



YBCO Synthesis and Characterization (Electrical Transport Option)

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Description: Superconductivity is an exciting phenomenon whereby certain materials at low temperatures demonstrate zero electrical resistance and the expulsion of magnetic field, also known as the Meissner effect [1]. In this lab, students will synthesize and electrically characterize their own polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductor, the first material with a superconducting critical temperature (T_c) above liquid nitrogen's boiling temperature (77 K) [2]. The pursuit of high temperature superconductivity in this era created such a fervor that the 1987 American Physical Society March Meeting will forever be remembered as the "Woodstock of Physics," where on March 18, two thousand physicists and chemists crammed themselves into the New York Hilton ballroom and overflow rooms to listen to talks and hold discussions from 7:30 pm to 3:15 am [3].

Student Learning Outcomes

- Students will learn solid state reaction techniques and synthesize a polycrystalline ceramic sample of YBCO.
- Students will develop proficiency in attaching small wire leads to samples using silver paint.
- Students will operate the Electrical Transport Option (ETO) of the VersaLab cryostat.
- Students will apply foundational knowledge of relevant solid state physics to resistance vs. temperature characterization.

Materials List

On the following page are tables of the supplies and equipment that can be used to perform this activity. The catalog numbers and suppliers listed are merely suggestions, and instructors should feel free to obtain whatever materials are within their means and accessibility. The chemical quantities mentioned should easily last a semester.

Sample Synthesis and Heat Treatment

Item	Quantity	Catalog Number	Supplier
Y ₂ O ₃	50 g	205168-50G	Sigma Aldrich
BaCO ₃	500 g	237108-500G	Sigma Aldrich
CuO	25 g	203130-25G	Sigma Aldrich
Mortar and Pestle	1	12-950AA	Fisher Scientific
Balance with .01 mg accuracy	1	01-920-052	Fisher Scientific
Weighing Paper or Weighing Boats	1 pack	S402871 or 02-202-100	Fisher Scientific
Spatula or Scoopula	1	14-357Q	Fisher Scientific
Hydraulic Press	1	13-872	Fisher Scientific
13 mm Press Die	1	SDS13	Across International
Tube Furnace	1	10-472-53	Fisher Scientific
Air supply line	1		
Combustion Boat	1	07-680a	Fisher Scientific

Sample Mounting

Item	Quantity	Catalog Number	Supplier
Zoom Stereo Microscope	1	12-070-850	Fisher Scientific, Zeiss
Calipers	1	14-648-17	Fisher Scientific
25 μ m Diameter Pt Wire	5 m	10292	Alfa Aesar
Lighter	1		
Scissors	1		
Leitsilber 200 Silver Paint	30 g	16035	Ted Pella
Tweezers	2	17-447-102	Fisher Scientific
Thin stick or needle			
Apiezon H Grease	25 g	FAPGH00025	Fisher Scientific

Sample Measurement

Item	Quantity	Catalog Number	Supplier
Multimeter	1		
VersaLab	1	1300-001	Quantum Design
VersaLab ETO Module	1	1084-700	Quantum Design

YBCO Synthesis

1) Using the precursor compounds Y_2O_3 , $BaCO_3$, and CuO , have the students determine the required stoichiometric ratios to yield 2 grams of $YBa_2Cu_3O_7$. The oxygen content will be determined by the heat treatment, at which point also the C will be removed; therefore, have the students focus on the Y, Ba, and Cu ratios.

A successfully performed synthesis mixed the chemicals in proportions such that the atomic ratios of yttrium, barium, and copper are 1:2:3: $0.5Y_2O_3 + 2BaCO_3 + 3CuO + \rightarrow YBa_2Cu_3O_7 + CO_2$.

$$Y_2CO_3 = 0.2823g$$

$$BaCO_3 = 0.9868g$$

$$CuO = 0.5966g$$

2) Carefully weigh out the quantities required and place the compounds into a mortar bowl.

3) Grind the combined powder using the mortar and pestle, applying a circular motion as you grind.

4) Have the students search the physics and chemistry literature in order to come up with their own heat treatment recipes. It is often suggested to treat the powders multiple times with re-grinding in between heat treatments. When they have decided on their plan, use a chemical spatula or scoopula to remove the compound from the mortar and into a crucible. When heating the samples, it is suggested to provide oxygen flow via an air supply line.

In order to create a ceramic pellet, extract the powder from the crucible and place it in a die for pressing. An application of 10,000 psi for one minute should be sufficient.

