Introduction

Superconductivity & BCS Theory [1]

Superconductivity was first observed in 1911 by Kamerling Onnes, a major pioneer in the field of low-temperature physics. Onnes had been the first scientist to produce liquid helium only three years prior to this discovery, which gave him the cryogenic tools necessary to cool metals to the temperatures required for low-temperature superconductivity. Onnes observed that below a critical temperature $T_c$ the resistance of certain metals dropped to immeasurably low levels. In 1933, Meissner and Ochsenfeld discovered a second property of superconductors, now known as the Meissner effect, through which superconductors perfectly expel all magnetic flux from the bulk of the material (aside from a small penetration depth ~500 Å)—perfect diamagnetism.

While a set of phenomenological equations were written by the brothers F. and H. London in 1935 which described the bulk electrodynamic behavior of superconductors, a full microscopic understanding of the origins of superconductivity was not reached until 1957 with the publication of the BCS (Bardeen, Cooper, and Schrieffer) theory, for which the authors won the 1972 Nobel Prize in Physics. Leon Cooper has been a professor at Brown since 1958.

In 1956 Cooper showed that even a weak attraction between electrons near the Fermi energy of a degenerate fermion gas can overcome Coulomb repulsion and generate a bound state between two electrons of equal and opposite momentum and spin as a result of Fermi statistics. Cooper demonstrated that such a bound pair would have an energy less than the Fermi energy of the system. The distance that the Fermi surface retreats is equal to half of the pair binding energy (and is given by $\Delta$ as explained in the following paragraph). The 1957 BCS paper then demonstrated that the weak attraction necessary for this pairing is provided by interactions between electrons and phonons in the metal’s lattice structure. A simple physical picture of the process is that an electron’s negative charge attracts nearby positive ions in the lattice, which polarizes the medium and then attracts a second electron, providing an effective attraction between the two electrons sufficient to form a bound pair. These pairs, however, overlap strongly because the binding energy is much less than the Fermi energy.

BCS theory formally treats the pairing by introducing two spinless fermionic quasiparticles, essentially electron-hole pairs. These quasiparticles are named bogoliubons for Nikolai Bogoliubov, a Russian mathematician and physicist whose set of unitary transformations, now known as Bogoliubov transformations, are used to find solutions to the BCS equations in a homogeneous system. Under this formalism, the Hamiltonian can be expressed as that of a free quasiparticle fermion gas plus a mean-field interaction term which contains a negative binding energy due to the effective attraction. This binding energy is mathematically similar to the energy gap in semiconductors, and hence this is referred to as the superconducting energy gap $2\Delta$. The analogy to semiconductor theory is particularly apt as the energy gap is observed as a gap in the spectrum of quasiparticle excitation levels below the superconducting transition temperature $T_c$. One of the outstanding successes of BCS is the prediction of the temperature-dependence $\Delta(T)$ as

$$\Delta(T) \approx 3.06 k_b T_c \sqrt{1 - \frac{T}{T_c}}.$$
There are several techniques which have been used to measure the energy gap. At low temperatures, the specific heat depends exponentially on temperature, indicative of the thermal excitation of quasiparticles across the gap. Infrared transmission and reflection as a function of frequency clearly show the proper absorption at the gap energies. The technique used in this experiment, first used by Giaever in 1960 and for which he shared the Nobel Prize in 1973, proceeds as follows: two thin metal films are deposited on top of one another with only a very thin insulating oxide film separating them (~20Å). Due to the quantum mechanical probability of electrons tunneling through the insulating layer, a current will flow through the junction under applied voltages greater than the energy required to break a Cooper pair ($eV > \Delta$). This causes the current to drop sharply to zero as $eV \rightarrow \Delta$ at zero temperature. Through observation of the behavior of the $I$-$V$ curve of the junction, one can make direct observations of the energy gap.

For a more detailed theoretical discussion of BCS theory, consult Chapter 2 of Tinkham’s *Introduction to Superconductivity*.

