Conductivity Lab Overview

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1 Welcome to the solid state electrical conductivity lab!

The electrical conductivity (σ) defines the response of a system to an applied electric field. The conductivity measures the tendency of electrical charges to move through the solid because of the field. This of course is the empirical property that makes metals metallic and insulators insulate, depending on the values that it takes. It would be hard to overstate its technological significance. In this lab, you'll be simultaneously learning about the conductivities of various materials, while using some of those facts to measure temperature–and enable more measurements.

In practice, one extracts information about the DC electrical conductivity from the resistivity (ρ), which is the inverse of the electrical conductivity ($\rho = 1/\sigma$). For the purposes of this lab, you can begin thinking of the resistivity as a shape-independent, bulk property belonging to a kind of material. The approximate separation of bulk properties from geometric specifics is what allows people to make differently rated resistors from the same roll of wire.

You will find that the first thing you'll actually have to do is to calibrate a couple of commercial diodes for low temperature thermometry; but after that, you can measure whatever you want, subject to availability.

2 Techniques You Will Be Using

2.1 The 4-Wire Technique and Alternation

A voltmeter doesn't know what it's connected to. If you were to measure the voltage across the sample using the same leads with which you applied the probing current, you would also measure the voltage drop through the current leads. Since the leads are long and the sample resistance may be small, this can be a very significant source of measurement error.

The simplest solution to this problem is to apply the current with one pair of wires, and measure the voltage with a second pair.

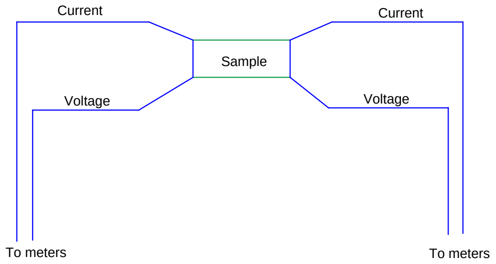

Figure 1: Four-Wire Schematic.

Another source of extraneous voltage is the *Seebeck effect* due to the thermal gradient down the voltage leads. Warm electrons diffuse faster down the wire, leading to a voltage proportional to the temperature difference. This material-dependent effect is the basis for the thermocouple thermometer, but for conductors (with small voltage signals) it's a nuisance because inevitable asymmetries in the lead wires will lead to a voltage offset. The solution to this problem is to alternate the direction of the applied current. In the average of the two measured voltages, this and other asymmetries cancel out.

The Keithley current source and voltmeter can be set up to alternate in what Keithley calls"Delta mode" (more information is in the **Keithley manual**). You can initiate these measurements either from the Keithley front panels, or from the scripts we have set up for you in Matlab (see the **Matlab Script Notes**). However for measurements of diodes and other intrinsically asymmetric devices, you should use the Keithley in DC mode.

2.2 Refrigeration

To get samples down to low temperatures, you have the use of a closed-cycle helium refrigerator. Compared to the cryostats used in the other low temperature labs, this system is more like a refrigerator in the sense of a kitchen refrigerator, with a compression/expansion cycle of a refrigerant fluid. The important details of how to operate this rather complicated bit of machinery are discussed in the **CTI Refrigerator Manual**. However, if everything is working properly, the instructions on **Cooling Down** should suffice.

For now, note that the refrigerator comes in two parts, connected by pressurized helium hoses. The big box contains a large pre-compressor; the heavy object to which these leads go is called the *cold head.* It is so clunky because it contains a motor that drives heat-exchanging fluid displacers back and forth. Once it's been wired up, the sample to be measured is thermally anchored to the coldest part of the cold head–the tip of the *cold finger.* The thermometer that you calibrated put into good thermal contact with the sample. Note that all of the lead wires are thermally anchored all the way down the cold finger to prevent unmitigated thermal conduction from the feedthrough plugs to the sample.

Next, two heat shields are placed around the sample. These fairly isothermal surfaces both slow radiative heating from the tip of the cold finger and ensure that the environment around the sample is at a constant temperature. Finally comes the outer tail, which pressure-seals around the shielded cold finger. Once this is done, a vane pump gets most of the atmosphere out of the sealed-off space (otherwise the remnant vapor pressure of the eventually frozen air would leak heat to the sample). At this point, with everything canned up and evacuated, you are ready to start the refrigerator.

