

HEAT CAPACITY OF METALS

1.0 References

C. Kittel, "Introduction to Solid State Physics" (John Wiley, N.Y.)

H. M. Rosenberg, "Low Temperature Solid State Physics" (Oxford 1963)

W. A. Harrison, "Solid State Theory" (McGraw Hill, N.Y. 1970)

N. W. Ashcroft and N. D. Mermin, "Solid State Physics" (Holt, Rinehart & Winston, 1976)

2.0 Introduction

In this experiment you measure the specific heat of Ni and Nb between 4.2 and 300K. You will learn experimental techniques appropriate for low temperatures and the handling of cryogenic fluids.

3.0 Theory

The specific heat is the change of total energy with temperature

$$C = \frac{\partial E}{\partial T} \quad (1)$$

and thus consists of contributions of a variety of elementary excitations at different temperatures. Above the Debye temperature all phonons are excited, and the heat capacity of nearly all solids approaches the constant value

$$C = 3Nk_B = 25 \text{ J mol}^{-1} \text{ deg}^{-1} \quad (2)$$

where N is the number of atoms in the sample. At sufficiently low temperatures only the acoustic phonons are excited and the phonon part of the specific heat is proportional to T^3 . In metals there is in addition an electronic contribution proportional to T so that at sufficiently low T

$$C = \alpha T^3 + \gamma T \quad (3)$$

The two terms can be separated at low T by plotting C/T against T^2 below $T \approx 18\text{K}$, but above T_C . The $T = 0$ intercept of this plot yields γ which is proportional to the density of electronic states at the Fermi energy. The slope of the plot is α from which one determines the Debye temperature.

Niobium becomes superconducting at $T_C \sim 9\text{K}$. At this critical temperature a gap opens up in the electronic density of states as a result of Cooper pair formation. The Bardeen-Cooper-Schrieffer theory predicts a sudden increase of the electronic heat capacity

$$(C_S - C_n)/C_n = 1.43 \quad (4)$$

as the metal becomes superconducting followed by a rapid decrease of C_S below T_C . Here the subscripts s and n designate the superconducting and the normal state, respectively. For several superconductors, including Nb, this discontinuity is larger than predicted, as shown in Fig. 1. The discontinuity is caused by a sudden change in entropy at T_C .

4.0 Equipment

4.1 Samples

Two cylindrical samples of Ni and Nb, about 1" long and 0.5" diameter, are mounted vertically in a stainless steel tube as shown in Fig. 2. Their masses are $27.89 \pm 0.05\text{g}$ for Ni and $24.20 \pm 0.05\text{g}$ for Nb.

Ideally one would like to cool the samples to very low temperatures, then isolate them thermally completely from their surroundings, and measure the temperature rise ΔT caused by a known amount of energy ΔE provided. We have to approximate this ideal situation as well as we can by holding the samples with very small, thermally insulating supports and by using very thin and long electrical leads which make contacts to the heater wire and the thermometer. Moreover, the heat capacity of the heater, the thermometer as well as of any glue and other material attached to the sample must be small compared to that of the sample. Alternatively, these additional contributions must be measured or calculated separately and subtracted. We shall list these materials below.

Each sample rests on a toothpick and is constrained sideways by thin rubber rings that are slipped over four 1/16" diameter brass posts that hold the sample cage. The temperature of each

sample is measured by a DT-500 Silicon diode thermometer, 0.2 cm x 0.2 cm x 0.1 cm coated with a thermally conducting compound, and attached to the top of the sample.

One layer of cigarette paper is glued with GE 7031 varnish around each cylindrical sample to provide thermal contact but electrical insulation to the heater wire which is wound around it. This heater is a thin manganin wire (30 Ω /foot). Thermal contact is provided with a thin coat of GE 7031 varnish. Manganin is an alloy of copper and manganese and was chosen because its resistance is relatively independent of temperature. At 300K the manganin heater of the Ni sample has a resistance of about 86.7 Ω , that of the Nb sample about 87.6 Ω . The electrical leads to the heater have a total resistance of 8.0 Ω . These 8 Ω have to be subtracted from your measurements on the outside terminals in order to determine the true resistances of the manganin heaters. Table 1 shows the temperature dependence of the resistance for manganin.

Table 1

<u>T(K)</u>	<u>R(T)/R (300K)</u>
300	1
250	0.997
78	0.945
34	0.916
4.2	0.887

The heater wires are connected to a heat pulser which allows you to apply a 5 second pulse of a known current. The current is user selectable from 5mA to 300mA.

Knowing the resistance of the heater wire, the magnitude and duration of the current you can calculate the power dissipated into the sample. The resultant increase in temperature is measured by the Si-diode and can be read, in Kelvins, from the front panel of the LakeShore Cryotronics temperature readout.

Contacts to the Si-diode thermometer and the heater are made with 6 cm long No. 38 copper wires wound in the shape of a short spiral. A typical temperature dependence of the forward

voltage of the DT-500 silicon diode with 10 μ A constant current is shown in Fig. 3. The Lake Shore sensor unit provides a digital readout in Kelvins as well as an analog voltage.

Heat contact between the samples and their surrounding is provided by admitting about 1 Torr helium gas into the sample chamber. Heat isolation is achieved by evacuating the sample chamber.

