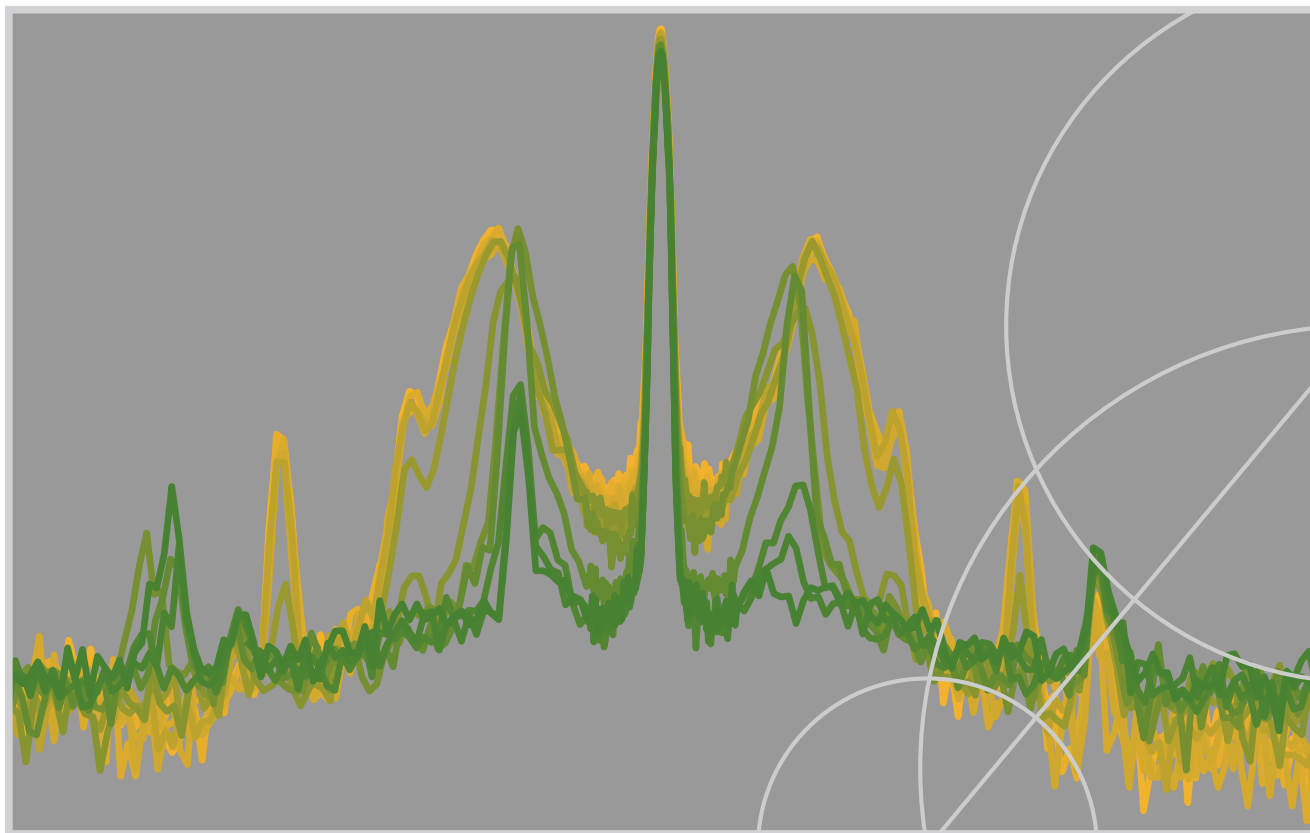




Master's thesis

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Structural investigation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ Following staging as a function of temperature



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List of abbreviations

Below is a list of abbreviations used in the report, with explanations of their meaning. The given page numbers are locations of their first mention.

N_A	Avogadro's constant, equal to 6.022×10^{23} 1/mol	118
amu	Atomic mass unit, equal to 1 g/(mol· N_A)	118
BW5	X-ray triple-axis instrument at DORIS, HASYLAB, DESY, Germany	47
DESY	Deutsches Elektronen Synchrotron in Hamburg, Germany	47
DMC	Neutron powder instrument at SINQ, PSI, Switzerland	55
DORIS	Doppel-Ring-Speicher storage ring at DESY, Germany	47
FWHM	Full width at half maximum	71
HASYLAB	Hamburger Synchrotronstrahlungslabor at DORIS, DESY, Germany	47
HTSC	High-temperature superconductor/superconductivity	7
HTT	High-temperature tetragonal	15
HWHM	Half width at half maximum	71
ILL	Institute Laue Langevin in Grenoble, France	30
ITfC	International Tables of Crystallography, [143]	15
LTO	Low-temperature ortorhombic	15
LTSC	Low-temperature superconductor/superconductivity	7
PG	Pyrolytic graphite	23
PSI	Paul Scherrer Institute in Villigen, Switzerland	30
r.l.u.	Reciprocal lattice units	15
RITA-II	Neutron triple-axis instrument at SINQ, PSI, Switzerland	52
RTSC	Room-temperature superconductor/superconductivity	11
SINQ	Spallation neutron source at PSI, Switzerland	30
Å	Ångström, a unit of length equal to 10^{-10} m	13

Preface

This thesis for the degree of MSc (Master in Science) is written as part of Pia Jensen Ray's 4+4 PhD studies, where MSc studies and PhD studies are combined. As such, this is not a finished work, and will be expanded with the remaining two years of the PhD time.

The work presented in this thesis is an analysis of staging data for several different samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, taken over several years at the hard X-ray instrument BW5 at DESY, Hamburg, Germany, as well as a comparison with data from the triple-axis neutron spectrometer RITA-II at SINQ, Paul Scherrer Institute, Villigen, Switzerland. A preliminary comparison with reciprocal space mappings of several different superstructures taken at the neutron powder diffractometer DMC at SINQ, Paul Scherrer Institute, Villigen, Switzerland, will also be shown.

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— Pia Jensen Ray
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Abstract

The cuprate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ – a high-temperature superconductor – was discovered almost three decades ago. However the mechanisms behind the superconductivity in the material for different doping values x and y are still not fully understood. A small part of this large puzzle is added to the pile with this thesis, where results on the structure for several different samples are presented.

The emphasis in this thesis is on a specific superstructure thought to be connected to the ordering of interstitial oxygen, known from the isostructural compound $\text{La}_2\text{NiO}_{4+y}$ as staging. Four single crystal samples with different co-doping values are investigated by the use of both X-rays and neutrons.

Staging is observed for all four samples at low temperatures with X-ray measurements. The sample with strontium doping $x = 0.00$ shows several co-existing staging levels with staging numbers between 2 and 8, with the highest contribution from a staging level between 4 and 5. The co-doped samples show increasing staging number with increasing x . It is found that the staging belongs to a structural phase assumed in space group $Fmmm$, while the unstaged fraction of the samples are in the $Bmab$ space group. These two structural phases are found to have significantly different lengths of the long crystal axis for the two low x samples, in the order of a fraction of a percent, while the two higher x samples had a difference of only a small fraction of a permille.

The temperature dependent phase transitions for both the $Bmab$ structure and the staging reflections are investigated between 5 and 300 K. The critical exponents for the $Bmab$ reflections are found to be significantly lower than results from similar materials in literature, although with transition temperatures consistent with literature for comparable sample compositions. It is found that the critical exponents for the staging reflections increase for increasing doping while the transition temperatures decrease, both consistent with results on the isostructural $\text{La}_2\text{NiO}_{4+y}$.

Results from previous neutron measurements are found to be consistent with the X-ray measurements in this work, and measured reciprocal space maps from this work show a large variety of other superstructure reflections which will be interesting to investigate in the future.

Resumé

Den kobber-holdige perovskit $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ - en højtemperatur superleder - blev opdaget for snart tre årtier siden. Til trods for dette er mekanismerne bag superledningen i materialet for forskellige dopingværdier x og y stadig ikke fuldt forstået. Denne afhandling tilføjer nu, med de præsenterede resultater for strukturen af flere forskellige $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ prøver, endnu en brik til dette puslespil.

Der fokuseres her på en specifik superstruktur, der formodentlig er forbundet til ordningen af doped oxygenatomer i mellempositioner af grundmaterialets krystalstruktur. Denne superstruktur er kendt som *staging* fra materialet $\text{La}_2\text{NiO}_{4+y}$, der har samme grundstruktur som $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$. Fire forskellige enkeltkrystaller med forskellige co-dopingværdier bliver undersøgt med både røntgenstråling og neutroner.

Staging observeres i alle fire prøver ved lav temperatur med røntgenmålingerne. For prøven med strontiumdoping $x = 0.00$ ses der staging med niveau mellem 2 og 8, med det højeste signal fra stagingen mellem 4 og 5. Der ses staging med højere niveau for højere strontium doping x i de tre andre prøver. Det bliver fundet at staging-strukturen hører til en strukturel fase, formodentlig i rumgruppen *Fmmm*, mens den ikke-stagede del af prøverne er i *Bmab* rumgruppen. Det blev fundet at disse to strukturelle faser har signifikant forskellige længder af den lange krystalakse for de to prøver med lavest x , i størrelsesordenen af en brøkdelt af en procent, mens de to prøver med højere x kun har en længdeforskel på en lille brøkdelt af en promille.

De temperaturafhængige faseovergange for refleksionerne fra både *Bmab* strukturen og staging strukturen bliver undersøgt mellem 5 og 300 K. De kritiske eksponenter for *Bmab* refleksionerne blev fundet til at være signifikant lavere end resultater fra lignende materialer i litteraturen, dog med overgangstemperaturer der er konsistente med disse. For stagingstrukturen findes kritiske eksponenter der stiger med stigende doping x , mens overgangstemperaturerne falder for stigende x - hvilket er i fin overensstemmelse med resultater for $\text{La}_2\text{NiO}_{4+y}$.

Det blev fundet at resultater fra tidligere målinger med neutroner er konsistente med resultaterne fra røntgenmålingerne i denne afhandling. Målte planer i det reciprokke rum fra denne afhandling viser desuden en stor samling af andre superstrukturer der vil være yderst interessante at undersøge i fremtiden.

I

Introductions and theory

“

Physics is still the discipline farthest away from the art of stamp collecting.

— *Ekaterina Shamonina*
Metamaterials 1:1, p. 12 (2007)

”

Introduction to the project

This thesis is written such that a physics master student should be able to understand it, given that they have some background in solid state physics.

The general books that I have used throughout this project have been *Superconductivity: Physics and Applications* by Fossheim *et al.* [1] for superconductivity, *Magnetism in Condensed Matter* by Blundell [2] for magnetism, *Crystal Structure Determination* by Massa [3] and chapter 8.1 of *International Tables for Crystallography Volume A: Space-group symmetry* by Wondratschek [4] for crystallography, *Elements of Modern X-Ray Physics* by McMorro *et al.* [5] for X-ray scattering, *Neutron Scattering: Theory, Instrumentation, and Simulation* by Lefmann [6] and *Introduction to the Theory of Thermal Neutron Scattering* by Squires [7] for neutron scattering, and *Structural Phase Transitions: I. Landau Theory* by Cowley [8] and chapter 18 of volume 23 (part C) of *Methods of Experimental Physics* by Cowley [9] for phase transitions.

1.1 Motivation

The ceramic material $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ is a superconductor, capable of transporting electricity with no resistance below a critical temperature T_c of around 40 K, [12]. The parent compound, La_2CuO_4 , can be doped by chemical substitution of Sr^{2+} for La^{3+} and/or by intercalation of O^{2-} into the structure, and this family of materials has been investigated for both its superconducting and magnetic properties since the 1980's.

New superconducting compounds have since been found to have higher critical temperatures - for $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$, another cuprate, up to $T_c = 138$ K, [13, 14], and even 164 K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ at high pressure, [15]. The naturally simpler single-layer structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ however, makes it a good model system to investigate the cuprates. Adding the fact that the intricate details of the workings of the superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ have still not been understood, it makes it an even more interesting system to work with.

In conventional superconductors working at lower temperatures, there are no important structural effects since the coherence length ξ is much longer than the penetration depth λ , [1]. This is not the case for these high-temperature superconductors, since these have $\xi \ll \lambda$. Because of this, knowing the structure of the HTSCs is an important part of understanding their physical properties and their superconductivity fully - which is why this thesis will work with exactly this.

1.2 The project

This project deals with the superstructure known as staging, which has been observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ both by the use of neutrons and X-rays.

The main emphasis of the thesis will be the analysis of X-ray data, with a comparison to similar already part-analyzed neutron data taken on the same samples. Neutron data measured to obtain overview reciprocal space maps of the relevant reciprocal space regions will also be presented, mainly as a base for comparison and as an outlook for work to come.

The X-ray data will be analyzed in order to understand the phase transitions of both the underlying structure and the staging superstructure, giving an insight into how the materials behave over temperature changes and how they form long range order.

1.3 Reading guide

This thesis is separated in parts, reflecting the type of content in the collected chapters. In part I, I focus on introducing concepts used in this project:

In Chap. 2, I introduce superconductivity and give a motivation as to why this subject is still important and interesting to work with even a century after its discovery. In Chap. 3, I explain relevant parts of crystallography, and go through the lattice systems that are important for this work. In Chap. 4, I go through neutron and X-ray scattering, focusing on scattering from crystals. In Chap. 5, I briefly explain phase transitions. In Chap. 6, I write more about the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ compound, and give a small review of earlier results.

In part II, I go through the instruments and experimental methods used to gather data:

In Chap. 7, I introduce the X-ray instrument BW5 (DORIS, HASYLAB, DESY, Germany) and the neutron instrument RITA-II (SINQ, PSI, Switzerland), and explain what was done to measure staging patterns on four different $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ samples. In Chap. 8, I introduce the neutron instrument DMC (SINQ, PSI, Switzerland) and explain how it was used to measure planes in reciprocal space for several different samples.

In part III, I go through measurements and explain my analysis of the data in detail:

In Chap. 9, I focus on the staging measurements from the different experiments, and go from raw data to temperature-dependent overviews of the patterns. In Chap. 10, I present some of the measured reciprocal space planes, and relate them to the staging measurements.

In part IV, I discuss and conclude on the analyzed data:

In Chap. 11, I go through the results in an overview, discussing what they could mean. In Chap. 12, I conclude on the overall project and give an outlook of what to do next.

Finally, in the appendices I show relevant material that did not make it into the main text – such as calculations and more detailed figures of the data. References to these appendixes are in the main text where relevant.

Superconductivity

Superconductivity is a state of matter where the DC electrical resistance abruptly goes to zero and magnetic fields are expelled below a critical temperature T_c .

In this chapter, I will go through a bit of the history of the discovery of superconductivity, and briefly elaborate on the different types of superconductors and how they are thought to work. Finally, I will mention a few applications of superconductors.

2.1 Conventional superconductivity

Superconductivity was first discovered by Heike Kamerlingh Onnes in 1911, [16, 17]. After his successful experiments to liquify helium in 1908, he continued to work with pure metals at low temperatures, and hence found that the electrical resistance of extremely pure mercury dropped to zero below a critical temperature T_c of 4.2 K, see Fig. 2.1. Onnes continued working on other pure metals, and soon added both lead and tin – as well as many others – to the list, bringing the maximum T_c further up to 7 K.

2.1.1 The Meissner effect

The magnetic effects in superconductors were extensively studied after the discoveries of Onnes. In 1933, Walther Meissner and Robert Ochsenfeld found that superconductors are perfect diamagnets, meaning that they have magnetic susceptibility $\chi = -1$, below a certain critical field H_c , [18].

This second characteristic defining property of superconductors, now called the Meissner effect, means that magnetic flux lines will be expelled from the superconductor, keeping the magnetic field $\mathbf{B}$ inside the material at zero, as illustrated in Fig. 2.2. The expulsion happens by induced surface currents, so-called shielding currents, that cancel out the applied field inside the sample, and since the resistance in a superconductor is zero, these currents can run freely as long as they are below a critical current I_c .

The magnetization $\mathbf{M}$ of the superconducting material will, in this instance, be the perfect opposite of the applied field $\mathbf{H}$ inside the material, since

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = 0 \quad \Rightarrow \quad \mathbf{M} = -\mathbf{H}, \quad (2.1.1)$$

which can also be seen directly from the perfect diamagnetism, $\chi = dM/dH = -1$.

When the applied field exceeds H_c , the superconducting state will break down, and the material returns to its metallic state.

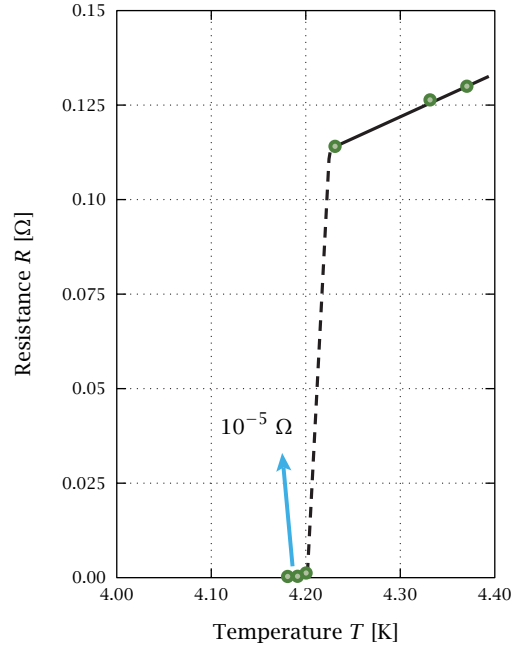


Figure 2.1: Kamerlingh Onnes' measurements of resistance versus temperature in mercury from 1911, showing the superconductivity below 4.2 K. Adapted from Onnes [16].

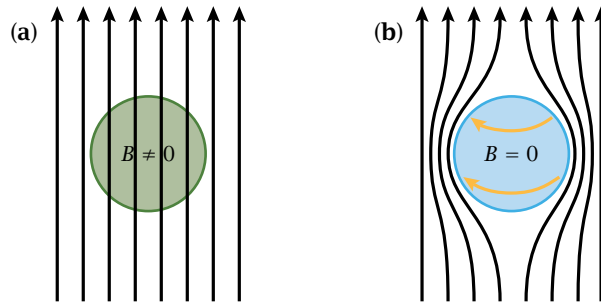


Figure 2.2: Illustration of magnetic field lines for a superconductor in the (a) normal state, where the flux lines go through the sample, and the (b) Meissner state, where the shielding currents (shown in yellow) make it so the resulting magnetic field inside the sample is zero.

2.1.2 BCS theory

Up until 1957, superconductors had not been understood on a microscopic level, but this was changed by John Bardeen, Leon Neil Cooper, and John Robert Schrieffer with their quantum mechanical theory now known as the BCS theory, [19, 20].

This theory describes how electrons couple in bosonic pairs, so-called Cooper pairs, [21], mediated by lattice vibrations in the crystal they travel within, phonons. In simple terms, as sketched in Fig. 2.3, the positively charged ions in the lattice are attracted to the negatively charged electron traveling through the lattice, creating an overall area of positive charge density after the electron has passed by. Since the ions are heavy, they are relatively slow at moving back to their original arrangement, and a second electron is attracted to the net positive charge, hence following the first electron through the lattice. In practice, the two electrons are then correlated with each other via phonons in the lattice.

Electrons with opposite spin and momentum (as to not violate the Pauli exclusion principle) pair up in Cooper pairs, and since electrons are fermions, the collected pair behaves as a boson. In a superconductor, there will be a lot of these pairs, and they can overlap strongly and form a

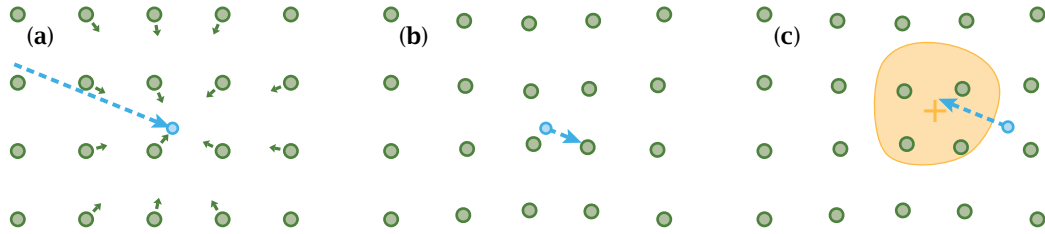


Figure 2.3: Very simple illustration of mediation of a bosonic pair of electrons via phonons. (a) An electron travels through a lattice of positively charged ions, attracting them. (b) While the electron travels, the ions displace slightly towards it, creating an area of positive charge density. (c) After the electron has left, the ions are still slightly displaced for a short period, attracting a second electron.

highly collective Bose-Einstein-like condensate, behaving with phase-coherence below T_c . Since they act as a condensate, breaking up even one of the pairs would require that all the pairs be broken up. This is also called the energy gap, since there is a certain minimum energy needed to excite the system above the Fermi level, as opposed to electrons in a normal metal, which can be excited with an arbitrarily small energy. Hence, the usual resistance that single electrons would feel from moving through the lattice will not be felt by electrons in the condensate, resulting in superconductivity – where the electron flow as a whole does not experience any resistance.

2.2 High-temperature superconductivity

For a long time, it was believed that superconductivity could not occur above 30 K, [22, 23], since the BSC theory does not allow Cooper pairs to form above this temperature. The Coulomb repulsion between the electrons become too large compared to the binding through the phonons.

However, in 1986 – following investigations of oxide superconductors such as the Nb-doped perovskite SrTiO_3 , [24–26] – Johannes G. Bednorz and Karl A. Müller discovered a new class of superconductor, [27]. They found that the ceramic material $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ was superconducting below T_c of 30 K, later precised to 35 K, [28]. Not only was this the first time a ceramic – which is generally a very bad conductor – had been seen to be superconducting, but this was outside the range of superconductivity at the time, and well above the previous record-setting value $T_c = 22.3$ K for Nb_3Ge from 1973, [29].

This new type of superconductor, the first of the high-temperature superconducting (HTSC) cuprates, started a worldwide race of discoveries of new higher and higher temperature superconductors, both for copper-oxide based and other types of materials – as illustrated on the timeline in Fig. 2.4. It seems that the mediation of superconductivity is still Cooper pairs, but the “glue” that keeps them together seems of a different nature than the phonons used in the BCS theory, [30].

2.2.1 Type-I and type-II superconductors

The HTSCs are type-II superconductors, as opposed to the conventional low-temperature superconductors (LTSC), which are type-I. This classification comes from the Ginzburg-Landau theory, which is a macroscopic theory describing superconductivity from the point of free energies, following Landau’s theory of phase transitions, [31, 32]. It was originally published in 1950 by Vitaly L. Ginzburg and Lev D. Landau, [33, 34], and later derived again from the BCS theory by Lev P. Gor’kov, [35, 36]. This theory defines two characteristic lengths: the penetration depth λ and the superconducting coherence length ξ . The penetration depth^{*} determines how an

^{*} λ is sometimes called the London penetration depth, since it originates from the London equations for electromagnetic fields in superconductors, [37].

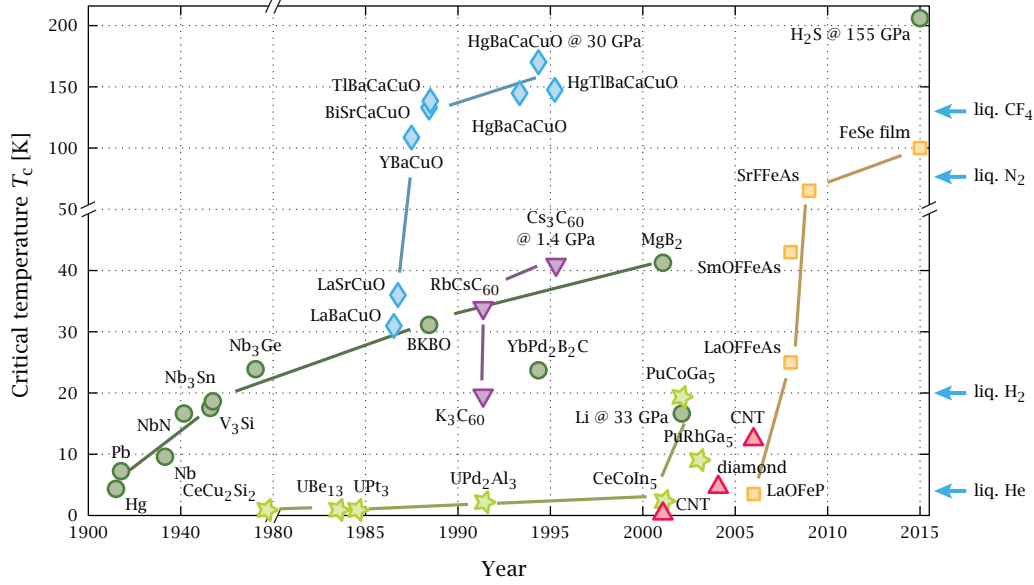


Figure 2.4: The history of some of the discovered superconducting compounds. Note in particular the BCS superconductors (green circles), the cuprates (blue diamonds), and the iron-based superconductors (yellow squares). Note also the change in the axes at around year 1980 and $T_c = 50$ K. Partly based on figures from [137] and [1, Fig. 2.1].

external magnetic field decays inside a superconductor (or, in turn, how far into the superconductor the screening currents occur), while the coherence length determines how the density of electrons in the superconducting state can be excited and recover again without breaking superconductivity.

The ratio of λ and ξ is the Ginzburg-Landau parameter,

$$\kappa = \frac{\lambda}{\xi}, \quad (2.2.1)$$

and type-I and type-II superconductors are split up by the value of κ by

$$\text{type-I: } \kappa < \frac{1}{\sqrt{2}}, \quad \text{type-II: } \kappa > \frac{1}{\sqrt{2}}. \quad (2.2.2)$$

The HTSCs are furthermore classified as extreme type-II superconductors, meaning that they have $\kappa \gg 1$, or $\xi \ll \lambda$, and they are not well described by the BCS or Ginzburg-Landau theories.

As illustrated on Fig. 2.5, type-II superconductors do not follow the Meissner effect all the way to H_c , but instead break into a mixed state when the applied field reaches H_{c1} , [38, 39]. In this state, the magnetic flux penetrates the material partially, and continuously penetrates more and more until the sample is in the normal state at H_{c2} .

The mixed state is also called the vortex state, since the field lines tend to penetrate in vortices of quantized units of flux $\Phi_0 = h/2e$ (h being Planck's constant, and e the electron charge), as shown in Fig. 2.6, [40, 41]. The density of these vortex lines rises with rising external field, until the superconducting areas of the sample collapse at H_{c2} . Interestingly, these vortices can order into lattices, see *e.g.* [42].

2.2.2 Cuprates

After Bednorz and Müller's discovery of superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, an important milestone was reached in 1987, when Paul Ching-Wu Chu *et al.* found that T_c could be raised to above 40 K when applying pressure, [43]. This effect can also be achieved by replacing some

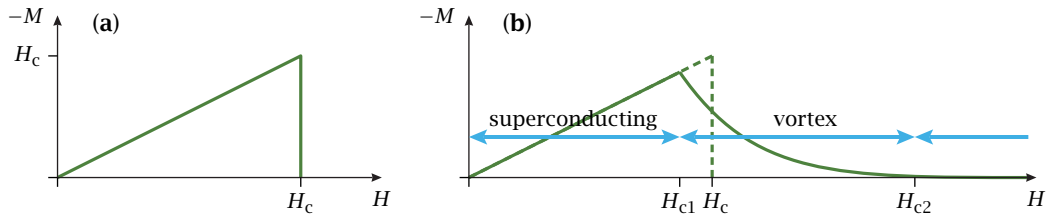


Figure 2.5: The magnetization M of a superconductor as a function of applied field H . (a) For a type-I superconductor the magnetization is the opposite of the direct field until the critical applied field H_c (the Meissner effect), while (b) for a type-II superconductor it will start to break down in a vortex state from H_{c1} until it breaks down fully at H_{c2} .

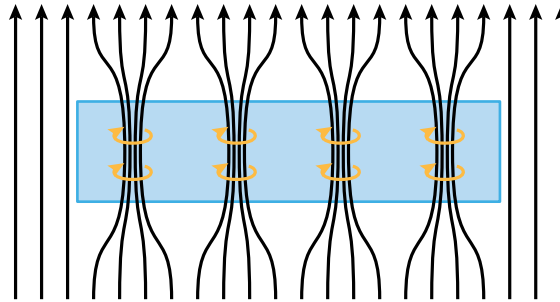


Figure 2.6: Illustration of magnetic field lines for a type-II superconductor in the vortex state, where the flux lines enter the sample in a vortex lattice, where shielding currents (shown in yellow) shield the bulk of the superconductor from both the field outside and the penetrating field lines.

of the atoms in the material with smaller ones with the same chemical properties,^{*} leading to the discovery that T_c could go as high as 38 K at ambient pressure when replacing Ba with Sr, [12, 44], for the first time observing superconductivity in the oxygen-stoichiometric version of the compound that I work with in this thesis. I will go into more detail on the oxygen-codoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ compound in Chap. 6.

During the following year, it was found that structures containing Y instead of La results in the critical temperature leaping to above 90 K for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, [45, 46]. This was a breakthrough of historic proportions – superconductivity at temperatures above liquid nitrogen (77 K) suddenly made applications of superconductivity much more realistic.

Now, decades later, thousands of scientists have published an impressively large number of research papers on the subject,[†] exploring new compounds to push T_c higher and trying to understand the HTSCs. A superconducting transition temperature as high as 138 K was observed for $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ in 1994, [13, 14], and even 164 K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ under pressure, [15], still holding the official record for cuprates to this day. It was very recently discovered that H_2S can exhibit BCS superconductivity at extreme pressures with a T_c of up to 203 K, [47] – hence giving H_2S the overall critical temperature record for now.

All of the HTSC compounds mentioned so far belong to the same family of materials, the cuprates. These materials are ceramics containing parallel weakly coupled copper-oxide (CuO_2) layers. In these layers, each Cu atom can relinquish one loosely bound electron which can then move around in the layer as a conduction electron. These electrons order into an anti-ferromagnetic Mott insulator, where electron-electron interactions do not allow conduction

^{*}Applying pressure to a crystal will compress the unit cell slightly. Replacing atoms with smaller atoms will instead cause the unit cell to shrink slightly from within, resulting in the same overall effect.

[†]A simple search on Web of Science (<http://webofknowledge.com>) for publications with topics *superconduct** suggests almost 250 000 articles at the time of writing this.

Compound	T_c [K]	Planes	Reference	Fig.
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$	39	1	Dover <i>et al.</i> [12]	(a)
$\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$	93	2	Wu <i>et al.</i> [45], Cava <i>et al.</i> [46]	(b)
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_9$	120	1	Hazen <i>et al.</i> [48]	(c)
$\text{Tl}_2\text{Ba}_2\text{CuO}_6$	81	1	Sheng <i>et al.</i> [49]	
$\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$	110	2	Hazen <i>et al.</i> [50]	
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$	125	3	Parkin <i>et al.</i> [51]	(d)
$\text{HgBa}_2\text{CuO}_{4+\delta}$	94	1	Putlin <i>et al.</i> [52]	
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	135	3	Schilling <i>et al.</i> [53], Huang <i>et al.</i> [54]	
$\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	138	3	Sun <i>et al.</i> [13], Dai <i>et al.</i> [14]	(e)

Table 2.1: An overview of a selection of cuprates and their critical temperatures at ambient pressure, along with the number of CuO_2 planes in the unit cell. The figure letters refer to the unit cells shown in Fig. 2.7.

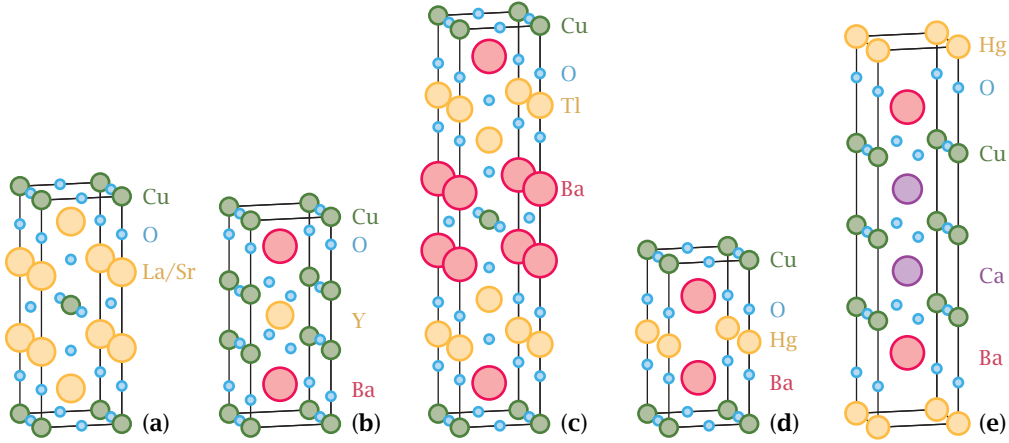


Figure 2.7: Unit cells of some typical cuprates, to show the CuO_2 layers for comparison with Tab. 2.1. (a) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, (b) $\text{YBa}_2\text{Cu}_3\text{O}_6$, (c) $\text{Tl}_2\text{Ba}_2\text{CuO}_6$, (d) $\text{HgBa}_2\text{CuO}_4$, (e) $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$.

electrons to move. The CuO_2 layers are separated by neighboring layers of atoms, *e.g.* lanthanum, yttrium, strontium, or barium, which help stabilize the structure, and at the same time dope extra electrons or holes (“stealing” electrons) into (from) the CuO_2 layers, thus changing the conduction properties. Because these layers provide the charge carriers to the CuO_2 layers, they are also often called the charge reservoirs.

A list of selected superconducting cuprates and their critical temperatures – as well as the number of CuO_2 layers in the structure – is shown in Tab. 2.1, with a few examples of the structures shown in Fig. 2.7.

Note that the number of unit cells given in Tab. 2.1 on first glance looks like it is too low for some of the structures. For *e.g.* $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in Fig. 2.7(a), it is seen that there is seemingly three layers in the unit cell. The top layer is simply the bottom for the unit cell on top, but the structure is said to only have one layer, not two. This apparent discrepancy is explained by the fact that the cuprates follow the Ruddlesden-Popper structure $\text{AO}-n(\text{ABO}_3)$, in which A and B are cations and O oxygen anions. The unit cell is then a stacking of n layers of perovskite ABO_3 between rocksalt AO layers, and the number of layers in the cuprates refer to the stacking number n , [55]. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ this is exactly one, as expected.

The superconducting cuprates are very different from the conventional superconductors, in the fact that they are not traditional metals, but instead doped oxides that behave like bad metals. Often, the pairing for superconduction does not happen with electrons, but instead

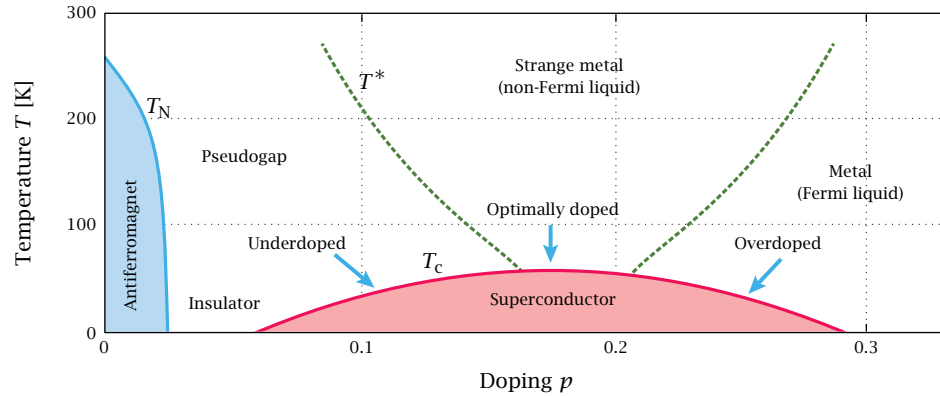


Figure 2.8: Typical phase diagram for a cuprate with doping parameter p , with the antiferromagnetic phase at low doping, a pseudogap above this separated by T^* to a metallic state, which is again split into a strange non-Fermi liquid metal and a normal Fermi liquid metal phase. The superconducting state is split into underdoped, optimally doped, and overdoped.

with the doped holes – which act as quasiparticles that pair up and behave like the Cooper pairs, but with opposite charge, [56]. The un-doped parent compounds are Mott insulators with antiferromagnetic order at low temperatures, and upon doping, the superconductivity (amongst several other interesting phases) appear, as shown in the phase diagram in Fig. 2.8. The complexity of the HTSC phase diagram is still the source of debate and research.

As seen in the timeline in Fig. 2.4, the maximum T_c of the cuprates (the blue points) skyrocketed in the late 1980's, but has since slowly stagnated, with the last record-setting T_c found more than two decades ago. Despite this, it is still not fully known what drives the pairing mechanism to get superconductivity in these materials – although multiple models have been presented, *e.g.* spin fluctuations [57, 58], spin-charge separation [59], stripe formation [60], and Fermi surface nesting [61].

2.2.3 Other high-temperature superconductors

For a long time, it seemed like all HTSC materials had copper-oxide planes. However, in the effort to realize higher transition temperatures, new novel superconducting materials such as Sr_2RuO_4 ($T_c = 0.93$ K), [62], $\text{LaFe}_4\text{Pn}_{12}$ ($T_c = 4.1$ K), [63], and KOs_2O_6 ($T_c = 9.6$ K), [64], were discovered.

In 2008, a break-through happened when Yoichi Kamihara and colleagues discovered superconductivity at 26 K for the iron pnictide $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$, [65]. This work of finding a fairly high critical temperature was based on their earlier work on LaOFeP , which was found to be superconducting at 3.2 K, [66]. This demonstrated a promising new platform for HTSCs apart from the cuprates, and since then the critical temperature for the iron pnictides has been rising steadily, as seen on the yellow points in Fig. 2.4.

Finding new materials in the HTSC line-up is extremely interesting, since it is possible to compare differences and similarities in the properties of the materials with the already known HTSCs – hence possibly getting closer to a full understanding of the superconductivity in all the materials, and getting closer to the ultimate goal of room-temperature superconductivity (RTSC).

2.3 Applications

The zero resistance of superconductors has useful and interesting consequences for applications ranging from electric cables and windmills to medical scanners and scientific equipment.

