University of Toronto

ADVANCED PHYSICS LABORATORY

HTC

High T_C Superconductors

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Please send any corrections, comments, or suggestions to the professor currently supervising this experiment, the author of the most recent revision above, or the Advanced Physics Lab Coordinator.

INTRODUCTION

A superconductor is a material that is both perfect conductor with zero resistance and a perfect diamagnet[1] expelling any magnetic field. Superconductivity was first discovered in pure metals, which have transition temperatures, T_c, to the superconducting state of a few Kelvin. Much later, some binary alloys, such as Nb_3Sn, were found to have much higher values of T_c, of order 20 K, and these are the superconductors now used in strong magnets. For many years after this, attempts to make materials with still higher T_c led nowhere. Then in 1986, Bendorz and Muller reported a much higher T_c in a ceramic based on CuO. Since then the field has flourished, with transition temperatures of newly discovered materials rising to the current record of 133 K ($-140°C$) at ambient pressure, and 203K (-70°C) at 90 GPa (10^6 atmospheres) pressure[2]. For their discovery, Bednorz and Muller were awarded the Nobel Prize in physics in 1987.

There are two set-ups for this experiment – "Make your own" and "Kit" – with different procedures. Make sure you know which version you are assigned to. Much of this write-up is relevant to both, but if a part applies only to one or the other, it is tagged with an "M" or a "K".

For "**Make your own**", you will prepare your own thin (few mm thick) samples of the "123" copper (or cupric) oxide superconductor $YBa_2Cu_3O_7$ (commonly known as "YBCO"). Here the "7" is nominal; the precise value 7-δ is critical as it controls the number of superconducting carriers in the sample. The preparation involves mixing metallic oxides followed by a solid-state reaction, otherwise known as the "shake and bake" technique. These samples are then tested for levitation and their resistivity studied as a function of temperature.

With the "**Kit**", you have several pre-made samples of YBCO and BSSCO (Bismuth strontium calcium copper oxide) superconductors, and you may study both resistivity and magnetization in these materials. Resistance measurements are sensitive to the one-dimensional path of least resistance, while magnetic susceptibility measure the volume characteristics of the sample. Until such time as this write-up is further updated, instructions will be provided by the supervising professor and the Colorado Superconductor manual. A "sand" cryostat is used for these measurements, which allows more gradual warming of the samples, but more care must be taken to avoid being splashed by liquid nitrogen during the initial cool-down.

Theory

Superconductivity is a quantum phenomenon that can occur in a normal metal if conduction electrons locally distort the atomic lattice in such a way that there is a short range effective attractive force between electrons. If this attractive force is stronger than the Coulomb repulsive force between a pair of electrons, weakly bound "Cooper pair" electron-electron states can form. These pairs form when thermal energies (~kT) are less than the pair binding energy $2E_g$, where E_g is the energy gap between an electron in a Cooper pair state and a normal conducting ground state. Since Cooper pairs are bosons with integer spin, they form a Bose-

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[1] Note that perfect diamagnetism (interior field **B**=0) does not follow from zero resistivity, which only implies d**B**/dt=0.

[2] A.P. Drozdov *et al.*, *Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system*, Nature 525 (2015) 73-76; http://dx.doi.org/10.1038/nature14964.

Einstein condensate quantum state that can't be scattered by the defects and excitations that cause normal electrical resistance, so the material has zero resistivity.

The energy gap $E_g(T, H)$ depends on temperature (T) and magnetic field (H), and a material only becomes superconducting below a critical temperature, T_c. According to standard BCS theory, the Cooper pair binding energy is $2E_g(T, H) \approx 7/2kT_c$.