The material should be a deep black by the end of the process.



Figure 1. Completed YBCO pellet.

A successful heat treatment cycle is:

Ramp up to 900 C in 4 hours.

Dwell at 900 C for 10 hours.

Cool to room temperature in 8 hours.

Re-grind the sample.

Ramp up to 930 C in 4 hours.

Dwell at 930 C for 15 hours.

Cool to room temperature in 10 hours.

Re-grind the sample and press into a pellet.

Anneal the pellet by ramping up to 955 C in 3 hours.

Dwell at 955 C for 5 hours.

Cool to room temperature in 7 hours.

Ramp the pellet one last time to 500 C in 2 hours.

Dwell at 500 C for 14 hours in order to set the oxygen content.

Cool to room temperature in 4 hours.

Measurement Background

Nearly all fundamental materials characterization methods rely on the proper measurement of current and voltage. As such, experimental setups must be considered in terms of their equivalent electronic circuits in order to properly characterize a physical quantity. The heart of such a circuit is Ohm's law, $V = IR$, where V is the voltage drop across and I is the current through a resistance value R . From the resistance, one can obtain the material resistivity, which is the intrinsic character of a material to hinder electrical conduction. In a typical sample measurement, the resistivity for a typical rectangular geometry is defined to be

$$\rho = \frac{RA}{L},$$

where R , A , and L are the resistance, cross-sectional area, and length of the sample, respectively.

The sample puck of the VersaLab (Figure 3) clearly depicts three channels with gold-plated pads labeled I+, V+, V-, and I- for four-wire resistance measurement. It should be noted that the ETO does not support the use of Channel 3. Two-wire measurement is also available using I+ and V-.



Figure 2. The VersaLab Puck. Notice the clearly labeled contact pads for the three measurement channels.

As a starting point, we consider the 2-leads measurement as illustrated below in Figure 3. In the 2-leads technique, current is applied to two electrodes attached to a load resistance. A voltmeter in parallel measures the entire voltage drop across the attached leads and the sample to be measured. This form of measurement occurs, for example, whenever a hand-held multimeter is used. However, the drawback behind this technique is that the lead resistances of the measuring device contribute to the voltage reading, i.e. the contact resistance is indistinguishable from the load resistance. In typical characterization of materials, this method has very limited uses.

Two-Wire Resistance Measurement

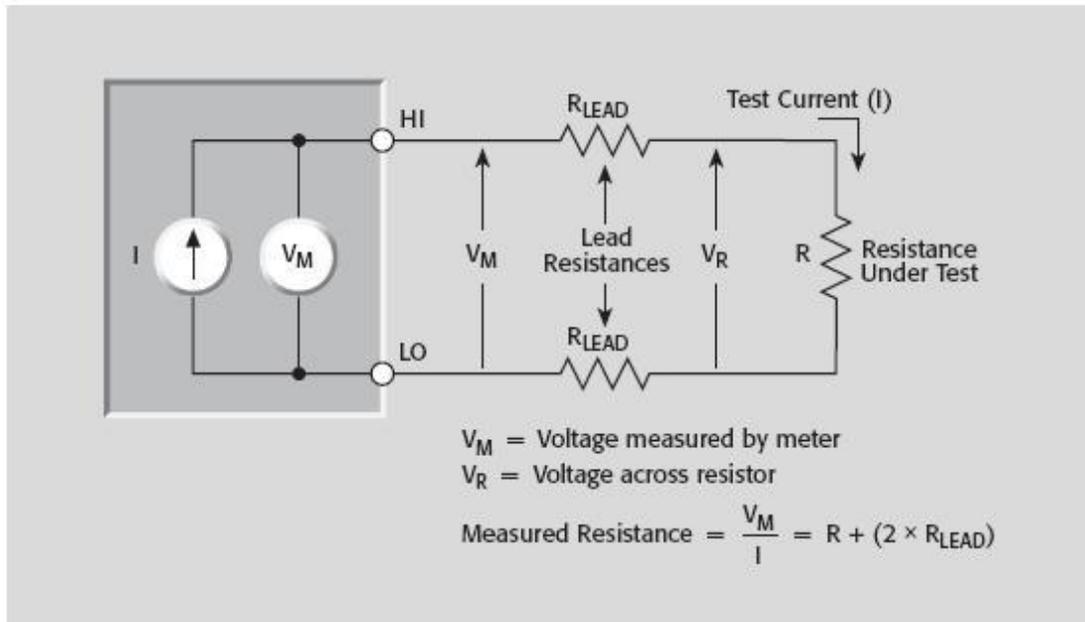


Figure 3. The circuit diagram for a typical 2-leads electronic configuration. Because the voltmeter is connected in parallel with the current source leads, the measured voltage drops occur over all leads and the sample, resulting in a total resistance measurement that encompasses every resistance in the circuit. [Adapted from 4]

