Growth and Annealing Study of High-Temperature Superconductor $HgBa_2CuO_{4+\delta}$

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Abstract

Monocrystalline samples of the superconductor $HgBa_2CuO_{4+\delta}$ (Hg1201) were grown and characterized by their critical temperature (T_c). Raw samples taken out from growth tubes have an inhomogeneous oxygen (and hence hole-dopant) concentration, which results in a broad T_c transition. Afterward, samples' doping levels are homogenized by a heating treatment process (known as annealing), which also increases sample quality. Such samples were prepared for future transport measurements in this manner.

Introduction

Since its discovery in elemental Mercury in 1911 [1], superconductivity has remained one of the most active areas of research in condensed matter and low-temperature physics. The superconducting state is characterized by two unique properties: zero electrical resistance within the material and the expulsion of all internal magnetic fields within the superconducting material—known as the Meissner effect [2]. Both of these effects are only observed when the material is cooled below a critical temperature, denoted T_c. The main difficulty with superconductivity is that the critical temperatures of many superconducting substances are well below room temperature; observed critical temperatures seemed to plateau around the early 1980's at about 20-30 Kelvin.

An exciting breakthrough occurred in 1986 when superconductivity was discovered in a class of complex copper-oxide compounds called the cuprates [3]. The critical temperatures of these compounds are far greater than those of traditional superconductors—as large as 160 K. The superconducting state of the cuprates is controlled by a process called doping, in which oxygen interstitials are carefully introduced to add or remove electrons from the material. By plotting the electron (or hole) doping concentration versus temperature, one can construct a phase diagram. A schematic of such a phase diagram is given in Figure 1.

A problem with high-temperature superconductivity is that the theoretical model that successfully explains traditional superconductivity fails to explain high-temperature superconductivity. Electron-phonon interactions, the traditional mechanism of the superconductivity, have been measured to be too small to account for superconductivity in the cuprates and other high-temperature superconductors (HTSCs) [4]. Therefore, a careful study of these HTSCs—specifically, the cuprates—is necessary in order to uncover the true source of the high-temperature superconducting state.

One cuprate stands out in particular as an exceptional compound to study: $HgBa_2CuO_{4+\delta}$ hereafter referred to as Hg1201. The δ in the chemical formula of Hg1201 corresponds to the interstitial oxygen atoms in the crystal structure (Figure 2).

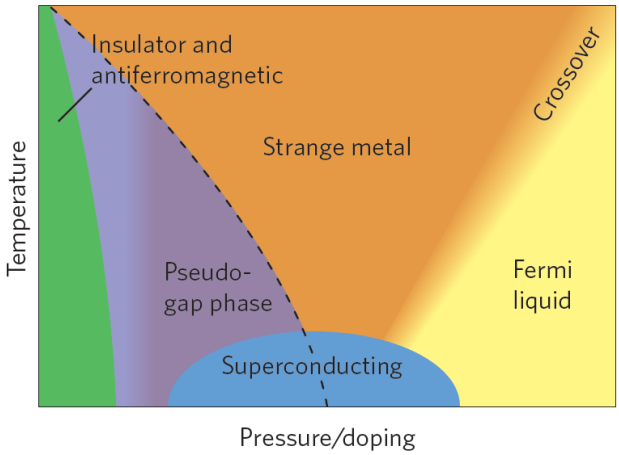

Figure 1 – Schematic phase diagram of Hg1201 with dependency on doping percentage and temperature. Note the superconducting "dome" (blue) [5].

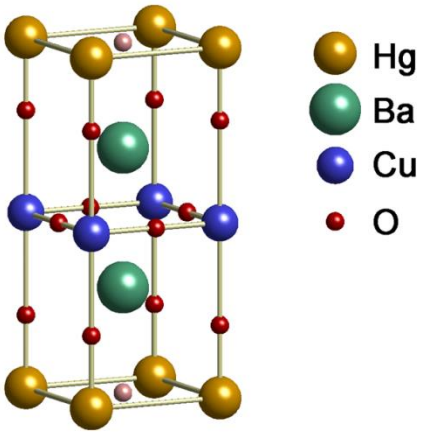

Figure 2 – Unit cell of Hg1201. The superconducting behavior is believed to originate in the CuO_2 planes.

