Resistance of the Superconducting Material YBCO

A Senior Project

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In this paper the synthesis and measurement of resistance versus temperature for samples of YBCO was tested. YBCO is a superconducting material that will have near zero resistance at low temperatures. Several small pellets and one large pellet were made. The small pellets that were made did not show superconducting behavior. Even though an initial x-ray diffraction and observation of the Meissner Effect indicated superconductivity, the small pellets showed semiconducting properties. Rather than a sudden decrease in resistance as the temperature was lowered, their resistance increased. This seemed to be due to degradation of the sample which was confirmed by taking an x-ray diffraction of crushed pellets.

History

The discovery of superconductivity was made possible by the first liquefaction of helium in 1908. Though at first this may seem unrelated to electrical properties, it provided the means to cool materials cold enough to reach a transition temperature (T_c), where superconductivity is present. Armed with a new tool to probe material properties at low temperatures, scientists began experimenting with liquid helium. In 1911, Heike Onnes was studying the resistance of solid mercury and found something that he did not expect. At 4.2 K, the resistance suddenly disappeared, which had never been seen before. This observation started a chain of new discoveries for several different superconductors and still continues today.

Seventy years after the discovery of superconductivity, the highest temperature superconductors were only near the 20 Kelvin range. In order for more practical uses of superconductivity to be put into motion, a higher temperature superconductor needed to be discovered. This occurred in 1986 when there was a major breakthrough that would eventually lead to the discovery of YBCO and more high temperature superconductors. Johannes Georg

Bednorz and Karl Muller discovered superconductivity in a sample of a LaBaCuO system at temperatures as high as 36 K[1]. This new breakthrough started research on similarly structured materials containing copper oxide planes. $YBa_2Cu_3O_7$ was later discovered by Chu, et al, which had a transition temperature beginning at 93 K and zero resistance at 80 K. These temperatures are high enough to be above the 77 K boiling point of liquid nitrogen. YBCO opened the possibility for more practical applications and hopes for even higher temperature materials.

Magnetization

The most famous characteristic of superconductivity is zero resistance. However, they are not the same as a perfect conductor. The difference between superconductivity and a perfect conductor can be seen in their magnetic properties. Magnetization refers to the magnetic field in a solid that is present due to an applied field. This magnetic field is created from the alignment of the magnetic moments created from nuclear spins and the motion of electrons in the material. Depending on which in more energetically favorable, the magnetic moments can either align to add strength to the applied field or decrease it. This can be described by:

$$M = \chi H \qquad \text{(eq1)}$$

In this equation M is the magnetization and H the applied field. The proportionality constant, χ, is known as the magnetic susceptibility and describes how the dipoles align. In a superconductor, this value is found to be negative one.

The total field, B, inside the material is:

[1] Brown, Ronald F. *Solid State Physics*. San Luis Obispo: El Corral Publications, 2006.

$$B = \mu_o(H + M) \qquad \text{(eq2)}$$

Since χ =-1 then M is equal to –H. This leads to the inside field in a superconductor being zero. The expulsion of magnetic fields within a superconductor is the defining characteristic of a superconductor and creates a phenomenon known as the Meissner Effect. When in the superconducting state levitation of a magnet over the surface of the superconductor is possible. If a magnet is placed near a superconductor, currents flow inside in a manner that creates a magnetic field to oppose the magnets field. If a superconductor was purely a perfect conductor, due to Faraday's Law a changing magnetic flux creates currents. The currents will create a field aligned opposite of the magnet that will persist since the resistance is zero. The result of this is similar to taking two magnets and trying to force like poles together; there is a repulsive force. A key difference is that in the superconductor, the orientation of the magnet is not important and can be done with the poles facing any direction, as the superconductor will always induce the opposite pole.

The previous description of the Meissner Effect makes a superconductor sound like the fabled perfect conductor from freshman physics. However, there is another aspect of the Meissner Effect that separates it from the perfect conductor. Take the case where a magnet is placed on the surface of a superconductor in the normal state and then cooled. As it passes into the superconductive state, the flux from the magnet does not change. If it were a perfect conductor, Faraday's Law would tell us that there would be no currents generated to lift up the magnet. However, if one were to do this, they would find that the magnet rises from the surface of a superconductor. This indicates that the Meissner effect is not purely a consequence of zero resistance and Faraday's Law. The full description of the Meissner Effect separates

superconductors from perfect conductors. In a perfect conductor the penetration of magnetic fields is allowed but in a superconductor it is not.

In order for the magnetic susceptibility to stay at negative one, a superconductor needs to be kept below a critical temperature, T_c, and the applied field less than the critical field H_c. If an applied magnetic field is stronger than the critical field, it can penetrate into the superconductor causing a quenching of the superconducting state. Even though the temperature may be below the critical temperature, it will no longer be superconducting. A superconductor that follows this behavior is known as a type I superconductor.

There also exists another classification of superconductors known as type II where there is the possibility of the magnetic fields penetrating into the material without the quenching of the superconducting state. At low fields and temperatures type II superconductors are in the Meissner state, behaving the same as a type I superconductor. Magnetic fields are excluded and the magnetization of the inside is zero. However, once the applied magnetic field reaches a critical field (H_{c1}), rather than the material leaving the superconducting state, magnetic flux lines enter without quenching the superconductor. When this happens the material is in what is called an intermediate state. These fields create regions in the material that are no longer superconducting, but the material as a whole stays in the superconducting state since electric currents can just flow around these regions. The regions forced into the normal state form an ordered lattice with a quantized amount of magnetic flux. As the applied magnetic field is increased, the superconductivity is eventually quenched by what is called the high critical field (H_{c2}).

YBCO is similar to a type II superconductor in that it has both a Meissner state and an intermediate state. However, there are some differences in the way the intermediate state operates. As with the type II superconductor, the flux penetration can form an ordered lattice. The main difference from the type II classification is when either the applied field or temperature becomes high enough, the lattice of flux tubes begins to break down and move around. Since the flux tubes can now move, they can interact with currents causing them to lose some energy. A measurement of resistance is, in essence, a measurement of how much energy an electron has lost passing through a material. If the currents can now interact with the flux tubes, there is a slight increase in resistance. Movement of the flux tubes broadens the superconductive transition into the superconductive state. This is why in the higher temperature superconductors the transition may not be as sharp. The migration of the flux tubes, called flux creep, can be slowed down by flux pinning. This is achieved by using metal dopants which help to pin the flux tubes down to a single location. When this happens the effect on resistivity is like they are still in an ordered lattice but they are no longer organized. Rather the structure of the flux tube is analogous to glass, since glass has no repeatable structure. The flux tubes still stay in a single location but there is no sort of ordered lattice.

Theory

The path to the understanding of superconductivity can be described as difficult at best. It was once thought that superconductivity had been fully explained with models such as those presented in the Bardeen, Cooper and Schrieffer theory (BCS). The discovery of the high temperature superconductors challenged this theory, making the phenomenon once again a

mystery for the high temperature superconductors. Even though BCS theory explains the low temperature superconductors well, a new theory is needed for the higher temperature superconductors. As Philip Anderson, a physicist involved in superconductivity, put it "the consensus is there is absolutely no consensus in the theory of high T_c superconductivity[2]."

A useful step in trying to understand superconductivity is in understanding BCS theory. Though it fails to completely explain high temperature superconductivity, the interactions presented by the theory still has some relevance to higher temperature superconductors.

One particularly important observation leading to the BCS theory was the discovery of the isotope effect. The benefit of using different isotopes in a sample is that they provide similar bonding and have the same amount of electrons, but the mass is different. The different masses of these isotopes caused a change in the measurement of the critical temperature. If lighter isotopes were used, the transition temperature increased. The transition temperature was found to be proportional to the inverse square root of the atomic mass. Going back to a mass on a spring, as the mass on the spring is varied, the frequency of oscillation varies. The frequency of oscillation is also related to the inverse square root of mass. This seemed to be more than a simple coincidence and gave insights into the way electrons interacted with atoms in the superconducting state. These results pointed to the importance of vibrating atoms in the conditions required for superconductivity.

An important theoretical development came from the idea that the electrons may be able to form pairs even though they should repel each other via electrostatics. In 1956 Leon Cooper

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[2] Brown, Ronald F. *Solid State Physics*. San Luis Obispo: El Corral Publications, 2006.

proposed such a theory that would eventually lead to the full BCS theory. What he proposed is that at very low temperatures there was some mechanism that created pairs with a bonding energy that would normally be overcome by the lattice vibrations. He proposed that there was a small attraction between electrons that would allow pairs to form. It was when the lattice vibrations where small enough so the energy involved did not rip the pairs apart, would pairing occur. This seemed to be a reasonable approach due to the low temperatures needed to induce superconductivity seemed to match the vibrational energy of the lattice. Cooper showed that electron pairs can be attractive if certain conditions for the electrons' wave functions were met. First they needed to have equal and opposite ground state vectors, which leads to them having the same magnitude of momentum. Another condition that needed to be met was the spins of these electrons had to be oppositely aligned. When this is the case the electrons are traveling in opposite direction but somehow are able to interact in a way so that they lower their energy.

The mechanism for the pairing was needed to complete the theory. A reasonable approach was to combine the observations from the isotope effect and the theoretical developments from Cooper. While John Bardeen was working with his graduate student Robert Schrieffer, they were able to come up with a possible mechanism to do so. First it is useful to understand how a single electron interacts with the lattice. At low temperatures quantum mechanical effects become more apparent in the vibrations of the lattice. The vibrations become quantized into discrete energy packets known as phonons. Phonons and electrons can interact, which ends up being key in the BCS theory of superconductivity. In order to form a pair, they exchange a virtual phonon as they travel onward. One electron interacts with the lattice and causes a light distortion in the system, which is then passed on to another electron traveling in the opposite direction. When the first electron interacts with the lattice, the second one responds

so that there is no loss in momentum to the lattice. With no total momentum lost, this explains zero resistance since the main source of resistance in a material is loss of energy to the lattice.

The presence of cooper pairs changes the lattice band structure of the material. In a metal, electrons fill up the conduction band up to a certain point called the Fermi level. Bound Cooper pairs in the lattice introduce a small energy gap in the Fermi level in a superconductor that can be described by the BCS theory. This is referred to as the superconducting gap.

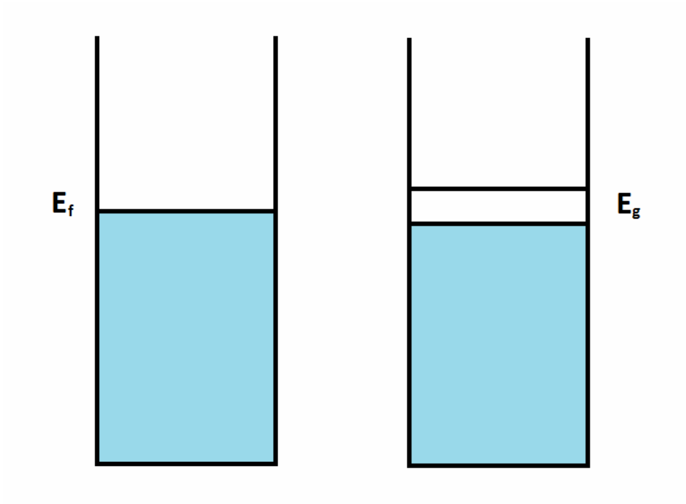

Figure 1: Electron band structure of a metal (left) vs a superconductor (right)

The energy related to the gap in the electron band structure of a superconductor is related to the binding energy of the cooper pairs. Experiments have been done that show evidence of this gap. Using either light in the infrared or microwave spectrums produced from a monochrometer, the amount of light reflected from the surface of a superconductor has been measured. Initially all the incident light is reflected, but as the energy is increased at a certain wavelength the amount of reflected light begins to decrease. The decrease corresponds to the light having enough energy to cause transitions across the superconducting gap. This wavelength can then be used to measure the bonding energy of the cooper pairs.