The standard 4-leads technique illustrated in Figure 4 typically overcomes this drawback. The load resistance to be measured has four contacts attached. Measurement current is applied via the two outermost contacts whereas the two innermost contacts are connected to a voltmeter. In principle, the voltmeter input is at high impedance, thereby preventing the flow of measurement current in the innermost leads. As a result, the voltage drop that is recorded occurs between the two inner electrodes, eliminating any resistive contribution from the electrodes themselves. This is a very elegant technique from an electronics standpoint, but in reality, the voltage reading is heavily dependent upon the contact geometry and quality.

Four-Wire Resistance Measurement

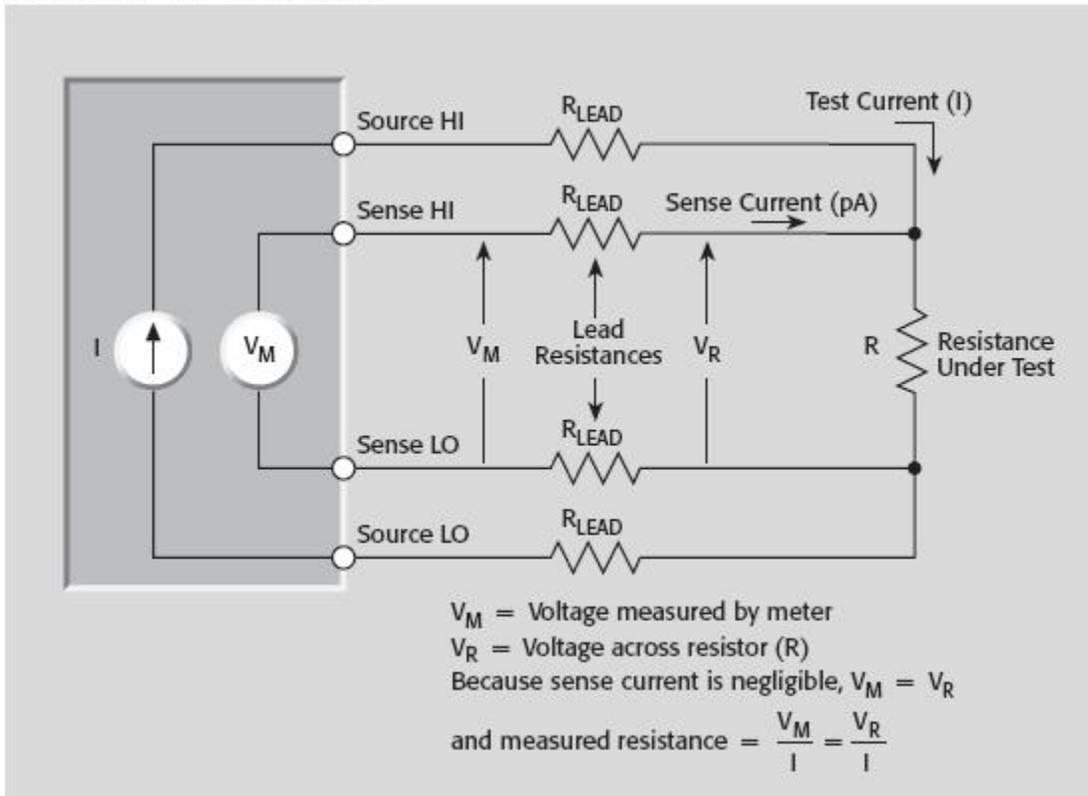


Figure 4. The circuit diagram for a typical 4-leads electronic configuration. Here, the voltmeter is attached to the sample via two leads separate from the current leads. Due to the negligible current in the voltmeter leads, the voltage drop, hence measured resistance, occurs only across the sample under test. [Adapted from 4]

YBCO Sample Preparation and Mounting

1) Cut a piece of weigh paper or cigarette paper in order to cover the gold plated sample holder on the VersaLab puck. This will prevent the sample from shorting. Apply a thin layer of thermal grease to the gold area, lay the paper on top of it, and add another layer of grease over the paper. It is recommended to use Apiezon H grease.

