

RUBIDIUM IODIDE BELOW 20$^{\mathrm{O}}$K

by

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INTRODUCTION

Thermal expansion measurements yield quantities necessary to establish the volume and temperature dependence of the free energy of a solid. If the Helmholtz free energy can be written as a volume dependent cohesive energy plus a term which depends on both volume and temperature, the lattice thermal expansion coefficient β is given by

$$\beta = \frac{\gamma_L \, C_v \, K_T}{V}$$

where γ_L is the Grüneisen constant and is related to the volume dependence of the lattice frequency spectrum, C_v is the specific heat at constant volume, K_T is the isothermal compressibility, and V is the volume. γ_L and its temperature dependence can be calculated theoretically in some instances, and data are needed to check these calculations.

At low temperatures, $\theta_D/10$ (θ_D being the Debye temperature) and below, γ_L usually is temperature independent as are K_T and V, so to a first approximation, β may be considered proportional to C_v. The specific heat at low temperatures is given by

$$C_v = 234 \; Nk \; (T/\theta_D)^3 \; \text{ergs/deg.-mole.}$$

Thus for a typical solid β would be of the order of $10^{-7}/^{\circ}K$ at $10^{\circ}K$. However, in some solids, e.g. sapphire and germanium,

the thermal expansion coefficient may be as low as $10^{-9}/^{\circ}K$ in this region. For this reason an apparatus designed to measure thermal expansion at low temperatures ($1^{\circ}K$ to $20^{\circ}K$) must be able to detect a relative change in the length of a solid of the order of one part in 10^{10} (for a 10 cm long sample, $0.1\overset{\circ}{A}$).

Experimental methods based on x-ray diffraction or optical interferometry techniques do not have the sensitivity necessary to measure expansion coefficients as small as $10^{-8}/^{\circ}K$. Three very different types of apparatus have been developed which do have this sensitivity. First, a double grid arrangement has been used with one grid moving with respect to the other (1). The relative transmission of light through this combination is measured using a differential photocell. However, fractional angstrom accuracy was not obtained. A modification of the above principle which uses a tilting mirror to shift the optical image of one grid with respect to the other has been tried at room temperatures. The detection of sample expansions of $10^{-4}\overset{\circ}{A}$ has been claimed (2), but only at room temperature, however.

A second method involves plating the top surface of a sample and using this surface as one plate of a variable

capacitor in a capacitance bridge (3). This method is one of the most sensitive now in use for measuring low temperature thermal expansion, and fractional angstrom changes in length can be detected. The major limitation of this method involves the stability of the capacitor plates.

The method used in the present work consists of using a linear variable transformer to measure the expansion of the sample (4,5). As the sample changes length the motion is transferred to the secondary coil of the transformer and the off-balance voltage detected using a mutual inductance bridge. Changes in length to a precision of $0.1\overset{o}{A}$ can be detected and an accuracy of $\pm\ 0.3\overset{o}{A}$ is maintained within the calibration accuracy.

DISCUSSION OF APPARATUS

The apparatus in general is based on that described by Carr (4) with several major modifications which will be discussed below. Figure 1 is a schematic representation of the primary components of the equipment and their relationship to each other. The equipment may be divided into three basic systems; thermal expansion measurement, sample heater and thermometry.

The thermal expansion sample is placed in an evacuated sample chamber and a thermal break is provided at the ends of the sample to insulate it from the bath temperature. The sample is warmed a few degrees above the bath temperature by means of a heater which is wound around the sample. As the sample expands due to this warming the motion is transmitted to the secondary coil of a variable transformer via a mylar diaphragm at the top of the sample chamber and a quartz rod between the diaphragm and the coil. The base of the sample is rigidly attached to the primary coil of the transformer and since the whole apparatus is immersed in superfluid liquid helium II the only expansion due to the heating is that of the sample.

The variable transformer is constructed in such a manner

Figure 1.   General electrical and mechanical schematic
            drawing of the thermal expansion measuring
            apparatus

THERMAL EXPANSION SCHEMATIC DRAWING
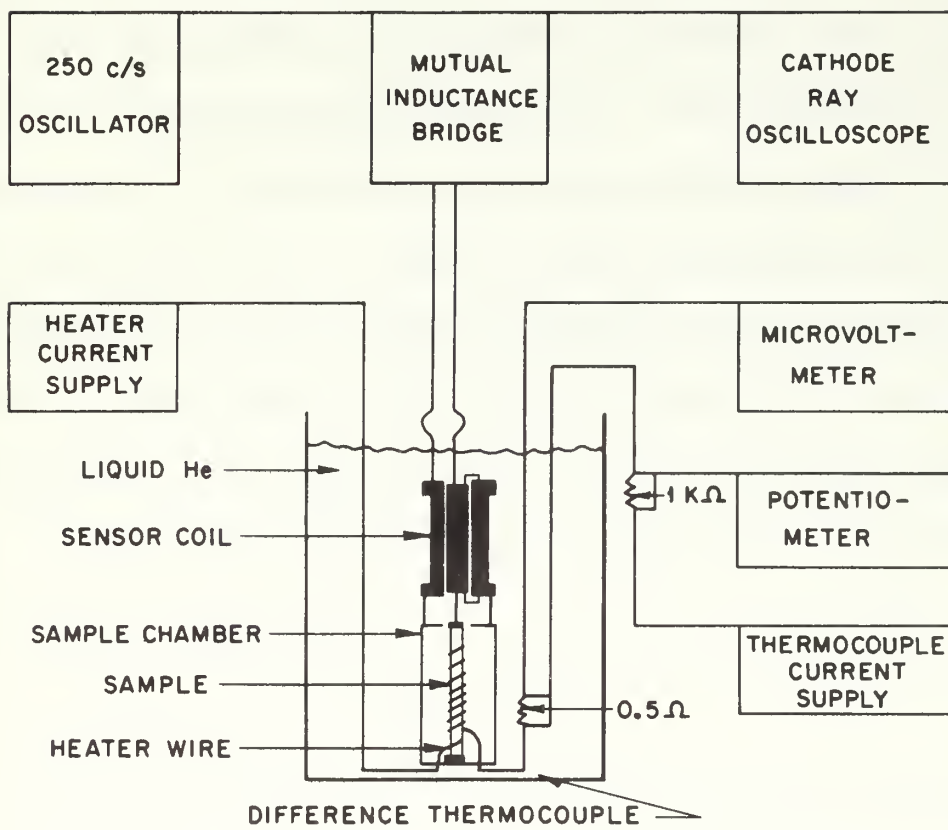
that when the secondary coil is moved axially from the cen-
ter position with respect to the primary coil a linear off-
balance voltage is produced. This voltage is measured with
a mutual inductance bridge (6). Therefore, with a proper
calibration the change of length of the sample can be meas-
ured directly.

The temperature of the sample is measured with a Au-Fe
versus Cu difference thermocouple (7). One junction of the
thermocouple is attached to the sample and the other junction
is in the helium bath. Since the bath temperature can be
determined from vapor pressure readings and the thermocouple
voltage is measured by potentiometric methods, the absolute
temperature of the sample can be found. A detailed discus-
sion of the various equipment components will be given in
the following sections.

Sample Chamber

Once the general size of the sample has been determined,
four basic problems must be solved; a diaphragm to transmit
the motion of the sample, a method for insulating the sample
from bath temperature, a method for taking up the differential
contraction between the sample and the sample chamber upon
cooling down from room temperature, and the development of a

continuous-lead vacuum-tight connector for the electrical leads into the sample chamber.

The first two problems will be discussed only briefly since their solutions are the same as used by Carr (4). The diaphragm consists of a mylar disk glued to the top of the sample chamber with epoxy glue (see Figure 2). The mylar maintains its elasticity at low temperatures, so any motion transmitted to it from the sample will be transferred to the quartz spacer rod and thus to the secondary coil.

Since the sample chamber is evacuated, there will be no heat transfer from the helium bath to the sample by gas conduction in the sample chamber. It is necessary, however, to maintain good mechanical contact between the sample and the diaphragm and at the same time to insulate the sample thermally from heat conduction through this mechanical contact. This is accomplished by making use of the poor thermal conductance which is found between two hard surfaces which are in mechanical contact. Sapphire disks were glued to both ends of the sample, to the base of the sample chamber, and to the inside of the mylar diaphragm. The disks at the top of the sample and on the diaphragm have polished surfaces, and although they maintain contact these surfaces provide for a