Unburdened with a heat load, the refrigerator is meant to cool the tip of the cold finger down to around 10K over $60-90$ minutes. Once your sample has reached base temperature, you can heat it by using the heater control on the Lakeshore thermometer box. This puts current through a stretch of NiCr wire in thermal contact with the sample holder. The Lakeshore box uses a Proportional-Integral-Derivative (PID) feedback algorithm, driving the thermal mass of the thermometer like a damped harmonic oscillator to establish the appropriate current through the heater coil.

3 Temperature Measurement

Well and good: but how to establish what the temperature is? What's required is a well-characterized and repeatable measurement that overlaps a trusted temperature scale at the high end, but persists to lower temperatures–or is simply more convenient.

Over a wide range of temperatures helium provides a decent thermodynamic temperature standard. Down to about 30 K, platinum has a very linear resistivity, and to measure the resistance of a twist of Pt wire is certainly more convenient than using a gas bulb. The usual choice for creating a continuous calibration curve for Pt resistors is the phenomenological *Callendar-Van Dusen function*:

$$R(T) = R_0(1 + AT + BT^2 + C(T - 100)T^3).$$

Here the term with C is applied only for $T < 0^\circ$ centigrade. This equation has four parameters, which you can determine for a particular bit of wire by comparing the measured

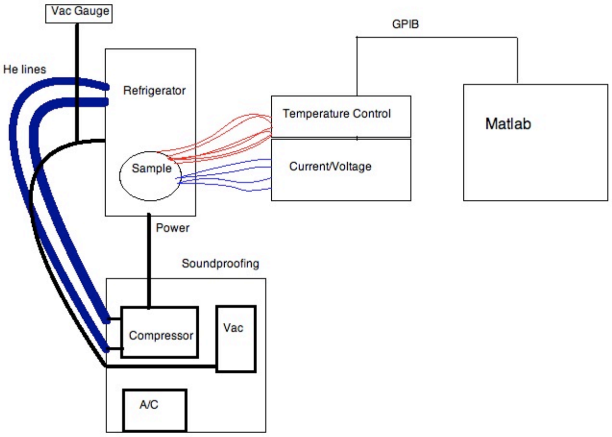

Figure 2: Rig Block Diagram.

resistances at *fixed points*, determined by phase transitions. Two obvious fixed points are the temperature of water in equilibrium with ice, and the temperature of water in equilibrium with vapor, at a well-defined pressure. But since thermometers based on this scale are common, you could establish the first three Callendar-VanDusen constants by measuring the resistance of your Pt in equilibrium with a mercury expansion thermometer at at least three different temperatures. The last constant requires a measurement at low temperature. A convenient fixed point here is the temperature of boiling liquid nitrogen at (approximately) one atmosphere, which is about 77 K.

3.1 Diode Thermometry

Below 30 K, the resistivity of a platinum sample becomes noticeably less linear and drops away as phonons freeze out. On the other hand, the resistivity of a semiconductor diode increases as thermally excited carriers freeze out. Hence, just where platinum thermometers become useless, the appropriate semiconductor thermometer becomes more sensitive. In principle, one calibrates the temperature/voltage function of the diode using a gas bulb thermometer, or against a previously calibrated Pt resistor–but many diode thermometers remain sensitive below the condensation temperature of He (about 4.2 K).

Your refrigerator currently has two diode thermometers installed. These are fairly standardized and almost prefectly interchangeable. Nevertheless, it's a good idea to recalibrate them before taking data.

4 Microscopic Models of Electrical Conductivity

4.1 The Drude Model

The standard classical mechanical model for the conductivity/resistivity of solid materials is called the Drude model. In the DC version of this model, which should be familiar from your introductory physics courses, the electron is treated like a little charged ball, bouncing along through the material under the influence of an accelerating electric field. After every bounce, the velocity is reset to some random value consistent with the temperature of the lattice. Unless there is something to stop the electrons–some sort of boundary or tether–they will tend to rattle on their way forever, with a bias in the direction of the electric field. So in the absence of an explicit binding force, this DC model describes a metallic conductor. The presence of a binding force implies electrical insulating behavior.