It can be seen that Hg1201 has simple tetragonal structure, unlike most of the other cuprates. The electronic properties of Hg1201 are also less prone to disorder effects. This is because the disorder is mostly confined to the HgO spacer layers of the crystal; the HgO layers are located relatively far from the CuO_2 layers, and it is suspected that it is the CuO_2 layers that are responsible for the superconducting behavior of the cuprates [6]. Additionally, the crystal structure remains the same across a wide variety of temperatures (no phase transitions occur), again making Hg1201 a good candidate to study. The purpose of this experiment was to grow good quality crystals of Hg1201 and to control their doping levels using a process called annealing.

Crystal Growth

The following solid-gas-state chemical reaction takes place when Hg1201 crystals form:

$$2Hg + O_2 + 4BaO + 2CuO \rightarrow 2HgBa_2CuO_4$$

The mercury comes from powdered mercury (II) oxide. However, because barium (II) oxide naturally reacts at ambient atmospheric conditions and produces unwanted byproducts in that reaction, a precursor is used. This precursor is produced by sintering a very fine mixture of

barium (II) nitrate and copper (II) oxide powders at 900ºC with a constant oxygen gas flow. The chemical formula of the precursor is Ba_2CuO_3, and this compound is more stable than barium (II) oxide.

Next, 2.14 grams of the precursor is placed inside a zirconium crucible in an inert atmosphere, and this crucible is then inserted into a quartz tube. 1.50 grams of mercury (II) oxide is also inserted into the tube, but outside of the crucible. (It was noted during the growth improvement process that impurities decreased when the HgO and precursor were separated.) Additionally, approximately forty milligrams of magnesium (II) sulfate hydrate is added to the quartz tube. This is done because it was observed that larger crystals were produced if water vapor was present during the reaction. However, this also produces more impurities in the final product. A quartz plug is then welded above the crucible under a high vacuum (600 – 700 mTorr) with a hydrogen-oxygen gas flame and placed in a furnace where the reaction took place. A rendering of a sealed quartz tube in a growth furnace is given in Figure 3.

The quartz tube is heated in the furnace according to the growth profile given in Figure 4. The first part of the heating process, where the tube is heated to 800ºC for ten hours, decomposes the mercury (II) oxide into vaporous mercury and oxygen gas. To allow for the correct partial pressures of oxygen and mercury, the quartz plug is sealed approximately ten centimeters from the bottom of reaction chamber. The mercury and oxygen gas then react with the precursor to form Hg1201. Pressure inside the reaction chamber tends to maximize during this part of the heating process due to the vaporization of both mercury and oxygen. However, the pressure decreases soon afterwards as the mercury gas is absorbed during the creation of Hg1201. The temperature is then increased to and held at 1020ºC for a brief period to melt and mix the Hg1201. After this, the temperature is slowly decreased to allow for the formation of Hg1201 crystals around nucleation sites. The temperature is then quickly lowered to allow for the safe removal of the tube from the furnace. The quartz tube is broken open using a hammer to remove a small cone at the bottom of the crucible. This cone contains the Hg1201 crystals. The cone is then placed in a water vapor rich environment to allow undesired byproducts to decompose and facilitate the crystal picking process.

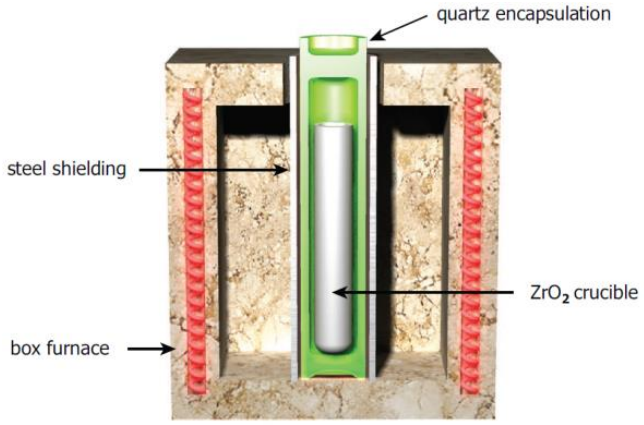

Figure 3 – Schematic of growth crucible inside growth furnace. Precursor is placed inside the crucible, while the HgO and $MgSO_4$ hydrate are placed outside of the crucible but inside the tube [7].