There is another peculiarity of the cooper pairs that allows superconductivity to exist in the BCS theory. If the pairs where to traverse the lattice in a motion independent of each other, there would be nothing to prevent the cooper pairs from being scattered in the lattice. The mechanism that prevents this is the result of the cooper pairs not only having the same wavelength, but also being in phase with one another. This means that the wave function of every pair will achieve a maximum and minimum at the same time and point acting like a tidal wave of electrons moving through the lattice. The in phase motion of the cooper pairs prevents scattering, since in order for one pair to be scattered several other pairs must be scattered as well. Robert Schrieffer, from the BCS theory, used the analogy of couples sliding down a bumpy hill to illustrate why this works. If each couple were to slide down individually, some would fall off their sleds when hitting bumps, which is analogous to scattering in the lattice. However, if the couples were then to link arms and then slide down, when one couple where to hit a bump they would be supported by their neighbors and not fall down. It would require a bump strong enough to pull all of the couples down in order to stop their motion.

In classic superconductors the mobile charge is the cooper pairs of electrons with a negative charge of two electrons. However, in superconductors such as YBCO, it is better to think of the cooper pairs as being the pairing of holes rather than electrons. Holes are the absence of an electron in the level that would be full of electrons. It is easier to consider the movement of these holes than the collective movement of all the electrons. Using holes as a charge carrier means that the charges that move are positive rather than negative. Holes in the cuprate superconductors come from the Cu^{2+} and Cu^{3+} states that are present. The number of holes in the copper-oxide conduction planes is influenced by the ratio of these two states. This ratio can be changed by the amount of oxygen present in the planes. The superconductive state is dependent

on the concentration of holes that are present and will only happen if a certain concentration is met. This is why varying the oxygen content in YBCO varies the critical temperature since when this is done the concentration of holes is affected.

Though the BCS theory had success in the description of early superconductors that were discovered, the mechanisms behind the theory do not seem to adequately describe the high temperature superconductors. One particular difference is that the magnetic properties of copper seem to influence the onset of superconductivity in the cuprates. Although copper atoms in their metallic form do not have a magnetic moment associated with them, the charged copper ions in the cuprate superconductors do. In YBCO, if the less magnetic zinc is substituted for the copper ions, the transition temperature decreases. If a magnetic ion, such as nickel, where substituted into the lattice, the change in the transition temperature would be less. This indicates that the ion's magnetic properties have an effect on the transition temperature. Further evidence for magnetism's involvement in superconductivity comes from the observation that current passes through the same orbitals in the copper ions that are responsible for the atoms magnetic properties. Also, as anti-ferromagnetism increases in a superconductor the transition temperature decreases. That is to say when the magnetic moments of the ions are aligned so that they are pointing in opposite directions the superconductivity decreases. Magnetic interactions also seem to point to why superconductivity is present in the CuO_2 planes and not in the CuO planes for YBCO. The hybridization of the bonding orbitals in the CuO_2 planes leaves sufficient space for magnetism to be intact in the anti-bonding band. However, in the CuO planes there is only one anti-bonding orbital per copper which doesn't allow for magnetism. The shape of these orbitals changes the way the magnetic moment of an electron in the valence band can be oriented.

Through the use of tunneling spectroscopy, the mechanisms behind high temperature superconductivity can be further investigated. In one particular study, A. Mourachkine used this technique to look at the energy gaps that appear during both the superconductive and normal states of $Bi_2Sr_2CaCu_2O_8$. The experiment found that there were two energy gaps. One of the gaps (Δ_p) is reminiscent of the energy gap from the BCS theory in that it is related to the pairing of electrons. However, the other gap in the superconductive state is what separates it from the BCS theory. This second gap (Δ_c) is most likely related to the coherence of the cooper pairs. A critical observation of these gaps is at what temperatures these gaps appear. As with a superconductor that behaves according to the BCS theory, it would be expected that these gaps would both appear at the critical temperature where superconductivity begins. They found that this was not the case. The gap that correlates to the binding of the cooper pairs actually appears at a temperature higher than the critical temperature. This indicates that if the material where to be acting in a manner predicted by the BCS theory, it would be in a superconductive state. The reason superconductivity is not present goes back to the analogy of couples sliding down a hill. Though cooper pairs can form at higher temperatures, the pairs lack any coherence and thus there is no superconductivity. The pairs need to be in phase with each other or the pairs that are formed are scattered by the lattice. Once they begin to become coherent, analogous to the sliding couple linking arms, superconductivity can appear. The second gap Δ_c appears at the critical temperature and seems to be related to the coherence of the cooper pairs. Once coherence begins the pairs are linked and scattering from the lattice is more difficult. Further observation of Δ_c backs up the importance of magnetism in the superconductive state of high temperature superconductors. The long range phase correlation of the cooper pairs in the cuprates is due to the spin fluctuations. As the temperature is increased, the magnetic moments due to spins in the

lattice can flip direction more easily. The lack of structure due to random fluctuations in spin causes the cooper pairs to no longer travel together in a coherent manner destroying the superconductivity.

YBCO Structure

The structure of YBCO plays an important role in superconductivity. YBCO has a layered structure consisting of copper oxygen planes with yttrium and barium atoms in the crystal structure as well. The resulting crystal structure is similar to a perovskite with a unit cell consisting of stacked cubes of $BaCuO_3$ and $YCuO_3$.

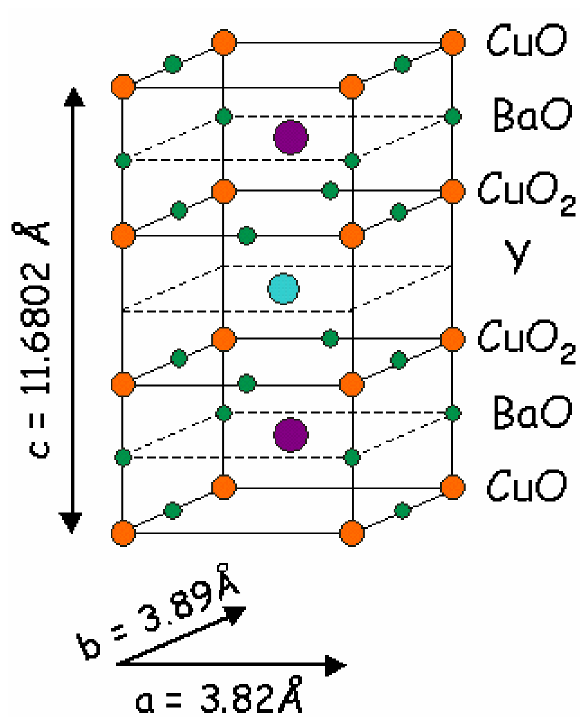

Figure 2: Structure of YBCO[3]

[3] *Crystal Structure. Hoffman Lab.* Harvard University. Web. <http://hoffman.physics.harvard.edu/materials/Cuprates.php>.

Figure 2 shows the structure and the chemical composition of the planes created. One important thing to note is the two different planes of copper and oxygen. The planes above and below the yttrium atoms have 2 oxygen atoms per copper where yttrium has planes near it with one copper per oxygen. These planes that are one to one are said to be oxygen deficient since when compared to a complete perovskite structure there are two oxygen atoms missing.

The superconductivity of the system seems to arise from these copper oxide layers since they are common to the copper oxide superconductors. The two planes of CuO_2 are separated by an atom of yttrium, a distance of 3.2A. The current that flows through a superconductor flows through the two CuO_2 planes. The distance between the copper atoms in these planes makes it easier for charge to hop between ions than from plane to plane. The consequence of this is that the current flow in a sample is affected by the orientation. If a single crystal were to be produced, its properties would be highly dependent on the orientation and would provide the best performance when current flows parallel to the planes. In-between these conduction layers there are barium, yttrium and additional copper oxygen pairs. Though these layers are not where currents flow through the material, they play an important role in the superconductivity. It is in these layers where a charge reservoir is created providing the electrons that will become pairs and carry current through the material.

The critical temperature of a YBCO sample can be affected by the amount of oxygen in the unit cell. For YBCO to be superconductive, it needs to have a chemical formula of $YBa_2Cu_3O_{7-x}$ where x is less than .5. $YBa_2Cu_3O_{6.5}$ does not go superconducting until the oxygen content is raised. Once the oxygen content is sufficient, superconductivity appears and as the oxygen content is increased and so does the transition temperature. This happens until the form

$YBa_2Cu_3O_7$ is reached. The changes in the oxygen concentration seem to have an effect on the bond lengths in the CuO_2 planes. According to Robert Cava et al, the changes in bond length correlate with a change in x. As the bond length is varied by the change in oxygen concentration, the critical temperature changes as well. This demonstrates that the superconductive state is heavily dependent on the structure of the copper oxygen planes if a small change in their structure affects the onset of superconductivity.

YBCO

In this paper, the synthesis of YBCO and the measurement of resistance as a function of temperature was attempted. Several pellets were made and what became apparent as the tests were conducted was the importance of the electrical connections to the YBCO. In the quest for good electrical leads, another problem appeared where the sample degraded to the point where superconductivity was no longer present. This was confirmed by x-ray diffraction that the material had changes since it was initially made.

Synthesis

The sample of YBCO created in this paper was created by combining yttrium oxide, barium carbonate, and copper (II) oxide. The chemical formula for the reaction is:

$$Y_2O_3 + 2\ BaCO_3 + 3\ CuO \rightarrow 2\ YBa_2Cu_3O_7$$

The ingredients were mixed together with a mortar and pestle to the ratio of the balanced equation above. After being ground together for thirty minutes, the powder was placed in an oven at 900^{o} C for 24 hours. Once removed the sample was reground for 15 minutes and placed back in the oven. The next day it was removed, reground and then pressed into pellets. The resulting pellets were placed in the oven at 900^{o} C once more for 24 hours. This was to harden the pellet and homogenize them. After verifying that the pellets stayed together, they were then placed back in at 450^{o} C for 24 hours. The purpose of this step was to uptake as much oxygen into the sample as possible since the properties of the superconductive state are dependent on the oxygen concentration of the sample.

The method used creates random orientations of YBCO grains. Since the properties are dependent on the orientation of the copper planes, a random orientation of the grains does not have as low of a resistance. For this experiment this method was sufficient, but if one were to create a better sample the orientation of the grains would be important. Grain alignment could be achieved several different ways. First by applying pressure, the grains can be compressed into a particular orientation. Another way is to embed the grains in a composite material such as an epoxy resin. Once embedded, a strong magnetic field could be used to orient the grains. Third, an oriented sample can be produced by melting a granular powder sample then by using an oven where the temperature varies regularly across the sample for reforming of the material.

There are also different preparation methods for the creation of YBCO. One possibility is substituting barium carbonate with barium oxide. This substitution provides some advantages over barium carbonate. The decomposition temperature of barium oxide is lower and also acts as an internal oxygen source. This aids with the annealing process making it easier to get the $YBa_2Cu_3O_7$ form. Also since there is no carbon in barium oxide, there is no formation of carbon

dioxide in the process. This is desirable since carbon dioxide can react with the YBCO to form non-superconducting phases at the grain boundaries. These slight differences result in a sharper transition into the superconducting state according to Rao et al. This method was not used due to the availability of materials in lab.

Meissner Effect

The first test was to see if the readymade sample of YBCO could levitate a magnet. Figure 3 shows the levitation of a magnet over a large disk showing the presence of the Meissner effect and confirming that the sample does show superconducting properties.