Figure 2. Sample chamber and continuous lead connector

SAMPLE CHAMBER

CONTINUOUS LEAD CONNECTOR

1 INCH
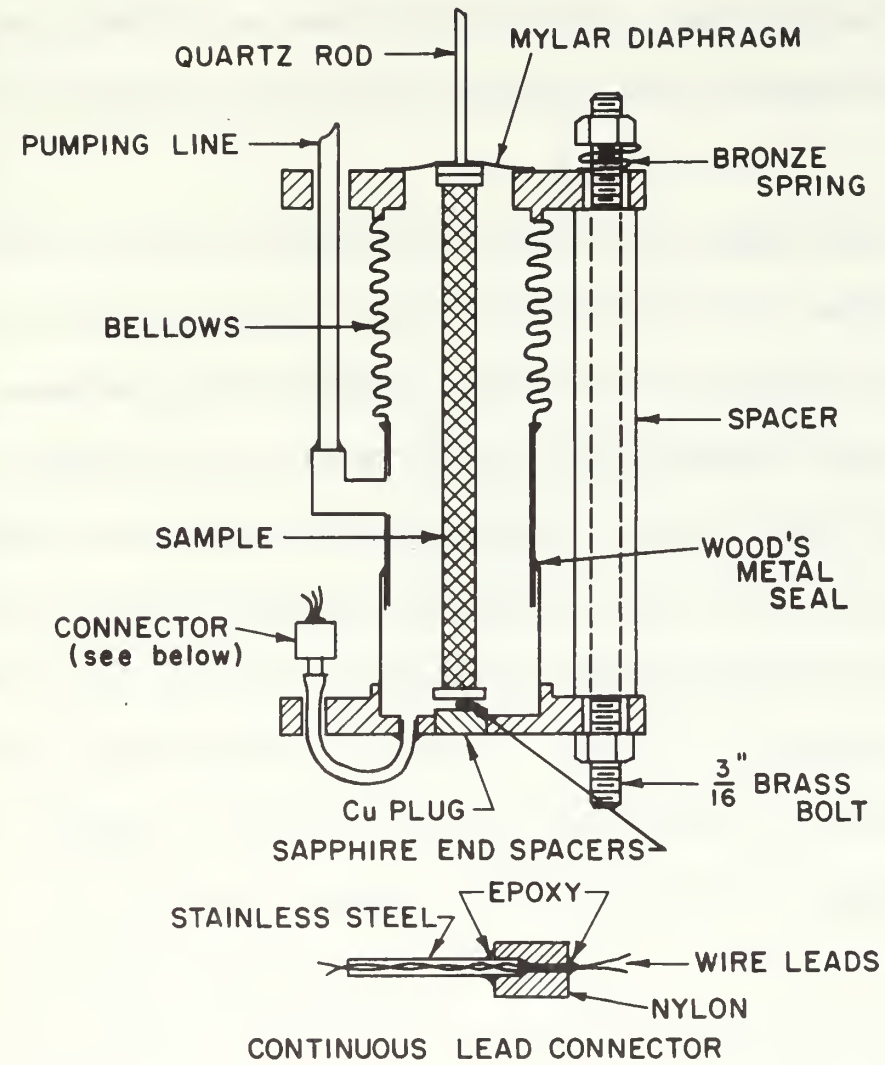
good thermal break. The disks at the bottom of the sample
and on the base of the sample chamber are indented and a 1 mm
ball is placed between them in these indentations. This not
only provides for a good thermal break, but also acts as a
gimbal bearing to alleviate stresses due to small misalign-
ments.

Differential contraction between the sample and the
sample chamber can be a major problem, since in cooling from
room temperature to helium temperature the sample could
either contract too little and possibly rupture the diaphragm
or become too loose and not maintain contact with the dia-
phragm. If the differential contraction is not too great,
allowance for this can be made by adjusting the tension on
the diaphragm from the sample by changing the length of the
sample chamber. This will not be sufficient if the differ-
ential contraction is large, and in either case reproducible
tension on the diaphragm is impossible.

The present sample chamber uses a stainless steel bel-
lows and spacers with a thermal expansion which is approxi-
mately the same as that of the sample (see Figure 2). The
spacers are placed between the flanges of the sample chamber
and spring loaded. Since the bellows allows the sample

chamber to change length, this length is the same as the spacers at any given temperature. Thus, there is only a very small differential contraction between the sample and the sample chamber, and consistent loadings can be accomplished.

With the incorporation of a thermocouple as the primary thermometer in the system it became necessary to use a continuous-lead vacuum-tight connector to insure that thermoelectric voltages were not developed where the electrical leads left the sample chamber. Hollow pin connectors, which were tried previously, were found to develope leaks a majority of the times that they were cooled to liquid nitrogen temperatures.

A connector was developed for this purpose (see Figure 2) by fitting a 1/8 inch steel tube into a hole drilled in a short section of 3/8 inch diameter nylon rod. These two pieces are glued together with Armstrong A-4 epoxy adhesive taking care that all surfaces are wetted. A 1/32 inch hole is drilled through the nylon and the wires are passed through and glued with the epoxy adhesive, again making sure that all surfaces of the wire are wetted. The stainless steel tube is soldered to a copper adapter and the wires pass through a copper tube into the sample chamber.

It was found that this connector is extremely durable and will not develope leaks even when subjected to sudden quenching in liquid nitrogen and immediate warming. This is because the material with the larger thermal expansion is on the outside. Of the four connectors used thus far all have been vacuum-tight even to superfluid liquid helium II.

Heater Supply

The temperature of the sample is raised by passing a small current through a 40 Ω heater wire (number 44 manganin) which is wound around the sample and attached with G.E. 7031 adhesive. The power used is of the order of 30 milliwatts at 30°K. A center tap and each end of the sample are connected to a low current power supply in such a manner that current can be passed through either the whole heater or only through one half. This is done so that thermal gradients across the sample can be detected by comparing "end only" measurements with "total" measurements.

The current supply is a transistorized current source which will provide direct current from 0 to 400 ma in four ranges to a low resistance load. A change in line voltage of 30 volts or a doubling of the load will change the current by

only 0.1%. This stability is necessary since small fluctuations in the heater current will produce significant fluctuations in temperature.

Thermometry

In low temperature thermal expansion measurements it is generally necessary to have an absolute temperature determination of $\pm$ 0.01°K and a relative temperature difference in some instances precise to $\pm$ 0.001°K. In this experiment these criteria are met by the use of a Cu versus Au-Fe difference thermocouple referred to the bath temperature (7) and a direct current nulling circuit. The bath temperature is found from vapor pressure measurements and is generally regulated with a giant manostat (4) at 1.89°K to better than one millidegree. The Cu versus Au-Fe thermocouple has a constant sensitivity of 13.6 µv/°K above 5.5°K, which decreases to about 11 µv/°K at 2°K.[1] Above 20°K the calibration is accurate to only $\pm$ 0.1°K, while below 20°K the calibration is good to nearly $\pm$ 0.01°K. Therefore, for an absolute temperature determination of $\pm$ 0.01°K in the 2°K to 20°K region

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[1]Appreciation is expressed to Mr. T. F. Stromberg and Dr. D. K. Finnemore for making available the Cu versus Au-Fe thermocouple calibration. Ames, Iowa (private communication, 1964).

thermocouple voltages of up to 300 μv must be measured to ± .1 μv, while for relative temperature differences a sensitivity of ± 0.01 μv must be possible. Since these voltages are on the lower ranges of commercial potentiometers, and because of the possibilities for stray thermoelectric voltages, an auxillary potentiometer or direct current nulling circuit was used (see Figure 3).

One junction of the thermocouple is wound around the sample two or three times and is attached to the sample with G.E. 7031 adhesive to insure good thermal contact. The other junction is taped to the outside of the sample chamber where it is in contact with the superfluid liquid helium II. A nulling circuit is constructed by placing a small resistor r_d (about 0.5 Ω) in series with one of the two copper thermocouple leads. These leads then go to a Kiethley microvoltmeter. An independent pair of leads is used to pass a small current through this resistor to produce sufficient voltage to "buck-out" the thermoelectric voltage. The null is detected on the microvoltmeter. The voltage drop V_S due to the current passing through a standard resistance, R_S = 1000 Ω, which is placed in series with the current source, is used to measure the nulling current. It is readily seen that

Figure 3.   Thermocouple circuit

THERMOCOUPLE CIRCUIT
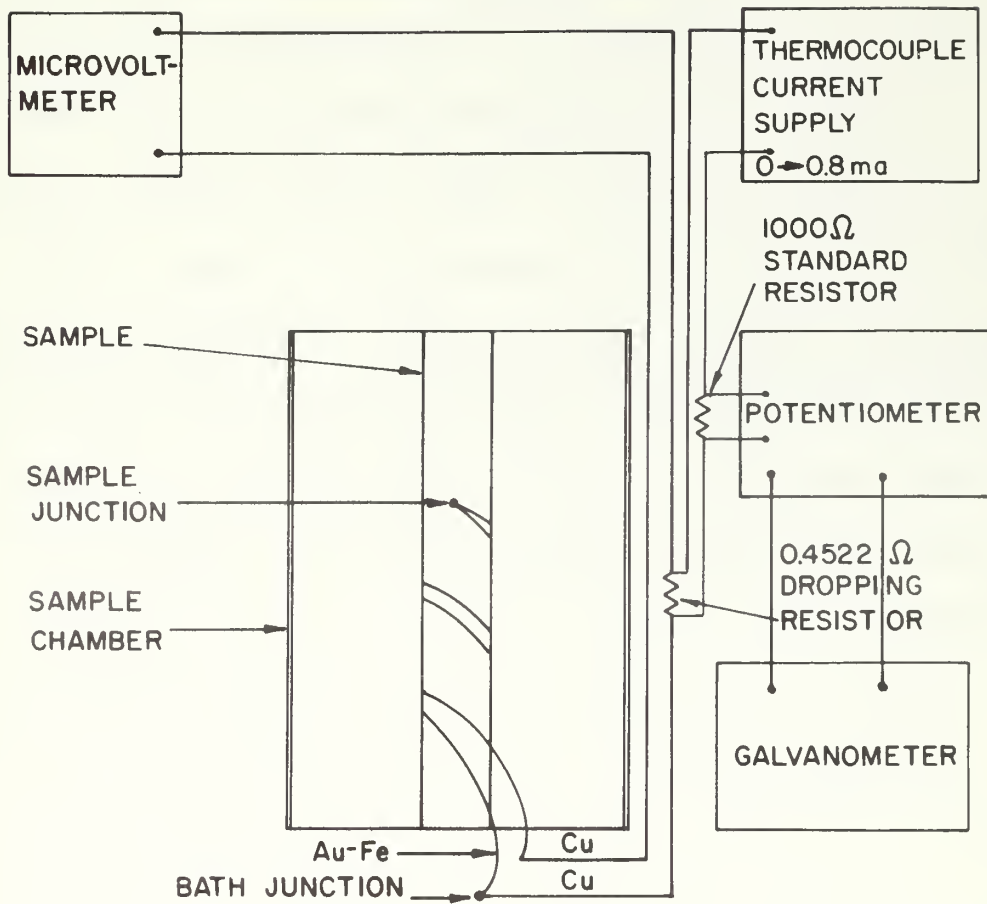
the bucking voltage V_b is given by

$$V_b = \frac{r_d}{R_s} V_s.$$

The largest temperature that would be measured is about
30°K. This corresponds to about 450 μv, so the voltage across
the standard resistor would be of the order of 900 mv. This
is well within the capabilities of a commercial potentiometer.
On the other hand the maximum sensitivity in V_s needed to
meet design criteria would be 200 μv for $\pm$ 0.01°K and 20 μv
for $\pm$ 0.001°K. Again these voltages are easily obtained with
a standard potentiometer. Thermoelectric voltages developed
at connections in the current supply or potentiometer would
be negligible compared to these voltages. All other connec-
tions in the circuit with the exceptions of the sample junc-
tion and the connection at the null indicator are in helium II
and therefore have small constant thermoelectric voltages.
The connection at the null indicator is thermally anchored
to a copper plate and encased in styrofoam. The total stray
voltages indicated at the microvoltmeter are of the order of
2 μv, and do not vary more than $\pm$ 0.1 μv over six hours.
These voltages are measured and used to correct the differ-
ential thermocouple voltages.

