

# Characterisation of x = 0.06 and x = 0.07 doped $La_{2-x}Sr_xCuO_4$

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## Abstract

 $La_{2-x}Sr_xCuO_4$  single crystals with hole doping x = 0.06 and x = 0.07 has been prepared and grown with the Travelling Solvent Floating Zone. The chemical content has been monitored through x-ray experiments and data from these experiments has been refined and show that the powder of both doping value from which the crystals were grown could be described well with the orthorhombic Bmeb space group, which confirms previous studies by Radaelli et al.

The effect of annealing the crystal after growth has been tested through magnetic moment measurements, which seem to indicate some effect from the annealing as the value of  $T_c$  was 6.4 K for the annealed x = 0.06 sample and 8.2 K for the unannealed x = 0.06 sample. The actual doping of the crystals has been tested through temperature dependent neutron diffraction experiments, which showed doping values of  $0.0664 \pm 0.0006$  and  $0.0752 \pm 0.0003$  and indicates that the inconsistencies in the TSFZ method produced crystals with different doping value than intended.

## Preface

The work described in this thesis has taken place in a period of time stretching back to before the summer of 2014, when Henriette Wase Hansen and Mette Kiehn Grønborg finished their work with  $La_{2-x}Sr_xCuO_4$  as part of their master and bachelor thesis. Henriette grew the x = 0.07 used in this thesis, while comitted to the project. The authors of this thesis joined the project that summer of 2014, and participated in the preparation and growth of underdoped  $La_{2-x}Sr_xCuO_4$  crystals under supervision from master student Monica Lacatusu and Ph.D. student Henrik Jacobsen. Monica continued the work on her own in the autumn of 2014, a period in which the single crystal of doping x = 0.06 used in this thesis was made. In November of 2014 these crystals were used in a neutron scattering experiment at PSI, the results of which has been a motivation for the work done in this thesis. The work on this bachelor thesis began in the spring of 2015, and is both a part of the bigger, ongoing project as well as a thesis on it own. As such, we will both be using data from older experiments as well as the ones we participated in.

In the thesis we will use standard notation with regards crystal structures and scattering. As such we denote the crystal vectors as  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$ , the reciprocal lattice vectors as  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$ , the incoming and reflected scattering vector as  $\mathbf{k}_i$  and  $\mathbf{k}_f$ , the scattering vector as  $\mathbf{q}$  and the reciprocal lattice vector as  $\boldsymbol{\tau}$ . Planes are written as (hkl), while directions are written with brackets as [hkl]. Crystallographic notation follows the latest edition of International Tables for Crystallography. As such we will use Cmce and Bmeb as the name for space group 64 and its variation.

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## 1 Introduction

Since the discovery of high temperature superconductors with transition temperature above 30 K in 1986 a massive amount of research has been performed on the subject [13]. The idea of a superconductor operating at room temperature is very appealing due to application in the industry, since keeping superconducting materials at very low temperatures is costly and extensive. The BCS-theory that explains superconductivity in low temperature superconductors does not apply above 30 K and so the mechanisms behind the high temperature superconductors are still a mystery, making it necessary to study the subject in all its forms for the dream of a superconductor at room temperature to come true.

This thesis will focus on the characterization of the compound  $La_{2-x}Sr_xCuO_4$ , or LSCO for short, which comes from the antiferromagnetic insulator  $La_2CuO_4$  and is hole-doped with Strontium, specifically hole-doped with x = 0.06 and x = 0.07. LSCO is just one of many high temperature superconductors, but it is one of the most examined due to its relatively simple crytal structure. This makes it ideal to study in detail, even though the transition temperature is only up to 37.5 K at the optimal doping value [1].

In an experiment performed in November 2014 at PSI by Monica Lacatusu et al., two crystals with these specific doping values showed perviously unseed behaviour.

When looking in to the process of making the crystals it turned out, that these crystals where made the same way as the crystals from Yamada et al. article from 1998 [12], except that they had not been annealed.

Therefore, the further structural studies in this thesis will include characterization of both annealed and unannealed crystals with doping of x = 0.06 and x = 0.07 grown with the Travelling Solvent Floating Zone, or TSFZ, in order to see, if the annealing makes a difference for the proporties of the crystal and maybe holds a key in the further understanding of the high temperature superconductor mystery.

## 2 Crystals and diffraction

This section will cover the basics of crystal strutures needed to understand scattering experiments on crystals. It will be followed by the theoretical background of scattering experiments in general as well as the two methods used in this thesis, neutron and x-ray diffraction.

#### 2.1 Crystal structures

In this section, a general theory for crystal structures will be presented.

A crystal can be described as a lattice, which can have different forms, where the most simple example is the square lattice. A lattice is an extended structure, defined by the three translation vectors, **a**, **b** and **c** that spans a parallelepiped known as a unit cell. **a**, **b** and **c** are also called the basis vectors, and the internal angles between them are known as  $\alpha$ ,  $\beta$  and  $\gamma$ . A unit cell is the smallest cell in the lattice, which, when repeated, can form the whole lattice extending in theory to infinity. In practice there will be some limit to the size of a crystal, but as this limit is very large, the possible physical extent of a crystal might as well be said to be infinite. The repetition of the

unit cell means, that the crystal is the same at point  $\mathbf{r}'$  as when viewed in point  $\mathbf{r}$ , where  $\mathbf{r}' = \mathbf{r} + x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$  and x, y and z integers, see chapter 1 in [3]

Based in a given lattice, different atoms can be placed at the lattice sites forming an actual crystal. The repetition of the atoms and their position in the lattice is what creates a macroscopic crystal.

#### 2.1.1 Space groups

The combinations of unit vectors and internal angles are almost infinite, but can be grouped into 230 space groups containing lattices, that share one or more symmetry properties. The 230 space groups are further more divided into 7 larger crystal systems as seen in figure 1. An example could be the tetragonal crystal system, to which the LSCO crystal belongs at temperatures above a critical phase transition temperature, which contains 67 space groups[21][10]. These space groups all share the property that their basis is a prism with a square of side length  $a \times a$  as its base and a height of c. The two lengths a and c cannot be equal, as the crystal would then belong to the cubic crystal system, see figure 1. The internal angles between the two a-axes and the one c-axis are all 90°, and thus this group has both a 4-fold symmetry axis along the c-axis and two mirror symmetry axes across its rectangular sides.

Another crystal system relevant for the LSCO crystal is the orthorhombic, which contains 58 space groups, and are defined as any lattice where all internal angles are orthogonal and none of the three sides of the otherwise cubic cell are equal. It differs from the tetragonal space groups by having the side lengths  $a \neq b$ . As LSCO is cooled below the cirtical phase transition temperature, it will change from having a tetragonal structure to the orthorhombic [21].

A thorough description of all the 230 space groups can be found in the International Tables for Crystallography [10].



Figure 1: The 7 different crystal systems and their characterisations [31]

#### 2.1.2 Planes and the reciprocal lattice

Planes in a lattice describe the orientation of the crystal, and exist where three lattice points relative to the basis vectors  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  are connected by a plane. Any plane can

be referred to by its Miller indices h, k and l, which are the inverse intercepts of the three vectors in the plane.