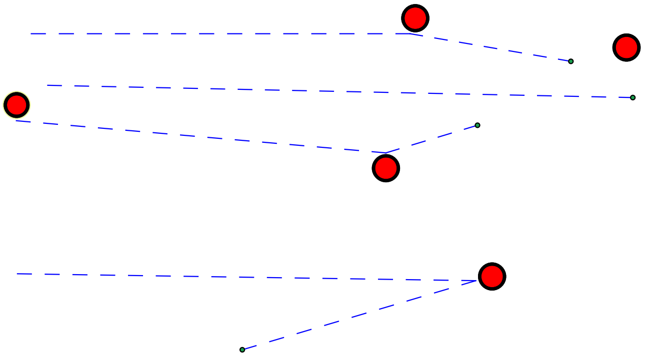

Figure 3: The Drude picture of a metal. Electrons are tiny, charged pinballs rattling past obstacles in the general direction of the applied field.

For AC voltages, the distinction between conductors and insulators is muddied, because AC currents in metals go back and forth anyway. Nevertheless, one expects a qualitative difference based on the notion that bound, oscillating electons should have a resonance frequency (corresponding to the "spring constant" of their tether). So one can generally define a metal in the Drude model as a material for which at least one "resonance" occurs at zero frequency: at least one "spring constant" is set to zero.

It's pretty simple to derive the full AC-DC Drude model for conductivity. To start, assume that a single charge carrier (mass m and charge q) is accelerated under the influence of an electric field with a form $E(t) = E_0 \cos \omega t$, while it is also subject to a restoring force kx (x is the displacement from equilibrium) and a dissipative force fv (v is the velocity). Solve the Newtonian equation to find the amplitude and maximal speed of the steady-state solution. One slick way to do this is to imagine the complex field $E(t) = E_0 e^{i\omega t}$ and take the real part at the end of the calculation. This works because the differential equation is linear. Next note that the classical expression for the electrical current density j is just $j = nq < v >$, where n is the number density of the charges, and the brackets indicate a sample average. Plugging in your expression for v, you'll get

$$\jmath(t) = \frac{nq^2 \times i\omega E_0}{k - m\omega^2 + i < f > \omega} \times e^{i\omega t}.$$

The proportionality between j and E is the frequency-dependent conductivity ($\sigma(\omega)$ for the frequency ω). If you rationalize the denominator and take the real part of your answer, you will find that it falls into two pieces: one part of the current is in phase with the electric field (goes like $\cos(\omega t)$) and the other is $\pi/2$ out of phase (goes like $\sin(\omega t)$). What does this mean?

jE has the units of a power density. Over a cycle, the out-of-phase product $\sin\cos$ averages to zero, but the in-phase $\cos^2$ averages to $\frac{1}{2}$. This nonzero part is the cycle-averaged power transmitted to the current. Where does it go? Its proportionality to $< f >$ is an important hint. Recall that f represented a damping force on a single oscillating charge. What we have described here is a steady state: the kinetic energy of the current is dissipated by the frictional force. By contrast, the out-of-phase part determines the energy flow into and out of the electromagnetic fields with no net absorption.

Because we initially assumed $k \neq 0$, we have described a DC insulator. However the same analysis goes through with $k = 0$, so the expression for the DC conductivity for conductors is just the $k = 0$ limit of the general expression. This leads to another familiar interpretation of the averaged dissipation coefficient $< f >$. Given that the additional velocity of a charge accelerated in a DC field E for time τ should be $qE\tau/m$, the current density should be $nq^2E\tau/m$. Comparing the two expressions for the DC current density shows that $< f >= m/\tau$. In other words, $m/ < f >$ is the average time for the uniform acceleration of an electron by the external field, before the electron hits some obstacle and decays out of the current.

4.2 "Perfect Conductors"

Things get a bit subtle when we try to imagine what would happen for a perfect DC conductor ($k = 0$ and $< f >= 0$ simultaneously). Imagine a sequence of graphs of the in-phase part of the conductivity as $\tau \to \infty$ and $< f >\to 0$. The typical Lorentzian narrows, and the peak at $\omega = 0$ simultaneously increases, in such a way that the total area under the curve remains constant. If we rescale the ordinate, we get closer and closer to what seems a perfectly thin spike at $\omega = 0$. This $< f >\to 0$ limit is a Dirac δ-function. For a perfect conductor, with no dissipation, the in-phase conductivity happens at zero frequency. Because τ represents the amount of time for which an electron retains the energy that the field gives it, and (for constant m) $< f > \to 0$ makes $\tau \to \infty$, a perfect conductor would be a great place to store kinetic energy, transmit energy without loss, etc. If only life were that easy!