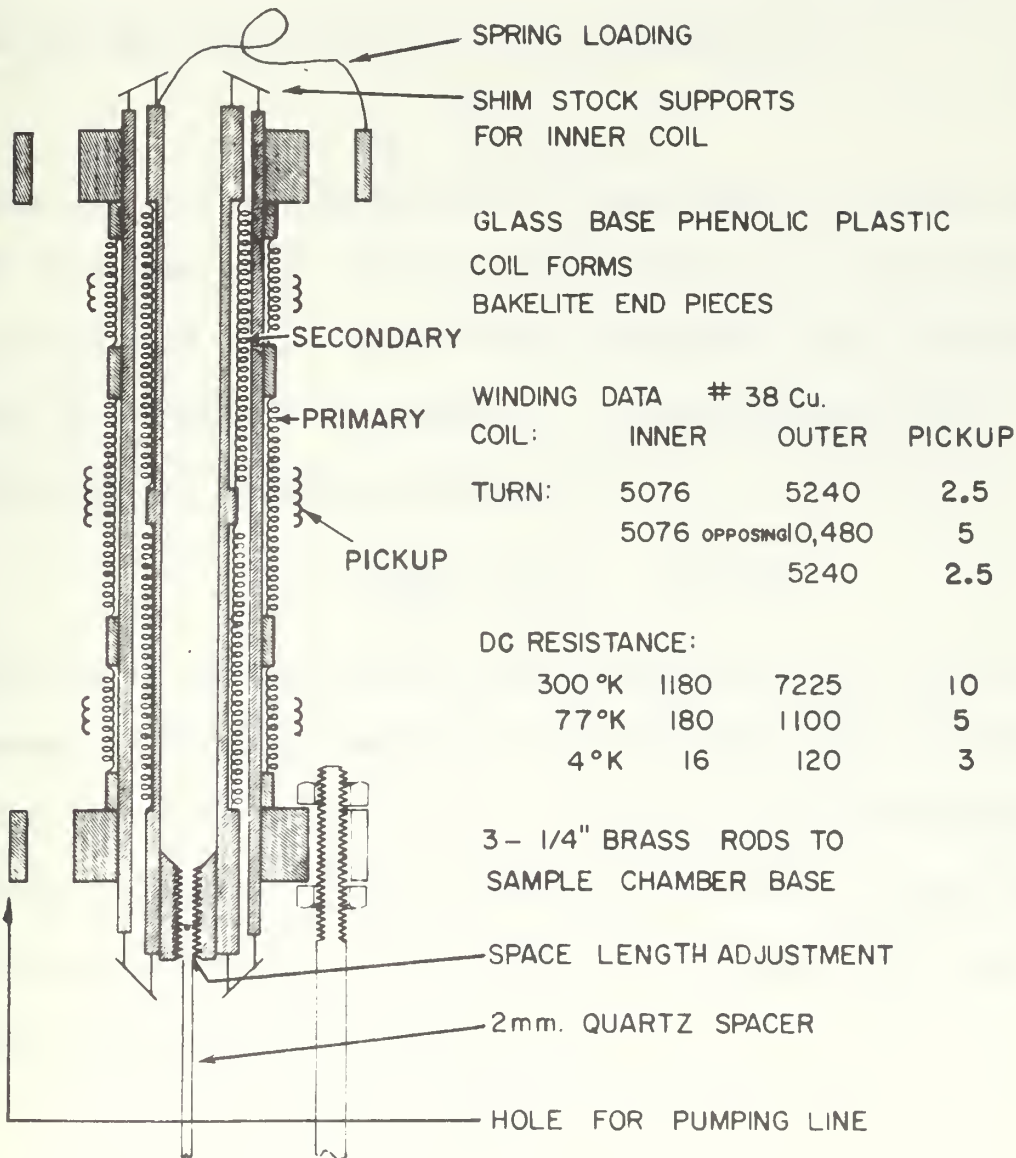The current source must be stable over short periods of

time (during a measurement). Since the maximum current is only 0.8 ma, a bank of nine mercury cells connected in series has been quite successful in providing the voltage for a standard d.c. current supply.

Variable Transformer

The same basic sensor coil is used in the present experiment as was used by Carr (4). The transformer consists of a fixed primary coil and a movable secondary coil (see Figure 4). An additional small pickup coil was wound about the primary turns so that a modified mutual inductance bridge can be used. All three coils were astatically wound to prevent pickup of other frequencies. The primary and pickup coils have the ends wound in a clockwise direction and the middle section wound in a counter-clockwise direction. The secondary coil has its two halves wound in opposite directions. When the secondary coil is situated midway with respect to the primary coil there is no net flux linkage. As the secondary coil is moved with respect to the primary a small voltage is induced whose phase differs by π depending upon the direction of movement. The magnitude of this voltage is proportional to the coil offset. Since the sample is

Figure 4. Linear variable transformer and winding data

VARIABLE TRANSFORMER

SPRING LOADING

SHIM STOCK SUPPORTS
FOR INNER COIL

GLASS BASE PHENOLIC PLASTIC
COIL FORMS
BAKELITE END PIECES

SECONDARY

PRIMARY

PICKUP

WINDING DATA   # 38 Cu.

COIL:	INNER	OUTER	PICKUP
TURN:	5076	5240	2.5
	5076 opposing	10,480	5
		5240	2.5

DC RESISTANCE:

300 °K	1180	7225	10
77 °K	180	1100	5
4 °K	16	120	3

3 - 1/4" BRASS RODS TO
SAMPLE CHAMBER BASE

SPACE LENGTH ADJUSTMENT

2 mm. QUARTZ SPACER

HOLE FOR PUMPING LINE

attached mechanically to the secondary coil, the voltage will

be a direct measurement of the sample expansion.

A simple calculation can be used to determine the volt-

age output of a transformer of this type. The magnetic field

on the axis at the center can be expressed by

$$B_O = \frac{\mu_O}{2} \, n_p \, I_p \, \gamma,$$

where μ_O is the permeability of free space, n_p is the number

of turns per meter of the primary coil, I_p is the primary

current, and γ is a factor which depends on the end windings

and is a function of geometry. In the existing coil $\gamma = 1.6$.

The magnetic coupling is given by

$$M = \frac{A \, n_s}{I_p} \, (2z' \, B_O - 2z' \, B_\ell)$$

where A is the mean area of the secondary coil, n_s is the

number of turns per meter of the secondary coil, B_O is the

magnetic field at the center of the coil, B_ℓ is the magnetic

field at the end of the secondary coil, and z' is the small

displacement from the null position. However $(B_O - B_\ell)$ is

just $B_O\gamma$ since B_ℓ is negative, so

$$M(z') = \frac{2A \, n_s}{I_p} \, B_O \, z' \gamma.$$

The induced voltage in the secondary then is given by

$$E(z') = -M \frac{dI_p}{dt} = 4\pi f \, A \, n_s \, z' \, B_O\gamma$$

where f is the frequency of the primary current. Thus the
change in voltage with a change in displacement is given by

$$\frac{dE(z')}{dz'} = 4\pi f \ A \ n_S \ B_0 \gamma.$$

The dimensions and total turns data are given in Figure 4,
f is 250 c/s, and I_p is 0.1 amperes. Substituting in these
values one obtains

$$\frac{\Delta E}{\Delta z'} = 75 \quad m\mu v/0.1 \overset{o}{A}.$$

By approximation methods it was deduced that the magnetic
field and thereby the off-balance voltage should be linear
within the expected calibration error, i.e. 0.5%, over a range
of one millimeter from the balance point.

Mutual Inductance Circuit

It was apparent in the earlier work (4) that a greater
range of measurement and more convenience in taking data
would be necessary for an extension of this work. For these
reasons a ratio transformer was used in a modified mutual
inductance circuit instead of the more conventional Hart-
shorn bridge.[1] The modified mutual inductance circuit uses

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[1]Appreciation is expressed to Dr. R. H. Carr and Dr. A.
M. Thompson for their suggestion to use a ratio transformer
in the mutual inductance bridge. Chippendale, NSW,
Australia (private communication, 1963).

a fraction of the primary coil voltage from a pickup coil as the input into the ratio transformer. A fraction of this voltage is used to produce a null in the secondary loop by bucking out the induced voltage in the secondary coil (see Figure 5). The ratio transformer reading will be a direct indication of the induced secondary coil voltage and hence of the change in length of the sample. The ratio transformer used in the present experiment is the Gertsch model 1101 R. This instrument is essentially an auto transformer used as an A.C. voltage divider. The ratio transformer will divide the input voltage by increments of 10^{-7}, so if the desired least change in length is $0.1 \overset{O}{A}$ the bridge range will be 100 microns. The linearity of the ratio transformer is considerably greater than the sensor coil calibration being of the order of .001% of the reading. The input impedance is 350 KΩ at 250 c/s and the dial settings (covering 7 decades) are read-out and range from -1 to X settings.