Superconductors expel magnetic fields through the Meissner effect, but a sufficiently high field can destroy the superconducting state. The magnetic field sufficient to force a bulk superconductor to revert to its normal state at temperature T is known as the critical field, $H_c(T)$:

$$\frac{H_c(T)}{H_c(T=0)} = 1 - \left(\frac{T}{T_c}\right)^2 \tag{1}$$

Type I superconductors have a single critical field H_c, but Type II superconductors have two apparent critical fields, H_{c1} & H_{c2}, with $(H_{c1} H_{c2})^{1/2} \approx H_c$. Below H_{c1}, all magnetic field is excluded as for a Type I superconductor. Above H_{c1} but below H_{c2}, the superconductor is in a mixed state where magnetic field exists in "vortex" filamentary normal regions within the superconducting material. The material is completely normal above H_{c2}. All known high temperature superconductors (e.g. the ones studied in this experiment) are Type II.

Between H_{c1} and H_{c2}, a Type II superconductor resists changes in the number of vortex filaments it contains, so it can be levitated or suspended in a magnetic field. See Ma et al. for more information on the forces on Type II superconductors in non-uniform magnetic fields. Figure 10 of Brandt[3] shows how the magnetization of a short cylinder depends on the aspect ratio (diameter/length) and exhibits hysteresis, i.e. differs for H increasing and decreasing.

Whether a superconductor is Type I or II depends on the ratio $\kappa = \lambda_L/\xi$. λ_L is the London penetration depth which parameterizes how external magnetic fields are exponential damped below surface of a superconductor. ξ_0 is the intrinsic coherence length over which the superconducting electron density cannot vary significantly, and is related to the typical separation of the electrons in a Cooper pair. A superconductor is Type II when the penetration depth is greater than the coherence length. The critical field values are related to κ:

$$H_{c1} \approx \Phi_0/(\pi \lambda^2) \approx H_c/\kappa, \qquad\qquad H_{c2} \approx \Phi_0/(\pi \xi^2) \approx \kappa H_c \tag{2}$$

where $\Phi_0 = hc/(2e)$ is the minimum quantum of flux inside a superconductor.

Resistivity and magnetization measurements give complementary information on a superconducting sample. For example, the resistance will be zero as long as there is a superconducting path through the sample, even if most of the sample is normal, either because the sample is inhomogeneous or because it is a Type II superconductor in the mixed state. Magnetization measurements are sensitive to what volume of the sample is superconducting, although the relationship is only linear below H_{c1}.

For a further introduction on superconductors, see the Superconductivity Chapter in Kittel, and for more details see Poole et al., Sharma, or Tinkham.

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[3] E. H. **Brandt**, *The Vortex Lattice in Conventional and High-Tc Superconductors*, Brazilian Journal of Physics 32 (2002) 675-684; http://www.scielo.br/pdf/bjp/v32n3/a02v32n3.

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Safety Reminders

- Barium Carbonate is poisonous. Before working with $BaCO_3$, you must read its Material Safety Data Sheet (MSDS) available in the cabinet or online.
- Eye protection, dust mask, and vinyl gloves must be worn when grinding the powders, any spilled powder must be cleaned up and properly disposed of. You must wash your hands when finished.
- Eye protection, gloves, and proper footwear, e.g. no sandals, must be worn when working with cryogenic liquids or dewars.
- Before pouring or using liquid nitrogen, always assess what might happen to you or other students if there was a spill. For example, you do not want to be in a situation where knocking over a small cryostat on the table would pour liquid nitrogen onto a student's lap
- When pouring liquid nitrogen (LiN) into a small dewar, it is best to place the small dewar on the floor so that any spills or splatters will be far away from your eyes and from clothes that might absorb and hold spilled LiN against your skin causing more severe burns.
- When pouring LiN into a sand cryrostat on the table with the sample already embedded in the sand, the liquid nitrogen may initially bubble vigorously with increased risk of splashes, so be particularly careful.
- If the helium gas tank were to fall over and have its valve knocked off, it would turn into a deadly torpedo capable of smashing through concrete walls. The helium gas bottle must always be properly secured in its cart.
- Compressed gas can propel dust or ends of hoses at high velocities, so eye protection must be worn when turning on the helium gas. Make sure all hoses are properly attached and not damaged before slowly turning on the helium. If you are not familiar with gas bottle regulators, ask your TA, Instructor or Technologist for guidance.