When working with crystals as a part of a scattering experiment it is however often easier to describe the planes in reciprocal space. In reciprocal space, a lattice can be formed by the reciprocal lattice vectors  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$ , defined as

$$\mathbf{a}^* = \frac{2\pi \mathbf{b} \times \mathbf{c}}{V_0} \tag{1}$$

$$\mathbf{b}^* = \frac{2\pi\mathbf{c}\times\mathbf{a}}{V_0} \tag{2}$$

$$\mathbf{c}^* = \frac{2\pi\mathbf{a}\times\mathbf{b}}{V_0}.\tag{3}$$

Here,  $V_0 = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$  is the volume of the unit cell in real space. The reciprocal lattice exist in its own space and any point in reciprocal space can be described by its reciprocal lattice vector given by the Miller indices and reciprocal basis vectors as  $\boldsymbol{\tau}_{hkl} = hb_1 + kb_2 + lb_3$ . Any plane can now be identified only by its miller indices (hkl). The distance between lattice points in the reciprocal space corresponds to the Miller indices and is given by

$$d_{hkl} = \frac{2\pi}{|\boldsymbol{\tau}_{hkl}|}.$$
(4)

Miller indices can also be used to refer to the orientation of a crystal. Instead of referring to the scaling of the three reciprocal basis vectors in the reciprocal lattice, they can denote the smallest set of integers, that have the same ratio as the components of a vector in the given direction. In this case, the Miller indices will be written as [hkl], and the direction [100] would be the direction pointing along the  $a_1$ -axis [3]

#### 2.2 Diffraction

Diffraction is a powerful tool when characterising and analysing crystals. Experiments can be divided into two main groups, single crystal and powder experiments. As the name suggest, the first covers any experiment done on a larger, single crystal while the latter includes experiments done on a polycrystalline powder. Using the scattering processes of particles interacting with a crystal is one of the least intrusive ways of examining it, since the beam of particles will not destroy the material. X-rays, neutrons and electrons are all usable particles for scattering, since they behave as waves, which will interfere. Furthermore, the energies and wavelengths of these waves are suitable to analyse structures in the nanometre scale, which is necessary in order to characterise a crystal [15]. The results from using scattering on a single crystal will come in the form of Bragg peaks as governed by Braggs law. It will be the position of these peaks along with knowledge of the orientation of the crystal that will provide the information about the crystal structure. As crystal powders actually consist of several small crystals spread randomly, but uniformly, across the powder sample, it will be like looking at all possible orientations at once. Instead of having rather well defined Bragg peaks, the diffraction pattern will instead reveal itself as diffraction cones of varying opening angles [15].

The fundament of diffration is that any particle also behaves itself as a wave.

The wave will hit the planes in the lattice and be scattered mostly by either the nuclei in neutron diffraction, or the electron cloud for x-ray. The scattered waves will then move away from the atom as spherical waves, which will then interfere with each other. The condition for constructive interference between the initial and scattered wave is governed by Braggs law, which reads, in direct space:

$$n\lambda = 2d\sin(\theta),\tag{5}$$

where n is an integer,  $\lambda$  is the wavelength of the incoming beam,  $\theta$  half the conventional scattering angle and d the distance between crystal planes as shown in figure 2. This means, that the phase of reflections from parallel planes only will be equal for certain values of  $\theta$ . It is only at these values that the waves will add up and result in a reflected beam to be measured.

The reciprocal scattering vector  $\mathbf{q}$  is given by

$$\mathbf{q} = \mathbf{k}_{\mathbf{i}} - \mathbf{k}_{\mathbf{f}} = \Delta \mathbf{k},\tag{6}$$

where  $\mathbf{k_f}$  is the final wave vector and  $\mathbf{k_i}$  is the initial wave vector. When the wave vectors are such that  $\mathbf{q} = \boldsymbol{\tau}$ , there will be a reflection from that point in the reciprocal lattice.

In the scattering experiments, the angle between the incoming beam and the scattering vector is set by adjusting the angle between the beam and detector,  $2\theta$  [3]. See figure 2 for an illustration.



Figure 2: Left: Bragg scattering on a lattice with spacing d in real space. Right: Bragg scattering in reciprocal space where  $\mathbf{q} = \boldsymbol{\tau}$ .

#### 2.3 Neutron scattering

Scattering with neutrons is a particularly useful experimental method when one wishes to investigate a crystal. The neutron is neutrally charged and therefore scatters of the nuclei due to the strong, nuclear force. In other words, is does not "see" the electron cloud. As opposed to the use of x-ray scattering, the neutron scattering method enables one to detect even light elements such as hydrogen.

Furthermore, the neutron possesses a magnetic moment, which will cause the neutron to scatter off the crystal's magnetic moment, allowing the measurement of magnetic structures [22]

#### 2.3.1 Elastic neutron scattering

In elastic scattering,  $k_i = k_f$ . The elastic neutron scattering has a cross section derived from the interference of the neutron waves from two nuclei, and can be summed up over all unit cells to yield the final expression

$$\frac{d\sigma}{d\Omega} \left| nucl.el. = N \frac{(2\pi)^3}{V_0} \exp(-2W) |F_N(\mathbf{q})|^2 \sum_{\tau} \delta(\mathbf{q} - \boldsymbol{\tau}),$$
(7)

where N is the number of unit cells  $\exp(-2W)$  is the Debye-Waller factor and  $F_N(\mathbf{q})$  the nuclear structure factor given by

$$F_n(\mathbf{q}) = \sum_i b_i exp(i\mathbf{q} \cdot \Delta_i),\tag{8}$$

where  $\Delta_i$  is the position of the i'th atom in the unit cell and  $b_i$  is an isotope specific quantity [22].

The delta function in 7 holds the condition for constructive interference, and thus Braggs law, since  $\mathbf{q}$  must be equal to  $\boldsymbol{\tau}$  in order to not be zero. It is worth mentioning, that the cross section can be equal to zero even if  $\mathbf{q} = \boldsymbol{\tau}$  and that is if  $|F_N(\mathbf{q})|^2$  is equal to zero.

By calculating the structure factor for different planes, it can be shown whether they will give rise to constructive interference. In this way one will know, which peaks are allowed in reciprocal space, and can be measured during experiments. Similarly, it is also possible to determine if a reflection should not be allowed.

#### 2.4 X-ray diffraction

X-ray diffraction is scattering with photons as electromagnetic waves. The photons "see" the electron clouds surrounding the atoms in the lattice, and it is therefore the electron density that is responsible for the scattering as opposed to the nucleus in neutron diffraction. From this, one can determine the mean position of the atoms in the lattice. The x-ray signal will change directly as a function of the number of electrons, and as such this method is not very useful when looking at different isotopes of the same chemical element. It is also not very good at detecting lighter elements such as the oxygen in LSCO as compared to more electron rich elements like lanthanum, strontium and copper. X-ray facilities are much more common than neutron facilities, as they are easier and less expensive to produce. As such, x-rays are used much more often, while complimentary neutron data can be harder to do. [22].

#### 2.4.1 The Laue method

Laue scattering is the original form of diffraction discovered by Max von Laue, and differs from the later developed x-ray diffraction methods because it uses a fixed angle and a wide range of wavelengths, a so called white x-ray or polychromatic beam. Because the crystal is stationary with respect to the incoming beam, the spacing  $d_{khl}$  and angle  $\theta$  are fixed [24] [14]. This means that each set of planes "picks" out the particular wavelength, that satisfies Braggs law and reflects this to a detector. In this project, a Laue camera is used with the Laue back reflecting method. Back reflection means that the x-ray beam is reflected inside the crystal and back on to a detector, which is placed between the source and the crystal. This a good method to align a single crystal, i.e. determine the orientation of the crystal, since the symmetry of the reflected pattern on the detector is directly connected to the symmetry of the crystal [14]

## 3 LSCO

#### 3.1 Superconductivity

This section will give a short introduction to superconductors, the theory behind the low temperature superconductor and some of the properties that apply to both low and high temperature superconductors.