The calculated voltage of the null signal is 7.5 x 10^{-8} volts. The voltage developed across the pickup coil is given by

$$E = -M \frac{dI_p}{dt}.$$

If this is to be the input voltage to the ratio transformer

Figure 5. Mutual inductance bridge circuit diagram

MUTUAL INDUCTANCE BRIDGE
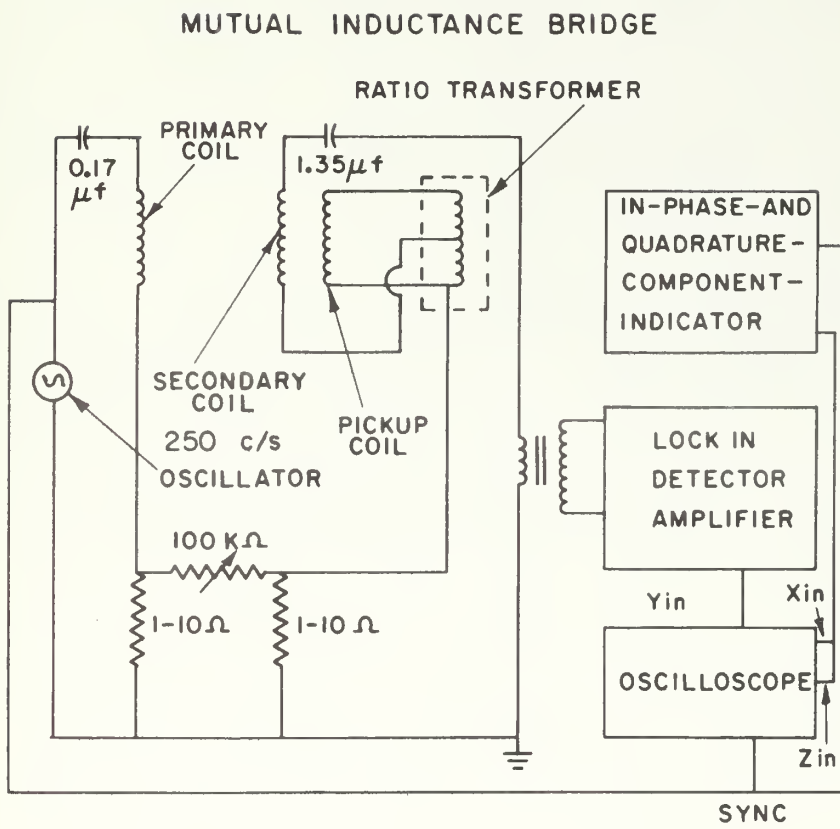
then the number of turns on the pickup coil is given by

$$N_{pk} = \frac{7.5 \times 10^{-8} \times 10^7}{2 \pi f \mu_o \, n_p \, I_p \, A \gamma}$$

or twenty turns. To insure that the required sensitivity was obtained a factor of two was introduced and the pickup coil was wound with 10 turns.

The alternating voltage source is a 250 c/s tuned-plate oscillator designed and built at the A.E.C. Laboratories at Ames, Iowa. The self-inductance of the primary coil is 2.3 henries so the primary loop is tuned for series resonance with a 0.17 μf capacitor. This allows a lower output voltage from the oscillator to be used for a given primary current. The output of the oscillator can be varied from 0 to 50 volts p-p and is normally operated at 10 volts p-p to produce 0.1 amperes in the primary circuit. The gain is stable within 0.1% and although a change in gain will affect the balance point it will not change the calibration. Frequency stability is important and the oscillator is stable to $\pm$ 0.01 c/s over a twenty-four hour period.

Two small dropping resistors (5 Ω) are included in the circuit to null out any resistive component present. The amount of quadrature voltage is regulated by a 100 KΩ rheostat that will control the amount of current in the resistive

loop. Reversing switches (not shown in figure) are provided in the primary, secondary, and pickup loops so that the proper polarity of the loops can be obtained without rewiring and certain systems checks can be made more conveniently.

The null voltage in the secondary loop is impedance-matched to a narrow band, low noise lock-in amplifier-detector (8) through a S.I.E. model TI 5384 impedance matching transformer. The transformer is wired in parallel and provides for an impedance match from the 20 Ω resistance of the secondary coil to the amplifier and it provides a gain of 200 in voltage. The 300 millihenries self inductance of the secondary coil is tuned with a 1.35 microfarads capacitor. The input impedance of the amplifier can be varied by an attenuator from 2 KΩ to 1 megohm to an open grid position. The amplifier is very satisfactory for this type of circuit since its low noise ($\pm$ .03 μv) and very low microphonic response are necessary for the detection of the minimum 2 μv input voltage from the matching transformer at a null signal. The null can be observed either on a d.c. ammeter or the output of the amplifier or on a monitoring oscilloscope. For greater visual sensitivity in "reading" the oscilloscope an in-phase-and-quadrature-component-indicator is used (9).
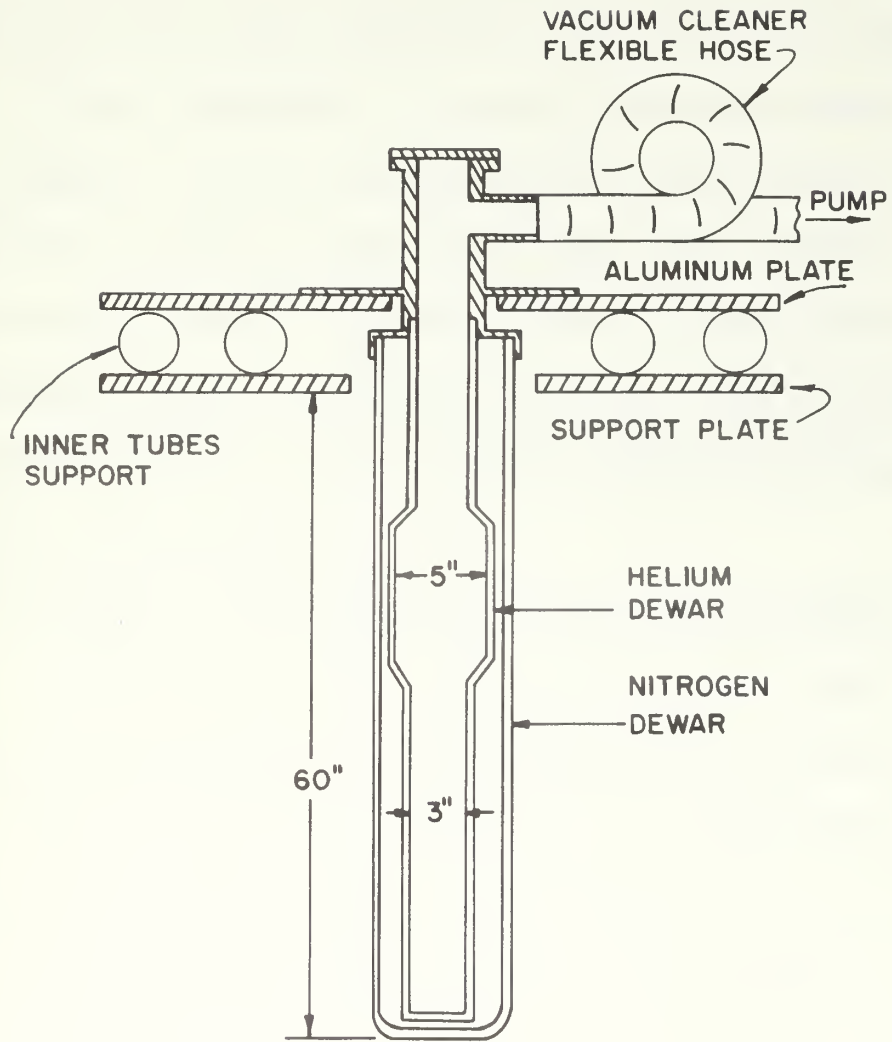
Dewar System

For an experiment of the present sensitivity dewar design becomes quite important for the elimination of magnetic, eddy current, and vibrational effects. The use of a glass dewar system eliminated the magnetic and eddy current problems and a simple innertube dewar suspension has eliminated a greater part of the vibrations.

The magnetic and resistive properties of a stainless steel dewar system can affect the balance point of the sensor coil. If the temperature distribution of the dewar were constant and the coil was constant in position with respect to the dewar these would not be a problem. However, it was found that as the evaporation rate changed due to a higher power input to the sample, etc., both the inductive and resistive balance points would "drift" up to $5\overset{o}{A}$/min. The use of a glass dewar system effectively has eliminated balance point drift due to these causes.

The present glass dewar system was designed with a large bulge to contain sufficient liquid helium for a five or six hour run (see Figure 6). The long tail of the dewar was designed so that very long samples (up to 35 cm) could be used to increase sensitivity. In this case there still would be

Figure 6. Glass dewars and suspension system

DEWAR   SYSTEM

sufficient liquid helium above the sensor coil for a two or three hour run.

The dewar system which weighs 200 pounds is suspended rigidly from a 1/2 inch thick aluminum plate. This plate is supported on two small innertubes which lie on the support frame. These innertubes act as very effective dampers for the frequencies of the order of 20 c/s which form the major vibrations external to this experiment. Any swinging motion of the dewar system is damped quickly by these innertubes. The pressure in the innertubes is of the order of five pounds per square inch and may be varied to adjust the damping constant of the system.

