The Preparation, Testing and Analysis of YBa$_2$Cu$_3$O$_{8-x}$
## *An investigation of superconductivity*

Background

Electrical conductivity in solids is a phenomenon generally identified with the metals and a few unusual allotropes of other elements such as carbon in the form of graphite. Whether approached through simple models which describe the lattice structure of these materials as floating in a "sea of electrons" or by more rigorous means such as band theory, electrical conductivity in a solid depends on the free movement of electrons. These electrons must be loosely bound in the solid lattice or else be relatively easy to "unseat" so that movement may begin.

In metals, which represent the typical case, good shielding enables valence electrons to move more or less freely though a sample given a "push" (i.e., when an electric potential is applied to a sample). This is not the sort of behavior to be expected from other types of solids (with the few exceptions noted earlier) since the forces binding other kinds of solids together either rely on localized electrons to maintain bonds (ionic or covalent network solids) or else consist of weak interactions arising from the polarity of molecules in which the electrons are again localized in (typically covalent) bonds (molecular solids).

The nature of electrical conductivity in metals and the factors that help or hinder the movement of electrons through the three-dimensional lattice has been studied for a long time. Early chemists and physicists knew that conductivity is influenced not only by the amount of energy needed to start electrons moving but also by obstacles that electrons might encounter in the lattice. For example, impurities or other dislocations in a metal lattice can cause atoms to be "out of place". In an ordered lattice electrons might have a "straight shot" between planes of atoms but if one if out of place, they could encounter a barrier to free movement.
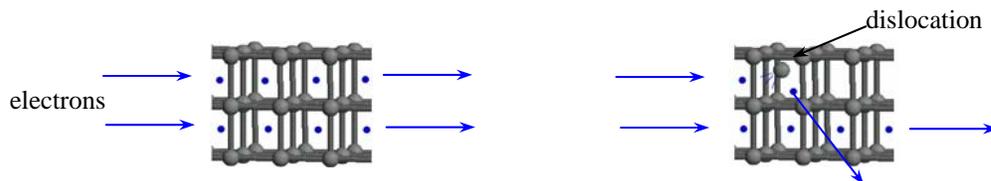

Temperature affects conductivity for similar reasons. Despite the macroscopic appearance of metal samples, the atoms *do* move within the lattice relative to one another, even in a sample at rest. Vibrations in the lattice due to thermal energy can randomly narrow or widen the "avenues" through which electrons travel but it is the narrowing which eventually limits conductivity as the temperature increases. This particular behavior suggests that improved conductivity should result at lower temperatures, an idea which is relatively easy to test experimentally. Tests show that electrons *do* move with fewer hindrances when metals are colder although the extent of the effect is different for each metal. The question which interested physicists and chemists was this: does the effect continue to a point where the resistance to the flow of electrons vanishes or is there a leveling-off effect?

A thorough testing of this question waited on the development of better refrigeration technologies. In 1908 the Dutch physicist Heike Onnes successfully liquefied helium by cooling it to -269°C (4 K). As he became more adept at producing larger quantities of the very cold liquid he began to experiment with metals and conductivity. In 1911 while working with very pure mercury he first observed a behavior he later called *superconductivity*: at 4.2 K the resistance to current flow in a mercury wire dropped to zero. In a later experiment with a loop of lead wire at 4 K, Onnes initiated an electrical current flow in the loop and then removed the potential source. A year later (with the loop cooled daily by constant additions of liquid helium) the current was still flowing, undiminished. Onnes was awarded a Nobel prize in 1913 for his discoveries.

Although fairly exotic, superconductivity became a "hot" topic among many physicists. How did it work? What other behaviors marked this new state? One answer to the second question came in 1933 when Meissner and Ochsenfeld showed that not only did current run indefinitely through superconducting metals but they were also perfectly *diamagnetic*. This means that magnetic fields cannot penetrate superconductors: they are repelled. As a magnet is brought near a superconductor it induces a current (this is essentially how a normal generator works, magnets constantly move in and out of wire coils) which does not stop. This current then creates a "mirror image" magnetic field which exactly balances the external field. This behavior is known as the *Meissner effect* and is a simple and dramatic test for superconductivity: magnets levitate over superconductors.