The samples are not completely thermally isolated from their environment. There is some heat transferred to the samples through the heater and diode wires for example. This effect is negligible near room temperature but causes a significant temperature drift at liquid helium temperatures that must be accounted for. The current and voltage outputs from the heat pulser, and an analog output from the LakeShore temperature readout, are also hooked up to a Keithley 2700 scanning DMM. The scanner, controlled by computer, can then be used to repeatedly scan and record the temperature and heater voltages and currents before, during and after the application of a heat pulse to a sample. Using this data the temperature change due to thermal coupling with the environment can be determined.

4.2 Admitting And Pumping Helium Thermal Exchange Gas

Helium gas provides good thermal conduction between the samples and the surrounding liquid He. All other gases become frozen at 4.2K. One needs no more than 1 Torr He gas because the thermal conductivity of gases becomes independent of pressure as soon as the mean free path gets smaller than the container dimensions. Fig. 4 shows the pump and gas handling system attached to the sample chamber. The mechanical forepump must run before you turn on the turbomolecular pump. When you switch off the turbomolecular pump at the end of the experiment, it keeps on running for 5 minutes because of its rotational inertia. Keep the turbomolecular pump clean and under vacuum by closing both entrance and exit valves before turning off the turbomolecular pump.

You admit a small amount, about 1 Torr He gas to the sample chamber by first putting some He gas into the small volume between valves V1 and V2 while V1 is closed; then close V2 and open

V1 for a short time and close V1 again. If you do not overfill the sample chamber with He gas then the turbomolecular pump has no trouble evacuating the chamber for heat insulation.

The sample chamber has to be evacuated and supplied with a few Torr of He gas before you start cool-down by filling liquid nitrogen into the outer dewar which is called the liquid nitrogen dewar. The liquid He cryostat and the cool-down procedure will be described next.

4.3 Liquid Helium Cryostat And Its Operation

A simple all-purpose liquid He cryostat is sketched in Fig. 5. It consists of two Dewar vessels, one inside the other. The outer one has a permanently sealed vacuum jacket and will be filled with liquid nitrogen. The inner dewar has a vacuum jacket which is connected to a pump and an air line for the following reasons. The vacuum jacket of the inner Dewar thermally isolates the liquid helium inside this innermost Dewar from the temperature of liquid nitrogen. The vacuum jacket of the liquid He dewar is not permanently sealed because some He diffuses through the Pyrex glass and then acts as a thermal conductor. Therefore before starting any cooling, this inner vacuum jacket has to be pumped with a forepump, backfilled with air and pumped again at least three times. After the last pumping of this helium Dewar vacuum jacket and after closing the pump valve there is only some air but no He in the vacuum jacket. This last bit of air will freeze out as soon as liquid He is put into the inner He Dewar, thus providing an excellent vacuum in the jacket (unless you forgot to close the valve of the vacuum jacket). The operation of the He cryostat will be described in simple logical steps. You might wish to use this as a check list.

1. Check the electronics of your experiment. Everything has to be in working order before you begin the cool-down. Measure the resistance of the heaters at room temperature.
2. Pump out air from the liquid He Dewar and fill in He gas with a small overpressure (about 0.1 atmosphere overpressure).
3. Pump the vacuum jacket of the He Dewar, backfill with air, pump and backfill with air... three times... finally pump and close vacuum jacket valve.

4. Pump sample chambers with turbomolecular pump. Calculate the number of Joules needed to achieve a temperature rise of about $\Delta T = 2\text{K}$ at room temperature. Measures the specific heat of Nb and Ni at room temperature.
5. Close the valve to the turbopump, and admit about 1 Torr He gas into sample chamber by first admitting He gas into the small volume between valves V1 and V2 while V1 is closed. Then close V2 and open briefly V1 and close V1 again.
6. Fill the outer dewar with liquid nitrogen. Close the opening with a ring of tissue or paper towel to prevent moisture from condensing in the liquid N₂. Refill liquid nitrogen as needed to keep the liquid level within 2" from the rim.
7. At about 4 temperatures, about 260K, 220K, 180K and 140K, evacuate sample chamber with the turbopump, measure the specific heat (probably with less Joules) of both samples. Determine the resistance of the heaters. Subtract the 8 Ω of the leads from your measurements. Subsequently admit about 1 Torr of He gas so that sample can proceed cooling down.
8. After 45 minutes you will notice that the rate of cooling has decreased. Perhaps the sample is near 110K. Pump out He gas from sample chamber with turbomolecular pump and measure the specific heat. Determine the resistance of the heaters. Subtract the 8 Ω of the leads from your measurements. When everything is working well, close valve of pump and readmit about 1 Torr He gas into sample chamber by way of valves V1 and V2. You are now ready to transfer liquid Helium.
9. Check that the He Dewar has about 0.1 atmosphere overpressure. Blow He gas through the liquid Helium transfer line and close valve of transfer line (rotating brass section).
10. Release the He gas overpressure of the He Dewar and open the valve of the He Dewar to the outside atmosphere to allow He vapor to escape during transfer.
11. Insert transfer line into liquid He storage vessel and into your helium Dewar with the valve end of transfer line (rotating brass section) into your helium Dewar.
12. Tighten the O-ring seals around both sides of the transfer line.