On the  $8^{th}$  of April 1911 the Dutch physicist Heike Kamerlingh Onnes became the first person to observe the sudden drop to zero in the resistivity in a piece of solid mercury at the ultra-cold temperature of 4 K [25].

Following the initial observation of this sudden drop in resistivity, several studies followed spreading to other materials in what would be known as the field of superconductivity. As the resistivity in a mercury coil dropped below the 4 K temperature limit, an electric current sent through it would remain lossless even after removing the original source of the current. The superconductor is in other words a perfect conductor with infinite conductivity. The temperature at which the resistance drops has been named the critical temperature,  $T_c$ , and marks the phase transition of the material going to the superconducting state [15].

#### 3.1.1 The Meissner-Ochsenfeld effect

Another phenomenon in superconductors is the repulsion of any magnetic field the superconductor is placed in during phase transition and the magnetic field cannot penetrate the sample when it gets below  $T_c$ , see figure 3. This effect was first found in 1933 by physicists Robert Ochsenfeld and Walther Meissner [30], and happens because the magnetic induction inside the material is zero. Currents are created on the surface, and they induce a field that exactly cancels out the applied field [25]. This unique effect is called the Meissner-Ochsenfeld effect and it only happens in a superconductor below  $T_c$ . A consequence of this is that the susceptibility of a superconductor is  $\chi_m = -1$  below  $T_c$ , and the superconductor is then a perfect diamagnet [25]:

$$\mathbf{M} = -\mathbf{H}.\tag{9}$$

#### 3.1.2 Type I and Type II superconductors

There are two ways a superconductor can transition from the superconducting state to normal, when a magnetic field is applied. This leads to two types of superconductors; Type I and Type II.



Figure 3: Left: The Meissner-Ochsenfeld effect for a spherical superconductor. The lines are magnetic flux lines [32]. Right: Vortices formed on the surface of a superconductor, as seen from the side [33]

In Type I superconductors there is a critical value of the applied field,  $H_c(T)$ , above which the field penetrates the entire sample. The sample returns to its normal state when the field is above  $H_c(T)$  [1].

In a type-II superconductor there are two magnetic field transitions;  $H_{c1}(T)$  and  $H_{c2}(T)$ . Below  $H_{c2}(T)$ , the sample is superconducting and will exhibit complete Meissner-Ochsenfeld effect. Between the two transition values, in the so-called mixed state, the field penetrates the sample in flux lines ordered in tube-like regions, where the current screens the flux, see figure 3. The state inside the flux is normal and the state in between the tubes is superconducting. The tubes are called vortices and the flux in each vortex is exactly one flux quantum,  $\Phi_0 = \frac{h}{2e}$  [25].

#### 3.1.3 BCS-theory and Cooper pairs

In 1957, J. Bardeen, L.N. Cooper and J.R. Schrieffer published the first microscopic explanation of superconductivity; the BCS-theory [25].

The main part of this theory is the description of electrons condensing into Cooper pairs. Electrons near the Fermi surface will at sufficiently low temperatures be attracted to one another by coupling to the lattice vibrations, phonons, and form pairs of electrons. The pairs have spin zero and are therefore bosons, even though the single electron is a fermion. When the temperature decreases below  $T_c$ , the Cooper pairs are formed and condensate in the sense that they all go into the same quantum state known as the Bose-Einstein condensate. This lowers the energy of the whole system creating an energy gap,  $\Delta$ . The Cooper pairs are then charge carriers and can move in the superconductor without any loss of energy. The energy gap  $\Delta$  is approximately the same energy it takes to break a Cooper pair, and disappears above  $T_c$  [25] [13]. The BCS-theory predicts that a superconducting state can exist at no higher temperature than approximately 30 K for any superconductor, since the phonons are no longer able to connect the electrons into Cooper pairs above this temperature. This theory is therefor not able to explain high-temperature superconductors, where  $T_c$  can be as high as 130 K and so another theory for hight-temperature superconductors is needed to explain the superconducting proporties that still exist here.

#### 3.1.4 High temperature superconductors

Since 1911 the field of superconductors has been ever increasing. This has led to the discovery of many superconducting materials [25] [13] as well as the development of several theoretical explanations for the phenomena eventually leading to a total of 8 Nobel prizes [27].

One of these was the 1987 Nobel price awarded to researchers Georg Bednorz and Karl Alex Müller, after their discovery of the existence of a new type of superconductors. The new type had critical temperatures as high as 35 K, much higher than those previously observed in various metallic superconductors [29].

This new type of superconductor has simply been named High Temperature Superconductors, or high- $T_c$ , and are all Type II. It was at first found in La<sub>2-x</sub>Ba<sub>x</sub>CuO<sub>4</sub> which belongs to the group of copper-oxides known as cuprates. The cuprates are ceramic crystals, and the superconducting cuprates each share some fundamental structural properties. This discovery was very surprising, since all the cuprates are poor conductors at room temperature, and the mother compound  $La_2CuO_4$  is an insulating antiferromagnet [13] and not a metal. A lot of the superconducting cuprates have somewhat similar structures to that of one of the most famous high  $T_c$  superconductors, the YBCO crystal, found to have a critical temperature as high as 92 K, the crystal consisting of  $YBa_2Cu_3O_{7-x}$  was ground breaking [5] since the discovery opened up for the possibilities of industrial use since 92 K is in the temperature range of liquid nitrogen, which is much cheaper to produce than liquid helium which would have been needed otherwise. YBCO, like LSCO, includes a CuO<sub>4</sub> copper-oxygen group, which placement in the different crystal layers seem to hold some of the key to understanding all the high- $T_c$  superconductors. However, the mechanisms behind high- $T_c$  superconductors are still not fully understood.

#### 3.2 LCO and LSCO structure

This section will describe the LSCO crystal, its structure and basic properties. LSCO has a relatively low  $T_c$  of 37.5 K at the optimal doping, and is in that sense not a good high  $T_c$  superconductor, but it is easier to study than e.g. the YBCO crystal, which has a more complex structure [1]. It does however share some structural properties with both YBCO and other high  $T_c$  superconductors, as it too is based on the same, basic perovskite crystal structure [5].

The LSCO crystal is based on the mother compound La<sub>2</sub>CuO<sub>4</sub>, or LCO for short. LCO in itself is not a superconductor but an antiferromagnetic insulator. The structure is Low Temperature Orthorhombic, LTO, below  $\simeq 500$  K with space group Bmeb [18] and High Temperature Tetragonal, HTT, above with space group I4/mmm [21]. The different crystal layers lie parallel to the *ab*-plane, were the copper-oxide planes lie in between the lanthanum-oxide planes along the *c*-axis. At 10 K, the length of the orthorhombic lattice vectors are a = 5.34, b = 5.42, c = 13.10 and the angles between the three vectors are all 90° [8] The entire LCO structure can be seen in figure 4, which includes the octahedra suspended by copper and oxygen.

LCO only becomes a superconductor by hole doping the compound. When hole doping a material, one creates charge carriers by replacing some of the atoms, with atoms of lower oxidation level [13]. The atoms with lower oxidation will then attract



Figure 4: The structure of LCO, with clearly marked  $CuO_4$  octrahedra. In the strontium doped LSCO, some of the lanthanum will be replaced with strontium [2]

the loosely bound electrons from the atoms with higher oxidation, leaving "holes" able to transport electrons, making the material conducting. In LSCO, this takes place by replacing some of the lanthanum atoms with strontium. Lanthanum has an oxidation level of 3+ while strontium has an oxidation level of 2+.