The question of how it all worked was given a first approximation in 1957 by three American physicists: John Bardeen, Leon Cooper and Robert Schrieffer. Their so-called *BCS* theory is complex and owes much to an understanding of quantum mechanics but the rudiments can be explained with a few ideas. According to the theory as an electron passes through the lattice it distorts it since the metal ions [remember, the atoms have given their valence electrons to the general bonding pool or "sea"] are attracted to the passing electron:

normal alignment	distortion due to electron flow
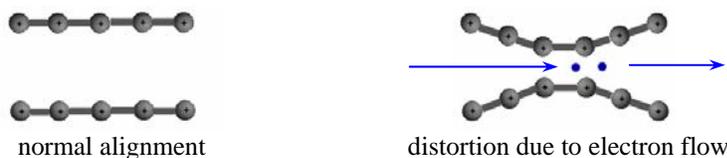
The distorted lattice draws in a second following electron because the positive charges are now more concentrated at the distortion and thus these two electrons travel together as a pair through the lattice, riding a wave of distortion, followed by other pairs, etc. The orderly travel of this "train" of electron pairs through the flexing lattice structure gives rise to the superconducting behavior, according to the BCS theory. In 1972 the three physicist were awarded the Nobel Prize for their work and theory.

The promise of superconductivity as a valuable commercial or industrial tool seemed remote. It remained largely a laboratory curiosity with a few researchers working on exotic metal alloys, trying to coax the phenomenon out of them at higher and higher temperatures. Approximately 20 K remained the highest known critical temperature for superconductivity until 1986.

Bednorz and Müller, working for IBM in Zürich, were studying a class of metal oxide ceramics known with the *perovskite* crystal structure in that year:
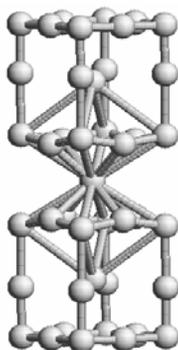
To their surprise the normally non-conducting ceramics showed signs of superconductivity at low temperatures, beginning at 35 K! Soon many scientists were synthesizing variations on the basic structure, looking for not only a higher critical temperature but also some clue as to how the process was working.

The perovskite crystal structure is like a sandwich. In the first metal oxide formulations the superconductors employed metals like lanthanum and barium in the "bread" layers and copper and oxygen for the filling. Not understanding exactly how the process was working it became a guessing game of trial and error to make substitutions in the lattice structure, hoping for the desired effect.

Paul Chu was fascinated by the new work and began to experiment with the ceramics. He initially tried compressing the material and found that he could raise the critical temperature to 70 K by applying tremendous pressures (10,000 atm). While this would never be practical commercially, it seemed to suggest that making an oxide with layers that were closer together might raise the critical temperature. He tried replacing the barium with strontium which has a smaller ionic radius. The critical temperature went from 35 K to 40 K without applied pressure. But when he tried calcium it went back down. At the end of 1986 and the beginning of 1987 Chu synthesized the ceramic formula that is part of this experiment, substituting yttrium for the lanthanum and leaving the barium alone. On testing he found it had a critical temperature around 90 K. While this is still very cold it is warmer than the boiling point of liquid nitrogen (77 K), a much cheaper cooling agent than liquid helium.
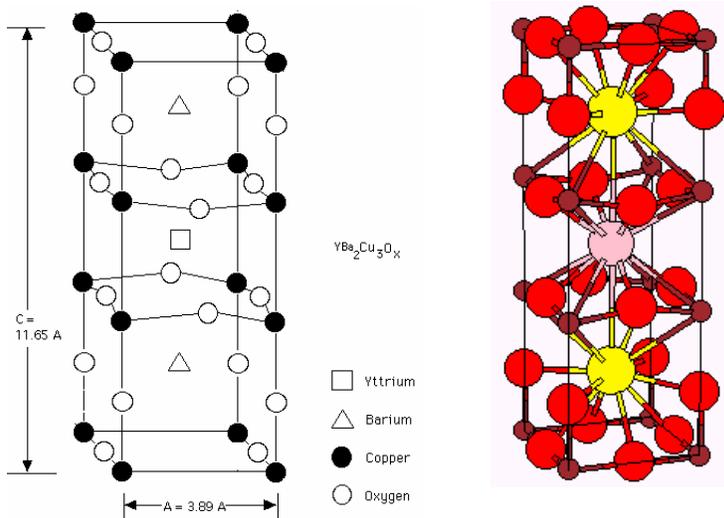
Since that time many other varieties of perovskites have been made with the hope of pushing the temperature even higher. Critical temperatures upwards of 130 K have been achieved but the materials--like Chu's original formulation--generally lack the physical properties needed for commercial applications. They are brittle and cannot easily be made into wires. Work continues on the engineering part of this problem and new technologies such as thin-film deposition have shown some promise.

