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Experiment 11

A High-Temperature Superconductor, $YBa_2Cu_3O_{7-x}$

M. Stanley Whittingham

Notes for Instructors

Purpose

To prepare $YBa_2Cu_3O_{7-x}$ and observe its properties in liquid nitrogen.

Method

Stoichiometric amounts of Y_2O_3, BaO_2, and CuO are ground together and heated at high temperature. The product is cooled in liquid nitrogen and its conductivity and effect on a small magnet are observed. *See* Chapter 9.

Materials

Yttrium oxide, Y_2O_3

Barium peroxide, BaO_2

Copper(II) oxide, CuO

Furnace (capable of operating up to 1000 °C)

Pellet press

Alundum combustion boats (VWR or Fisher Chemical)

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Liquid nitrogen

Foam cup

Plastic forceps

Small, strong magnet

Four-probe conductance test circuit and voltmeter (*See* Figure 6.)

A High-Temperature Superconductor, $YBa_2Cu_3O_{7-x}$

Purpose

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Introduction

H. Onnes, a Dutch physicist, discovered in 1911 that mercury loses all resistance to electrical flow when cooled to about 4 K; thus, a current once started will flow continuously. Such a phenomenon is known as superconductivity. At ordinary temperatures, metals have some resistance to the flow of electrons, because atomic vibrations scatter the electrons. As the temperature is lowered, the atoms vibrate less and the resistance declines smoothly, until, if the material can become a superconductor it reaches a so-called critical temperature, T_c. At this point, the resistance drops abruptly to zero (Figure 1). If an electrical current is started in a superconducting ring, it will continue forever.

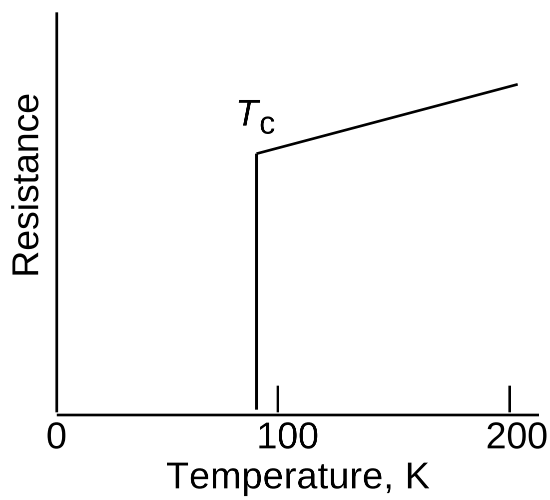

Figure 1. Electrical resistance of a $YBa_2Cu_3O_{7-x}$ superconductor.

Superconductors are also perfectly diamagnetic (i.e., they expel a magnetic field from their interior); this property was discovered in 1933 and is known as the *Meissner effect.* When a magnet approaches a superconductor, it induces a current in the superconductor. Because there is no resistance to the current, it continues to flow and thus induces its own magnetic field which then repels the magnet's field. If the magnet

NOTE: This experiment was written by M. Stanley Whittingham, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY, 19302.

is sufficiently small and strong, the repulsion will be enough to counterbalance the pull of gravity and the magnet will levitate above the surface of the superconductor. In the $YBa_2Cu_3O_{7-x}$ superconductor, there is actually some penetration of the magnetic field that helps to provide a stable levitation position for the magnet above the superconductor pellet.

Even though until recently the highest known critical temperature was only 23 K, observed in the intermetallic compound Nb_3Ge, superconductors found a number of applications. The most common of these is for superconducting magnets for nuclear magnetic resonance instruments used for medical imaging and in the research laboratory; you may find these in many chemistry departments. These instruments require liquid helium as the refrigerant, which is scarce and expensive. In a major breakthrough in 1986 (which resulted in a Nobel Prize in 1987), J. G. Bednorz and K. A. Müller at the IBM research labs in Zurich discovered superconductivity at over 30 K in copper-containing oxides. A massive worldwide research effort culminated in the discovery of a metallic oxide of yttrium, barium, and copper that was superconducting at about 92 K. This meant that liquid nitrogen (b.p. 77 K), which is cheaper and easily handled in a Dewar flask (the laboratory version of a Thermos bottle), could be used as a coolant rather than liquid helium. Related oxides have now been found that superconduct at temperatures up to 130 K.