Depending on the doping, the LSCO crystal will become superconducting at a certain temperature as shown in figure 5.



Figure 5: Left: The transition temperature between the normal and superconducting phase for LSCO as a function of doping [34]. Right: The structure phase diagram of LSCO with the structural transition temperature as a function of doping value [21]

## 4 Making of LSCO crystal

#### 4.1 Mixing of powder and preparation of rod

This section will give an overall view of how the process of preparing and growing a LSCO crystal using the Travelling Solvent Floating Zone method was in this project.

The process described here is a part of a larger LSCO project, where the purpose is to produce LSCO single crystals in the doping region x = 0.02 - 0.07. The crystals used for further studies in this paper had doping values of x = 0.06 and x = 0.07respectively, and were grown before the work on this thesis began. We have however been part of the preparation and attempted growth of other LSCO crystals, and as such the following should be read as a description of the general proces.

## 4.2 Powder

Three types of rods needed to be made; a feed rod, a seed rod and a solvent rod with a larger copper content, in order to start the floating zone process. Two types of LSCO powders was needed for this; one for the feed and seed rod and one for the solvent rod.

Both powders were made by mixing three existing powders; CuO (copper (II) oxide), SrCO<sub>3</sub> (strontium carbonate) and La<sub>2</sub>O<sub>3</sub> (lanthanum (III) oxide). All of these should have a purity of 99.99 % or higher, and the ratio between these powders was different in accordance to the type of rod grown from it as well as adjusted to give a certain doping of the final crystal.

#### 4.2.1 The feed and seed rod

When mixing the powder for the feed and seed rod, the ratio between the different powders was decided by the stoichiometry of the chemical formula for LSCO;  $La_{2-x}Sr_xCuO_4$ . The ratio between molecular mass of the four elements are then 2x:x:1:4, and multiplying the ratios with the molecular masses will give the needed amount of powder in grams following the equation

$$m = M \times n. \tag{10}$$

The molar masses of the included elements can be seen in table 1, while the actual calculation used to make a batch of x = 0.06 powder is presented in table 2.

Chemical element	Molar mass $/[g/mol]$
La	138.90547
$\operatorname{Sr}$	87.62
Cu	63.546
0	15.999

Table 1: The molar masses of the elements in LSCO.

The different powders were weighed in a glove box with argon at a 10 mbar pressure. The mixed powders were then removed from the glove box and mixed by adding ethanol to the powders and placing it on a magnetic stirrer until all ethanol had evaporated. This was to let the powders mix more properly.

	CuO	$SrCo_3$	$La_2O_3$	
М	79.55	147.63	325.81	
n	1.04	0.06	0.97	
m	82.73	8.86	316.03	
Doping value $x = 0.06$				

Table 2: An example of the calculations done prior to the mixing of a new powder. The final mass should be adjusted to a more reasonable amount.

The dry powder was calcinated in a furnace at 950°C for two days. This temperature is below the melting point of LSCO at approximately 1320°C, but high enough as to make the separate powders react and form a crystal structure [1]. The cooled powder was then crushed in a mortar in order to secure a homogeneous powder.

This process was repeated, and the powder was then subject to a x-ray diffraction experiment at the facility at Risø to detect whether the powders had fully reacted. If this was the case, there should be no La<sub>2</sub>O<sub>3</sub> left in the sample. The presence of La<sub>2</sub>O<sub>3</sub> would be revealed as a peak at scattering angles  $26^{\circ}$  and  $30^{\circ}$ , and if these were found, the powder had to be calcinated a third time, to create an environment where the last powder could react [1]. An example of the x-ray diffraction plot can be seen in figure 6, where plots from after second and third calcination has been included. One can clearly see that the peak at  $26^{\circ}$  and  $30^{\circ}$  has disappeared after the third annealing showing that all of the powder had reacted.



Figure 6: X-ray diffraction plot from x = 0.04 doped LSCO from a previously made powder. The red line is the data from powder that has only been calcined twice. The blue line is data from pwder that has been calcined three times.

When the powder had fully reacted, a dense rod had to be pressed from it. The rod was made by sealing one end of a silicon tube and then filling it with the powder by the use of a small funnel. The tube was regularly shaken in order to pack the powder as densely as possible. When the tube had been filled to approximately 12 cm it was cut and sealed and placed in a waterproof condom, which would have all the air in it removed forming a waterproof shelter around the rod. To stabilize the rod during the pressing, it was placed in a copper tube of the same width and height before being

submerged into the water of a hydrostatic press. The rod was then pressed uniformly from all directions and carefully removed from the silicon tube with a scalpel.

A small hole, approximately 1 mm, was drilled in one end of the rod to secure a platinum wire. The rod was then suspended vertically from this wire and sintered in a vertical furnace at 1100 degrees for 2 days. The result should be a straight and homogeneous rod, ready to be placed in the mirror furnace for the actual crystal growth, but this was not always the case and if not, the process had to be repeated. This is because a uniform rod is essential in the actual growth of the single crystal in the mirror furnace.

The solvent pill was grown following the exact same procedure, but contained a much higher amount of copper in order to secure a high copper content during the beginning of the growth. The pill was then used to start the process of crystal growth, which requires melting of the feed and seed rods. The solvent rod was smaller both in length and circumference as compared to the seed and feed rods, and the sintering took place in a regular furnace.

#### 4.3 Crystal growth

Samples of large, single crystals are needed for most of the experiments done in this project, and one of the most common methods of growing these is that of the Travelling Solvent Floating Zone, or TSFZ for short [6]. As the name suggests, this method involves a melted, solvent zone moving longitudinal across the rod. The melting is performed in a mirror furnace, which uses reflective mirrors to concentrate its heating to a very specific point, see figure 7. In this furnace, the content of the feed rod will be gradually transferred to the melted zone, which will solidify into the LSCO crystal structure, with the solvent pill providing a steady flow of copper in the beginning [11].

The process started with the merging of the seed and feed rod. The two pressed powder rods were mounted within the mirror furnace, see figure 7. The crystals used in this projects were all grown at Risø, where the seed rod was mounted in the upright holder with the feed rod placed directly above it.

As the heat was turned on, the two rods were made to rotate counter directional around their longitudinal axes. The solvent pill was placed between them, initiating the growth with its high copper content. The molten ends of the feed and seed rods were then brought together, creating an hourglass shaped transfer zone.

After the melted zone was established, the actual growth can begin.

The liquid will settle into a crystalline structure when it solidifies, after having been completely melted. To secure that it will solidify into the LSCO structure, a steady flow of copper into the melted zone is needed. This was constantly provided by the feed rod, while the large content of copper in the solvent pill secured the growth of the LSCO structure from the beginning of the process. The focus of the heat was slowly moved upwards along the feed rod, moving the melted zone with it and leaving the bottom of the zone to slowly cool. The speed at which the mirrors moved is called the growth rate, and is usually around 1 mm an hour. See figure 7 for a photograph of the process.

In this way, the melted zone traversed the entirety of the feed rod until the whole length had been completely melted and solidified again. This was a very lengthy process, which required constant supervision as the molten zone was very fragile and might



Figure 7: Left: A schematic overview of growing in the mirror furnace [9]. Right: A photograph taken during the growth of the LSCO x = 0.06 crystal

react very drastically to wrong temperatures or growing speeds. Typical problems could be droplets forming because of too high temperatures or grinding due to too low temperatures. Grinding between the upper and lower parts of the rod might also happen because of too fast a growing speed, if the new parts of the rod does not spend enough time in the focus of the mirrors heat to totally melt. In this case, the liquid part of the rod might still contain grains of solid material, which will result in an uneven result [9].