**Tunneling Current [1]**

In the general case, if a potential (voltage) is applied across two metal films separated by a thin insulating layer, a current will flow between them as a result of quantum mechanical tunneling. The applied voltage shifts the chemical potential of the two films relative to one another, creating a current from tunneling given by

$$I_{1\rightarrow 2} = A \int_{-\infty}^{\infty} |T_{12}|^2 \rho_1(E)f(E)\rho_2(E+eV) [1 - f(E+eV)]dE$$

where $I_{1\rightarrow 2}$ is the current tunneling from metal 1 to metal 2, $|T_{12}|$ is the magnitude of the tunneling matrix element, $\rho_1(E)$ and $\rho_2(E+eV)$ are the energy-dependent densities of states of the two metals, and $f(E)$ is the Fermi function

$$f(E) = \frac{1}{e^{\frac{E-E_F}{k_BT}} + 1}$$

which gives the probability of an electron state of energy $E$ being occupied. The product $\rho_1(E)f(E)$ gives the number of occupied states in metal one and $\rho_2(E+eV)[1 - f(E)]$ gives the number of available states in metal 2. Assuming that the tunneling matrix element is constant, the total current is given by

$$I = I_{1\rightarrow 2} - I_{2\rightarrow 1} = A|T|^2 \int_{-\infty}^{\infty} \rho_1(E) \rho_2(E+eV) [f(E) - f(E+eV)]dE$$

If the metals are both in the normal (non-superconducting) state, we can make a free particle approximation in which we treat the density of states as a constant, so at zero temperature the current becomes

$$I = A|T|^2 \rho_1(0) \rho_2(0) \int_{-\infty}^{\infty} [f(E) - f(E+eV)]dE = A|T|^2 \rho_1(0) \rho_2(0)eV.$$
This demonstrates a regular Ohmic current where the current is proportional to the applied voltage (for low voltages).

In a superconductor, however, the density of states is not constant, but rises very rapidly at the edges of the energy gap. The current in a normal metal-superconductor junction like you will be investigating is thus given by

\[ I = A|T|^2 \rho_2(0) \int_{-\infty}^{\infty} \rho_{1s}(E)[f(E) - f(E + eV)] dE \]

Numerical evaluations of this integral gives \( I - V \) curves as shown in Figure 1. At zero temperature, there is no current when the potential difference \( eV \) is below the value of the energy gap \( \Delta \). When the voltage is increased beyond that level, there is a sharp increase in current. The sharpness of the change in current as \( eV \to \Delta \) is dulled by the presence of nonzero temperature, as depicted by the dotted line in Figure 1 below.

![Figure 1: I-V curve of the superconductor-normal metal junction. The thick solid line shows the current in the normal-superconducting junction at zero temperature, and the dotted line at finite temperature. The thin solid line shows the conductivity of a normal-normal junction. [1]](image-url)
A conceptual picture of the difference between the normal and superconducting junctions is given in figure 2 above. With no applied bias, both systems reach equilibrium states in which the chemical potentials of the two metals, denoted by the Fermi energies $E_F$, align. In the normal metal to normal metal junction, a current flows for any value of the applied potential. However, in the superconductor, there is a gap of width $\Delta$ on either side of the Fermi energy which must be overcome in order to reach available electron states, as shown in figure 3 below. If the potential is increased by $\Delta$ in the normal metal, then the superconductor states above the gap become available to the electrons in the normal metal and a current is observed. If the potential is increased by $\Delta$ in the superconductor, there is a breaking of some Cooper pairs and resultant tunneling into the metal.

Figure 2: (a) Normal to Normal and (b) Normal to Superconducting Junctions. The opening of the energy gap at the onset of pair formation can be seen as the difference between the two images. [2]

Figure 3: Normal to Superconducting Junctions at a) zero bias and b) bias equal to the energy gap $V = \frac{\Delta}{e}$. Note that due to the equilibrium positions of the chemical potentials under zero bias, one must only apply a bias of $\frac{\Delta}{e}$ and not $2\frac{\Delta}{e}$ to generate a current. Also note that the chemical potential of the system can be shifted in either direction to generate a current. [2]
In this experiment, the voltage bias of the junction is ramped continuously and passes through the value of the energy gap in both directions. The observed $I$-$V$ curve allows for direct measurement of the gap as a point of discontinuity in the slope of the curve. The procedure is repeated at various temperatures in order to measure the temperature dependence of the gap.

**Oxide Layer**

The appearance of different metals in bulk varies, but this is not as true for thin metal films. The metallic for this experiment must be clean, free of fingerprints (both below and on the surface) and have a mirror-like finish. The heat generated during evaporation tends to warm the substrate. If the bell jar is vented before the substrate is cool enough, then the metal film will fog as a result of rapid oxidation. Fogging may also occur if the slide is too close to the boat during evaporation. The films should be opaque to ordinary room intensity light, but they may pass the high intensity light coming from the boat during evaporation.