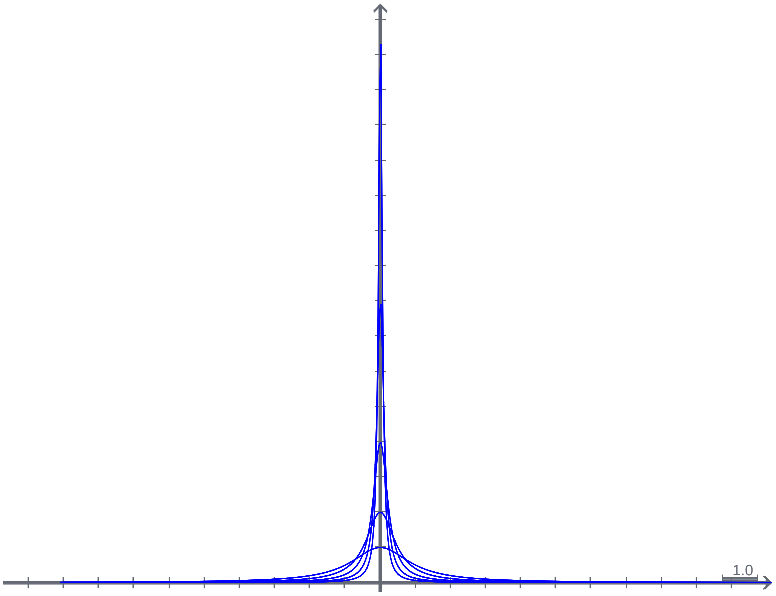

Figure 4: The in-phase part of $\sigma(\omega)$ for a metal ($k = 0$) as $< f > \to 0$ ($\tau \to \infty$).

4.3 Temperature dependences of the Scattering

4.4 Impurity Scattering in Metals

The idea of perfect metallic conductivity is no relic of the Drude model. The quantum mechanical treatment of the electron states in a lattice also implies that a single electron need not scatter out of its eigenstate. So why do metals exhibit finite τs? There are many mechanisms to consider. The simplest to imagine is impurity scattering. An electric field gives a directed momentum to a conduction electron; the scattering centers mix up momenta. Hence if impurity scattering were the only scattering process, one would expect a mean free path of about the average impurity spacing, and a corresponding *impurity scattering resistivity* that could be made as low as one wished by careful materials processing.

To be specific, consider the following ballistic model for impurity scattering. Call the density of impurities N_i. Define the *mean free path*, L, as the length for which a charge carrier on average hits one impurity. Actually, it's easier to imagine the impurities sweeping toward the charge carrier. Supposing that the radius of one impurity is r_i, then $L \times \pi r_i^2 N_i \sim 1$. But $L = v\tau$, where v now stands for the average speed. So $\tau \sim \frac{1}{vN_i}$. All else being constant, $N_i \to 0$ implies $\tau \to \infty$.

For a fixed N_i, we might expect to be able to understand temperature dependence from the variation of v. If, as you might expect for a classical gas, v were something like $\sqrt{k_B T/m}$ (with $k_B T >> E\tau$) then you might expect the impurity resistance to increase with temperature.

In fact the proper speed to use at all temperatures for which the metal is solid is the Fermi speed, v_F, which for classical particles would correspond to a temperature on the order of 10^4 to 10^5 K. The fact that in metals the impurity resistivity is largely independent of temperature is a consequence of the fact that electrons do not obey classical statistics.

If $\tau \sim \frac{1}{v_F N_i}$, then you can estimate v_F in a crystal of a metal by introducing a controlled density of impurities. As an exercise, see if you can work out the details of how you would extract v_F from a data set of ρ versus N_i.