The growing stopped, when the end of the feed rod was reached. At this point, the crystal may be placed in a furnace to be annealed, but during the growth of the x = 0.07 and x = 0.06 crystals this was not done at first.

As further investigation of these specific crystals seemed to show some previously unseen Bragg peaks when investigated in neutron experiments at the RITA II experiment at PSI in November 2014, interest was focused partly on the process of annealing the crystals. As this seemed to be one of the things distinguishing this set of crystals from ones previously grown, parts of some of the non-annealed crystals has later been annealed.

The annealing of the crystal was performed in a cylindrical furnace at Department of Energy Conversion and Storage at Risø. It followed the temperature scheme shown in figure 8. First, the sample was heated to 1173.15 K at a rate of approximately 3.6 K/min and then stayed at this temperature for 3000 minutes before being cooled by 1.7K/min until it reached 773.15 K. It then stayed at this temperature for another 3000 minutes, and was then set to reach room temperature at its own rate. The entire annealing was done in a flow of oxygen at approximately 0.2 liters per minute, such that any lack of oxygen in the crystal might be minimized.

The stability of the crystal was tested by leaving the crystal exposed to air overnight, to see whether any leftover LaO would react with the oxygen and crumble. The same



Figure 8: The annealing scheme used for both the small x = 0.06 sample used in the VSM measurements as well as the larger single x = 0.07 crystal used for further experiments at PSI

thing will happen if, for some reason, a single crystal has not been grown, as described in [11]

If nothing happens, then the crystal was deemed stable enough to be prepared for further experiments.

## 5 Magnetic moment measurements

By doing measurements of the magnetic moment on a crystal, even more can be said about its attributes including finding the critical temperature of the transition to the superconducting state due to the Meissner-Ochsenfeld effect, that will make any magnetic field from the sample drop to zero below  $T_c$ . By doing the measurements on a piece of unannealed crystal and subsequently annealing it and repeating the measurements, any impact from that process on the critical temperature can be detected.

The unannealed and annealed crystal has the same structure, the only difference might being, that the unannealed crystal have an oxygen content of  $O_{4-y}$ , where y is not zero.

A change in  $T_c$  will be a strong indicator, that the annealing process indeed did result in a higher content of oxygen. This measurement will also confirm that this crystal is in fact superconducting.

#### 5.1 Measuring of magnetic moment by VSM

The data were collected at the Department of Energy Conversion and Storage at Risø using a Vibrating Sample Magnetometer, VSM for short. A small piece of the x = 0.06 doped crystal, previously cut from the original x = 0.06 doped crystal, was chosen because of its suitable size for the VSM, which can only measure on small samples because of the rapid movements during the measurements. The crystal was mounted in the VSM with the help of head of lab Jean-Claude Grievel.

The VSM machine works by oscillating the sample mounted on a non-magnetic rod between two fixed coils. The sample is magnetized by the applied field created by the coils. As the sample oscillates, it will create a magnetic field vibrating with it, creating a changing magnetic flux in the coils, which can be detected and analysed. The VSM used in this experiment also had the ability to cool down and heat the sample while collecting data, which will give us the magnetic moment as a function of temperature [23]. As optimally doped LSCO only becomes superconducting below 37,5 K [1], the sample would have to be cooled well below this, to make sure to reach the critical temperature of this underdoped sample.

The sample is first cooled from 250 K and down to 5 K at a rate of -5 K/min. After this temperature is reached, a magnetic field of approximately 0.2 T is applied, and the sample is again heated at a rate of 5 K/min until it reaches 250 K. The final step is repeating the cooling from 250 K to 5 K at the same rate and the same constant magnetic field as in the heating. After this, the measurements are stopped, and the sample left to reach room temperature before being removed. The data used were collected during the heating, and are examples of so-called zero field cooled measurements.

## 5.2 Results

The results were all analysed using Matlab and can be seen in figure 9. The  $T_c$  was found by making two linear fits of the data below and above the drop and then calculate the temperature at which they cross. Before the annealing, the superconducting transition temperature is 6.4K according to this method, while it was 8.2 K after.



Figure 9: Left: An overview of the data from the x = 0.07 sample before annealing in blue and after annealing in red. The black lines show the fit to two sets of data before and after the sudden drop in magnetic moment. Right: A detailed view of the data around the sudden drop in magnetic moment

As seen in figure 9 there is a high peak around 45-80 K in both measurements. This is because of the oxygen surrounding the sample in the machine and can be ignored, since it is not a consequence of the samples themselves and it has no effect on the transition temperature of the samples. It is also seen, that the unannealed plot has an offset at much higher temperature than the annealed plot,  $\simeq 25$  K compared to  $\simeq 12$  K, but both of them has similar drops at  $\simeq 6$  K.

#### 6 Scattering measurements

In this project we have used diffraction data from both x-ray and neutron experiments. Some of this data was collected during the time of our commitment to the LSCO project and some of it was provided by others connected to the project and has been collected in previous stages.

#### 6.1 X-ray

This chapter describes the two different x-ray diffraction experiments performed on the two crystals, both of them at University of Copenhagen. The first is to find the space group af the crystal and the second is a part of the alignment process for the further neutron diffraction experiments.

#### 6.1.1 Powder

X-ray diffraction was performed on the x = 0.06 powder used to grow the crystal using the Bruker V8 Venture instrument in the HCØ-building at University of Copenhagen with a beam of wavelength  $\lambda = 1.54$  Å. Maria Retuerto Millan and Niels Vissing Holst from the Department of Chemistry collected the data. The data is a spectrum with intensity as a function of scattering angle, see figure 10 and reveals the Bragg peaks resulting from the scattering of the x-ray beam. The data was treated through the process of Rietveld refinement using the software Fullprof.

Rietveld refinement works by comparing experimental data with a theoretical model, the so called space group, fitting experimental and structural parameters until it suits the collected data. This require some idea of how the structure is, since one will have to start with a space group as a theoretical model that is not to far from the one the crystal actually has. By refining a set of data with regard to different structures, the best fit can be found, and Fullprof then creates a .CIF-file, that contains the information from the refinement.

How good a structure fits the experimental data is quantified as the Bragg R-factor, which is monitored throughout the entire refinement process. It is defined as follows

$$R_B = \frac{\sum |I_{\text{observed}} - I_{\text{calculated}}|}{\sum |I_{\text{observed}}|},\tag{11}$$

where  $I_{\text{observed}}$  and  $I_{\text{calculated}}$  is the measured and calculated intensities of the peaks respectively.

Some things must be chosen by the user of the program, for example the line profile to which the data should be fitted. In this case the pseudo-Voigt shape function was used. It is a linear combination of the Lorentzian and Gaussian functions, and is often used when fitting x-ray data [17]. There will also be option regarding the type of instrument used, when collecting the data, as well as the option to do other types of refinement, than the Rietveld method.

The refinement was run through several cycles, each of them doing the set of refinement calculations over and over again. Between cycles more and more factors was included as a quantity to refine, changing its  $R_B$  value by each cycle, getting closer and closer to an acceptable value, until the value no longer changed from cycle to cycle. If the model describes the data well, the  $R_B$  should be around 5 or less To begin, factors like scaling and background noise was refined. The line-profile itself was refined, as the program can fit the different components of the line shape equation, which describe different geometrical aspects of the peak. Afterwards factors regarding e.g. the placement of the atoms was refined as well [17]. An example of refinement of the x = 0.06 powder data can be seen in figure 10.