At times the bath temperature must be decreased to as close to 1^OK as possible and this makes a three inch diameter pumping line necessary. A rigid pumping line would defeat the purpose of the dewar suspension, so an eight foot section of wire-reinforced flexible vacuum cleaner hose was installed. Since the hose will contract when it is evacuated, a loop was formed to take up this contraction (see Figure 6). All other small pumping lines have a small section of rubber hose in them to maintain the flexibility of the system.
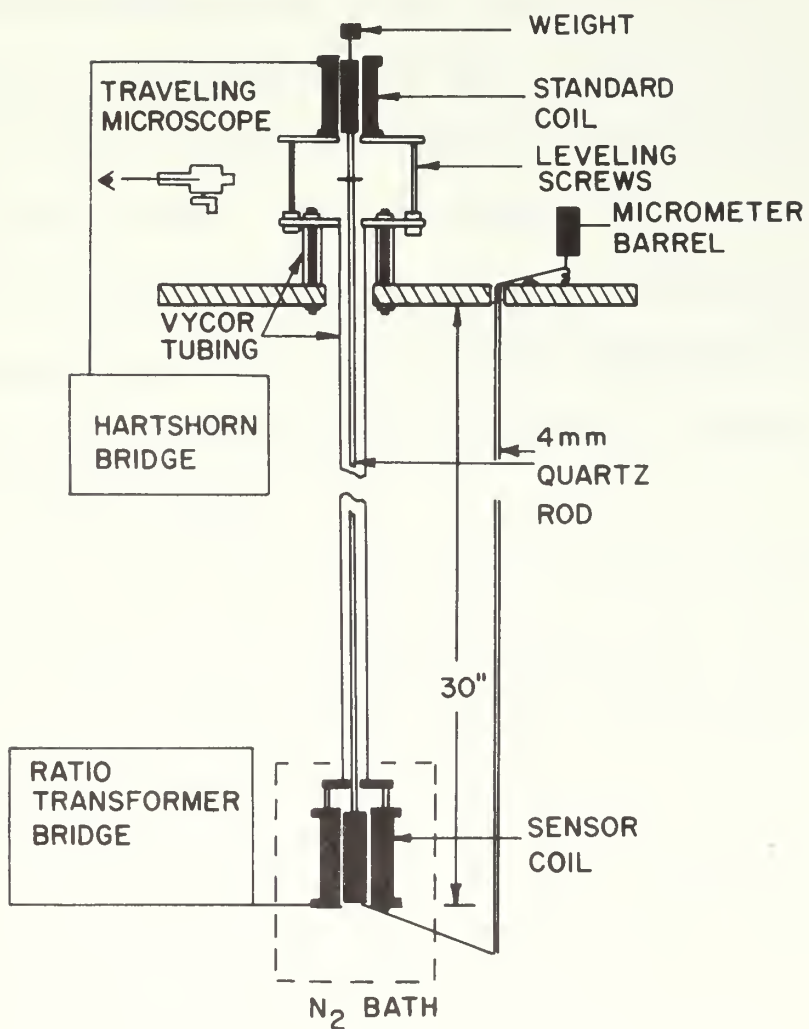
CALIBRATION

The smallest detectable change in length anticipated was of the order of 0.05Å and, consequently, the total bridge range was expected to be of the order of 50 microns. An interferometric method of calibration, similar to that of Carr (4), could be used to obtain a calibration precise to 0.5 percent. However, a more convenient method was devised using a second variable transformer which was used as a transfer "standard". This "standard" transformer has a 2 mm range, and is linear to 0.1 percent. It was calibrated against a traveling microscope after which it was used for the calibration of the sensor coil.

This "standard" transformer (10) is constructed similar to the sensor coil, but has a longer range and no pickup coil. The motion of the secondary coil was detected by means of a Hartshorn bridge operating at a frequency of 33 c/s (6). This bridge is divided into 28 "turns" with a least count of 10^{-3} turns. A 40 micron coil motion produces a mutual inductance change of approximately one turn. A traveling microscope was used to read the motion of a razor edge which was attached rigidly to the movable secondary coil of the "standard" (see Figure 7). The position of the razor edge

Figure 7. Calibration apparatus

COIL CALIBRATION APPARATUS

could be determined to ± 2 microns which, over the 1.1 mm range of the bridge, gives an accuracy of 0.2 percent. These calibration data are shown in reduced form in Figure 8a.

Once the "standard" transformer was calibrated, the primary and secondary coils of the "standard" transformer and the sensor coil respectively were connected rigidly. A micrometer barrel was used to produce a change of position of the secondary coils between settings, and the sensor coil was placed in liquid nitrogen to take into consideration the thermal contraction of the coil between $300^{\circ}K$ and $77^{\circ}K$, and to increase the sensitivity of the bridge by reducing the resistance of the coils.

The sensor coil then was calibrated over the ratio transformer range. The "standard" transformer bridge could be balanced to ± 0.04 microns, giving a 0.08 percent uncertainty, while the ratio transformer could be read to about the same precision. Therefore, the total accuracy of the calibration should be about 0.4 percent. These calibration data are shown in Figure 8 also.

The calibration of the "standard" transformer is 39.5 ± .1 microns per turn and the calibration of the sensor coil

Figure 8a. Standard coil versus traveling microscope
           sum plot

Figure 8b. Standard coil versus ratio transformer sum plot
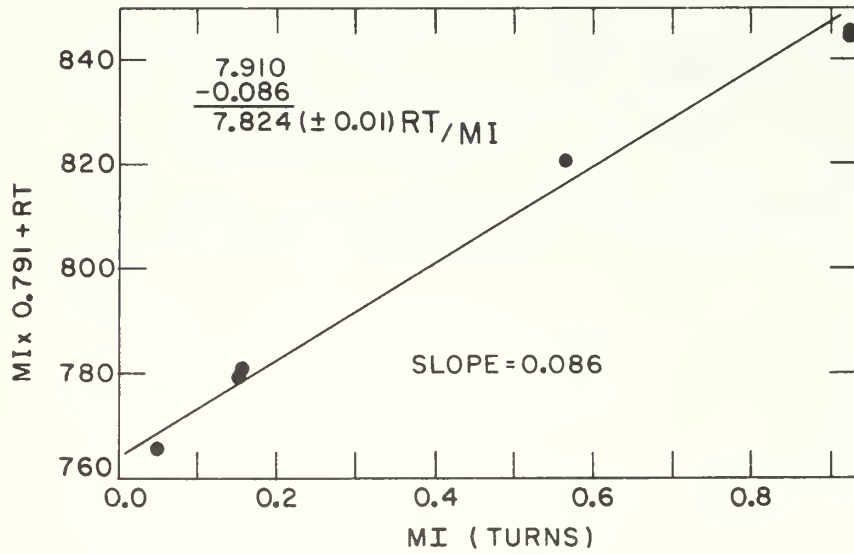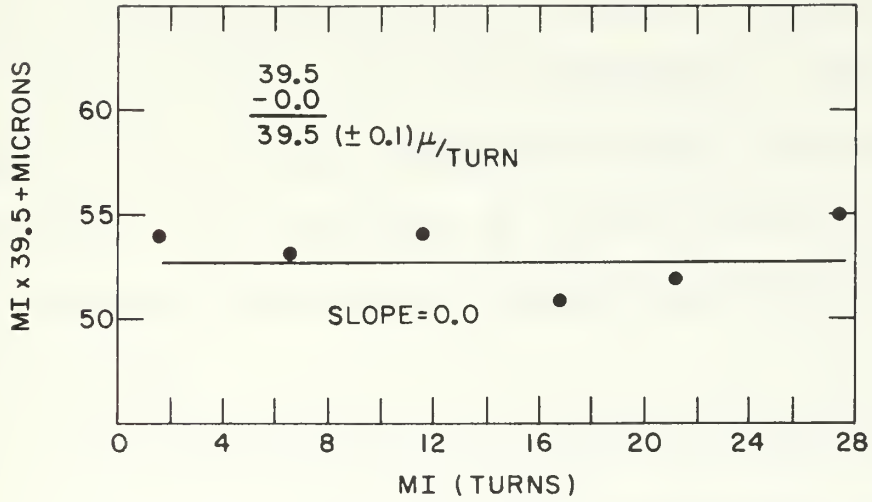
is 0.783 ($\pm$ .0015) ratio transformer bridge length per
Hartshorn bridge turn. Therefore, the final calibration of
the sensor coil was found to be 50.49 $\pm$ 0.30 microns per
ratio transformer bridge range with, roughly, 0.6 percent
accuracy. Therefore, the smallest change of length which
can be seen is 0.05$\overset{o}{A}$ on the ratio transformer. This is only
possible at liquid helium temperatures where the sensitivity
is increased as the resistance of the coil windings decrease.
Due to vibrations the present smallest increment which can
be seen is 0.1$\overset{o}{A}$.

It should be emphasized that the use of this calibration
depends upon the fact that a variable transformer remains
linear (or becomes more linear) as the range of motion de-
creases. Therefore, the calibration obtained over a larger
range can be trusted when making small measurements.

EXPERIMENTAL PROCEDURE

The various components of the system have been described above. The inter-relationship of these can be appreciated better through a description of the procedure involved in the performance of an experiment. Four steps are involved; sample preparation and loading, systems checks at 77°K, liquid helium transfer and pumpdown, and the method of taking data.

The samples used in this experiment are usually 10 cm in length and about 1/4 inch in diameter. The ends are cut normal to the sample axis and the sapphire disks are glued to the ends with G. E. 7031 adhesive. The heater wire is wound around the sample, glued and the thermocouple is attached in the same way making sure that good thermal contact is maintained along two or three inches of the sample. All electrical connections are made, the sample is mounted on the sapphire ball, and the sample chamber is assembled. After the spacers have been installed and the sensor coil bolted onto the sample chamber a fore-pump vacuum is pumped on the sample chamber. The sample chamber then is flushed with N_2 gas and pumped several times, the glass pumping line is sealed off, and the excess glass is

removed with a gas-oxygen torch. The whole apparatus then is placed in the dewar where it rests on the bottom. This is done so the measurements will not be affected by small changes in the dewar length.