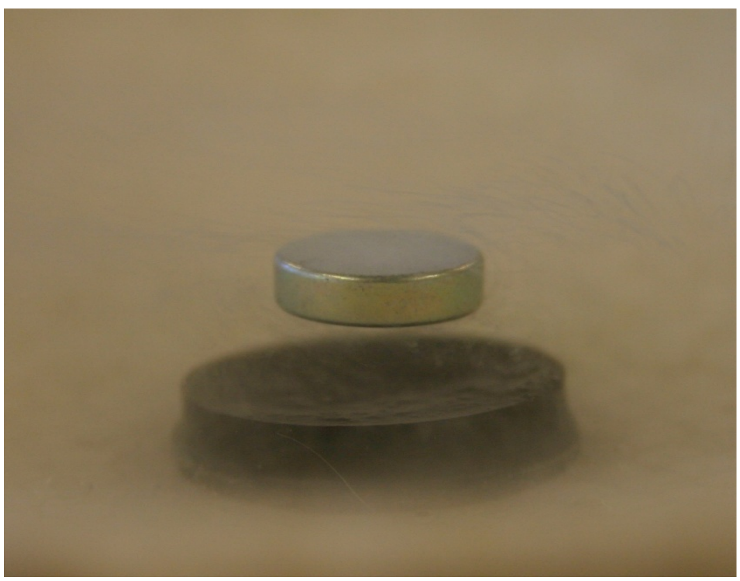

Figure 3: Levitation of a magnet over YBCO

X-Ray Diffraction

Through x-ray diffraction the structure of a crystalline solid can be determined. A specific wavelength of light is incident on a crystalline solid at different angles. If the angle is just right, constructive interference can take place showing up as a peak in the diffraction data.

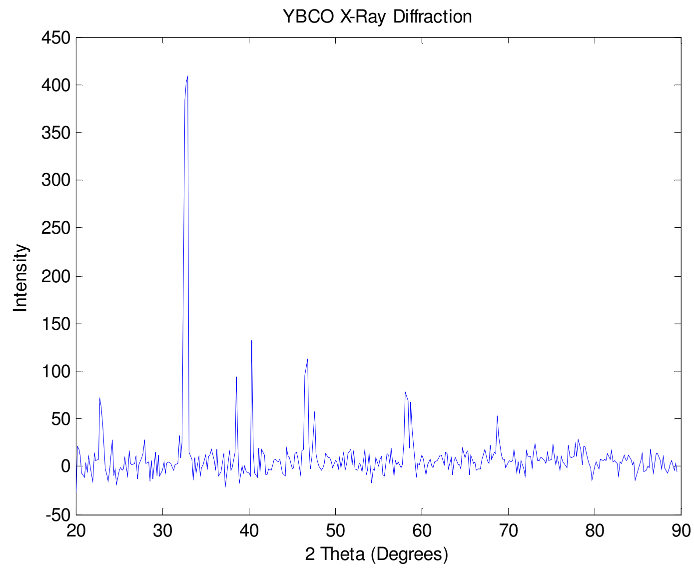

Figure 4:

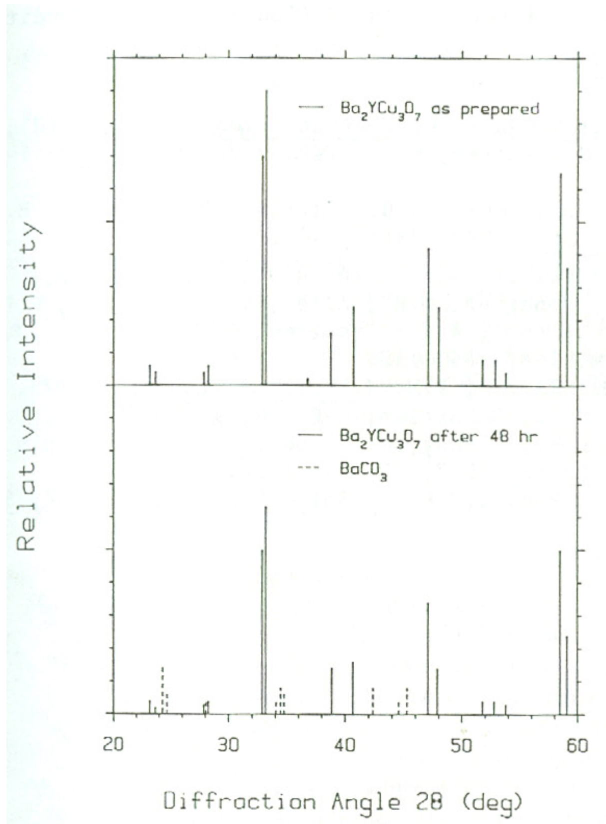

Figure 5: Known x-ray diffraction taken from Davison et al figure 11

The diffraction pattern of the YBCO that was made matches a known diffraction in figure 5. In the measurement, the resolution of the equipment seems to have caused the two peaks near 33 to merge together. Comparing figures 4 and 5 the sample also appears to be the correct phase of YBCO.

Resistivity Measurements

The resistance as a function of temperature was measured in order to observe the superconductive transition in samples of YBCO. A block diagram of the setup can be seen in figure 6. A Cryomech CP510 compressor system, seen in figure 8, was used for cooling the

samples. Resistance measurements were done with a Keithley 2400 series multimeter and temperature measurements with a Cryocon 32b. The resistance was measured using a four wire resistance measurement. In this mode a known current is passed through the sample from two outside wires. Two more wires are attached between the current wires that read the voltage across that part of the sample. From these two values the resistance can be calculated using ohms law. This method eliminates the resistance of the lead wires. Resistance and temperature measurements were controlled by a program in Labview. A vacuum pump was attached in order to make an insulating vacuum around the sample. A vacuum layer allows the sample to be cooled without heat from the outside environment interfering.

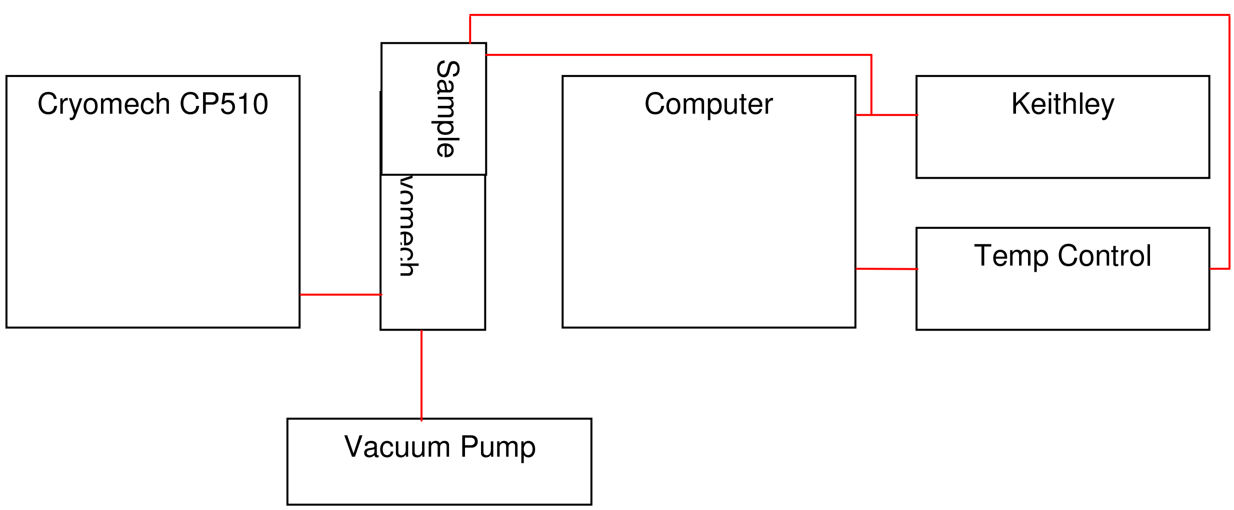

Figure 6: Experimental Setup Block Diagram

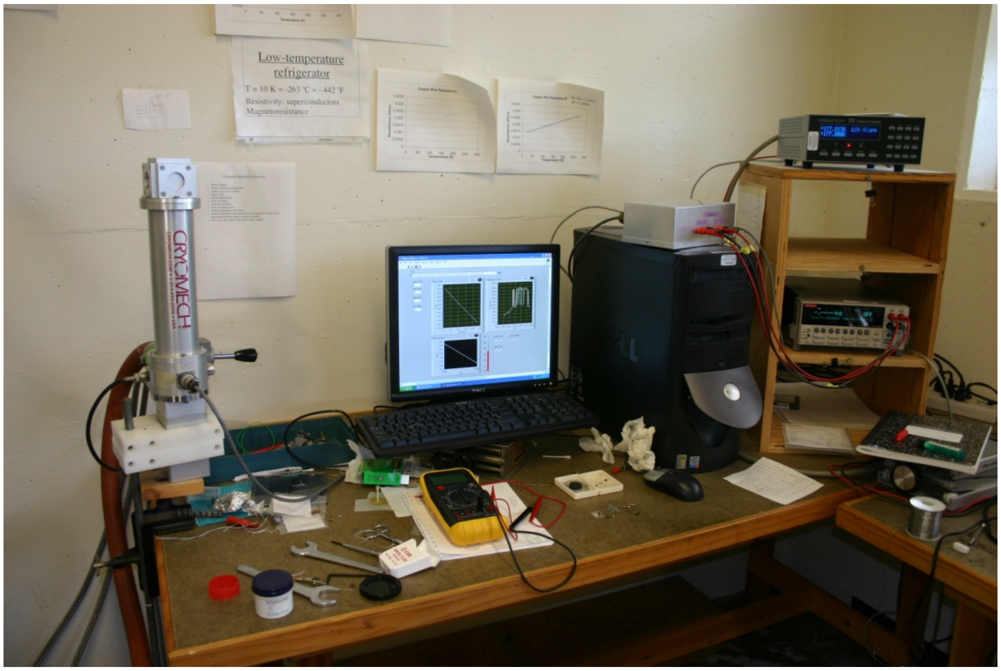

Figure 7: Table with the majority of the equipment.

Figure 8: Cryomech CP510

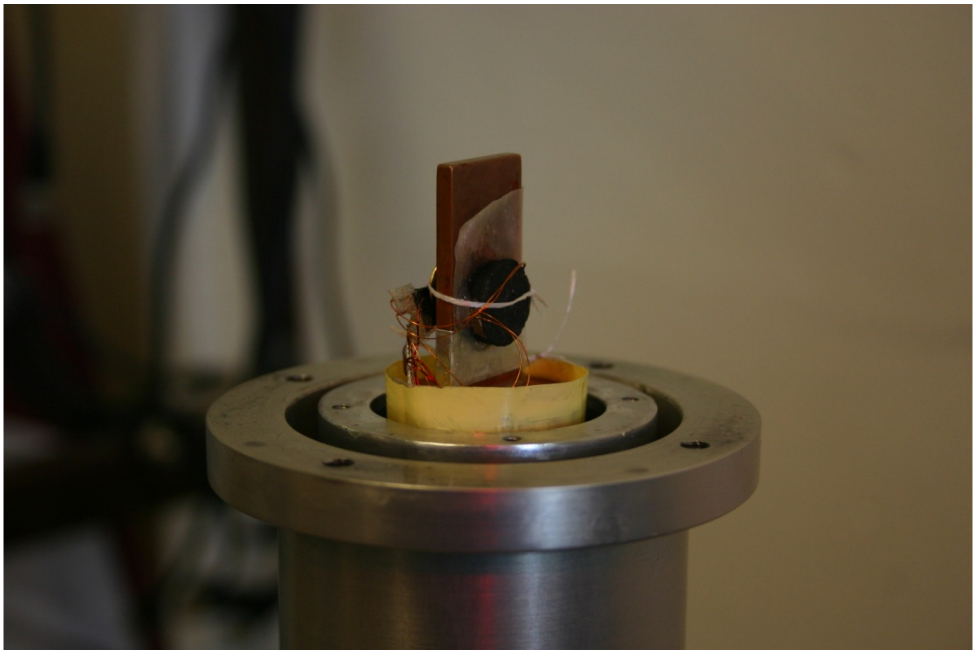

Figure 9: Sample attached for measurement.