Meanwhile, the search for a coherent explanation of how these materials become superconducting continues. With a working model it might be easier to make materials with even higher critical temperatures and perhaps more desirable physical properties. What is known about the so-called "1-2-3" superconductor of Chu (containing yttrium, barium and copper in a ratio of 1:2:3) is that there are different oxygen-copper environments in the crystal structure. The amount of oxygen in the formula is important. In the typical ceramic the ratio of Cu to O is very close to 3:7. If the ratio of Cu:O increases to 3:6.7 then the critical temperature falls to 60 K. With a ratio of 3:6.4, the solid becomes a semiconductor. The one-dimensional Cu-O chains is where the variable oxygen content occurs. The technique used in the synthesis of this structure must either include a ready supply of oxygen or allow for slow cooling so that oxygen may diffuse into the structure. The two-dimensional Cu-O pyramidal structures seem to be where the superconductivity originates, but just exactly how is not yet well understood.

The synthesis of the ceramic oxide superconductors is amazingly simple. Powdered oxides, carbonates or nitrates of the metals are ground together in a mortar and pestle until homogeneous. Experience shows that prior drying of the compounds is important as is a thorough mixing. Since the reactants are solid and they do not actually melt in the firing process it is important to produce a mixture which is as uniform as possible (in addition to having the correct stoichiometry of metals).

Once the materials are well mixed they are packed into heat resistant vessels [porcelain crucibles in this experiment] and placed in a furnace, heated to 920-930°C for 12 hours and then slowly allowed to cool to below 100°C before removal from the furnace. The resulting material is brittle and somewhat porous. Some methods call for regrinding and then pressing the material into pellets for an additional firing. In this experiment the physical characteristics of the material are not as important so a single firing is sufficient. The ceramics are sensitive to moisture and are stored in a desiccator when not in use.

The determination of the critical temperature, T_c, is most easily done by observing the temperature at which the Meissner effect takes place. Measuring very low temperatures is often done with *thermocouples*. A thermocouple at its most basic is two dissimilar metal wires twisted together at opposite ends to form two junctions. In 1821 Thomas J. Seebeck demonstrated that if the two junctions are kept at different temperatures a small voltage is produced in the wire loop. The voltage depends on the identity of the metals and the temperatures. If the temperature of one junction is held constant a calibration of voltage vs. temperature for the second junction may be made.

The "Seebeck effect" is quite complicated but can be conceptualized by considering what happens when one end of a wire is heated. Electrons which may need just a small amount of energy to move freely in the conduction band will begin to do so, migrating toward the colder end of the wire. This flow of electrons results in an electric potential between the two ends of the wire. There is more to it, but that is enough to give some context to the use of a thermocouple in this experiment. [interestingly, the phenomenon works in the *reverse* as well, i.e., running a voltage through a thermocouple causes the temperature of one junction to rise while the other drops! This is known as the *Peltier effect*.]

The different oxygen-copper environments of the 1-2-3 superconductor allow for an unusual method of analysis of the final product after it has been tested for the Meissner effect. The copper ions in the lattice are not all the same! Some have an oxidation state of +2 while others are in the unstable state of +3. A structure with superconducting properties has an average copper oxidation state of $+\frac{7}{3}$. Studies show that this fractional average results from a 2:1 ratio of Cu(II):Cu(III). By careful manipulation of experimental conditions it is possible to selectively analyze for these different copper ions and thus determine whether the sample was prepared properly (and to some extent how homogeneous it is).