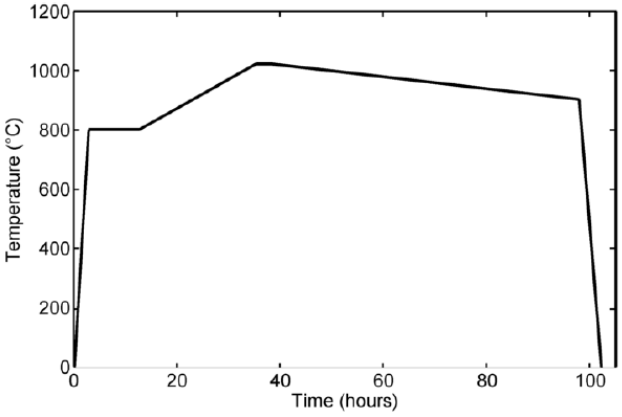

Figure 4 – Growth profile for Hg1201, which was formed at 800ºC. The sample then was melted and cooled [8].

Measurement of Critical Temperature

Measurements of samples are done using a Magnetic Properties Measurements System (MPMS) which utilizes SQUID magnetometry. This instrument cools samples to below their critical temperatures and measures small changes in their magnetic moments. Above the critical temperature, the diamagnetic component of the magnetic moment is zero. However, when the temperature of the sample reaches the critical temperature, the magnetic moment becomes extremely large and negative due to the aforementioned Meissner effect. By measuring the magnetic moment across a wide range of temperatures, the critical temperature of the sample can be determined.

There exist some deviations from ideal superconducting behavior in as grown Hg1201 samples that are investigated in the measurement process. First, due to inhomogeneity and impurities within an Hg1201 crystal, the superconducting transition does not occur instantaneously at the critical temperature; rather, there is a small range of temperatures over which the superconducting transition occurs—the sharper the transition, the higher the sample quality. (The specific T_c is taken as the temperature at which the magnetic moment is at the half

of its maximum.) Second, the Meissner effect is not fully realized in as grown samples. This is because magnetic flux vortices are pinned at impurities within the sample when it is cooled below T_c in an applied magnetic field. This effect can be quantified by taking the ratio of the magnetic moment of the sample with an applied magnetic field (field-cooled, or FC) to the magnetic moment of the sample in the absence of the magnetic field (zero-field-cooled, or ZFC) below the T_c. For better quality, annealed samples, this ratio is closer 0.5-0.95. Third, samples are not usually completely uniformly doped to the same extent. Consequently, some parts of the sample superconduct earlier than others. This leads to a gradual sloping in the SQUID data before the primary component of the superconducting transition. However, this can be remedied by annealing.

A sample labelled SM1 was prepared according to the growth procedure outlined above. SQUID data for the sample is given in Figure 5. The sample had a T_c of 78 K with a T_c-width of 4 K, which is typical of as-grown samples. Its FC/ZFC ratio was 0.15, which was also typical of samples grown in the lab. Both of these indicate that the sample was of good quality. Sources of impurities include precursor reactions with the atmosphere, as well as the water vapor that came from the magnesium (II) sulfate hydrate. The sample can be further improved upon by annealing, which is discussed next.

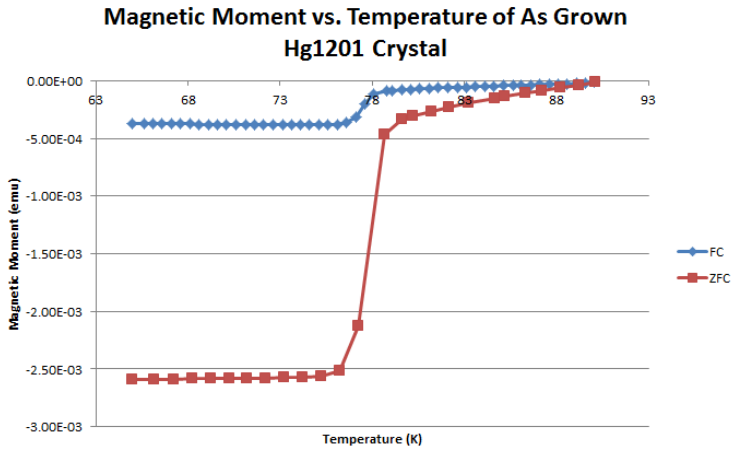

Figure 5 – SQUID data for the sample SM1. Field-cooled and zero-field-cooled data are given, which are used to compute the FC/ZFC ratio. The superconducting transition is easily noticed and occurs around 78 K, and the width of the transition is 4 K.