13. Put a small amount (0.05 atmosphere) of He gas overpressure on the liquid He storage vessel and open the valve (rotating brass section) of the liquid He transfer line. Since there is overpressure on the liquid He in the storage vessel whereas the He Dewar is open to atmosphere, liquid He is forced out of the storage vessel through the transfer tube into the He dewar. The evaporating He can escape into the room because you kept the valve open. You notice the first transfer by the cooling of the pipe and the escape of He gas through the open valve between the He Dewar and the room. You will also notice that the temperature of your sample first increases a bit and then plunges to low temperatures.
14. Now you have to watch the rise of the level of liquid He in your He Dewar. Switch on the fluorescent light. You have to get ready to stop the flow before it is full because it takes you some time to stop it. When the Dewar is 1/2 - 2/3 full, switch off the He gas overpressure on the storage vessel and close the transfer line valve (rotating brass section).
15. Release any overpressure of the storage vessel. You now can pull out the transfer tube and right away close the transfer openings with the plugs on both the storage vessel and on your He Dewar.
16. Put the transfer tube in a safe place, it is a delicate and expensive object. Move the storage vessel to a safe place.
17. Measure the resistance of the heaters at the temperature of Helium. Do not forget to subtract the 8Ω resistance of the leads.. Keep the outer nitrogen Dewar filled with liquid nitrogen.

4.4 Heat Capacity Measurements

The circuit sketched in Fig. 6 allows you to select a current and time interval and thus to subject the sample to a known heat pulse ΔE . You measure the resultant temperature rise ΔT . However, first pump out the sample chamber so that the sample is thermally isolated from its environment. The heat capacity measurements at room temperature and down to about 110K have already been described in the previous section, F 4, 7 and 8. Important note: Remove or disconnect

the meter used for determining the heater resistance before measuring heat capacity. We now describe the procedure for the temperature ranges 4 - 16K and 16 - 100K.

4.4.1 Measurements Between 4K And 16K.

Most of the interesting physics occurs here and you use these data to determine α and γ of Eq. (3). The heat capacity of the samples is very small. As soon as you evacuate the sample chamber with the turbopump, the sample temperature will be rising even without a heat pulse because of radiation heating coming down the stainless steel tube from the top which is at room temperature and because of heat conduction through the electrical leads. Because of the small heat capacity start with a small current pulse such as 5 mA. Since you measured the manganin heater resistances near 4.2K as well as at higher T, you need not measure them between 4.2K and 16K. Keep the turbopump pumping the sample chamber while you take measurements between about 4K and 16K.

You can measure $\Delta E/\Delta T$ despite the drift in temperature if you record the drift before and after the electrical heat pulse and carry out the appropriate extrapolations as shown in Fig. 7. Particularly at low temperatures, high accuracy and many data points are needed in order to separate the contributions of electrons and of phonons and also to determine the rapidly changing specific heat curve near and below the superconducting critical temperature of Nb. Measure first Ni between 4.2K and 16K and then Nb between 4.2K and 16K, each will take less than 10 minutes.

You can always return to $T = 4.2\text{K}$ and start over again by

- (a) closing the valve to the turbomolecular pump,
- (b) admitting about 1 Torr of He gas to the sample chamber through valves V2 and V1, and
- (c) when you are ready to resume your measurements, by pumping out the He gas with the turbomolecular pump.

As previously mentioned, low temperature data is collected using a computer controlled scanning DMM. Before starting the Data Acquisition (DAQ) software, first make sure that the Keithley 2700 DMM is turned on and *Rear Input* is selected on the front panel. The DMM should

be connected to the computer via serial cable. Start the DAQ by double clicking on the CvsT_DAQ icon on the desktop. Alternatively you can start the program from the Start Menu. On startup the program will initialize the DMM for serial data transfer and configure the scanner.

The right hand side of the DAQ window normally shows user selectable plots of all the data that has been scanned and is stored in memory. Using the pull down menus, located at the top of each plot, you can select which of the four scanner channels gets displayed on each plot. Immediately after a new scan four plots showing the data collected from each channel will momentarily replace the normal two plot display.

The left hand side of the DAQ window contains a tabbed control panel. There are four tabs, selectable by the mouse, which allow you to display various information and control panels. The available displays are:

- *Instructions.* Displays a short set of instructions for using the DAQ software.
- *Configure Scanner.* This tab allows you to change the default voltage and current ranges for the scanned channels.
- *Operate Scanner.* Collecting and saving data is accomplished from the controls in this tab.
- *Exit.* Allows you to gracefully exit the DAQ software.

Once the DAQ is setup and the samples are at 4.2K use the following procedure to collect data.

1. Make sure that the heat pulser and the LakeShore temperature readout are both set to the same sample, either the Ni or the Nb. Failure to double check this could result in heat pulses being sent to one sample while monitoring the temperature of the other sample. This would be a sub-optimal data collection strategy.
2. From the DAQ software initiate a scan by clicking the *Start Scan* button. The scanner should start making rapid clicking noises.

3. Five seconds after initiating the scan press and release the momentary toggle switch on the heat pulser box to start a 5 second heat pulse.
4. At the end of the scan the data will be transferred to the computer. Immediately following the transfer the data from all four scanner channels will be displayed graphically and you will be given the option to keep or discard the data. The four channels scanned include the Si Diode voltage, the heater current, the heater voltage to the Ni sample and the heater voltage to the Nb sample. A good scan should show a distinct change in the Si Diode voltage in synchronization with the current pulse. The heat pulse should be well centered in the data stream with about 5 seconds of pre- and 5 seconds of post-pulse data. If the data looks acceptable select *keep* scan and the data will be held in the computers memory.
5. You can now go back to step 1 and repeat the process for another scan. Repeated heat pulses will continue to heat the sample. In this fashion you can work your way up to ~16K and then start over with the other sample at 4.2K.