Resistance Measurement of Metals

In order to test the operation of the setup, it was useful to use something that would have an easily predictable result. A good candidate for this was copper since the temperature dependence of the resistivity is approximately linear. The equation that approximates this is:

$$R = R_o[\alpha(T - T_o) + 1] \qquad \text{(eq3)}$$

where α for copper is 3.9×10^{-3} C^{-1}.

The first test used a copper block. This particular block was used because it had easy to measure dimension and it had leads already attached to it.

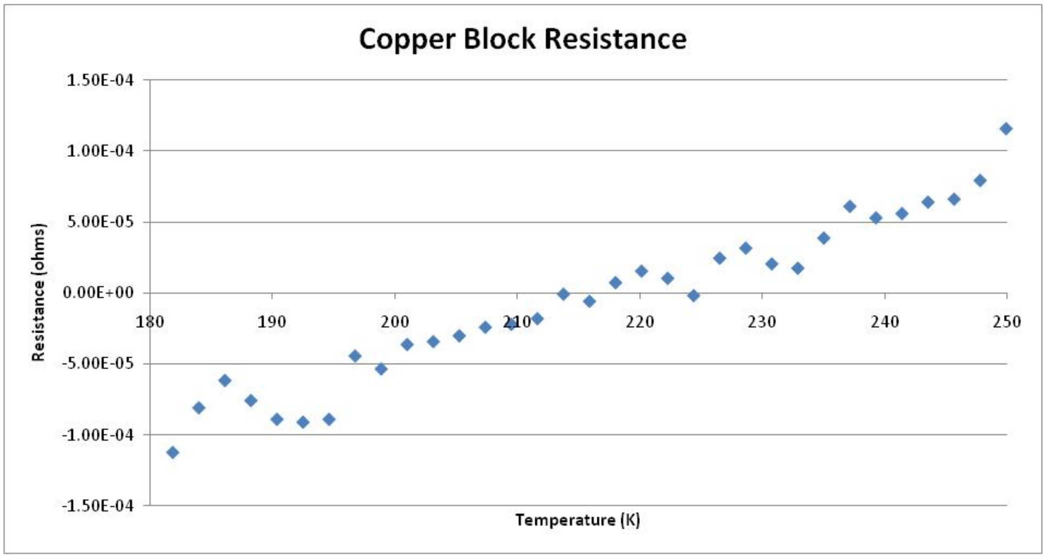

Figure 10: January 8 Copper Block Test

Figure 10 shows the results from this run. The sample was not cooled down to 10 K because of the observation of negative resistance. After reading further into the manual for the Kiethley the minimum measurable was 100 micro-ohms, which is where this sample began. It seems the negative resistance was a product of the resistance not being in the measureable range of the setup.

The next test was done with a piece of copper wire, which had a larger resistance. Data was taken as the sample cooled and the other as it warmed up.

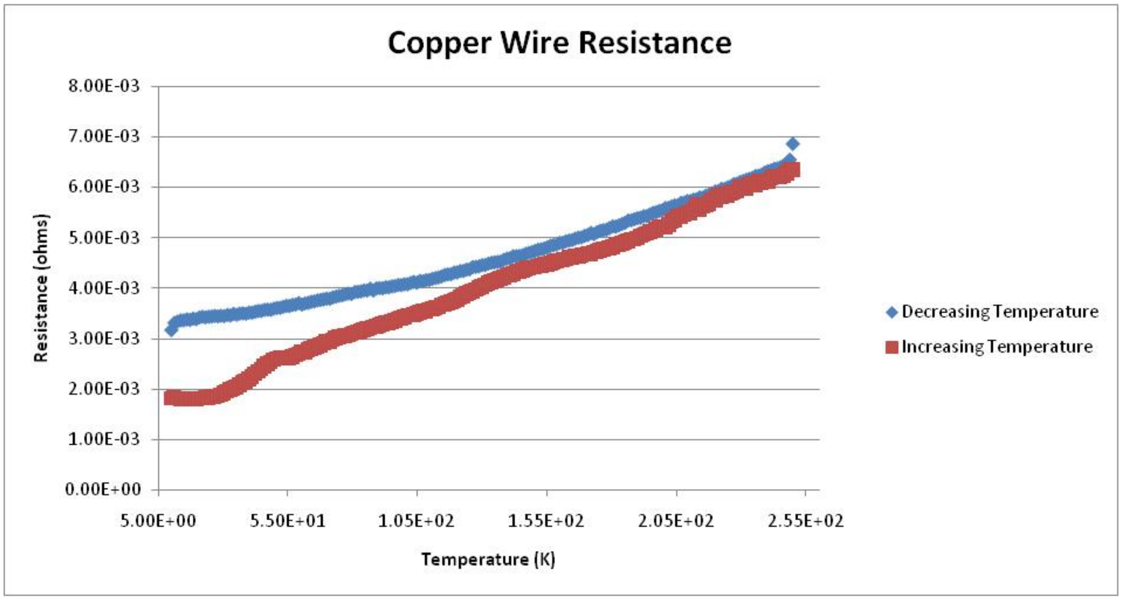

Figure 11: January 15 Copper Wire Test

Although the data in figure 11 seemed close to linear, the two runs produced different results which indicated that there was a problem. The cause for this difference seems to be the way that the sample was mounted. The copper wire was attached to the mount with vacuum grease. This worked at room temperature, but the grease doesn't hold together at the low temperatures reached causing the sample to fall off the mount. As the sample heated up, the measured temperature did not reflect the actual temperature of the attached wire, so this may have been the cause of the different lines.

In the next test a couple of things were tried. First, in order to prevent the sample from falling off, it was tied to the mount with dental floss. In the previous run, the sample may not have reached thermal equilibrium when the resistance was measured. To test this, a "for" loop was placed into the program that made multiple measurements at a given temperature.

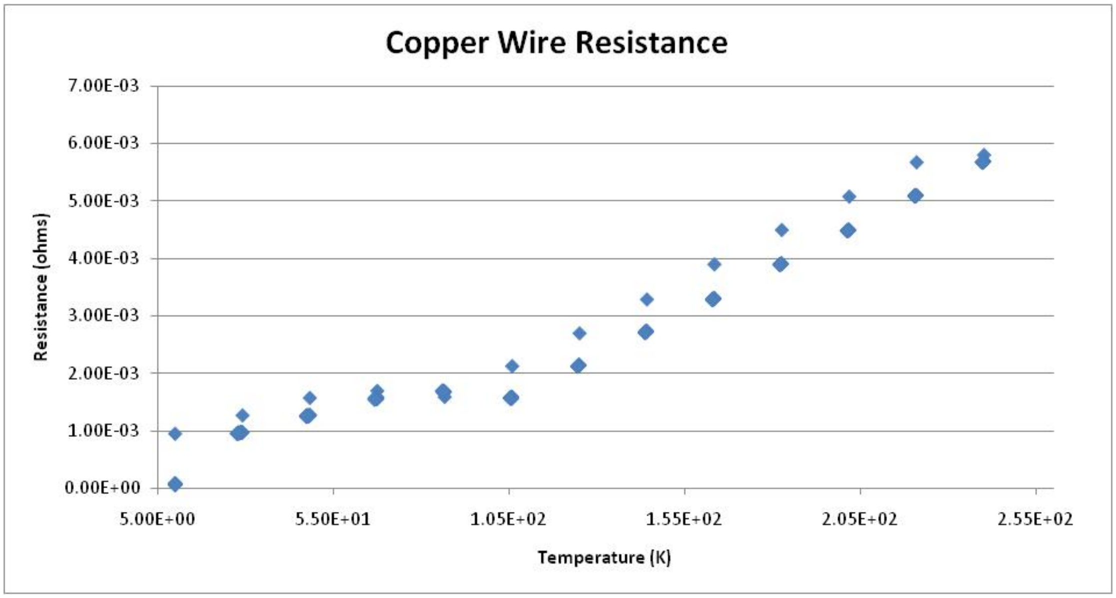

Figure 12: January 22 Copper Wire Test

Twenty measurements were taken at each temperature as the temperature was lowered. Figure 12 shows that nineteen of the data points were close to each-other while a single point was higher. Upon closer inspection of the data, the higher point had the same value of resistance as the previous temperature's nineteen identical data points. A serious error was found in the order that the program did things. The program first measured the resistance and then changed the temperature. After the temperature reached its next value, it then measured the temperature and then paired it with the earlier resistance measurement. Rather than trying to fix the program, it seemed easier to rewrite it and add in other features as well.

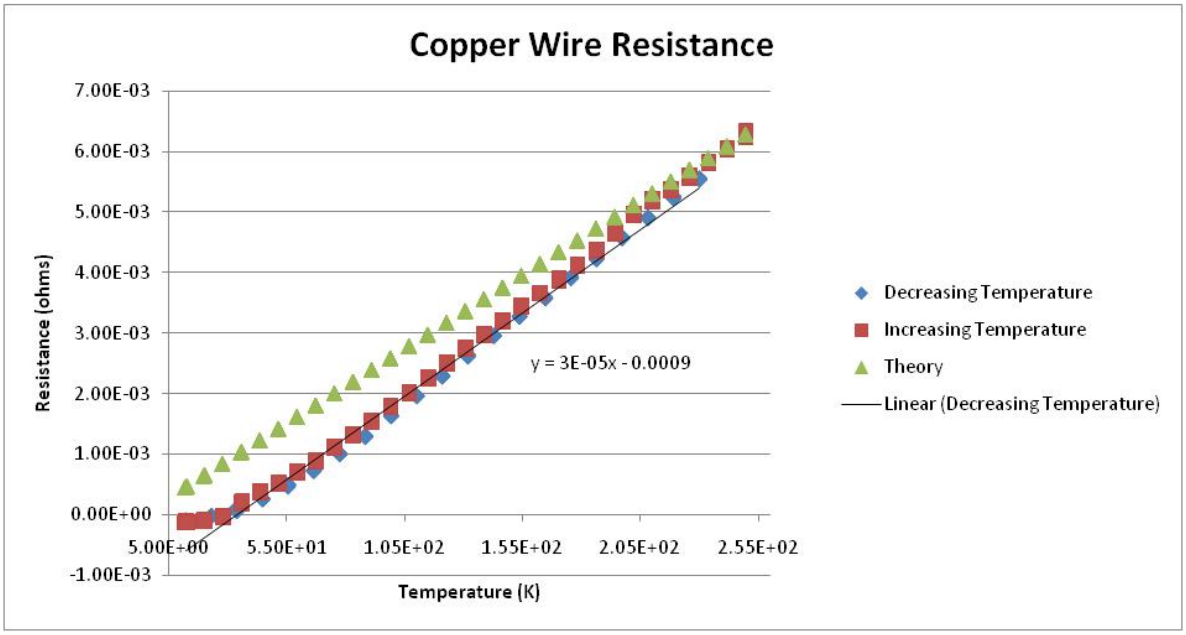

Figure 13: January 28 Copper Wire Test

The next test produced a linear result in both the heating and cooling runs, which can be seen in figure 13. The slope changes near the lower temperatures. However, this could be a result of the equipment's calibration, which was later found to be off. The theoretical points where calculated from the equation stated earlier and the values for R_o and T_o where picked from the highest temperature measurement that was made. Using the slope of the line fitted to the data the value for α of the wire was found to be around 4.3×10^{-3} C^{-1}. Compared to copper's value of 3.9×10^{-3} C^{-1}, this seems plausible. The material of the wire was assumed to be copper and with impurities the value of α could be affected. However since the measured results seemed close enough to theory and produced a linear result, the test of YBCO was the next step.