The ground ceramic material dissolves readily in dilute HCl. Under ordinary conditions any Cu^{3+} present is immediately reduced to Cu^{2+}:

$$2\ Cu^{3+}_{(aq)} + H_2O_{(l)} \rightarrow 2\ Cu^{2+}_{(aq)} + \tfrac{1}{2}\ O_{2(g)} + 2\ H^+_{(aq)} \qquad [1]$$
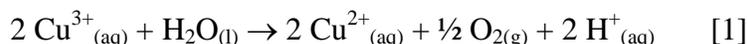
This amount of Cu^{2+} adds to that already present and so any determination of copper content at this point will give the total copper in the sample.

A common analytical method for quantifying copper (and other metals) involves treatment of the metal ion with iodide (which acts as a reducing agent):

$$2\ Cu^{2+}_{(aq)} + 4\ I^-_{(aq)} \rightarrow 2\ CuI_{(s)} + I_{2(aq)} \qquad [2]$$
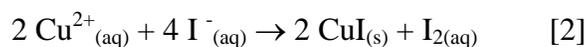
Excess iodide is used in the step above to ensure a complete reaction and to keep the I_2 that is formed in solution. [the primary iodine species in such solutions is actually I_3^- but for the sake of simplicity this is represented as $I_{2(aq)}$ in the discussion here]

Standard iodometric titration involves the reduction of the I_2 formed with thiosulfate using a starch indicator near the end of the reaction to signal when the I_2 is completely reduced:

$$I_{2(aq)} + 2\ S_2O_3^{2-} \rightarrow 2\ I^-_{(aq)} + S_4O_6^{2-}_{(aq)} \qquad [3]$$
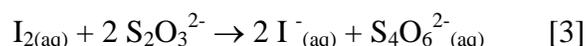
The previous two reactions taken together reveal a 1:1 mole ratio between copper(II) and thiosulfate using this procedure.

If excess iodide is present when the dilute HCl is first added, any Cu^{3+} present is reduced by the I^- rather than water:

$$2\ Cu^{3+}_{(aq)} + 6\ I^-_{(aq)} \rightarrow 2\ CuI_{(s)} + 2\ I_{2(aq)} \qquad [4]$$
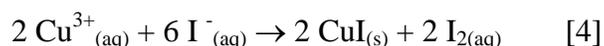
Thus it forms twice the amount of I_2 as any Cu^{2+} present which is still reduced in the manner of reaction [2]. Had this Cu^{3+} been converted to Cu^{2+} first as in reaction [1] it would have only produced one mole of I_2 so it is as if this part of the copper has reacted twice, i.e., the total moles of iodine liberated in the second method are from the total copper present plus the amount of Cu(III) measured "again" (Cu^{2+} + 2 Cu^{3+}). The first method gives Cu^{2+} + Cu^{3+} and therefore the difference between the two methods gives the amount of Cu^{3+} alone. That provides enough information to determine the value of "x" in the formula for the ceramic.

Samples which exhibit the Meissner effect may not be completely homogeneous so it is possible to have a functioning superconductor and yet obtain values for "x" from the gross sample which indicate it might not work. In addition, error is introduced through careless handling of samples during titration since I⁻ in acidic solution is readily oxidized by oxygen in the air. To minimize this effect the titration is generally done under an inert atmosphere (nitrogen gas will be used in this experiment).

The Experiment

There are four parts to this experiment:

- preparation of the ceramic mixture
- firing of the ceramic [outside of lab time]
- testing for the Meissner effect and determining T_c
- analysis of the Cu content of the ceramic

The following non-locker materials will be provided:

- mortar and pestle
- solid Y_2O_3, $BaCO_3$, CuO
- numbered crucible
- sample holder w/thermocouple
- multimeter w/cables
- small rare-earth magnet
- plastic forceps
- liquid and gaseous N_2
- approx. 0.03 M $Na_2S_2O_3$
- 1.0 M HCl
- solid KI
- starch indicator
- parafilm
- gas delivery tubing and nozzle

The Chemicals

Yttrium(III) oxide is a white powder which is soluble in dilute acids. It is used in mantles for gas and acetylene lights.