When the system has reached equilibrium at 77°K the resistances of all the leads are checked to be sure that there are no shorts or open circuits. Then the mutual inductance, thermocouple, and heater circuits are checked out. A long adjust rod which passes through a hole in the lid of the dewar is used to turn a screw which adjusts the position of the secondary in the primary. Thus, a rough balance can be obtained while the apparatus is in the dewar. This is necessary since differential thermal contractions during cooling will change the balance point considerably more than the 50 micron ratio transformer range. While the apparatus is at 77°K the dewar is pumped out and the change in balance point noted. Although there will be some change in balance point due to temperature change and the compressibility of the sample, a large change in balance would indicate either a leak in the sample chamber or a loss of contact between the sample and the mylar diaphragm. If these checks are successful liquid helium is transferred. At this point all resistive

checks are made again. A rough balance is made with the adjust rod which is then pulled out of the dewar. The mutual inductance circuit, the heater, and the thermocouple circuit are checked again and if correct the helium bath is pumped down through the manostat (4). When the manostat is regulating all checks are made again and the system is allowed to run for ten or fifteen minutes to come to equilibrium.

The method of taking data involves three steps; the establishment of a base point, the heating of the sample, and the return to the base point. The base point is obtained by taking the ratio transformer and potentiometer readings at zero current. A fixed amount of current then is passed through the heater, and when the sample comes to a temperature equilibrium (10 to 60 seconds for most samples) the ratio transformer and potentiometer readings are taken. The base point is then redetermined by shutting off the heater current and reading the ratio transformer and potentiometer settings when equilibrium has been reached again. This process is repeated using various current settings until data points have been taken throughout the desired temperature range. In this manner a Δl versus T curve may be plotted and the data evaluated.

The base point is determined continuously to eliminate the effect of small uniform drifts in the balance points. These drifts are caused by the change of the hydrostatic pressure on the sample as the helium evaporates, temperature changes in the electronics, and small constant vibrations transferred to the sample chamber. Of course, large changes in balance due to sudden large vibrations will negate the balance point. A few "end only" points will be taken during each run to insure that there are no effects due to thermal gradients across the sample. Samples with low thermal conductivity cannot be measured in this apparatus.

Another method of taking data consists of moving the base point from one temperature to another (using a set value of heater current other than zero current) and taking the data points for only small temperature differences. In this manner the linear thermal expansion coefficient

$$\alpha = \frac{1}{\ell_0} \left(\frac{\Delta \ell}{\Delta T} \right)_T$$

can be obtained directly as a function of temperature. This is most useful where the thermal expansion is not a simple function of temperature, e.g. negative expansion over a small temperature range.

RESULTS AND ANALYSIS

A convenient approach to the study of thermal expansion
is to consider the lattice frequency distribution to be a
function of volume (11). In this way a simple thermodynamic
development may be used. The following relationships,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

can be combined to give

$$\frac{\beta}{K_T} = \left(\frac{\partial S}{\partial V}\right)_T$$

where $\beta = \left(\frac{\partial \ln V}{\partial T}\right)_P$ and $K_T = -\left(\frac{\partial \ln V}{\partial P}\right)_T$ are the volume
coefficient of thermal expansion and isothermal compressi-
bility, respectively.

If a lattice free energy of the form

$$F(V,T) = U_O(V) + kT \sum_{i=1}^{n} f_i \left(\frac{\nu_i(V)}{T}\right)$$

is assumed, where U_O is the internal energy at absolute zero,
k is the Boltzmann constant, and ν_i is the frequency of the
phonon of the ith mode, it can be shown that β is given by

$$\beta = \Sigma \frac{\gamma_i C_i K_T}{V}$$

where C_i is the lattice specific heat and $\gamma_i = -\dfrac{d \ln \nu_i}{d \ln V}$

is the volume dependence of the frequency of the ith mode.

The Grüneisen constant is a weighted average of the γ_i's and

is given by

$$\gamma_L = \frac{\Sigma\, C_i \gamma_i}{\Sigma\, C_i} \, ,$$

so the thermal expansion coefficient is given by

$$\beta = \frac{\gamma_L\, C_v\, K_T}{V} \, .$$

A similar development can be made for the electronic

contribution of the thermal expansion for a metal, giving,

$$\beta_e = \frac{\gamma_e\, C_e\, K_T}{V}$$

where

$$\gamma_e = \left(\frac{d \ln \mathcal{N}(E_F)}{d \ln V}\right)_T$$

is the electronic Grüneisen constant and

$$C_e = \frac{2\pi^2\, k^2}{3}\, \mathcal{N}(E_F) T$$

is the electronic specific heat for the free electron model.

$\mathcal{N}(E_F)$ is the density of states at the Fermi surface. There

may be other contributions to the thermal expansion such as

those due to magnetic effects and spin pairing and in general

the total thermal expansion coefficient is given by

$$\beta = \beta_L + \beta_e + \beta_m + \beta_p + \ldots.$$

For dielectric solids the only contribution of import-
ance is the lattice thermal expansion. At low temperatures
the lattice specific heat is proportional to T^3 and to a good
approximation K_T and V are temperature independent, so

$$\beta = A_L T^3.$$

In isotropic materials (cubic crystal structure) the linear
thermal expansion coefficient α_L is given by $\beta/3$. This is
not true for an anisotropic material where α_L is a function
of direction.

Originally it was expected that sapphire would follow
the theoretical $\beta = AT^3$ low temperature behavior as no con-
duction electrons or significant magnetic contributions
should be present. However, earlier work by Carr (4) indi-
cated that the thermal expansion coefficient of a normal 60°
orientation single crystal was proportional to $T^{2.2}$. There-
fore a thorough investigation of the thermal expansion of
sapphire was undertaken. Sapphire has a hexagonal crystal
structure and its thermal expansion is anisotropic. Due to
the symmetry of the hexagonal structure, measurements on only
two samples are necessary to determine the thermal expansion
completely. For this reason a sample with the C-axis 60°
from the sample axis and a sample with the C-axis parallel

to the sample axis were obtained from Linde Company. The

sample sizes are shown in Table 1.

Table 1. Summary of successful runs

Run number	Sample	Reference temperatures	Sample length
IS	60° sapphire	1.89°K	10.04 cm
IIS	C sapphire	1.89°K, 12.93°K	10.40 cm
IIIS	C sapphire	1.89°K	10.40 cm
VS	60° sapphire	1.89°K	10.04 cm
IR	RbI	1.36°K, 1.89°K	5.46 cm
IIR	RbI	1.89°K	5.46 cm
IIIR	RbI	1.17°K, 1.89°K 8.10°K, 15.0°K	5.46 cm

The thermal expansions of sapphire from $1.89°K$ to $18°K$

are shown in Figure 9 and the data are presented in the

Appendix. The values of the linear thermal expansion coef-

ficients obtained are $\alpha(60°) = 1.78(\pm 0.02) \times 10^{-11}T^{2.2}/°K$

and $\alpha(C) = 0.42(\pm 0.01) \times 10^{-11}T^{2.6}/°K$. Since the crystal

structure of sapphire is hexagonal Voight's rule,

$$\alpha(\Phi) = \alpha_\perp \sin^2\Phi + \alpha_{||} \cos^2\Phi,$$

was used to determine the thermal expansion coefficient in

Figure 9. Sapphire thermal expansion
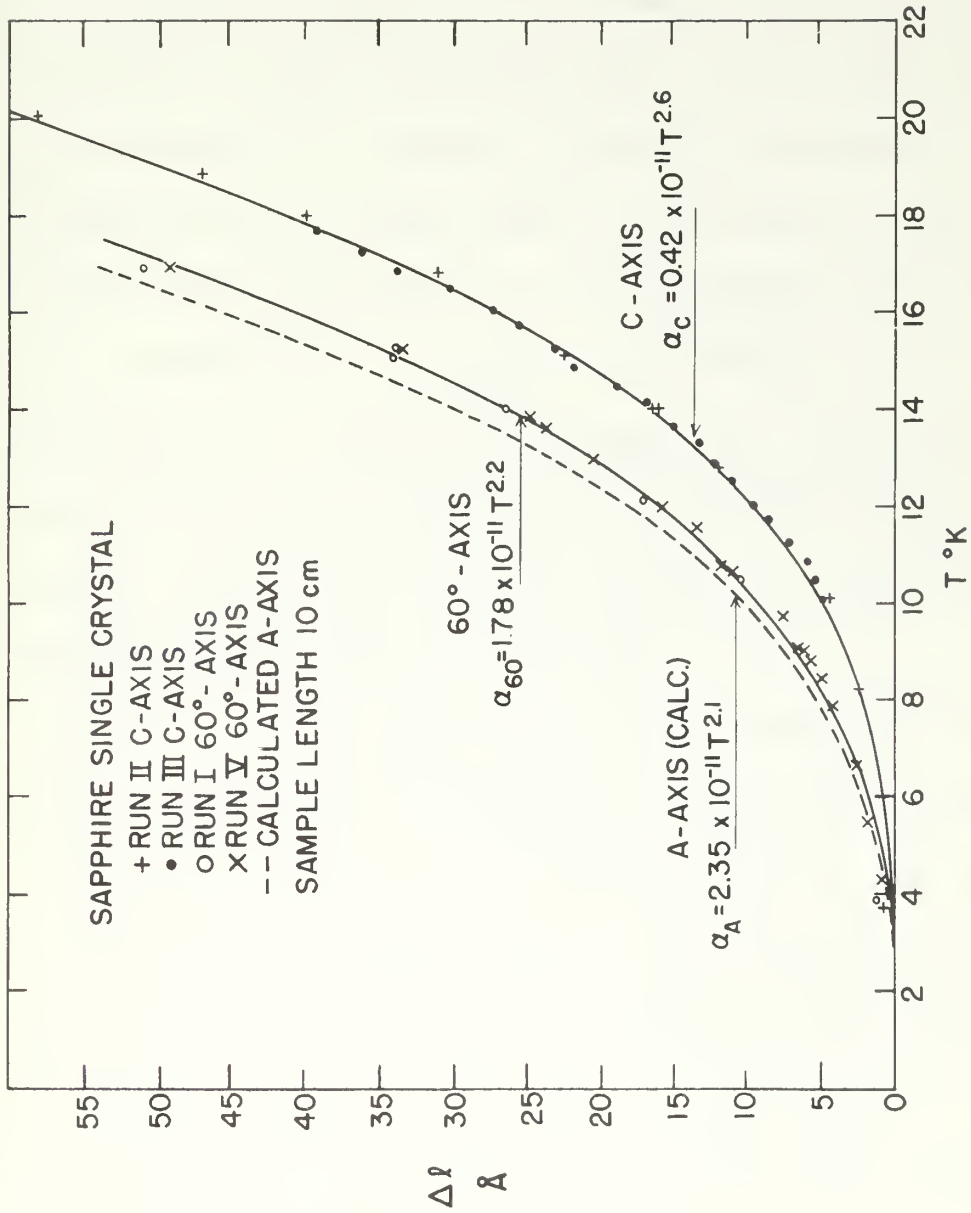
the basal plane. In this way it was determined that $\alpha(A) =$ 2.35 x $10^{-11}T^{2.1}/^{o}K$ and the volume coefficient β is 5.4 x $10^{-11}T^{2.15}/^{o}K$ to about $20^{o}K$. Aside from the fact that the thermal expansion of sapphire is extremely small there are two interesting results from these data. First, the temperature dependence of the thermal expansion coefficient is not T^3 as predicted by the Debye theory, but in fact varies from $T^{2.1}$ to $T^{2.6}$ depending upon the crystallographic direction. Since the coefficient is proportional to $\gamma C_V K_T/V$ and K_T and V are essentially not a function of temperature, the discrepancy between experiment and theory must be due to γ or C_V. Unfortunately no data for either of these quantities exist for sapphire in this temperature range.

