High T_c Superconductivity of $GdBa_2Cu_3O_7$

Daniel E. Roberts

Partner: Josh Hone

Abstract

We report on sample preparation and investigate the superconductivity of high-T_c-cuprate-superconductor $GdBa_2Cu_3O_7$. An x-ray diffraction pattern of the sample indicates that $GdBa_2Cu_3O_7$ was indeed prepared. We found that the critical temperature of superconductivity for $GdBa_2Cu_3O_7$ is nearly $92K$. We also observed the Meissner effect within the cuprate superconductor and found the superconducting volume fractions for 36 and 48 hour oxygen annealings to be 28% and 30%, respectively.

Introduction

The purposes of this lab were to gain experience making a high-T_c superconductor, become familiar with the procedures involved in determining the superconductivity of a material, and observe the Meissner effect, which is the expulsion of an external magnetic field from the sample.

Familiar conductors, such as copper, are metal and can be thought of as a mass of positive charge immersed in a bath of electrons. Conduction occurs in these materials because the valence electrons are loosely bound and therefore move freely about the metal moving from one atom to another. In the band theory of solids, the conduction band and the valence band overlap so that the valence electrons require no extra boost of energy to reach the conduction band, unlike semiconductors.

Superconductors are not just materials that conduct better than typical conductors like copper, and the conduction process is not due to an intrinsic overlap of the conduction and valence bands. In fact at room temperatures (and much cooler temperatures for that matter) superconductors are poor conductors or insulators. Indeed, high-T_c superconductors are typically ceramic materials, and such materials usually serve as insulators. However when the temperature is reduced to below the critical temperature of the superconductor, the material under goes a second order (continuous) phase transition and becomes superconducting. The phase transition causes electrons in the material to pair up, forming Cooper pairs. These Cooper pairs allow the flow of charge without resitance. At this point the material conducts better than any conventional conductor; so much so that the resistance of the superconductor is zero. Unlike conventional metallic conductors with loosely bound valence electrons, high-T_c superconductors typically have very complex structures and are tightly bound. However it is this tightly bound structure that, below T_c, makes possible the superconductivity.

Superconductors are diamagnetic. Diamagnetism is usually observable in materials with no unpaired electrons in the atomic orbitals, where paramagnetism does not exist. When a diamagnetic material is magnetized by an external magnetic field, bound currents are induced in the material that generate a magnetic field that opposes the external magnetic field. So the magnetic field inside a diamagnetic material is less than the external field. Superconductors are so strongly diamagnetic that the bound currents induced by an external magnetic field generate an opposing field large enough to completely cancel the external field. So the external magnetic field is expelled from the superconductor. The expulsion of external magnetic fields by a superconductor is called the Meissner effect. If the external magnetic field is strong enough, it will break up the Cooper pairs, thus destroying the superconductivity.

The superconducting material we prepared, $GdBa_2Cu_3O_7$, is a cuprate superconductor. This means that the material has copper and oxygen planes in its lattice structure. Cuprate superconductors are often annealed in oxygen to increase the oxygen content of the sample which increases the superconducting volume fraction and reduces the magnetic susceptibility of the sample, thus making a better superconductor. All high-T_c superconductors are cuprate materials. High-T_c superconductors have critical temperatures between roughly $70K$ and $130K$. Superconductors that are not high-T_c have critical temperatures from about $20K$ and below. For example, aluminum superconducts below $1.2K$[1].

The remainder of the report will discuss the preparation of the sample, the x-ray diffraction analysis confirming $GdBa_2Cu_3O_7$ was prepared, measurement of the superconducting volume fraction, T_c, and the observation of the Meissner effect, and finally a conclusion.

$GdBa_2Cu_3O_7$ Sample Preparation

The $GdBa_2Cu_3O_7$ sample was prepared by the following chemical reaction:

$$\frac{1}{2}Gd_2O_3 + 2BaCO_3 + 3CuO \ \rightarrow \ GdBa_2Cu_3O_{6.5} + 2CO_2. \tag{1}$$

Eq. 1, while balanced, does not appear to yield the correct compound. The first term on the right side of the equation has 6.5 oxygen, not 7. However, because it is impossible experimentally to mix perfect molar ratios in a reaction,this discrepancy has no influence on the result of the sample, and therefore $GdBa_2Cu_3O_7$ will be produced.

The molecular weight of $GdBa_2Cu_3O_{6.5}$ is $726.5381g/mol$. A $1.5g$ sample is therefore $2.0646 \times 10^{-3} moles$. The molecular weights of Gd_2O_3, $BaCO_3$, and CuO are $362.498g/mol$, $197.3362g/mol$, and $79.5454g/mol$ respectively. For $2.0646 \times 10^{-3} moles$ of $GdBa_2Cu_3O_{6.5}$, $\frac{1}{2} \times 2.0646 \times 10^{-3} moles \times 362.498g/mol = 0.37421g$ of Gd_2O_3 are required. The $\frac{1}{2}$ is the coefficient in front of Gd_2O_3 in Eq. 1. A similar procedure for $BaCO_3$ and CuO shows that $0.814841g$ of $BaCO_3$ and $0.49269g$ of CuO are required. We measured and used $0.3742 \pm 10^{-4}g$, $0.8116 \pm 10^{-4}g$, and $0.4924 \pm 10^{-4}g$ for Gd_2O_3, $BaCO_3$, and CuO respectively. Their error arises from the uncertainty in the balance used.

The compounds were ground together for 30 minutes, then pressed into a tablet, and baked at $900°C$ for 48 hours. The sample was then ground, pressed, and baked again in order to ensure uniformity of the compound and increase the oxygen uptake of the sample.