4.5 Carrier Freezeout in Semiconductors

In nonmetals, the freeing of a charge requires an activation energy. As the temperature increases, one expects a population of thermally excited carriers. Recall that the Drude-model conductivity $\sigma = \frac{nq^2\tau}{m}$. The number of electrons at energy ϵ follows the Fermi distribution $n(\epsilon) = \frac{1}{e^{\epsilon/k_B T}+1}$. In a semiconductor ϵ includes the *band gap* Δ. Typically, $\Delta \sim 1\text{eV}$ (1.6×10^{-19}J). Hence for $T << \Delta/k_B \sim 10^4$ K, $e^{\epsilon/k_B T} >> 1$. In other words, the activated electrons in a semiconductor approximate a Maxwell-Boltzmann gas. Inserting the density of states factor $\epsilon^{1/2} d\epsilon$, we calculate for the total number of free carriers at temperature T,

$$n \propto \int_{\Delta}^{\infty} e^{-\epsilon/k_B T} \epsilon^{1/2} d\epsilon \propto T^{3/2} e^{-\Delta/k_B T}.$$

The calculation of the scattering time is a bit more complicated than it is for conductors. Here is one way to grasp the main result. For a Maxwell-Boltzmann gas, the *thermal wavelength* corresponding to kinetic energy $\frac{1}{2} k_B T$ of each quantum mechanical particle (of mass m) is

$$\lambda_T = \sqrt{\frac{\hbar^2}{2mk_B T}}.$$

This defines a thermal volume V_T per particle of $\lambda_T^3 \sim (k_B T)^{-3/2}$. Now $N_i V_T$ will be the number of scatterers in the same volume, so you would expect that for the impurity scattering rate, $1/\tau \propto (k_B T)^{-3/2}$, and $\tau \propto (k_B T)^{3/2}$.

The reason the analysis of the scattering time for semiconductors differs from that in metals is that for metals, the charge density n is much larger (on the order of one electron per unit cell) and basically independent of T. Maxwell-Boltzmann statistics are no longer a good approximation. So for metals, the appropriate temperature to use for the "thermal wavelength" would be the Fermi temperature T_F (typically $T_F \sim 10^4$K), which is proportional to $n^{2/3}$. In other words, the average spread of the charge carrier wavepackets is metals about a lattice constant–much smaller than the typical impurity spacing–and so in metals the ballistic approach works better.

So for semiconductors, we'd expect $\sigma \propto T^3 e^{-\Delta/k_B T}$.

4.6 Phonon Scattering in Metals

Even a perfect atomic lattice will support normal modes, known as *phonons*, which cause local variations in the density that act as scattering centers. So the average density–of these density variations–should also limit the mean free path and contribute to the resistivity. Electrons will scatter from other electrons. As long as there is something from which to scatter, and an open state for the electron to go into (recall that electrons are Fermi particles) our Drude-model currents, once set up, will eventually decay.

Faced with the multiplicity of scattering mechanisms, you might not be surprised that the general computation of the electrical resistivity of a metal can turn into a very complicated undertaking. The total scattering rate should be something like the sum of all the different rates taken individually. That is, $\frac{1}{\tau_{total}} = \frac{1}{\tau_{impurity}} + \frac{1}{\tau_{phonon}} + \ldots$. In other words, all else being constant, the various resistivities of the material should add like resistors in series. There is some hope of disentangling the major contributions because each mechanism has a characteristic temperature dependence.

To understand the temperature dependence of phonon scattering, you must consider again the totality of electron states in momentum space. You must also have a notion of the spectrum of phonon states.

As you add electrons to a system, Fermi exclusion forces the newer electrons into higher and higher momentum states. For a completely isotropic material, you'd end up with a ball of momentum states, filled out to the *Fermi wavevector* k_F. The elastic scattering of an electron at this *Fermi Surface* from a phonon of wavevector q leads to a loss of momentum

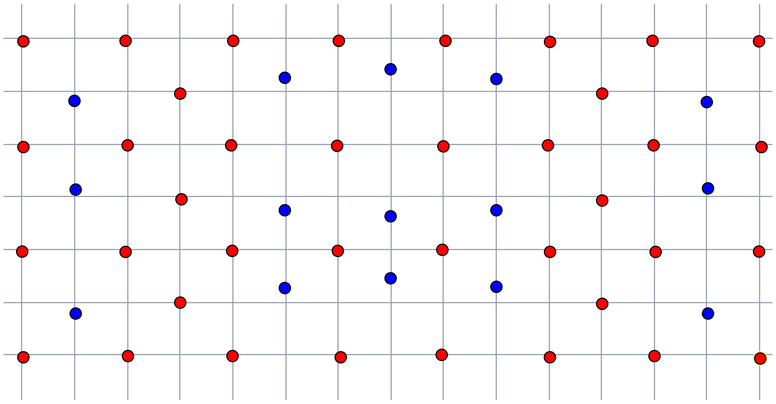

Figure 5: Cartoon of a particular phonon on a centered square lattice. The blue atoms are displaced from their equilibrium lattice positions.