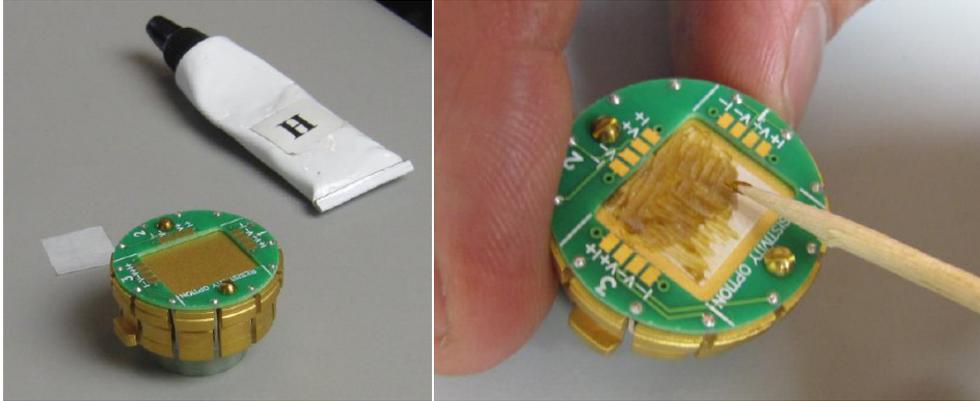


Figure 5. Apiezon H grease and paper application in order to prevent a short to the sample, keep the sample in place, and provide good thermal contact.

2) Measure the thickness of the pellet.



Figure 6. Thickness measurement of pellet in order to determine the cross-sectional area for the resistivity calculation.

3) The pellet should encompass the entire area of the sample puck. Choose whether you wish to connect the pellet to Channel 1 or Channel 2, as Channel 3 is not used with the ETO. You may opt to measure two samples at the same time, but that will require sawing or breaking pellets into smaller samples.

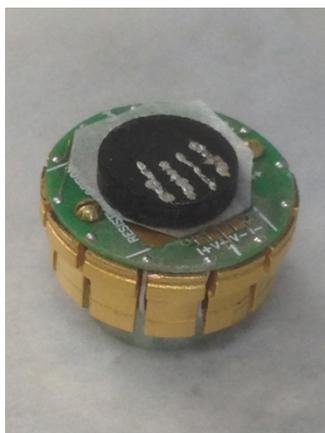


Figure 7. Sample mounted on the VersaLab puck with contacts already in place.

4) Obtain a strand of Pt wire and anneal it by running a lighter flame over it. This will soften the wire and make it easier to work with. Cut the wire with some spare length to connect the samples to the puck channel pads.

5) Using tweezers and a microscope, attach four Pt wires to your sample. The two inner wires will measure voltage while the two outer wires measure current. Silver paint will be used to attach the wires, so before getting started, it is useful to place a drop of silver paint on weighing paper or a glass slide and get a feel for how its viscosity changes as it dries. Use a thin stick or needle to play with this and see if you can control placing a small droplet of paint on a surface.

When you are ready to work with the sample, one method to attach leads is to lay individual wires in the locations that you want and placing a droplet of silver paint at the location with the small stick or needle. This is sufficient to measure the bulk properties of the sample, but painting stripes across the entire face of the pellet will allow for greater bulk measurement coverage.

Any mistakes can be remedied with a cotton tip soaked in ethanol or the creative use of a needle, stick, or razor blade when the silver paint has dried. In an extreme case, the surface layer of the pellet can be sanded off.

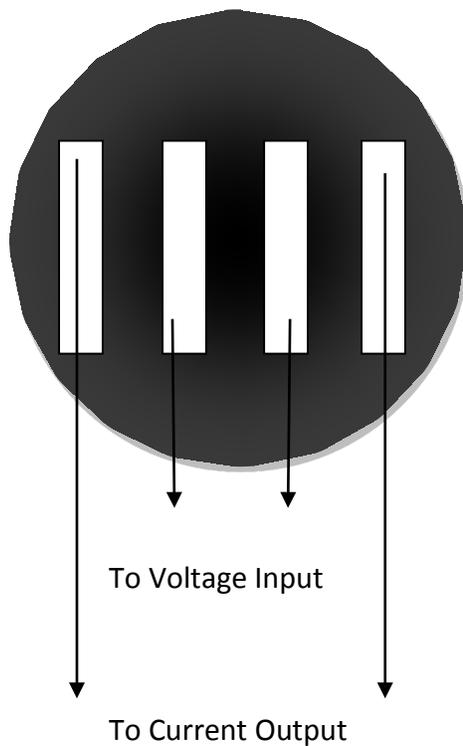


Figure 8. Four-lead measurement configuration for the sample pellet.