Note that as you take multiple scans the data are appended into one long data stream until you choose to *Save* the data. The two default plots which the DAQ displays will show the entire data stream which resides unsaved in memory. It is **highly recommended** that you save your data periodically, a counter in the DAQ indicates the number of unsaved scans which are currently in memory.

Saved data will be written to an ASCII text file as 9 columns of numbers, the first column is an arbitrary scan number with the first scan in the file numbered 1. Each individual channel of data is represented by two columns of numbers, one containing the actual scanned reading and the other containing the time stamp associated with each reading. Once you save, all data in memory are deleted.

Note that the data from the Si Diode will be voltages that need to be converted into temperatures. Each of the two Si diodes used in this experiment, one for the Ni sample and one for the Nb sample, has its own calibration curve as supplied by the manufacturer for temperatures

below 80 degrees K. The calibration data for the two diodes is available from the kerstenlabs.uchicago.edu web site, available from on-campus only.

Repeat the measurements between 4.2K and 16K until satisfied. Note: Do not choose ΔT too small. A good choice is $\Delta T/T \approx 0.02$.

4.4.2 Measurements Between 16K And 100K.

In this temperature range measurements are very easy. The heat capacity has become so large that the temperature rise between heat pulses is negligible. You therefore no longer need the scanning DMM, however, you may continue to use it if you so choose. Continuously pump the sample chamber with the turbomolecular pump. If you prefer you can record data at these temperatures by hand in your notebook. Read the temperatures before the heat pulse and a short time afterwards when the temperature is nearly steady again. Always remember to note down heat pulse current $I(\text{mA})$ and duration $\Delta t(\text{sec})$. Take say 10 data points for Ni then 10 data points for Nb, then again 10 data points for Ni and 10 data points for Nb and so on covering the range from 16K to 100K.

This finishes your experiment because you have measured the heat capacity between 110K and 300K while cooling with liquid nitrogen.

4.5 Shutting Equipment Off When Finished

1. Switch off Keithley DMM, heat pulser, Lakeshore silicon diode thermometer, and other electronic components on table.
2. Close turbomolecular pump valve to sample chamber. Close the valve between turbo pump and rotary forepump. Switch off turbopump.
3. Make sure that top of liquid nitrogen Dewar is closed with tissue to prevent moisture from condensing into it.
4. Turn off rotary pump and open air relief valve (See Fig. 4). Close air relief valve.

4.6 A Note Of Caution Concerning The Lakeshore Digital Temperature Readout

The silicon diode temperature sensors are very convenient for this experiment because they are small, have a small heat capacity and a good voltage response as a function of temperature as illustrated in Fig. 3. There is, however, one peculiar feature in the digital readout circuit which provides temperature in Kelvin. The smooth voltage - temperature curve of Fig. 3 is approximated by a series of tangents. As the temperature changes, the instrument moves from one tangent to the next. This change causes a discontinuity in the slope of the $V(T)$ curve. For most applications this algorithm works well. However, our data analysis, explained by Fig. 7, is sensitive to the slope $\Delta V/\Delta T$. Thus, while the true slope changes smoothly, the digital readout changes discontinuously. In order to by-pass this problem, we measure the actual Si diode voltage, not the digital readout in the most sensitive temperature range.

5.0 Evaluation Of Results And Of Experiment

Estimate the systematic and statistical errors of your results.

Question 1.

Give a physical argument explaining why the electronic specific heat is proportional to T and why the low T part of the phonon contribution is proportional to T^3 . Why does the specific heat approach a constant value above the Debye temperature Θ_D and what is the physical meaning of Θ_D ?

You probably need not be reminded that Eq.(3) applies only to the low temperature range in which the metal is normal and not superconducting.

Question 2.

Compare your measured Heat capacities with the literature values. From the literature values calculate the density of electronic states $D(E)$ at the Fermi level E_F in units $\text{cm}^{-3} \text{eV}^{-1}$.

Question 3.

What gives rise to the change in temperature of the sample at low temperatures when no energy is supplied via the heater (the background drift of the sample temperature)?

Question 4.

Estimate the heat received by the sample at low temperatures from radiation and by heat conduction through the wires connecting the heater and the thermometer with your electrical circuitry. What fraction of the total heat capacity is due to the heater wire, the cigarette paper, the glue, and the Si-diode thermometer (see data provided in section 5.1)?

Question 5.

In order to get a feel of the different values of the heat of vaporization per cm^3 of liquid He and liquid N_2 calculate how many cm^3 of liquid He evaporates when you cool the nickel sample from 100K to 4.2K and from 300K to 100K. What volume of liquid N_2 would evaporate in cooling the nickel sample from 300K to 100K? The heat of vaporization and density of cryogenic liquids are listed on p. B-365 of the CRC Handbook of Chemistry and Physics 65th edition.

5.1 Materials Attached To Each Sample

$0.0159 \pm 0.0002\text{g}$ cigarette paper

$0.0331 \pm 0.0002\text{g}$ nichrome wire

$0.0172 \pm 0.0002\text{g}$ GE 7031 varnish

Three 7cm long 0.0086cm diameter copper wires connecting the diode thermometer and the heater to three 100cm long 0.025cm diameter copper wires that connect to the top of the apparatus.