Even though RTSC has still not been achieved, superconductors are still used in a variety of applications already.

The largest current application of superconductors is in the field of NMR and MRI instruments, where superconductors are used to produce large and stable high magnetic fields. Such high field magnets are also used in large scale research facilities. Typically, these instruments use LTSCs cooled with helium, since the current known HTSCs are too expensive for the instruments to be cost-effective even when including the possible lower cost of cooling. A further complication is the fact that the currently known HTSC materials are often too brittle to use in large-scale applications. A RTSC, or even just a cheaper HTSC, would make the need for helium unnecessary in these instruments, and would be a great benefit for both hospitals and researchers.

There are of course many other current applications of superconductors – both LTSCs and HTSCs have been used to make cables for transport of electricity over long distances, [67, 68], and applications in transformers, [69], generators, [70], energy storage, [71], and many others have also been seen. Most of these would greatly gain in both the form of lower cost and simpler maintenance, if cheaper, less brittle, and easier malleable higher temperature superconductors were to be found.

Crystallography

A crystal is a solid material consisting of atoms or molecules arranged into a repeating pattern in three dimensions. Crystallography is the science of investigating these patterns in terms of a unit cell that describes the lattice.

In this chapter, I will explain the terminology of crystallography and briefly elaborate on symmetries and space groups. These results will be used further when explaining scattering in Chap. 4.

3.1 Atomic lattices

In order to describe a crystal, a lattice and unit cell have to be set up. The lattice is a coordinate system spanned by the lattice vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, such that each lattice point $\mathbf{r}$ can be written as

$$\mathbf{r} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}, \quad (3.1.1)$$

where the n_i 's are integers. The lattice parameters* are the lengths and interaxial angles of the lattice vectors, a , b , c , α , β , and γ , as shown in Fig. 3.1. Typical inter-atomic distances in crystallography are in the order of Ångström (shortened Å), which is 10^{-10} m, whereas the lattice vector lengths are up to a couple of hundred times this length for protein crystals.

The lattice vectors span a single unit cell, and repeating this unit cell in each lattice point will construct the crystal on an infinite lattice, ignoring the crystal surface as well as any defects and imperfections. The lattice can always be chosen in such a way that the unit cell is the smallest possible repeating volume (giving the primitive unit cell), but this is not always the most convenient.

The atom positions in the unit cell are described in terms of fractional coordinates x , y , z of the lattice parameters a , b , c - *e.g.* an atom in the center of the unit cell is written as $(1/2, 1/2, 1/2)$. The atom position vector is written for atom i as

$$\Delta_i = x_i\mathbf{a} + y_i\mathbf{b} + z_i\mathbf{c}, \quad (3.1.2)$$

such that the absolute position of atom i in unit cell j is

$$\mathbf{r}_{i,j} = \Delta_i + \mathbf{r}_j \quad (3.1.3)$$

with $\mathbf{r}_j$ from Eq. (3.1.1). The position of each of the N atoms in the unit cell, the basis Δ_1 , Δ_2 , ..., Δ_N , is then folded with the lattice (by translating to all $\mathbf{r}_j$) to create the full infinitely repeating crystal.

*The lattice parameters are also called cell parameters and lattice constants/angles.

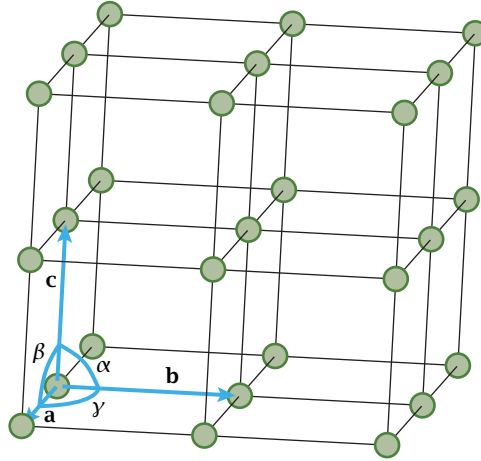


Figure 3.1: The basis vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and their angles α , β , γ in a crystal lattice, here with lattice points shown in green. A single unit cell is spanned between the three vectors.

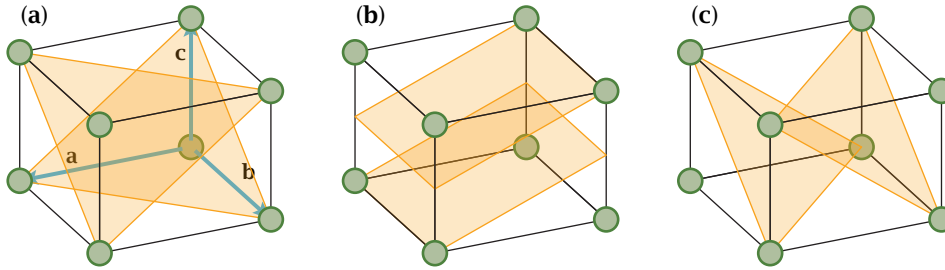


Figure 3.2: Simple examples of two neighboring planes in a single unit cell of a crystal with lattice vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$: (a) (111), (b) (102), and (c) $(\bar{1}11)$.

3.1.1 Crystal planes and Miller indices

When the crystal has been defined with the lattice and basis, crystal planes can be defined as families of parallel planes with the same distance to each other in the crystal, intersecting atoms and lattice points in the crystal.

A family of crystal planes is specified by three integers as (hkl) , the Miller indices. These correspond to the inverse values of the intersections between the lattice vectors and the plane closest to the origin,* *e.g.* a plane that intersects in $\mathbf{a}/2$, $\mathbf{b}/3$, $\mathbf{c}/2$ will have Miller indices (232) – see also the example in Fig. 3.2. Negative values are often written by overstriking the relevant index, *e.g.* $(\bar{2}01)$.

3.1.2 Reciprocal space

When working with scattering on crystals, it is often simpler to work in the so-called reciprocal space as opposed to real-space. Here, the reciprocal lattice vectors are defined as

$$\mathbf{a}^* = \frac{2\pi}{V_0} \mathbf{b} \times \mathbf{c}, \quad \mathbf{b}^* = \frac{2\pi}{V_0} \mathbf{c} \times \mathbf{a}, \quad \mathbf{c}^* = \frac{2\pi}{V_0} \mathbf{a} \times \mathbf{b}, \quad (3.1.4)$$

where $V_0 = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ is the volume of the real-space unit cell.

Each point in the reciprocal space corresponds to a family of planes in the real space, known by their Miller indices (hkl) . A point in the reciprocal space is then written as the reciprocal vector

$$\boldsymbol{\tau}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*. \quad (3.1.5)$$

*In case the plane intersects origo, the nearest plane away from this is chosen.

The real-space distance between two nearest planes can be calculated from the Miller indices (hkl) and the corresponding reciprocal lattice point as

$$d_{hkl} = \frac{2\pi}{|\boldsymbol{\tau}_{hkl}|}. \quad (3.1.6)$$

The Miller indices can be used to refer to the orientation of a crystal, in which case they are written as $[hkl]$. With this notation, $[001]$ would indicate the direction of the $\mathbf{c}^*$ axis.

Often, positions in reciprocal space will be given in reciprocal lattice units, or r.l.u. for short, instead of the other typical unit, $\text{\AA}^{-1}$. This simply means that the units are in the lengths of the reciprocal lattice vectors, a^* , b^* , and c^* , and it will be stated which lattice vector is used for the unit in the given context.

3.2 Symmetries and space groups

It turns out that the arrangement of atoms or molecules in a crystal lattice follows certain symmetries. Mathematically, these can divide all crystal structures into a collection of similar structures with same structural properties. Several symmetry operations are used to describe these structures: reflections, rotations, improper rotations, screw axes, and glide planes.

All the different possible crystal symmetries are divided into 230 space groups, which represent the symmetry operations and translations that build up the crystal. The full list with names, numberings, and descriptions of all these space groups are kept in the *International Tables of Crystallography* (ITfC) published by the International Union of Crystallography (IUCr), [143].

3.2.1 Crystal systems and Bravais lattices

The 230 space groups are divided into seven crystal systems, differentiated by how the symmetry elements of the space groups restrict the shape of the unit cell. These are cubic, tetragonal, orthorhombic, monoclinic, triclinic, rhombohedral,* and hexagonal, as listed in Tab. 3.1.

The crystal systems are again split up into the 14 Bravais lattices, which combine the seven crystal systems with the different types of possible centerings of lattice points. These are, as illustrated in Fig. 3.3, primitive (shortened as P), which simply has lattice points at the edges of the unit cell; body-centered (shortened I), which has an extra lattice point[†] in the center of the unit cell; face-centered (shortened F), which has extra lattice points at the center of each of the faces of the unit cell; and base-centered (shortened A , B , or C), which has two extra lattice points at the center of a pair of parallel faces. Auguste Bravais found in 1850 that the combination of crystal systems and lattices, as shown in Tab. 3.1, can describe all possible crystal symmetries.

3.2.2 The two $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ crystal systems

Both the tetragonal and the orthorhombic crystal systems are important for this thesis, since $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ has phases in either one. The system is tetragonal at high temperatures (the so-called high-temperature tetragonal phase, HTT), and orthorhombic at low temperatures (the low-temperature orthorhombic phase, LTO).[‡]

*The rhombohedral crystal system is the same as the trigonal lattice system, with a few distinctions that I will not go into detail with.

[†]The extra lattice point is compared to the primitive unit cell. In theory, for the centered lattices, it is possible to choose a primitive unit cell with fewer lattice points – but choosing the centered lattice instead makes the symmetries easier to work with.

[‡]Some cuprates also have another low-temperature tetragonal phase (called LTT), but this is not the case for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$.

Crystal system	Unit cell lengths	Unit cell angles	Lattice centerings
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	P, I, F
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P, I
Ortorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P, C, I, F
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta > 90^\circ$	P, C
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	P
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	P
Rhombohedral	$a = b = c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	P

Table 3.1: Relations of unit cell lengths and angles for the seven different crystal systems. The lattices are the P (primitive), C (base-centered), I (body-centered), and F (face-centered).

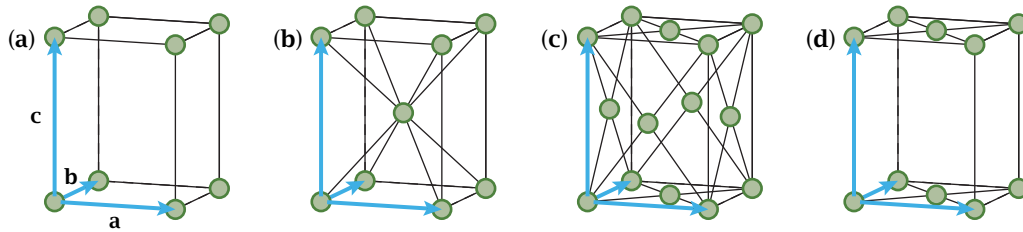


Figure 3.3: Illustrations of the (a) primitive (P), (b) body-centered (I), (c) face-centered (F), and (d) base-centered (here C) lattice centerings, with the lattice vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$.

Tetragonal space groups

Following Tab. 3.1, it is seen that the tetragonal space groups are fairly simple, with two lattice vectors that are the same length, $a = b$, and a different length last axis c . The lattice angles are all 90° , and the lattice centering is either primitive or body-centered.

Tetragonal crystals have the center of the unit cell as the center of symmetry. They have the possibility of a four-fold rotational symmetry parallel to the c axis, as well as two-fold rotational symmetries parallel to the a and b axes and 45° to these, see Fig. 3.4(a). As illustrated in Fig. 3.4(b), there are in total five possible mirror planes in the structure; one lying parallel to the ab plane and four lying perpendicular to this, parallel to the a and b axes, as well as 45° to these.

The seven different combinations of these symmetry operations, making up all the possible symmetries in the tetragonal space groups, are listed in Tab. 3.2.

Ortorhombic space groups

Again looking at Tab. 3.1, it is seen that the ortorhombic space groups have only a few changes from the tetragonal space groups. The two equal length lattice vectors are no longer the same length, $a \neq b$, and both base-centered and face-centered lattice centerings are possible.

Ortorhombic crystals have fewer symmetries than tetragonal crystals since the $\mathbf{a}$ and $\mathbf{b}$ axes have different lengths and hence break some of the tetragonal symmetries. As shown in Fig. 3.5(a), they have three possible two-fold rotational symmetries parallel to the three lattice vectors – corresponding to the four-fold rotational symmetry from the tetragonal symmetry having changed into a two-fold and the two diagonal symmetries disappearing. Further, they have three possible mirror planes, perpendicular to each other and lying parallel to the axial planes – while the two 45° mirror planes from the tetragonal symmetry disappears, see Fig. 3.5(b).

The three different combinations of these symmetry operations, making up all the possible symmetries in the ortorhombic space groups, are listed in Tab. 3.2.

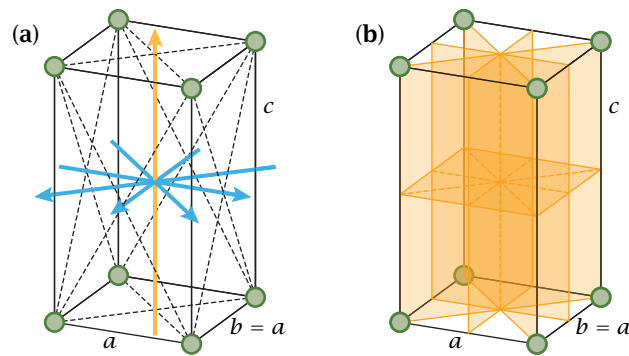


Figure 3.4: Symmetries of tetragonal crystals. (a) Rotation axes, with the four-fold rotation axis shown in yellow and the two-fold rotation axes in blue. (b) Mirror planes. Note that both rotation axes and mirror planes all go through the center of the unit cell, since this is the center of symmetry.

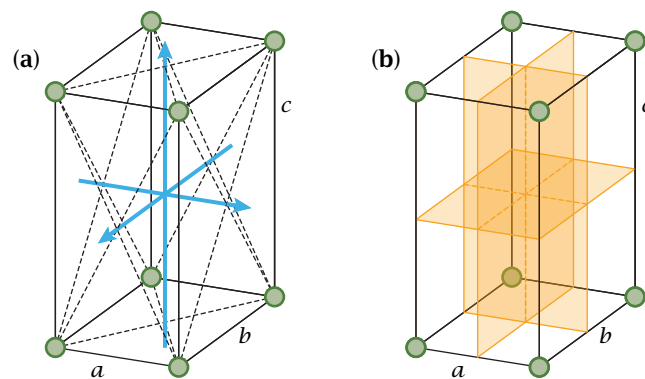


Figure 3.5: Symmetries of orthorhombic crystals. (a) Rotation axes. (b) Mirror planes. Note that both rotation axes and mirror planes all go through the center of the unit cell, since this is the center of symmetry.

Crystal system	Crystal class	Description
Tetragonal	4	Four-fold rotation around c
	$\bar{4}$	Four-fold rotation around c combined with mirroring in the center of symmetry (rotoinversion)
	4/m	Four-fold rotation around c combined with mirror plane perpendicular to c
	422	Four-fold rotation around c and two-fold rotations around a , b , a + b , and a - b
	4mm	Four-fold rotation around c and mirror planes perpendicular to a , b , a + b , and a - b
	$\bar{4}2m$	Four-fold rotation around c combined with mirroring in the center of symmetry (rotoinversion), two-fold rotations around a and b , and mirror planes perpendicular to a + b and a - b
	4/mmm	Four-fold rotation around c combined with mirror planes perpendicular to c , a , b , a + b , and a - b
Orthorhombic	222	Two-fold rotations around a , b , and c
	mm2	Mirror planes perpendicular to a and b and two-fold rotation around c
	mmm	Mirror planes perpendicular to a , b , and c

Table 3.2: The seven tetragonal and three orthorhombic crystal classes. The tetragonal crystal classes are written in the order of **c**, **a** (and **b** because of the symmetry), and **a + b** (and **a - b** because of the symmetry), while they are simply in the order of **a**, **b**, and **c** for the orthorhombic system.

4

Scattering

Scattering is a common name for a group of experimental methods where a beam of known particles is used to interact with a sample. Looking at how the particles change with the interaction gives information about both static and dynamic properties of the sample. Typical probing particles to use for scattering are X-rays, neutrons, and electrons – which each have their own strengths and weaknesses.

In this chapter, I will go through the basic theory of scattering, explain diffraction on crystals, and then explain X-ray and neutron scattering in particular – since these are the methods used to obtain data for this thesis. Finally, I will touch upon the differences between these two methods, and on how to choose between them.

4.1 Definitions

Imagine an incident beam of particles, typically sent towards a sample. The flux Ψ is defined as the number of particles passing through a unit area per second, and is used as the measure of the intensity of the beam.

4.1.1 Scattering cross section

The cross section is a property describing how much the sample interacts with the beam, by giving how many particles end up where and with which properties after the interaction – ignoring the incident beam. The partial differential cross section is defined as

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{\text{particles scattered per second into a solid angle } d\Omega \text{ in a given direction, with final energy between } E_f \text{ and } E_f + dE_f}{\Psi_0 d\Omega dE_f}, \quad (4.1.1)$$

where Ψ_0 is the initial flux. This is a measure of the efficiency of the scattering process as seen from the given direction, where the flux of the incident beam and the size of the detection area have been normalized away.

If the energy of the particles is not analyzed, an integral over dE_f is performed, and the differential cross section is obtained instead,

$$\frac{d\sigma}{d\Omega} = \int_0^\infty \frac{d^2\sigma}{d\Omega dE_f} dE_f = \frac{\text{particles scattered per second into a solid angle } d\Omega \text{ in a given direction}}{\Psi_0 d\Omega}. \quad (4.1.2)$$

The total cross section can be found in a similar way, by also integrating over all directions, getting

$$\sigma = \int_{\text{all directions}} \frac{d\sigma}{d\Omega} d\Omega = \frac{\text{particles scattered per second}}{\Psi_0}. \quad (4.1.3)$$

This expression is the total ability of a sample to scatter the probing particles, although typically given per atom or nucleus* instead of for the full sample at once. The unit of the cross section is area, and it can be thought of as the effective area of the sample atoms or nuclei that the particle beam interacts with in the sample.

4.1.2 Elastic scattering

The incoming wave ψ_i at the point $\mathbf{r}$ is approximated by a complex plane wave of the form

$$\psi_i(\mathbf{r}) = e^{ik_i \cdot \mathbf{r}}, \quad (4.1.4)$$

where $\mathbf{k}_i$ is the incident wave vector, defined simply as the vector pointing in the direction of the beam with length $2\pi/\lambda$, with λ being the wavelength of the beam. Depending on the probe being used, the wavelength can be calculated from the energy of the probing particles, as indicated in Fig. 4.1.

Scattering any wave of a sample consisting on a single object which is small compared to the wavelength – *e.g.* a nucleus – will result in a spherical scattered wave as illustrated in Fig. 4.2(a). Hence, assuming a sample placed at $\mathbf{r}'$, the scattered (final) wave ψ_f at the point $\mathbf{r}$ is written

$$\psi_f(\mathbf{r}) = \psi_i(\mathbf{r}') \frac{-b}{|\mathbf{r} - \mathbf{r}'|} e^{ik_f |\mathbf{r} - \mathbf{r}'|}, \quad (4.1.5)$$

where b is the scattering length – a measure of the scattering strength of the sample. The actual measured intensity is not the wave function directly, but instead typically the differential cross

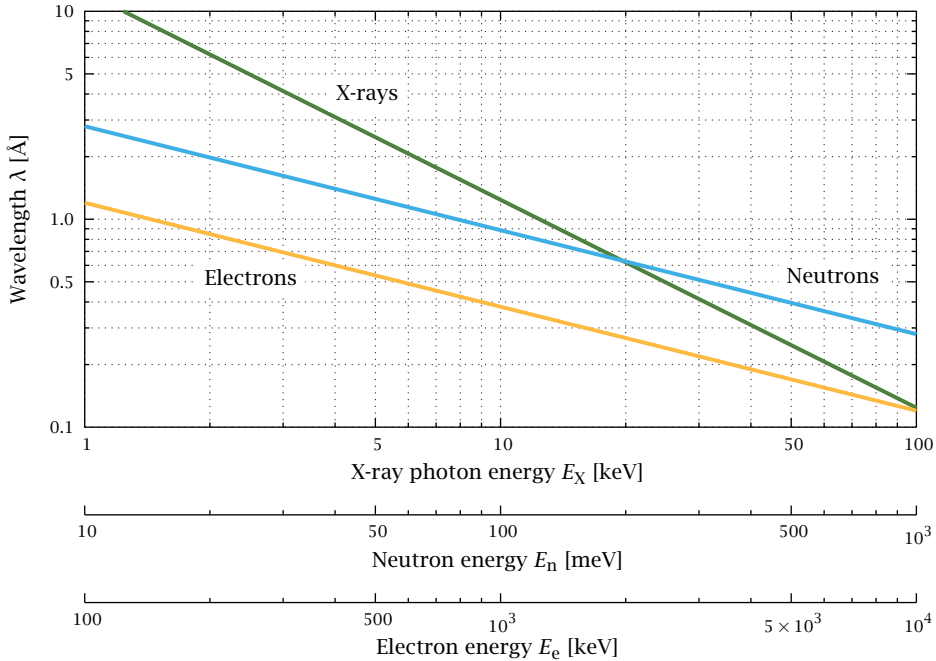


Figure 4.1: Particle energies E versus wavelengths λ for three different scattering probes, in typical units using the relations $\lambda[\text{\AA}] = 12.4/E_X[\text{keV}]$ (or Eq. (4.4.1)), $\lambda[\text{\AA}] = 0.28/(E_n[\text{eV}])^{1/2}$ (or Eqs. (4.5.1) to (4.5.2)), and $\lambda[\text{\AA}] = 12/(E_e[\text{eV}])^{1/2}$. Partly based on [10, Fig. 1, p. 47].

*Different probes interact with different parts of the atom, and hence see different cross sections – more on that when I go through the particular probe types in Sects. 4.4 to 4.5.

section from Eq. (4.1.2), where the modulus squared of the wave function, $|\psi(\mathbf{r})|^2$, gives the number of scattered particles in the beam. Assuming elastic scattering, where no energy is exchanged between the sample and the probing particle beam, the final scattering vector length is the same as the ingoing, $k_f = k_i$, and it can be shown that $d\sigma/d\Omega = b^2$ and $\sigma = 4\pi b^2$.

If there is more than one object in the sample, interference between the scattered spherical waves will take place, and the resulting scattered wave will be a sum of the individual contributions,

$$\psi_f(\mathbf{r}) = \sum_j \psi_i(\mathbf{r}_j) \frac{-b_j}{|\mathbf{r} - \mathbf{r}_j|} e^{ik_f|\mathbf{r} - \mathbf{r}_j|}. \quad (4.1.6)$$

Here it has been assumed that the individual objects in the sample only pose a small perturbation to the incident beam, so that the incoming wave can be seen as having the same flux on each of the $\mathbf{r}_j$ positions.

Inserting Eq. (4.1.4), the sum can be rewritten with a few tricks, applying a coordinate system with an origo far away from the sample compared to the inter-sample distances: $r \gg |\mathbf{r}_i - \mathbf{r}_j|$ for any two i, j . It is then permissible to rewrite $k_f|\mathbf{r} - \mathbf{r}_j|$ to $\mathbf{k}_f \cdot (\mathbf{r} - \mathbf{r}_j)$ since the components of the $\mathbf{r}_j$'s parallel to $\mathbf{k}_f$ are much bigger than the perpendicular components. This also lets $|\mathbf{r} - \mathbf{r}_j|$ get rewritten to r in the denominator in the final step,

$$\psi_f(\mathbf{r}) = \sum_j e^{i\mathbf{k}_i \cdot \mathbf{r}_j} \frac{-b_j}{|\mathbf{r} - \mathbf{r}_j|} e^{i\mathbf{k}_f \cdot (\mathbf{r} - \mathbf{r}_j)} \quad (4.1.7)$$

$$= \sum_j \frac{-b_j}{|\mathbf{r} - \mathbf{r}_j|} e^{i[\mathbf{k}_i \cdot \mathbf{r}_j + \mathbf{k}_f \cdot (\mathbf{r} - \mathbf{r}_j)]} \quad (4.1.8)$$

$$= \sum_j \frac{-b_j}{|\mathbf{r} - \mathbf{r}_j|} e^{i[(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}_j + \mathbf{k}_f \cdot \mathbf{r}]} \quad (4.1.9)$$

$$= e^{i\mathbf{k}_f \cdot \mathbf{r}} \sum_j \frac{-b_j}{|\mathbf{r} - \mathbf{r}_j|} e^{i\mathbf{q} \cdot \mathbf{r}_j} \quad (4.1.10)$$

$$= e^{i\mathbf{k}_f \cdot \mathbf{r}} \sum_j \frac{-b_j}{r} e^{i\mathbf{q} \cdot \mathbf{r}_j}. \quad (4.1.11)$$

Here, the scattering vector, as illustrated on Fig. 4.2(b), has been defined by

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f. \quad (4.1.12)$$

In the figure, the scattering angle 2θ between the incident and final beam has also been indicated.

The actual measured (elastic) scattered intensity from a sample can then be shown to be

$$\frac{d\sigma}{d\Omega} = \left| \sum_j b_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \right|^2. \quad (4.1.13)$$

4.2 Diffraction from crystals

In the case of scattering from a crystal, the object positions $\mathbf{r}_j$ can be split up using Eq. (3.1.3) to $\Delta_i + \mathbf{r}_j$, where the Δ 's form the basis of the atom positions in the crystal and the new $\mathbf{r}$'s are the lattice points. This means that the cross section in Eq. (4.1.13) can be rewritten to

$$\frac{d\sigma}{d\Omega} = e^{-2W} \left| \sum_{\substack{\text{atoms } i \\ \text{cells } j}} b_i e^{i\mathbf{q} \cdot (\Delta_i + \mathbf{r}_j)} \right|^2 \quad (4.2.1)$$

$$= e^{-2W} \underbrace{\left| \sum_{\text{atoms } i} b_i e^{i\mathbf{q} \cdot \Delta_i} \right|^2}_{F_{\text{u.c.}}(\mathbf{q})} \underbrace{\left| \sum_{\text{cells } j} e^{i\mathbf{q} \cdot \mathbf{r}_j} \right|^2}_{S_N(\mathbf{q})}, \quad (4.2.2)$$

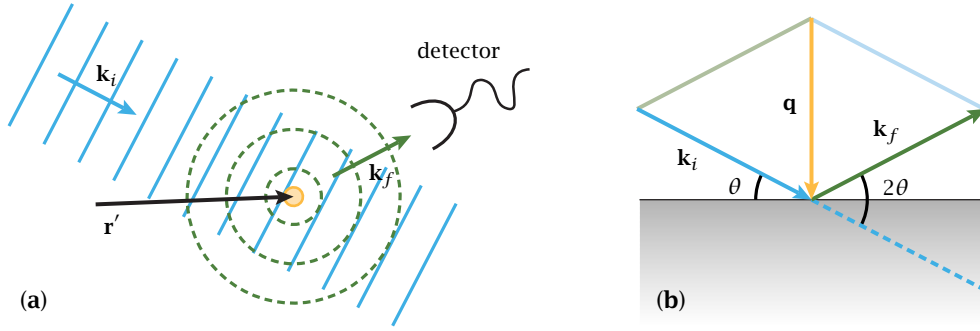


Figure 4.2: A simple look at scattering vectors and angles. (a) A plane wave with wave vector $\mathbf{k}_i$ scattering from a single-object sample placed in $\mathbf{r}'$, resulting in a spherical wave with wave vector $\mathbf{k}_f$ in the direction of the detector. (b) Subtracting $\mathbf{k}_i$ with $\mathbf{k}_f$ gives the scattering vector $\mathbf{q}$.

where the extra term $\exp(-2W) \leq 1$ is the site-independent Debye-Waller factor, which takes into account that the atoms vibrate slightly around their crystal positions. The Debye-Waller factor is close to unity for low temperatures as well as for low values of q .

4.2.1 The unit cell structure factor

The first sum in Eq. (4.2.2) contains the unit cell structure factor (often simply referred to as the structure factor)

$$F_{\text{u.c.}}(\mathbf{q}) = \sum_i b_i e^{i\mathbf{q} \cdot \Delta_i}, \quad (4.2.3)$$

which only depends on the positions of the atoms in the crystal. In a typical diffraction experiment, the goal is to measure $|F_{\text{u.c.}}(\mathbf{q})|^2$ and then use this to calculate back to get the Δ_i 's, solving how the atoms are positioned in the unit cell.

There is one big problem with this approach though; the so called phase problem. Because the measured value is $|F_{\text{u.c.}}(\mathbf{q})|^2$, instead of $F_{\text{u.c.}}(\mathbf{q})$ directly, the complex phases are lost. Because of this it is not possible to do a direct calculation back to the Δ_i 's, and several different possible sets of Δ_i 's can even give the same value of $|F_{\text{u.c.}}(\mathbf{q})|^2$.

A large part of crystallography is devoted to solving the phase problem, which is needed to solve a crystal structure. The steps are typically to start out with a model structure and calculate the resulting structure factors at given $\mathbf{q}$ positions, comparing to the observed structure factors at those $\mathbf{q}$. This results in a density map of the unit cell where it is possible to see if any atoms are missing or wrong, and it is then possible to refine the model in order to make the density map fit better and better - resulting in the best possible model. There are several different ways to do this, which is covered well in text books, *e.g.* *Crystal Structure Determination* by Massa [3].

4.2.2 The Laue condition and Bragg's law

The second sum in Eq. (4.2.2) is called the lattice or cell sum $S_N(\mathbf{q})$, and sums up all the lattice points in the crystal, ignoring crystal boundaries. Performing this near-infinite sum, it turns out that only when the scattering vector $\mathbf{q}$ coincides with a reciprocal lattice vector $\boldsymbol{\tau}$ - as defined in Eq. (3.1.5) - will the sum element be non-zero. This rule,

$$\mathbf{q} = \boldsymbol{\tau}, \quad (4.2.4)$$

is called the Laue condition, and is illustrated in Fig. 4.3(a). Only when the incident and final wave vectors lie in a way that they hit a reciprocal lattice point, will scattering occur.

In real space, the Laue condition corresponds to the situation illustrated in Fig. 4.3(b). An incoming beam is scattered off a family of lattice planes with interplanar distance d at an angle

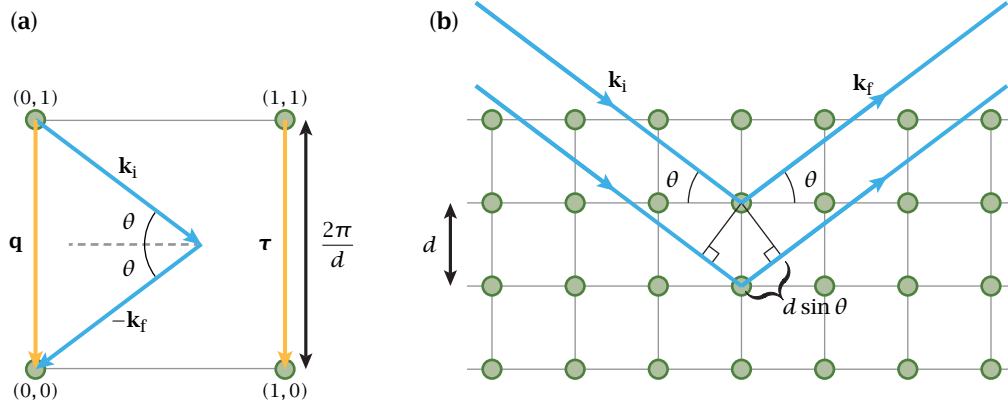


Figure 4.3: Illustrations to help show the requirements for constructive interference. (a) In reciprocal space, the Laue condition requires $\mathbf{q} = \boldsymbol{\tau}$, while (b) in real space, the Bragg condition requires $n\lambda = 2d \sin \theta$.

θ . There will only be constructive interference if θ is such that the extra distance traveled by the lower beam, $2d \sin \theta$, is an integer number n of wavelengths λ . This rule,

$$n\lambda = 2d \sin \theta, \quad (4.2.5)$$

is called the Bragg law. For a few more details on this derivation, see Appx. A.1, and for the proof of the equivalence of the Laue and Bragg conditions, see Appx. A.2.

One very simple application of Bragg's law is a monochromator, which is an optical device used to pick out a specific energy of a white beam.* A typical source used for scattering experiments will send out many wavelengths in the same beam, and for particular experiments it is necessary to have only one specific (and known) wavelength on the sample. A monochromator is simply a known crystal, typically lead, silicon, or pyrolytic graphite (PG), put into the incoming beam at an angle θ (as illustrated in Fig. 4.2(b)) where the Bragg law is met for the wanted wavelength. The sample is then placed at an angle 2θ from the incoming beam, where the monochromatic beam will be.

4.2.3 The structure factor for specific crystal symmetries

The Laue and Bragg conditions both say the same thing: diffraction can only take place when the conditions are met such that $S_N(\mathbf{q}) \neq 0$. However, the structure factor $F_{\text{u.c.}}(\mathbf{q})$ determines whether or not there will actually be diffraction in the given spot, and how big it will be. If $|F_{\text{u.c.}}(\mathbf{q})|^2 = 0$, there will be no diffraction, even if the Laue and Bragg conditions are met.

Depending on the given crystal structure, there are certain reflection patterns that are always present independent of the actual unit cell contents – simply given by the symmetry. Some of these for the general translational symmetry elements are summarized in Tab. 4.1. These conditions tell when $|F_{\text{u.c.}}(\mathbf{q})|^2 \neq 0$, not what the value is when it is non-zero. Adding to these, specific space group symmetries will have their own reflection patterns – which is a great help when initially trying to get a structural model for a crystal from a measured reflection pattern. Below, I will go through some of the space groups used for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$.

$I4/mmm$

The tetragonal space group $I4/mmm$ (number 139 in ITfC) is of the $4/mmm$ crystal class, and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ is in this space group when in the tetragonal state.

*Calling a beam “white” means that it contains a continuum of energies – using the naming convention known from optical light.

Symmetry element		Condition for reflection to be present
Primitive lattice	P	none
Base-centered lattice	A	$k + l = 2n$
	B	$h + l = 2n$
	C	$h + k = 2n$
	I	$h + k + l = 2n$
Body-centered lattice	I	$h + k + l = 2n$
Face-centered lattice	F	$h + k, h + l, k + l = 2n$

Table 4.1: Some systematic reflection conditions due to translational symmetry elements of the lattice symmetries. Here n is an integer.

Apart from the $h + k + l = 2n$ condition given in Tab. 4.1, there are several other reflection conditions for scattering from crystals with the $I4/mmm$ space group. These are given in Tab. 4.2.

It is worth mentioning that in order to work together with the following orthorhombic space groups, sometimes a larger unit cell is chosen where the lattice vectors coincide with the orthorhombic cell, [144]. This unit cell, $F4/mmm$, has the **a** and **b** lattice vectors rotated 45° around the **c** axis and enlarged so the unit cell side is $\sqrt{2}$ times the $I4/mmm$ side length. The reflection conditions for this unit cell are also shown in Tab. 4.1.

Bmab

The orthorhombic space group $Bmab$ is of the mmm crystal class. This is the typical space group to use for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ in the orthorhombic phase, although sometimes $Cmca$ (number 64 in ITfC) is used instead*. $Cmca$ and $Bmab$ are related by a different choice of unit cell basis vectors – $Bmab$ is a variant of $Cmca$ chosen to keep the notation closer to $I4/mmm$ by making the **c** axis the same.

The $Bmab$ choice of basis vectors has $a < b < c$, and is switching the **b** and **c** axes, with a change of sign with respect to the $Cmca$ space group, following

$$\{\mathbf{abc}\}_{Cmca} = (100/001/0\bar{1}0)\{\mathbf{abc}\}_{Bmab} \quad (4.2.6)$$

When nothing else is mentioned, I will be using the $Bmab$ notation rather than the $Cmca$ notation in this thesis.

Often, even when $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ is in the tetragonal phases, the $Bmab$ space group is still chosen. This is a bigger unit cell with less symmetry, and will in the tetragonal case have $a = b$, but when using this unit cell for both the orthorhombic and tetragonal phases, it is easier to follow what happens through the transition.

Apart from the $h + l = 2n$ condition given in Tab. 4.1, there are several other reflection conditions for scattering from crystals with the $Bmab$ space group. These are given in Tab. 4.2 along with the same rules for $Cmca$ for comparison.

Fmmm

The orthorhombic space group $Fmmm$ (number 69 in ITfC) is also of the mmm crystal class. This space group is typically used for a secondary phase with disordered tilts as a reaction to interstitial oxygen, [72].

Apart from the $h + k, h + l, k + l = 2n$ condition given in Tab. 4.1, there are several other reflection conditions for scattering from crystals with the $Fmmm$ space group. These are given in Tab. 4.2.

*Note that $Cmca$ ($Bmab$) has actually been renamed to $Cmce$ ($Bmcb$) in newer versions of ITfC because of an ambivalence with the naming scheme. I have chosen to keep the old naming scheme in this thesis, to not be conflicting with older literature.

<i>I4/mmm</i>	<i>F4/mmm</i>	<i>Cmca</i>	<i>Bmab</i>	<i>Fmmm</i>
$hkl : h+k+l = 2n$	$hkl : h+k, h+l, k+l = 2n$	$hkl : h+k = 2n$	$hkl : h+l = 2n$	$hkl : h+k, h+l, k+l = 2n$
$OkI : k+l = 2n$	$OkI : k, l = 2n$	$OkI : k = 2n$	$OkI : l = 2n$	$OkI : k, l = 2n$
$hOl : h+l = 2n$	$hOl : h, l = 2n$	$hOl : h, l = 2n$	$hk0 : h, k = 2n$	$hOl : h, l = 2n$
$hk0 : h+k = 2n$	$hk0 : h, k = 2n$	$hk0 : h, k = 2n$	$hOl : h, l = 2n$	$hk0 : h, k = 2n$
$h00 : h = 2n$	$h00 : h = 2n$	$h00 : h = 2n$	$h00 : h = 2n$	$h00 : h = 2n$
$Ok0 : k = 2n$	$Ok0 : k = 2n$	$Ok0 : k = 2n$	$00l : l = 2n$	$Ok0 : k = 2n$
$00l : l = 2n$	$00l : l = 2n$	$00l : l = 2n$	$Ok0 : k = 2n$	$00l : l = 2n$
$hhl : l = 2n$	$hhl : h+l = 2n$			
	$hh0 : h = 2n$			

Table 4.2: Reflection conditions for specific space groups, not showing the special conditions for specific atom sites. Here n is an integer. Grey values are only there for completeness, since they are equivalent of the condition above them because of the symmetry. The conditions for *I4/mmm*, *Cmca*, and *Fmmm* are directly from ITfC, while the conditions for *Bmab* are derived from the *Cmca* conditions.

