

High Temperature Superconductors

A brief history, theory, and formula

Mark Bush

H3

DAWN OF SUPERCONDUCTORS

Dutch physicist Heike Kamerlingh Onnes was interested in how materials behaved when cooled to near absolute zero temperatures. On July 10, 1908, Onnes successfully operated the first liquefier of helium, which exhibited a boiling point of approximately 4.2K (Doss, 1989). Onnes was interested in how materials behaved when cooled to nearly absolute zero temperature. Kamerlingh Onnes conducted experiments with conductors and liquid helium, believing that the electrical resistance would steadily decrease alongside the decrease of temperature. The experiments validated Kamerlingh Onnes's hypothesis. His production of extreme cryogenic temperatures led to his discovery of superconductors. Superconductors are materials that have no resistance to the flow of electrons and remain to this day one of the last frontiers of scientific discovery. The reasons for this are that the limits of superconductivity have not yet been reached, but also the theories that attempt to explain superconductor behavior are incomplete. Kamerlingh Onnes immediately appreciated that his new discovery potential had important technological implications centered in particular on the production of high magnetic fields. It is well known that passage of an electrical current gives rise to a magnetic field to produce an electromagnet. The disadvantage, however, of using normal metals is that such materials have a finite electrical resistance and a passage of large currents would burn out the material. Kamerlingh Onnes hypothesized that a superconductor can deliver a high current with zero electrical resistance and hence, no joule heating. Joule heating is the process by which the passage of an electric current through a conductor releases heat. Joule heating is caused by interactions between the moving particles that form the current and the ions that make up the body of the conductor. Charged particles in an electric circuit are accelerated by an electric field but give up some of their kinetic energy each time they collide with an ion. The increase in the

kinetic energy of the ions manifests itself as heat and a rise in the temperature of the conductor. However, Kamerlingh Onnes observed that passage of a large current produced a magnetic field which destroyed superconductivity. The superconducting electromagnets ceased to be superconducting in magnetic fields which exceeded a few hundredths of a Tesla. There is a limit, known as the critical current density, to the amount of current that can be carried.

THE MEISSNER EFFECT

In 1933, Walter Meissner and Robert Ochsenfeld discovered that magnetic flux was not only excluded, but actually expelled from superconductors. This indicates that superconductivity is a magnetic phenomenon. Prior to the Meissner-Ochsenfeld discovery, it had been wrongly assumed that the fundamental property of superconductors was zero resistance; magnetic properties were considered to be the secondary effect (Dahl, 1986). By Faraday's Law of electromagnetism, when a magnet is moved towards a superconducting sample, a current is induced on the surface layer of the conductor. This current in turn generates a magnetic field, which is exactly equal and opposite in sense to that of the magnet. This is the principle on which the electric generator operates. But, in a superconductor the induced currents exactly mirror the field that would have otherwise penetrated the superconducting material - causing the magnet to be repulsed. This phenomenon is known as strong diamagnetism and is today often referred to as the "Meissner effect." The Meissner effect is so strong that a magnet can actually be levitated over a superconductive material. Since diamagnetism is a measure of the ability of a material to shield its interior from an applied magnetic field, the complete exclusion of flux means that a superconductor is a perfect diamagnet. Perfect diamagnetism, in addition to zero resistivity, is a fundamental and equally basic property of the superconducting state.

According to Maxwell's induction equation, the field in the superconductor would behave according to:

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

However, infinite conductivity would require that $E = 0$, which would lead to:

$$\frac{\partial B}{\partial t} = 0$$

This is equivalent to stating that the magnetic field induction inside the superconductor could not change; that is, any magnetic field present would be trapped when the material became perfectly conductive. The field that is exerted by a superconductor does not change with time and neither is the induced current. Therefore, conductivity could be seen as infinite. However, the infinite conductivity model is not sufficient enough to explain the Meissner effect and applying the relevant electromagnetic equations derived by James Maxwell requires that the magnetic flux inside a completely superconducting body cannot change and this in turn would imply that any magnetic flux present inside the superconductor before it is cooled into the superconducting state would remain frozen in it. Instead, its explanation is better understood as a quantum-mechanical phenomenon as proposed by F. London (London, 1950).