Figure 10: A picture from the Fullprof program showing the final fit between x-ray data from the x = 0.06 powder and the Bmeb space group. The red dots are the data, the black line the fit, the blue line shows any difference between the two and the green lines are the angles at where the theoretical space group allows peaks.

The results from fitting the data to two different space groups can be seen in table 3.

Space group	Space group nr.	Crystal system	a	b	c	$R_B$
Bmeb	64	Orthorhombic	5.35	5.37	13.19	5.28
I4/mmm	139	Tetragonal	3.79	3.79	13.19	16.7

Table 3: This table shows the result of refinement of the x = 0.06 powder x-ray data collected at HCØ. By comparing the  $R_B$  values, it seems that the Bmeb structure fits the data best.

#### 6.1.2 Laue

In order to prepare the crystals for the neutron diffraction measurements the crystals were alignment to find the orientation of the samples, the a,b and c-axis respectively. This is necessary to do with the Laue camera beforehand, because the neutron instruments at PSI only measure in one dimension at a time which means, that a misalignment of just a few degrees will make the neutron beam miss the peak.

The Laue backscattering method was used on the annealed and unannealed x = 0.07 doped crystal and the unannealed x = 0.06 doped crystal and was performed using the Laue camera at the Niels Bohr institute at the University of Copenhagen. The camera is by Photonic Science Limited, PSL. All data was processed using the viewer software provided by PSL.

The annealed x = 0.07 crystal had at this point already been aligned in the *ac*-plane, but interest in measuring both the  $(0\ 1\ 0)$  required it to be aligned in the *ab*-plane as well. In practice, this was done by preparing two separate sample holders for the one crystal, the old one with markings of the *ab*-orientation and a new one with markings of the ac orientation. The sample will be held in place by coiling a piece of thick wire from the sample holder around it, making sure that the crystal is held there securely. See figure 11 for a photograph of the crystal in the sample holder



Figure 11: Left: A schematic of the backscattering Laue camera used in the experiment [35] Right: The mounted crystal in the sample holder with a and c axes marked on the foot.

Measurements were done at 30 kV and 20 mA with an exposure time of 25-30 seconds.

The first crystal was the piece of annealed x = 0.07 LSCO single crystal. The first picture clearly showed the presence of the *c*-axis, as it contains a pattern with 4-fold symmetry, and for the orthorhombic crystal structure, the *c*-axis is the only one to have this. See in figure 12 top right. The symmetric center of the pattern is right at the direction of the *c*-axis, and would be in the center of the beam, with the large, visible lines from the *a* and *b*-axes completely horizontal and vertical. There are to sets of axes in the pattern, each of them consisted of a set of two very visible lines perpendicular to each other. The two sets of axes represent respectively the orthorhombic and tetragonal cells, and have an angle of 45 ° between each other. The crystal needed to be aligned in the orthorhombic notation, and as such it was needed to distinguish between the two.

In real space, the side a in the tetragonal structure is smaller than the corresponding side a in the orthorhombic structure. In reciprocal space, this means that the side  $a*_{tetragonal} = \frac{2\pi}{a_{tetragonal}}$  will be larger than the side  $a*_{orthorhombic} = \frac{2\pi}{a_{orthorhombic}}$ . This difference in length will shift the relative distance between the spots. If the distance between the x-ray source and the sample is held constant, the length between the two spots will be larger in the orthorhombic system. The angle of the crystal with regards to the incoming beam was changed by carefully turning the sample holder around its vertical axis, while the angle with respect to the horizontal line was changed by physically manipulating the wire holding the crystal until the x-ray beam hit the center of the c-axis and the lines where horizontal and vertical. By placing the c-axis in the center of beam and then rotating 180 degrees around the vertical axis, the center of the c-axis should still lie in the center. If not, it will mean that there is an offset in the angle between the beam and the c-axis, which could then be corrected.

The other two axes were also found by recognizing the pattern from the orthorhombic a-axis, placing the beam in the middle of the axis and turning the crystal 90° to find the b-axis. All axes was marked on the mount of the crystal as seen in figure 11 to the left. Also, the quality of the alignment was checked by increasing the distance between the source and the crystal. Doing this enlarged any offset in the angle between the beam and centered axis and the offset was corrected. The annealed x = 0.07 and the unannealed x = 0.06 doped crystals were aligned using the same method.

See figure 12 for pictures of three different orientations in the crystal. Here the symmetry of the crystal is clearly visible, and each dot represents a set of planes in the crystal. The orthorhombic *a*-axis is turned  $45^{\circ}$  around the *c*-axis relative to the tetragonal *a*-axis.



Figure 12: Top left: A Laue picture of one of the crystals with no known orientation visible. Top right: The c-axis in the unannealed x = 0.07 doped crystal. Bottom left: The orthorhombic *a*-axis in the unannealed x = 0.06 doped crystal. Bottom right: The tetragonal *a*-axis in the unannealed x = 0.06 doped crystal

#### 6.2 Neutron

In order to find the exact doping value of the crystals, one needs to find the structural transition between the orthorhombic state and the tetragonal state, which is temperature and doping dependent. This was the aim of the neutron diffraction experiment and it was performed at the neutron spallation facility SINQ at the Paul Scherrer Institut, PSI, in Switzerland. The crystal analysed was the x = 0.06 doped crystal and two x = 0.07 crystals, one annealed and one unannealed. The same crystals used in the previous experiments in this thesis. When measuring the temperature dependence of the (1 0 4) peak in the unannealed samples, one can see when the transition from orthorhombic to tetragonal state happens and then find the doping value. According to the phase diagram seen in figure 5, the transition will occur for x = 0.06 and 0.07 at T = 396 and T = 373.5 respectively.

The instruments used at PSI were the two-axis diffractometer Morpheus and the two-axis test diffractometer Orion [20][19]. Two-axis spectrometry uses elastic scattering and the possibility of varying the position of the detector with regards to the incoming beam as well as rotating the sample itself to some degree, to acces a wide range of possible peaks. The sample was mounted on a eulerian cradle, making it possible to rotate in the three directions  $\omega$ ,  $\chi$  and  $\phi$ . Varying  $\omega$  will rotate the sample around its vertical axis,  $\chi$  around the horizontal axis and  $\phi$  rotates the entire setup in the plane between the horizontal and vertical axes.

#### 6.2.1 Orion

Orion is a cold neutron test diffractometer connected to a beam of neutrons, that is sent trough a pyrolytic graphite monochromator to get a wavelength of  $\lambda$ =2.214 Å. At PSI it is mainly used for alignment, which was also the purpose when used at this stay.

The three crystal had already been aligned by the use of Laue backscattering in Copenhagen, but after transporting them to PSI the quality of the alignment should be checked again, and any misalignment realigned by the use of neutrons. Also, The Laue back reflecting method can only align down to an error of 1-2 degrees, and an alignment down to a half degree is needed in the neutron diffraction experiments. The aligning was checked by using the variable angles of the sample holder to scan across the area of any peak known to exist in the structure [19]. The exact angle was calculated before scanning, the peak was found in the  $\omega$  angle and then a  $\chi$ -scanning was made to see, if the peak was centred in the scattering plane. The crystals had to be aligned near perfectly in the scattering plane before being moved to Morpheus for further testing. as physical limitations will make it impossible to rotate in any direction other than the vertical scattering plane. This was done in practice by finding the  $(2 \ 0 \ 0)$  and  $(0 \ 0 \ 4)$ peaks which both have high intensities and are therefore easier to detect. Furthermore, finding these peaks will also make sure that the crystals were aligned in the *ac*-plane which is necessary in order to find the  $(1 \ 0 \ 4)$  peaks for the temperature dependent measurements. Aligning with Orion was a rather quick process, as all the crystals showed good alignement from the Laue backscattering experiment.