YBCO Resistance Tests

The first sample tested had leads that were attached with silver epoxy cured for an hour at 160^{o} C per the instructions. These leads were also placed in four separate locations for a four wire resistance measurement. The small wires used to attach the four leads were found to be weak and prone to breaking so in later samples 2 pieces of larger wire were attacked with silver epoxy and then the four leads soldered onto the larger wires. The resistance of the larger wires should be small in comparison to the superconductor in its normal state so the superconductive transition would still be viewed. This method of attaching leads was carried out for the rest of the samples as well. Some of the samples can be seen in the figure below.

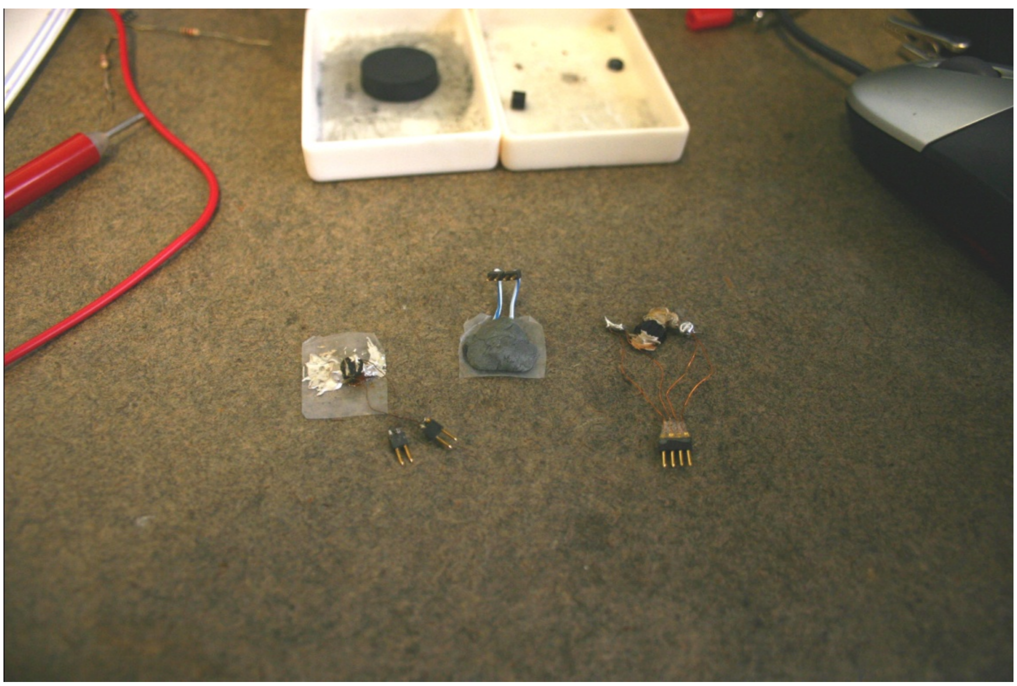

Figure 14: In order from left to right samples one, two and three. Also in the background are the large disk used for observation of Meissner Effect and pellets for later samples.

Sample 1

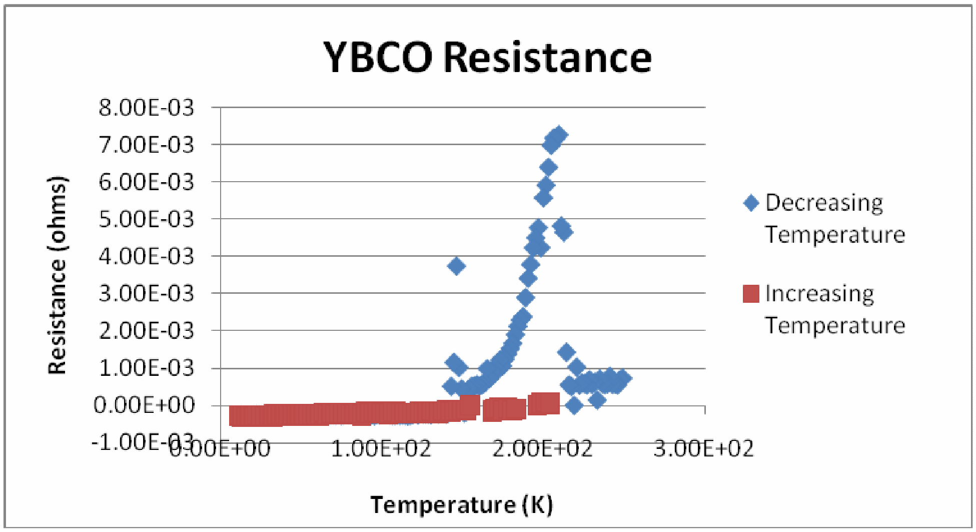

Figure 15: February 4, 2010 test of sample 1

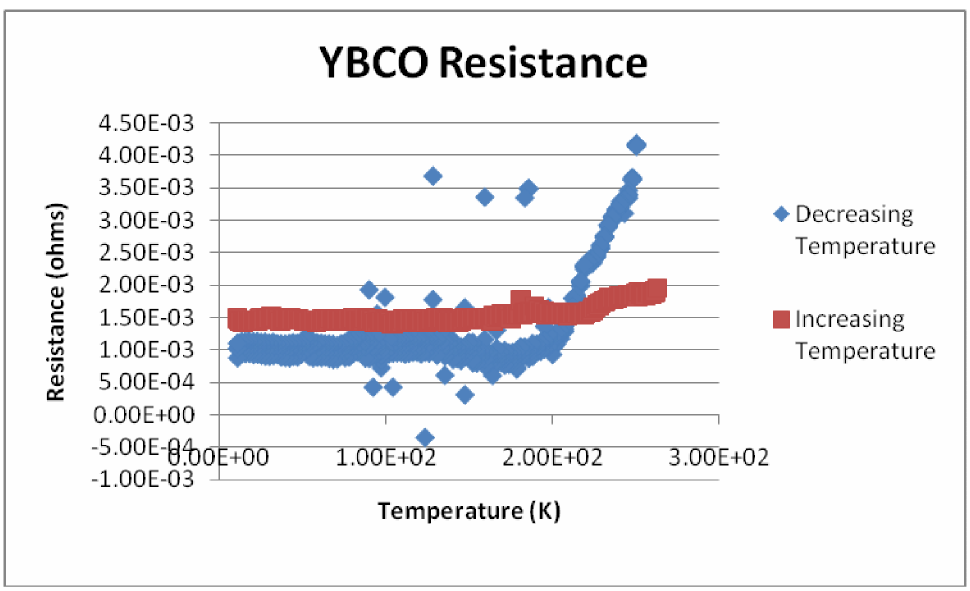

Figure 16: February 5, 2010 test of sample 1

The two figures above are representative of the type of data that was collected for the first sample. The first curious feature of the first two graphs is the apparent superconductive transition near two hundred degrees. However, when the sample was heated up this change in resistance was not observed. Aside from an obviously wrong temperature, this pointed to the transition being some artifact of the setup. In a study by Torrance et al, they observed a similar transition at 170 when measuring the resistance of YBCO. They concluded that the change in resistance was due to temperature dependant current contacts. Supposedly, a change in contact resistance causes the voltage source to not behave as an ideal current source throwing off measurements. They also found that these anomalies began to decrease as the sample was cycled. This may explain why the increasing temperature runs of the first two pictured did not show a large increase in resistance where the decreasing runs showed a large drop. In my experiment, the first set of data was taken as the temperature decreased.

Sample 2

For the next sample a different method was used to attach the leads. Rather than using the silver epoxy, a circuit repair glue called “nickel print” was used. The mechanical strength of the nickel print was not as good as the silver epoxy and in order to protect the leads, they were covered with epoxy putty.

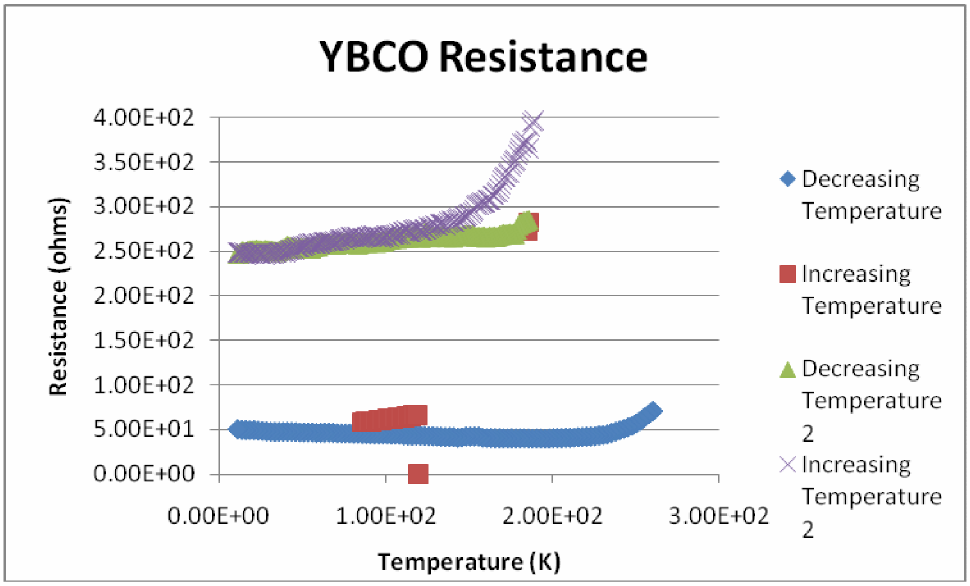

Figure 17: February 23, 2010 test of sample 2 with second increasing temperature run cut off