THE LONDON BROTHERS

The brothers Fritz and Heinz London carried out a theoretical analysis of a superconductor in a magnetic field. Heinz London realized that alternating current must penetrate a short distance into the superconducting metal, and derived the correct formula for this depth, now known as the penetration depth, in which there is some penetration of flux. Magnetic flux near the surface decays exponentially inwards. The penetration depth is determined by the

superfluid density which is an important quantity which determines the critical temperature in high-temperature superconductors. If some superconductors have some node in their energy gap, the penetration depth at 0 K depends on magnetic field because superfluid density is changed by magnetic field and vice versa (Doss, 1989). Fritz London correctly predicted that, at sufficiently high frequencies, the superconducting electrons would not shield their normal counterparts, and Joule heating would occur. The total current flowing in the superconductor is simply the sum of the normal and superconducting components:

$$\mathbf{J} = \mathbf{J}_s + \mathbf{J}_n$$

The normal electron current obeys Ohm's law, that is,

$$\mathbf{J}_n = \sigma \mathbf{E}$$

Where σ is conventional temperature-dependent electrical conductivity (London, 1950). If one considers an electron with mass 'm' and charge 'q' in an applied electric field, E, the force relationship is:

$$\mathbf{F} = m \frac{d\mathbf{V}}{dt} = q\mathbf{E}$$

The current density, J, is nqV where 'n' is the density of electrons so that

$$\frac{d\mathbf{V}}{dt} = \frac{1}{nq} \left(\frac{d\mathbf{J}}{dt} \right) = \frac{q}{m} \mathbf{E}$$

and

$$\frac{m}{nq} \frac{dJ}{dt} = qE$$

so that

$$\frac{dJ}{dt} = \left(\frac{nq^2}{m} \right) E = \left(\frac{1}{\Lambda} \right) E$$

Fritz London, using his brother's results, came to the conclusion that superconductivity required a new relationship between the superconducting current flow and the magnetic field. From the above development

$$\Lambda = \frac{m}{n_s q^2} = 4\pi\lambda$$

Where 'm' is the mass of the superconducting charge carrier (fancy term for electron), n_s is the electron density, and λ is the penetration depth of superconductors. The London equation may be rewritten:

$$E = 4\pi\lambda^2 \frac{\partial J_s}{\partial t}$$

This equation replaces Ohm's law for superconductors. When the current density J_s is not changing with time, the electric field is zero. Since static supercurrents can flow with a zero electric field, the expression properly describes the superconductive state (London, 1950).

BCS THEORY

During the period from 1930 to 1950, a considerable effort was expended by theorists in their attempts to understand the mechanism of superconductivity, and a variety of talented

individuals attempted to explain the strange behavior with the quantum mechanical models. Superconductivity involves the interactions between enormous numbers of electrons. American physicists John Bardeen, Leon Cooper, and John Schrieffer worked on a microscopic theory of superconductivity based on a condensation of electron pairs into "Cooper Pairs" (Ginzburg, 1991). Electron-pairing was the premise of this theory which sought to satisfy the Pauli Exclusion Principle. The theory asserts that, as electrons pass through a crystal lattice, the lattice deforms inward towards the electrons generating sound packets known as "phonons". These phonons produce a trough of positive charge in the area of deformation that assists subsequent electrons in passing through the same region. This is analogous to rolling a bowling ball up the middle of a bed. 2 people, one lying on each side of the bed, will tend to roll toward the center of the bed, once the ball has created a depression in the mattress. And, a 2nd bowling ball, placed at the foot of the bed, will now, quite easily, roll toward the middle.

Below the critical temperature, pairing of electrons close to the surface is the more stable configuration in the superconducting state and reduces the total energy of the system. This is why pairing takes place. An electron pair does not behave like a point particle but instead influences the other Cooper pairs around it. The spheres of influence of the pairs overlap extensively. The electrons are continually exchanging partners with each other; that is the same as saying that the pairs interact with each other. A superconductor can then be visualized as a giant quantum state in which electrons are in a condensed state that has more order and is lower in energy than that of the electrons in a normal metal. BCS theory proposes that the formation of the superconducting state only relies on the electrons near the surface.