Barium carbonate is a heavy, white powder which is poisonous. Almost insoluble in water, it is soluble in dilute acids. The compound is used in rat poison, in ceramics, paints, enamels, optical glasses and in the manufacture of paper.

Copper(II) oxide (black copper oxide) consists of black to brownish-black powder or fine crystals. It is practically insoluble in water but is soluble in dilute acids. It is used as a pigment in glass, ceramics and enamels. The compound also is used in copper metallurgy and in correcting copper deficiencies in soil.

Nitrogen (discovered in 1772) makes up about 78% of the air by volume. It is found frequently in volcanic or mine gases. The gas and liquid are odorless and colorless and are sparingly soluble in water. The gas combines with oxygen and hydrogen on sparking to produce ammonia and nitrogen monoxide. It combines directly with lithium metal and many of the alkaline earth metals to form nitrides. The gas is used in the manufacture of ammonia, nitric acid, for filling high temperature thermometers, and as an inert atmosphere in laboratory procedures. The gas is not toxic but in high concentrations it functions as an asphyxiant. Contact with liquid nitrogen can result in severe frostbite and the material should be handled with care.

Hydrochloric acid is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes colored yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odor of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form).

Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur. Ingestion can be fatal.

Potassium iodide is a white solid, slightly deliquescent, and prone to oxidation in air. It is used in the manufacture of photographic emulsions, and in table salt and some drinking water to help prevent iodine deficiency disease.

Sodium thiosulfate (photographer's "hypo") is most commonly obtained as a pentahydrate in colorless, odorless crystals or granules. It melts at 48°C and has a tendency to form supersaturated solutions. The compound dissolves silver halides and many other salts of silver. It is used as a fixer in photography, for extraction of silver from ores, as a mordant in dyeing and printing textiles and in the manufacture of leather. The compound has relatively low toxicity. Large doses orally cause purging.

Starch (soluble starch, *amylodextrin*) is a white, odorless, tasteless powder which is soluble in water when heated. It is frequently used in the lab as an indicator for iodometric analysis since it forms an intense blue-to-black complex with I_2 but not with I^-.

Technique Discussion

The preparation of the sample mixture is straightforward. Stoichiometric quantities of the compounds (0.75 g Y_2O_3, 2.62 g $BaCO_3$, 1.58 g CuO) are placed into--better, measured into--a mortar. The powders are ground deliberately for 20 minutes. Grinding with a mortar and pestle is tedious business but is absolutely necessary if a near-homogeneous product is to result. *Grinding is not hammering*. Grinding means moving the pestle firmly about the bottom and sides of the mortar, continually turning the solid material over (without spilling) and pressing it down again. A somewhat circular motion is best. It is a good idea to occasionally scrape the side of the mortar with a scoop so that material which has been pushed up the sides is returned to the main mixture. Because the inevitable motion of the mortar on the benchtop will leave permanent scratches be sure to use the masonite square underneath the mortar when grinding.

The finished product is transferred to a crucible with your locker number on the bottom. When as much material as possible has been transferred use the back end of the pestle to tamp the powder down firmly, leaving a smooth top with no "fringes" of solid up around the sides. The crucibles then go into a desiccator. Over the following weekend they will be heated in a furnace as described in the Background section.

The sample holder for determining the critical temperature (T_c) of your sample is constructed from PVC plumbing fittings with a small hole drilled into the side for a thermocouple wire as shown in the see-through diagram below:

washer

ceramic pellet

foam bushing
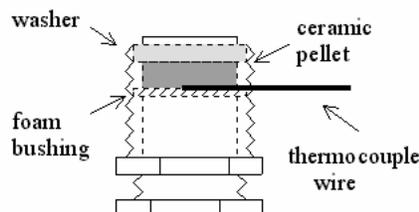
thermocouple wire

The thermocouple system consists of a sample and reference junction, prepared by twisting the ends of the *constantan* (Cu-Ni alloy) and copper leads tightly together and immersing the reference junction in an ice-water bath ($0^{o}C$). The copper lead of the <u>sample junction</u> is attached to the + terminal of a multimeter and the copper lead of the <u>reference junction</u> is attached to the - terminal:

to (-) on multimeter →
(Cu)