(as measured from the current direction)

$$\Delta k = k_F(1 - \cos\theta)$$

and this loss can be averaged over the Fermi surface:

$$< \Delta k >_{\mathbf{Surface}} = 2\pi k_F^2 \int_0^{\theta_{\mathbf{Max}}} n(\theta)(1 - \cos\theta) sin\theta d\theta.$$

The scattering rate out of a current is really a rate of momentum loss, so $\frac{1}{\tau} \propto < \Delta k >$.

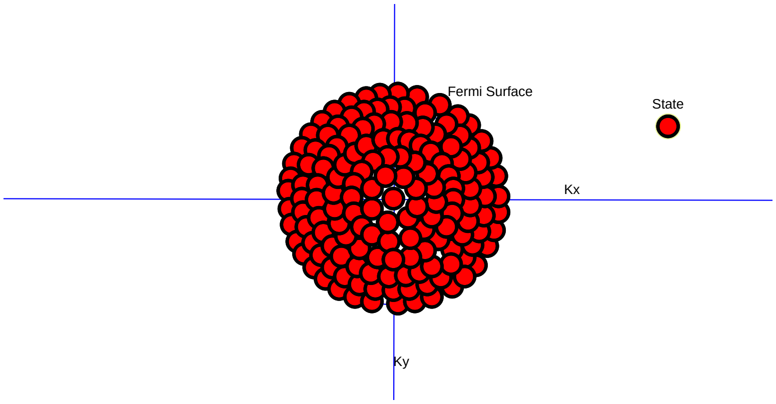

Figure 6: Fermi Sphere. The idea is that each state owns a particular volume of wavevector space, so they must stack up in energy.

$n(\theta)$ is the number density of phonons available for scattering (and corresponds to N_i in the previous section). Since phonons are Bose particles, their occupation number as a

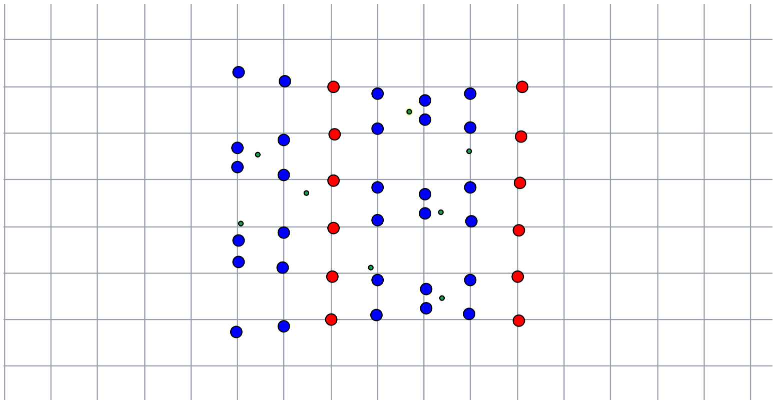

Figure 7: Electrons scattering from phonons (point particle picture). The lattice ions in blue are displaced from their equilibrium positions. Electrons (tiny green dots) are drawn to regions of temporarily higher positive charge density.

function of temperature is

$$n_q \sim \frac{1}{e^{E_q/k_BT} - 1} \sim k_BT/E_q$$

with the last expression as a very crude approximation for phonons of energy $E(q)$ and momentum q.

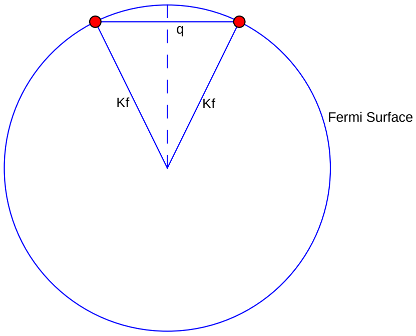

Figure 8: Phonon scattering cartoon (momentum space version). Here q is the phonon wavevector and the initial and final electron states are taken to be on the Fermi surface.