The superconducting compound, $YBa_2Cu_3O_{7-x}$, is readily prepared by heating an intimate mixture of yttrium oxide, barium peroxide, and cupric oxide at approximately 930 °C for 10–12 hours. In this stage the crystalline structure is formed by the interdiffusion of ions, but it has a deficit of oxygen ($x \approx 0.5$). By cooling the material to 500 °C and annealing at this temperature for 10–12 hours, it reacts further with oxygen from the air; x is reduced to less than 0.1. The overall reaction (with only the metal ions balanced) is given by

$$1/2\ Y_2O_3 + 2\ BaO_2 + 3\ CuO \rightarrow YBa_2Cu_3O_{7-x}$$

This compound is often called the “1-2-3” material from the molar ratios of Y:Ba:Cu. The heating–cooling synthesis sequence is shown graphically in Figure 2.

The unit cell structure of $YBa_2Cu_3O_7$ is shown in Figure 3; although it appears complex, its basic building block is the simple perovskite structure. The main feature of the structure that is thought to be important in the superconductivity is the existence of the CuO two-dimensional sheets, extending through the material. Identify these sheets in Figure 3.

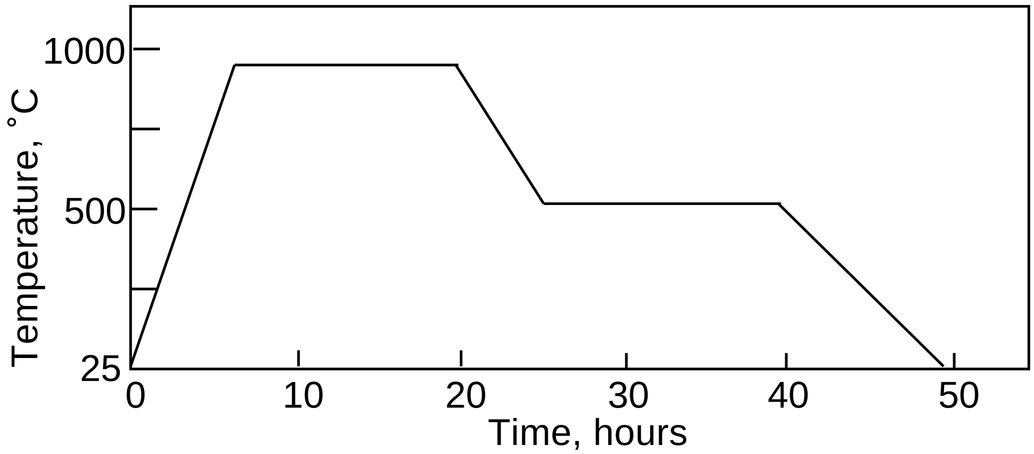

Figure 2. Heating-cooling sequence for synthesis of the 1-2-3 superconductor.

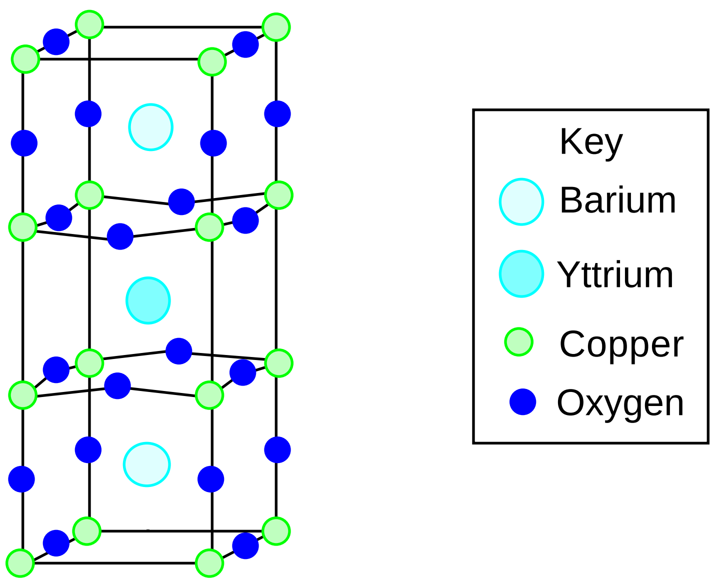

Figure 3. Unit cell of $YBa_2Cu_3O_7$.