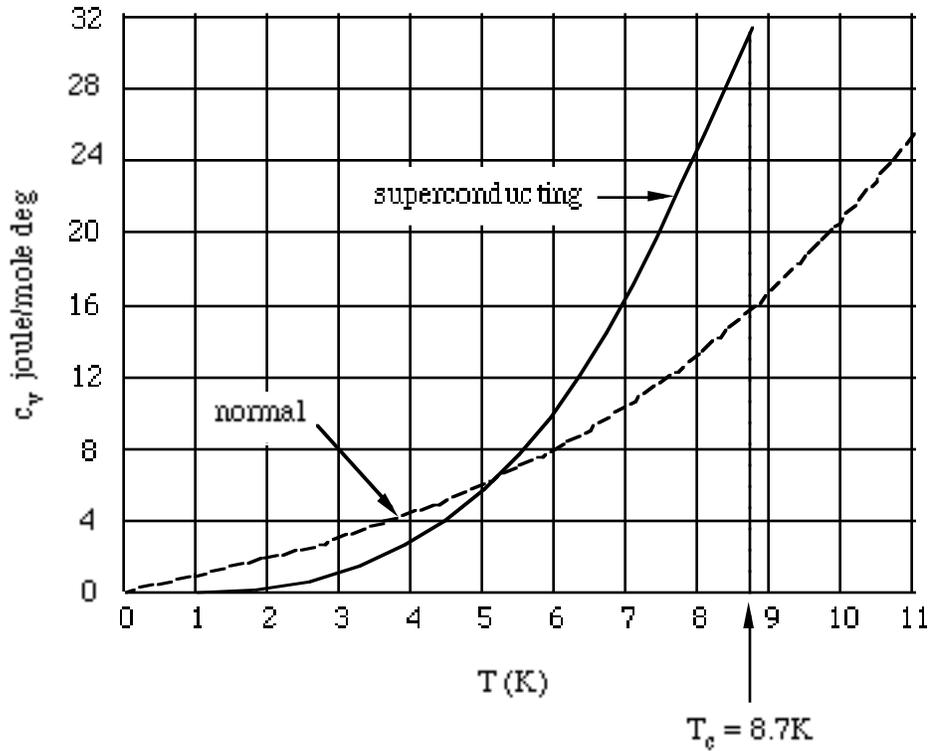


Fig. 1 Specific heat of normal and superconducting Nb at low temperatures. The normal state was achieved by applying a large magnetic field. -- H.M. Rosenberg, Low Temperature Solid State Physics Oxford, 1963, page 159.

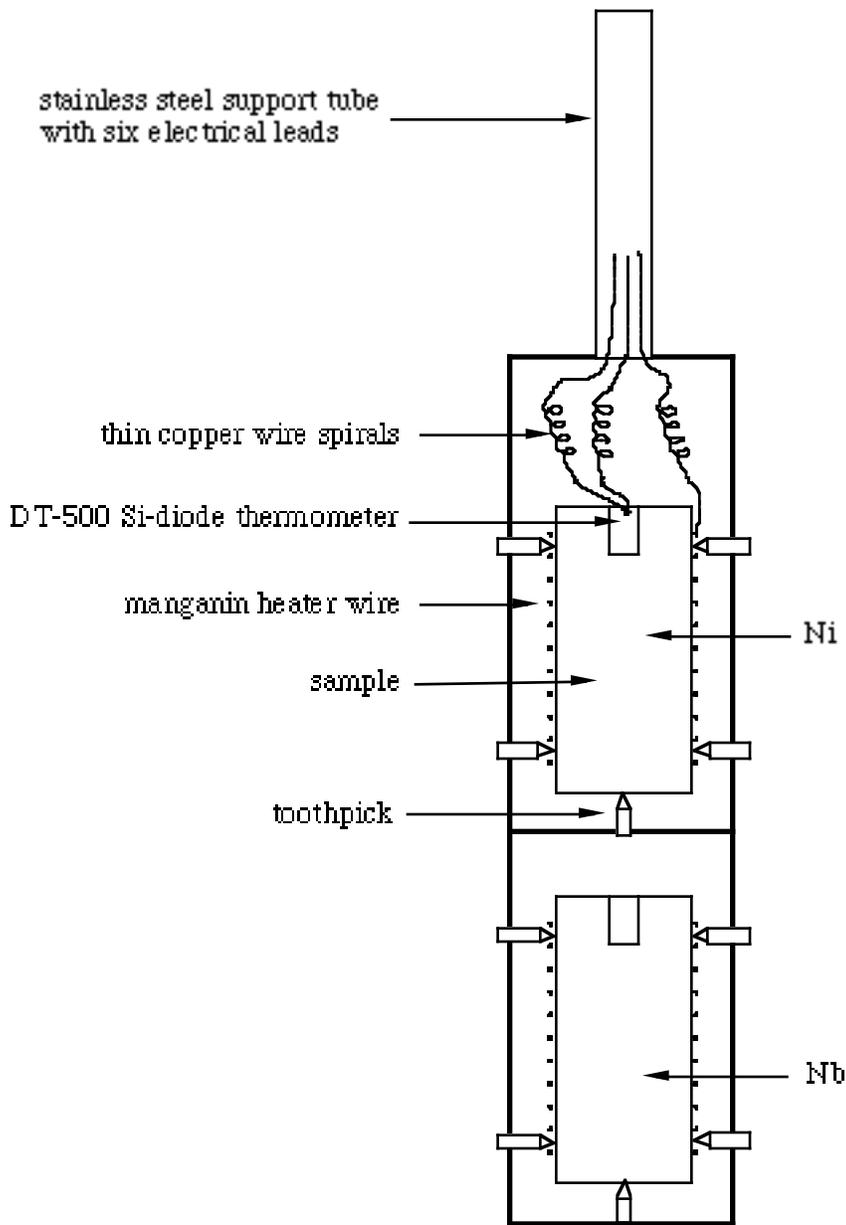


Fig. 2 Niobium and Nickel samples mounted above one another. Electrical connections to top sample are shown. This sample holder is inserted in 7/8" diameter thin wall stainless steel tube (not shown) which is the sample chamber.