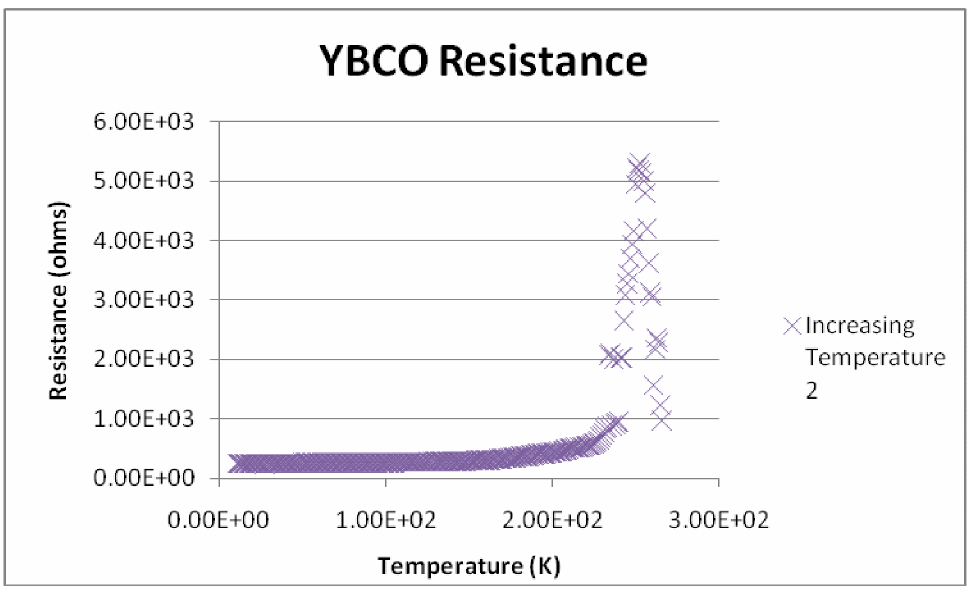

Figure 18: February 23, 2010 test of sample 2 second increasing temperature run

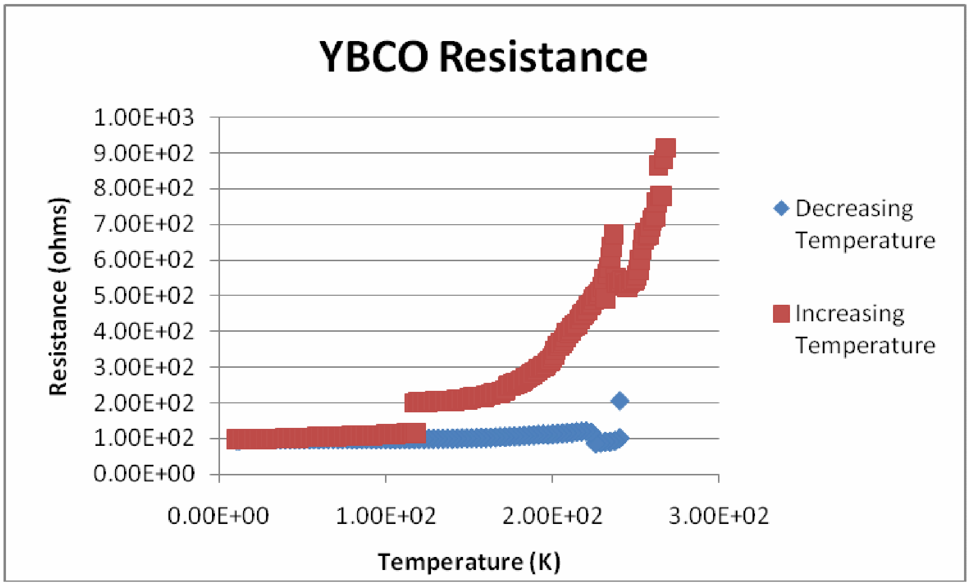

Figure 19: February 24, 2010 test of sample 2

Measurements of resistivity for the sample prepared with the nickel print showed no improvement in measurements over the epoxy putty other than the resistance values seeming more plausible than the previous sample. The previous had a resistance that seemed too low at higher temperatures where this one gave values that seemed consistent with placing multi-meter probes on disks of YBCO. The curve in figure 19 is similar to figure 4 in Torrance et al where they show what an anomaly looks like. Their anomaly shows the resistance dropping by a large amount from room temperature and then showing a proper superconductive transition at the correct transition temperature. Above 200 Kelvin in the February 24 test, the results seem to be due to the contacts. This appears to be the case since there are large jumps in the resistance values of the increasing run as the temperature changes. A correct curve would not have jumps near 250 Kelvin like this curve does. Near 118 Kelvin, the temperature decreases by a factor of two in a manner that looked like a superconductive transition. However, this temperature is too high for a YBCO transition to superconductivity and without another run where this is observed

it is not possible to say anything for certain. The transition observed is most likely the result of the contacts and just happened to occur close to the transition temperature of YBCO.

Thermistor Test

In order to test the calibration of the temperature readings, a thermistor from RadioShack was placed in the setup. On the back of the thermistor's packaging it listed temperature and resistance pairs that could be compared to measurements.

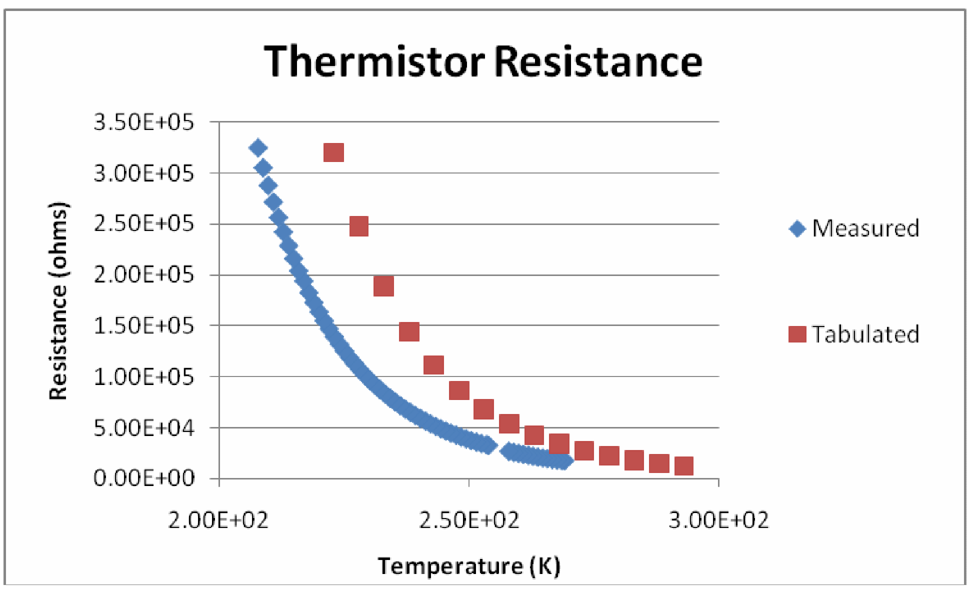

Figure 20: Thermistor Test

The thermistor test indicates that the calibration of the temperature readings is off. According to the above figure, the equipment reports a temperature that is lower than the actual temperature of the sample. Sadly, the thermistor could not be used to measure the temperature differences at low temperatures. However, it does provide an indication that the reported

temperature is incorrect. Proper calibration did not seem as important as creating a sample with good leads. Once a sample showed a superconductive transition, focus could be turned to proper calibration. The calibration did not affect the previous results for the copper wire. Since all that was important for that test was the slope of the line, shifts of the line to the left or right did not affect the end result. Also, when the theoretical curve was generated it was fixed to one of the measured data points.

Sample 3

The next sample was produced using the silver epoxy again. This time the epoxy was cured for 3.5 hours at 220^{o} Celsius in hopes that the silver would diffuse more into the superconductor.

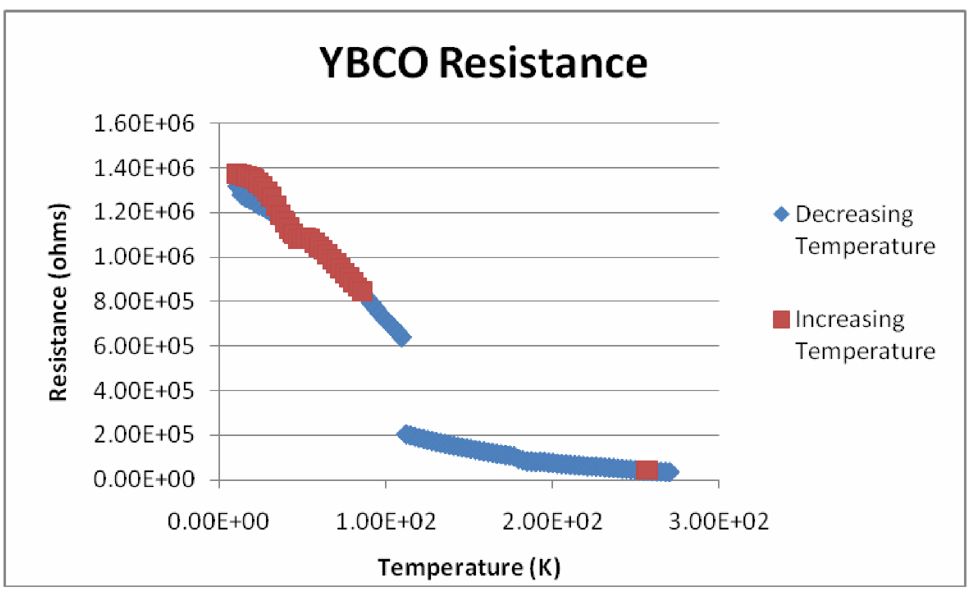

Figure 21: March 1, 2010 test of sample 3

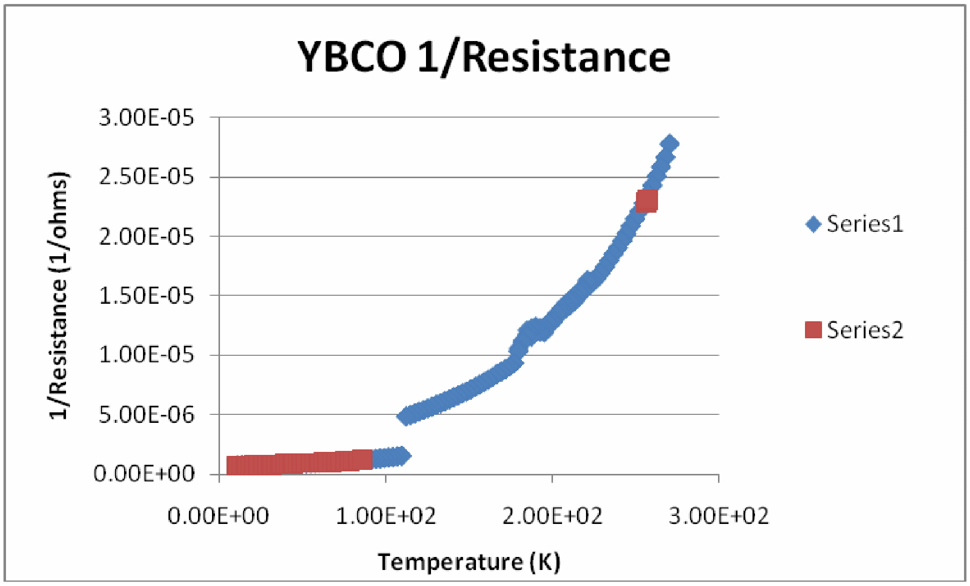

Figure 22: March 1, 2010 test of sample 3 with inverted resistance

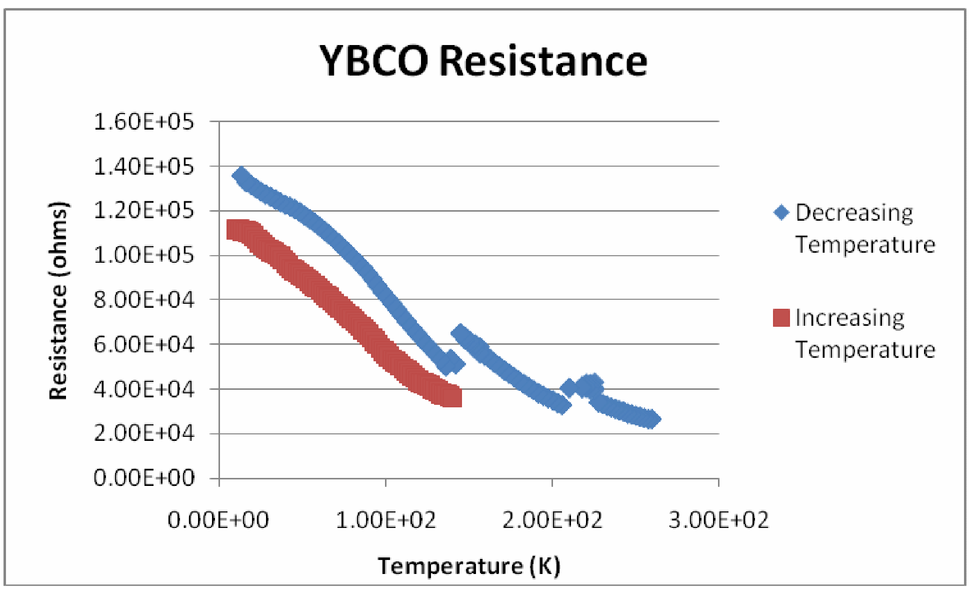

Figure 23: March 2, 2010 test of sample 3

The resistance measurements of sample 3 showed unexpected results. Rather than the resistance decreasing as the temperature was lowered, it increased. In figure 22, the data shows a gap near 110 Kelvin that made me think that there was a wiring problem. The reason for this is a

four wire resistance measurement looks at the voltage and current across a sample and determines resistance from that. If the calculation of resistance were performed incorrectly (I/V), then the resistance may be inverted. However, when making a graph of 1/R this does not seem the case. The inverse of the resistance versus temperature showed a correct shape but the resistance was far too low to make sense. For the next run the wires were re-soldered to the leads. This test showed the same sort of problem with the resistance.