4.3 Diffraction from disordered crystals

So far, I have been describing crystals as infinite perfectly repeating lattices with perfectly placed atoms, but the crystals in nature are not always so immaculate. There are many effects that can affect the crystal structure to be distorted in many different ways, which will all alter the scattering from the structure. Here, I will simply focus on twinning and modulation, which are both important for the work done in this thesis.

4.3.1 Twinning

Twinning happens when a crystal contains two or more single crystals of the same lattice and unit cell, but with different orientations, grown together in a way that they have a real axis (and hence a reciprocal plane) or a real plane (and hence a reciprocal axis) in common. The relation between the single crystal twins is described by a twin element, which is basically a symmetry element which only acts between the twin domains, instead of acting on each unit cell. Twinning can happen in several different ways – *e.g.* by applying stress or temperature changes to a sample and hence going through a phase transition (transformation twins) or by the natural growing of the crystal (growth twins).

The scattering pattern from a twinned crystal will often be split into several separate reflections, as illustrated in Fig. 4.4(a) for a four-domain twinned crystal. I will go further into detail with the specific twinning happening in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ in Sect. 6.3, where I will also illustrate the twinning in real space.

4.3.2 Modulated structures

A crystal structure can be modulated, which means that a part of the structure cannot be described with the usual ordering of the normal translational lattice, but instead show a continuous variation of atom positions, site occupations (on average, how many times the atom is actually there in the unit cell), or displacement factors (describing the variations of the atom position over time) over the unit cells.

The modulation can usually be described by a suitable periodic function, and often a sine function is used. The modulation can be divided into two different categories: commensurate and incommensurate.

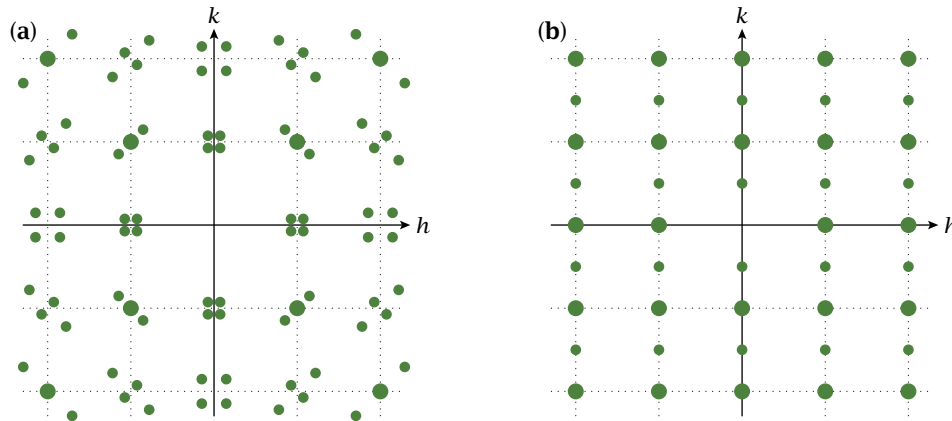


Figure 4.4: Examples of $(hk0)$ reciprocal space patterns from (a) an orthorhombic crystal with four twin domains rotated around the c axis in relation to each other, and (b) a commensurately modulated structure, where an element repeats itself only every two unit cells along b . The dots represent the reflection positions, not intensities, and the gridlines indicate integer h and k values.

Commensurate modulation

If the wavelength of the periodic function describing the modulation is a rational small multiple of the basic unit cell length, the modulation is commensurate, and the resulting effect is a so-called superstructure, where the resulting diffraction pattern has reflections between the usual structural positions – at $1/n$ distances along the reciprocal lattice vectors. The crystal system can be described with a correspondingly big supercell, made up of n unit cells completing a full period of the modulation.

Repeating the super cell with simple translation (as is usually done for the simple unit cell), the new – bigger – structure is no longer modulated. A simple example of this type of modulation is shown in Fig. 4.4(b).

Incommensurate modulation

If the wavelength is, however, an irrational multiple of the unit cell, the modulation is incommensurate, and a supercell cannot be chosen directly. The reflection pattern for this type of modulation will typically contain so-called satellite reflections grouped around the main reflections in sometimes very intricate patterns.

For both types of modulation, the superstructure reflections are indexed with so called propagation vectors, which relate the superstructure reflection to the corresponding normal reflection. For the example modulation in Fig. 4.4(b), this would be $\mathbf{q} = (0, 1/2, 0)$. For an incommensurate modulation, the propagation vector can not be written with nice fractions, and will instead be irrational.

4.4 X-rays

The most commonly used probe for scattering is X-rays – electromagnetic radiation with wavelengths in the region between 0.1 and 100 Å. X-rays with small wavelengths (up to 1 Å) are typically referred to as hard X-rays, and are used for crystallography. Larger wavelength X-rays are less useful, since they are very easily absorbed instead of being scattered.

The most important property of an X-ray beam is the wavelength λ - or wave vector $k = 2\pi/\lambda$ - which can also be expressed as the energy E by

$$E = \frac{hc}{\lambda} = \hbar ck, \quad (4.4.1)$$

where h (and $\hbar = h/2\pi$) is Planck's constant and c is the speed of light. The relation between these different expressions of the energy of the X-ray beam is shown in Fig. 4.5, where the different naming conventions for hard and soft X-rays are also indicated.

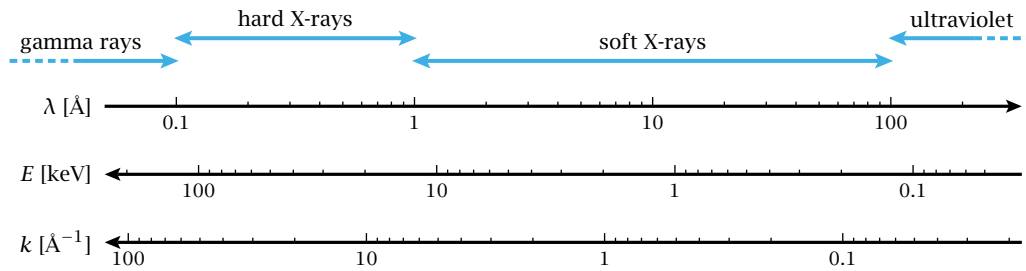


Figure 4.5: Relating different energy units for X-rays. Hard X-rays and the high-energy end of the soft X-rays are what is typically used for crystallography. Note that the wavelength axis (λ) goes in the opposite direction of the others.

X-rays scatter from the electrons in the sample material via an electromagnetic interaction. This means that the scattering length b in the diffraction results above - Eqs. (4.1.5) to (4.2.3) - is replaced with a $\mathbf{q}$ dependent expression,

$$-r_0 f^0(\mathbf{q}) = -r_0 \int \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r}, \quad (4.4.2)$$

where $r_0 = 2.82 \times 10^{-5}$ Å is the Thompson scattering length of the electron. The integral $f^0(\mathbf{q})$ is called the atomic form factor*, and is the Fourier transform of the distribution of electrons in the atom, $\rho(\mathbf{r})$. For $\mathbf{q} = 0$, the atomic form factor is equal to the atomic number, Z , while $f^0(\mathbf{q})$ tends to zero for higher $\mathbf{q}$ lengths.

This means that the measured scattering of X-rays from a given atom will be proportional to Z^2 , following Eq. (4.1.13).

4.4.1 Extinction

It is sometimes necessary to take extinction into account when doing single crystal diffraction experiments. Real crystals are not perfect, but really consist of a mosaic of small perfect blocks with a thin distribution of orientations around some average value - called mosaicity.

If the size of the mosaic blocks are large, the risk of a scattered beam being scattered a second time, or even multiple times, increases. These multiply scattered beams can interfere destructively with each other, resulting in the integrated intensity from the diffraction being reduced. This is called primary extinction.

When the X-ray beam enters the crystal, some of it diffracts from the top layers of the crystal structure, while other parts of the beam go deeper, gradually being reflected in deeper and deeper layers, and finally a part of the beam might transmit all the way through the sample. The reflections from the deeper layers will naturally see a smaller flux in the incident beam, since some of the beam has already been reflected - and hence again the integrated intensity from the diffraction is reduced. This is called secondary extinction.

*I am here ignoring the energy-dependent dispersion corrections f' and f'' , which should be added to f^0 to get the total atomic form factor $f(\mathbf{q}, \hbar\omega) = f^0(\mathbf{q}) + f'(\hbar\omega) + if''(\hbar\omega)$ which takes resonant scattering and dissipation into account. These are only important at very specific energies, dependent on the given atomic element.

Extinction happens for crystals that are “too” perfect – meaning that they consist of very few mosaic blocks, resulting in both primary and secondary extinction being large effects. If instead the crystal is “ideally imperfect”, the mosaic blocks have the right size and angular distribution to let the integrated intensity from the scattering be large, but not too imprecise. Even in this scenario, secondary extinction can still be a significant effect, and might only be eliminated by use of a smaller sample.

4.4.2 X-ray production

X-rays used for crystallographic research are often produced in local laboratories, where X-ray tubes with rotating anodes (typically made of copper, chromium, or molybdenum) generate X-ray radiation from bremsstrahlung as well as fluorescent radiation specific for the anode material (typically the K_α and K_β lines, which have energies between 5 and 9 keV, [145]). However, when a highly collimated and small, or a higher energy, beam is needed, these types of X-ray sources are not the best option – instead the experiment is moved to a synchrotron.

Synchrotron radiation is a generic term used to describe radiation from charged particles at relativistic speeds, forced to travel along a curved path. Typically, electrons or positrons are kept in a storage ring, travelling around the ring in a controlled closed orbit by bending magnets. The synchrotron radiation is produced either directly at the bending magnets, or by insertion devices such as wigglers and undulators, which use alternating magnetic fields to force the electrons into oscillating paths, emitting even more radiation.

An important property for X-ray sources is the so-called brilliance, which is an attempt to collect some of the many properties the beam can have into one quantity,

$$\text{Brilliance} = \underbrace{\frac{\text{photons per second}}{\text{mm}^2 \text{ source area}}}_{\text{flux}} \underbrace{\frac{1}{\text{mrad}^2}}_{\text{divergence}} \underbrace{\frac{1}{0.1\% \text{ bandwidth}}}_{\text{monochromaticity}}. \quad (4.4.3)$$

The divergence is the angular spread in the beam, set by the vertical and horizontal beam slits, while the monochromaticity is the photons which fall within a bandwidth of 0.1% of the central wavelength given by the monochromator.

Typical 3rd generation synchrotron sources have brilliances of more than ten orders of magnitude larger than rotating anode sources at the K_α line. A new type of pulsed X-ray source, the free electron laser, even exceeds this with several more orders of magnitude.

4.5 Neutrons

A much less common probe to use for scattering is neutrons – the neutrally charged nuclear particle. Neutrons are not usually found in their free form, since they are unstable outside nuclei and decay to protons with a mean lifetime of 885.7(8) s, [146]. However, different more or less violent reactions can force them out of their nuclei to be used as a scattering probe.

Neutrons scatter from the nuclei in the sample material via the strong nuclear force. The scattering length b will depend on the element and isotope of the nucleus in a non-trivial way, and has been tabulated for most isotopes, [147].

Just as for X-rays, the wavelength λ (or wave vector $k = 2\pi/\lambda$) is the main property of a neutron beam. This works by seeing the neutron – a particle – as a wave with a corresponding de Broglie wavelength,

$$\lambda = \frac{h}{m_n v}, \quad (4.5.1)$$

where v is the speed of the neutron, m_n is the neutron mass, and h is Planck's constant. The calculation of the corresponding energy is a little more complicated than Eq. (4.4.1) for photons,

$$E = \frac{h^2}{2\lambda^2 m_n} = \frac{\hbar^2 k^2}{2m_n}, \quad (4.5.2)$$

with $\hbar = h/2\pi$. Finally, it is also possible to give the energy of the neutron as an equivalent temperature by

$$T = \frac{E}{k_B}, \quad (4.5.3)$$

where k_B is Boltzmann's constant.

The relation between these different expressions of the energy of the neutron beam is shown in Fig. 4.6, where the different naming conventions for temperatures for the neutrons are also indicated.

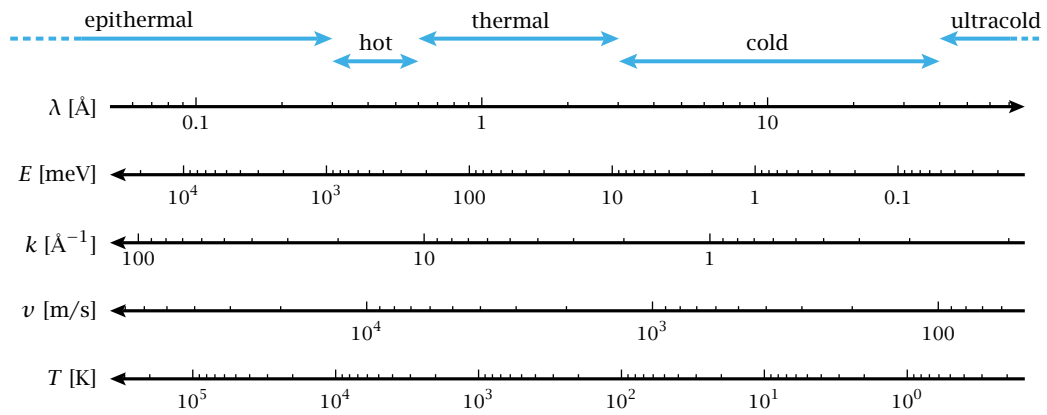


Figure 4.6: Relating different energy units for neutrons. Typically, neutrons in the thermal region are used for crystallography. Note that the wavelength axis (λ) goes in the opposite direction of the others.

4.5.1 Incoherent scattering

It is worth noting that neutrons interact with the nuclear spin, which results in an overall incoherent scattering which gives a constant non-interfering scattering of neutrons in all directions. This scattering is usually not included in the tabulated scattering lengths, but is instead listed as a incoherent scattering cross section for any given element.

4.5.2 Inelastic scattering

Since neutrons with typical wavelengths around inter-atomic distances in crystals at the same time have energies comparable to elementary excitations in the same materials, they are often used for inelastic scattering as well, where they deliver or receive energy in the scattering interaction. In this way, it is possible to measure both static structure and dynamic behavior in the same measurement, which is difficult to do with X-rays.*

4.5.3 Neutron production

Neutrons used for crystallographic research are most often produced at one of two source types: spallation sources or nuclear fission reactors.

*It is possible to do inelastic X-ray scattering at very specific resonant energies, by doing X-ray Raman scattering, or by certain triple-axis setups, [73], but I will not go into detail with this here.

The oldest type of the two – the fission reactor – relies on the chain reaction of the fission process

$$^{235}\text{U} + n \rightarrow \text{D}_1 + \text{D}_2 + 2.3n + Q, \quad (4.5.4)$$

where the daughter nuclei D_1 and D_2 can be a range of elements, and the released energy Q is of the order 200 MeV. The excess neutrons coming out of each reaction is on average 1.4, [74].

The most powerful reactor neutron source in the world is located at Institut Laue Langevin (ILL) in Grenoble, France, and yields a power of 58.3 MW [153]. These sources are typically continuous, with the notable exception of the source in Dubna, Russia. Here, reflectors mounted on a spinning wheel create a pulsed beam by making the reactor become periodically overcritical, yielding a power of 1850 MW during the pulse, [138].

In order to get a really high neutron flux from a fission reactor, it is necessary to develop cooling materials to remove the heat quickly enough to keep the fission reaction cross section large. However, for really large fluxes, this is simply not possible – and spallation sources have to take over. Spallation sources instead rely on 1-3 GeV proton accelerators bombarding a target consisting of heavy neutron-rich nuclei, such as tungsten, mercury, or lead. The heavy nuclei are destroyed in the process, releasing in the order of 10 to 12 neutrons per proton, [75].

Spallation sources are typically pulsed, with pulses ranging from 1 μs to 3 ms, with 20 to 60 pulses per second, [76]. An exception to this is the semi-continuous source SINQ at the Paul Scherrer Institute (PSI) in Villigen, Switzerland, where a continuous proton beam hits a lead target.

For both source types the neutrons are of high energy when they are just produced, and have to be slowed down in order to be useful for scattering. This is done in moderators consisting of materials with a high density of hydrogen nuclei. Neutrons entering a moderator collide with the hydrogen nuclei and lose energy, eventually exiting following a Maxwellian energy distribution given by the temperature of the moderator.

4.6 Choosing between X-rays and neutrons

X-rays interact with the spatial distribution of electrons in the material via an electromagnetic interaction, while neutrons interact with the atomic nuclei via the strong nuclear force. The obvious large difference from this is the fact that X-rays have the same scattering length for different isotopes, while neutrons will have different scattering lengths, see Fig. 4.7. Scattering lengths for X-rays are simply calculated* using $b = r_0 Z$, while for neutrons it is tabulated, e.g. $b_{1\text{H}} = -3.74 \text{ fm}$ and $b_{2\text{H}} = 6.67 \text{ fm}$.

A selection of a few other pros and cons of the two types of probes are shown in Tab. 4.3.

While X-rays are easy and fairly cheap to produce in a small laboratory and possible to produce at enormous intensities at synchrotrons, neutrons are difficult to obtain – hardly possible at smaller laboratories, and hence experiments have to be performed at large facilities. With X-rays, only a small sample mass is needed because of this huge flux, whereas relatively large samples are needed in neutron experiments. It is also worth noting that because of the difference in interaction strength, typical X-ray experiments are very short compared to typical neutron experiments of similar investigations. Because of incoherent scattering, neutron experiments will inherently have large background signals compared to X-ray experiments, which should also be factored in when choosing.

However, neutrons do not get absorbed as quickly as X-rays because of the lower interaction rate, and the sample environment can be created out of less absorbing metals which would still be opaque for X-rays (unless the X-ray energy is very high). Hence, neutrons are better for uses

*The $b = r_0 Z$ is of course only for $\mathbf{q} = 0$. For other $\mathbf{q}$, the atomic form factor f^0 from Eq. (4.4.2) has been calculated as an approximate function $\sum_{n=1}^4 a_n \exp(-b_n q^2 / (4\pi)^2) + c$, where a_n , b_n , and c are tabulated.

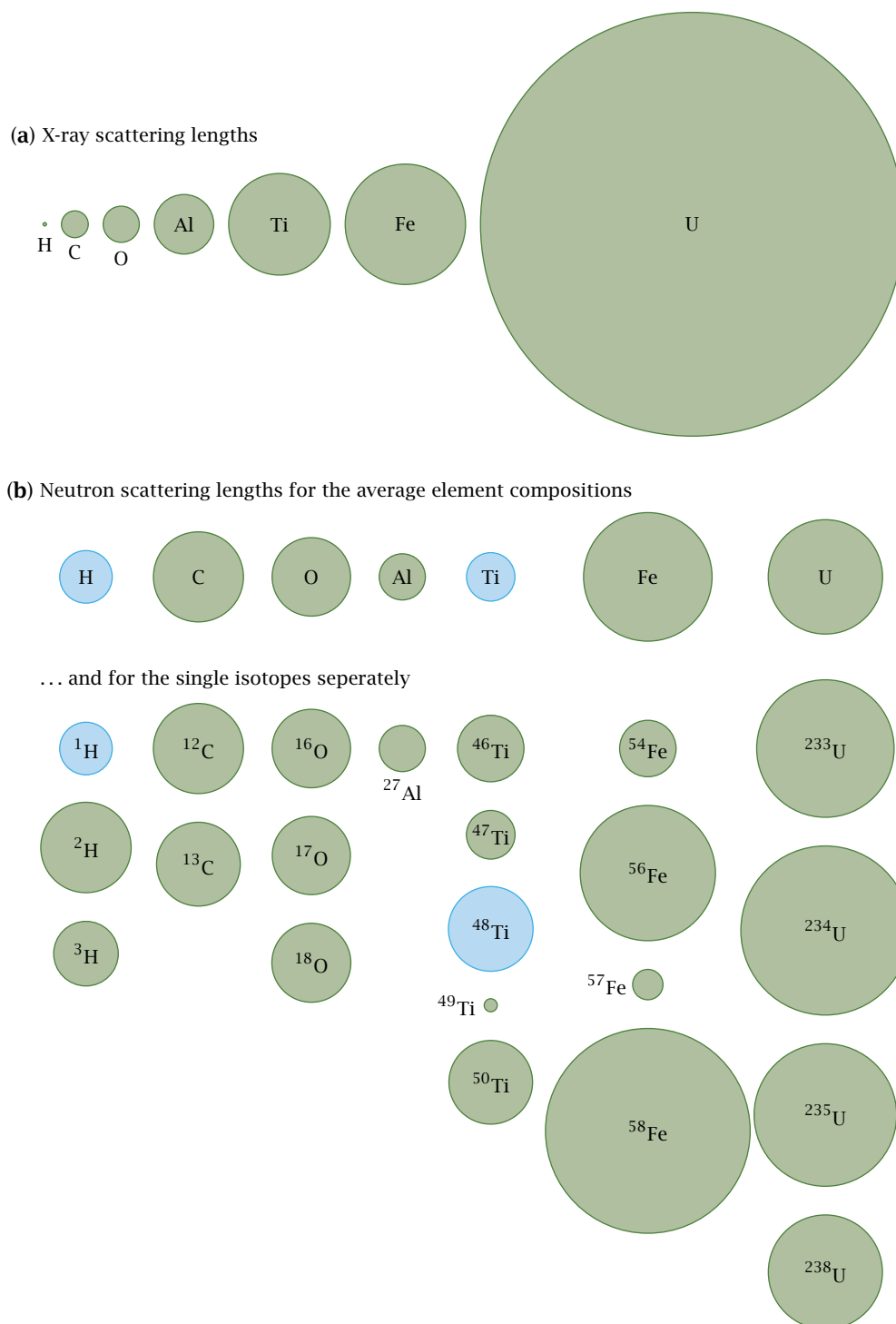


Figure 4.7: Illustration of some typical (a) 100 keV X-ray and (b) thermal neutron scattering lengths. Values are proportional to the area diameters (different factors multiplied on X-rays and neutrons, though) and blue areas indicate negative values. X-ray data from [148, 149] and neutron data from [147].

	X-rays	Neutrons
Distinguishing isotopes	✗ No	✓ Yes
Easy to produce	✓ Yes	✗ No
Required sample size	✓ Small	✗ Big
Measurement times	✓ Short	✗ Long
Low background	✓ Yes	✗ Perhaps (incoherent scattering)
Absorption	✗ High	✓ Low
Light elements visible	✗ No	✓ Yes
Scattering at high q	✗ Low	✓ Yes
Sees magnetism	✗ Very little	✓ Yes

Table 4.3: A few positive and negative impacts of choosing either X-rays or neutrons for crystallographic scattering experiments.

where the sample environments are extreme, as when high pressures, large magnetic fields, or very low temperatures are needed. Neutrons are also more interesting to use when working with light elements, and contrast matching is possible by balancing isotope concentrations. It is also necessary to consider that the scattering falls off towards zero for higher scattering angles (higher q) for X-rays, while it stays independent of the angle for neutrons.

Finally, neutrons interact with magnetic structures in the sample at a comparable strength of the interaction with the spatial structure, and can hence be used to investigate magnetic phenomena – something which is very hard to do with X-rays.

5

Phase transitions

A phase transition is the transition of matter from one state to another under the influence of for instance temperature, pressure, or applied magnetic or electric fields. To mention a few examples, the transition could be between a solid and a liquid, a paramagnet and a ferromagnet, or a normal metal and a superconductor.

In this chapter, I will briefly go through temperature driven phase transitions and explain the importance of the critical exponents describing these.

5.1 The order parameter

A system can typically be described by a so-called order parameter μ as a measure of the symmetry (or order) which disappears in the system at the phase transition. The magnitude of the order parameter will be zero when fully in the disordered phase, and non-zero when in the ordered phase.

Examples of order parameters are the net magnetization for magnetic phase transitions and atomic displacements for structural transitions.

For magnetic transitions, the system usually changes from a high-temperature disordered phase with randomly oriented atomic magnetic moments into a low-temperature ordered phase with the magnetic moments in a well defined structure.

For structural transitions, the system commonly changes from a high-temperature ordered phase into a low-temperature phase which is a distorted version of the high-temperature phase. This means that the symmetry is broken such that some of the symmetry operations of the high-temperature phase are not symmetry operations of the low-temperature phase.

5.2 First order phase transitions

The order of a phase transition is traditionally given by the order of the lowest differential of the free energy which shows a discontinuity at the transition. A first order phase transition has a discontinuity in the first derivative of the free energy, *e.g.* in the volume, entropy, or magnetization.

Such transitions are characterized by a latency where the system releases or absorbs energy in a coexistence region, where some parts of the material have gone through the transition while other parts have not. Only after a fixed amount of energy has been exchanged has the full system transitioned to the new phase. A well-known example of this is water boiling, where the

water does not instantly turn into vapor, but instead is a turbulent mixture of liquid water and steam bubbles at a constant temperature until enough energy (the latent heat of vaporization) has been transferred for the whole system to change into steam.

5.3 Continuous phase transitions

A continuous phase transition,^{*} also called a second order phase transition, is traditionally considered to have a discontinuity in the second derivative of the free energy, *e.g.* in the compressibility or heat capacity. In reality, the free energy is actually not analytical in the transition point, which makes the name “second order” slightly deceptive.

In a simple sense, a continuous phase transition happens as follows: While still in the initial ordered phase, small domains of the disordered final phase gradually grow already a distance from the critical temperature (or critical field, etc.) for the transition. At the actual phase transition the disordered domains have grown together into a large volume stretching through the full system, covering about half of the total system volume. After the transition, the domains that are still in the ordered phase will gradually break up into smaller and smaller domains, each growing smaller until the system is fully disordered.

Examples of temperature dependent continuous phase transitions are many magnetic transitions and the superconducting transition.

5.3.1 The critical exponent

A continuous phase transition can be described by quantitative Landau theory (equivalent to mean field theory), [31, 32], where the free energy is written in polynomial expansions as powers of the relevant order parameter. When the phase transition becomes more complicated (*e.g.* including long range interactions) and cannot be described by Landau theory, it can instead be described by a more general renormalization group theory, [77, 78].

With both Landau and renormalization group theory – often referred to collectively as describing Landau-like behavior – the magnitude of the order parameter μ will follow a power law of the temperature T towards the transition point at the critical temperature T_c . This takes the form

$$\mu(T) \propto \begin{cases} \left| \frac{T - T_c}{T_c} \right|^\beta & \text{for } T \leq T_c \text{ (ordered phase),} \\ 0 & \text{for } T \geq T_c \text{ (disordered phase),} \end{cases} \quad (5.3.1)$$

where β is a so-called critical exponent.[†] The fraction $(T - T_c)/T_c$ is often called the reduced temperature t . Widely varying phase transitions follow this very general power law, which seems surprising – but has nonetheless been verified over and over with experiments and theory alike.

Note that the measured intensity from a scattering experiment will typically be $I \propto \mu^2$, and hence in literature it happens that β is replaced by 2β . In this thesis I will always use the notation β to denote the critical exponent for the order parameter as written in Eq. (5.3.1).

5.3.2 Universality classes

The value of β gives important information about the nature of the phase transition. If the system follows Landau theory directly, β will equal $1/2$ – but this is often not the case. All

^{*}The “continuous” in this name comes from the fact that it is continuous in the first derivative of the order parameter, as opposed to first order phase transitions.

[†]There are a number of other critical exponents defined similarly to β , describing the behavior following changes in magnetic field etc., but I will not go into further detail with this here. Because of this, β is sometimes alternatively named simply the order parameter exponent, since it determines the behavior of the order parameter as a function of temperature.

	Landau	2D Ising	3D Ising	3D XY	3D Heisenberg
d	any	2	3	3	3
D	any	1	1	2	3
β	$1/2 = 0.5$	$1/8 = 0.125$	0.326	0.349	0.367
Ref.	Blundell [2]	Blundell [2]	Blundell [2]	Campostrini <i>et al.</i> [84]	Blundell [2]

Table 5.1: Examples of critical exponents for various models of system dimension d and order parameter dimension D .

types of phase transitions can, however, be split up into categories by characterizing them into so-called universality classes with three pieces of information: the dimensionality of the system, d , the dimensionality of the order parameter, D , and whether the forces of the system are long or short range.

It turns out that each universality class, independent of the smaller details of the systems, have the same critical exponents. For example, the critical exponents for the phase transition between a gaseous and liquid phase is independent of the chemical composition of the liquid, [79, 80].

Most systems with $d = 1$ do not have continuous phase transitions, while all systems with $d \geq 4$ – and many long range interactive systems – follow Landau theory exactly. The specific case of $d = 2$ and $D = 1$ can be solved with the 2D Ising model, however most real systems have $d = 3$ and short range interactions, which turns out to be hard to solve exactly. Some examples of the value of β for different model systems are given in Tab. 5.1.

Most $d = 1$ systems cannot have phase transitions, [81], however a few specific examples defy this. Examples are the “un-zipping” of DNA molecules, [82], and the roughening of “steps” on a crystal surface cut at a small angle to a close-packed plane, [83].

5.3.3 Saturation of the order parameter

At low temperatures some systems tend to no longer follow the power law in Eq. (5.3.1). Instead, the order parameter shows a temperature-independent behavior below the so-called saturation temperature T_s , [85].

This effect is illustrated in Fig. 5.1, where the order parameter plateaus off in the low-temperature region instead of following the power law.

5.3.4 The critical scattering region

At temperatures close to the transition temperature T_c , sometimes fluctuations will dominate the system, and the order parameter will no longer follow the simple power law from Eq. (5.3.1), [86]. This effect comes from the mixing of phases happening close to the transition, as explained in the beginning of this section.

This effect is also illustrated in Fig. 5.1, where the order parameter does not fall as sharply as expected in the temperature region close to T_c .

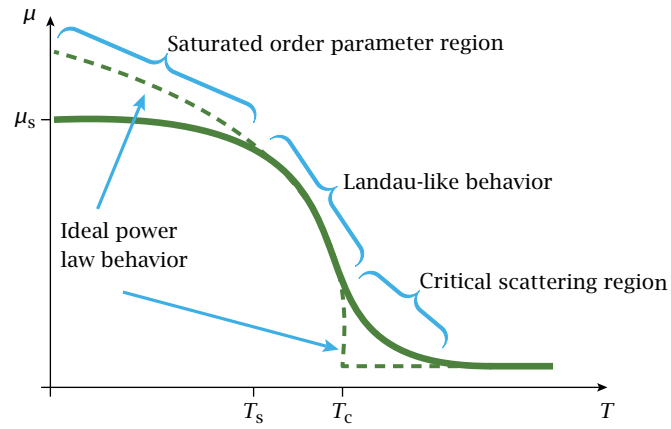


Figure 5.1: Illustration of a typical phase transition deviating from the ideal Landau-like power-law behavior. The order parameter μ saturates to μ_s at low temperature T , starting the deviation from the Landau-like behavior at the saturation temperature T_s , and there is critical scattering close to the critical temperature T_c .

The $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ compound

As mentioned in Chap. 2, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compound was first seen to be superconducting in 1987 when replacing Ba with Sr in the superconducting $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ compound. It was later found that doping the mother compound La_2CuO_4 with O also lead to a superconductor, and investigations has continued with co-doping with both Sr and O to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$.

In this chapter I will go through some of the properties of this family of compounds, mentioning in particular results on the structural nature.

6.1 The mother compound La_2CuO_4

The mother compound of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, the undoped material La_2CuO_4 , is an antiferromagnetic Mott insulator, [87]. A Mott insulator is a type of material where the conductivity vanishes for temperatures tending towards zero, while standard band theory would instead predict it to be metallic, [88].

The room-temperature crystal structure was first solved by Longo *et al.* [89] and later refined further by Grande *et al.* [90] to be a slightly distorted K_2NiF_4 structure (in the ortorhombic *Bmab* space group). The structure has oxygen in an octahedral coordination around the Cu^{2+} ions, as illustrated in Fig. 6.1 (where the ortorhombic unit cell is shown – this can be compared to the tetragonal unit cell shown in Fig. 2.7(a) on p. 10). As mentioned earlier in Subsect. 2.2.2 on cuprates, La_2CuO_4 is a layered perovskite, formed by layering two-dimensional sheets of CuO_2 planes with LaO between the planes.

The oxygen octahedra are seen to tilt around the $[110]$ or $[1\bar{1}0]$ directions (in tetragonal notation, meaning around *a* in ortorhombic notation). This distorts the structure from a simple tetragonal structure to an ortorhombic with the same *c* axis, as illustrated in Fig. 6.2, where the structure change is illustrated for a single CuO_2 layer, also showing the unit cell choices.

6.2 Doping

Hole-doping the mother compound changes it from an insulator – with one electron per Cu^{2+} – to a metal, [91]. In practice, the doping removes electrons from the copper-oxide planes (inserts holes), allowing electrons to move freely in the planes, and hence opening up for superconductivity.

The classic way of hole-doping La_2CuO_4 is by substituting Sr for La, creating random substitution sites in the crystal structure. Another way to hole-dope is by intercalating oxygen,

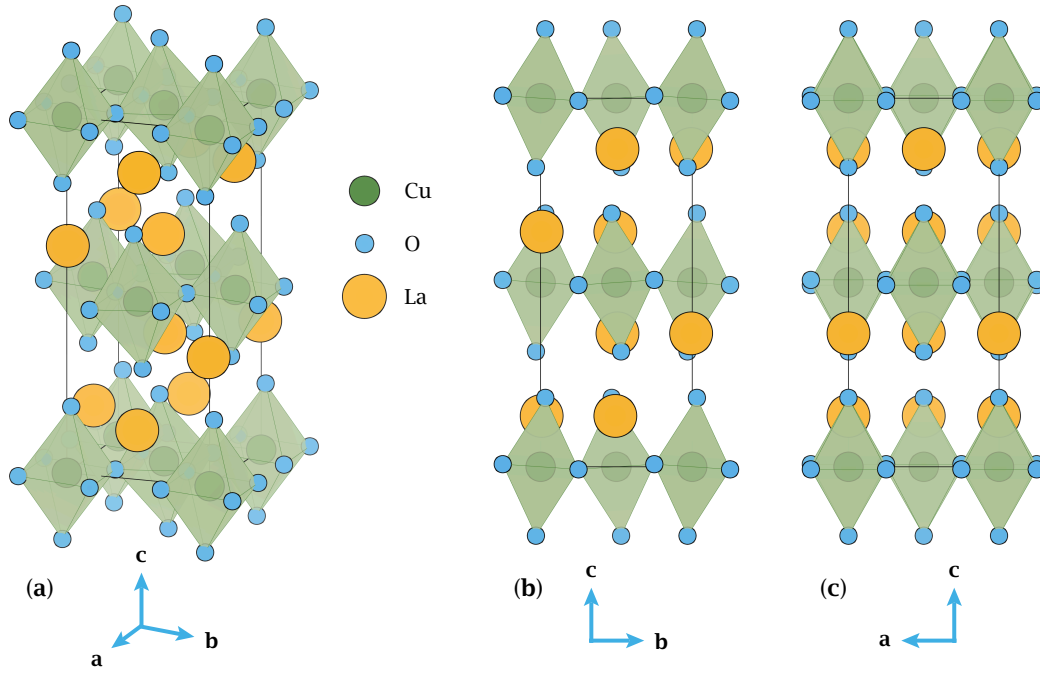


Figure 6.1: The $Bmab$ crystal structure of La_2CuO_4 as solved by Grande *et al.* [90] (see also Tab. B.2). The full view in 3D is shown in (a), while a rotated view from (b) the a axis and (c) the b axis show the octahedral tilts that are only around the a axis. Figures are created using VESTA, [163].

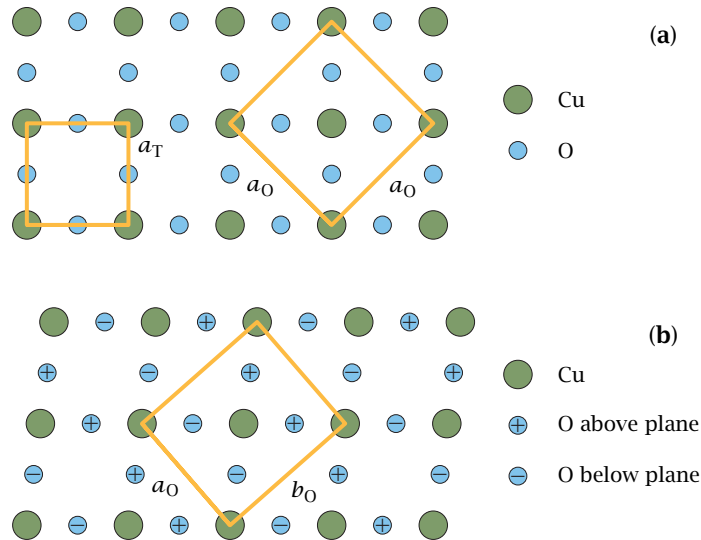


Figure 6.2: (a) The copper-oxide plane as seen along the c axis, showing the tetragonal (left) and orthorhombic (right) unit cell conventions. (b) When crossing the tetragonal to orthorhombic phase transition, the oxygen atoms are displaced above and below the copper plane because of the oxygen octahedral tilt, now only described with the orthorhombic unit cell, where $a_O < b_O$.