The oxide between the layers usually forms within minutes after the first layer (aluminum) is exposed to the air. One may vary the oxide thickness by either leaving the film exposed for a longer time or by heating the film or both. The oxide is usually so thin that no significant fogging of the finish is noticed. In the case of active metals such as tin and indium, an oxide forms more rapidly you may observe fogging after a time. These active metals are usually the top layer so that this rapid oxidation is not important.

The films should be used as soon after completion as possible. Prolonged exposure to air degrades them and they frequently become useless. They also do not ordinarily perform properly after temperature cycling, i.e., between room and liquid helium temperatures. Their properties can usually be preserved if they are kept in an environment at liquid nitrogen temperature (oxidation rate is significantly reduced).

The way to ensure success, of course, is to be very careful about the cleanliness of the vacuum chamber. Use a Kimwipe and alcohol to wipe down the chamber door and O ring every time the door is opened. Be sure that a suitable vacuum before evaporating in order to ensure the films are free from impurities. **DO NOT use vacuum grease on the evaporator/vacuum system.** The above remarks concerning the required care of the slides should be taken quite seriously – they will save you time in the long run.

**Cryogenics & Evaporative Cooling**

You will employ cryogenic liquids to achieve temperatures at which lead becomes superconducting (7.2 K). Aluminum has a transition temperature of 1.1 K, which is not accessible with this cryogenic apparatus.

See Figure 7 below for a diagram of the cryogenic Dewar system being used in this experiment. The system is composed of two nested glass Dewars, the outermost of which is used to contain liquid nitrogen (77 K). Its jacket is permanently evacuated. The inner Dewar is for holding liquid helium (boiling point at atmospheric pressure is 4.2 K). The vacuum jacket on this Dewar has a valve allowing its vacuum to be flushed and adjusted. The slide with the tunnel junctions and wiring is hung by a stainless steel tube (low thermal conductivity) from the top of the cryostat.
You will reduce the temperature of the liquid helium through evaporative cooling techniques which exploit the relationship between temperature and vapor pressure. Beginning with the Clausius-Clapeyron relation which characterizes the phase transition between liquid and gaseous helium, we see

\[ \frac{dP}{dT} = \frac{L}{T\Delta V} \]

Where \( P \) is the pressure, \( L \) the latent heat of the transition, and \( V \) the resulting change in volume. If we assume that the volume of a comparable number of atoms in the liquid state is negligible compared to in the gaseous state, we can assume that \( \Delta V = \frac{nk_BT}{p} \) from the ideal gas law. Inserting this into Clausius-Clapeyron,

\[ \frac{dP}{dT} = \frac{LP}{nk_BT^2} \]

\[ P = Ae^{-L/(nk_BT)} \]

From this it can be seen that by reducing the vapor pressure of the gas above the liquid helium, one can induce a reduction in the temperature of the liquid. In this case, only the most energetic (“hottest”) atoms will leave the liquid and enter the gas phase, inducing an overall reduction in mean energy of the liquid—a cup of coffee left out cools by the same mechanism. The rate at which energy leaves the liquid phase is given by the product of the rate at which atoms leave the liquid phase and the latent heat of the liquid (\( \dot{Q} = \dot{n}L \)) Assuming that the volume of the chamber is constant, the rate at which particles cross the liquid-gas boundary is proportional to the vapor pressure. Hence

\[ \dot{Q} \propto LP \propto e^{-L/(nk_BT)} \]

We see that the cooling power drops exponentially with temperature, so we expect the temperature achieved by this process to hit some kind of asymptotic lower limit—about 1.5 K for this experiment.

Normal liquid helium (above 2.2 K) is not a sufficiently good thermal conductor to establish equilibrium on the time scale of minutes. However, in this temperature regime, convection can act as an effective thermalization process. As you decrease the vapor pressure, the helium near the top of the fluid will cool as explained above, whereas the temperature of the helium on the bottom will lag. Since the density of liquid helium increases with decreasing temperature, as the pressure is changed a density gradient is formed in the liquid as well. So as the pressure is decreased, a stratification develops between the cold, dense layer of helium above and the hot, less dense helium below.

The temperature and pressure gradients in the liquid will be sufficient for the top and bottom of the liquid to achieve equilibrium by undergoing convection, much like processes which occur in a lava lamp or in the sun (bubbles of hot light material float up from the lower layers due to
density gradients and heat the cold upper layers.) After reducing the pressure, give the helium a few seconds to thermalize before taking measurements. It is advisable to decrease the pressure monotonically and not bring it back up to “double check” a higher temperature, as this will create a layer of hotter, less dense helium on top and one of colder, denser helium below. In this case, the denser, colder helium will stay on the bottom and will not convectively thermalize the container, making the pressure-temperature relationship invalid at the depth of the sample.