Annealing of Samples

The hole concentration of samples can be altered after they are grown by a process known as annealing [9]. This is accomplished by placing the sample in a furnace under some elevated temperature and gas condition. For example, to increase the hole concentration, samples are annealed under a constant flow of oxygen gas; to lower the hole concentration, samples are annealed with nitrogen or kept inside a vacuum. By adjusting the hole concentration by annealing, different regimes of Hg1201's phase diagram can be explored—not just the superconducting dome. Samples are typically annealed for several weeks to several months at a time to insure that the sample is uniformly treated.

SQUID data for an annealed sample (not SM1) is given in Figure 6. The critical temperature of this sample is about 91 K, with a width of 3 K. This is a sharp transition, indicating the sample is of high quality. Additionally, its FC/ZFC ratio is 0.57, which suggests that the sample is relatively free of impurities. It can also be seen that there is less sloping behavior on the upper portion of the graph; this shows that the sample is uniformly doped. This sample is therefore successfully annealed and ready for future measurements.

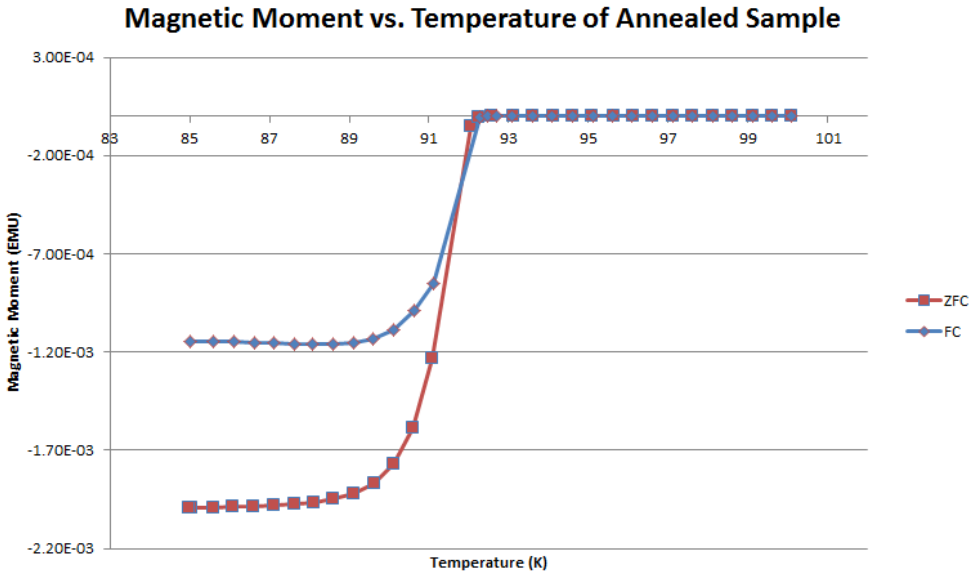

Figure 6 – SQUID data for a sample annealed at 300ºC and 3 barr of oxygen partial pressure. This sample had a T_c of 91 K and a transition of 3K. Note the flattened upper portions of the curves, an indication of uniform doping.

Conclusion

The data obtained from this study show that the crystal growth method that has been developed is a reliable way to produce high quality, monocrystalline Hg1201 samples. Now that these samples are able to be produced in such a consistent manner, the natural extension is to perform different measurements to uncover the nature of the superconductivity of Hg1201. Such measurements include the Hall effect, thermoelectric power, and magnetoresistance. These measurements can also be used to explore different regimes of the phase diagram, such as the pseudogap and strange metal phases.

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