#### 6.2.2 Morpheus

To find the doping value of the crystals, temperature dependent measurements on the  $(1 \ 0 \ 4)$  peak were performed on the unannealed x = 0.06 and x = 0.07 crystal. It is

important to know the doping value in the characterisation of the crystals, since this gives important data on the structure and what kind of crystal it is.

The transition between LTO and HTT can be identified by the presence of the  $(1 \ 0 \ 4)$  peak, which only exists in the HTT state and disappears as the structure goes to LTO at lower temperatures [21]. By knowing the temperature at which the  $(1 \ 0 \ 4)$  peak disappears one can find the exact doping value.

Morpheus is an instrument with a lot more options than just varying the scattering and sample angles as at Orion. Morpheus uses a different monochromator than Orion, and operates at wavelenght  $\lambda$ =5Å. When set up for measurements of single crystals, the detector has three variable slits, the first two being placed before the crystal and the last between the crystal and the detector [16]. The slit openings can be varied in size by moving the left, right, top or bottom sides. A large opening will allow a lot of neutrons to pass, but this will come at the cost of increased background noise and a lower resolution. Instead, each of the slit positions was varied while measuring the intensity of a peak. The intensity will at first rise as a function of the opening, but at some point it will flatten into a plateau. The onset of this plateau was then kept as the actual slit position.

The sample was mounted in a cryo-furnace. This made it possible to heat and cool the sample to as low as around 20 K and up to around 600 K.

#### 6.2.3 Results

All measurements were done by counting the detected neutrons for a given angle. By dividing the count number by the monitor count, the intensity could be compared for different sets of measurements. The monitor is a detector placed before the sample, detecting a small fraction of the incoming neutron and thus provide a count for how many neutrons have passed in the beam. Figure 13 shows the  $(1\ 0\ 4)$  peak fitted with a Gaussian as a function of temperature for both the x = 0.06 and 0.07 crystal.

The maximum for each of these peaks were then fitted to the general power function describing a phase transition as a function of temperature [4];

$$f(x) = A \left(1 - \frac{T}{T_c}\right)^{2\beta} + B, \qquad (12)$$

where the amplitude A, background B, critical exponent  $\beta$  and  $T_c$  are free, but the latter is at first based on a guess and since optimized by feeding the fitted value into the function, until it reaches a stable value. See figure 14.

The transition temperature was found to be  $382 \pm 1$  K and  $362 \pm 1$  K for the x = 0.06 and x = 0.07 crystal respectively. The transition temperature as a function of doping was found by using the data presented in 5. As we did not have access to the original data, each point was positioned by eye in a web plot digitizer [28] and then afterwards fitted to a 2nd order polynomial function. This function had an  $R^2$ -value of 0.99, so the fit was good. Even though there was a small uncertainty in each point in the plot digitizer that was not included in the final error calculation, the resulting doping value from this fitted function is still a good estimate since it can be concluded that the errors from the digitizer are small compared to the ones from the experiment itself. The uncertainty in the transition temperature results in the doping lying in the range of 0.0658-0.0670 and 0.0749-0.0755 through error propagation, the minima of



Figure 13: Intesity of the  $(1 \ 0 \ 4)$  peak as a function of  $\Omega$  for different temperatures. The open circles are data points and the lines show fits to a Gaussian. The color of the markers corresponds to a temperature as shown in the colorbar to the left. Left: Data and fits for the unannealed x = 0.06 crystal. Right: Data and fits for the unannealed x = 0.07 crystal



Figure 14: The intensity of th  $(1 \ 0 \ 4)$  peak as a function of temperature. The black circles are data points and the red line is the best fit to the powerlaw 12. Left: Data and fit from the unannealed x = 0.06 crystal. Right: Data and fit for the unannealed x = 0.07 crystal

these still above the expected values. The actual doping of the x = 0.06 and x = 0.07 crystal is therefor  $x = 0.0664 \pm 0.0006$  and  $0.0752 \pm 0.0003$  respectively. The fitting of this function to the data returned an uncertainty of the transition temperature of  $\pm 1$  K on both crystals

## 7 Discussion

## 7.1 Preparation of the crystals

The preparation of the crystals was overall succesful and produced rods, that could be used in the growing of crystals with the TSFZ method. During the preparation of the crystal powders and rods, there were several sources of uncertainties. Together they might have lead to the achieving of a doping different from the one wanted, which is the case in this project. This is however not a problem if one does not need a crystal with an exact doping value since the doping can be measured relatively easy afterwards.

## 7.1.1 Making the powder batch

As mentioned, the process of making the rod had sources of uncertanties, as many actions were not timed, controlled and repeated in the same way. This however did not affect the results in this case, but it is recommended for further growing of crystals, that all steps are monitored and done in the same way to minimies unknown variables.

## 7.1.2 Making the rod

Pressing a straight rod from the powder was required to get a stable crystal growth, but was hard to achieve. Only after the growth of the x = 0.06 and x = 0.07 crystals used in this thesis, an improved, perforated, copper tube was constructed, which has shown to greatly improve the pressed rod. If it was possible to combine this with an even higher pressure, the chances of destroying the pressed rod while removing it from its tube would also be greatly reduced and the rod would be more uniform, making the growing in the mirror furnace more stable and successful.

As the whole process was eventually successful, these points are only considerations for future growing of LSCO crystals.

## 7.2 Crystal growth

The TSFZ method described by [9] was a successful way to grow large single crystals, and two large crystals were produced. The method contains some difficulties, as the many factors of starting and maintaining the stable floating zone varied from time to time. A critical uncertainty comes from the melting of the rod in the TSFZ method because a not uniform feeding rod will make the mixing of the feeding rod and the solvent pill inhomogeneous. If the feeding rod is thicker at one point, more LSCO will mix with the constant copper content in the solvent pill and the relative copper content in the grown crystal will be smaller. This will create a crystal were the doping can alter in the crystal itself. It can be a problem since further measurements of the doping value might give a doping only valid for that part of the crystal. Again, this stresses the importance of a uniform feed rod.

#### 7.3 Magnetic moment measurements

According to the VSM experiment, the annealed and unannealed samples have a  $T_c$  of 6.3 K and 8.4 K respectively. By comparing these two numbers, as well as looking at the two graphs in figure 9, it seems clear that there are differences between the two sets of data. Both the absolute value of the magnetic moment above  $T_c$  as well as the

slope at  $T_c$  are different, and this should be contributed to the annealing process since nothing else was changed in between the two measurements. But, there are no errors on the two  $T_c$  values, since there was no error on the data collected, and this makes a comparison of the two values of  $T_c$  imprecise.

The different  $T_c$  result is also interesting because the unannealed crystal might have an oxygen content of  $O_{4-y}$  which would mean that it has more electrons and therefore lower hole doping compared to the annealed sample. The lower content of oxygen should therefore decrease the doping value of the crystal and thus decrease the transition temperature [34]. This is not the case in this experiment and it suggests that something unexplained is happening in the unannealed crystal.

Another interesting result is the fact that the unannealed plot has an offset at  $\simeq 25$  K compared to an offset at  $\simeq 12$  K in the annealed plot even though they both drop at  $\simeq 6$  K. This shows that the unannealed crystal is inhomogenous since parts of the crystals goes below  $T_c$  before other parts, creating the higher offset. This also indicates that the structure of the unannealed crystal is different from the annealed which could be due to the lack of oxygen atoms, but possibly something else as well.