Warm-up Exercises

1. Calculate the weights of BaO_2 and CuO required to react *stoichiometrically* (1Y:2Ba:3Cu) with 0.60 g of Y_2O_3 to produce $YBa_2Cu_3O_7$. (Do not balance the amount of oxygen.)
2. What is a superconductor? Discuss two major physical properties usually associated with superconducting solids.

Procedure

Wear eye protection.

CAUTION: The chemicals used in this experiment are toxic. Avoid creating or breathing dust when grinding. Avoid eye and skin contact. Wash your hands thoroughly after handling.

Weigh out onto a piece of weighing paper 0.60 g of yttrium oxide, Y_2O_3, and transfer it to a small *dry* beaker. Weigh out stoichiometrically equivalent amounts (you calculated these as a warm-up exercise) of barium peroxide, BaO_2, and cupric oxide, CuO, transferring each in turn to the same beaker.

These three materials must now be thoroughly mixed to obtain good results. *In a hood* place the powdered materials in a mortar. Mix and grind the material with a pestle for about 10 minutes; use a spatula to scrape the material off the sides of the mortar when it cakes there. Your final powder should be a uniform color with no lumps and no black or white spots or patches visible. What color is your powder? Why must you mix the starting powders?

Scrape the powdered mixture onto a creased piece of weighing paper. Divide the mixture in half using a second piece of weighing paper. Make two pellets with this powder: your instructor will show you how to press each mixture into a pellet using the pellet press. (The pressed pellet is quite fragile and may shear crosswise or crumble when ejected from the die. If it shears or crumbles, crush it in your mortar and re-press it.)

The pellets will be placed in an alundum (a form of Al_2O_3) boat and heated in a furnace. The furnace will be heated to 930 ^oC over a period of about 8–12 hours, held at 930 ^oC for 12–16 hours, allowed to cool to 500 ^oC and held there for 12–16 hours. Finally the furnace will be turned off and allowed to cool to room temperature. (See Figure 2.) The cooled pellets, in their beakers, will be stored in a desiccator until the next laboratory period.

The finished pellet should be dark gray to black. A dark green material is a second phase, of composition Y_2BaCuO_5, which does not superconduct.

Model Building

The properties of a superconductor obviously will depend on the structure and packing of the atoms in its crystalline form. X-ray and neutron diffraction studies were most important in the elucidation of the 1-2-3 oxide structure, which belongs to a structural family known as perovskites. Perovskites, ABO_3, generally have a ratio of two metal atoms, AB, for three oxygen atoms.

Perovskite Structure

The perovskite structure is named after the mineral $CaTiO_3$. This structure is made up by corner-sharing of TiO_6 octahedra with Ca ions in the large cavities at the corners of the unit cell.

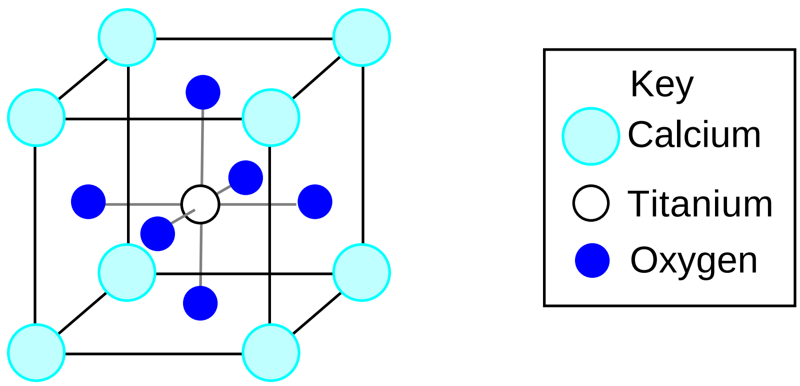

Figure 4. The perovskite structure of $CaTiO_3$.