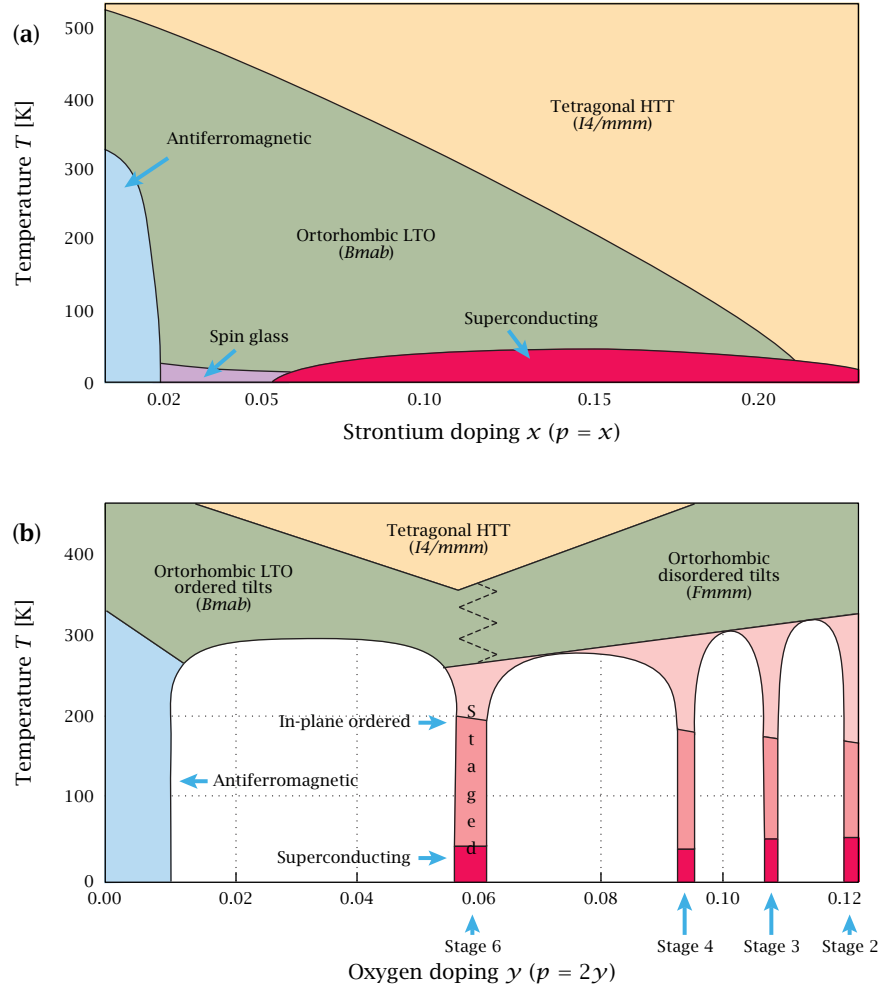


Figure 6.3: Phase diagrams when doping La_2CuO_4 with either (a) strontium to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ or (b) oxygen to $\text{La}_2\text{CuO}_{4+y}$. The concentration p of holes per Cu atom in a CuO_2 sheet is given in parenthesis on the two first-axes, [92]. Adapted from [72, Fig. 1].

yielding the compound $\text{La}_2\text{CuO}_{4+y}$. Whereas the superconductivity in the first type of hole-doping is strongly and non-monotonically dependent on the amount of Sr doping as shown in Fig. 6.3(a), the transition temperature by oxygen doping seems to be almost constant and just above the optimal for Sr doping alone as shown in Fig. 6.3(b). This could be a consequence of clustering and superstructures of the intercalated oxygen. In the following, I will go a little more into detail with the different doping types.

6.2.1 Doping with strontium to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

Hole-doping the mother compound La_2CuO_4 by substituting La^{3+} with Sr^{2+} results in a superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with critical temperature T_c depending on the doping x , as found by Dover *et al.* [12]. As seen in Fig. 6.3(a), the superconductivity appears at doping $x = 0.055$, [93], and optimal doping resulting in the highest T_c is $x = 0.15$, [94]. The superconductivity disappears completely at $x = 0.28$, [95], and the material behaves as a metal above this.*

*There is also a small anomalous dip in T_c close to $x = 0.125$, which happens for several La-based cuprates, but this is not of interest to this thesis.

6.2.2 Doping with oxygen to $\text{La}_2\text{CuO}_{4+y}$

Hole-doping the mother compound La_2CuO_4 by intercalating O^{2-} results in a superconductor $\text{La}_2\text{CuO}_{4+y}$ with critical temperature higher than with the optimal Sr doping. This was first discovered by Grant *et al.* [96], who saw $T_c \approx 40$ K, although at the time they did not think that the cause was interstitial oxygen. Following Fig. 6.3(b), the material becomes superconducting at a doping of $y \approx 0.055$ with a critical temperature $T_c \approx 32$ K, while higher doping values result in several other separate superconducting phases with critical temperatures as high as $T_c = 45$ K, [72].*

The phase diagram for $\text{La}_2\text{CuO}_{4+y}$, Fig. 6.3(b), is full of miscibility gaps[†], where the oxygen ions phase-separate into oxygen-rich and oxygen-poor regions below 290 K, [99, 100], as well as a wider variety of structures than that for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The reason for this is the mobility of the intercalated O^{2-} ions, which phase separate into regions of oxygen-rich and oxygen-poor regions at temperatures down to 200 K, [100].

6.2.3 Co-doping to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$

Doping with both Sr and O results in a compound which seemingly follows the superconductivity for the O doping, by having a critical temperature $T_c \approx 40$ K independent of the Sr doping, [101].

Just as $\text{La}_2\text{CuO}_{4+y}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ exhibit both antiferromagnetic and superconducting phases, leaving a miscibility gap in the phase diagram similar to what is seen for $\text{La}_2\text{CuO}_{4+y}$. There is no general consensus whether these phases appear in two distinct structural phases or simply exist as different electronic phases in the material as argued by Wells *et al.* [100] and Mohottala *et al.* [102], respectively.

6.3 Crystallographic properties

Where the mother compound La_2CuO_4 is orthorhombic (in the $Bmab$ space group as mentioned in Sect. 6.1) up to a temperature of around 533 K, [89, 90], doping stabilises the tetragonal phase and decreases the orthorhombic distortion, resulting in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ having the phase transition from the LTO to the HTT phase at lower temperatures, depending (monotonically for Sr doping) on the doping, [103], as can also be seen in Fig. 6.3.

As was earlier mentioned, when the compound is doped with interstitial oxygen, it will sometimes phase separate into oxygen-rich and an oxygen-poor phases. This has led to several different combinations of space group choices, such as $Fmmm$ by Radaelli *et al.* [98], $Bmab$ by Rial *et al.* [104], $Fmmm$ in combination with $Bmab$ by Jorgensen *et al.* [105] and Radaelli *et al.* [99], and several different $Bmab$ phases by Chaillout *et al.* [106]. Most of these investigations used powder samples instead of single crystal samples, and it was found that any further conclusions on the space groups would be resulting from measurements on single crystals, [106], however the results are still up for discussion even after these experiments. For now, it seems like the oxygen-rich phase is either in the $Bmab$ or $Fmmm$ space group, while the oxygen-poor phase is widely agreed to be in the $Bmab$ space group, [107]. I will go more into detail on one possible interstitial oxygen superstructure relevant to this discussion, staging, in Subsect. 6.3.2.

For both Sr and O doping, some researchers further report undistorted octahedral tilts, [104, 108], while others report distorted octahedra upon tilting, [105, 106, 109].

*Several experiments give different doping values for different critical temperatures, [92, 97, 98], and hence the superconducting phases presented in Wells *et al.* [72] (as in Fig. 6.3(b)) still need more refinement.

[†]A miscibility gap is, in general, a region in a phase diagram where the compound exists as two or more separate phases, splitting up into other areas of the phase diagram.

Reflection (<i>hkl</i>)	<i>F4/mmm</i> HTT	<i>Fmmm</i>	<i>Bmab</i> LTO	<i>Pccn</i> LTLO	<i>P4₂/ncm</i> LTT
(111)	✓	✓	✓	✓	✓
(200)	✓	✓	✓	✓	✓
(020)	✓	✓	✓	✓	✓
(002)	✓	✓	✓	✓	✓
(014)	✗	✗	✓	✓	✓
(104)	✗	✗	✗	✓	✓
(110)	✗	✗	✗	✓	✓
(100)	✗	✗	✗	✗	✓
(010)	✗	✗	✗	✗	✗

Table 6.1: Overview of a choice of reflections which are allowed and forbidden in different space groups for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$. The two greyed out last columns are for related compound such as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ or $\text{La}_{1.875}\text{Ba}_{0.125-x}\text{Sr}_x\text{CuO}_4$, [110]. Note that because of twinning the reflections might be seen even in the forbidden positions, because *h* and *k* get interchanged. Table from Udby [154, Tab. 2.1].

Other HTSC cuprates have several other crystallographic phases than the earlier mentioned HTT and LTO phases for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, and a small overview of forbidden and allowed reflections for some of these can be seen in Tab. 6.1, to give an idea of how to quickly distinguish them.

It is in generally accepted that the doped interstitial oxygen are placed in the $(1/4, 1/4, 1/4)$ sites of the ortorhombic unit cell, [100, 111], albeit sometimes with a slight displacement along *c*, [101, 104]. See also Tabs. B.3 and B.4 for a couple of structure solution examples, where the interstitial oxygen position is given both for only oxygen doped and co-doped compounds.

6.3.1 Twinning from HTT to LTO

At high temperatures $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ is in the tetragonal (HTT) phase (for suitable values of the dopings *x* and *y*). Cooling the sample down will result in a transition to the ortorhombic (LTO) phase, by tilting the CuO_6 octahedra as mentioned in Sect. 6.1. Because of this tilting, the **a** and **b** axes change to become shorter and longer, respectively (see e.g. [105, Fig. 2]), and the (110) mirror plane from the tetragonal cell is lost, replaced by twin laws. As briefly mentioned in Subsect. 4.3.1, this change in the lattice parameters can result in twinning of the crystal structure, where several domains of different orientations occur in the same crystal, [112].

An example of a (110) twin domain boundary is shown in Fig. 6.4(a), where the tetragonal and ortorhombic lattice parameters are also shown for the bottom right of the two domains, for comparison with Fig. 6.2(b). The two twin domains result in the reciprocal plane shown in Fig. 6.4(b), and a corresponding plane will result from the corresponding perpendicular $(1\bar{1}0)$ twin domain boundary, giving the total reciprocal plane shown in Fig. 6.4(c). Note that the dots in Fig. 6.4(b) and (c) do not show the intensities of the reflections, but simply the positions, and that these reciprocal planes are using the tetragonal notation.

It is possible to calculate the angular distance Δ between two twin reflections by using the illustration in Fig. 6.5,

$$\frac{\Delta}{2} = 90^\circ - 45^\circ - \alpha, \quad \tan \alpha = \frac{a}{b}, \quad (6.3.1)$$

combined to the final result

$$\Delta = 90^\circ - 2 \arctan \frac{a}{b}. \quad (6.3.2)$$

Note that the *a* and *b* here can be both in tetragonal and ortorhombic notation, since the difference is simply a factor of $\sqrt{2}$ on both, cancelling out the difference.

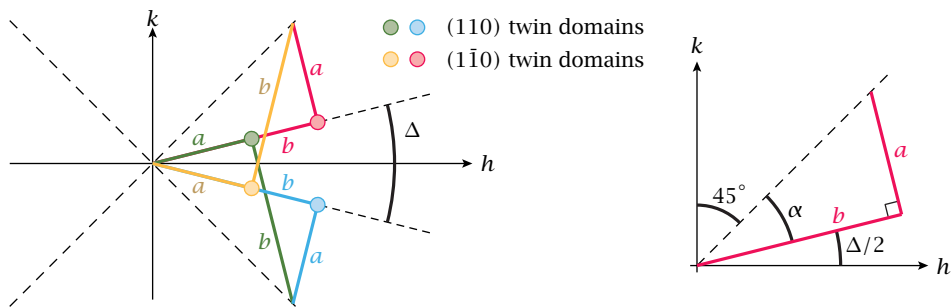
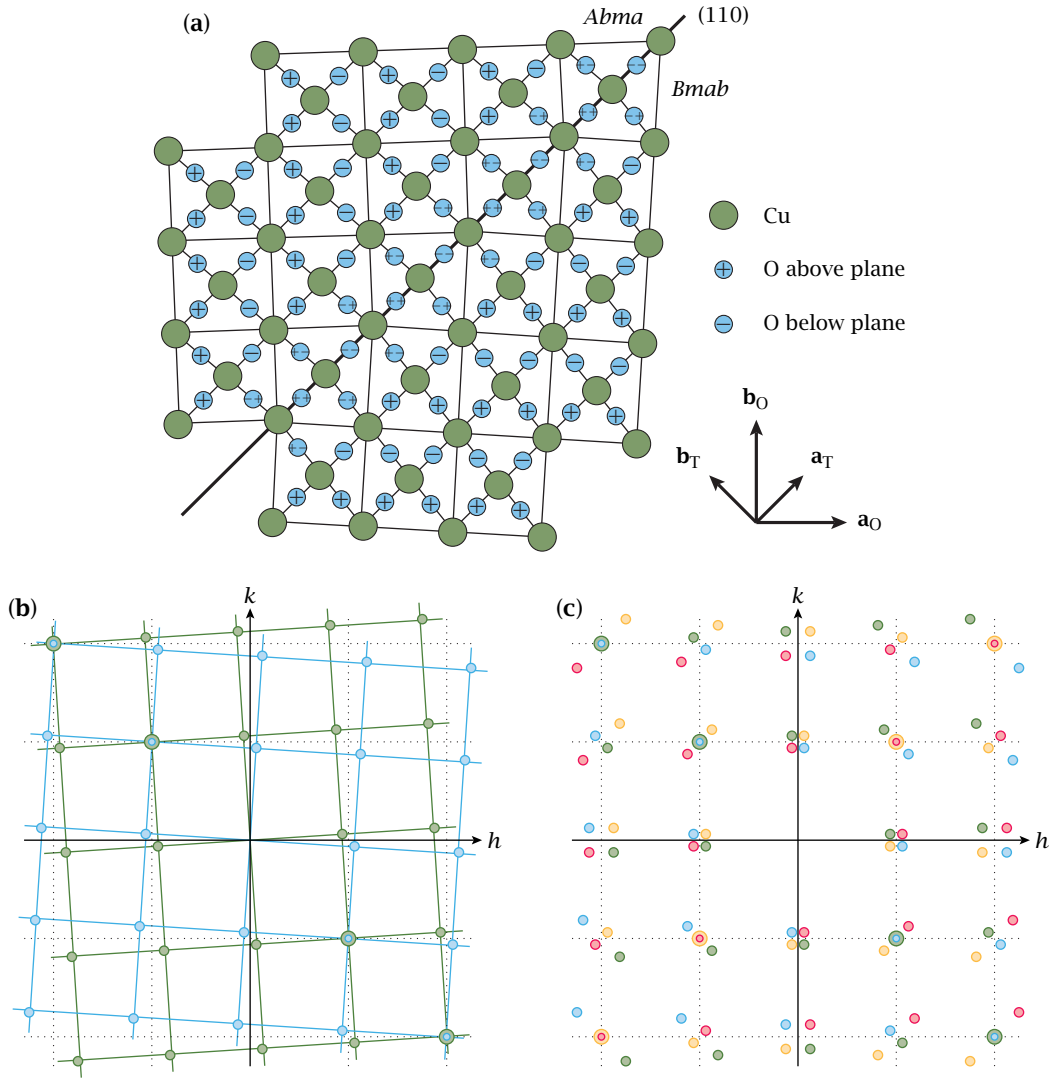


Figure 6.5: The reciprocal space plane $(hk0)$ (tetragonal notation) as in Fig. 6.4(c), but with a larger a/b ratio to exaggerate the splitting, showing how the angular separation Δ is found. Note that the angle between the $\mathbf{a}$ and $\mathbf{b}$ lines for the same point are always 90° . Figure based on [154, Fig. 4.8].

For a typical twinning in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ at 10 K, where the lattice parameters are $a \approx 5.32 \text{ \AA}$ and $b \approx 5.36 \text{ \AA}$ (see Tab. 7.1 in Chap. 7), this angle will be 0.4° .

6.3.2 Staging

For the oxygen-rich phase ($y \geq 0.055$) the LTO phase seems to have an additional superlattice modulation along the c axis from the intercalated oxygens between neighbouring layers of LaO , [100]. This superstructure is consistent with a superstructure known from $\text{La}_2\text{NiCuO}_{4+y}$, [113], called staging after the well-investigated stacking phenomenon in graphite, [114].

Following Fig. 6.6, the modulation happens as follows: within the planes, the CuO_6 octahedra are ordered like in the mother compound, and perpendicular to these planes (along c) the local ordering is also the same. However, there are broad antiphase boundaries parallel to the CuO_2 planes consisting of layers where the CuO_6 tilts are reversed. These antiphase boundaries are presumed to be caused by layers of interstitial oxygen in the favorable positions caused by the strong in-plane coupling of the octahedra because of their corner sharing: if one octahedra reverses tilt because of an interstitial oxygen, this might propagate through the entire CuO_2 plane.

The stage number n refers to the induced periodicity of n CuO_2 layers, although non-integer staging numbers can also occur by mixing of several layerings. The staging numbers for different dopings y in $\text{La}_2\text{CuO}_{4+y}$ can be seen in Fig. 6.3(b). It should be noted that in reality, the staging is a simplified picture, since data points more towards a smearing out of the boundaries in a sinusoidal fashion, [72].

The staging is exactly what I am looking into in this thesis. As explained in Subsect. 4.3.2 a superstructure of this type will result in scattering between the integer (hkl) points in reciprocal space belonging to the average structure. In this particular case, the staging peaks will be along l , since this superstructure is along c . The distance from the integer (hkl) point, Δl , will be given by the reciprocal of the staging number,

$$\Delta l = \frac{1}{n}, \quad (6.3.3)$$

in units of l .

Note also that the staging has, so far, only been well investigated for $\text{La}_2\text{CuO}_{4+y}$. In this thesis, I work with co-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, to see how the Sr doping might affect the superstructures. Note also that $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ exhibits many other superstructures apart from the staging, *e.g.* satellites along $\mathbf{a}^*$, [115]. I will show some of the overview data we have obtained in Chap. 10.

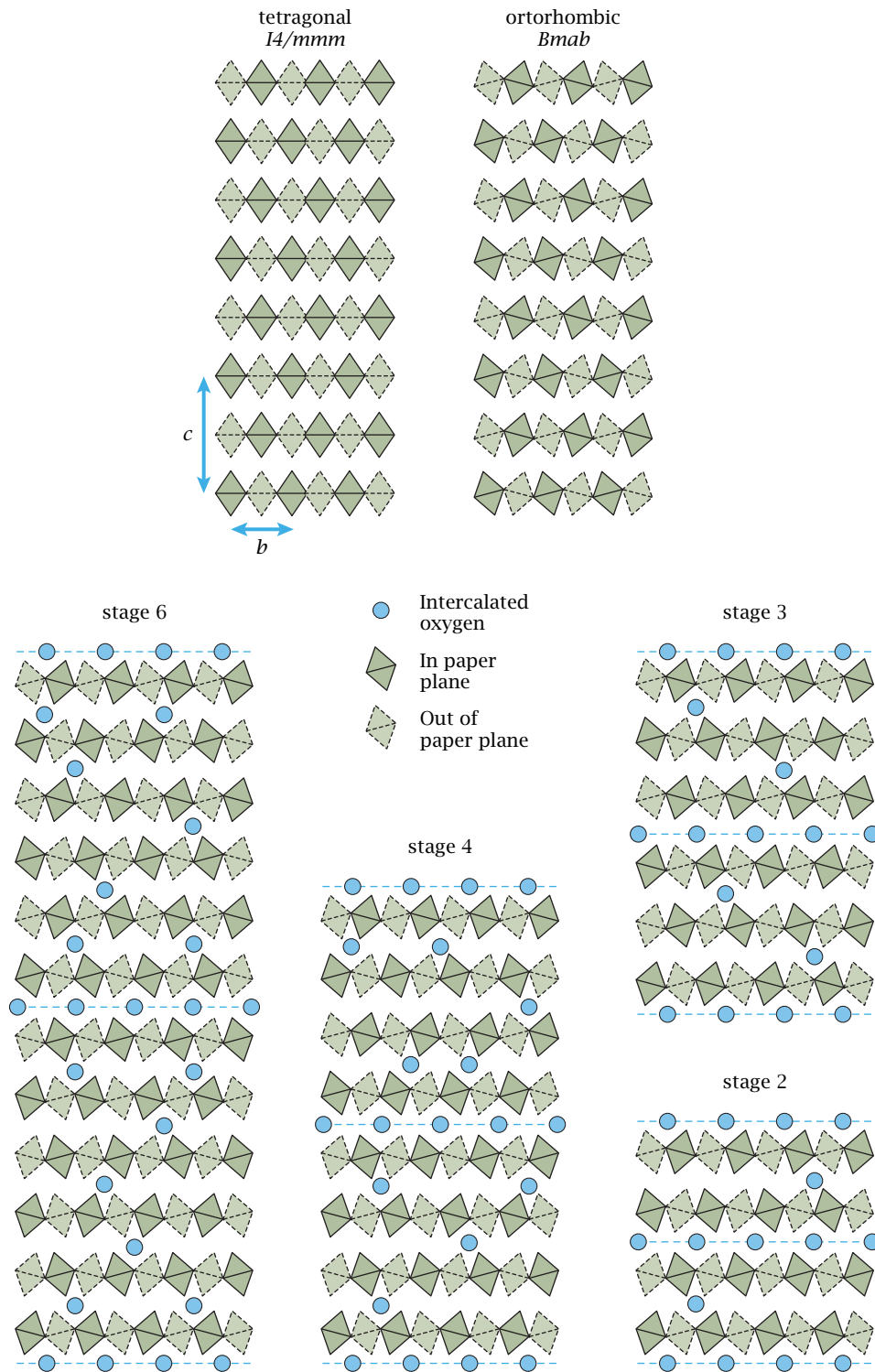


Figure 6.6: Illustration of some CuO₆ tilt structures and staging levels, as seen from the a axis (La ions are omitted). Note that the $Bmab$ structure is as shown for a single unit cell in Fig. 6.1(b), although here the tilt angles are exaggerated for clarity. Note also that the indicated b and c lengths are for the orthorhombic unit cell (corresponding to $F4/mmm$ for the tetragonal symmetry). The dashed octahedra are displaced $a/2$ out of the paper, while the interstitial oxygen are displaced $a/4$ out of the paper. Figure inspired by [72, Fig. 2], [100, Fig. 2], and [113, Fig. 2].

II

Experiments

Measuring staging patterns

In this chapter I will go through which samples were used, how the used instruments work, and how the staging measurements were obtained on these instruments. The data from these measurements will be presented and analyzed in Chap. 9.

7.1 The samples

Measurements have been performed on four different $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ single crystal samples, with Sr doping values $x = 0.00, 0.04, 0.065$, and 0.09 . All samples have been co-doped with O by electrolysis in an NaOH solution over several months, making sure that they were maximally oxygenated into the super-oxygenated regime (where the critical temperature for superconductivity is measured to an onset temperature of $T_c = 40$ K).

Photos of the samples with their crystal axes indicated are shown in Fig. 7.1. Further information about the samples is shown in Tab. 7.1. Note that between the main measurements in 2006 and the extra measurements in 2008 the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample broke into several smaller pieces such that only a smaller piece, weighing 0.018 g, was used in the latter experiment. This breaking up is very common for oxygenated samples, since the oxygenation makes the crystals more brittle.

The samples were all glued onto copper holders using GE varnish, which is good at maintaining a hold even at very low temperatures. Both $\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ were mounted in the $(a_T + b_T, c)$ plane,* while $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ was mounted in the (a, b) plane. Note, however, that most of the full reciprocal space was accessible on four-circle setups.

7.2 The BW5 instrument

Up until October 2012 the X-ray triple-axis instrument BW5 was situated on a high-field wiggler on one of the straight sides of the positron storage ring DORIS III at HASYLAB (DESY) in Hamburg, Germany, [139]. Since then the storage ring has been replaced by the third generation synchrotron radiation source PETRA III with a new suite of instruments, [155, 140]. In this section I will explain how the instrument worked (following Bouchard *et al.* [116] and Zimmermann [168]), and how the measurements used for this thesis were produced.

*By $a_T + b_T$ it is meant one of the orthorhombic axes, which are typically not distinguishable at room temperature.

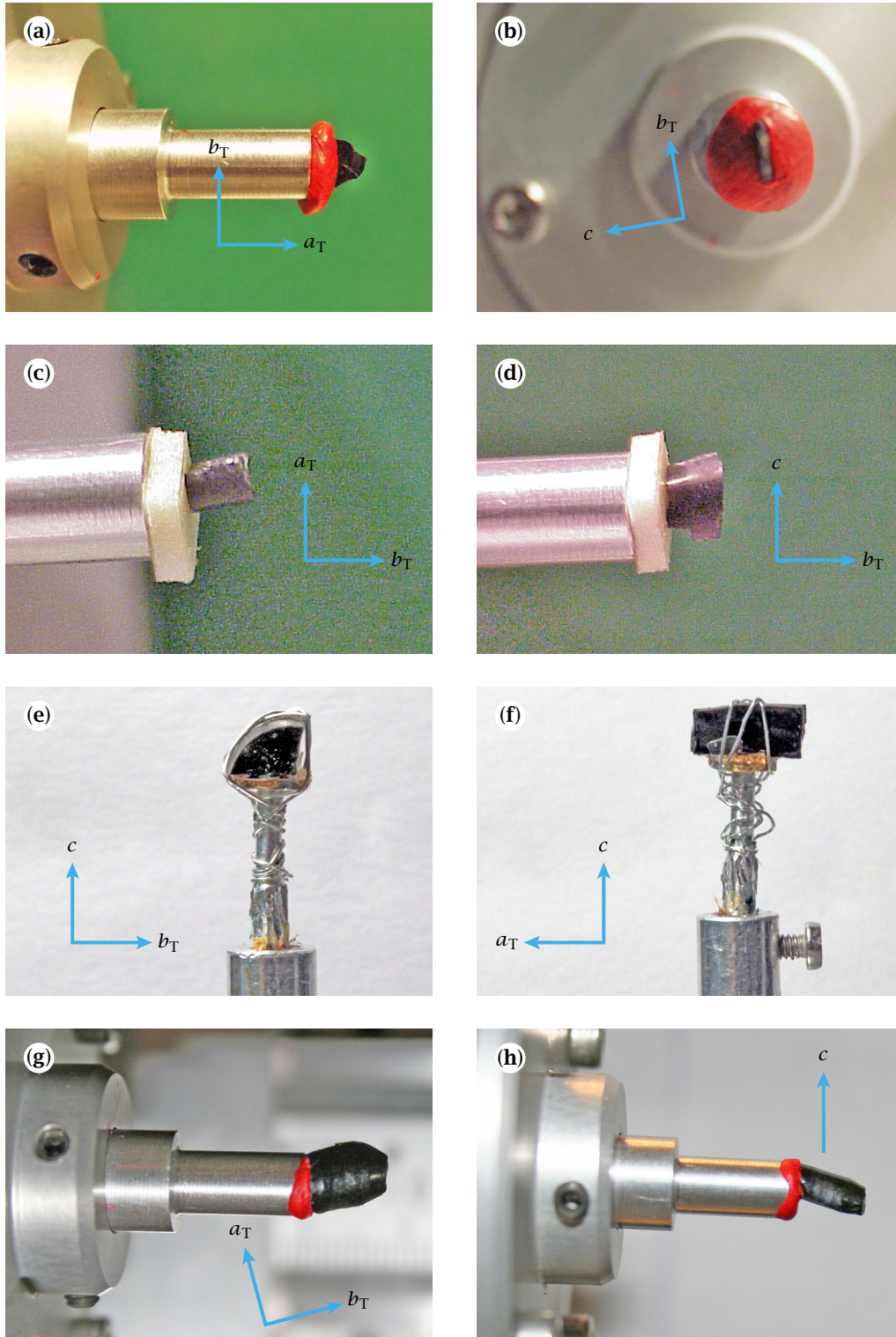


Figure 7.1: Photos of the samples with crystal axes indicated. Note that the a and b axes are in the tetragonal notation, whereas the orthorhombic axes would be a 45° rotation of these around the c axis). (a/b) $\text{La}_2\text{CuO}_{4+y}$, (c/d) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ (broke into three parts before 2008 measurements), (e/f) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and (g/h) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$. Photos (a-d) and (g-h) by Linda Udby. Note that the holders used for measurements on BW5 are *not* the holders shown here.

Sample	Doping x	Mass m [g]	a [Å]	b [Å]	c [Å]	Approx. size (shape) [mm×mm×mm]
La ₂ CuO _{4+y} sLSCOc_0	0.0	0.025	5.30(3) 5.326	5.37(3) 5.326	13.20(3) 13.233	0.5 × 2.5 × 3.5 (irregular disc)
La _{1.96} Sr _{0.04} CuO _{4+y} sLSCO_0.04ABC sLSCO_0.04B	0.04	0.068 0.018	5.32(3) 5.3583	5.38(3) 5.3583	13.19(1) 13.1963	2 × 3 × 3.9 (irregular cylinder)
La _{1.935} Sr _{0.065} CuO _{4+y} sLSCO_0.065A	0.065	0.093	5.32(2) 5.355	5.36(3) 5.355	13.15(3) 13.135	2 × 2 × 2 (quarter cylinder)
La _{1.91} Sr _{0.09} CuO _{4+y} sLSCO_0.09	0.09	0.417	5.33(2) 5.355	5.34(3) 5.355	13.14(2) 13.135	2.8 × 5.1 × 6.5 (half cylinder)

Table 7.1: Information about the samples used in the data collection for this thesis. Grayed out sample names are referring to the naming used during the experiments, defined in [154, Tab.4.1]. Note the La_{1.96}Sr_{0.04}CuO_{4+y} crystal which split up into smaller pieces before 2008, where only one smaller piece was used. Lattice constants are using the orthorhombic notation and are from low temperature neutron measurements, [154]. The grayed out lattice constants are the initial values given to the BW5 instrument, which were not further refined.

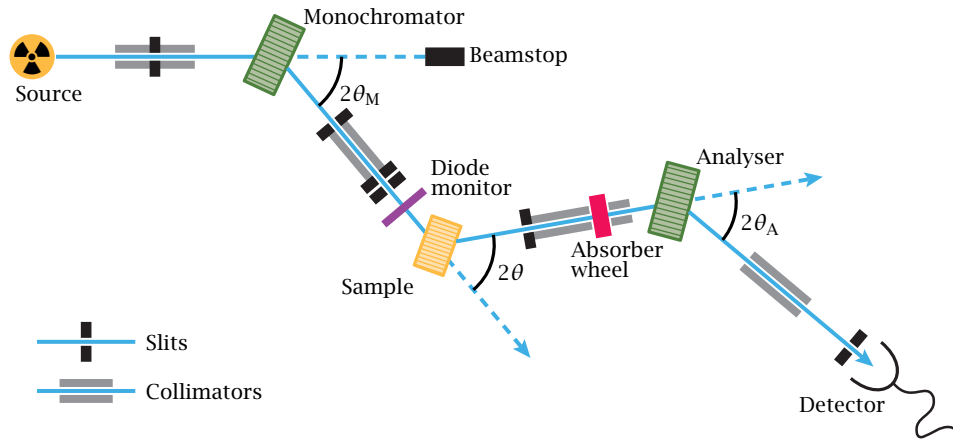


Figure 7.2: Simple illustration of the triple-axis X-ray instrument BW5, as seen from above. Angles are exaggerated for the sake of illustration. Figure based on information from Bouchard *et al.* [116, Fig. 1 and 7] and Zimmermann [168].

7.2.1 An overview of the instrument

The BW5 instrument follows the general layout for triple-axis scattering instruments, and is sketched in Fig. 7.2. The instrument uses a Laue transmission geometry, which is common for triple-axis neutron instruments, but not as much for similar X-ray triple-axis instruments with lower energies – which more often uses a direct Bragg geometry.*

The X-ray beam enters the instrument from the wiggler through a set of collimators and slits defining the beam shape before hitting the monochromator.

The monochromator is typically a SiGe gradient crystal used with the (111) reflection to get an X-ray energy of around 100 keV (0.124 Å). Such a gradient crystal has a controlled homogeneous “gradient” of the lattice parameter over the crystal depth, which enhances the crystal reflectivity, [117]. The transmitted beam is caught by a beamstop, while the reflected beam continues towards the sample position through another set of collimators and slits. Before hitting the sample, the beam is sent through a diode monitor which is used as a measure of the intensity of the incoming beam in data treatment.

*For the Bragg geometry, the scattered beam is seen as coming out of the crystal surface that the incident beam hits, whereas for Laue transmission geometry, the scattered beam is observed on the “back side” of the crystal. On neutron triple-axis instruments, it is possible to do both because of the low interaction strength of the neutrons.

The now monochromatic beam hits the sample at the sample position at an angle of $2\theta_M$ to the incident beam, with one of several possible sample environments installed. For the measurements used in this thesis, a displacive cryostat was installed in order to cool down to sub-10 K temperatures. This cryostat was mounted on top of a four-circle setup to allow for fine tuning of the sample alignment with (χ, ψ) angles of up to $\pm 15^\circ$. Rotation of the sample on the sample position is named ω .

The scattered X-rays are sent from the sample position through yet another set of collimators and slits in the scattering angle 2θ to the incoming monochromatic beam. An absorber wheel with different choices of exchangeable absorbers is also mounted here, making it possible to choose between different orders of magnitude in the intensity on the detector. Before hitting the detector, however, the beam is scattered yet again on the analyser crystal in a setup identical to the monochromator setup. The analyser improves the reciprocal space resolution and makes sure that the detected X-rays are only the elastically scattered by only reflecting energies equal to the energy picked by the monochromator. This way, unwanted energies from *e.g.* fluorescence are also removed.

The detector is finally positioned at an angle of $2\theta_A$ to the beam from the sample, after another set of collimators. The detector is a Ge solid state detector, which generally has a background count rate of less than 1 cts/s, and works linearly up to around 6×10^4 cts/s (usually a safe margin of counts up to 4×10^4 cts/s is used).

Often, X-ray instruments are chosen to have the scattering plane be vertical because of polarization effects, but this is not a big problem for the small Bragg angles that the 100 keV beam gives (in the order of a few degrees), and hence the BW5 instrument was chosen to have the scattering plane be horizontal – a common choice for neutron scattering instruments. Because of this it is possible to install heavy sample environments on the sample position.

Also important to note is the fact that the hard X-rays used on BW5 makes it possible to use more advanced sample environments, *e.g.* ILL “Orange” cryostats or big magnets which are usually only possible to use on similar neutron instruments, [118]. This is not normally possible for X-ray instruments because of the strong interaction with the material (*e.g.* the cryostat surface), but this interaction is weaker for higher energies. For a typical cryostat used on BW5, the loss to absorption due to the sample environment is less than 20%, see Appx. A.3.

7.2.2 Measurements

Measurements were done over a number of years by different people, as listed in Tab. 7.2. The data selected for use for this thesis is only a fraction of the total data measured at the experiments, and hence I will limit my description to how the selected data were obtained.

For all of the experiments, the gradient SiGe (111) monochromator and analyser – both with a mosaicity of 40 arcsec – were used, set to an energy close to 100 keV. For each of the mentioned measurements below, the cooling rate was controlled to be no faster than 2 K/min, in order to allow the oxygen to order. Unless otherwise stated, when measurements were running the temperature was held constant.

2006 experiment: $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$

The measurements on the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ crystal were done between January 31 and February 2, 2006. A few measurements on the $\text{La}_2\text{CuO}_{4+y}$ crystal were also performed, but these data are not used in this thesis. A full beam time report has been compiled by Linda Udby, [156], but I will here mention a few relevant details.

The energy setting of the monochromator and analyser was set to 99.704 keV, and the beam size before the monochromator was $1 \text{ mm} \times 1 \text{ mm}$.

Period	Instrument	Participants	Samples	Reference
31.01.2006- 06.02.2006	BW5, DESY, HASYLAB	L. Udby, N. H. Andersen, Ch. Niedermayer, M. von Zimmermann	$\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, $\text{La}_2\text{CuO}_{4+y}$	Udby <i>et al.</i> [156]
28.11.2007- 03.12.2007	BW5, DESY, HASYLAB	L. Udby, N. H. Andersen, S. B. Emery, M. von Zimmermann	$\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$	Udby <i>et al.</i> [157]
03.10.2008- 10.10.2008	BW5, DESY, HASYLAB	L. Udby, N. H. Andersen, T. B. S. Jensen, M. von Zimmermann	$\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$	Udby <i>et al.</i> [158]
21.07.2005- 04.08.2005	RITA-II, SINQ, PSI	H. E. Mohottala, L. Udby, B. O. Wells, Ch. Niedermayer, N. B. Christensen, N. H. Andersen	$\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$	Mohattala <i>et al.</i> [159]
29.10.2005- 07.11.2005	RITA-II, SINQ, PSI	L. Udby, K. Lefmann, N. B. Christensen, Ch. Niedermayer	$\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$	Udby <i>et al.</i> [160]
03.10.2006- 19.10.2006	RITA-II, SINQ, PSI	L. Udby, N. B. Christensen, Ch. Niedermayer	$\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$	Udby <i>et al.</i> [161]
19.06.2008- 26.06.2008	RITA-II, SINQ, PSI	L. Udby, J. i Hjøllum, N. B. Christensen, Ch. Niedermayer	$\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$	Udby <i>et al.</i> [162]

Table 7.2: An overview of staging measurement experiments. M. von Zimmermann and Ch. Niedermayer were the instrument responsables for BW5 and RITA-II, respectively.

The temperature dependence of the staging peaks around the B_{mab} position (014) was measured at 19 temperatures during cooling from 270 to 10 K, by scanning along l from 3.1 to 4.9 r.l.u. with no attenuation (overview in Fig. D.1(b) in Appx. D). The same measurements were done again while heating, with results consistent with the cooling measurements.* The peak was not aligned before each temperature measurement, but it was later concluded that there had been no change in the length of the b axis during cooling (only the a axis got smaller), meaning that all the (014) scans were still properly centered along b .

Several B_{mab} position peaks were also measured at low temperature, varying l around (012), (032), and (034), concluding that they had similar staging peaks to (014), [156, Fig. 12].