Also, it is interesting to note that although at low temperatures the thermal expansion is greater in the basal plane than along the C-axis, due to the power of the temperature dependence the thermal expansion will ultimately be greater along the C-axis. This "cross-over" should occur at $35^{o}K$ although data were not taken in this region for the C-axis crystal as it was felt that the "cross-over" temperature would be much higher.

In practice the Grüneisen constant is a definite function

of temperature, and in some solids may even become negative

(12,13). An insight into this behavior may be obtained by

considering the phonon dispersion curves of a hypothetical

solid (see Figure 10). The left hand curve of the figure

(direction [x, y, z]) depicts the more typical mode of the

solid. As pressure is applied the curve rises and $\gamma_i =$

$- \dfrac{d \ln \nu_i}{d \ln V}$ is positive. However the curve on the right

(direction [a, b, c]) lowers at large k values upon the

application of pressure and γ_i will be negative for these
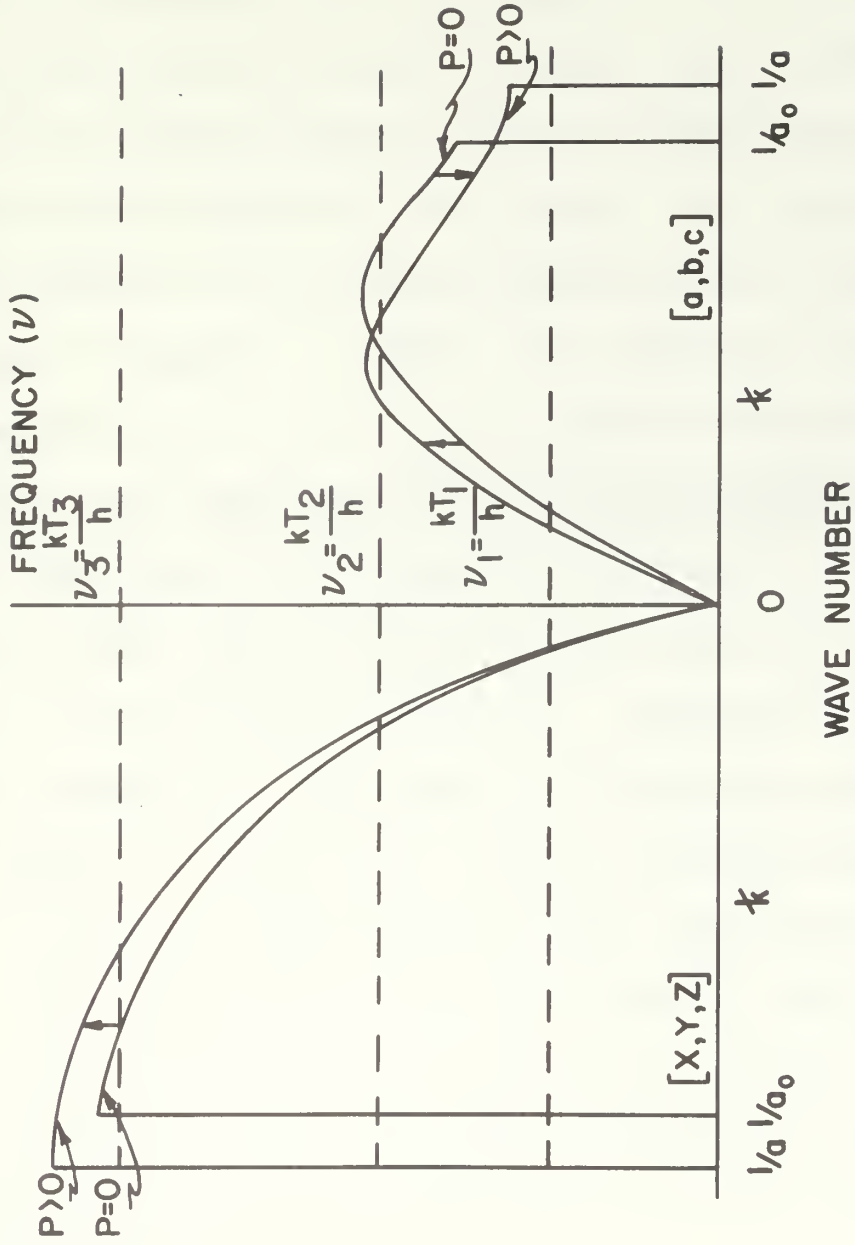
modes.

If there were only two types of dispersion curves in the

solid, the following behavior might result. The maximum fre-

quency excited always is of the order of kT. Hence, at low

temperatures, ν_{max} might correspond to ν_1 in the figure so

that the only excited states are those with positive γ_i's,

and the thermal expansion is positive. However, as ν_{max}

increases to ν_2 the modes of large k values with negative

γ_i's are occupied on the right hand curve. Since these

negative γ_i's are larger than those at smaller k values, γ_L

and, thus, the thermal expansion may become negative. As

ν_{max} increases to ν_3, even though the modes with negative

γ_i's are still occupied many more states of positive γ_i have

of temperature, and in some solids may even become negative

(12,13). An insight into this behavior may be obtained by

considering the phonon dispersion curves of a hypothetical

solid (see Figure 10). The left hand curve of the figure

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and, thus, the thermal expansion may become negative. As

ν_{max} increases to ν_3, even though the modes with negative

γ_i's are still occupied many more states of positive γ_i have

Figure 10. Phonon dispersion curve for an arbitrary solid

PHONON DISPERSION CURVES

been occupied and γ_L is positive again. At the present time
it is not possible to calculate these dispersion curves theo-
retically.

RbI is a compound which has negative γ's in some modes
(14). In fact, there is reason to believe that in some
samples γ_L is negative between 4^OK and 6^OK (15) giving a
negative thermal expansion in this region. One experimental
run was completed on the original apparatus which demonstrated
this negative expansion. However, that sample was destroyed
in an accident and it has not been possible to reproduce
these data. The sample used in the present experiment was
obtained from Daniels[1] who originally predicted a negative
expansion in RbI, and the results obtained from 1.17^OK to 8^OK
for three runs are shown in Figure 11. Although there is no
negative expansion for this sample, an inflection point
exists between 4.5^OK and 6.5^OK. Also, the overall expansion
in this temperature region is 40% greater than that obtained
earlier. White[2] has found a negative expansion from 2^OK to
9^OK and it is believed that his results are typical of the
thermal expansion of RbI. The large discrepancies between

[1]Daniels, W. B. RbI. Princeton, New Jersey (private
communication, 1963).

[2]White, G. K. RbI. Sydney, Australia (private communi-
cation, 1964).