However, in the superfluid phase (below the $\lambda$ point at 2.2 K) the thermal conductivity of helium increases drastically and the fluid can be assumed to be isothermal at all times—you will see no convection bubbles below 2.2 K.

**Figure 4: Cryogenic Dewar system**
Procedure
Junction Preparation

The junctions consist of thin metallic films which are deposited on ordinary glass microscope slides. The thin-film tunneling probe allows three junctions to be tested at once. The probe is equipped with a lucite slide holder that has eight spring-loaded gold contacts.

1. The evaporator with which you will deposit the metallic films uses a turbo molecular pump that spins on magnetic bearings at about 50K RPM - for comparison, the average car engine will fail above 7K rpm. This pump is worth about $30K and can be easily destroyed if it receives a significant bump. Please be careful when working with or around the evaporator. Do not operate the evaporator without first receiving personal instruction from one of the lab staff or TAs; the instructions for using the teaching lab’s evaporator (Edwards 306A) should also be read carefully before use. The thin film patterns (shown in Figs. 1-3) are generated by placing aluminum masks between the source and the glass slide. The masks are held above their respective source material and rotated under the slide in sequence. To keep the chamber clean, always keep it under vacuum when not in use.

2. Make sure the slides are extremely clean. As delivered the slides should be sufficiently clean, but touching them with ungloved hands, even just by the edges, will make the slides dirty. Unfortunately, chances are you will have to wash a slide.
   a) Clean it very carefully with a series of washings in acetone and alcohol. Pour about 1/4” of acetone from the large brown bottle into a clean glass beaker. Do the same with alcohol in another clean glass beaker. Do not use the solvents from the plastic squeeze bottles.
   b) Place a slide in the acetone and gently agitate the beaker. Using tongs pick up the slide by one corner and let the acetone drain off. Place the slide in the alcohol and repeat the process. You should go back and forth between the acetone and alcohol several times until you are convinced the slide is clean. Always use alcohol last.
   c) After the last alcohol cleaning use the tongs to place the slide in the desiccator containing calcium chloride. Position the slide with one corner down making as little contact with other objects as possible. Place the lid on the desiccator and wait for the slide to dry. Note: The acetone and alcohol you use must be very pure, since any contamination present tends to leave a filmy residue.

3. You will need to prepare all the materials in the evaporator before you begin. This includes placing the materials to be evaporated in boats suspended between the connection terminals, putting the shields in place (and making sure they don’t touch the “hot” post on the right,) and putting the masks in place. Make sure the boats and masks are properly aligned and that the connection terminals are tight. See the TAs for access to the materials to be evaporated and the boats to hold them. Make sure the liquid nitrogen trap on the evaporator system is full before any evaporations are performed.

4. Once the metals, masks, and shields are in place, you are ready to pump down the vacuum chamber of the evaporator. Press “cycle” and wait a few minutes for the pumping to finish. Once the chamber pressure reaches about 8*10^{-6} torr, you can begin the evaporation process. Remember to proceed in the correct order (Cr, Al, oxidize, Pb.)

5. You will monitor the thickness of your evaporations with a thickness monitor. Before performing the evaporations, ensure that the thickness monitor is set to the correct density and Z-factor for the material you will be evaporating. These are listed on the evaporator
control panel.
6. Before performing evaporations, you will want to burn off any impurities in the metal by putting the evaporator’s shield into the blocking position and setting the current slightly (0.5-1 A) below the nominal melting currents marked on the evaporator for ~30s. You will then move the shield to the open position and increase the current to just above the nominal melting value.
   a. Chromium pads should be deposited first as pictured in Figure 5. Chromium is used since it forms a hard film which is scratch resistant. Make the Cr contacts about 1K-2K Å thick at a deposition rate of about 2-10 Å per second.

   ![Figure 5: Chromium pad arrangement](image)

   b. Aluminum (Al) is used to make the single long strip down the center of the slide. The film you create here will remain normal even at liquid helium temperatures. Use a deposition rate of 5-20 Å/sec to achieve a final thickness of 800 - 1800 Å. Al films are continuous after 200 Angstroms so the device will function as needed as long as you exceed this thickness. You will then create the insulating oxide layer on top of the Al by venting the system back to atmospheric pressure (leave the door closed!) and leaving it there for 5-30 minutes. Afterwards, pump the chamber back down and proceed to the Pb evaporation.

