Annealing study of the cuprate superconductor $HgBa_2CuO_{4+\delta}$

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Abstract

Growths of the cuprate superconductor $HgBa_2CuO_{4+\delta}$ were carried out. In an attempt to reach extreme doping levels (i.e., T_c below 45 K), an entire boule was annealed at 680°C and 480 mTorr for a period of 1 month. The end result was unsuccessful, with a final T_c of about 83 K.

Introduction

The cuprate superconductors are among the most widely studied materials in condensed matter physics. This is due to the interesting properties they display at different temperatures and doping levels. Some of these properties are summarized in the generic temperature versus hole-doping cuprate phase diagram shown in Figure 1.

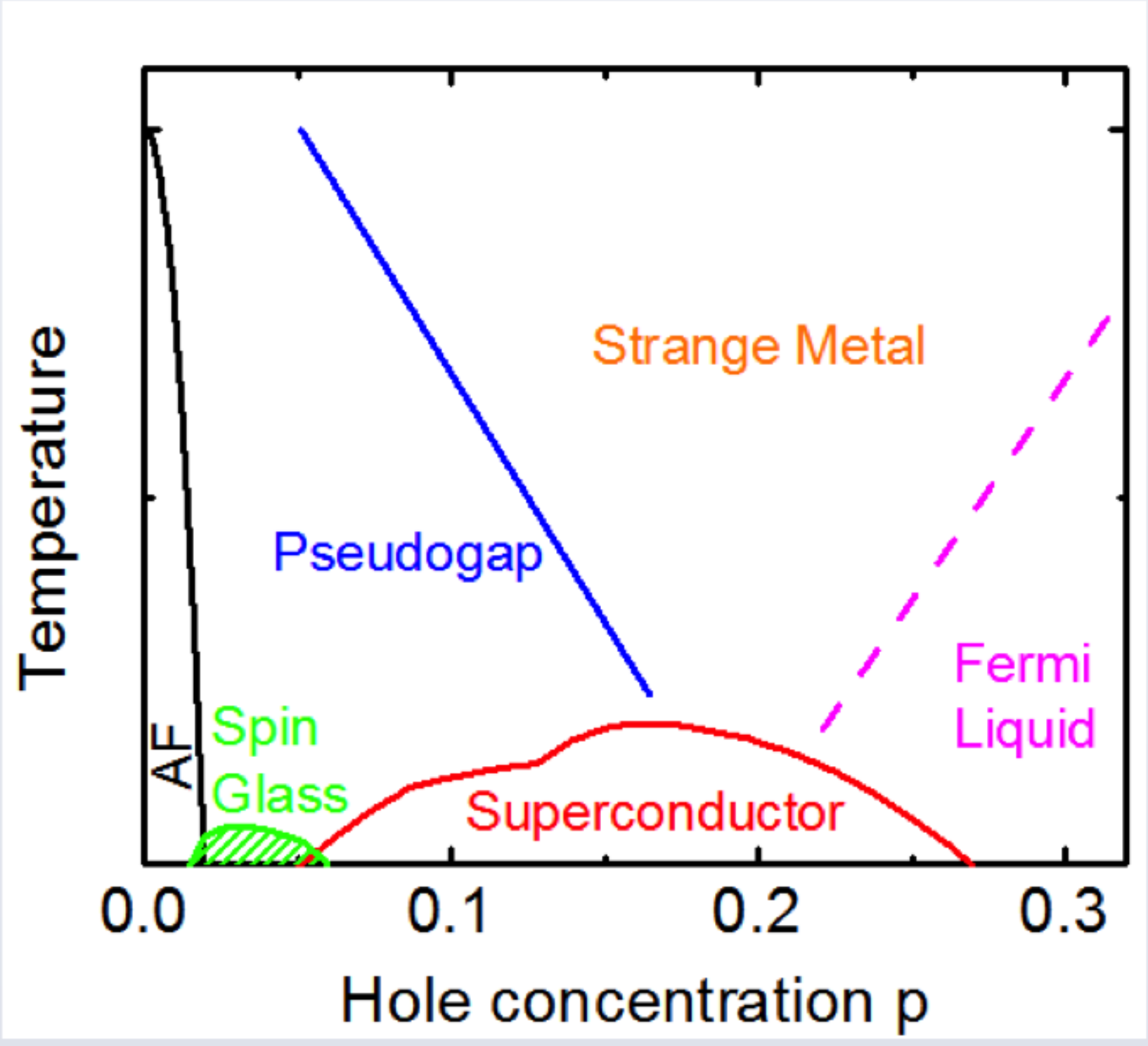

Figure 1: Generic phase diagram of the cuprates. The superconducting phase corresponds to the "dome" below the red line, which represents the superconducting transition temperature T_c. The other phases display interesting properties, but they are not the focus of this study.