2007 experiment: $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$

The measurements on the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ crystals were done between November 28 and December 3, 2007. A full beam time report has been compiled by Linda Udby, [157], but I will here mention a few relevant details.

The energy setting of the monochromator and analyser was set to 99.9995 keV, and the beam size before the monochromator was $1 \text{ mm} \times 1 \text{ mm}$ for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample and $2 \text{ mm} \times 2 \text{ mm}$ for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample. The larger beam size was because of the large size of the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample, following Tab. 7.1.

For the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample, only six measurements along l around the B_{mab} position (014) was measured, during heating up the sample from 25 to 300 K after a long list of other measurements (overview in Fig. D.1(c) in Appx. D). The scanned interval was for l from 3.75 to 4.25 r.l.u. after centering ω , θ and 2θ , χ , and ω again on the central peak for each temperature, to make sure of the alignment. No attenuation was used for these measurements.

*Because of time restraints, however, I only present the data from cooling in this thesis.

The (004) and (020) peaks were measured as a function of temperature as well (at smaller temperature intervals), both with an attenuation of 12 and an alignment on ω , θ and 2θ , χ , and ω again before the actual measurements. The temperature was allowed to change during both measurements, but limited to a rate of 0.75 K/min such that the longest lasting of these scans had a temperature gradient of less than 2 K. The (020) measurements ended up being important for more than alignment purposes because they show extinction in the sample – and hence give the transition temperature from the HTT to LTO phase more accurately than the (014) measurements were able to. I will go more into detail on this in Chap. 9.

For the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample, the temperature dependence along l around (014) was measured at 19 temperatures during heating from 15 to 300 K with an attenuation of 4 (overview in Fig. D.1(d) in Appx. D). The scanned interval was for l from 3.95 to 4.05 r.l.u. after centering ω , θ and 2θ , χ , and ω again on the central peak for alignment at each temperature.

The (022) and (020) peaks were also followed as a function of temperature, with an attenuation of 12 for the former and 14 for the latter, and an alignment with ω , θ and 2θ , χ , and ω before each measurement. The temperature was allowed to change during the (020) measurements, but only with a rate of 0.7 K/min such that the longest lasting of the scans had a temperature gradient of less than 1.5 K.

2008 experiment: $\text{La}_2\text{CuO}_{4+y}$ (and $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$)

Finally, the measurements on the $\text{La}_2\text{CuO}_{4+y}$ crystal were done between October 3 and 10, 2007. Measurements were also done on the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ crystals, but only a few measurements for the former mentioned will be used in this thesis. A full beam time report has been compiled by Linda Udby, [158], but I will here mention a few relevant details.

The energy setting of the monochromator and analyser was set to 99.9996 keV, and the beam size before the monochromator was 1 mm $\times$ 1 mm.

For the $\text{La}_2\text{CuO}_{4+y}$ sample, the temperature dependence of the staging peaks was measured along l around the *Bmab* position (014) at 13 temperatures heating from 10 to 300 K (overview in Fig. D.1(a) in Appx. D). The measurements were done both at a long interval with l from 3.1 to 4.9 r.l.u., and a more narrow interval between 3.9 and 4.1 r.l.u. with smaller point distance to resolve the central peak better. Before each measurement, the sample was aligned on (220) and (004) by centering in ω , θ and 2θ , χ , and ω again, in order to fix alignment changes caused by the temperature change.

The (020) peak was also measured as a function of temperature with no attenuation, after centering on the peak in ω , θ and 2θ , χ , and ω again for each temperature.

For the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample, the (020) and (004) peaks were followed as a function of temperature, both with an attenuation of 12 and alignment on ω , θ and 2θ , χ , and ω again before the actual measurements.

7.3 The RITA-II instrument

The neutron triple-axis instrument RITA-II is situated on the SINQ neutron source at PSI in Villigen, Switzerland. In this section I will very briefly explain how the instrument works, following Lefmann *et al.* [119] and the instrument website [141]. Several measurements similar to the BW5 measurements were performed for the same samples by Linda Udby, and details of these experiments can be found in her thesis, [154].

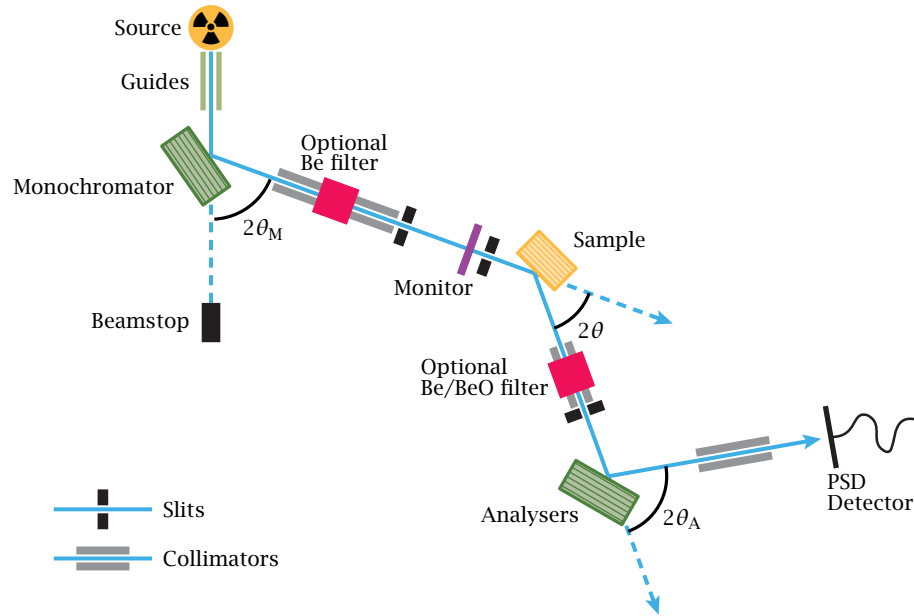


Figure 7.3: Simple illustration of the triple-axis instrument RITA-II, as seen from above. Figure based on information from Lefmann *et al.* [119] and PSI [141].

7.3.1 An overview of the instrument

The RITA-II instrument follows a typical layout for triple-axis scattering instruments, just like BW5, and is sketched in Fig. 7.3. The instrument is at the end of the thermal neutron guide 1RNR13, where the vertically focusing PG(002) monochromator can provide neutrons with energies between 2.5 and 20 meV. Any transmitted beam is caught by a beamstop behind the monochromator, while the reflected beam continues at an angle $2\theta_M$ to the incident beam, towards the sample position through a set of collimators and adjustable slits. An optional Be filter to remove higher-order neutrons is also possible here.

The intensity of the monochromatic beam is detected by a monitor right before the sample position. At the sample position it is possible to insert sample environments ranging from furnaces and pressure cells to cryostats (such as the standard ILL “Orange cryostat”) and cryomagnets.

The scattered beam continues at the scattering angle 2θ through a second optional cooled Be or BeO filter with built in radial collimation. It then hits the flexible nine-bladed PG(002) analyser through a set of slits. This advanced analyser makes it possible to record data in several different modes, *e.g.* a monochromatic focusing mode and a flat mode.

The position sensitive ^3He detector plate is located at the scattering angle $2\theta_A$ from the analyser, after a rough radial collimator to separate the signals from the individual analyser blades. This detector is fairly large, 500 mm $\times$ 300 mm.

7.3.2 Measurements

Measurements were done over a number of years as listed in Tab. 7.2. Since I only show results from these experiments for comparison with the BW5 data, I will not go into detail with how they were obtained here – this can be found elsewhere, [154, 159–162].

Mapping out reciprocal space

In this chapter I will outline how the reciprocal space maps, giving overviews of several superstructures – including staging – were measured. I will keep this short since the data has not been fully analyzed yet and is simply here for comparison and outlook of what is still to be done. The data will be presented in Chap. 10 with a short discussion of what was observed.

8.1 The DMC instrument

The neutron powder diffractometer DMC is situated on the SINQ neutron source at PSI in Villigen, Switzerland. In this section I will briefly explain how the instrument works, following Schefer *et al.* [120] and the instrument website [142], and describe how it was used to measure reciprocal space maps for several of our samples.

8.1.1 An overview of the instrument

The DMC instrument follows a simple two-axis scattering layout, as sketched in Fig. 8.1. The instrument is situated at the cold neutron guide RNR12, where the vertically focusing PG(002) monochromator* can provide neutrons with energies between 3 and 15 meV (between 2.3 and 5.1 Å). The transmitted beam is sent on through the guide system to another instrument, while the reflected beam continues at an angle $2\theta_M$ to the incident beam, towards the sample position through several set of slits and an optional collimator.

The intensity of the monochromatic beam is measured by a monitor in the beam before the sample position. It is possible to install a variety of sample environments in the sample area, amongst them the standard ILL “Orange” cryostat (on top of a three-circle setup to allow for fine tuning of the sample alignment with (χ, ψ) angles of up to $\pm 15^\circ$), which we used for all our reciprocal space mapping measurements.

In front of the detector is an oscillating radial collimator, covering the full angular span of the detector. The detector itself is interesting, since it uses 400 linear position-sensitive BF_3 counters in a large “banana” array spanning 79.8° at a radius of 1.5 m. The angular distance between the detectors is 0.2° , and it is normal to measure once, rotate the detector 0.1° in the horizontal plane, and measure again, in order to get a better angular resolution.

*It is also possible to instead use a Ge crystal, scattering on the (311), (511), or (400) planes.

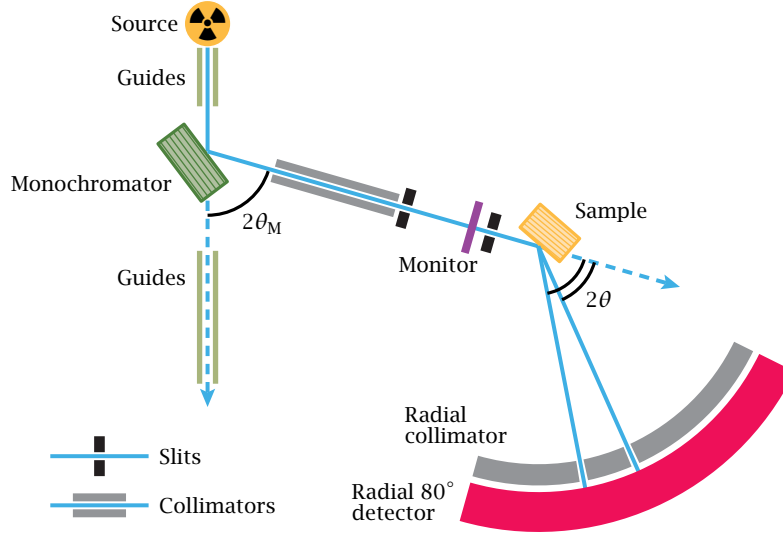


Figure 8.1: Simple illustration of the powder diffraction instrument DMC, as seen from above. Figure based on information from Schefer *et al.* [120] and PSI [142].

Period	Instrument	Participants	Samples
12.11.2012- 17.11.2012	DMC, SINQ, PSI	P. J. Ray, L. Udby, K. Lefmann, M. Frontzek	$\text{La}_2\text{CuO}_{4+y}$
05.07.2013- 07.07.2013	DMC, SINQ, PSI	L. Udby, U. B. Hansen, M. Frontzek	$\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$
24.11.2013- 28.11.2013	DMC, SINQ, PSI	P. J. Ray, M. Frontzek	$\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$, $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$

Table 8.1: An overview of reciprocal space mapping experiments. M. Frontzek was the instrument responsible for DMC.

8.1.2 Measurements

Measurements* have been done over a number of experiments, as outlined in Tab. 8.1. The samples are the same, or other crystals of the same composition, as the samples used at BW5 as presented in Chap. 7. Crystals were mounted in the (a, b) and the (b, c) planes on aluminium holders, using aluminium thread and GE varnish.[†]

In order to map out slices of reciprocal space, a sample is placed in the cryostat, and counts are then recorded in the channels of the detector as a function of the horizontal rotation of the crystal, ω . In this way a $(2\theta, \omega)$ map is collected, which can then be transformed into the reciprocal lattice directions of the given crystal orientation. Measurements were done for a low temperature (either 2, 5, or 10 K), a medium temperature of 100 K, and room temperature (300 K), for both the (a, b) and (b, c) alignments, for most of the samples. A full overview of the measurements is presented in Appx. E.

*The used samples were not all the same samples as the samples measured on at BW5 and RITA-II, but the compositions are the same, so I will not go into further details with this here, since I do not perform any deeper analysis of the reciprocal space map results.

[†]Araldite glue covered with a small amount of Gd_2O_3 was used for the $\text{La}_2\text{CuO}_{4+y}$ sample at the November 2012 experiment, which resulted in a features in the background.

III

Results and analysis

Staging measurements

In this chapter I will go through the measurements that were done on BW5, analysing them to see the phase transitions. I will also show some of the complementary neutron results taken on RITA-II from Udby [154].

Unless otherwise stated, peak fits have been done with the *iFit* data analysis framework, [164], while power law fits are done with the *spec1d* software package, [165], both for *MATLAB*, [166].

9.1 Initial treatment of BW5 staging data

The raw (014) l -scan data for all four samples at all the measured temperatures can be seen in Appx. D, where they are shown plotted individually (with an overview in Fig. D.1 and the individual plots in Figs. D.2 to D.13).

For the $\text{La}_2\text{CuO}_{4+y}$ sample the measurements were split up into a wide scan and a narrower central scan with a closer density of measurements. In order to treat these scans as one, they have been combined into a single dataset for each temperature.* All data has been normalized to the monitor value. The only other initial treatment of the raw data was to remove a few erroneous points where the detector had zero counts as an obvious error. For the $\text{La}_{1.96}\text{Sr}_{0.04}\text{-CuO}_{4+y}$ sample at $T = 70$ K there was one of these points, while for the $\text{La}_2\text{CuO}_{4+y}$ sample there were two points at $T = 10$ K, one point at $T = 30$ K, and one point at $T = 290$ K. These removed points are marked with red in the raw data in Figs. D.2 to D.13.

The data for each sample has been plotted together as an overview in Fig. 9.1, and on a logarithmic scale in Fig. 9.2. To be able to compare the data more directly, they have also been plotted in this way, but with the same l axis limits, in Figs. D.14 and D.15.

9.1.1 Correcting for changing lattice parameter

With the exception of the $\text{La}_2\text{CuO}_{4+y}$ measurements, each l scan at each temperature was aligned on the central (014) peak in order to scan at the correct position in reciprocal space. For the $\text{La}_2\text{CuO}_{4+y}$ sample, it was concluded that even though the alignment was not done, the position was still correct, [158]. These alignments did, however, not change the UB matrix of the instrument, and hence the positions in reciprocal space written down in the data files did not have the correct values. The position of the (014) peak should always be at $l = 4$ in the

*Combining the data is done after normalizing to the monitor value, using the `combine()` command from the *spec1d* software package for *MATLAB*, [165, 166].

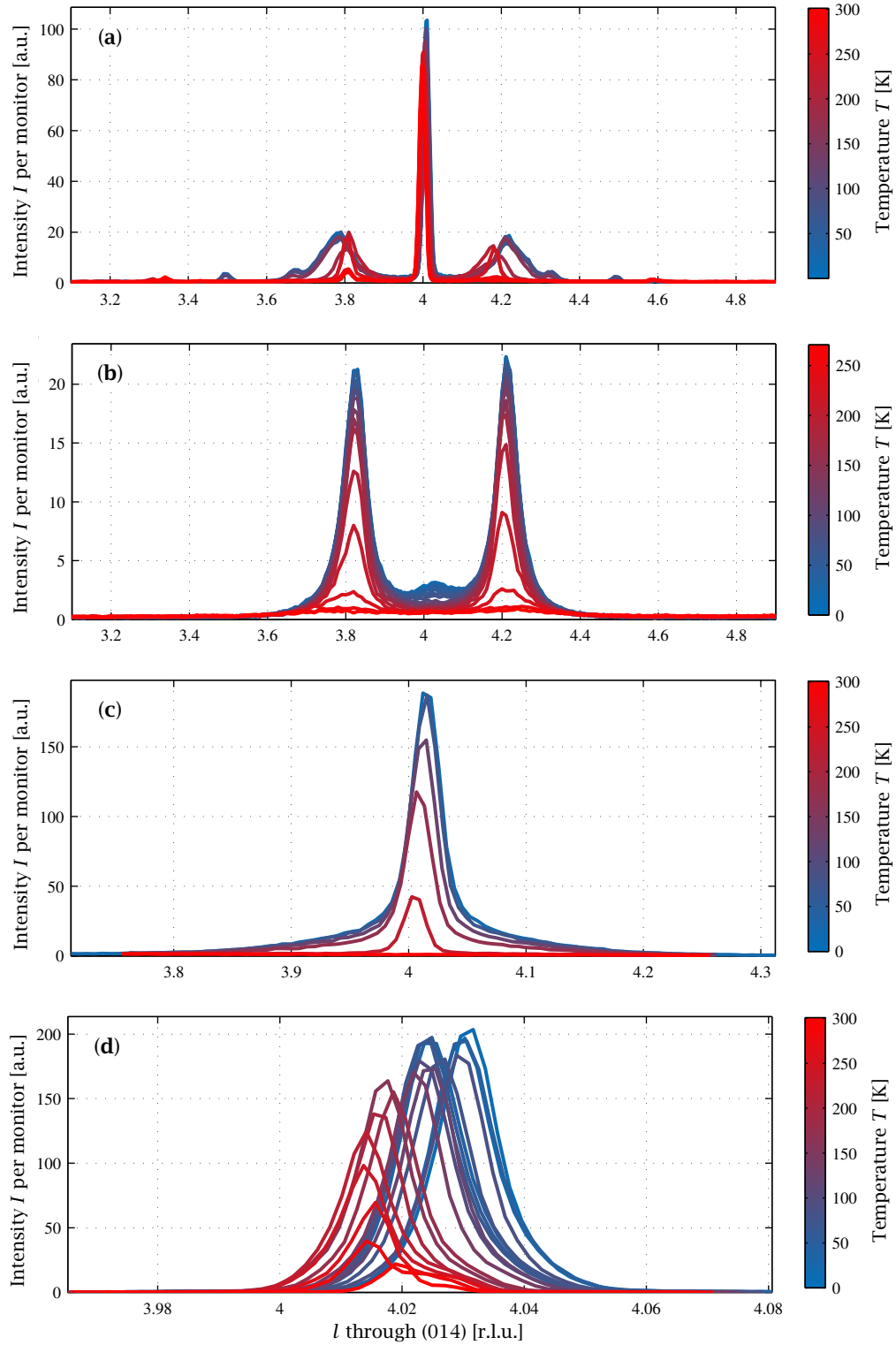


Figure 9.1: Measurement on the (a) $\text{La}_2\text{CuO}_{4+\gamma}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ crystals along l over the (014) peak on BW5 before any correction of the instrument lattice parameter. The curve color shows the temperature, with blue being colder and red being warmer. Note the different l axis intervals on the graphs - the plots are shown all with the same interval in figure Fig. D.14.

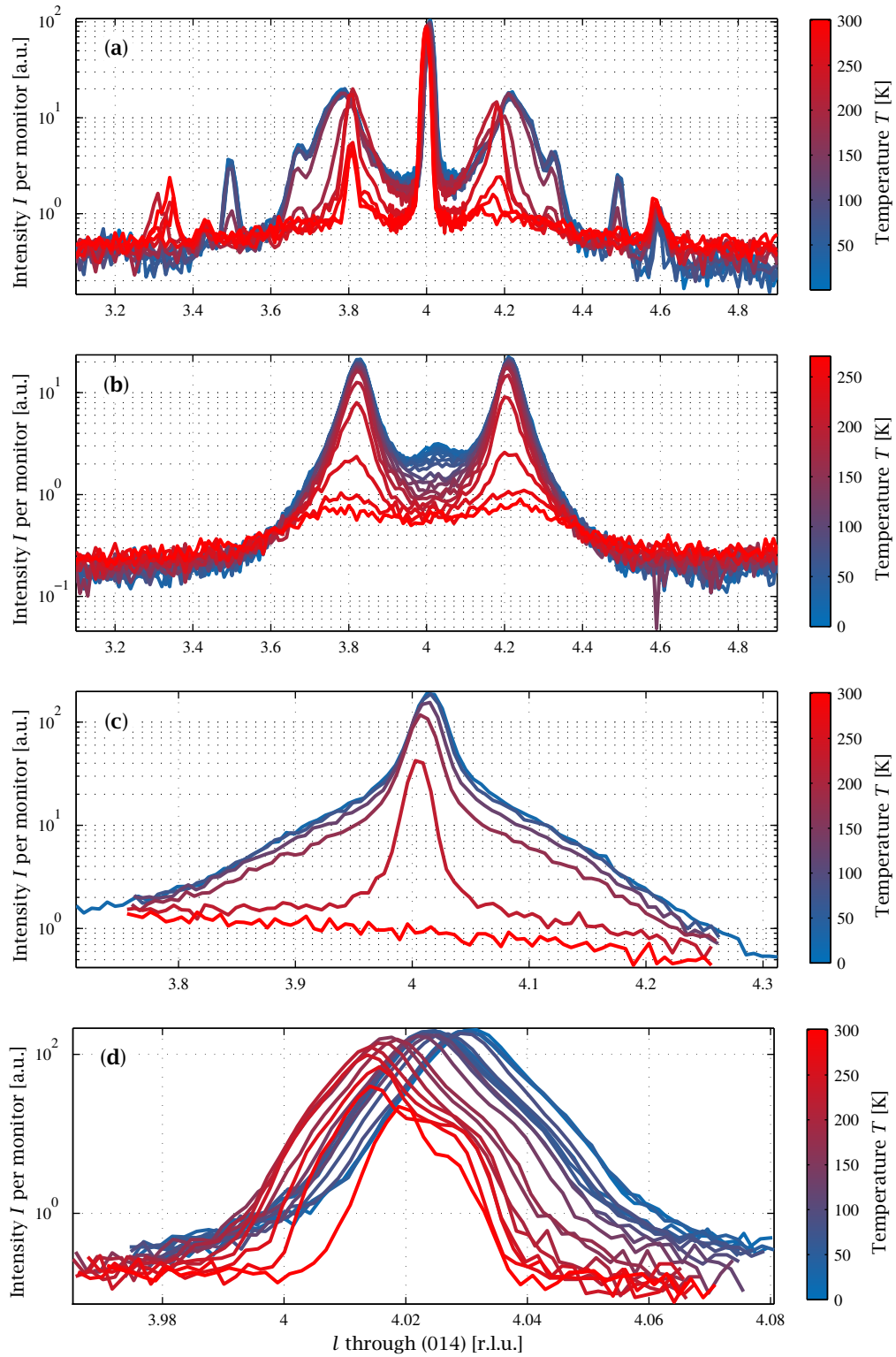


Figure 9.2: As figure Fig. 9.1, but with the intensity on a logarithmic scale. (a) $\text{La}_2\text{CuO}_{4+\gamma}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$. These plots are shown all with the same l axis in figure Fig. D.15.

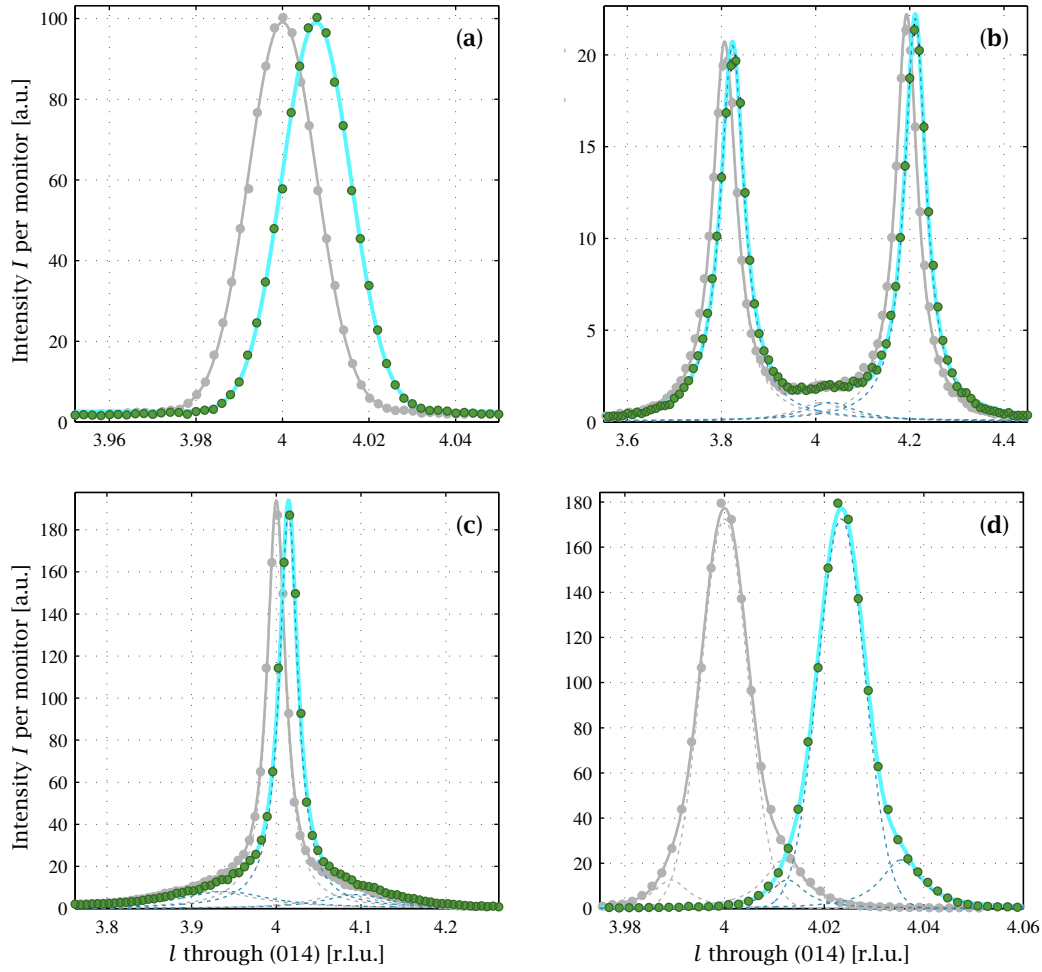


Figure 9.3: Examples of fits done to find the correction on the l axis. (a) $\text{La}_2\text{CuO}_{4+y}$ at 100 K, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ at 70 K, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ at 75 K, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ at 100 K. The green points are the original data, with the total fitted curve in blue (with the single peaks shown as dashed lines). The gray data is scaled on the l axis to get the fitted curve (also shown in gray) centered around $l = 4$. Note that the error bars are smaller than the points.

measurements, but this is not the case in the data files. The scans are centered around the immediate central point of the scan at the current temperature, but the l value of the data has to be corrected: the reciprocal lattice points are a bit off at lower temperatures, where the lattice parameters have changed slightly.

To correct for this, the position of the central peak of the data in each scan has been found with a fit. This value has then been used as a factor on the l axis in order to center the data correctly – as if the lattice parameter had actually been recalculated at each temperature. Examples of these fits for one temperature for each sample have been shown in Fig. 9.3, while an overview of the fitted positions for all of the datasets is shown in Fig. 9.4.

For $\text{La}_2\text{CuO}_{4+y}$ the fitting function was simply a Gaussian* on a restricted narrow central cut-out of the scan, between $l = 3.95$ and 4.05 r.l.u., see Fig. 9.3(a). The fitting function had to be a little more complicated for the three other samples, where the full measured intervals were taken into account.

*For an overview of the functions used in this thesis, see Appx. C.

For $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ the fitting function was two Lorentzians around a common center, with a Lorentzian with a free center between these (see Fig. 9.3(b)). Since the inner central peak is very small (especially for higher temperatures where it almost disappears), and hence very difficult to fit precisely, the mid-point of the two outer peaks was used for the correction of the l axis.

For $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ the fitting function was a central Lorentzian with two more Lorentzians in the shoulders around another free common center (see Fig. 9.3(c)). The position of the first mentioned was used for the correction of the l axis. One exception, however, was the $T = 300$ K dataset, which does not show a peak. I have tried fitting it with a simple Lorentzian on a sloping background, but there is no trace of a peak, and hence the l axis for this temperature has simply been scaled to a linearly extrapolated point from the central positions of the three lower closest temperatures.

For $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ the fitting function was like the function for $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, except that the central peak was fitted with a Gaussian instead of a Lorentzian (see Fig. 9.3(d)).

From the peak positions it is possible to calculate the length of the sample axis c from the one given to the instrument initially (following Tab. 7.1). Naming the instrument value for the lattice parameter c_{instr} and the real lattice parameter c_{real} ,

$$l_{\text{center}} \frac{2\pi}{c_{\text{instr}}} = 4 \frac{2\pi}{c_{\text{real}}} \quad \Rightarrow \quad c_{\text{real}} = \frac{4c_{\text{instr}}}{l_{\text{center}}}, \quad (9.1.1)$$

where l_{center} is the center position found for the dataset as shown in Fig. 9.4. The found values are shown in Fig. 9.5. The low temperature values in this figure can be compared with the values from Tab. 7.1 as shown in Tab. 9.1.

The $\text{La}_2\text{CuO}_{4+y}$ value matches easily within the uncertainty, but for the other samples the neutron values are significantly larger, although the general trend of higher Sr doping meaning a shorter lattice parameter is still seen. This discrepancy of the higher Sr doped lattice parameters between the neutron results and these will be discussed further in Sect. 11.1.

The full datasets after the correction are shown in Figs. 9.6 and 9.7, to compare with the uncorrected full datasets in Figs. 9.1 and 9.2. As was done with the uncorrected data, the corrected data has also been plotted with the same l axis limits in Fig. D.16 and Fig. D.17.

For comparison, the central regions of the data is shown before and after the scaling of the l axis has been done in Figs. D.18 to D.21. The data after the scaling is now clearly centered around $l = 4$ as was expected.

Sample	Lattice parameter c from neutrons [Å]	Lattice parameter c from X-rays [Å]	Temperature T for X-ray lattice parameter value [K]
$\text{La}_2\text{CuO}_{4+y}$	13.20(3)	13.2038(11)	10.279(10)
$\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$	13.19(1)	13.1367(7)	9.331(19)
$\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$	13.15(3)	13.0857(2)	25.001(4)
$\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$	13.14(2)	13.0346(1)	15.003(15)

Table 9.1: A comparison of lattice parameter lengths c for the four samples from neutron experiments, [154] (also given in Tab. 7.1), with the found lattice parameters for the lowest temperature as shown in Fig. 9.5, using Eq. (9.1.1). Note that the X-ray lattice parameter for $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ is found for the mid-point between the large staging peaks - not the center of the smaller central peak.

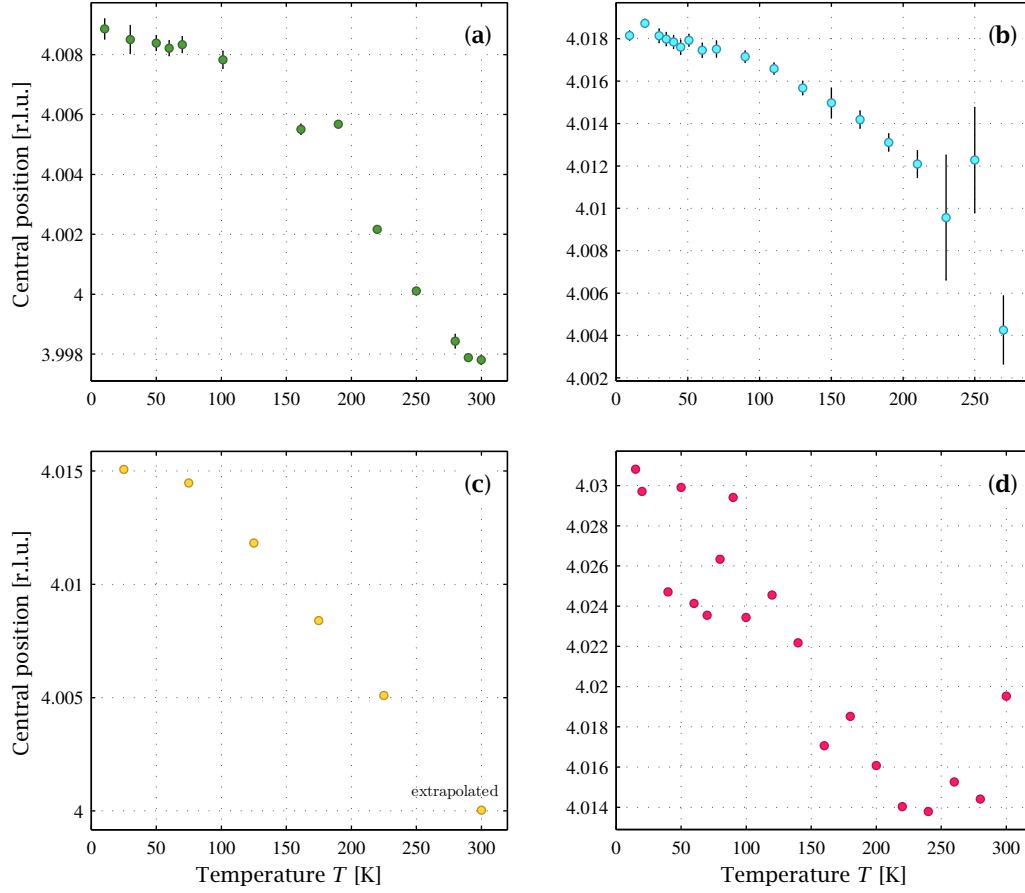


Figure 9.4: Overview of the peak center positions before the l axis correction. (a) $\text{La}_2\text{CuO}_{4+y}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$. Note that the $T = 300$ K point for $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ is an extrapolation from the other points, since no peak was observed.

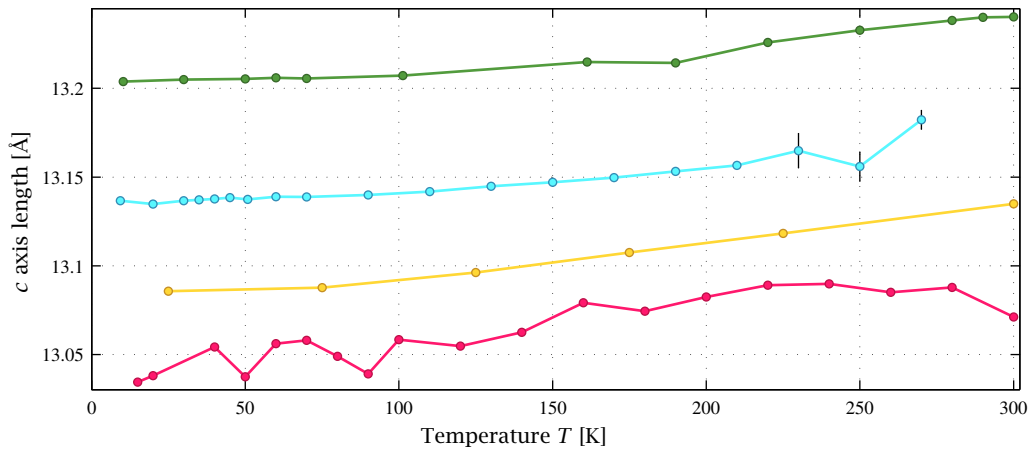


Figure 9.5: Found lattice parameter lengths c from the l axis corrections on BW5 data following Fig. 9.4. Green points are $\text{La}_2\text{CuO}_{4+y}$, blue points are $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, yellow points are $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and red points are $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$.

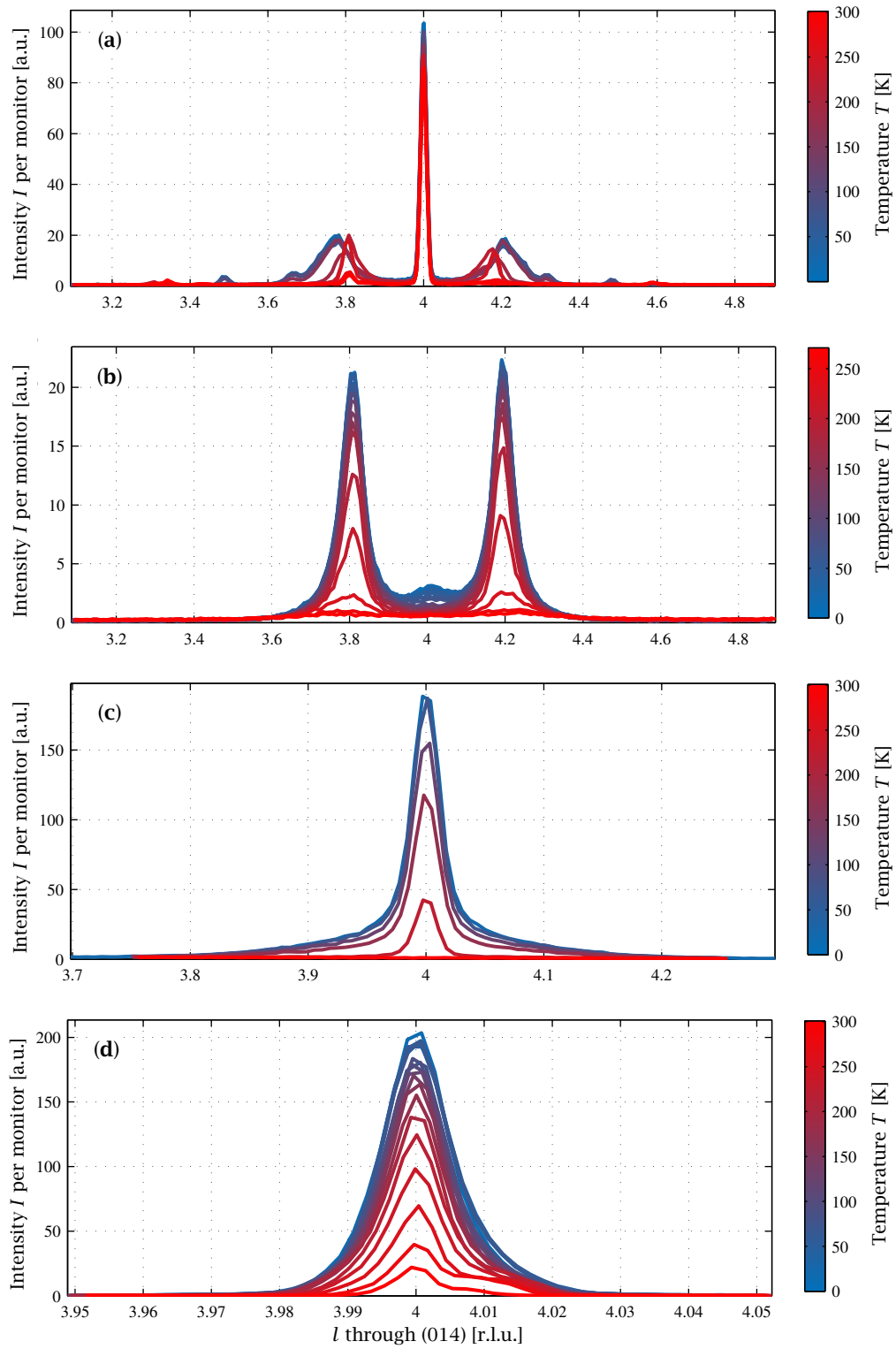


Figure 9.6: Measurement on the (a) $\text{La}_2\text{CuO}_{4+\gamma}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ crystals along l over the (014) peak on BW5 after correction of the first-axis, see also Figs. D.18 to D.21. The curve color shows the temperature, with blue being colder and red being warmer.