Study the structure in Figure 4 or use a model (for the SSMK, build alternate perovskite using template C) to answer the following questions.

1. What is the coordination number of:

   Calcium_______ Titanium_______ Oxygen_______

2. Show that the unit cell of this compound corresponds to the formula $CaTiO_3$. Remember that an ion shown as part of a unit cell does not contribute a whole ion to the cell unless it is wholly enclosed within the cell, as the Ti ion is here. (Remember: How many unit cells is each atom in?)

3. Determine the oxidation state of the Ti if Ca and O have their normal oxidation states.

4. How does the structure of WO_3 differ from that of $CaTiO_3$?

Structure of the Superconductor $YBa_2Cu_3O_7$

The 1-2-3 superconductor has a structure similar to perovskite. The resulting unit cell consists of three stacked cubic unit cells with Y and Ba sharing the Ca positions, and Cu taking the Ti positions; it is considered to be orthorhombic rather than cubic, having an almost square base but rectangular sides (a = 3.817 Å, b = 3.882 Å, c = 11.671 Å, where a, b, and c are lengths of the sides of the unit cell.)

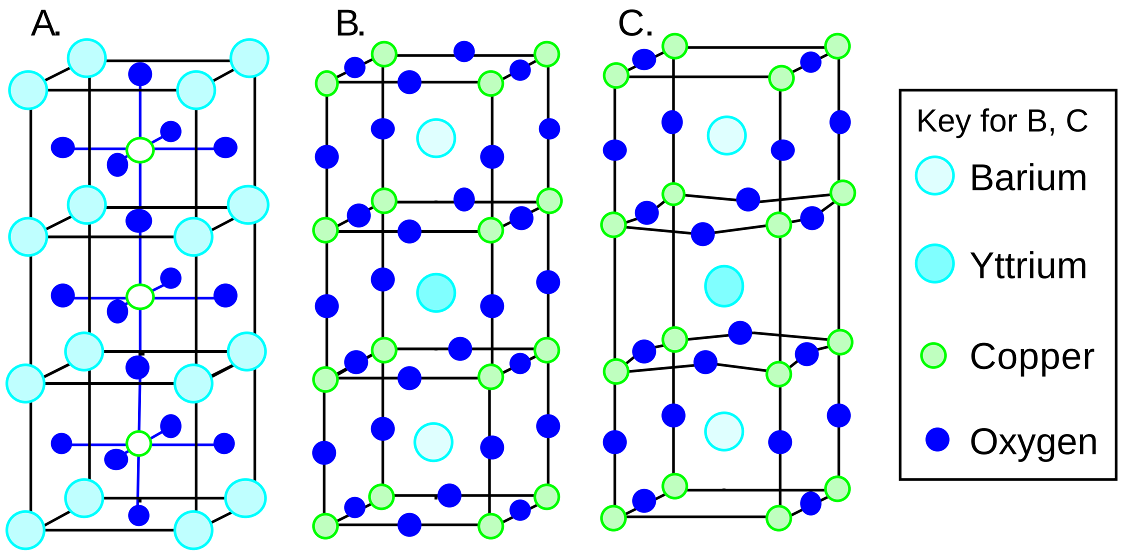

Figure 5. Idealized structure of $YBa_2Cu_3O_7$ obtained from X-ray diffraction data, showing evolution from the perovskite structure shown in Figure 4. A: Stacking of three perovskite units. B: Shift of origin. C: Removal of oxygen to give correct chemical composition. (Reprinted with permission from Whittingham, M. S. *Mater. Res. Soc. Bull.*, p 41, August 1990.)

Study the structures in Figure 5 or use a model (for the SSMK use template C and modify the directions for perovskite) to answer the following questions.

1. Show that the unit cell obtained by X-ray diffraction analysis corresponds to the formula $YBa_2Cu_3O_7$.
2. The copper in $YBa_2Cu_3O_7$ may be considered to be a mixture of +2 and +3 oxidation states. If Y has a +3 oxidation state and Ba and O have their normal oxidation states, what fraction of the copper is in each of the two oxidation states?