NOTE: This is not a complete list of every hazard you may encounter. We cannot warn against all possible creative stupidities, e.g. juggling cryostats. Experimenters must use common sense to assess and avoid risks, e.g. never open plugged-in electrical equipment, watch for sharp edges, don't lift too-heavy objects, …. If you are unsure whether something is safe, ask the supervising professor, the lab technologist, or the lab coordinator. When in doubt, ask! If an accident or incident happens, you must let us know. More safety information is available at http://www.ehs.utoronto.ca/resources.htm.

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EXPERIMENTAL

Currently, students who bake their own samples can only make resistivity measurements, while students using the kit samples may focus on magnetization.

Recipe for "Bake your own" (M)

1. Weigh out about 1 g of Y_2O_3 and, separately, the appropriate amounts of $BaCO_3$ and CuO. Using the molecular weights of these compounds, very carefully[4] calculate the correct

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[4] Mistakes in this calculation are by far the most common reason for failed, i.e. non-superconducting, samples.

amounts to get YBa_2Cu_3 as the final product. Note that Carbon and Oxygen may react with the air and leave or enter the sample during baking.

2. Grind these materials in a mortar, doing the $BaCO_3$ first, and mix and grind together until no black or white streaks are left in the mix.

3. React the mixture at 900° C to 930° C in air for 15 hours in an alumina crucible. Take 3 hours to ramp up to 900° C. This ensures that the CO_2 will evolve before the solid-state reaction takes place. Then slowly ramp to 930° C over 15 hours. After the oven has cooled down remove the sample, grind and repeat the reaction for another 15 hours soaking at 930°C.

4. Press the powder into pellets using the hydraulic press. Note that the powder will compress by about a factor of two. Hold the pellets at about 2000 lbs of pressure for 5 minutes before releasing the pressure. If the pellet breaks when extracted, hold the pressure longer and perhaps increase the pressure to 2500 lbs.

5. Sinter the pellets in flowing oxygen following this procedure: 3 hours to ramp up to 930° C, hold there for sintering for 10 hours. Slowly cool to 700° C over 8 hours, hold here for 6 hours then cool to 400° C over 10 hours. Finally turn off the furnace. This procedure will ensure that the oxygen concentration will saturate at approximately $YBa_2Cu_3O_{6.95}$, the desired composition.

6. You should now have some high T_c superconducting samples!

Test if sample is superconducting

To test whether a sample – either one you've made or one provided to you - try to levitate it, cooled with liquid nitrogen, on top of a powerful magnet. If it floats - success! It floats because a superconductor expels all magnetic field from its interior: $B = 0$ (Meissner effect). This corresponds to a diamagnetic moment on the pellet which is opposite to the magnet's polarity therefore repelling it.

If the sample does not actually float above the magnet with a space between it and the magnet, either the sample is not superconducting or the repulsion force is not great enough to overcome gravity. If this is the case, make an effort to explore the magnetic properties of the sample at liquid Nitrogen and room temperatures. Even a partial Meissner effect will correspond to zero resistivity in this type of superconductor (Type II).

Resistivity

The resistivity of a thin sample – either one you've made or one provided – can be measured as a function of temperature and the superconducting transition observed.

Attaching leads to "bake your own" sample (M)

Attach the sample to the resistance probe with double sided tape. Glue the thermocouple onto the sample with Duco cement. Then attach the 4 leads to the sample with silver paint and/or epoxy. A 4-wire resistance measurement normally uses two outer leads to provide an alternating current. The voltage across the two inner leads should be proportional to the current across the two outer leads, with the same period and phase. This method allows for sensitive resistance measurements and eliminates systematic errors caused by thermal emf and resistance of the leads

and connections themselves. Use small amounts of silver paint and Duco cement in order to minimize the electrical pad size.

Four probe method

Use the 4-wire method of measuring resistance and monitor the resistance and temperature as the probe is slowly cooled down to liquid nitrogen temperature. Prepare a plot of the results which should reveal T_C, the point at which R $\rightarrow$ 0. An AC current is preferable, and a typical circuit is shown in Figures Figure 1 & Figure 2. If a DC current is used one must reverse the current and take two measurements at each temperature in order to subtract out the thermal EMFs. If you use AC and a step-ohm resistance box, do not use high frequencies as the circuitry of the box may exhibit reactance. Keep $f \leq 100$ Hz.