A photograph of the mounted samples is attached to the wall near the experiment.

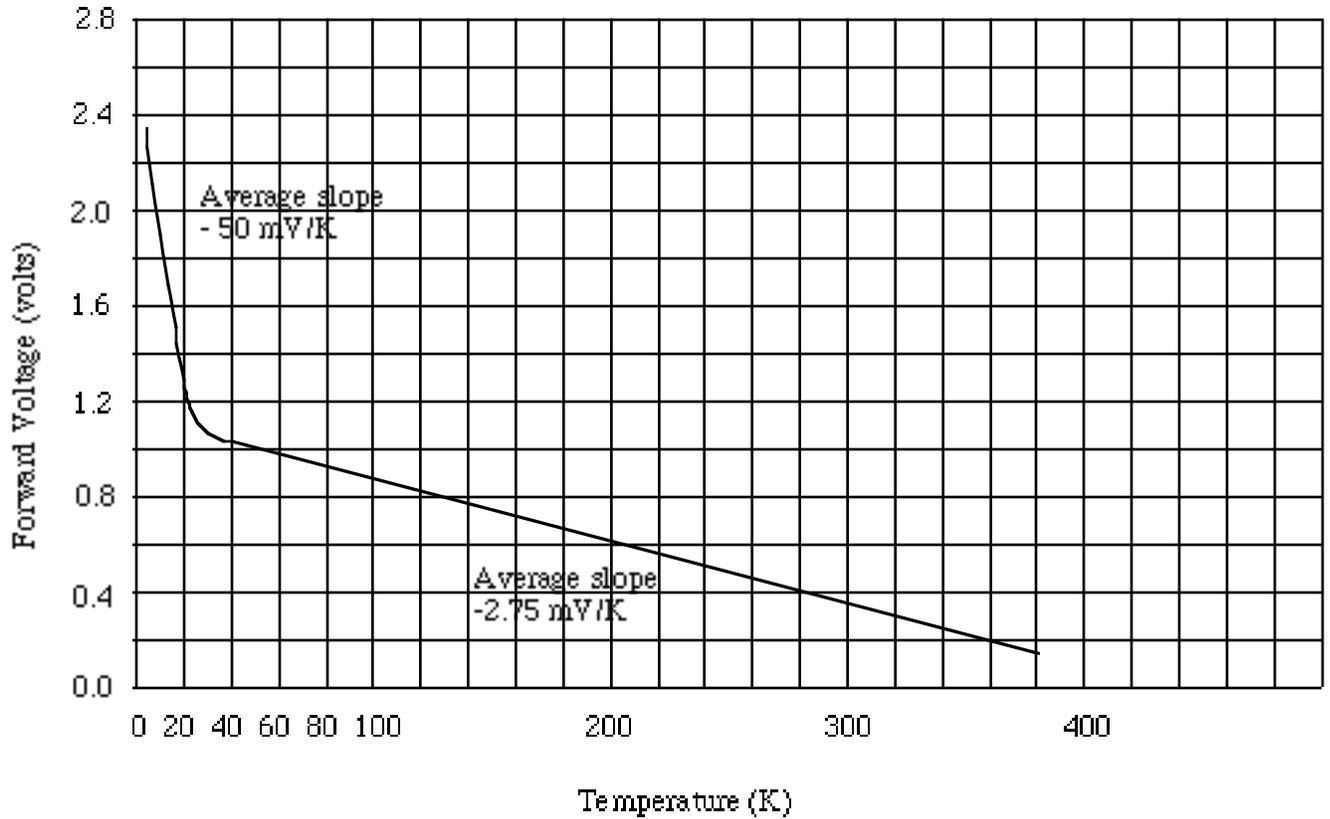


Fig. 3 Typical Temperature response curve of DT-500 silicon-diode Sensor with 10 μ A excitation current.

Note: The I(V) characteristics of a p-n junction diode is $I = C \exp(-e\phi/kT)[\exp(eV/kT) - 1]$, where ϕ is the built in barrier potential of the p-n junction. As the temperature T decreases, an increasing forward bias voltage V is needed to supply a constant current $I = 10 \mu$ A.