It is highly desirable to be able to probe the different regimes of the phase diagram by studying crystals with suitable hole concentrations. The hole doping level of the material can be adjusted through an annealing process that modifies the density of oxygen interstitials within a crystal.

The Nearly Ideal Cuprate $HgBa_2CuO_{4+\delta}$

The material of interest in this study is hole-doped $HgBa_2CuO_{4+\delta}$ (Hg1201). This compound is ideal to study for several reasons. First, it has a simple tetragonal crystal structure, as shown in Figure 2. This structure remains the same throughout wide doping ranges, in contrast to other cuprate compounds. Second, Hg1201 is less susceptible to disorder due to the relatively large distance between the Hg planes and the CuO_2 planes (oxygen interstitials reside in the Hg planes, and the large distance between these neighboring planes means that the disorder caused by dopants has less effect on overall properties). Third, the CuO_2 planes themselves have a simple, flat structure. Because of these simple characteristics, the measured properties of Hg1201 tend to be those intrinsic to the quintessential CuO_2 planes [6].

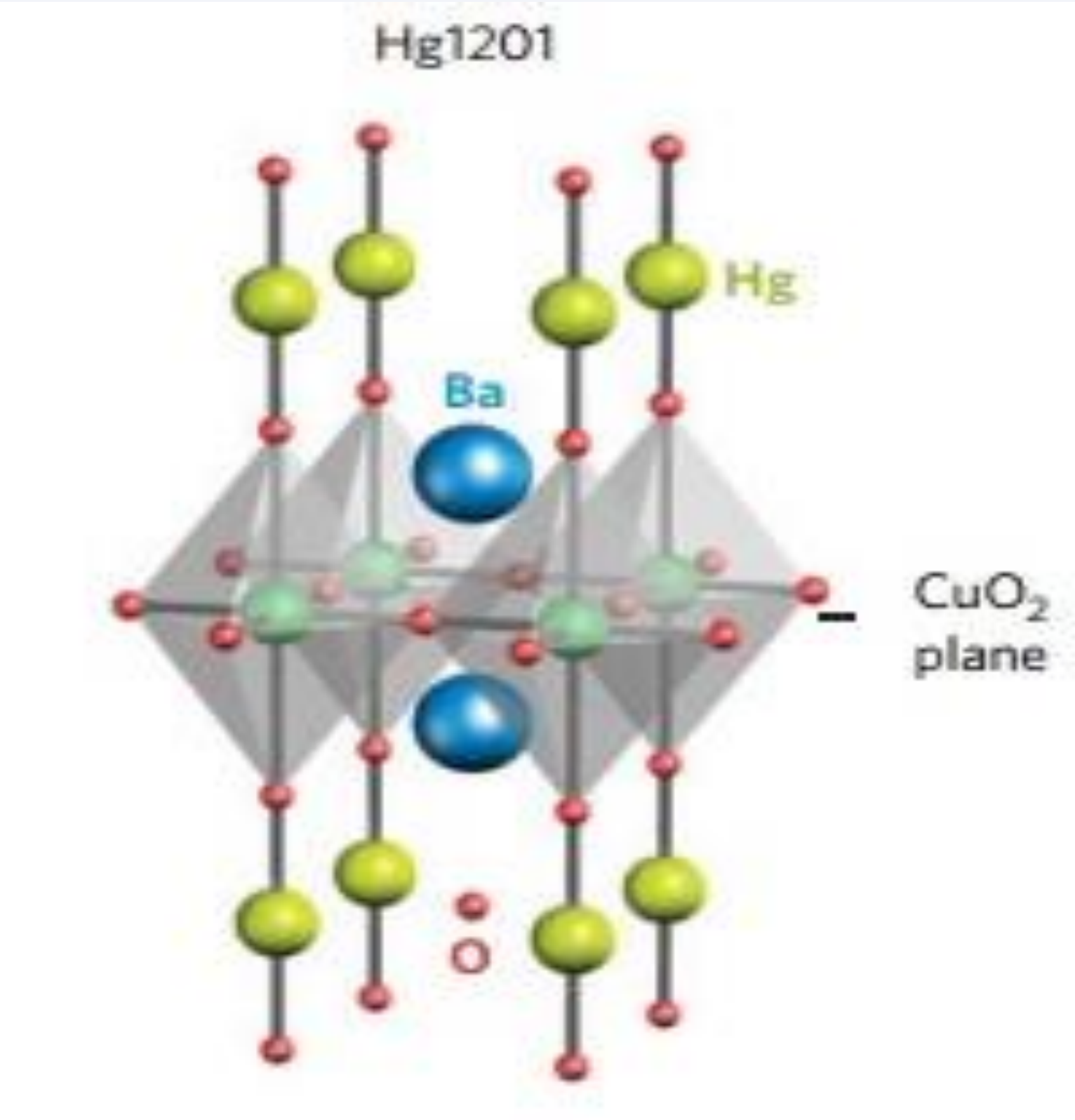

Figure 2: Unit cell of Hg1201. The CuO_2 plane lies in the middle, surrounded by Hg planes on top and bottom. Oxygen interstitials are inserted in the Hg planes. An interstitial oxygen dopant can be seen in the bottom plane. Reproduced from [11].

Annealing

The oxygen content of Hg1201 is changed through the process of annealing. Keeping crystals in an oxygen-rich or oxygen-poor environment at some elevated temperature (e.g., 300+°C) yields relatively high (overdoping) and low (underdoping) oxygen (and hence hole) concentrations, respectively. Single crystals of Hg1201 have never been sufficiently underdoped to yield a Tc below 45 K, due to harsh required conditions that lead to Hg vacancies, causing disorder in the compound. Normally, crystals are annealed after they are picked out from the boule that forms as a result of the reaction. However, this does not need to be the case. The purpose of this study is to attempt to obtain underdoped crystal with Tc below 45 K by annealing the boule as a whole in the hope that this will minimize Hg vacancies [3].

Materials and Methods