Figure 11. Thermal expansion of RbI from 1.17°K to 8°K
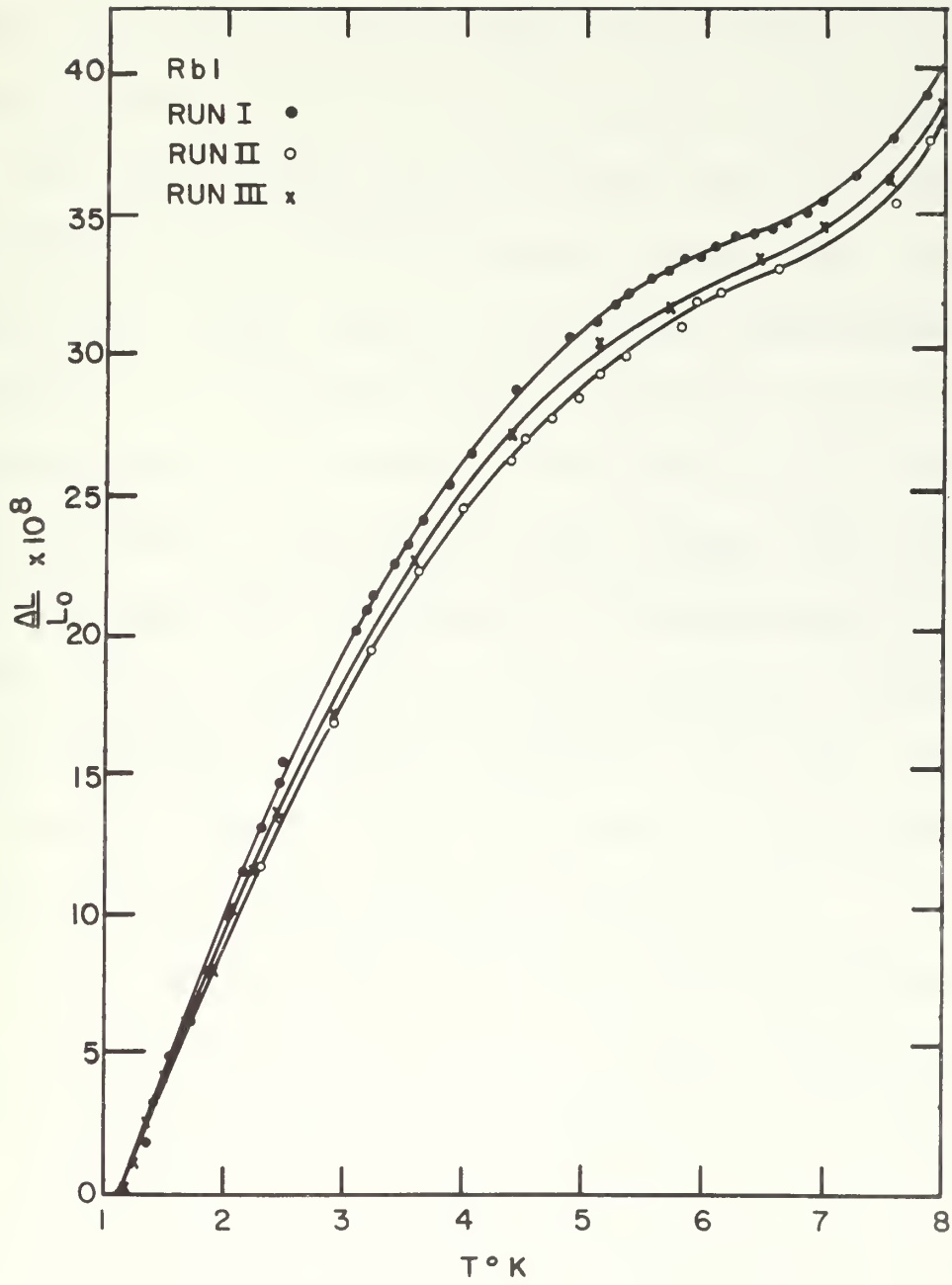
his results and the results obtained in this apparatus are believed due to the glued sapphire end spacers. When the sample was removed from the sample chamber there were fractures on the ends due to the differential contraction.

The value obtained for the thermal expansion coefficient at $1.5^{\circ}K$ is $9.9 \times 10^{-8} (^{\circ}K)^{-1}$, whereas White found a coefficient in this region equal to zero within experimental accuracy. It is believed that the increase in the thermal expansion due to the strain in the crystal may be reflected in an increase in the specific heat although there are no data to support this hypothesis. The separation of the curves between the three runs is not understood although they correspond to a higher pressure on the sample ends due to loading. The upper curve corresponds to the highest pressure and the curves merge again above $8^{\circ}K$.

Data were also taken from $8^{\circ}K$ to $30^{\circ}K$ and although the expansion is quite large no anomalies were observed (see Figure 12). The temperature dependence of the thermal expansion coefficients in this region varies from $T^{4.3}$ to $T^{3.5}$ with increasing temperature. The thermal expansion coefficients of this sample at $17.5^{\circ}K$ and $28.4^{\circ}K$ are $4.73 \pm 0.04 \times 10^{-6} (^{\circ}K)^{-1}$ and $16.35 \pm 0.05 \times 10^{-6} (^{\circ}K)^{-1}$ respectively.

Figure 12. Thermal expansion of RbI from 8°K to 22°K
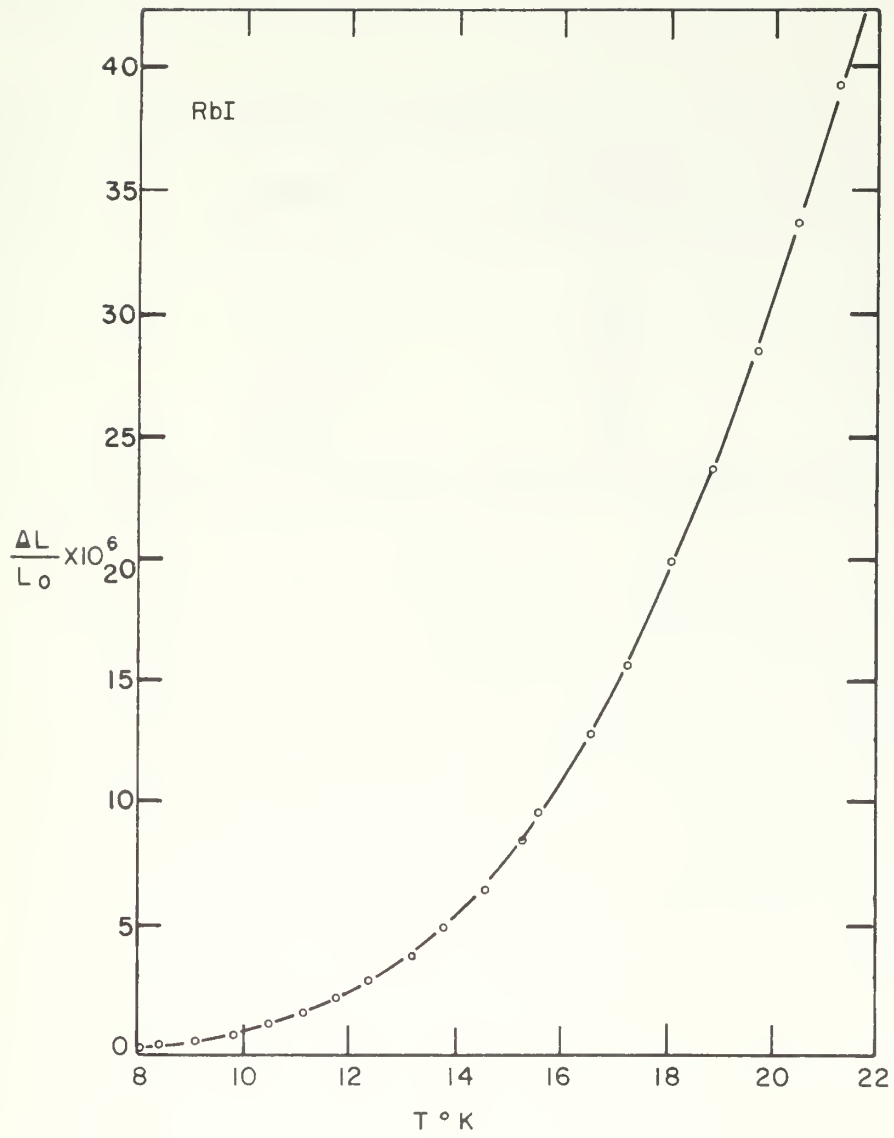
These values are 50% greater than those given by Schuele (14)
and 25% greater than those found by White. A spectrographic
analysis of the samples used in this experiment yielded very
low impurity levels (see Table 2).

Table 2. Spectrographic analysis

Element	Amount	Element	Amount
Na	$< 0.1\%$	Ca	Trace
K	$< 0.1\%$	Cu	Trace
Rb	35.5%	Fe	Trace
Cs	$<1.0\%$	Mg	Faint trace
Al	Trace	Si	Trace

CONCLUSIONS

The sensitivity and range of the original mutual in-
ductance thermal expansion measuring apparatus have been
extended by the modifications discussed above. The sensi-
tivity, $\pm$ 0.2$\overset{\text{o}}{\text{A}}$, is necessary to detect expansions of the
order of 1 part in 10^{10}, such as occur in sapphire at 3°K.
The bridge range has been extended from 600$\overset{\text{o}}{\text{A}}$ to 50 microns.
This is necessary for the measurements of the thermal expan-
sion of substances like RbI which at 20°K has 600 times the
total expansion of sapphire. The extension of the lower
limit of the helium bath temperature to 1.17^{o}K by installing
a 3 inch pumping line is very useful in determining the low
limit behavior of solids with low θ_D's. The versatility of
the original apparatus has been greatly increased by these
improvements and it is hoped that the thermal expansion of
a large variety of substances can be studied routinely.

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ACKNOWLEDGMENTS

APPENDIX

Sapphire Thermal Expansion Data

$60°$-axis   L = 10.04 cm

ΔL	T	ΔL	T
	Run I		Run V
32.9Å	15.25°K	6.0Å	9.02°K
16.6	12.11	4.9	8.42
1.0	3.88	4.1	7.84
33.3	15.01	2.4	6.65
92.4	20.9	2.0	5.41
140.5	23.7	.8	4.31
60.1	18.04	15.3	11.99
25.8	13.98	13.0	11.52
10.1	10.47	10.6	10.60
49.9	16.92	7.0	9.71
123.0	22.7	5.5	8.80
261.9	28.7	19.9	12.95
528.7	35.1	24.2	13.83
		6.4	9.05
		11.4	10.76
		23.0	13.56
		32.8	15.18
		48.3	16.96

Sapphire Thermal Expansion Data

C-axis   L = 10.40 cm

ΔL	T	ΔL	T
Run II		Run III	
.5Å	3.67°K	4.7Å	10.06°K
2.3	8.20	21.0	14.81
15.7	14.01	35.4	17.25
39.2	18.00	29.5	16.47
57.1	20.04	24.9	15.70
46.0	18.84	21.2	14.86
30.4	16.79	16.5	14.11
22.0	15.12	12.9	13.30
16.0	13.98	10.8	12.49
11.6	12.77	8.3	11.68
4.2	10.05	5.7	10.84
		5.2	10.42
		7.0	11.22
		9.3	11.99
		11.6	12.85
		14.7	13.62
		18.4	14.42
		22.5	15.22
		26.6	16.03
		32.9	16.81
		38.3	17.62