   ![Figure 6: Aluminum strip](image)

   c. Lead (Pb) is used to make the three short strips that run across the slide. These films will go superconducting at liquid helium temperatures. Be aware that lead melts at a very low temperature compared to the other metals used. It is relatively easy to evaporate all of it while attempting to burn off impurities. Deposition rates of 5-20 Å/sec or even a little higher are fine. Final depositions of 800 - 1800 Å are typical. The Pb film will be continuous once you have reached ~700 Å.
7. Once you have prepared a slide, record a 4-wire I-V curve for all three junctions at room temperature. Use this data to calculate the room-temperature resistance of the junctions; typically, a successful junction will have a room-temperature 4-wire resistance of .01-10 ohms.

Cooling Down
You may not start the cooling process before receiving permission and detailed instructions on the procedure, the apparatus and handling cryogens. Cooling down takes ~2 hours and is somewhat complicated.

The jacket of the LHe (inner) Dewar has a glass valve which allows air to be added or removed. At the beginning of the cooling process the jacket will be evacuated and then a small amount of air (a few Torr) will be admitted to the jacket to increase thermal conduction during the precool phase (cooling from 300 K to 77 K). Next LN2 will be put in the outer Dewar. Once the LN2 has been added, do not open the glass valve! If the glass valve is opened while either Dewar is at cryogenic temperatures, leave it open. Closing the glass valve while either of the Dewars is at cryogenic temperatures can and has created a bomb. The gas admitted to the LHe Jacket will liquefy once the LHe is added, creating a better vacuum in the LHe jacket than could be achieved with the lab vacuum pump.

Measuring the Energy Gap
There are a variety of ways to investigate the $I-V$ characteristics of these junctions. The simplest way is to employ an adjustable voltage source (a function generator with output of at least 0 ...30 mV, 0 ...100 mA) for biasing the junction, and a differential amplifier for measuring the junction voltage. This is called a 4-wire or 4-point measurement—see the appendix for an explanation of why this is necessary. The current can be monitored by observing the voltage across a 1-100 $\Omega$ resistor in series with the junction. This latter voltage may be observed on the y input of the oscilloscope. The output of the differential amplifier should be on the x input. A computer with a 16 bit A-D converter can be used instead of an oscilloscope. (See Figure 8.) Note that the differential amplifier has adjustable frequency filters. Be sure that the sweep frequency of the function generator is well within the band pass of the amplifier.

- Record an $I-V$ curve for all three junctions at 77 K before transferring helium. This will also ensure that your junctions are still working properly. There is significant thermal contraction in the cooling process, so the contacts may become disconnected.

- Though you are not allowed to transfer liquid helium from the storage Dewar to the research cryostat without staff assistance, you will be involved in the process. You will be given specific instructions before the process. If you have any concerns or doubts about your role in the transfer, ask for clarification before starting the procedure.
Lower temperatures can be achieved by pumping down the vapor pressure above the LHe, as described in the section on cryogenics. There are five different valves in the Dewar system. You will use two of them for the cooling process, a small one then a large one—the TA’s will show you which valves to use. Do not touch adjust any of the other valves. Use the small valve to reduce the pressure to the values listed below. When the small valve no longer efficiently reduces the pressure, open the large valve.

Record an $I-V$ curve for all three junctions at approximately 760 Torr (4.2 K), 350 Torr, 50 Torr, 35 Torr, 5 Torr and then as low as the pump will go. Be sure to take all measurements above the Lambda point before going through the lambda point. The liquid helium can be observed through slits in the silvering of the Dewars. Pay close attention to the dramatic change in boiling when the liquid becomes superfluid at what is called the $\lambda$ point at 2.2 K.

From your data estimate the superconducting energy gap and its temperature dependence.

Figure 8: Electronic Apparatus

References
On Superconductivity in General (Introductory) Including Simple Tunneling Discussions:

On BCS Theory (Introductory):

Original References:


Appendix
4-Wire Measurement
Four-wire measurements are used to very accurately measure the voltage across a particular circuit element. The current through the junction also runs through the films in order to reach the junction; these films will have a finite resistance. By Ohm’s law, there will be a voltage drop across the film as this current flows. For the following discussion, refer to figure A. If you measure the voltage difference between points A and B, where the function generator is attached, you would not only measure the voltage drop across the junction, but also the voltage drop across resistances R1 and R2 as the current travels through them. However, since the input impedance of the multimeter is on the order of 1-10 Mohms, only a negligible current flows through resistances R3 and R4, and hence there is a negligible voltage drop across them. This means that a voltage measurement across C and D will be almost exactly that across the junction.

![Figure A: 4-point measurement](image)