← to sample holder
(Cu-Ni)

to (+) on multimeter
(Cu)

ice water
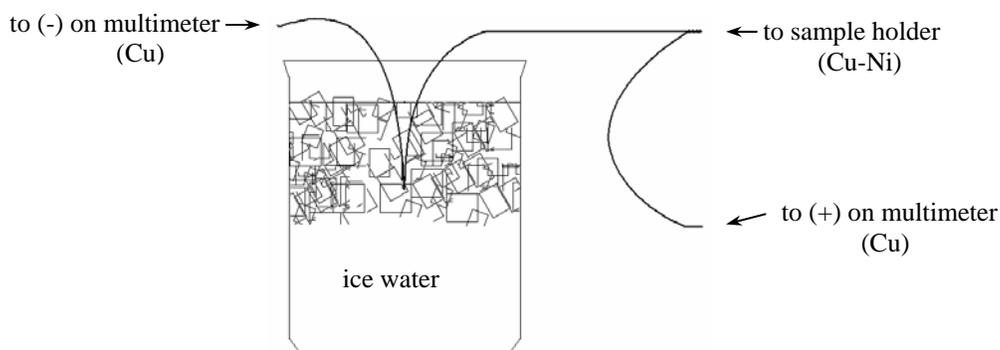
The sample holder is placed on an expanded polystyrene support and the sample junction of the thermocouple is threaded through the hole and centered. The ceramic disk is then placed over the thermocouple and fixed in place by screwing down the inner cylinder securely against the disk. If the thermocouple has been connected correctly the reading on the meter should be approximately 0.7-0.8 millivolts (i.e., 0.0007-0.0008 volts). If the voltage is negative the wires are connected backwards. If no voltage is registered check the connections of the thermocouple wires to the multimeter cables. The wires are very fine and sometimes the clips from the cables do not "bite" into them.

Liquid N_2 is poured onto the ceramic until it has been cooled to approximately 77 K (the boiling point of nitrogen). The voltage reading should then be near -5.5 millivolts. The small magnet may then be placed over the ceramic to detect the Meissner effect. A more pronounced effect is obtained this way as opposed to placing the magnet on the ceramic and then cooling it with liquid nitrogen.

If the Meissner effect is observed the voltage should be recorded while the magnet is floating. The ceramic is then allowed to warm while the voltage on the multimeter is monitored. The voltage is recorded again when the magnet just falls to the surface of the ceramic. Because the thermocouple is below the ceramic and the surface will warm up faster than the bottom, several determinations of T_c should be made in order to obtain a good estimate of the value.

When it is convenient to do so the _dry_ ceramic should be reground as finely as possible. Unless the powder is very fine it will not dissolve in the second titration procedure and this will cause hopelessly lagging endpoints (and likely invalidate the results entirely). A small amount of initial hammering is required to break up the disk with the pestle but this should be kept to a minimum and regular grinding should begin as soon as the sample grain size is small enough.

Sodium thiosulfate, for all its uses and virtues, is not a good *primary standard*. That essentially means it cannot be prepared directly from the stock bottle with a reliable concentration since the compound is generally hydrated and it will not withstand oven drying without decomposing. Therefore the solution to be used in the titration must first be standardized against something with a known concentration. This will be done by the instructor as a demonstration of the titration and the various techniques involved. The data for these determinations should be recorded. The next section in [ ] describes the preparation of the standard and the essentials of the titration.

[A standard copper solution is prepared from reagent grade copper wire (1.25 g-1.50 g) in a 250 mL volumetric flask. The wire is dissolved in nitric acid, warmed and diluted. After dilution and heating a small amount of urea is added to destroy any residual nitrogen oxides that interfere with the titration by oxidizing iodide ion. The mixture is then brought up to volume with 1 M HCl.