Properties of a Superconductor

Meissner Effect

Using the *plastic* forceps, remove the superconductor pellet from the beaker and place it in a cut-off foam cup. (If there is loose material on the pellet scrape it off gently with a spatula. If the pellet has sheared, use the thickest piece, and place it flat side up.) Then place a small magnet on top of the pellet with *plastic* forceps.

Obtain some liquid nitrogen in a second foam cup. **CAUTION: Liquid nitrogen is extremely cold: 77 K = –196 °C = –321 °F. Do not spill it on your skin or clothing. Severe frostbite or freezing of the flesh can occur. Remove clothing that becomes saturated with**

liquid nitrogen, because the liquid may be held within the spaces in the fabric and freeze the skin underneath.

Carefully pour some of the liquid nitrogen into the cut-off cup, covering the pellet. Some of it will boil away as the pellet, magnet, and cup cool; add more as necessary. When the pellet cools below the critical temperature, the magnet should "levitate" above the superconductor. Touch it gently with your forceps and it should spin.

Allow the liquid nitrogen to evaporate and the pellet and magnet to warm to room temperature.

Loss of Electrical Resistance

The loss of resistance below the critical temperature can be measured by measuring the voltage drop across the pellet in a circuit. The four-probe apparatus used is shown schematically in Figure 6. A battery generates a current, I, which passes through the pellet. The voltage drop, $V = IR$, along the pellet due to the pellet's resistance, R, at room temperature is measured with the voltmeter. When the material becomes superconducting, $R \rightarrow 0$, so $V \rightarrow 0$, and no voltage drop should be measured. (The resistor in the circuit prevents the battery from being shorted when the superconductor loses its resistance. A four-probe technique eliminates contact resistances.)

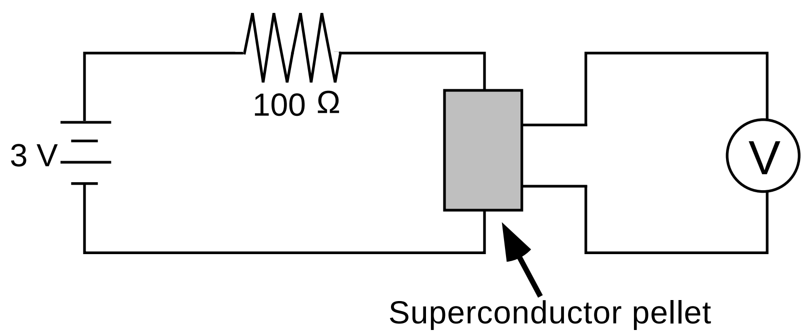

Figure 6. The four-probe conductance test circuit.

Carefully insert the pellet into the four-pronged holder. Connect the outer leads to the battery and the inner leads to the voltmeter.

After placing the holder in the foam cup, pour liquid nitrogen slowly and carefully into the cup as in the Meissner experiment. **CAUTION: The resistor in the test circuit becomes quite hot. Do not touch the resistor or spill liquid nitrogen on it. Thermal shock could cause the resistor to break, and you could burn your fingers.** When the pellet cools below T_c, it should become superconducting. What happens to the voltmeter reading at this point?

Disassemble the experiment as follows: (1) Disconnect the battery to prevent overheating the resistor, (2) let the nitrogen evaporate, (3) let the sample and holder return to room temperature, and (4) remove the sample from the holder.

Questions

1. Discuss your observations. Does your product exhibit the characteristics of superconductivity? Does it appear to be uniform? If not, what do you hypothesize went wrong? How would you identify the presence of additional phases?
2. Why did you compress your reactants into pellets for your solid-state reaction? Hint: What is the difference between reactions in solution and in the solid state?
3. The dream of the materials chemist is to discover a material that would be superconducting above room temperature, so that no refrigerant would be required. Suggest how the properties of such superconductors could be valuable in each of the following fields: computers, electronics, power generation, power transmission, and rail transportation.