Some forms of YBCO show semiconducting properties which is what was viewed in these tests. A characteristic of semiconductors is that the resistance begins to increase as the temperature is decreased. Even though this was a possibility, it did not seem to be likely since the second run did not match the first. Also, the x-ray diffraction conducted earlier showed that the YBCO produced was in the form needed for superconductivity. However, according to Neeraj Khare et al, it may be possible for the surface of the sample to have degraded to a form that is semiconducting and since this is where the contacts are attached it may explain the results.

Because the results obtained seemed strange, a second ohmmeter was used to measure the resistance of the YBCO samples at room temperature and placed in liquid nitrogen. When the resistance of sample three was measured at room temperature, it was found to be 31.6 kΩ. When cooled with liquid nitrogen the resistance increased to .377 MΩ. On a second cooling with liquid nitrogen, the resistance was found to be .492 MΩ. The difference between the first and second measurement shows that the measurement is not precise. Though these are not the exact same resistances reported by the Keithley at these temperatures, they are on the same order of magnitude. This was repeated several times with similar results showing that the strange measurements were not the result of the equipment but seemed to be related to the sample. Again the leads came into question.

Silver Epoxy Test

The leads seemed to be an issue, so the resistance of the silver epoxy was measured as a function of temperature. A large glob of the silver epoxy was placed between two leads. These were then attached to the meter.

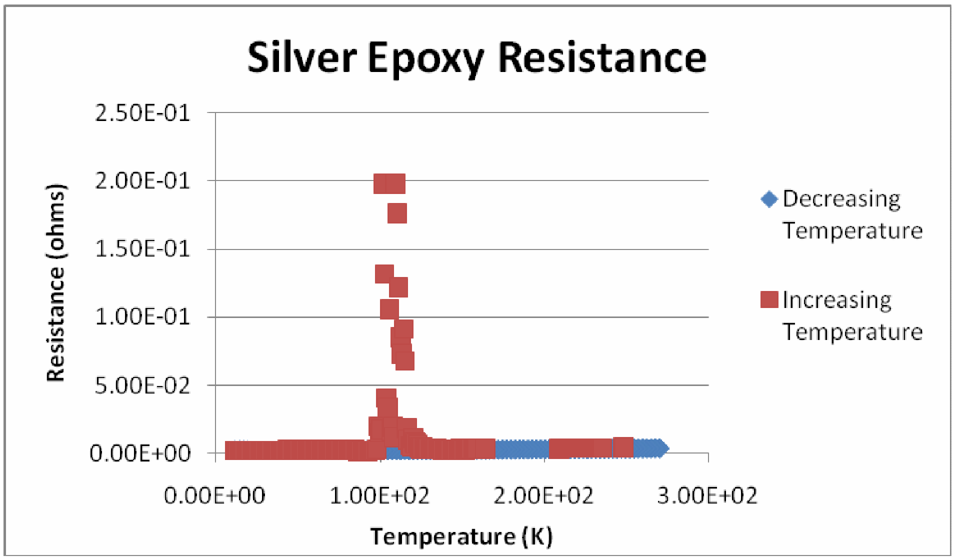

Figure 24: Silver epoxy test

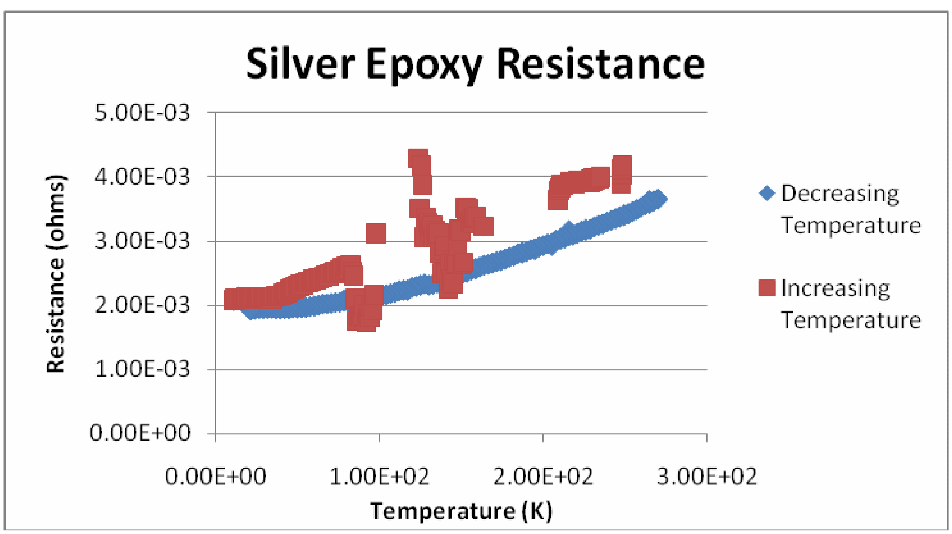

Figure 25: Silver epoxy test with peak cut off

The decreasing temperature run showed a mostly linear result, which would be expected from a metallic substance. On the increasing run the Keithley kept shutting off which may have caused the strange readings. However, even if these were correct measurements, the magnitude of the resistance is still not enough to explain the large values measured on the YBCO samples. At room temperature the YBCO samples have resistances in the kΩ range and the epoxy's resistance is on the order of 10^{-3} ohms. At the peak in figure 24, the resistance of the silver epoxy is on the order 10^{-1} ohms which is still small in comparison to YBCO. Since the resistance of YBCO is larger a transition should still be viewed. The problem does not seem to lie in the glue by itself but rather where it contacts the sample.

Sample 4

Sample 4 had leads made with silver epoxy again but went through different methods of attaching them. First, the silver epoxy was baked on the sample at 400^{o} C for 22 hours. The intent for this was to have the silver atoms mix into the sample. Also, according to Neeraj Khare et al, baking at higher temperatures adds oxygen to the surface that has degraded into a non-superconducting layer. Attempting to cure the silver epoxy at this temperature resulted in the silver epoxy becoming brittle and falling off of the YBCO.

Next the edges were sanded down to try and remove any semiconducting layer that may exist on the edge of the YBCO. The silver epoxy was cured at 280^{o} C for 23.5 hours. The result was the same as the previous attempt and the silver epoxy crumbled.

After that temperature failed to create a good bond silver epoxy was cured on the YBCO for 24 hr at 200^{o} Celsius. This sample did not break and could be tested.

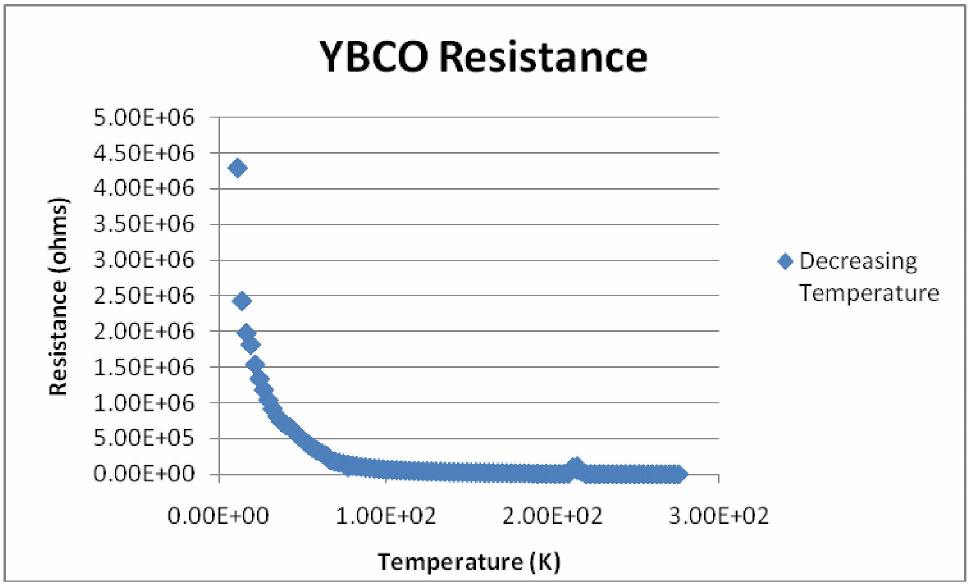

Figure 26: March 12 test of sample 4

This sample did not show a sign of superconductivity but rather semiconducting properties.

Sample 5

The pellet from sample 2 was extracted out of the epoxy putty and the previous leads sanded down. New leads were attached by placing the sample for one hour at 160 C and then for 15 minutes at 400^{o} C. Again a semiconducting result was obtained and the sample was then bathed in oxygen at 400^{o} C overnight. The purpose of this was to try and add some oxygen back into the superconductor. If, indeed, parts of it had been semiconducting, there was a chance that oxygenation could bring back the superconducting phase.

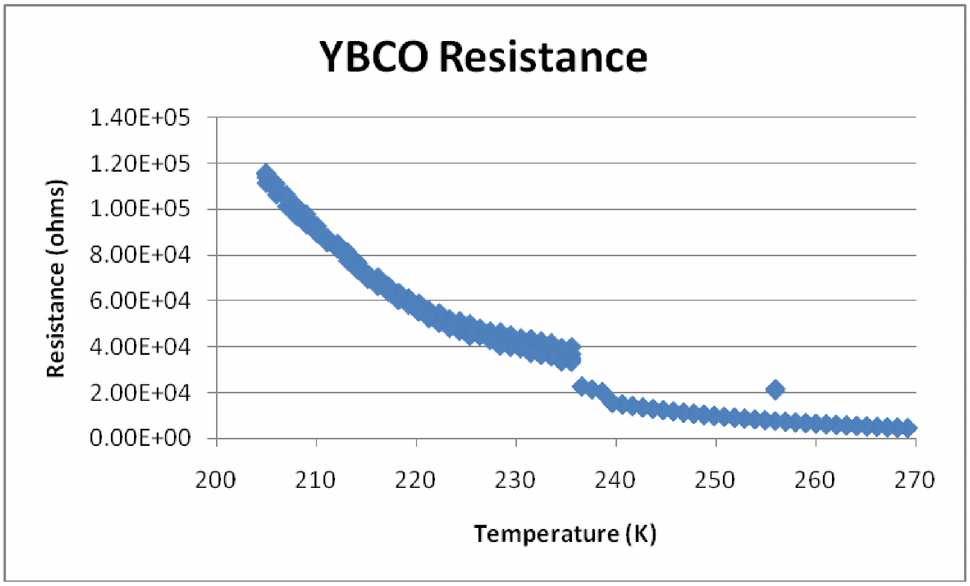

Figure 27: April 29 test of sample 5

Again, as seen in figure 27, the sample showed semiconducting properties for the resistance. In order to see if the sample had decayed, a pellet was ground up and an x-ray diffraction performed. The pellet used for the first diffraction was a pellet that had fallen apart after leads were attached. This sample had been heated for 14 days at 200° C. This was to hopefully allow diffusion of silver from the leads into the YBCO and oxygen into the sample as well. Since it fell apart, the resistance could not be measured and it will be referred to as sample 6.