At low temperatures, the distribution limits scattering to $\sin(\theta/2) < q/2k_F$. So the question is: what's the typical q at a temperature T? The answer is simple if we use the *Debye model* for the phonon spectrum. In the Debye model, the energy of a phonon of wavevector q is just cq, where c is the speed of sound in the crystal. The sound modes have a natural largest wavevector q_D ("D" for Debye) corresponding to the dimensions of a cell of the crystal, with a largest energy $E_D = cq_D$. By dividing E_D/k_B, we convert E_D to the *Debye temperature*, Θ_D. So to find the typical q_T at typical energy k_BT, we find its wavevector as a fraction of q_D: $q_T = q_D(T/\Theta_D)$.

Now in metals, typical Debye wavevectors are much smaller than typical Fermi wavevectors, so we can approximate $q_D/k_F \sim \theta$. Retaining the crude approximation that the number of phonons is proportional to T, you can calculate:

$$< \Delta k >_{\textbf{Surface}} = 2\pi k_F^2 T \int_0^{T/\Theta_D \times q_D/k_F} (1 - \cos\theta) sin\theta d\theta \sim T^5.$$

At high temperatures, the upper limit of the integral saturates at q_D/k_F, so the temperature dependence for $T > \Theta_D$ will be linear. A more careful calculation along the same lines yields the *Bloch-Gruniesen formula*

$$\frac{1}{\tau} = v_F \sigma_a \frac{\hbar^2 q_D^2 k_B}{M_a k_B^2 \Theta_D} \left(\frac{T}{\Theta_D}\right)^5 \int_0^{\Theta_D/T} \frac{4z^5 dz}{(e^z - 1)(1 - e^{-z})}.$$

In this formula, σ_a is the cross section for scattering from a single atom of the lattice. For more on Bloch-Gruneisen and its brethren, see the **Conductivity Theory References**, especially the **Approximation of the BG Transport Integral**, which is useful for actually fitting data.

Considering both phonon and impurity scattering together, you would expect the DC resistivity of a metal to increase as a function of temperature, and at low temperature decrease to a finite value. In terms of the Drude parameters, for metals, n is a constant. Likewise $\tau_{impurity}$ is constant, but τ_{phonon} changes. By fitting the ρ versus T data for a metal, you can estimate the experimental quantities, Θ_D, n, $\tau_{impurity}$, and the jumble of other constants that determines the overall scale for τ_{phonon}.

4.7 Superconductivity

While the idea of perfect metallic conductivity is understandable within the context of the Drude model for independent electrons, *superconductivity* (which by contrast is an actually attainable state) is not. While normal currents in a metal decay by scattering, for supercurrents there is an energy gap–analogous to the band-gap that makes insulators work–which means that scattering itself requires energetic activation. Hence materials in the superconducting state are qualitatively different from merely excellent regular conductors.

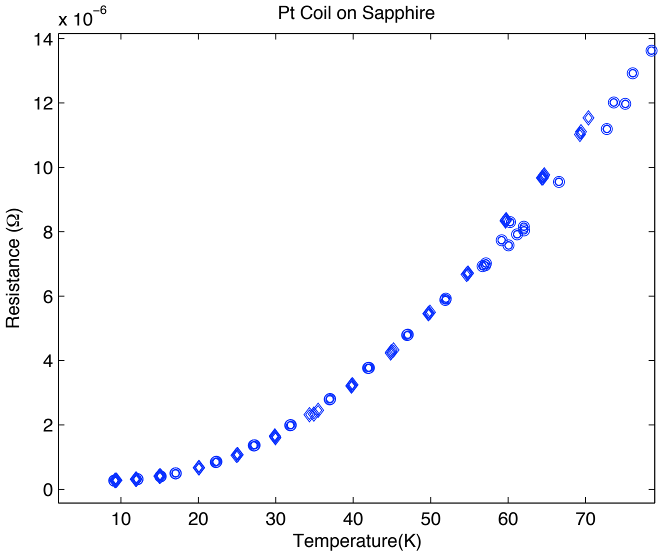

Figure 9: Resistance of a platinum wire at low temperatures, showing the effects of phonon freezeout. The scatter at higher temperatures results from time-dependent temperature gradients across the sample. With more patience, these damp away.