10.00 mL of the copper solution is pipetted into a 100 mL beaker. A stirring bar is added. The beaker is covered with a sheet of parafilm and set on a magnetic stirrer for titration. A small hole is punched through the parafilm to admit the buret tip. The buret is filled with the $Na_2S_2O_3$ solution. A second hole is punched in the film to admit the gas jet connected to the "Air" line (nitrogen gas is supplied through this line for the titration). 1.0-1.5 g of KI is dissolved in 10 mL of distilled water and added to the beaker while stirring by carefully lifting a corner of the parafilm. Nitrogen gas is then allowed to flow gently over the solution until the titration is complete. The buret tip or gas jet should _not_ be used to punch the holes as parafilm will frequently clog them.

Thiosulfate is added from the buret until the brown iodine color of the mixture is significantly faded (to about the color of a file folder). Then approximately 2 mL of starch is added. Titration continues until the blue-gray color is discharged. The final mixture is off-white, occasionally with a pink cast.]

For the two analyses it is most convenient if the sample masses are very close to one another. About 150-200 mg of sample powder is required in each case. For the total copper analysis the powder-- in the 100 mL titration beaker-- is mixed with 10 mL of 1 M HCl in the fume hood and set on a hot plate there until it boils for a few minutes to ensure all of the Cu^{3+} is reduced. After cooling to room temperature the mixture is treated like the standard copper sample described above.

For the determination of Cu^{3+}, the 10 mL of HCl is mixed with about 1.2 g of KI before adding it to the massed sample. This must be immediately placed under flowing nitrogen and stirred thoroughly *until all of the solid has dissolved* (about 1 minute). 10 mL of distilled water is added and the titration is then completed as for the other samples.

The Report

Your initial calculations should include:

1. The "best" value (or range) of T_c determined from the thermocouple data [table following]

2. The concentration of the standardized sodium thiosulfate solution

3. The total copper content of the oxide

4. The Cu^{3+} content of the oxide
   [note: if the sample masses for the two titrations were very different then the moles of copper
   should be compared on a per-gram-sample basis]

5. The value of "x" in the oxide formula

      Your conclusion to this experiment should include a description of the behavior of your sample. Did it exhibit the Meissner effect? Strongly, weakly, in some regions? The critical temperature determination should be compared to the known value for this superconductor. Discuss any differences. Finally, how does the ratio of Cu^{2+}:Cu^{3+} in your sample compare to the "ideal" value? How is this connected with the rest of your results?

Thermocouple Type "T" reference table
millivolts

°C	-9	-8	-7	-6	-5	-4	-3	-2	-1	0
-200	-5.739	-5.724	-5.710	-5.695	-5.680	-5.665	-5.650	-5.634	-5.619	-5.603
-190	-5.587	-5.571	-5.555	-5.539	-5.523	-5.506	-5.489	-5.473	-5.456	-5.439
-180	-5.421	-5.404	-5.387	-5.369	-5.351	-5.334	-5.316	-5.297	-5.279	-5.261
-170	-5.242	-5.224	-5.205	-5.186	-5.167	-5.148	-5.128	-5.109	-5.089	-5.070
-160	-5.050	-5.030	-5.010	-4.989	-4.969	-4.949	-4.928	-4.907	-4.886	-4.865
-150	-4.844	-4.823	-4.802	-4.780	-4.759	-4.737	-4.715	-4.693	-4.671	-4.648
-140	-4.626	-4.604	-4.581	-4.558	-4.535	-4.512	-4.489	-4.466	-4.443	-4.419
-130	-4.395	-4.372	-4.348	-4.324	-4.300	-4.275	-4.251	-4.226	-4.202	-4.177
-120	-4.152	-4.127	-4.102	-4.077	-4.052	-4.026	-4.000	-3.975	-3.949	-3.923
-110	-3.897	-3.871	-3.844	-3.818	-3.791	-3.765	-3.738	-3.711	-3.684	-3.657
-100	-3.629	-3.602	-3.574	-3.457	-3.519	-3.491	-3.463	-3.435	-3.407	-3.379
-90	-3.350	-3.322	-3.293	-3.264	-3.235	-3.206	-3.177	-3.148	-3.118	-3.089