GENERAL SCIENCE

The electrons in an atom produce magnetism. Although the magnet as a whole may be stationary, the magnet is composed of atoms whose electrons are in constant motion. Two kinds of electron motion contribute to magnetism: their spinning motion and their orbital motion (Stewart, 2011). Electrons spin about their own axes like tops. A spinning electron also revolves about the atomic nucleus which is charge in motion. So every electron is a tiny electromagnet. Hund's rule states that the lowest-energy electron configuration of an atom is the configuration with the maximum number of unpaired electrons in degenerate orbitals, all having the same spin. A pair of electrons spinning in the same direction makes up a stronger electromagnet. Conversely, a pair of electrons spinning in opposite directions, however, works against each other. Their magnetic fields cancel. This is in accordance with Pauli's exclusion principle which states that no two electrons in an atom can have the same set of four quantum numbers (Gilbert, 2009). This is why most substances are not magnets.

It is easy to establish an electric current in metals because one or more of the electrons in the outer shell of the atom in a metal are not anchored to the nuclei of that particular atom and can move freely within the lattice structure of the metal atom. This creates a "sea" of charge carrying electrons. This is called the "Free Electron Theory of Metals" (Ford, 2005). Such materials are called conductors. The electrons in metals make for good conductors due to their adjacent state in energy to empty states: application of an electric field causes these electrons to be accelerated into an unoccupied state and conduct current. At temperatures near absolute zero, certain metals acquire infinite conductivity (zero resistance to the flow of charge). These are superconductors (Hewitt, 1998). Because superconductors have no electrical resistance, electrons can travel through them freely and they can carry large amounts of electrical current for

long periods of time without losing energy as heat. Once an electric current is established in a superconductor, the electrons flow indefinitely. With no electrical resistance, current passes through a superconductor without losing energy. Superconductors expel magnetic field, and hence repel magnets. This repulsion can be stronger than gravity, which leads to levitation. Diamagnetism is the property of an object whenever an induced dipole is opposite the direction of the magnetic field. The opposition to the external field causes a repulsive effect (Stewart, 2010).

Helium has a critical temperature measured at 3K, which is very close to absolute zero. The reason why helium is so difficult to liquefy is due to the weakness of the interaction between its atoms, which reflects its inert nature as a noble gas. Helium has two protons and two neutrons in its nucleus around which orbit two electrons. A very weak interaction between helium atoms takes place via the van der Waals interaction and it is only at very low temperatures that this interaction is sufficiently strong enough to allow helium to condense into a liquid. Liquid helium changes its behavior at a temperature of around 2.2K. Above this temperature, liquid helium is violently agitating while below, it suddenly becomes quiescent (Ford, 2005). This change marks the transition of helium into a superfluid state. As a superfluid, helium behaves like a liquid but does not possess viscosity and is capable of infinite thermal conductivity. There are striking analogies between superfluidity in liquid helium and superconductivity; the former is a frictionless flow of atoms and the other is a frictionless flow of electrons.

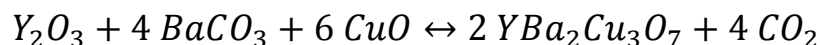
BUILDING THE SUPERCONDUCTOR

The formula used for this project was taken from an article in the *Journal of the American Ceramic Society* titled “Rapid Method for the Preparation of 1-2-3 superconductor.” The key ingredient in preparing superconductors is the rare earth metal that is used in synthesis.

Lanthanum, Bismuth, Thallium, Niobium and Yttrium are all materials that have a high critical temperature and are what keeps the superconductor intact as the raw materials undergo calcination—the process of ‘baking’ a superconductor in a high temperature oven. Rare earth elements are typically very expensive because any known quantity of them on Earth is not very concentrated and they are not commercially exploitable. This makes the rare earth element the limiting reactant in a high temperature superconductor, not because of stoichiometry but cost.

The materials used in the superconductor that ties into this paper are Yttrium Oxide, Barium Carbonate, and Copper (II) Oxide. Yttrium is purchased as Yttrium Oxide because of the toxicity of pure Yttrium. Not only is Yttrium Oxide air-stable, the oxygen in the compound plays a crucial role in the annealing process of superconductors (more on this later).