Synthesis and Anneal Preparation

To synthesize single-crystals of Hg1201, the flux method of crystal growth is used [10]. A mixture of Ba_2CuO_3 and HgO reacts at high temperature and pressure within a crucible that is placed inside a sealed quartz tube, resulting in the product $HgBa_2CuO_{4+\delta}$. The temperature is then raised past the melting point of the product. Slow cooling then allows for crystal nucleation. Hydrated $MgSO_4$ is also added to form larger crystals.

Once the synthesis is finished, the resultant boule is a hardened mixture inside which there exist single crystals. Normally crystals are picked out of the boule and prepared for annealing. Instead, in the present study the boule was sealed within a quartz tube and annealed as a whole. The conditions were 480 mTorr pressure and 600°C. The anneal took place over the course of a month.

Crystal Characterization

Once the annealing process was finished, crystals were picked out and their physical properties were characterized. For characterization, a Quantum Design, Inc. Magnetic Properties Measurement System (MPMS) was used to measure the magnetic moment of a sample over a range of temperatures. Below T_c, the moment is negative due to the Meissner effect, but above T_c the moment is rather small and positive. The location of this transition is how the T_c is measured. A sharp T_c indicates a good sample.

Another way to determine the quality of a sample is to measure the ratio of magnetic moments when the sample is cooled with an external magnetic field present (field-cooled, FC) and without one present (zero-field-cooled, ZFC). Ideally, these moments are the same, and the resulting ratio would be unity. However, in practice, samples contain impurities. When a sample is cooled in the presence of a magnetic field, vortices of flux are trapped at the sites of these impurities. These vortices produce small magnetic moments in the direction of the applied magnetic field, and effectively reduce the sample's diamagnetic signal [6]. Therefore, measuring the FC/ZFC ratio gives a rough estimate of sample quality because it reflects the relative presence of impurities.

Results

The T_c and FC/ZFC ratio of a sample from the boule anneal were measured. The results are shown in Figure 3 below.