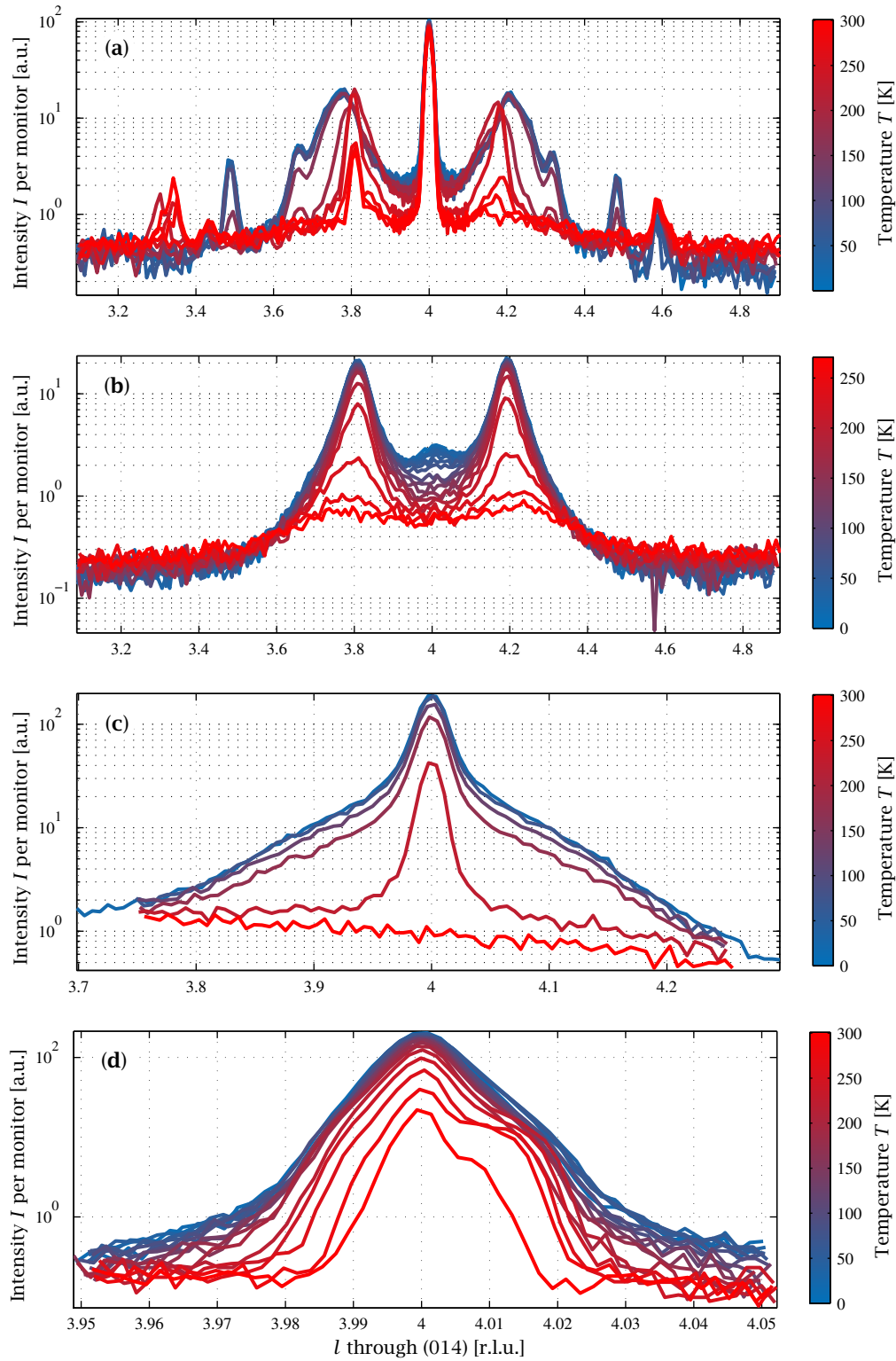


Figure 9.7: As figure Fig. 9.6, but with the intensity on a logarithmic scale. Measurement on the (a) $\text{La}_2\text{CuO}_{4+y}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ crystals along l over the (014) peak on BW5 after correction of the first-axis.

9.2 Fitting to find integrated intensities for BW5 staging data

After the correction of the staging data, it is now possible to fit the scans to obtain the total intensities of the contained peaks. Since the difficulty level of the data treatment was very different for the four samples, I will start with $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ which was the most straightforward. Then I will go over the data treatment for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ samples, and finally for the $\text{La}_2\text{CuO}_{4+y}$ sample, which was the most complicated.

In the following subsections the fitting functions are chosen empirically, based on which peak shapes gives a better fit. The desired end result is the integrated intensities of the reflections – not the peak shapes or resolution – and hence Lorentzians and Gaussians are used. It could have also been interesting to use Voigts (explained in further detail in Appx. C) for the fitting, however with the large number of fitting parameters already used this is an unwanted complication of the data analysis.

9.2.1 Fitting $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ peaks

The measured peaks for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample were shown in Fig. 9.6(b) and on a logarithmic scale in Fig. 9.7(b). In order to find the integrated intensity for each of the elements in the spectra, each full scan has been fitted with a constant background and three Lorentzians: one small central peak for the *B_{mab}* peak, and one larger peak on either side for the staging. The mid-point of the staging peaks and their distance to this are used as fitting parameters, instead of fitting the location of the two individual peaks directly. Examples of fits for the $T = 20$ and 230 K datasets are shown in Fig. 9.8.

The position of the central *B_{mab}* peak has been held fixed to the $T = 60$ K value for temperatures above this, since the peak intensity becomes very small at higher temperatures, making

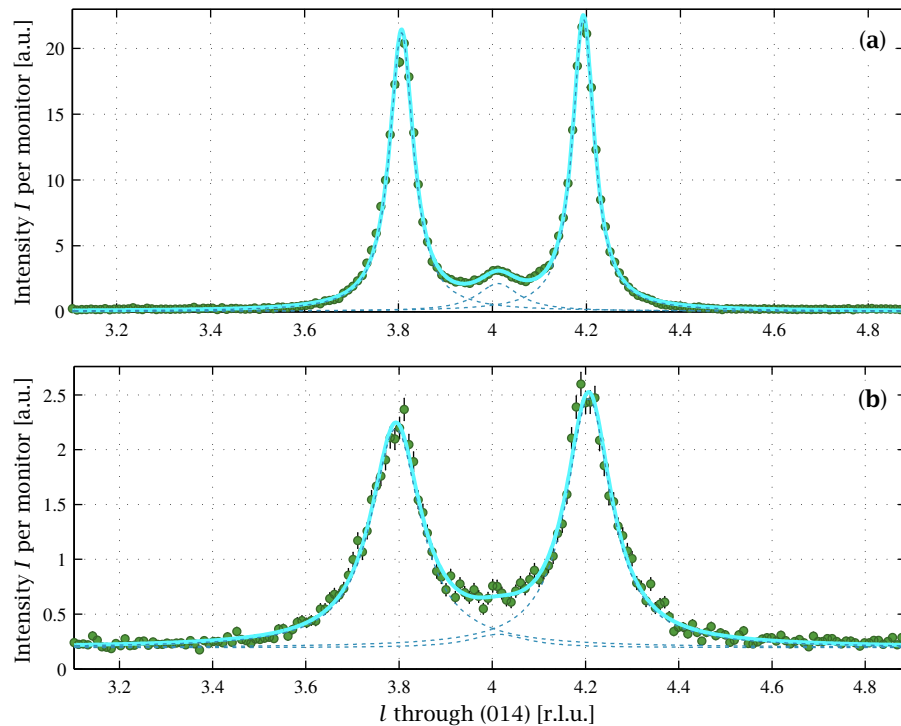


Figure 9.8: Examples of fits done for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ BW5 data, here for the (a) $T = 20$ K and (b) $T = 230$ K measurements. The individual peaks of the fit (plus the background) are shown as dashed lines, while the full fit is the solid blue line. For points without visible errorbars, the errors are smaller than the marker.

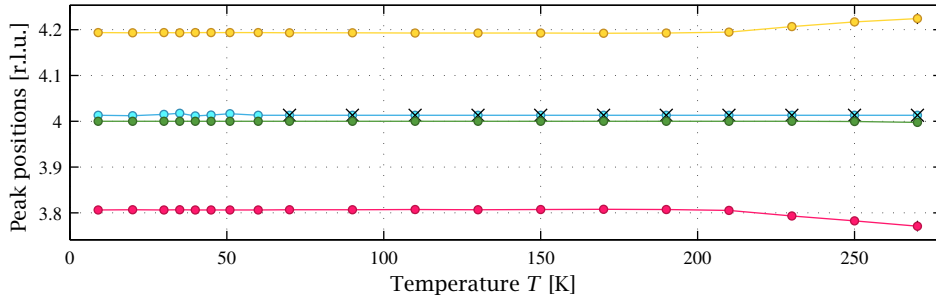


Figure 9.9: Positions of fitted peaks for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample. The blue points show the position of the central *Bmab* peak while the green points show the mid-point of the staging peaks, which are in turn positioned at the yellow and red points. The points with crossmarks indicate that the position was held fixed to the $T = 60$ K value. For points without visible errorbars, the errors are smaller than the marker.

the fit difficult. In the same way, the width of the *Bmab* peak is held fixed to the $T = 90$ K value for temperatures above this.

An overview of the positions of the fitted peaks is shown in Fig. 9.9. Note how the *Bmab* peak (shown in blue) is always at a higher value of l compared to the mid-point of the staging peaks (shown in green). This distance is $\delta l = 0.014(2)$ r.l.u., as determined from the fits at temperatures below 60 K, above which the *Bmab* position is held fixed in the fit (although the distance seems to stay the same all the way to the highest measured temperature, assuming that the *Bmab* peak is correctly positioned at the fixed value). This indicates that the superstructure is not a superstructure for the *Bmab* reflection, but instead possibly for a structural *Fmmm* phase (for which the central position is not an allowed reflection following Tab. 6.1) with a slightly longer lattice parameter c . I will go more into detail with this in Subsect. 11.1.1.

The distance between the staging peaks (their positions shown as yellow and red points) and their mid-point (green points) for temperatures below 200 K has an average value $\Delta l = 0.193(8)$ r.l.u., corresponding to a staging number of just above $n = 5$ following Eq. (6.3.3). Above 200 K, the distance slowly increases all the way up to $\Delta l = 0.227(10)$ r.l.u. for $T = 270$ K, corresponding to a staging number n of between 4 and 5.

The integrated intensities for the fitted peaks are calculated as explained in Appx. C and shown in Fig. 9.10. I will work further with these intensities in Sect. 9.4, where I find transition temperatures and critical exponents for all the samples together. As an initial observation, the staging peaks follow power laws nicely at $T > 150$ K (below which saturation takes a hold) – as is expected for a continuous phase transition, following Chap. 5 – while the central *Bmab* peak seems to fall very slowly, and might have a large amount of critical scattering. The transition temperature for the *Bmab* peak also seems much lower than for the staging peaks.

The widths of the fitted peaks are shown in Fig. 9.11. Since the intensity of the central *Bmab* peak was so small, and the width was hence kept fixed for higher temperatures, it is difficult to conclude anything for this parameter. For the staging peaks, however, the width seems fairly constant at low temperatures, but rising significantly when getting close to the phase transition.

9.2.2 Fitting $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ peaks

The measured peaks for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample were shown in Fig. 9.6(c) and on a logarithmic scale in Fig. 9.7(c). To find the integrated intensities for each of the elements in the spectra, each full scan has been fitted with a constant background plus three Lorentzians: a large central peak for the *Bmab* peak, and one small peak on either side for the staging. As for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample, the mid-point of the staging peaks and their distances to this

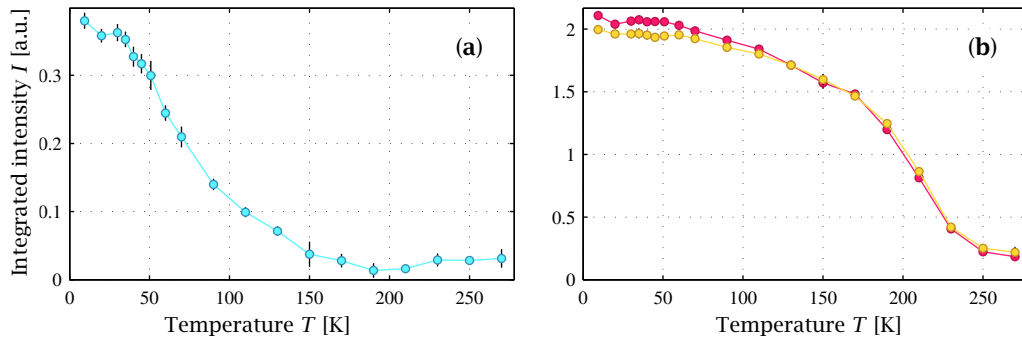


Figure 9.10: Integrated peak intensities of fitted peaks for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample for (a) the central $Bmab$ peak and (b) the staging peaks: red points for the low l and yellow for the high l peak (as in Fig. 9.9).

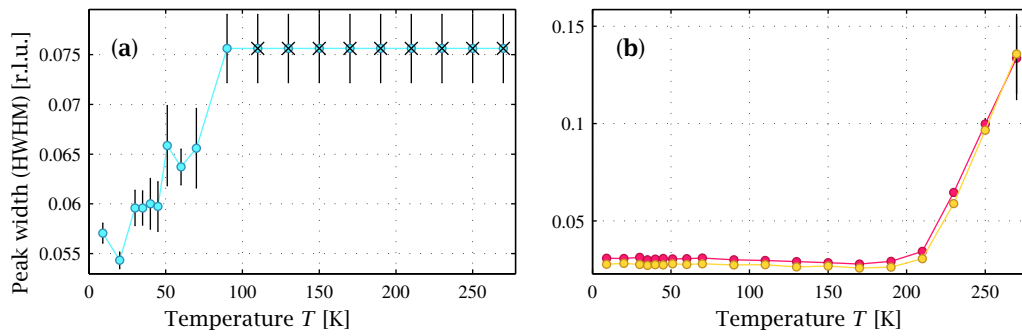


Figure 9.11: Widths of fitted peaks for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample for (a) the central $Bmab$ peak (held fixed at the $T = 90$ K value at temperatures higher than this, marked with crossmarks) and (b) the staging peaks: red points for the low l and yellow for the high l peak (as in Fig. 9.9).

are used as fitting parameters. Examples of these fits for the $T = 25$ and 175 K datasets are shown in Fig. 9.12. The $T = 300$ K data did not exhibit signs of a peak even when tried fitted with a single peak on a sloping background.

The choice of fitting two side-peaks in the shoulders of the central $Bmab$ peak – instead of a wide bottom peak below it – was simply because the former gave a slightly better fit. Fitting with a single Lorentzian, two Lorentzians, two Gaussians, or a Lorentzian and a Gaussian, all gave worse goodness-of-fit values for the fits than fitting with a central Lorentzian and a Lorentzian in either shoulder. This result could also be seen by eye, noticing how one or two peaks only could not account for both the width and the tails of the total signal. As an example, for the $T = 25$ K dataset the following correlations (a value between 0 and 1 given for an *iFit* fit, with higher values corresponding to a better fit) were found: 0.868 for one Lorentzian, 0.917 for two Lorentzians, 0.979 for two Gaussians, 0.921 for a Gaussian and a Lorentzian, and 0.995 for a Lorentzian with a Lorentzian on each side. With more time, it would be interesting to also do a full analysis with the latter mentioned fit function, especially if it is possible to get more data than the only six scans (one of them with no peak) that have currently been obtained from BW5.

The widths of the staging peaks were held fixed to the $T = 25$ K value for temperatures above this, since these peaks are so small in intensity that the fit is difficult. In the same way, the mid-point and distance to the mid-point for the staging peaks were kept fixed to the $T = 175$ K value for the 225 K scan.

An overview of the positions of the fitted peaks is shown in Fig. 9.13. The position of the $Bmab$ peak and the mid-point of the staging peaks – shown in blue and green, respectively – are very

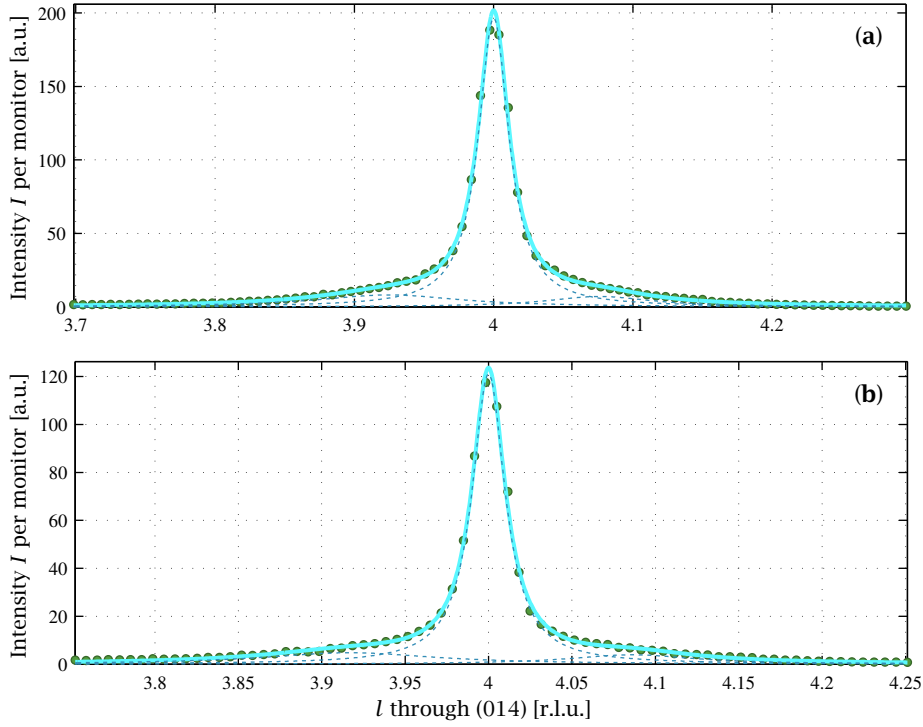


Figure 9.12: Examples of fits done for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ BW5 data, here for the (a) $T = 25$ K and (b) $T = 175$ K measurements. The individual peaks of the fit are shown as dashed lines (plus the constant background), while the full fit is the solid blue line. For points without visible errorbars, the errors are smaller than the marker.

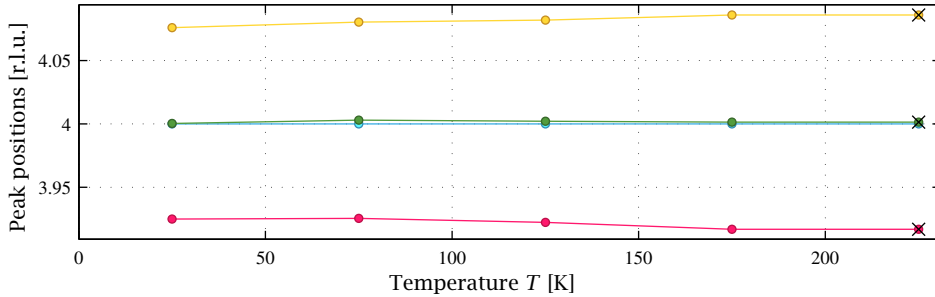


Figure 9.13: Positions of fitted peaks for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample. The blue points show the position of the central $Bmab$ peak while the green points show the mid-point of the staging peaks, which are in turn positioned at the yellow and red points. Note that no points are shown for the $T = 300$ K data since no peak was seen here. The crossmarks indicate parameters that were fixed to the value from the neighboring scan with lower temperature. For points without visible errorbars, the errors are smaller than the marker.

close to each other, with an average distance of only $\delta l = 0.0017(11)$ r.l.u. (not including the $T = 225$ K data, where the mid-point and distance to this for the staging peaks was fixed at the 175 K values). As opposed to the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample, though, here the $Bmab$ peak is at lower values of l compared to the mid-point of the staging peaks. With this very small δl , and the large uncertainty on the value, there is not much incentive to say that two structural phases, one $Bmab$ and one $Fmmm$ as was concluded for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample, are at play for this sample.

The distance between the staging peaks (their positions shown in yellow and red points) and their mid-point (green points) for the lowest temperature of 25 K was found to be $\Delta l =$

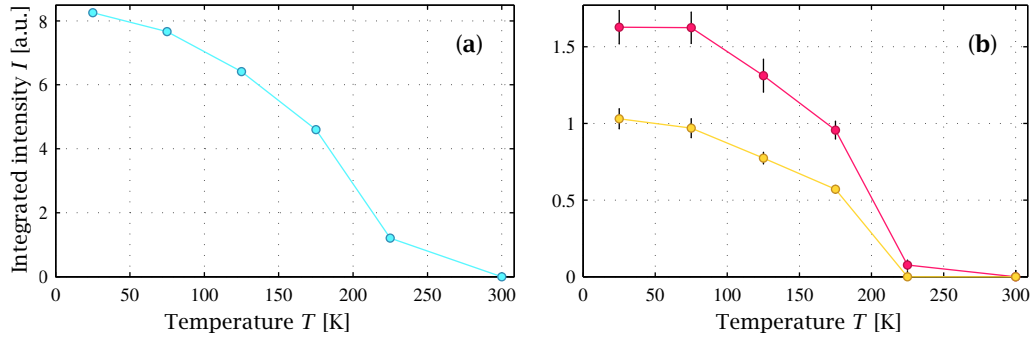


Figure 9.14: Integrated peak intensities of fitted peaks for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample for (a) the central $Bmab$ peak and (b) the staging peaks: red points for the low l and yellow for the high l peak (as in Fig. 9.13). For points without visible errorbars, the errors are smaller than the marker.

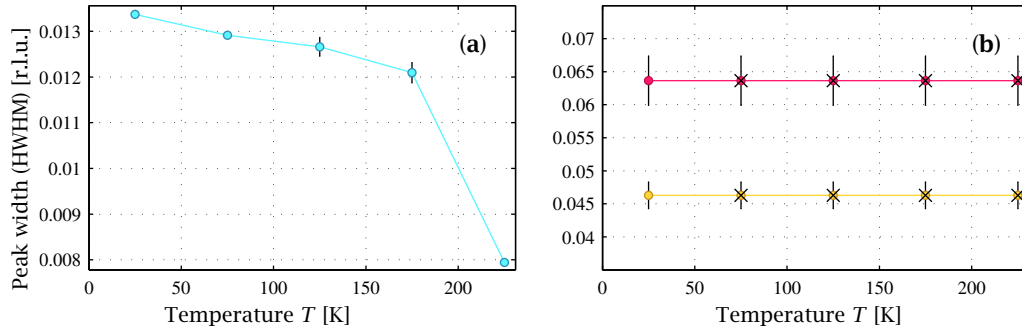


Figure 9.15: Widths of fitted peaks for the $\text{La}_{1.350}\text{Sr}_{0.650}\text{CuO}_{4+y}$ sample for (a) the central $Bmab$ peak and (b) the staging peaks: red points for the low l and yellow for the high l peak (as in Fig. 9.13). Both staging peak widths were held fixed at the $T = 25$ K value at temperatures higher than this (marked with crossmarks). For points without visible errorbars, the errors are smaller than the marker.

0.0755(14) r.l.u., corresponding to a staging number n larger than 13. For higher temperatures the distance grows slightly, to $\Delta l = 0.0847(11)$ r.l.u. for $T = 175$ K, corresponding to n between 11 and 12.

The integrated intensities for the fitted peaks are shown in Fig. 9.14. I will work further with these intensities in Sect. 9.4, however at a first glance they follow power laws well.

The widths of the fitted peaks are shown in Fig. 9.15. Since the intensities of the staging peaks were so small, and their widths were hence kept fixed for higher temperatures, it is difficult to conclude anything for these parameters. For the central $Bmab$ peak, however, the width is seen to decrease slowly before the phase transition, close to which it falls significantly.

Since the value for the staging number is fairly high, $n = 13$, it is interesting to take a look at correlation lengths for this sample. The widths found for the staging peaks were shown in Fig. 9.15(b) as half width half maximum (HWHM) values of around $\text{HWHM} = 0.055$ r.l.u.. A typical domain size D in a sample, connected to the measured reflection, is

$$D = \frac{2\pi}{\text{FWHM}} = \frac{\pi}{\text{HWHM}}, \quad (9.2.1)$$

where FWHM is the full width at half maximum. Using the value for the lattice constant given in Tab. 9.1 to get $\text{HWHM} = 0.055 \cdot 2\pi/c \approx 0.053 \text{ \AA}^{-1}$, it is then given that $D \approx 119 \text{ \AA}$, which corresponds to $119 \text{ \AA}/c \approx 9$ unit cells.

Since the staging number n only counts half a unit cell (as shown in Fig. 6.6 with *e.g.* stage 6 having three unit cells per level), this means that the correlation length in the sample is longer

than the staging number needs to order the oxygen, and it is concluded that staging is indeed possible with such a high value.

9.2.3 Fitting $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ peaks

The measured peaks for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample were shown in Fig. 9.6(d) and on a logarithmic scale in Fig. 9.7(d). In order to find the integrated intensities for each of the elements in the spectra, each full scan has been fitted with a large central Gaussian for the B_{mab} peak, and one small Lorentzian peak on either side for the staging. Again, the mid-point of the staging peaks and their distances to this are used as fitting parameters. Examples of these fits for the $T = 60$ and 220 K datasets are shown in Fig. 9.16. The mid-point between the staging peaks was kept fixed to the $T = 200$ K value for temperatures higher than this because of the low intensity of the staging peaks at these temperatures.

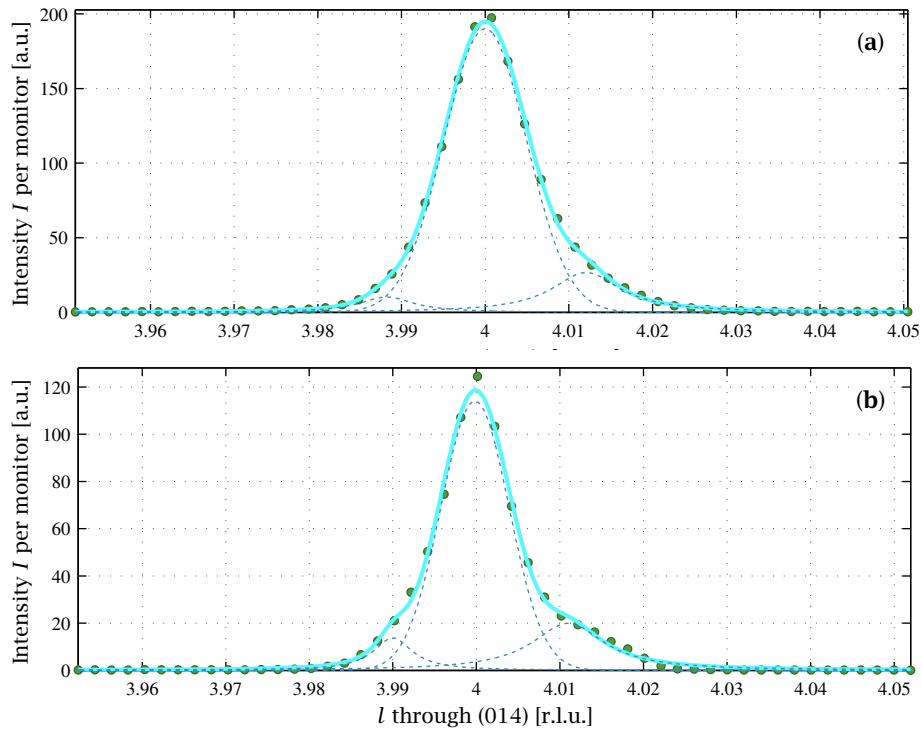


Figure 9.16: Examples of fits done for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ BW5 data, here for the (a) $T = 60$ K and (b) $T = 220$ K measurements. The individual peaks of the fit are shown as dashed lines (plus the constant background), while the full fit is the solid blue line. For points without visible errorbars, the errors are smaller than the marker.

The fitting function was chosen with a central Gaussian because of the shape of the main peak, with two Lorentzians in the shoulders of this peak to account for the asymmetry seen in the measured data. Several other fitting functions were used before the final chosen function, however a central Gaussian with Lorentzians in the shoulders gave the best results. Note also the strong asymmetry in the staging peaks in the shoulders, with the high l peak being much larger than the low l peak.

An overview of the positions of the fitted peaks is shown in Fig. 9.17. The position of the B_{mab} peak and the mid-point of the staging peaks – shown in blue and green, respectively – are, as for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample, very close to each other, with an average distance of only $\delta l = 0.00039(16)$ r.l.u. for temperatures below 200 K. The B_{mab} peak is at lower values of l compared to the mid-point of the staging peaks. As was mentioned for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$

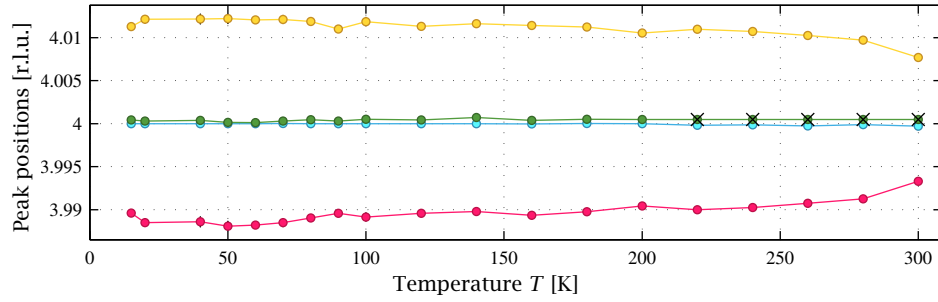


Figure 9.17: Positions of fitted peaks for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample. The blue points show the position of the central *Bmab* peak while the green points show the mid-point of the staging peaks, which are in turn positioned at the yellow and red points. The crossmark indicates a parameter that was fixed to the value from a lower temperature scan. For points without visible errorbars, the errors are smaller than the marker.

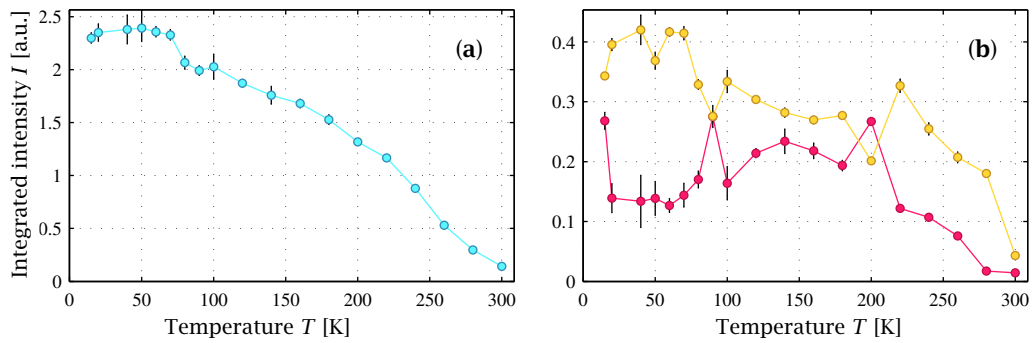


Figure 9.18: Integrated peak intensities of fitted peaks for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample for (a) the central *Bmab* peak and (b) the staging peaks: red points for the low l and yellow for the high l peak (as in Fig. 9.17).

sample, this very small δl value with a large associated uncertainty, leads to the conclusion that there is only a *Bmab* phase in this sample, as opposed to two structural phases.

The distance between the staging peaks (their position shown in yellow and red points) and their mid-point (green points) for temperatures below 200 K is on average $\Delta l = 0.011(3)$ r.l.u., which would correspond to a staging number of just above 89. For higher temperatures this distance becomes even smaller, all the way down to $\Delta l = 0.00719(2)$ r.l.u., corresponding to an n larger than 139, for $T = 300$ K. These values for n are both absurdly high, and most likely means that the fitted shoulder peaks are not actually from staging, but instead stems from random disorder.

The integrated intensities for the fitted peaks are shown in Fig. 9.18. I will work further with these intensities in Sect. 9.4, although at a first glance none of them follow a simple power law very well. They do, however, all fall with temperature: the *Bmab* peak might show two phase transitions instead of one - with a jump in the intensity around 70 K; while the staging peaks fall erratically, most likely caused by noise because of the very low intensities.

The widths of the fitted peaks are shown in Fig. 9.19. For the central *Bmab* peak the width generally falls with rising temperature. The staging peaks also have this general trend, although the high l peak width has a jump in width around $T = 220$ K.

Just like for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample, the value for the staging number for this sample is high, $n = 89$ and higher. It is again interesting to look at the correlation length for this sample. The widths found for the staging peaks were shown in Fig. 9.19(b) with values of

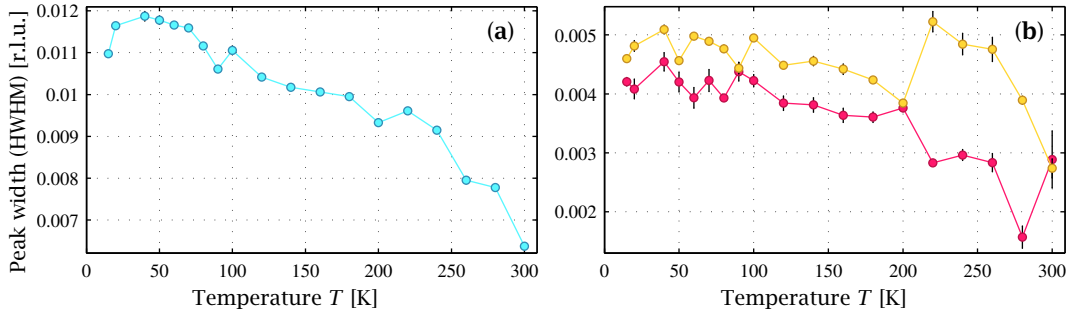


Figure 9.19: Widths of fitted peaks for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample for (a) the central *Bmab* peak and (b) the staging peaks: red points for the low *l* and yellow for the high *l* peak (as in Fig. 9.17).

around $\text{HWHM} = 0.0045 \text{ r.l.u.} = 0.0045 \cdot 2\pi/c \approx 0.0022 \text{ \AA}^{-1}$ for low temperatures (with c from Tab. 9.1). A typical domain size in the sample will then be given by Eq. (9.2.1) as $D \approx 1448 \text{ \AA}$, which corresponds to $1448 \text{ \AA}/c \approx 111$ unit cells.

This means that a staging number of $n = 89$ (needing interactions reaching out $n/2 = 44.5$ unit cells) is indeed possible within the domain sizes, as it was concluded similarly for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample. Even the very large staging number at higher temperatures, up towards 139, is not going against the domain sizes.

9.2.4 Fitting $\text{La}_2\text{CuO}_{4+y}$ peaks

The measured peaks for the $\text{La}_2\text{CuO}_{4+y}$ sample were shown in Fig. 9.6(a) and on a logarithmic scale in Fig. 9.7(a). To find the integrated intensities for each of the elements in the spectra, each full scan has been fitted with a constant background plus a central Gaussian with a smaller Lorentzian at the same center – the *Bmab* peak – and five pairs of Lorentzians – representing staging – fitted with a common mid-point and the same distance to this mid-point in the pairs. Examples of these fits are shown for the $T = 10, 161$, and 220 K datasets in Fig. 9.20.

The choice of fitting function was decided on the basis of the $T = 10 \text{ K}$ data, which show the fitted peaks most clearly. Several parameters were held fixed at higher temperatures: from 30 K and upwards, the distance from the mid-point to the innermost staging peaks at $\Delta l \approx 0.13 \text{ r.l.u.}$ (plotted with left-pointing triangles in the coming figures) was kept fixed to the $T = 10 \text{ K}$ parameter; from 60 K and upwards, the widths of the outermost staging peaks at $\Delta l \approx 0.6 \text{ r.l.u.}$ (up-pointing triangles) were kept fixed to the $T = 50 \text{ K}$ parameters; from 190 K and upwards, the widths of the outer shoulder peaks on the main staging peaks ($\Delta l \approx 0.33 \text{ r.l.u.}$, squares) were kept fixed at the $T = 161 \text{ K}$ parameters; from 220 K and upwards, the widths of the innermost staging peaks ($\Delta l \approx 0.13 \text{ r.l.u.}$, left-pointing triangles) and the distance between the mid-point and the three outermost staging peaks ($\Delta l \approx 0.33 \text{ r.l.u.}$, $\Delta l \approx 0.5 \text{ r.l.u.}$, $\Delta l \approx 0.6 \text{ r.l.u.}$, or squares, diamonds, up-pointing triangles) were kept fixed at the $T = 190 \text{ K}$ parameters; from 250 K and upwards, the widths of the $\Delta l \approx 0.5 \text{ r.l.u.}$ staging peaks (diamonds) were kept fixed at the $T = 220 \text{ K}$ parameters; for 300 K the widths, the mid-point of all the staging peaks, and the distance from the main staging peaks ($\Delta l \approx 0.2 \text{ r.l.u.}$, circles) to the mid-point were kept fixed to the $T = 290 \text{ K}$ parameters.