Combining the ingredients and balancing the equation yields:



The molar masses of the compounds and elements:

	Molar masses (g/mol)
Yttrium	88.906
Oxygen	15.999
Barium	137.33
Carbon	12.011
Copper	63.546
Copper (II) Oxide	79.545
Barium Carbonate	197.338
Yttrium Oxide	225.809

(Table 1: Molar masses pulled from the periodic table of elements (Gilbert, 2009))

If 30 grams of Yttrium Oxide are used, 104.86 grams of Barium Carbonate will be necessary for this reaction:

$$30g Y_2O_3 \times \frac{1 mol}{225.809 g} \times \frac{4 mol BaCO_3}{1 mol Y_2O_3} \times \frac{197.338 grams}{1 mol} = 104.86g$$

If 30 grams of Yttrium Oxide are used, 63.40 grams of Copper (II) Oxide are necessary for this reaction:

$$30g Y_2O_3 \times \frac{1 mol}{225.809g} \times \frac{6 mol CuO}{1 mol Y_2O_3} \times \frac{79.545 g}{1 mol} = 63.40 g$$

The ratio in this stoichiometry indicates that Yttrium-Barium-Copper-Oxide (YBCO) is a 1-2-3 high temperature superconductor. Since the stoichiometry holds true for YBCO, the ratios of the compounds used can be reduced to 10 grams of Yttrium Oxide, 20 grams of Copper (II) Oxide, 30 grams of Barium Carbonate.

The three compounds must be ground together with a mortar and pestle to create a powder mixture to allow the chemical process to take place. This mixture should ideally be heated between 925 to 1030 degrees Celsius for up to 18 to 24 hours. This first treatment may be done in a crucible or evaporating dish made of alumina or laboratory porcelain. The result of the first firing is a porous black or very dark gray lump. The coloration should be fairly even. An uneven green coloration indicates that the powders are not thoroughly mixed.

After the initial calcinations, the superconductor mixture can be reground to allow for the oxygen annealing phase of the procedure. The introduction of oxygen in this phase is what gives a superconductor its properties. A slow and steady oxygen flow must be present at all times during the annealing phase. A final temperature of 925 to 950 degrees Celsius for duration of 18 to 24 hours is recommended; temperatures above 1000 degrees Celsius deteriorate the superconductor structure and will make the material harder to grind. After this period, a steady

cooling process can take place. **A word of caution!** The cooling of the oven should be no more than a 100 degree per hour change while under constant oxygen flow. This ensures that as the superconductor cools, oxygen can still anneal to the YBCO. If, after a run through the oven, there is some green coloration in the superconductor, it is important to take the time and care in regrinding and mixing the material before starting on the next firing, otherwise, the same green coloration will reappear and another 24-plus hour will be spent heating the mixture and waiting for the cool down.

A word of caution! When working with Yttrium Oxide and Barium Carbonate, extreme caution and safe lab procedures must be exercised at all times. Safety goggles, vinyl gloves, surgeon/dust masks, lab coats and a ventilation hood must be readily accessible while working on any phase of the superconductor. Potential damage to the lab and serious personal injury may occur if the proper procedure is not practiced (attached to this paper are the MSDS for Yttrium Oxide, Barium Carbonate, and Copper (II) Oxide).