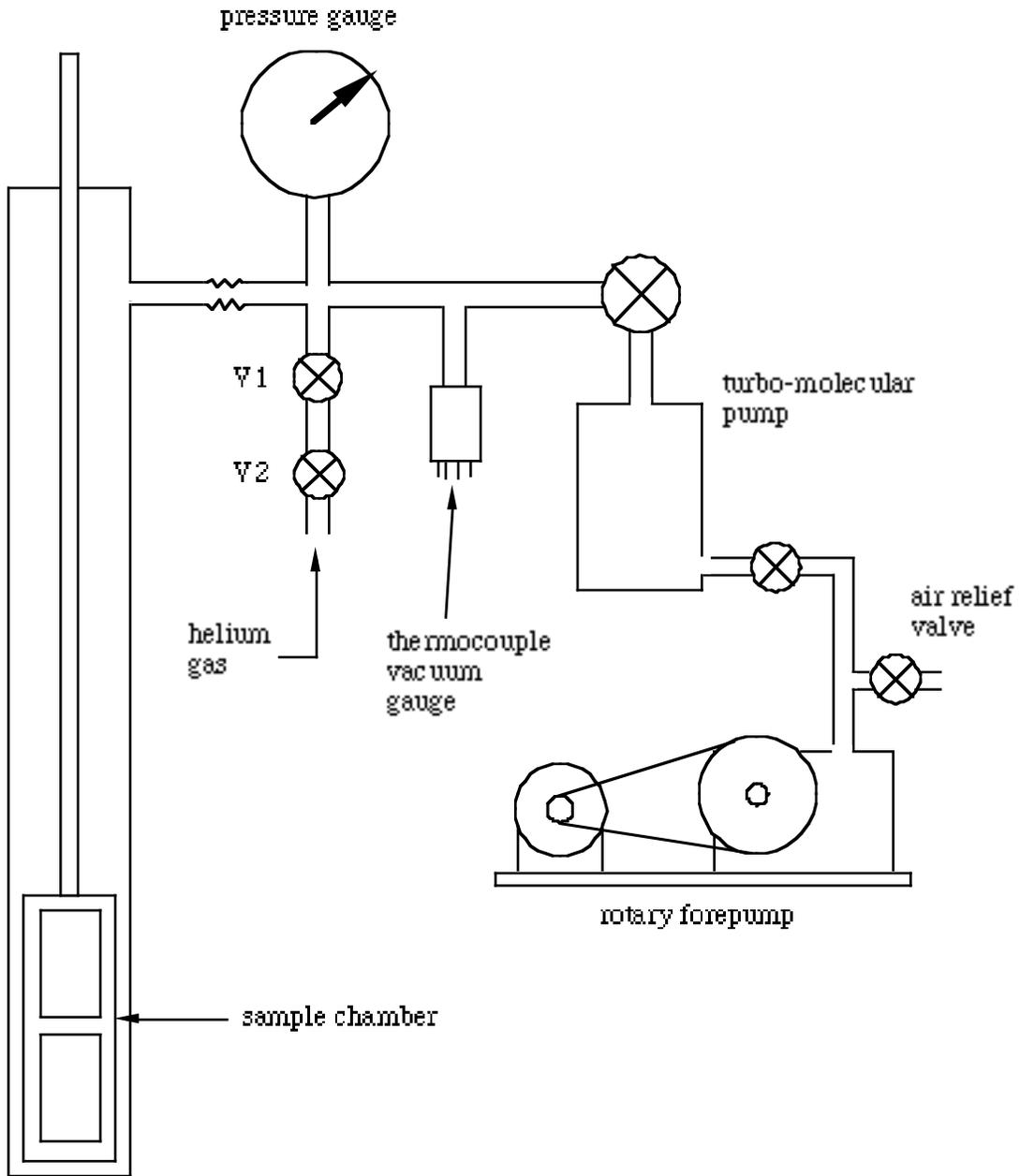


Fig. 4 Sample Chamber with pumps and He gas inlet valves.