An overview of the positions of all the fitted peaks is shown in Fig. 9.21. The positions of the *Bmab* peak and the mid-point of the staging peaks – shown in blue and green, respectively – are fairly close, with an average distance of $\delta l = 0.0094(7) \text{ r.l.u.}$ for temperatures below 250 K . For temperatures above this, the distance is first seen to get smaller, and then slightly larger. This

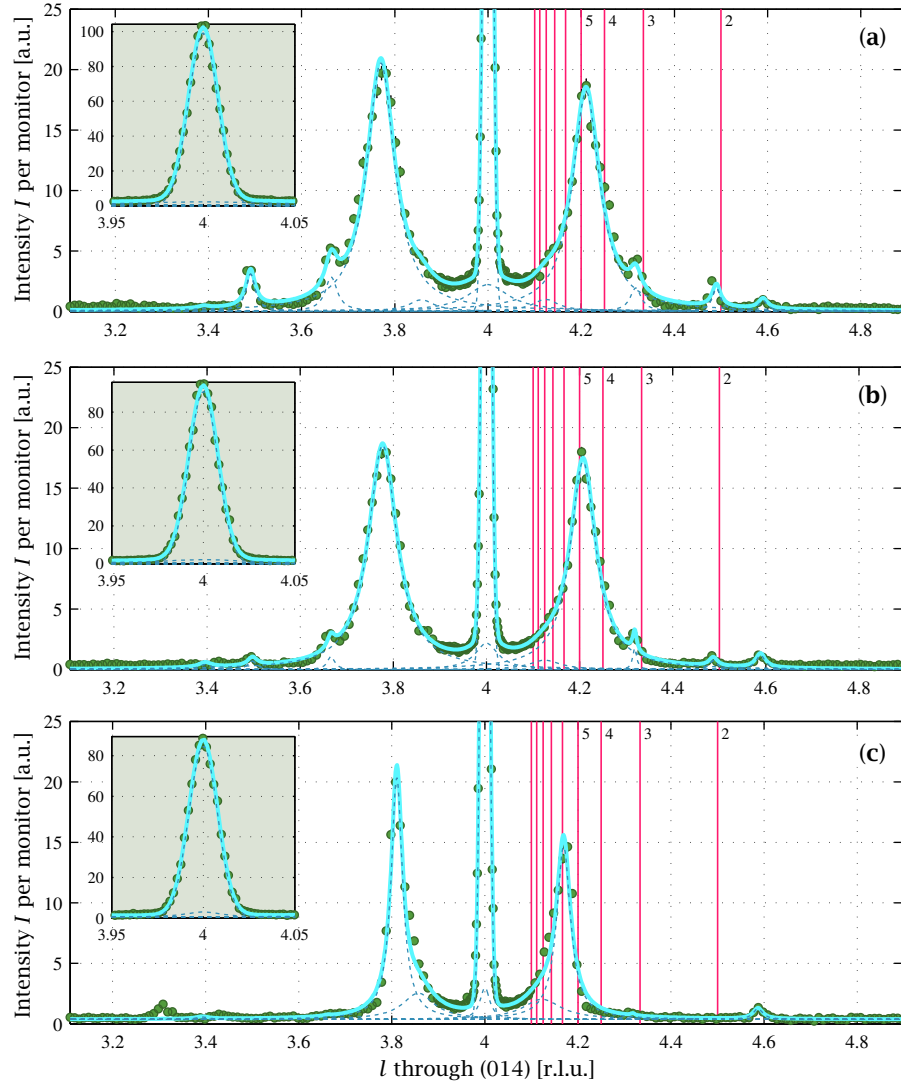


Figure 9.20: Examples of fits done for the $\text{La}_2\text{CuO}_{4+y}$ BW5 data, here for the (a) $T = 10$ K, (b) $T = 161$ K, and (c) $T = 220$ K measurements. The individual peaks of the fit are shown as dashed lines (plus the constant background), while the full fit is the solid blue line. The red lines in the background mark integer staging positions on the high l side up to $n = 10$, with n indicated in the top for the smaller values. For points without visible errorbars, the errors are smaller than the marker. The insets show zoom-ins of the central peak in its full height.

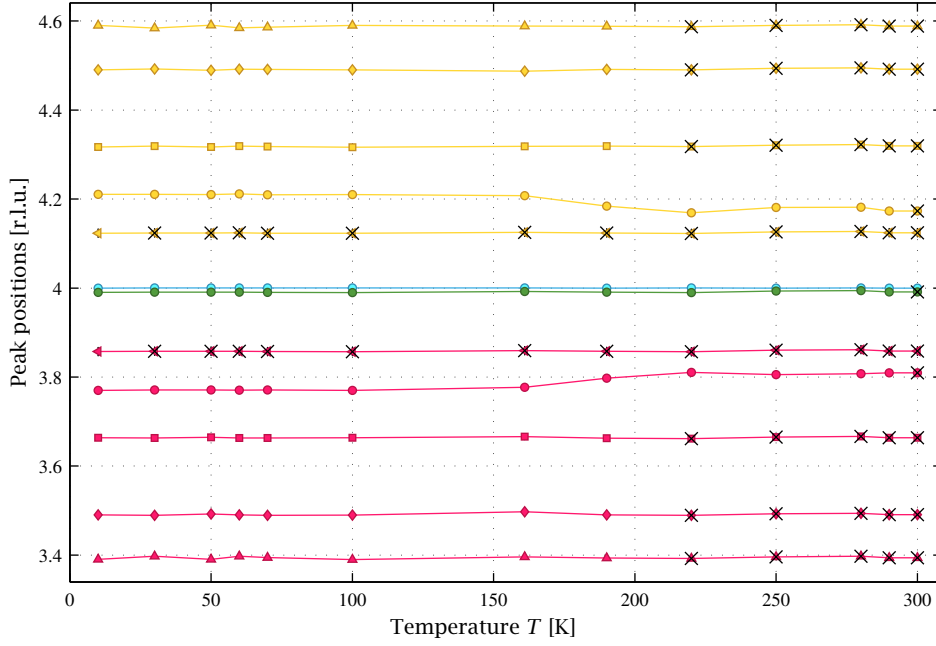


Figure 9.21: Positions of fitted peaks for the $\text{La}_2\text{CuO}_{4+y}$ sample. The blue points show the position of the central $Bmab$ peak while the green points show the mid-point of the staging peaks. The staging peaks are positioned at the other colored points, with the circle points being the large main staging peaks. For points without visible errorbars, the errors are smaller than the marker. Crossmarks over points indicate that the distance from the point to the mid-point were fixed to the value for the temperature lower than where the crossmarks start.

value for δl is small, but significantly larger than zero with the associated uncertainty, indicating that the superstructures are not connected to the $Bmab$ reflection, but instead possibly a structural $Fmmm$ phase, as was concluded for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample.

The distance between the staging peaks (their positions shown in yellow and red, with different symbols used for the different pairs), and their mid-point (green points) are as explained in the following: For the innermost staging peaks (left-pointing triangles, only fitted for 10 K) $\Delta l = 0.13(7)$ r.l.u., corresponding to a staging number n between 7 and 8. The uncertainty on this value is large because of difficulties in fitting the peak resulting from the very low intensities. The largest staging peaks (circles) have $\Delta l = 0.2159(16)$ r.l.u. for temperatures below $T = 170$ K, above which they are seen to move closer to the center, to about $\Delta l = 0.1793(4)$ r.l.u. at the smallest value at $T = 220$ K, corresponding to n just below 5 and between 5 and 6, respectively. The small peaks in the shoulder of the large staging peak (squares) have $\Delta l = 0.327(13)$ r.l.u. for temperatures below $T = 210$ K, above which the distance to the mid-point is kept fixed. This corresponds to a staging number of $n = 3$. The next peaks (diamonds) have $\Delta l = 0.500(6)$ r.l.u. for temperatures below $T = 210$ K, above which the distance to the mid-point is kept fixed. This corresponds to a staging number of $n = 2$. The outermost peaks (up-pointing triangles) $\Delta l = 0.597(5)$ r.l.u. for temperatures below $T = 210$ K, above which the distance to the mid-point is kept fixed. This corresponds to a staging number n between 1 and 2, which might indicate that these outermost peaks are not actually a superstructure of (014), but rather the surrounding integer (hkl) positions, here (013) and (015).

The integrated intensities for all of the fitted peaks are shown in Fig. 9.22. I will work further with some of these in Sect. 9.4, but I will go through the results here in a descriptive way.

As an initial observation the central $Bmab$ peak (shown both split up in the Gaussian and Lorentzian and as the total in Fig. 9.22(a)) does not follow a power law, but simply falls off

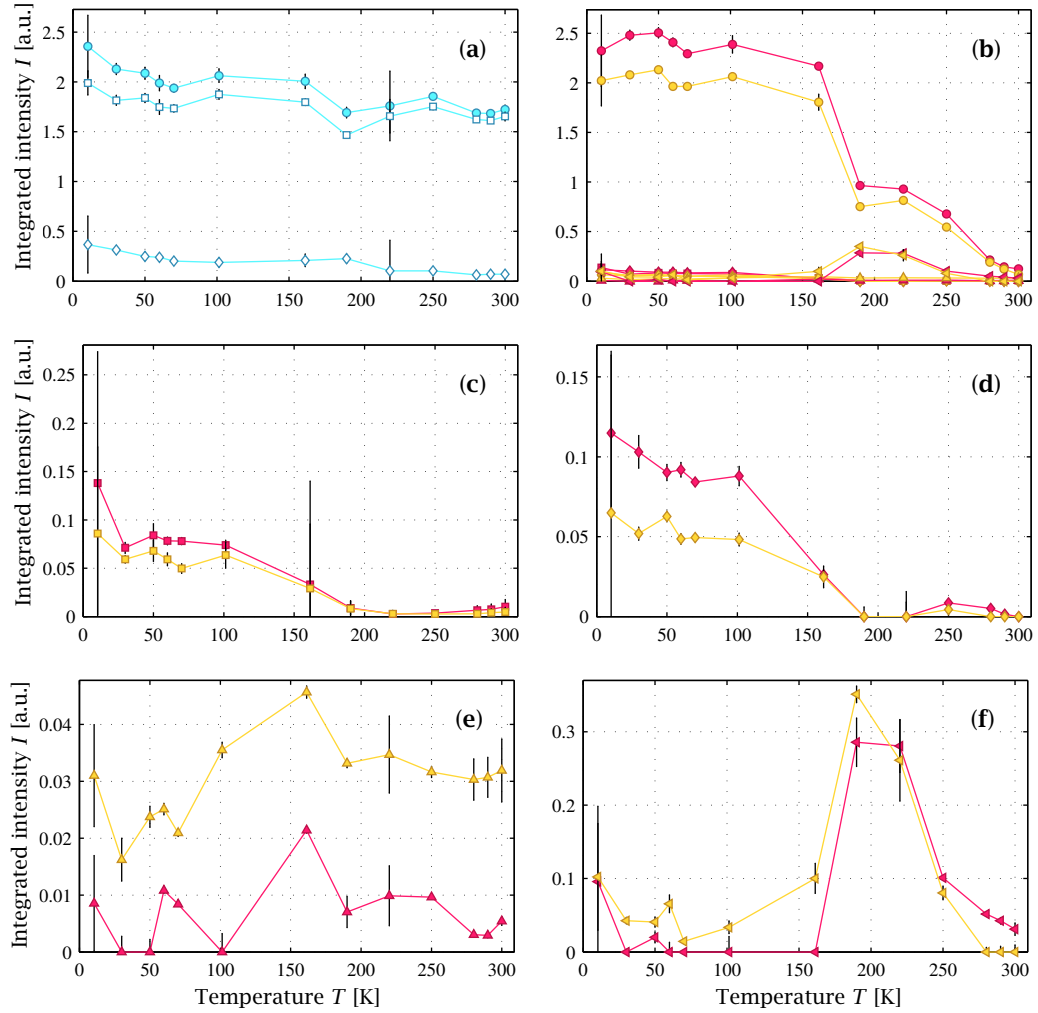


Figure 9.22: Integrated peak intensities of fitted peaks for the $\text{La}_2\text{CuO}_{4+y}$ sample. **(a)** The central $Bmab$ peak: empty diamonds for the Lorentzian tail, empty squares for the Gaussian main part of the peak, and filled circles for the sum of the two. **(b-f)** The staging peaks: red points for the low l and yellow for the high l peaks, with different symbols depending on the set of peaks following the symbols and colors of Fig. 9.21: the circles in **(b)** are the two large main staging peaks, the squares in **(c)** are the two $\Delta l \approx 0.33$ r.l.u. staging peaks, the diamonds in **(d)** are the two $\Delta l \approx 0.5$ r.l.u. staging peaks, the up-pointing triangles in **(e)** are the two $\Delta l \approx 0.6$ r.l.u. staging peaks, and the left-pointing triangles in **(f)** are the two $\Delta l \approx 0.13$ r.l.u. staging peaks. The smaller staging peaks are shown both in **(b)** for an easy comparison, and in their individual plots in **(c-f)**.

slowly with rising temperature. This is expected, since the HTT to LTO phase transition is above room temperature for the $\text{La}_2\text{CuO}_{4+y}$ sample.

The main staging peaks, shown with circle points in Fig. 9.22(b), seem to follow a power law, although the sudden fall at $T = 190$ K might be problematic. This fall could stem from a slight change in the peak shape that has not been resolved well enough, or maybe from these staging peaks actually consisting of a combination of $n = 4$ and 5. Note, however, that this fall in intensity coincides with the rise in intensity seen on the inner-most staging peak, as seen in Fig. 9.22(f).

The four smaller staging peaks are harder to conclude anything from. The data in Fig. 9.22(c) and (d) show a phase transition, although it is not very Landau-like. The intensities in Fig. 9.22(e) and (f) are so noisy that I cannot conclude much from them.

Finally, the widths of the fitted peaks are shown in Fig. 9.23. For the B_{mab} peak the width is shown for each of the two parts of the peak, and seems fairly constant. There is, however, a rise in the width for the Gaussian part in Fig. 9.23(b), which might indicate that a phase transition is close.

For the main staging peaks, in Fig. 9.23(c), the width seems to fall, but suddenly rise for the high l peak (yellow points). This rise might not mean much, though, since the intensity of the peak is very low at these temperatures. For the other staging peaks, the widths are kept fixed for many of the higher temperatures, although a small fall in width with temperature is seen in Fig. 9.23(d) with the opposite happening in Fig. 9.23(e).

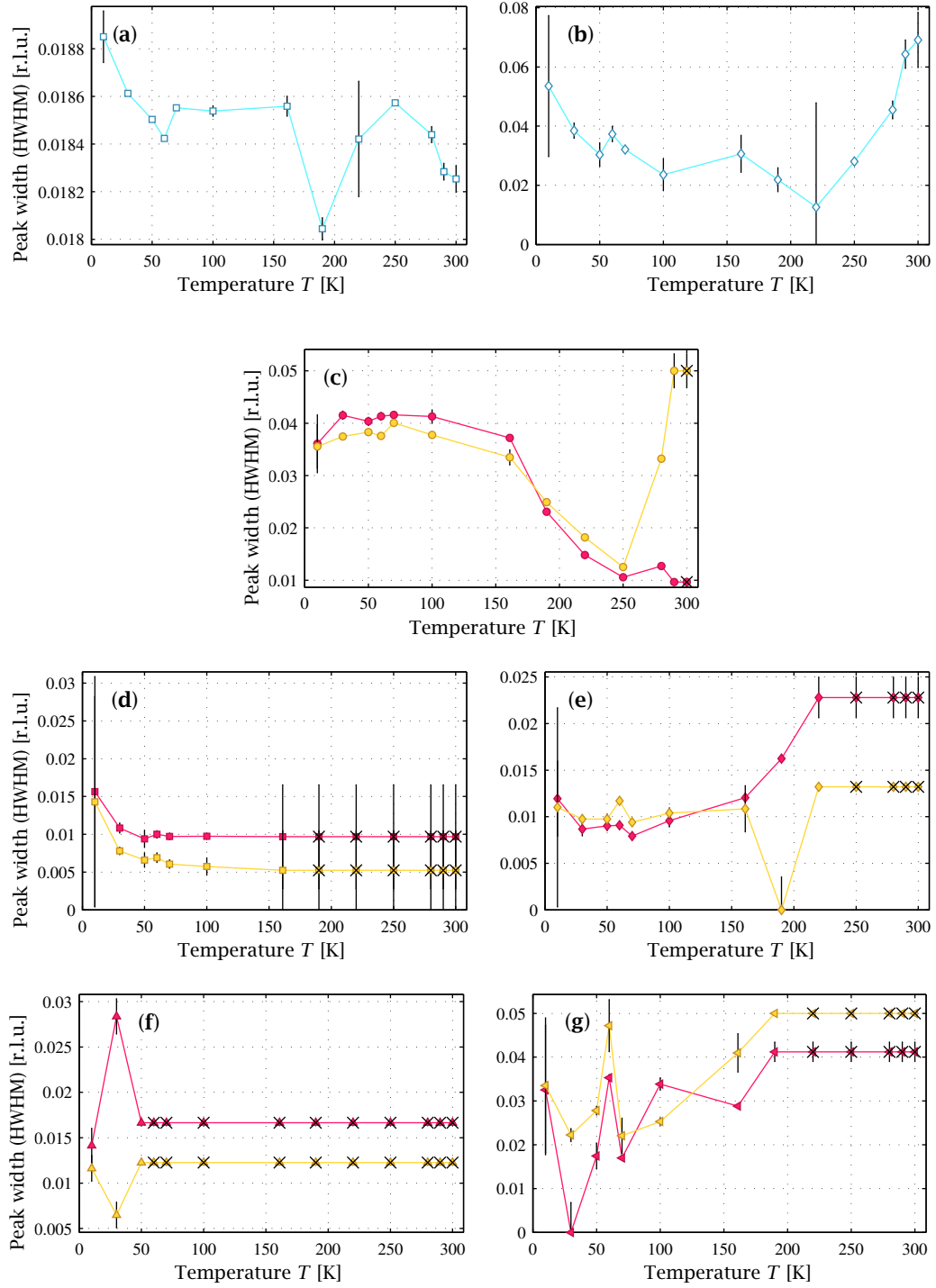


Figure 9.23: Widths of fitted peaks for the $\text{La}_2\text{CuO}_{4+y}$ sample. (a) The Lorentzian tail and (b) the Gaussian main part of the central $Bmab$ peak (following the symbols from Fig. 9.22(a)). (c) The main staging peaks. (d-g) The smaller staging peaks. All the staging peaks follow the symbols and colors from Fig. 9.21, with red points for the low l and yellow for the high l peaks: the circles in (c) are the two large main staging peaks, the squares in (d) are the two $\Delta l \approx 0.33$ r.l.u. staging peaks, the diamonds in (e) are the two $\Delta l \approx 0.5$ r.l.u. staging peaks, the up-pointing triangles in (f) are the two $\Delta l \approx 0.6$ r.l.u. staging peaks, and the left-pointing triangles in (g) are the two $\Delta l \approx 0.13$ r.l.u. staging peaks. Crossmarks over points indicate that the width was fixed to the value of the temperature lower than where the crossmarks start.

9.3 Alternative ways to find the transition temperature

In order to analyze the phase transitions and get out the transition temperature and critical exponent, data will be fitted with power laws as suggested in Chap. 5. However, some of the found temperature dependent integrated intensity datasets have very few useable points, or behave in a noisy way. In order to find the critical exponent for the phase transition for these it is helpful to determine the transition temperature first – in an alternative way than simply fitting with a power law to get both parameters out simultaneously. There are several ways to do this, but below I will explain the two methods I have used for the data analysis in this thesis, and then continue to fitting with power laws in Sect. 9.4.

9.3.1 Taking extinction and twinning at the phase transition into account

When going from the high temperature tetragonal (HTT) phase to the low temperature orthorhombic (LTO) phase, several new reflections show up in the data. These reflections were forbidden in the HTT phase, and going through the transition, more of the crystal is hence “seen”, simply from the change in the structure factor. This results in a lowering in intensity of the reflections that are allowed in both phases (but split up in the LTO phase), with a very sharp transition. On the other hand, twinning also happens at this transition, causing the sample to be divided into several domains, which will relieve extinction just as mosaicity would – also happening as a very sharp transition, but with the effect of increasing the intensity, [112, 121].

This sharp transition should be at the same temperature as the central *Bmab* peak of the (014) spectra show up, because this is where the crystal symmetry changes from HTT to LTO, and hence where the point (014) becomes an allowed reflection in reciprocal space (since it was forbidden for the tetragonal crystal symmetry following Tab. 6.1). As has earlier been mentioned, the staging peaks are likely a superstructure of another structural phase (*Fmmm*), and can show up at a different temperature than this. Hence, this method can only be used to find the transition temperature for the central peak, not the staging peaks.

Several measurements of fundamental peaks such as (020), (004), and (022) were taken as a function of temperature during the different experiments. In order to check for extinction effects for the samples, the (020) peaks were investigated for each of these. The raw data* is shown in Fig. 9.24.

The $\text{La}_2\text{CuO}_{4+y}$ sample did not show any significant change in intensity over temperature, however this is expected since the transition temperature from the HTT to the LTO phase is above room temperature for this doping.

It is also as expected that extinction is a small effect for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample, since this sample is very small – and the data does indeed not change much over temperature.

The data for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample shows a clear change when the temperatures get low, with the peak almost halving in intensity.

Extinction was expected to be a significant effect for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample, but as is seen in Fig. 9.24(d), the temperature dependence is more complicated, with the peak splitting up at lower temperatures, possibly because of twinning (which is expected to split the peak with about 0.1° , following the calculations shown in Appx. A.4).

To find the transition temperature for the HTT to LTO transition in $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ from the data in Fig. 9.24(c), each temperature scan has been fitted with a Gaussian plus a Lorentzian fixed at the same center. The integrated intensity of the sum of these two peaks as a function of temperature is shown in Fig. 9.25(a). The effect is clearly a smaller intensity on the fundamental peak when getting below the transition temperature, which either means that the extinction

*The raw data for the measured (004) and (022) peaks for some of the samples can be seen in Fig. D.22, but none of these showed any significant extinction effects.

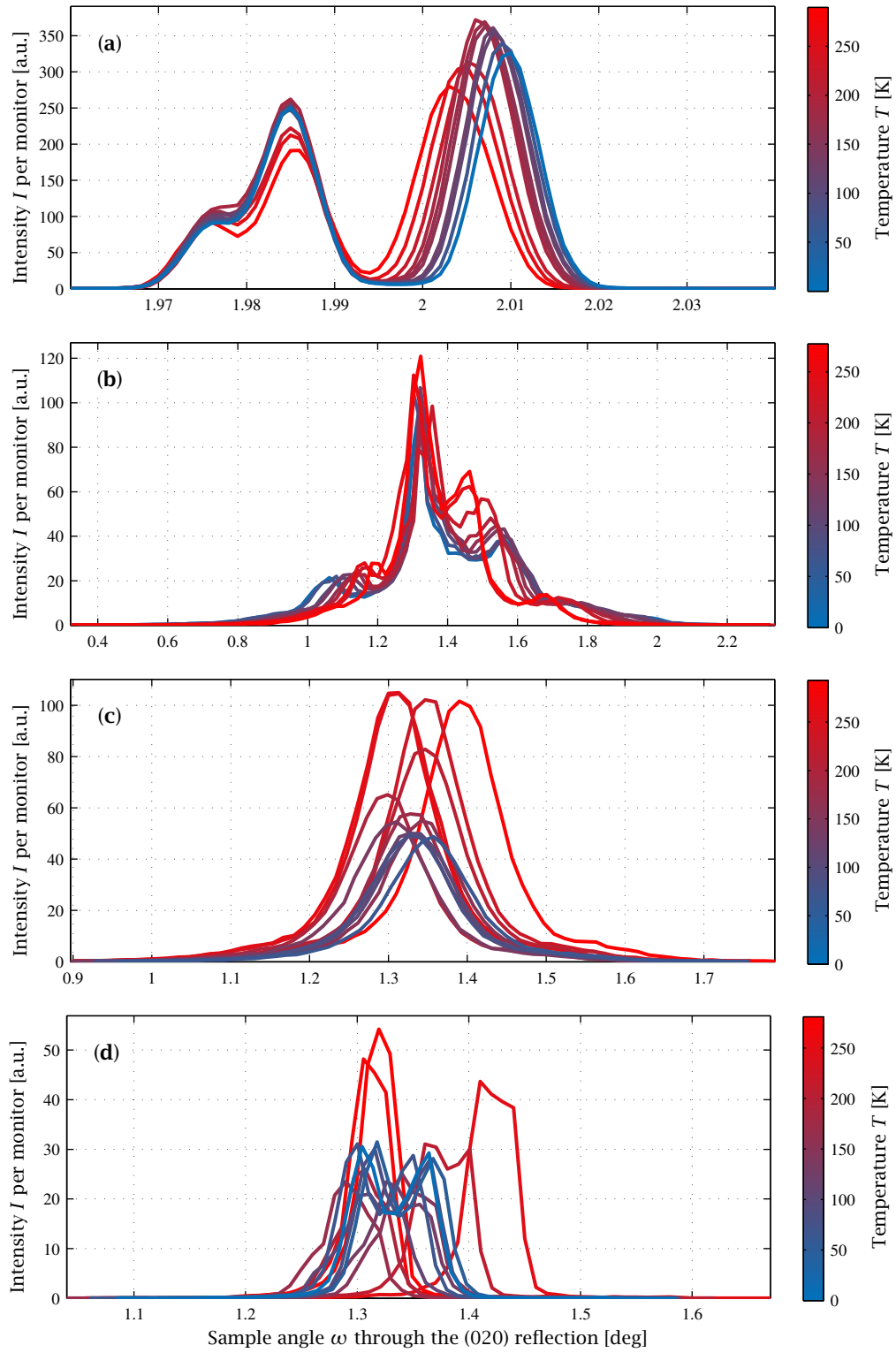


Figure 9.24: Measurement along ω over the (020) peak on BW5 for the (a) $\text{La}_2\text{CuO}_{4+\gamma}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ crystals.

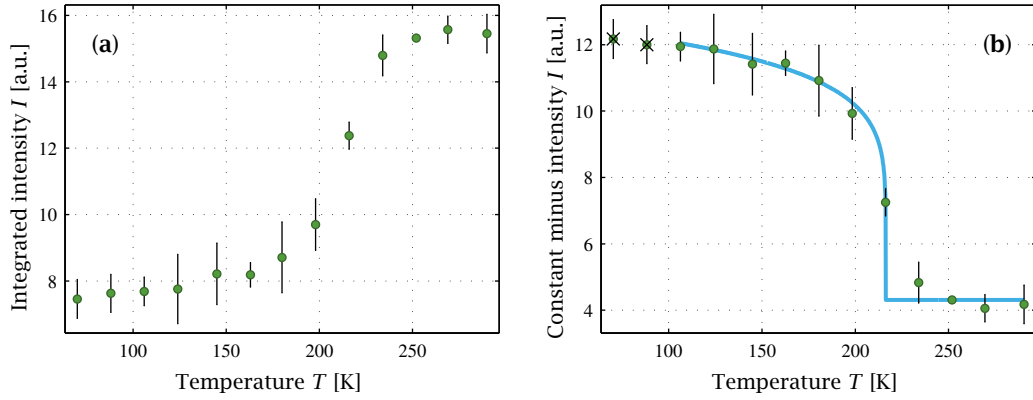


Figure 9.25: Integrated peak intensities for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ (020) peak scans shown in Fig. 9.24(c). (a) The intensities directly from the fits. (b) The intensities subtracted from an arbitrary constant in order to fit with a simple power law shown in blue. The transition temperature was found to be $T_{\text{HTT-LTO}} = 216.3(5)$ K. Crossmarks indicate points that are not used for the fit.

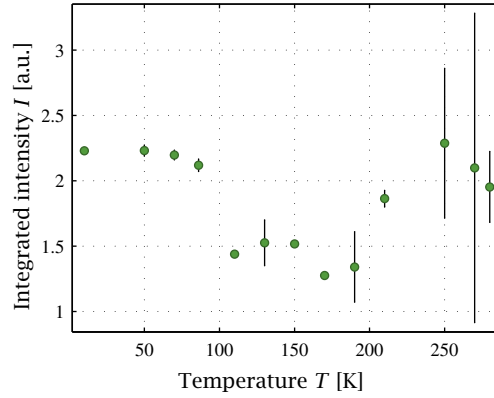


Figure 9.26: Integrated (020) peak intensities for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample, obtained with a double Gaussian fit of the peak in Fig. 9.24(d).

dominates, and the twinning – in this case – is not a large enough effect to counteract this, or simply that the structure factor changes significantly between the HTT and LTO phases.

In order to fit the intensities to a standard power law (as defined in Appx. C), these data are subtracted from an arbitrarily chosen constant, resulting in the fit shown in Fig. 9.25(b). This fit gave a transition temperature of $T_{\text{HTT-LTO}} = 216.3(5)$ K, which will be used later when working with the (014) peak data. Note however that the statistical uncertainty on this transition temperature, as found by fitting with *spec1d*, is very low and should probably be a little larger due to the model choice: the transition temperature is mostly determined by the one datapoint exactly at this temperature in Fig. 9.25(b).

The (020) peaks for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample in Fig. 9.24(d) were fitted in order to get the integrated intensities as well. Two Gaussians were used in order to take the peak splitting into account. The integrated intensities as a function of temperature can be seen in Fig. 9.26.

The results – significantly so at high temperatures – have large errorbars because of the poor resolution of the (020) peak measurements. However two things can be seen as general features: at temperatures lower than $T \approx 80$ K the intensity rises, coinciding with the temperature where the peaks visibly split up into two peaks instead of overlapping; and at temperatures above $T \approx 220$ K the intensity also rises. The low temperature effect is the opposite of what is seen in Fig. 9.25 for $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, meaning that the twinning relief of the extinction dominates

here. The higher temperature effect is just as was seen for $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, where the extinction dominates.

The effect at low temperature is much like was seen on the integrated intensities for the *Bmab* (014) peak for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample in Fig. 9.18(a), indicating that a small second phase transition might indeed happen at lower temperatures. By eye, the transition temperature for the higher temperature effect in Fig. 9.26, at around 220 K, also matches the behavior of the *Bmab* (014) peak.

9.3.2 Slope analysis of the integrated intensities

One measure of the position of the transition temperature is where the slope of the integrated intensities as a function of temperature is the highest (of course assuming that a phase transition is seen at all), [122]. In order to do this analysis, the integrated intensity data has been interpolated linearly, and then this data has been smoothed with a low-pass Butterworth filter* in order to be able to find the gradient in a meaningful way. The minimum of the gradient of this can then be found, and hence indicate the transition temperature.

This analysis has been done for all of the found integrated intensities, although it is only used directly in the further analysis for the main staging peaks of the $\text{La}_2\text{CuO}_{4+y}$ sample (shown in Fig. 9.27(a) and (b), giving $T_{\text{staging}} = 175(5)$ K for both), the central *Bmab* peak for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample (shown in Fig. 9.27(c), giving $T_{\text{HTT-LTO}} = 57(5)$ K), and the central *Bmab* peak for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample (shown in Fig. 9.27(d), giving $T_{\text{HTT-LTO}} = 247(5)$ K). The errors on these numbers have been estimated manually, since the used method was not very well developed.

Apart from these directly used results, it is also interesting to compare the slope analysis with the power fit analysis done on the rest of the integrated intensities. The analysis done for the $\Delta l \approx 0.33$ r.l.u. and $\Delta l \approx 0.5$ r.l.u. staging peaks for the $\text{La}_2\text{CuO}_{4+y}$ sample is shown in Fig. 9.28.

For the $\Delta l \approx 0.33$ r.l.u. staging peaks in Fig. 9.28(a) and (b) the slope analysis results in very low values because of the somewhat erratic behavior of the data. However, they both seem to have a second minimum around $T_{\text{staging}} \approx 175$ K.

For the $\Delta l \approx 0.5$ r.l.u. staging peaks in Fig. 9.28(c) and (d) the slope analysis give meaningful results with $T_{\text{staging}} = 121(5)$ K for the low l peak and $T_{\text{staging}} = 174(5)$ K, although it could be argued if they should both be around the 174 K value with the very wide minimum seen in the gradient of the low l results: I choose to set the low l transition temperature manually to 175(5) K because of this.

The remaining slope analyses are shown in Fig. D.23, and are mostly for comparison with the transition temperatures found directly from the temperature series for the (014) peak scans later.

For $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ the transition temperatures were found to be $T_{\text{staging}} \approx 212(5)$ K for the staging peak at low l and $T_{\text{staging}} \approx 214(5)$ K at high l with this method.

For $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, the method gave a transition temperature $T_{\text{HTT-LTO}} \approx 202(5)$ K for the central *Bmab* peak, and $T_{\text{staging}} \approx 202(5)$ K for both the staging peak at low and high l .

The results for the staging peaks for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample were both inconclusive, with a best guess that the transition temperatures are around 250 K or higher for both peaks.

*This is done using the functions `butter()` and `filtfilt()` for *MATLAB*, [166], with settings such that the smoothed data - evaluated by eye - seemed right.

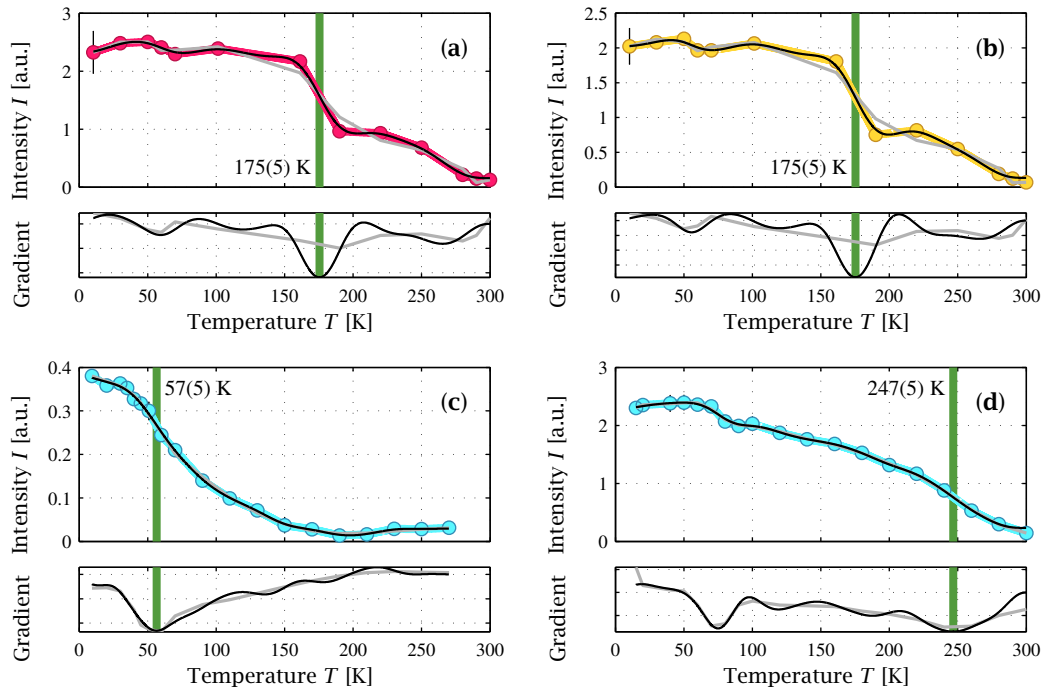


Figure 9.27: Slope analysis of integrated intensities of (a) the low l and (b) high l main staging peaks ($\Delta l \approx 0.2$ r.l.u.) of the $\text{La}_2\text{CuO}_{4+y}$ sample, (c) the central $Bmab$ peak of the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample, and (d) the central $Bmab$ peak of the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample. The integrated intensity points are plotted directly, while linearly interpolated points are shown as a colored line underneath. A smoothing filter has been applied to the data points (grey) and the interpolated points (black), resulting in the gradients shown in the bottom parts of each plot. The gradient minimum for the smooth data is marked by a green line.

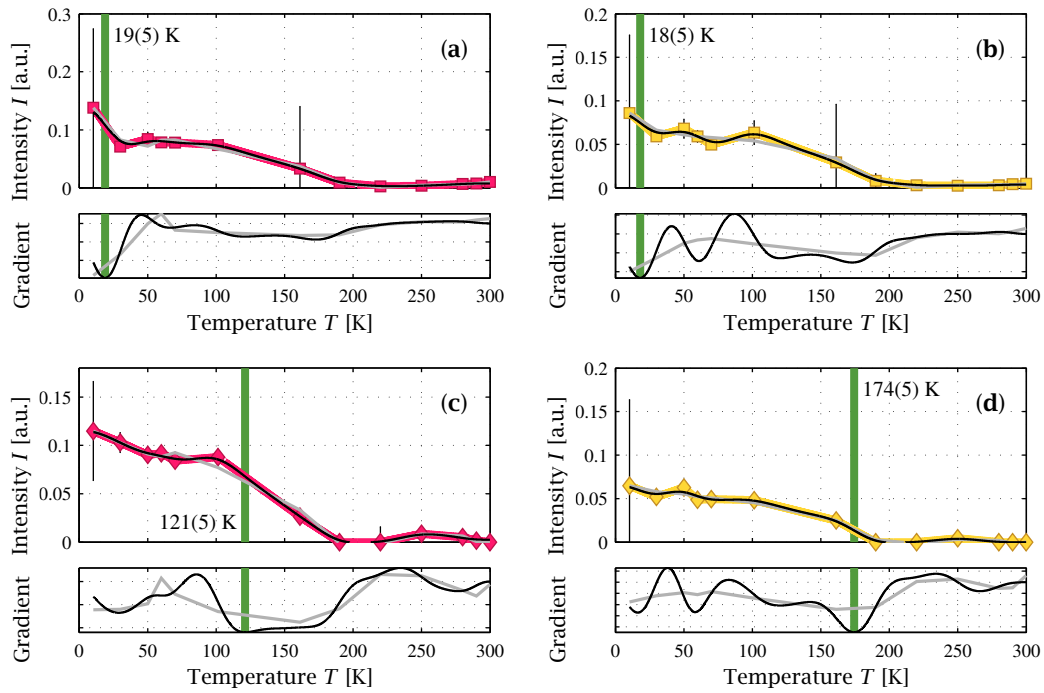


Figure 9.28: Additional slope analysis of the integrated intensity of some of the smaller staging peaks for $\text{La}_2\text{CuO}_{4+y}$. (a) The low l and (b) high l $\Delta l \approx 0.33$ r.l.u. staging and (c) the low l and (d) high l $\Delta l \approx 0.5$ r.l.u. staging. The method and coloring of the different elements are as explained in the caption of Fig. 9.27.