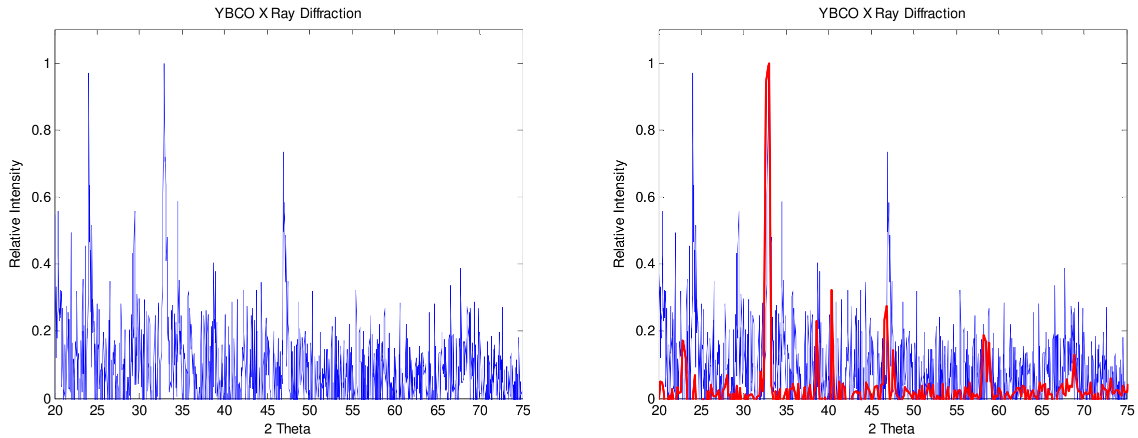

Figure 28: X ray diffraction of sample 6 (left) and earlier x ray diffraction overlaid (right)

The x-ray diffraction showed that the sample has changed from when it was first made. Though the main peak for the superconductive phase is present there are several additional peaks that were not present earlier. In sample six, figure 28 shows there is still a portion of the sample that is still in the correct phase. However, near the transition temperature if the slope of the resistance curve is like figure 26, then it is steep enough so that the superconductive transition for the parts in the correct phase is drowned out by the semiconducting phase.

To make sure that these peaks are not from crushed silver epoxy, a diffraction of the silver epoxy was taken.

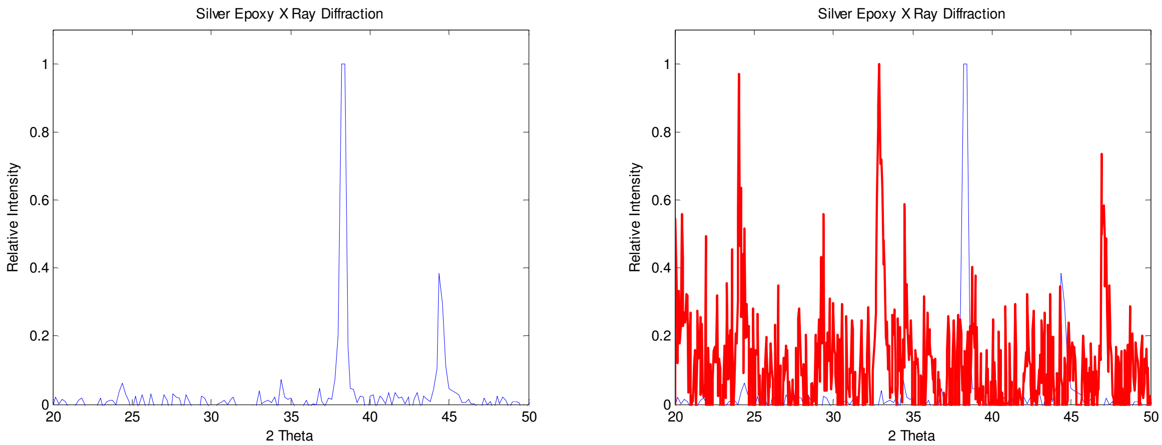

Figure 29: X-ray diffraction of silver epoxy (left) with sample 6 overlaid (right)

Figure 29 shows that crushed silver epoxy is not the cause of all the extra peaks. The x-ray diffraction of the epoxy shows only a few large peaks that could show up in the pattern for the sample. In order to see if the change in composition was exclusive to sample six, a test on sample four was performed as well.

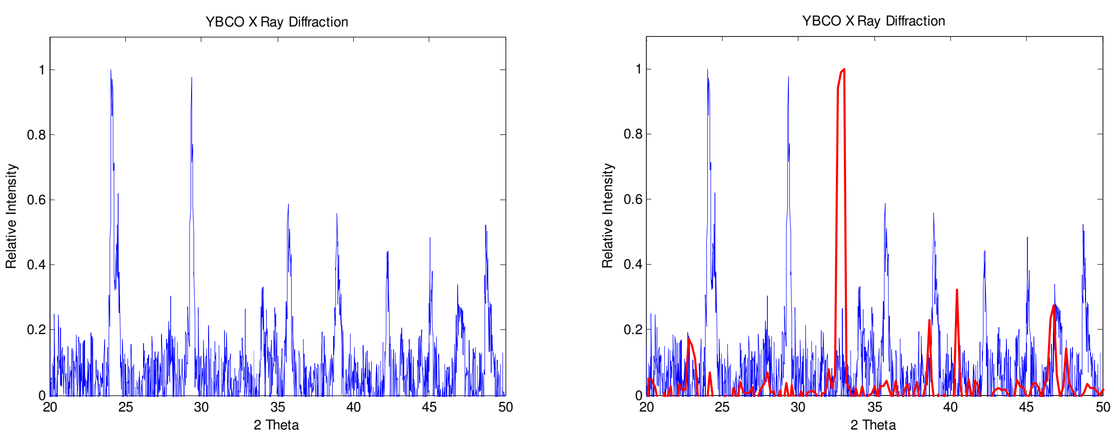

Figure 30: X-ray diffraction of sample 4(left) overlaid with original diffraction (right)

In figure 30 the x-ray diffraction of sample 4 has large peaks that are not due to the superconducting phase of YBCO. One other observation on sample four was the top of sample four was white. Normally YBCO has a black color. According to Rekhi et al., when they purposefully degraded YBCO with water the surface turned white. The white color and the x-ray diffraction both point to degradation of the sample causing superconductivity to not be observed.

What exactly caused the degradation is unknown. One clue rests with an x-ray diffraction of the large pellet that was used to float a magnet earlier.

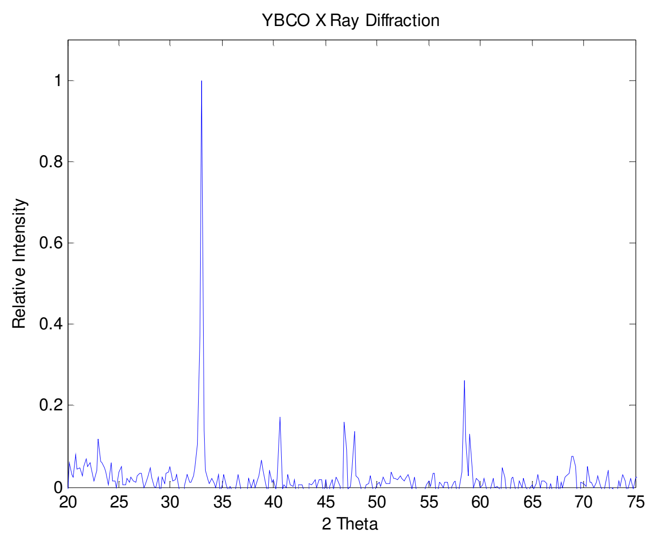

Figure 31: X-ray diffraction of large pellet

Figure 31 matches the know x-ray diffraction in figure 5. This means that the large pellet did not decay like the smaller ones did. Both were made with the same powder so they should have started off with similar compositions. What seems to have caused the degradation was the process of attaching leads. One possible explanation is that baking the samples at lower temperatures may have allowed for humidity in the air to decompose them. In Fitch et al.,

samples of YBCO were subjected to 100% humidity at 80 C in order to test the corrosion of YBCO. They found that after as little as two hours, the sample began to degrade and after 24 hours the superconductive phase was gone. In our experiment the leads were attached at 200 C for similar periods of time and the humidity in the air was high most of the time due to rain. It is not certain though if this is the exact cause since the temperature for attaching leads is over twice that of the study by Fitch et al. Interactions between the solvents in the silver epoxy and the surface could have an effect as well. The only thing that seems to be certain is the semi-conducting resistance measurements seem to be related to the process of attaching leads.

Conclusion

X ray diffraction data and the observation of the Meissner Effect indicate that the samples of YBCO prepared were initially superconducting. However, resistance measurements did not indicate the presence of superconductivity and instead showed semiconducting properties. In early tests, the resistance changed depending on whether the run was increasing or decreasing in temperature. In order to fix this, the method of lead attachment was changed. Finding the method that provided a good balance of mechanical strength and a good electrical connection became the main focus. Leads that were brittle and fell off were as useless as ones with a bad electrical connection.

Although resistance measurements in the superconducting phase were not successful, several important lessons were learned. The manner in which the leads are attached plays an important role. Bad connections can create noisy and nonsensical data or even false superconductive transitions. The method that gave the best electrical connection with silver

epoxy was to bake the silver epoxy for 24 hours at 200 degrees Celsius. However, this method of attaching leads may make a good connection but also could cause degradation of a sample.

In order for a good connection with an intact sample, a different method would be best. In Neeraj Khare et al., several different methods for lead attachment were approached. The best leads made were created from thermal evaporation of silver. Once a contact pad was made with silver, it underwent a two step heat treatment. The first step was baking it for 20 min at 780^{o} C and then for 550^{o} C for six hours. Then iridium was pressed on to the silver pads in order to provide something that copper wires could be soldered to. Trying a similar approach in the future would most likely allow a superconductive transition to be observed.

Bibliography

Brown, Ronald F. *Solid State Physics*. San Luis Obispo: El Corral Publications, 2006.

Crystal Structure. Digital image. *Hoffman Lab*. Harvard University. Web. <http://hoffman.physics.harvard.edu/materials/Cuprates.php>.

Davison Et Al. "Chemical Problems Associated with the Preparation and Characterization of Superconducting Oxides Containing Copper."

Fitch Et Al. "Water Corrosion of YBCO Superconductors." *J. Am. Ceram. Soc.* 72.10 (1989): 2020-023.

Ford, P. J., and G. A. Saunders. *The Rise of the Superconductors*. Boca Raton: CRC, 2005. Print.

Mourachkine, A. "Mechanism of High-Tc Superconductivity Based on Tunneling Measurements in Cuprates." *Journal of Physics and Chemistry of Solids* 67 (2006): 373-76.

Neeraj et a;. "Effect of Heat Treatment on Ag/YBCO Contact Resistance." *Pramana –J.* 33 (1989): L333-L338

Owens, Frank J., and Charles P. Poole. *The New Superconductors*. New York: Kluwer AcademicPlenum, 2002.

Rao Et Al. "Synthesis of Cuprate Superconductors." *Superconductor Science and Technology* 6 (1993): 1-22.

Rekhi et al. "Recovery of Superconductivity in the Water Degraded YBCO Samples." *Physica C 307 (1998): 51-60*

Ribeiro, R. A., and O. F. Lima. "Scaling Analysis of Magnetization Curves Based on Collective Flux Creep for YBCO." *Physics C* 354 (2001): 227-31.

Torrence Et Al. "Broad Search for Higher Critical Temperature in Copper Oxides." (1987).