Suggested Resistivity measurements

Measure the resistance in the normal state up to room temperature. What temperature dependence is observed? Is this typical of metals? Figure 1b of Rodriguez[5] shows how resistivity vs temperature can depend on the sample annealing time.

What happens to the resistance just above T_c? Can this be explained in terms of fluctuating superconductivity in the normal state? You may want to look at the paper by Eagles[6] or consult a text on superconductivity such as Tinkham (Chapter 8).

Make an absolute measure of the resistivity at room temperature. This can be done with the van der Pauw method[7]. Here one places the 4-wire leads around the edge of the sample of uniform thickness, d. Label the leads A, B, C and D. Passing a current through A to B and measuring a voltage across C and D yields a resistance $R_{AB,CD}$. Repeat this for another combination of current/voltage leads. Then solve the following equation for the resistivity ρ of the material under investigation.

$$\exp(-\pi R_{AB,CD}d/\rho) + \exp(-\pi R_{BC,DA}d/\rho) = 1 \tag{3}$$

As van der Pauw showed this method yields the resistivity for any sample shape of uniform thickness as long as the leads are mounted on the edge.

How does your value of the resistivity compare to that of copper? Are high-T_c compounds good metals? Extrapolate the normal state resistivity to $T = 0$. What does this value tell you about the material you have made?

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[5] J.E. **Rodriguez**, *YBCO samples as a possible thermoelectric material*, Physica Status Solidi 2 (2005) 3605–3608; http://dx.doi.org.myaccess.library.utoronto.ca/10.1002/pssc.200461769.

[6] D.M. **Eagles**, *Analysis of Resistance Data on a Good Ceramic Sample of YBa₂Cu₃O₇₋ₓ*, Jpn. J. Appl. Phys. 32 (1993) 1077-1081; http://m.iopscience.iop.org/article/10.1143/JJAP.32.1077/pdf.

[7] L.J. van der Pauw, *A method of measuring specific resistivity and Hall effect of discs of arbitrary shape*, Philips Res. Repts. 13 (1958) 1-9, http://socrates.berkeley.edu/~phylabs/adv/ReprintsPDF/SHE%20Reprints/01-Measuring%20Discs.pdf; *A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape*, Philips Tech. Rev. 20 (1958) 220-224, http://electron.mit.edu/~gsteele/vanderpauw/vanderpauw.pdf.
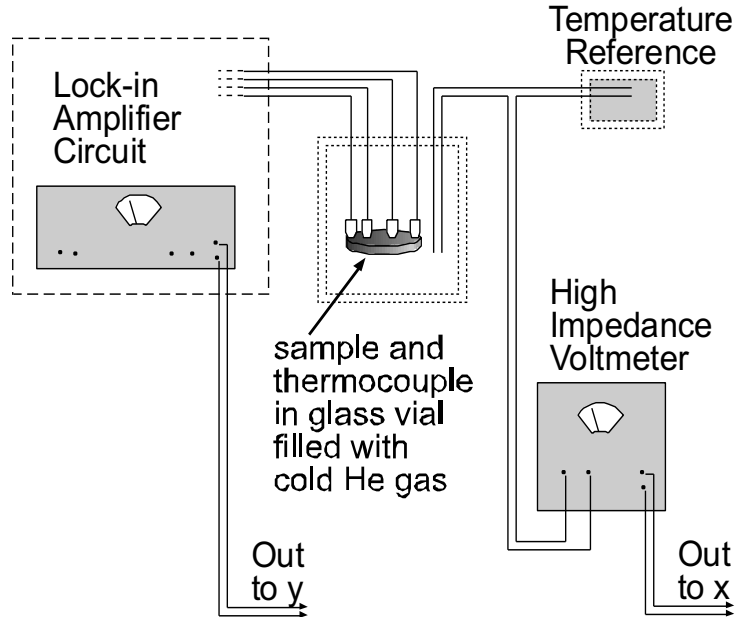
Figure 1: A schematic overview of a possible layout for simultaneous measurements of temperature and resistivity. See Figure 2 for "Lock-in Amplifier Circuit" details.
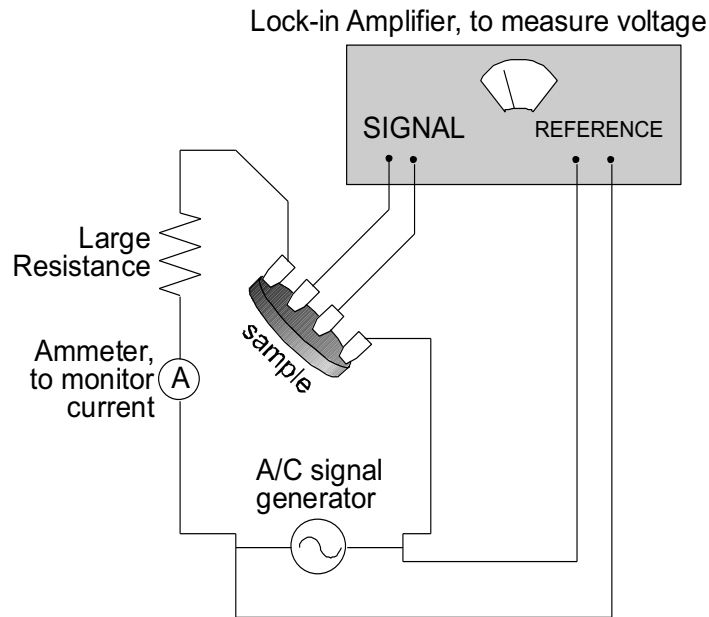