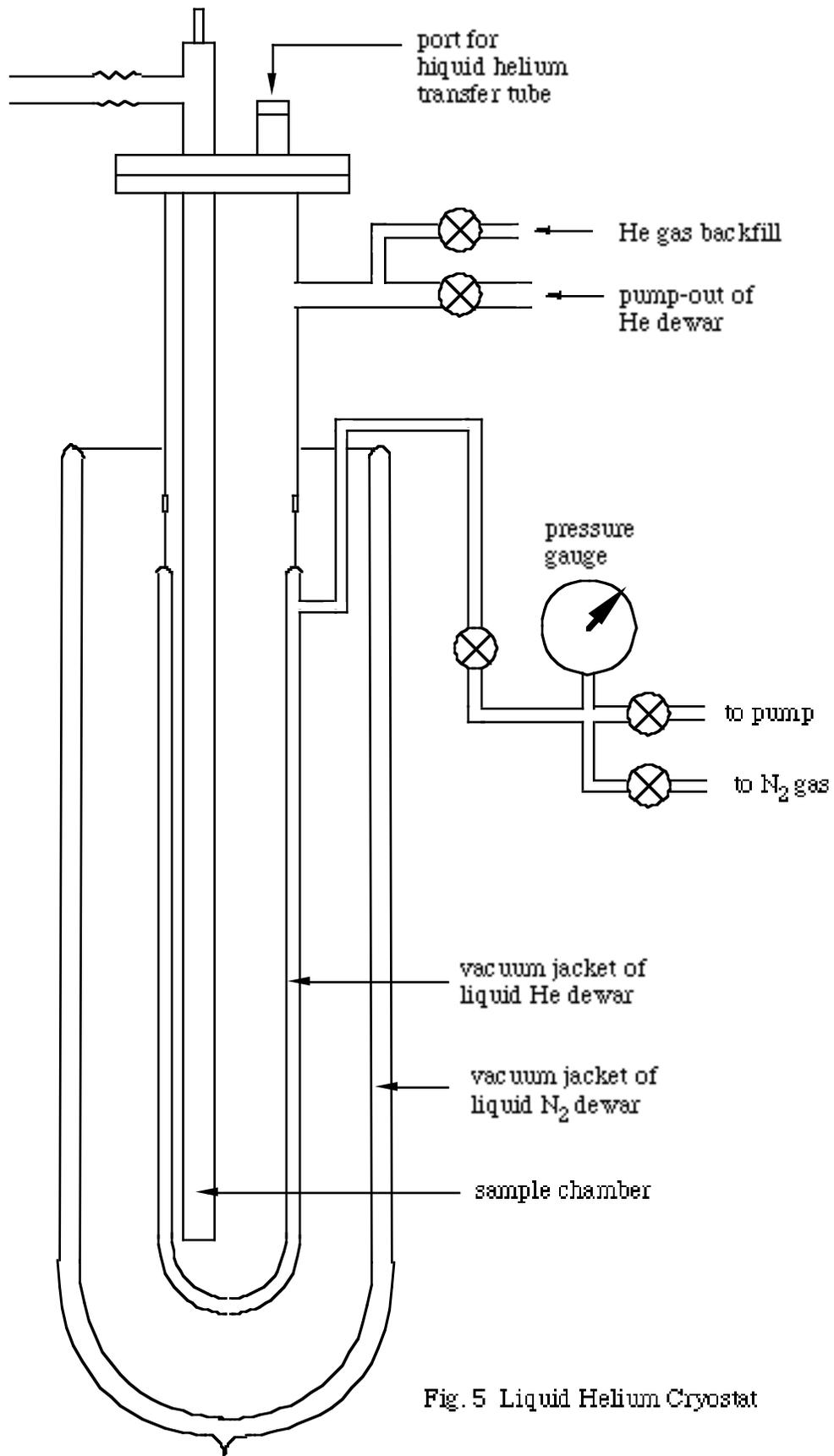


Fig. 5 Liquid Helium Cryostat

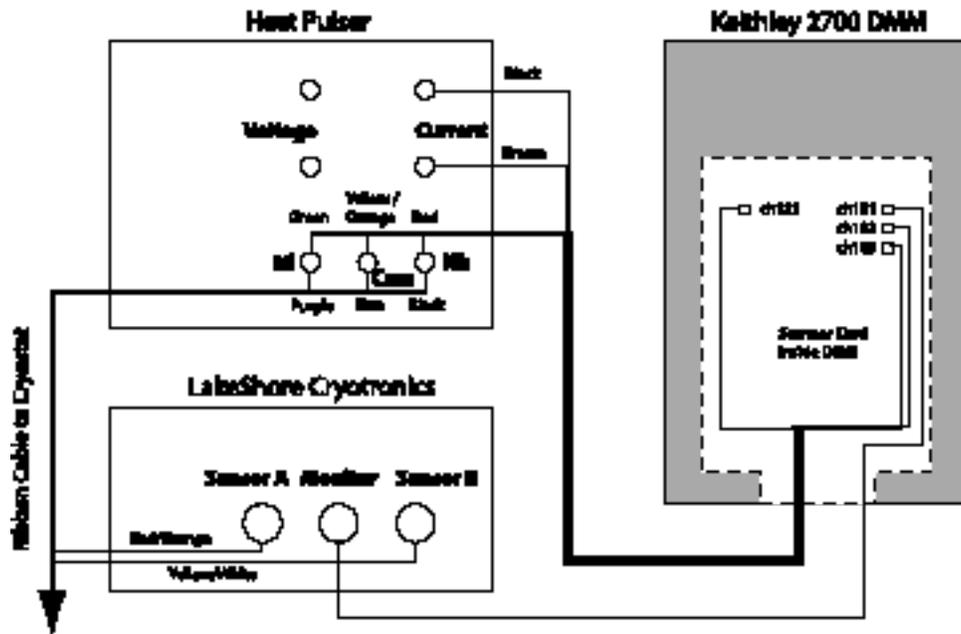


Figure 6. Heat capacity electrical connections.

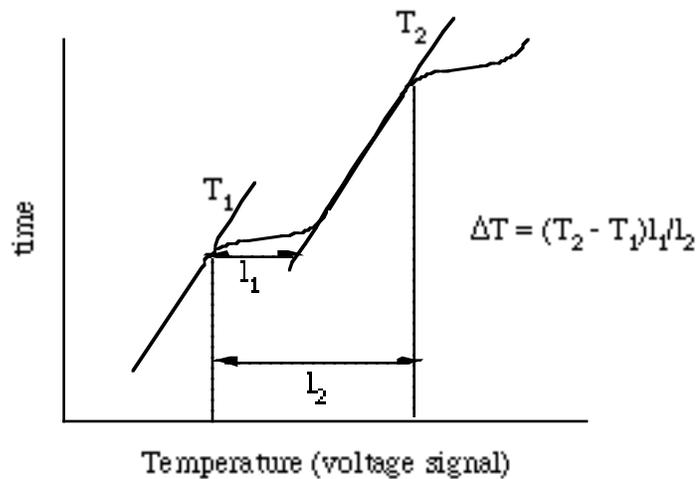


Fig. 7 Time trace of voltage on strip chart recorder for determining ΔT . At the moment of pressing the current pulser call out and write down the temperature on the chart. Also note down current and time duration of pulse (5,1) meaning 5 mA, 1 sec whenever you change these settings.