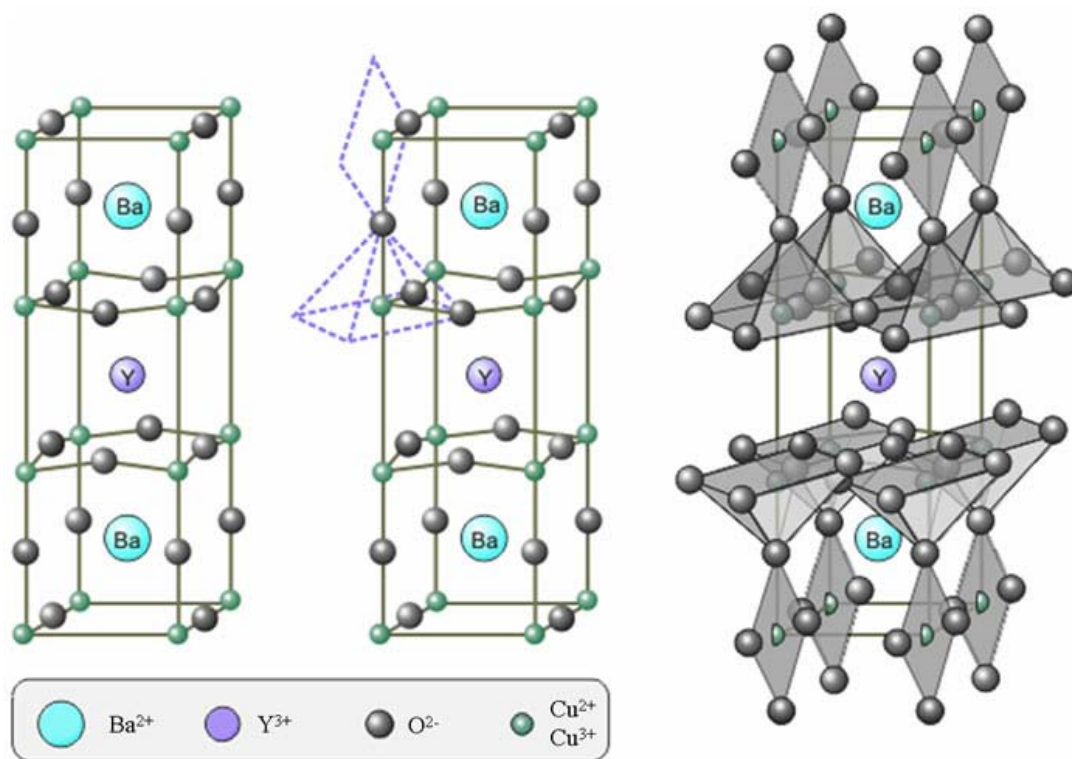
OXYGENATION

Oxygen stoichiometry is particularly important in determining the 1-2-3 superconductor's characteristics (or whether there are any superconducting phenomena to measure). The molecular structure of YBCO is typically either orthorhombic or tetragonal, depending on the oxygen stoichiometry (Mensah, 1992).



For values of δ less than ~ 0.6 , YBCO is orthorhombic, but when that value increases beyond ~ 0.6 , a transition to a tetragonal structure occurs. The tetragonal state, is not superconducting. As δ approaches 1.0, YBCO becomes a semiconductor at low temperatures (Mensah, 1992).

In YBCO, oxygen forms a Cu-O-Cu-O chain which is what is responsible for the superconductivity and generally speaking; increasing oxygen content of a superconductor increases the critical temperature substantially. As the superconductor is annealing, it must be under an oxygen rich atmosphere; not only does this create more Cu-O-Cu-O chains, but it also helps establish a reaction equilibrium in the superconductor.



(Figure 1: structure of YBCO before and after the oxygen doping (<http://www.fusione.enea.it/SUPERCOND/ybco.html.en>))

SPECIAL THANKS

Though the bulk YBCO superconductor that was proposed was not finished, I would like to take the time to thank the professors who assisted me on this project and helped point me in the right direction:

Dr. Mya Norman – Department of Chemistry and Biochemistry; for getting me in touch with the various other professors of the Chemistry department.

Dr. Rick Ulrich – Department of Chemical Engineering; for his willingness to oversee the safety aspects of the superconductor project and laboratory procedure

Dr. John Stewart – Department of Physics; for being patient with me on this project even past the intended due date

Works Cited

- Dahl, P. F. "Superconductivity after World War I and Circumstances Surrounding the Discovery of a State $B = 0$." *Historical Studies in the Physical and Biological Sciences* 1st ser. 16 (1986): 1-58. Print.
- Doss, James D. *Engineer's Guide to High-temperature Superconductivity*. New York: Wiley, 1989. Print.
- Ford, P. J., and G. A. Saunders. *The Rise of the Superconductors*. Boca Raton: CRC, 2005. Print.
- Gilbert, Thomas R. "The Periodic Table and Filling the Orbitals of Multi-electron Atoms." *Chemistry: the Science in Context*. New York: W.W. Norton, 2009. 328-32. Print.
- Ginzburg, V. L. "John Bardeen and the Theory of Superconductivity." *Journal of Superconductivity* 4.5 (1991): 327-30. Print.
- Hewitt, Paul G. *Conceptual Physics*. Reading, MA: Addison Wesley, 1998. Print.
- London, Fritz. *Superfluids. Vol. 1: Macroscopic Theory of Superconductivity*. Wiley: New York, 1950. Print.
- Mensah, Thomas O. *Superconductor Engineering*. New York, NY: American Institute of Chemical Engineers, 1992. Print.
- Stewart, John. "Magnetic Materials." *UPII Spring 2011 Course Guide Part II: Magnetism and Optics*. 2011. 357-61. Print.