Figure 2: A possible Lock-in Amplifier circuit to measure the resistivity of the sample. A n introductory video on the use of Lock-in is available at https://www.youtube.com/watch?v=oKmXaLlvr6c.

Magnetization (K)

The Colorado Superconductor kit has one or two high T_C samples wrapped in copper coils. As discussed in the Colorado Superconductor guide, measuring the AC impedance of the coil provides information on the magnetic susceptibility of the sample. As with resistivity, we

want to generally study how the susceptibility of the sample changes as a function of temperature, and measure T_C in particular. One challenge is that the samples are quite large, and the temperature is only measured (by a thermocouple) at the bottom of the sample (assuming the sample is vertical). If there is any temperature gradient across the sample, then the susceptibility will also vary accordingly, which smears out the relation between susceptibility and temperature.

Carefully measure the susceptibility of the kit sample as a function of temperature and frequency using the sand cryostat. You will need to decide what frequency to use; you may be able to theoretically reason whether higher or lower frequencies are better, but it is strongly recommended that you experimentally try different frequencies. To improve the measurement, one could try to measure the temperature variations across the sample, try to create a larger uniform temperature volume around the sample, or try to wrapping a coil around a smaller sample. Here are some suggestions, but it is not known at the present time (January 2016) how well how well any of them will work. Your Professor or Demo may have helpful suggestions, so talk to them.

- Try using another thermocouple (i.e not the one attached to the sample) to estimate how large and problematic the temperature variation across the sample might be.
- Place the sample inside a nitrogen gas filled test-tube dipped in liquid nitrogen (i.e. the method used by the "make your own" students). This may produce less temperature variation across the sample.
- Small, thin discs of YBCO created by students should be available. Check that the disc is superconducting (i.e. it shows the Meisner effect on the test magnet) before trying to wrap it in some configuration. A wide variety of wire is available from the lab technologists. A non-magnetic form, e.g. plastic, can be used around the disc. Try measuring the AC impedance of your coil. (One advantage of "rolling your own", is that you may be able to compare the impedance of the coil with and without the sample inside.)

REFERENCES

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M. **Tinkham**, *Introduction to Superconductivity*, 2nd Edition, Dover, 1996; https://app.knovel.com/web/toc.v/cid:kpISE00023/viewerType:toc/root_slug:introduction-to-superconductivity.