6) Measure the distance between the inner voltage contacts, which will give the length L in order to calculate the resistivity. Measure the length of the inner electrodes in order to determine the cross sectional area with the previous thickness measurement.

7) Place the sample onto the VersaLab puck and use silver paint to connect the other ends of the wires to either Channel 1 or Channel 2. The I and V pads are clearly labeled.

8) There are several methods to check the quality of the contacts, but the most straightforward would be to insert the puck into the sample test holder accessory for the VersaLab and measure the resistances between any two leads using a hand-held multimeter. Ideally, the contact resistances should be less than 100Ω .



Figure 9. Testing connections on the VersaLab puck via the sample test holder accessory.

Samples Measurement Using the ETO

Refer to your VersaLab manual to prepare the cryostat for operation.

1) Place the puck in the insertion tool and lock it into place. Make sure that the puck is snug and does not rotate once locked.

2) Make sure that the VersaLab is sample chamber is stable at 300 K with the magnet discharged. Use the VENT CONT command to vent the chamber, and then open the vacuum flange.

3) It is suggested to insert the puck with its keying notch aligned either to the right or left. When the tool has been inserted into the bottom, rotate the tool such that the notch will turn towards you. You should feel the puck drop slightly once the notch is properly aligned. Give the tool a gentle push downwards, release the lock, and lift out.

4) Replace the vacuum flange and activate the PURGE AND SEAL command. Once the chamber has been purged, use the ETO resistivity console to perform a quick 4 wire measurement of the sample or samples. If there is no reading, then a wire has broken in the process of mounting the puck.

5) Create a sequence to sweep temperature and measure resistance. In order to save time, you may use large temperature intervals to measure from 300 K to 100 K and then use finer temperature intervals to measure from 100 K to 50 K in order to properly catch the superconducting transition. You may refer to ETO measurement parameter guidance such as current, frequency, and autoranging in the transport newsletter:

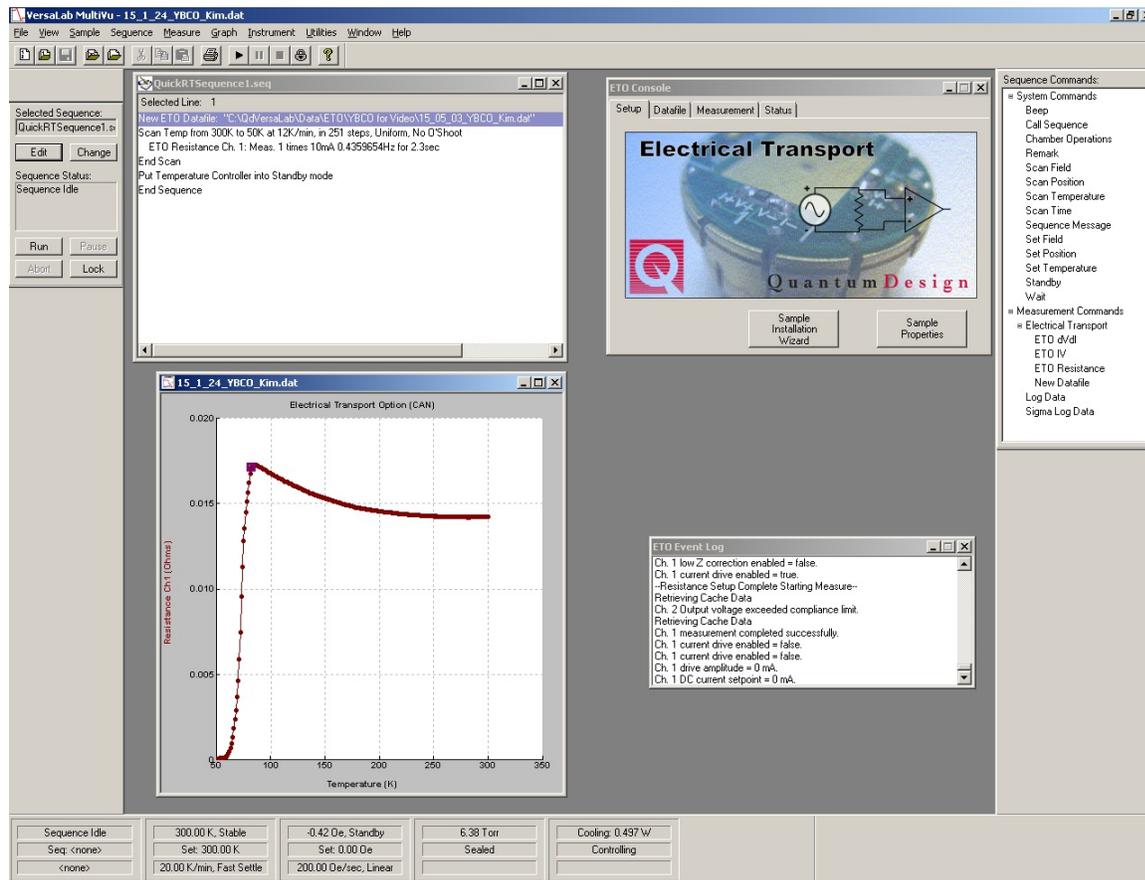


Figure 10. MultiVu interface for performing the measurement.

6) Run the sequence, and display the measurement in real time. Once the data has been acquired, have the students plot the resistivity vs. temperature using the dimensions of the sample and voltage lead placements that they have previously measured.

Data and Discussion

Ideal YBCO samples will possess resistance $< 1 \Omega$ at room temperature and a sharp transition temperature ~ 93 K.

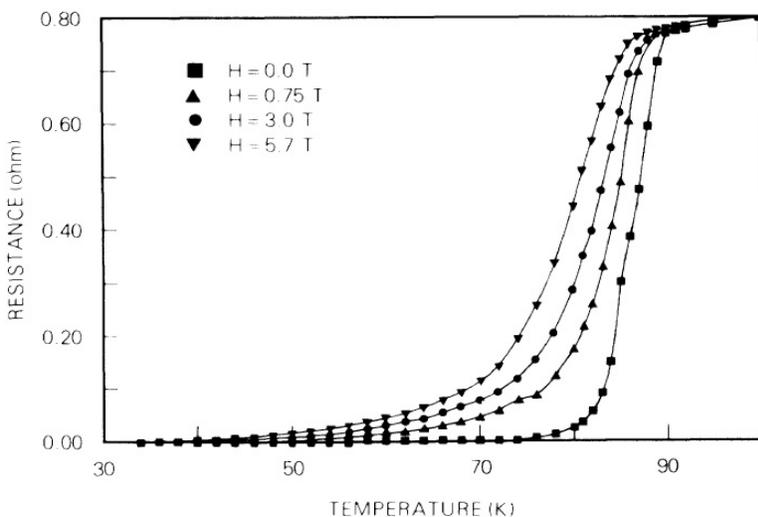


Figure 11. Resistance vs. temperature plots of YBCO under application of various magnetic fields [2].

Even if this is not achieved, it is possible to obtain sub-optimal superconducting samples with lower T_C and very broad transitions. Even mixed phase samples can reveal semiconducting properties and indication of superconducting domains. As such, this is a rich activity that illustrates the challenges of materials synthesis and engages the students in trying to explain the behaviors of their samples. The possibility of failure is exciting for the students, and instructors can make a competition out of this laboratory project. Most importantly, students should leave this activity well versed in fundamental techniques of condensed matter research.

Potential questions to ask students may include:

- 1) How is T_C determined from the data? What are some methodologies to obtain the exact temperature at which the onset of superconductivity occurs? *For example, students may plot the first derivative of their data with respect to temperature in order to see the onset of T_C .*
- 2) If the sample is not superconducting, does it demonstrate metallic or semiconducting behavior? How can this be concluded from the data, and what is the physical reasoning behind these particular resistance vs. temperature behaviors?
- 3) You may apply magnetic fields up to 3 T using the VersaLab. What effect does this have on the T_C , and why?
- 4) If the samples are very high impedance ($>10\text{ M}\Omega$), why does the standard 4-lead technique fail?
- 5) Compare your results with those of your peers. What methods are best for obtaining good superconducting YBCO?

References

- [1] For example, C. Kittel, *Introduction to Solid State Physics*, Wiley.
- [2] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang, and C.W. Chu, "Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure," *Physical Review Letters* **58**, 908-910 (1987).
- [3] K. Chang, "Physicists remember when superconductors were hot," *The New York Times*, March 6, 2007. http://www.nytimes.com/2007/03/06/science/06supe.html?_r=0
- [4] *Low Level Measurements Handbook*, 6th. Ed, Keithley.