#### 7.4 X-ray diffraction

The results from the powder x-ray refinement can be seen in table 3.

#### 7.4.1 Powder x-ray

The two .CIF-files, the powder x-ray diffraction data was refined with, correspond to the space groups Bmeb and I4/mmm. The Bmeb has previously been shown to fit the structure of LSCO at this doping (x = 0.06) [18]. As such, it would be assumed to be the best fit, which is also the case. As a rule of thumb, an  $R_B$  around 5 would indicate a good fit. As  $R_B=5.28$  for the Bmeb structure, it can be said to describe the crystal structure very well.

In the powder x-ray refinement, the three different refinements with the two different .CIF-files was all treated similarly, making a comparison between the  $R_B$  values possible. There are however still some factors, that could be refined for each of the structures. On of these is the occupancy of each of the elements, which describes the ratio between them. Refining these values allows the refining program FullProf to look for any different concentration of the element, that might fit the data better. Often this will not lead to reasonable results, as the refinement might end up with zero content of an element known for sure to be present in the sample.

#### 7.4.2 Laue diffraction

As mention in section 6.1.2, the Laue method is mostly a qualitative method to determine alignment of the crystals and was used as such in this experiment with succes. The unannealed x = 0.06 crystal was aligned in the *ac*-plane and the unannealed and unannealed x = 0.07 was aligned in both the *ab* and *ac*-plane. The alignment was done by eye and gave an error of approximately 1-2° which was acceptable in this case, since a more precise alignment was done with neutron scattering.

#### 7.5 Neutron diffraction

#### 7.5.1 Orion

The alignment done at PSI using the Orion instrument was quantitative, as it provided a comparable value between shifting of the sample in the form of a definite peak value. The alignment from the Laue experiment turned out to be good, since the crystals was all in the scattering plane with just a minor off set of a few degrees in the  $\chi$ -scan. The  $\chi$ -scan was made to ensure, that the crystal was aligned in the acquired scattering plane with en error of  $\simeq 0.5^{\circ}$ , since an offset of  $\simeq \pm 0.5^{\circ}$  in the  $\chi$ -scan of the sample was accepted. This method also made sure, that the found peak was indeed in the center and not just a part of the tail of the peak. The marking of the axes on the sample-mount turned out to be a good method, because when mounting the sample in the Morpheus instrument afterwards we knew where to scan to find the required peak.

However, the quantitative and precise nature of this alignment did not change the fact that the crystals became misaligned a few times afterwards because the mount itself either bend a little or became loose in the transportation between instruments, allowing for unwanted vertical and horizontal rotation of the crystal. It is therefore advised in future experiments, that the mount is as stable as possible with no chance of anything getting loose or bend, since this caused some troubles and confusion in this experiment.

#### 7.5.2 Morpheus

The results from the temperature dependent measurements at Morpheus can be seen in figure 13. The experiment showed that the actual dopings of the x = 0.06 and x = 0.07 crystal werer  $x = 0.0664 \pm 0.0006$  and  $0.0752 \pm 0.0003$  respectively.

An extensive amount of measurements were done on the x = 0.07 crystal, even after reaching a convergence in intensity of the (1 0 4) peak. This was done under the assumption, that the intensity of the peak would go to zero while this misunderstanding was cleared up before the second experiment, resulting in much fewer data points above the structure transition temperature for the x = 0.06 doped crystal. The second experiment should however have had more data in the high temperature range above the structure transition since this would have provided a better estimate for the background of the peak resulting in a lower error for  $T_c$  and the final result for the doping value.

The difference between the predicted doping and the one measured is rather big, especially for the x = 0.06 sample, and this could maybe be explained by the inconsistencies during growth.

During the stay at PSI, there were several setbacks to the measurements. Because of this, there were not enough time to measure the actual doping of the annealed x = 0.07 crystal. If this is done in the future, any difference between the two doping values might indicate an even larger effect of annealing on the crystal. Similarly, other samples could be annealed in order to investigate the effect of annealing for several dopings.

## 8 Conclusion

This thesis consisted of five experimental parts:

The first was the growing of the underdoped LSCO crystals. From the growing of the crystals it can be concluded, that the TSFZ method is a complicated but good method for growing large single crystals, with uncertainties that still needs further studying to limit. Despite these, it has been possible for Monica Lacatusu and others to grow large crystals of good quality, even though there were no successful attempts during our attachment to the project.

The two crystals used in this thesis were one with doping value x = 0.06 and one with x = 0.07. The two crystals were cut, and a part from each of them was annealed in order to compare the annealed and unannealed crystals.

The second was doing VSM measurements to find the magnetic moment as a function of temperature in order to find  $T_c$ , where the sample becomes superconducting, and see if the annealed and unannealed crystals has different  $T_c$ .

The magnetic moment measurements were performed on a small piece of the unannealed x = 0.06 crystal and the same piece was afterwards annealed and the measurements repeated. The plot shows a clear difference for the two measurements, see figure 9, and  $T_c$  was found to be 6.4 K before annealing and 8.2 K after which indicates, that there is a difference between the two.

The third was X-ray experiments on the powder to find the structure in form of space groups.

Refinement of the x-ray diffraction data on the powder that the x = 0.06 crystal was grown from showed, that the orthorhombic space group Bmeb is a good match because of an  $R_B$  value of 5.28 which confirmed previously studies [18]. The data was also refined with the tetragonal I4/mmm, since this space group had previously been used to describe the structure of LSCO at other dopings than x = 0.06 [18]. This refinement however had an  $R_B$  value of 16.7 respectively, and it can be concluded, that it is not a good description for the structure of the x = 0.06 doped LSCO crystal.

The fourth was the temperature dependent measurements with neutrons to find the exact doping value of the crystals as well as the alignment of the crystals as a preparation to this.

The alignment was performed with both a Laue camera and neutron diffraction at the Orion instrument at SINQ, PSI, on the unannealed x = 0.06 crystal and both the annealed and unannealed x = 0.07 crystals, since it was these crystals that were included in the further neutron diffraction experiments on the Morpheus instrument at PSI. The Laue alignment confirmed that the crystals were single crystals of good quality, and the neutron diffraction with the Orion instrument on SINQ, PSI corrected the alignment down to an error of  $\simeq 0.5^{\circ}$ .

The doping values for the unannealed x = 0.06 and unannealed x = 0.07 crystals were found by measuring the (1 0 4) peak's intensity as a function of temperature. This peak only exist in the orthorhombic structure and therefore disappears when the structure becomes tetragonal. Previous studies have shown this transition as a function between temperature and doping value of the LSCO crystal [21] and by converting this graph into a function from doping as a function of transition temperature a doping value was found for the two crystals, see tabel 4. The transition temperature was found from a power fit of the intensity as function of temperature.

As one can see, the actual doping values differs from the theoretical ones by 12.5 % and 9 % respectively, and this is possibly due to the inconsistencies in the growing of the crystals. From this it can be concluded, that the actual doping of future, grown

Theoretical doping	Transition temperature	Actual doping	Difference
0.06	$382 \pm 1 \text{ K}$	$0.0664 \pm 0.0006$	12.5~%
0.07	$362 \pm 1 \text{ K}$	$0.0752 \pm 0.0003$	9~%

Table 4: The results from the neutron diffraction experiment at Morpheus showing the theoretical doping values and the actual, measured doping value

crystals should be controlled by a structure transition experiment.

It can finally be concluded, that there appears to be a difference in the annealed and unannealed crystals according to the magnetic moment measurements. Further studies with measurements on both the annealed and unannealed crystals are needed, in order to see, if this can have an effect on the properties of the crystal.

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