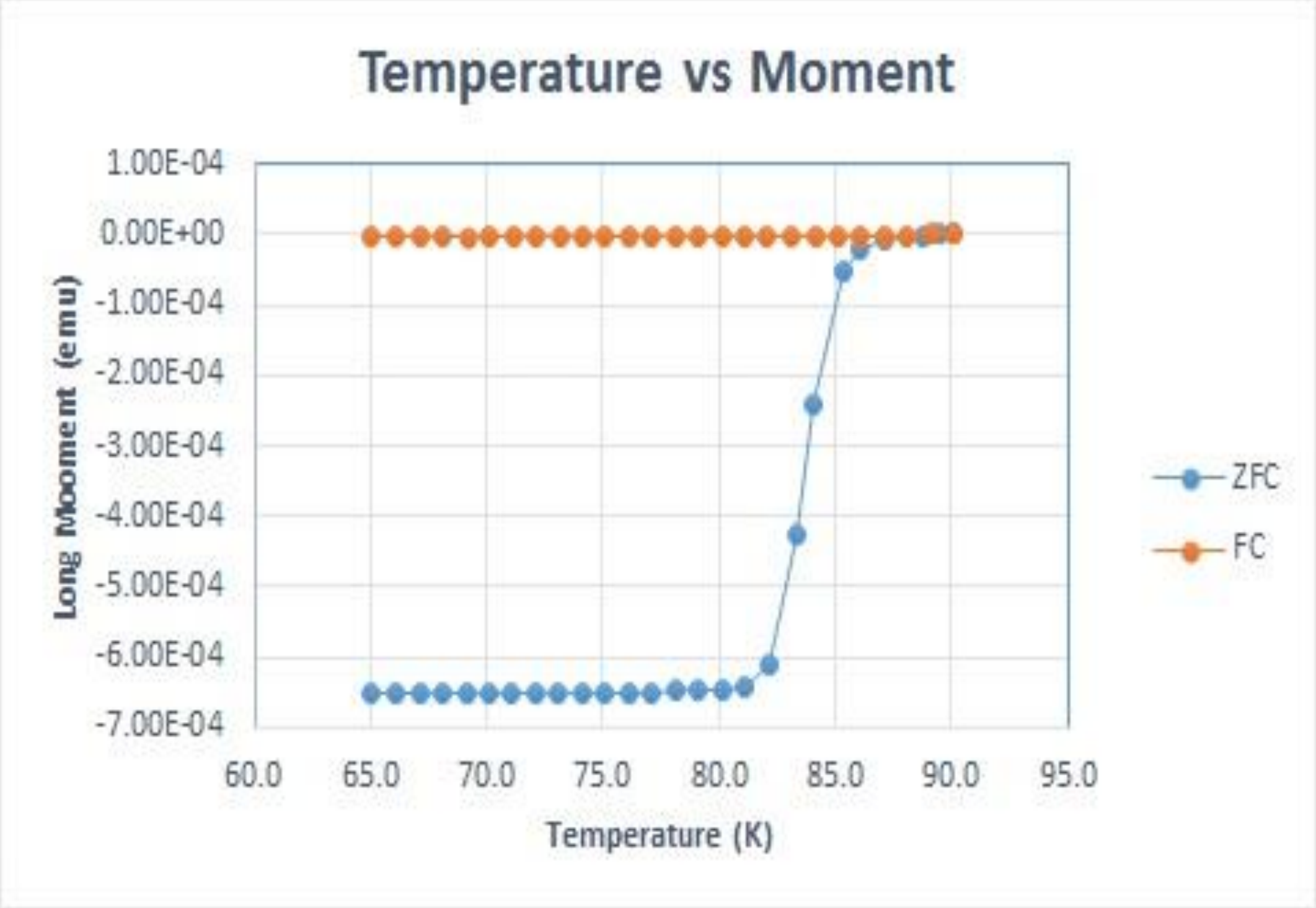

Figure 3: Measurements of FC (orange) and ZFC (blue) magnetic moments over a range of temperatures.

The transition temperature for this sample is about 83 K, with a width of about 2.5 K. Since the average T_c for as-grown samples is about 78 K, underdoped, the T_c has increased. This suggests an increase in doping level, contrary to what was expected.

The FC/ZFC ratio appears to be practically zero. It is currently unclear whether this is the result of the growth process or of the harsh conditions of the anneal. For single crystals, if the anneal conditions are especially harsh, the density of mercury deficiencies is known to increase, causing sample quality to deteriorate. It is possible that the same situation occurred with the boule, as the resulting FC/ZFC ratio is very poor.

Conclusion

The characterization results of the boule anneal clearly show an increase in T_c from 78 K to 83 K, which indicates an increase in the doping level, contrary to what was expected. This could possibly be explained by the escape of excess oxygen from the boule due to the low pressure, which would create a O partial pressure within the quartz tube and result in some oxygen entering the crystals as dopant. Regardless, this method of annealing clearly does not produce the desired result. The FC/ZFC ratio is also very poor, which could be attributed to Hg vacancies caused by the harsh annealing conditions or by a mistake during the growth.

It is still desirable to reach extreme doping levels. Since this tends to be prevented by the formation of Hg vacancies, one possibility for the future would be to anneal with Hg partial pressure, so as to prevent such vacancies.

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