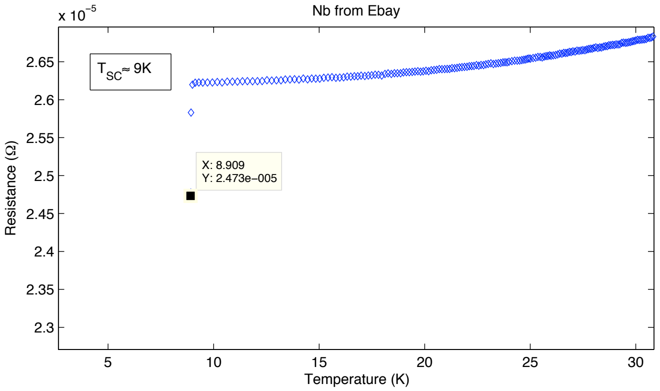

Figure 10: This ledge in the resistance indicates the onset of the SC transition to zero resistance. The sample was cut from Nb wire purchased from a jewelry supplier on an online auction site. The low temperature limit of the apparatus prevents you from seeing the full transition.

How does an energy-gapped state arise in a condutor, where the Drude electrons are "untethered?" In one fairly well-understood class of superconductors (Bardeen-Cooper-Schreiffer or BCS-type), the motions of the electrons become coordinated by sharing the energy benefit of lattice deformations. The overlap of the coordinated electron wavefunctions leads to a bulk coherent state, a quantum mechanical phenomenon, which is energetically favorable below the superconducting transition temperature T_{SC}. The electronic correlations themselves create a new "moving tether" between paired charges. But since all of the electrons are identical, they are *all* tethered into the same (macroscopic) quantum state.

Superconductors are therefore qualitatively different from "perfect" conductors where we picture each Drude electron moving on its own. The difference is especially apparent in a superconductor's response to an applied magnetic field. First consider the theoretical response of a perfect metal to a changing magnetic field. According to Faraday's law of induction, the changing magnetic field would induce current loops that oppose the change in the field. Hence the field in a perfect conductor would be stuck at its initial value. On the other hand, a superconductor tends either to expel (type I) or sequester (type II) magnetic field lines so that most of the sample volume is free of magnetic field. A superconductor spontaneously generates electric currents that keep magnetic fields from the bulk of the sample.

Here's a rough sketch of how this large diamagnetic response, known as the *Meissner effect*, comes about. So we don't have to worry about boundary effects, consider an infinitely long, thick slab of superconductor. It is always tempting to think of electrons like little balls of charge, with velocity $\vec{v}$, such that $\vec{j} = ne < \vec{v} >$. But to construct a localized particle out of waves requires a particular sum of momentum states. Superconductivity depends explicitly on the correlated multi-electron wavefunction, and this single-particle picture breaks down: the momentum states are added up in a very different way. Because of the energy gap between this ground state and the single-particle-like excitations, the applied vector potential can't change the shape of the wavefunction by much.

It seems paradoxical that current can both flow and not flow in the "ground" state, depending on whether we are applying a magnetic field. The resolution to this paradox resides in the difference between the $< m\vec{v} >$-momentum of a localized particle and the canonical momentum $-i\hbar\nabla$ in the Hamiltonian. In the presence of a vector potential $\vec{A}$, the operator for $m\vec{v}$ is modified from $-i\hbar\nabla$ to $-i\hbar\nabla - e\vec{A}/c$). Since the ∇ operator describes the shape of the wavefunction in space–which can't change because of the energy gap–the expectation value of current $< ne\vec{v} >$ must be proportional to $< -ne^2\vec{A}/mc >$. So the vector potential acts as a direct push on the *totality* of "particles" that comprise the superconducting state, resulting in something like a Galilean translation of a rigid solid. By applying the appropriate Maxwell's equations, you will find that this supercurrent exponentially screens out a magnetic field. For more about the superconducting state, see the **Superconductivity References**.

Superconductivity was first discovered in solid mercury by Heike Kammerleigh Onnes in 1911, soon after he had succeeded in the liquefaction of helium. Superconducting wires with the ability to carry large currents are used in the production of the very strong cryogenic electromagnets used in diagnostic NMR machines. In the 1980's, Bednorz and Muller discovered superconductivity at the relatively high temperature of 35 K in a layered copper-oxide. As part of this lab, you have the opportunity to make (or, if time doesn't permit, at least measure) a similarly structured compound that becomes supercondcuting anywhere from $70-90$ K, depending on the details of how you produce it (see the notes for **Making BSCCO**). Although the recipe for making this material is well known, there is as yet no consensus about the interaction which makes its superconducting transition occur.