After x-ray analysis confirmed the correct sample was made, and the superconducting volume fraction and magnetic susceptibility were measured, the sample was annealed in oxygen for 36 hours at $900°C$, and another sample was annealed in oxygen for 48 hours at $900°C$. The purpose of the annealing was to demonstrate the affect of duration of oxygen annealing on the superconducting volume fraction and magnetic susceptibility of the sample.

The sample not annealed in oxygen is referred to as air annealed.

X-Ray Diffraction Analysis

X-ray diffraction is a common method of determining the identity of a material. When x-rays are scattered from a crystal surface, a diffraction pattern, unique to that material, is formed. The uniqueness of the pattern arises from the fact that elements in a crystal form planes. These planes are defined by the placement of the atoms in the unit cell of the crystal. Because a material is defined by its elemental components, each unit cell and its corresponding planes are unique to that material.

The sample was placed in a quartz glass and the quartz was then placed in an x-ray spectrometer. The spectra obtained agree with previous results of Shaheen *et al.*[2] for the diffraction pattern of $GdBa_2Cu_3O_7$. The sample spectra also agreed with spectra in a library of previous x-ray diffraction results for $GdBa_2Cu_3O_7$. The diffraction pattern for $GdBa_2Cu_3O_7$ appears in Fig. 1.

Magnetic Measurement

A $28.4 \pm 0.1mg$ vial including sample was $180.2 \pm 0.1mg$. The sample was placed in a Superconducting QUantum Interference Device (SQUID), with an applied magnetic field of 50 Gauss, in order to measure the superconducting properties of the sample; namely the superconducting volume fraction and the magnetic susceptibility. The magnetic susceptibility, χ_m, is given by magnetization divided by auxiliary field, $\chi_m = \mathbf{M}/\mathbf{H}$, and is plotted as a function of the temperature in Fig. 2a and Fig. 2b.

χ_m is in units of $emu/gram$ where emu is "electromagnetic unit". For a sample with 100% superconducting volume fraction, the superconducting volum (SV) in units of emu/cm^3 is $SV_{100} = |\chi_m| \times sample\ density = |\frac{\mathbf{M}}{\mathbf{H}}| = \frac{1}{4\pi} \simeq 0.8$. From Fig. 2 we find that χ_m for the 36 hour and 48 hour oxygen annealed samples are roughly $-3.2 \times 10^{-3} \frac{emu}{g}$ and $-3.5 \times 10^{-3} \frac{emu}{g}$, respectively. The following equations, therefore, give the superconducting volumes for the 36 hour and 48 hour oxygen annealed samples, respectively:

$$SV_{36h} = -3.2 \times 10^{-3} \frac{emu}{g} \times 6.961 \frac{g}{cm^3} = 0.022, \tag{2}$$

$$SV_{48h} = -3.5 \times 10^{-3} \frac{emu}{g} \times 6.961 \frac{g}{cm^3} = 0.024. \tag{3}$$

And, therefore, the superconducting volume fractions for the 36 hour and 48 hour oxygen annealed samples are:

$$SVF_{36h} = \frac{SV_{36h}}{SV_{100}} = \frac{0.022}{0.08} = 28\%, \tag{4}$$

$$SVF_{48h} = \frac{SV_{48h}}{SV_{100}} = \frac{0.024}{0.08} = 30\%, \tag{5}$$

respectively. These results are quite good in that they show that the sample is a bulk superconductor. SVF values below approximately 20% are considered surface superconductors. This means that the majority of the superconducting material resides near the surface. Bulk superconductors have a superconducting phase that percolates through the sample and are therefore much better superconductors.

From Fig. 2, we also find that the critical temperature, T_c, below which $GdBa_2Cu_3O_7$ is in a superconducting phase, is roughly $92K$. This result agrees with that of Shaheen *et al.*[2].

The SQUID is an extremely accurate instrument and therefore any error in the measurements of χ_m or T_c would be exclusively due to the measurement of the mass of the sample.

Discussion and Conclusion

Fig. 2a is a plot of the magnetic susceptibility, χ_m, as a function of temperature for an air annealed sample, a sample that was annealed in oxygen for 36 hours, and a sample that was annealed in oxygen for 48 hours. Fig. 2b is the same plot only it enlarges the region around T_c where the phase change occurs. These plots demonstrate the Meissner effect, which is the expulsion of an external magnetic field by a superconductor. The negative magnetic susceptibility illustrates the diamagnetic nature of a superconductor, and therefore the fact that the magnetization of a superconductor is such that the magnetic field inside is reduced to zero.

Below $T_c = 92K$, $GdBa_2Cu_3O_7$ superconducts. The superconducting characteristics of these three samples are quite different. The air annealed sample reaches its maximum superconductivity much more gradually than the oxygen annealed samples. Therefore the phase change of a sample to superconductivity is much more definitive for samples with higher oxygen content.

The dynamic of the phase change to superconductivity does not appear to differ among the two oxygen annealed samples of different annealing times. However, the time of annealing does have an effect on the maximum (negative) value of χ_m of the samples, and therefore on the SVF. The SVF value for the 48 hour oxygen annealed sample is 30%, while the SVF value for the 36 hour oxygen annealed sample is 28%. Apparently, the longer a sample is annealed in oxygen the better it superconducts. A theory that explains why oxygen rich cuprate materials superconduct and do so at such high temperatures is still undeveloped.

In conclusion, we found the critical temperature of $GdBa_2Cu_3O_7$ to be $92K$. This value agrees with previous results [2]. We also observed the Meissner effect within the cuprate superconductor and found the SVF for a 36 hour oxygen annealing to be 28% and the SVF for a 48 hour oxygen annealing to be 30%.

Footnotes and References

1. http://hyperphysics.phy-astr.gsu.edu/hbase/solids/scond.html#c1
2. S.A. Shaheen *et al.*, J. Appl. Phys. **63** (8), 4187(1988).