9.4 Analysing the *B_{mab}* and staging phase transitions

The integrated peak intensities were shown for the four samples in Figs. 9.10, 9.14, 9.18 and 9.22. As explained in Chap. 5, these intensities should be fitted with a power law to find the transition temperature and critical exponent for the phase transitions. Saturation of the order parameter and critical scattering will have to be taken into account by only fitting some temperature regions of the data.

9.4.1 Choosing which part of the data to fit

As was described in Subsect. 5.3.3 the intensities tend to saturate for very low temperatures, which is especially seen for the $\text{La}_2\text{CuO}_{4+y}$ and $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ (staging) results here. The fits should be cut off such that these temperatures are not used. As a rule of thumb if the transition temperature is already known, the cut-off happens at T equal to a third of this, [85, Fig. 1]. If the transition temperature has already been found by alternative methods, such as looking at the (020) peak or the slope analysis, this value is used to determine the cut-off, and directly for the fit instead of fitting this parameter. If the transition temperature is not already known, this is simply a matter of trying out different cut-offs and evaluating which one gives the better and more realistic fit, combined with looking at the data by eye to evaluate if the results are meaningful.

The critical scattering happening close to the transition temperature, resulting in the intensity not falling as fast as was expected as explained in Subsect. 5.3.4, also has to be taken into account. This is done by omitting points above and close to the transition temperature, in order to ignore the smoothing of the transition and only fit the data unaffected by critical scattering. Several different cut-offs were tried for each fit, and the ones giving the best fits were chosen.

9.4.2 Fit results for the phase transitions

The final fitted integrated intensities for each of the peaks in the (014) scans are shown in Fig. 9.29, with overlapping axes for the staging peaks (left axis) and central *B_{mab}* peak (right axis shown in blue) for easier comparison. They are all fitted with power laws (as defined in Appx. C) as explained in the following. The results are also shown plotted on double logarithmic axes in Fig. D.24.

The $\text{La}_2\text{CuO}_{4+y}$ staging peak transition temperatures were held fixed to the values found with the slope analysis, as explained in Subsect. 9.3.2 and shown in Fig. 9.27(a) and (b). The *B_{mab}* peak for this sample was not fitted, since no clear phase transition is seen.

The $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ *B_{mab}* peak transition temperature was also held fixed to the value found with the slope analysis, as shown in Fig. 9.27(c). This was especially necessary for this peak, since the phase transition is so wide, possibly because of a large contribution from critical scattering.

The $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ *B_{mab}* peak transition temperature was held fixed at the value found with the (020) peak data, as explained in Subsect. 9.3.1 and shown in Fig. 9.25.

Finally, the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ *B_{mab}* peak transition temperature was also held fixed to the value found with the slope analysis, as shown in Fig. 9.27(d).

The fits done for the two main staging peaks for the $\text{La}_2\text{CuO}_{4+y}$ sample are slightly inaccurate, mainly because of the very few points that were useable for the fit. The critical exponents ended up being $2\beta = 0.06(4)$ and $0.09(5)$ for the low and high l peaks, respectively, but with reduced χ^2 values of 55 and 183, these values are not to be trusted.

However, looking at the double logarithmic plots in Fig. D.24(a) and (b), where the fitted points should lie on a straight line to follow the power law behavior, it seems that this is how

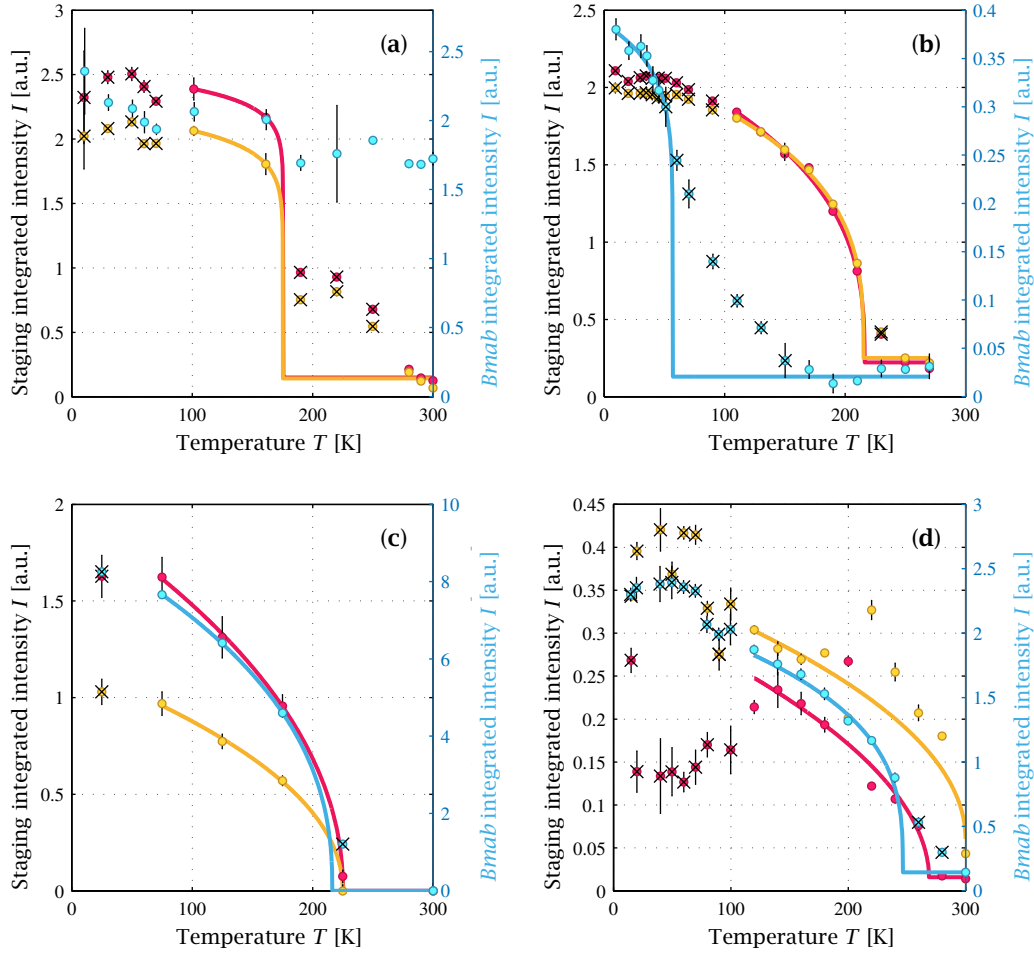


Figure 9.29: Integrated intensities fitted with power laws, with the *Bmab* peaks (shown in blue) and staging peaks (shown in red and yellow) on different axes to be able to compare them more easily. Crossmarks indicate points that are not used for the fit, either because of saturation (low T) or critical scattering (T close to transition temperature). (a) $\text{La}_2\text{CuO}_{4+y}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$.

good the fit can get with the low number of points available. The points omitted from the fit due to saturation also fall underneath the straight line, as expected.

The fits done for the staging peaks for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample were much better, with enough datapoints in the relevant temperature regions to get fits with reduced χ^2 values of 2.2 and 0.7, critical exponents 2β of 0.36(2) and 0.312(14), for the low and high l peaks, respectively. The transition temperatures T_{staging} were found to be 216.2(1.1) and 215.3(1.0) K, respectively, compared to the values from the slope analysis of 212(5) and 214(5) K.

The central *Bmab* peak was only fitted for narrow temperature intervals at low and high temperature, and gave a critical exponent of $2\beta = 0.12(4)$ with a reduced χ^2 of 1.3. Note that these very low reduced χ^2 values might indicate an over-estimation of the uncertainties of the datapoints, originating from the fitting routine used to fit the peak shapes – this is also true for the following results.

Looking at the double logarithmic plots in Fig. D.24(c) to (e), it is easily seen that these fits are well determined, with the points lying on a straight line, and the saturated point falling below this.

The fits done for the staging peaks for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample resulted in reduced χ^2 values of 0.04 and 0.23, critical exponents 2β of 0.48(18) and 0.48(15), and transition temperatures T_{staging} of 225.3(9) and 225(5) K for the low and high l peak, respectively. The transition temperatures can be compared to the ones found with the slope analysis, both at 202(5) K. The fit of the central *Bmab* peak gave a critical exponent of $2\beta = 0.41(3)$ with a reduced χ^2 of 0.02.

Again looking at the double logarithmic plots, now in Fig. D.24(f) to (h), the fits are well determined with the few available points.

The fits done for the staging peaks for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample were fairly inaccurate because of the very noisy data, resulting in fits with reduced χ^2 values of 58 and 77, critical exponents 2β of 0.52(6) and 0.50(8), and transition temperatures T_{staging} of 279(4) and 300(8) K for the low and high l peak, respectively. The fit of the central *Bmab* peak gave a critical exponent of $2\beta = 0.332(16)$ with a reduced χ^2 of 3, and a much better agreement with data.

Looking at the double logarithmic plots for these fits, shown in Fig. D.24(i) to (k), the central *Bmab* peak fit is well determined as expected.* The precision of the staging peak fits are clearly limited by the noisy data: the fits do, however, agree overall with a straight line.

A final overview of all of the results mentioned so far in this chapter is shown in Tab. 9.2, which also refers to the individual figures where the results were found.

Note how the transition temperature T_{staging} for each of the staging peak sets (low and high l) agree well. In the same way the staging peaks for all the different staging numbers agree well for the same sample, as seen for the $\text{La}_2\text{CuO}_{4+y}$ sample. In most cases, the direct fit and alternative method (slope analysis or (020) peak extinction analysis, when available) also agree, with exception of the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ staging peaks, where the slope analysis gave lower values. This could be interesting to investigate further, by measuring for more temperatures.

The critical exponents for the staging peaks are seen to increase for increasing Sr doping, while the critical exponents for the central *Bmab* peaks seem a little more erratic.

*Possibly with the hint of a second phase transition at low temperatures as was also mentioned earlier, indicated in the double logarithmic plot as low temperature points being above the line instead of below it (as would be expected for the saturation seen in the other samples).

Sample and peak	Staging distance Δl [r.l.u.]	Staging number n	Transition temperature [K]	Result from	Critical exponent 2β	Result from direct fit in
La₂CuO_{4+y}						
Central <i>Bmab</i>	$(\delta l = 0.0094(7) \text{ r.l.u., } Bmab \text{ higher in } l - \text{significant difference})$			Direct fit: Fig. 9.22(a)		
Low l staging	0.2159(16)	4.6	> 300	Slope analysis: Fig. 9.27(a)	0.06(4)	Fig. 9.29(a)
High l staging	—	—	175(5)	Slope analysis: Fig. 9.27(b)	0.09(5)	Fig. 9.29(a)
Low l staging	0.327(13)	3.1	~175	Slope analysis: Fig. 9.28(a)		
High l staging	—	—	~175	Slope analysis: Fig. 9.28(b)		
Low l staging	0.500(6)	2.0	175(5)	Slope analysis: Fig. 9.28(c)		
High l staging	—	—	174(5)	Slope analysis: Fig. 9.28(d)		
La_{1.96}Str_{0.04}CuO_{4+y}						
Central <i>Bmab</i>	$(\delta l = 0.014(2) \text{ r.l.u., } Bmab \text{ higher in } l - \text{significant difference})$			Slope analysis: Fig. 9.27(c)	0.12(4)	Fig. 9.29(b)
Low l staging	0.193(8)	5.1	57(5) (atypical)	Direct fit: Fig. 9.29(b)	0.36(2)	Fig. 9.29(b)
High l staging	—	—	216.2(1.1)	Slope analysis: Fig. D.23(b)		
			212(5)	Direct fit: Fig. 9.29(b)	0.312(14)	Fig. 9.29(b)
			215.3(1.0)	Slope analysis: Fig. D.23(c)		
La_{1.935}Str_{0.065}CuO_{4+y}						
Central <i>Bmab</i>	$(\delta l = 0.0017(11) \text{ r.l.u., } Bmab \text{ lower in } l - \text{no significant difference})$			(020) analysis: Fig. 9.25(b)	0.41(3)	Fig. 9.29(c)
Low l staging	0.0755(14)	13.2	216.3(5)	Slope analysis: Fig. D.23(d)		
High l staging	—	—	202(5)	Direct fit: Fig. 9.29(c)	0.48(18)	Fig. 9.29(c)
			225.3(9)	Slope analysis: Fig. D.23(e)		
			202(5)	Direct fit: Fig. 9.29(c)	0.48(15)	Fig. 9.29(c)
			225(5)	Slope analysis: Fig. D.23(f)		
La_{1.91}Str_{0.09}CuO_{4+y}						
Central <i>Bmab</i>	$(\delta l = 0.00039(16) \text{ r.l.u., } Bmab \text{ lower in } l - \text{no significant difference})$			Slope analysis: Fig. 9.27(d)	0.332(16)	Fig. 9.29(d)
Low l staging	0.011(3)	89.0	247(5)	Direct fit: Fig. 9.29(d)	0.52(6)	Fig. 9.29(d)
High l staging	—	—	279(4)	Direct fit: Fig. 9.29(d)	0.50(8)	Fig. 9.29(d)
			300(8)			

Table 9.2: Overview of the transition temperatures, critical exponents, and (low temperature) staging information found for the different peaks from the four samples on BW5, with references to figures showing how the results were found for the two first mentioned. Note that the staging distance Δl (and hence staging number n) is the same for the low and high l peaks for one set of staging peaks, and is hence only shown for one of them. The distance between the central *Bmab* peaks and the mid-points of the staging peaks, δl have also been shown. Note the La₂CuO_{4+y} *Bmab* peak transition, which was very atypical with a large amount of critical scattering and a very low transition temperature.

9.5 Results from RITA-II measurements

Measurements on the neutron instrument RITA-II were done for all four samples as a function of temperature, just like on BW5.

The results along with some examples of fitted data for a few temperatures are shown in Fig. 9.30(a) for $\text{La}_2\text{CuO}_{4+y}$, Fig. 9.30(b) for $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, Fig. 9.31(a) for $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and Fig. 9.31(b) for $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$. The initial analysis resulting in these figures was done by Linda Udby, [154].

The temperature series of the peak areas (integrated peak intensities) from the insets of the figures can be analysed in the same way as I did for the BW5 data, but I will here simply do a couple of observations for comparison with the results from BW5 – leaving the full analysis for the future.

For $\text{La}_2\text{CuO}_{4+y}$ it is seen that the central *Bmab* (014) peak does not change much in integrated intensity (black points in the third inset of Fig. 9.30(a)). This agrees well with the X-ray data, where the *Bmab* peak did not show a phase transition either.

The staging peaks are positioned between $\Delta l = 0.25$ and 0.3 from $l = 4$ (colored points in the first inset of Fig. 9.30(a)), corresponding to staging number $n = 4$ or a little lower. They have a slight tendency to a larger distance for higher temperatures. The larger Δl on RITA-II compared to the one on BW5 could be explained by the smaller peaks at $\Delta l \approx 0.33$ r.l.u. being explicitly fitted as a different set of staging reflections, which they were not for the RITA-II data because they were not directly seen – either because of the low flux or possibly a wider resolution. In the same way, none of the smaller staging peaks seen in the X-ray data were seen in the neutron data – it should, however, be mentioned that these *are* seen with neutrons in the reciprocal space maps presented in Chap. 10 for two different $\text{La}_2\text{CuO}_{4+y}$ samples.

The staging seems to have a transition temperature of $T = 300(10)$ K (colored points in the third inset of Fig. 9.30(a)), which does not seem to agree with the X-ray data – although the fit for the X-ray staging data for this sample had a very large uncertainty since only a few datapoints could be used close to the transition temperature.

For $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ the central *Bmab* (014) peak falls off at a fairly low temperature around $T = 110(25)$ K (black points in the third inset of Fig. 9.30(b)), although the interval with no data around 100 K limits the precision of this conclusion. The transition temperature was found to be $57(5)$ K with slope analysis on the X-ray data – and hence at least both neutron and X-ray data agree that the transition temperature is much lower than the one found for the corresponding staging peaks. Note also that the central peak is significantly larger for these neutron data from RITA-II compared to the X-ray data from BW5, which will be discussed further in Chap. 11.

The staging peaks are positioned close to $\Delta l = 0.2$ from $l = 4$ (colored points in the first inset of Fig. 9.30(b)) corresponding to staging number $n = 5$, again with a tendency for larger distance at higher temperatures – slightly more so than was seen for $\text{La}_2\text{CuO}_{4+y}$. This agrees well with the X-ray data. The staging peaks seem to have a transition temperature of around $T = 245(15)$ K (colored points in the third inset of Fig. 9.30(b)), seemingly around 20 to 30 K higher than what was observed for the X-ray data. The conclusion for the neutron data does not take critical scattering into account, however, which could lower the transition temperature somewhat.

For $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ the central *Bmab* (014) peak seems to fall off at a temperature of around $T = 220(20)$ K (black points in the third inset of Fig. 9.31(a)). This agrees well with the X-ray data.

The underlying broader feature was fitted with a single wide Gaussian for these data, and this seems to fall off at a slightly lower temperature, around $T = 210(20)$ K (colored points in

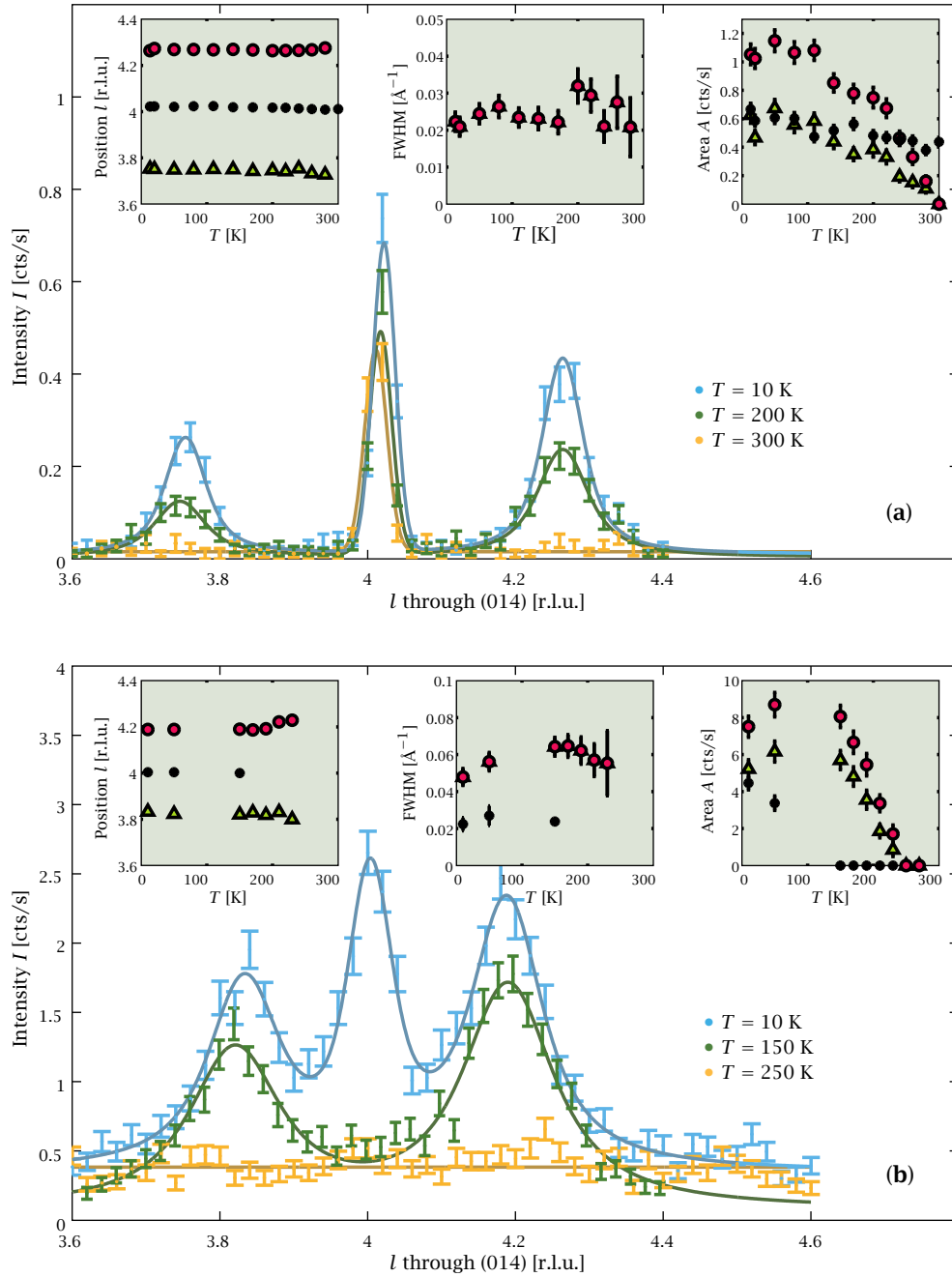


Figure 9.30: Results from RITA-II for $\text{La}_2\text{CuO}_{4+y}$ and $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$. (a) $\text{La}_2\text{CuO}_{4+y}$ fitted with a central Gaussian and two Voigts. (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ fitted with three Voigts. The fitted positions, widths and areas (integrated intensities) are shown in the inset plots (red circles are the right staging peaks, left-pointing triangles are the left staging peaks, black circles are the central peaks). Adapted from Udby [154, Fig. 4.10 and 4.12].

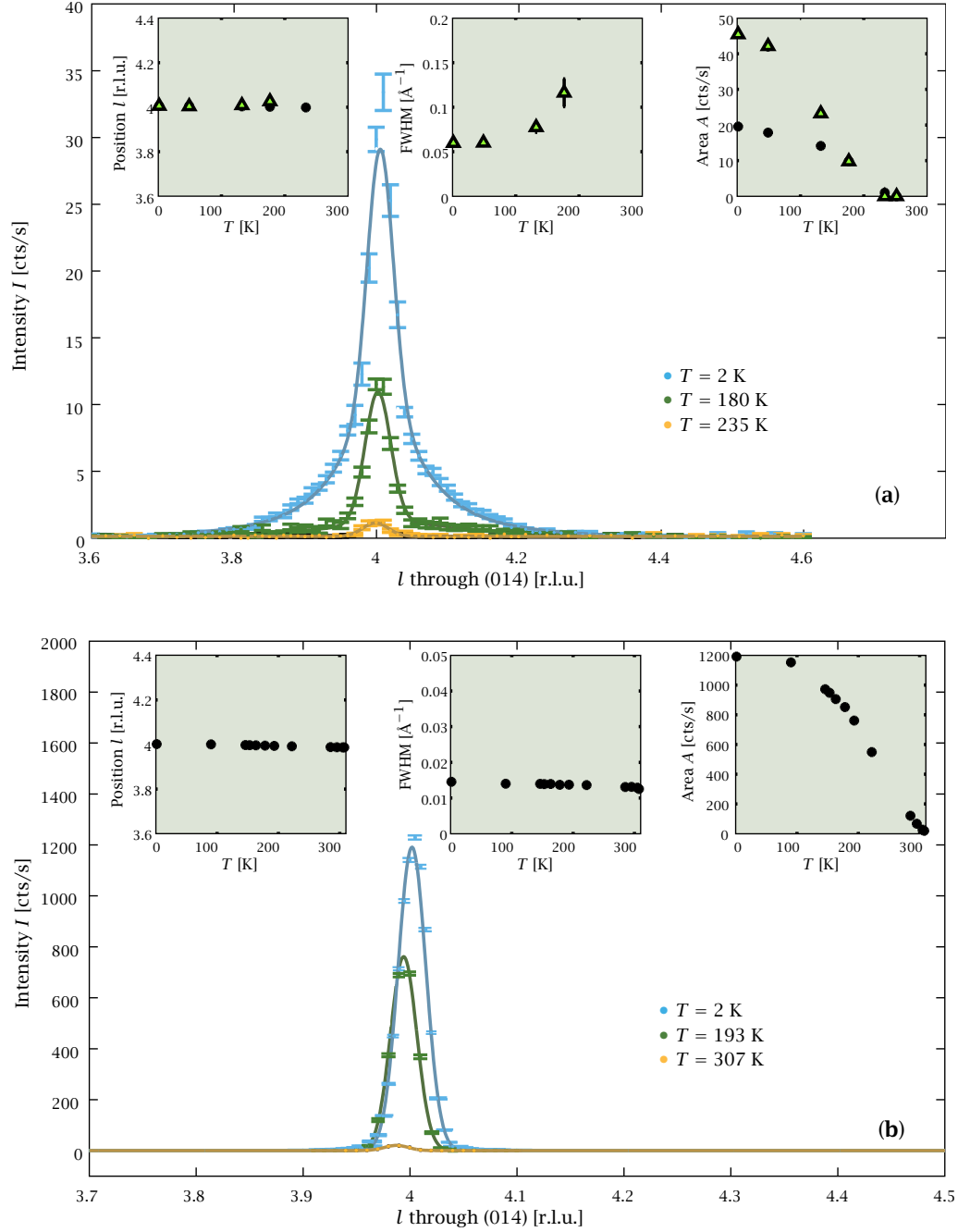


Figure 9.31: Results from RITA-II for $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$. (a) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ fitted with a Gaussian and a Voigt. (b) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ fitted with a Gaussian. The fitted positions, widths and areas (integrated intensities) are shown in the inset plots (left-pointing triangles are the wide bottom peaks for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample). Adapted from Udby [154, Fig. 4.14 and 4.16].

the third inset of Fig. 9.31(a)), agreeing with the transition temperatures found for the staging peaks in the X-ray data.

For $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ there was no visible staging in the neutron data, and the B_{mab} (014) peak falls off at around $T = 295(15)$ K (black points in the third inset of Fig. 9.31(b)). The found transition temperature does not fit perfectly with the X-ray data results for the central B_{mab} , which had $T_{\text{HTT-LTO}} = 247(5)$ K from the slope analysis. However the transition temperature for the staging peaks in these data do get close to room temperature, and hence might explain the discrepancy since the staging peaks are not resolved in the neutron data, and hence might simply be seen as an extra intensity in the central peak.

An overview of all of the neutron data results mentioned above is shown in Tab. 9.3, for later reference and for an easier comparison with the X-ray results in Tab. 9.2.

Sample and peak	Staging distance Δl [r.l.u.]	Staging number n	Transition temperature [K]	Result from
$\text{La}_2\text{CuO}_{4+\gamma}$				
• Central B_{mab}			> 300	Fig. 9.30(a)
▲ Low l staging	0.25-0.3	4 or lower	300(10)	Fig. 9.30(a)
● High l staging	—	—	300(10)	Fig. 9.30(a)
$\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$				
• Central B_{mab}			110(25)	Fig. 9.30(b)
▲ Low l staging	0.2	5	245(15)	Fig. 9.30(b)
● High l staging	—	—	245(15)	Fig. 9.30(b)
$\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$				
• Central B_{mab}			220(20)	Fig. 9.31(a)
▲ Underlying peak			210(20)	Fig. 9.31(a)
$\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$				
• Central B_{mab}			295(15)	Fig. 9.31(b)

Table 9.3: Overview of the transition temperatures and staging information found for the different peaks from the four samples on RITA-II, with references to figures showing the results.

10

Reciprocal space maps

10.1 Raw data from DMC

DMC is a neutron powder diffraction instrument, so the typical datafiles come out as intensity values with their respective 2θ values for each detector tube position. In order to get an overview from a single crystal dataset out of all these, it is necessary to first combine many of these datafiles, and then later transform this to a reciprocal space map.

10.1.1 Combining many datasets

The large number of 2θ spectra from each single measurement at each crystal rotation ω and detector position is combined into one single $(2\theta, \omega)$ dataset using the instrument software *csc*, which also corrects for the detector efficiency by using a standard vanadium normalization scan. An example of such a dataset is shown in Fig. 10.1 for the $\text{La}_2\text{CuO}_{4+y}$ sample at $T = 10$ K.

Note the intense lines at constant 2θ values close to 63° and 74° : these are powder lines from Al in the beam from the sample holder and sample environment. The lines have a small change in intensity for different ω , which is because of asymmetries in the sample holder.

The background also tend to change slightly with ω , differently from sample to sample depending on the sample holder and mounting. For the $\text{La}_2\text{CuO}_{4+y}$ sample, some of the sample holder was covered with Gd_2O_3 to mask glue (as mentioned in Chap. 8), and this stops a small part of the incoherent scattering and makes this effect even more noticeable. On the other hand, large amounts of glue on the holder can give a larger background due to the extra incoherent scattering from the hydrogen in the glue.

The streaks going through the more intense peaks along 2θ are faults in the multi-detector, where the tubes “saturate” when going through a Bragg peak. When this happens the neutrons diffuse and get caught up in the neighboring tubes.*

10.2 Transformed data as reciprocal planes

When the raw data has been collected and combined into $(2\theta, \omega)$ datasets as shown in Fig. 10.1, it is possible to transform it into reciprocal space planes using the software *TVtueb*, [167]. Here, two peaks are marked as known – say, the $(2\theta, \omega) \approx (55^\circ, -245^\circ)$ peak as (020) and the

*Technically this is not an actual detector saturation since all neutrons are still detected, albeit be it in the wrong detector tube. This effect is also called bleeding. In the reciprocal space maps I show in this thesis, the bleeding is especially visible because the colormaps used for plotting are chosen to show small effect, whereas the large Bragg reflections are cut off by ending the colormap long before their maximum intensity.

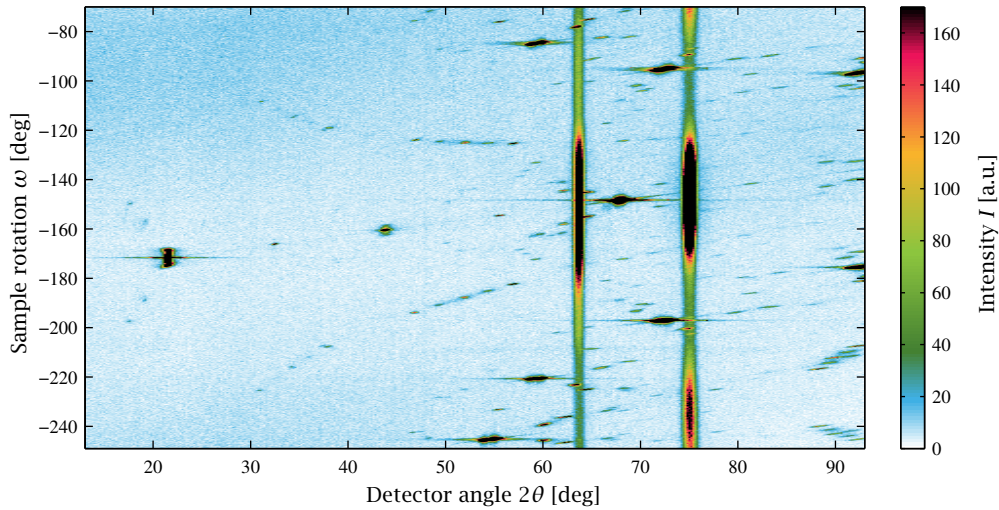


Figure 10.1: Example of a measured $(2\theta, \omega)$ plane for $\text{La}_2\text{CuO}_{4+y}$ at $T = 10$ K, created by combining many separate “powder spectra” from DMC with the *csc* program.

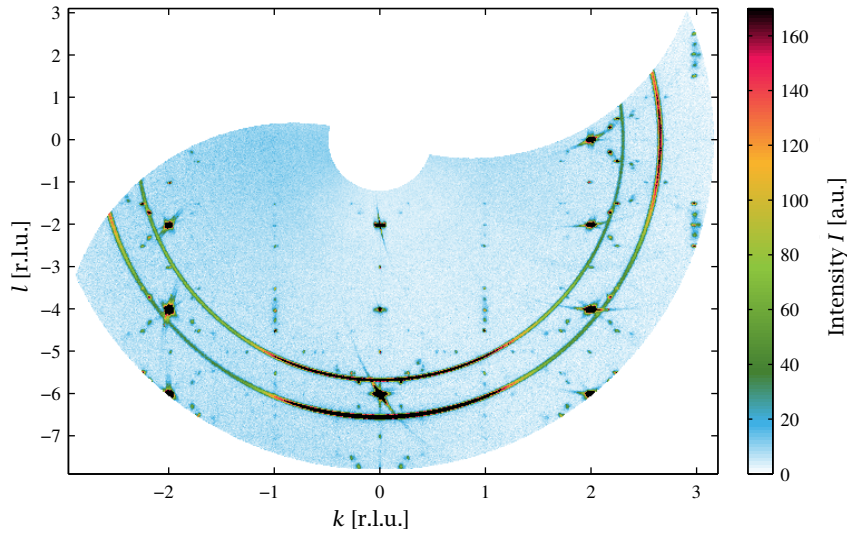


Figure 10.2: Example of a reciprocal space map for $\text{La}_2\text{CuO}_{4+y}$ at $T = 10$ K, created by transforming the data in Fig. 10.1 with the *TVtueb* program.

$(2\theta, \omega) \approx (67^\circ, -148^\circ)$ peak as (006) - and the program then calculates the transformation from the position of these. In this way, the data from Fig. 10.1 turns into a reciprocal space map as shown in Fig. 10.2.

Note how the powder lines now turn into rings - as is fully expected - and the detector saturation streaks turn into curves.

With *TVtueb* it is also possible to take symmetries into account, meaning that it is possible to use a two-fold rotational symmetry on the plane shown in Fig. 10.2 in order to get a clearer picture of the plane. This results in the plot shown in Fig. 10.3(a). The same treatment has been done on several other datasets for three crystals, although I will only shown the low temperature reciprocal space maps here, in Figs. 10.3 to 10.5 for $\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$, and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$, respectively. An overview of all of the measurements can be seen in Appx. E.

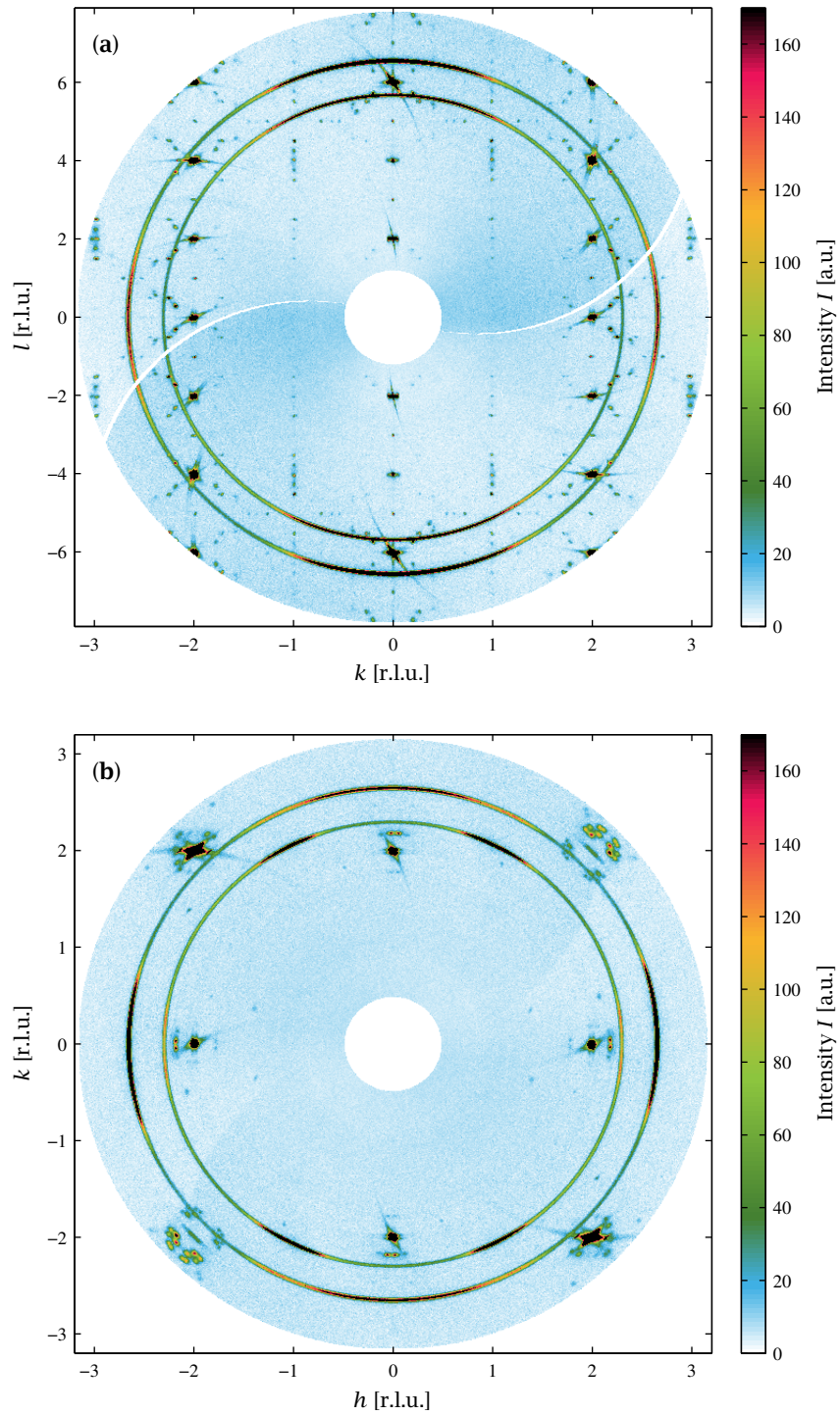


Figure 10.3: Symmetrized reciprocal space maps measured at DMC at $T = 10$ K for the $\text{La}_2\text{CuO}_{4+y}$ sample in two different settings; (a) $(0kl)$ plane and (b) $(hk0)$ plane. Measurements at several other temperatures can be found in Appx. E.

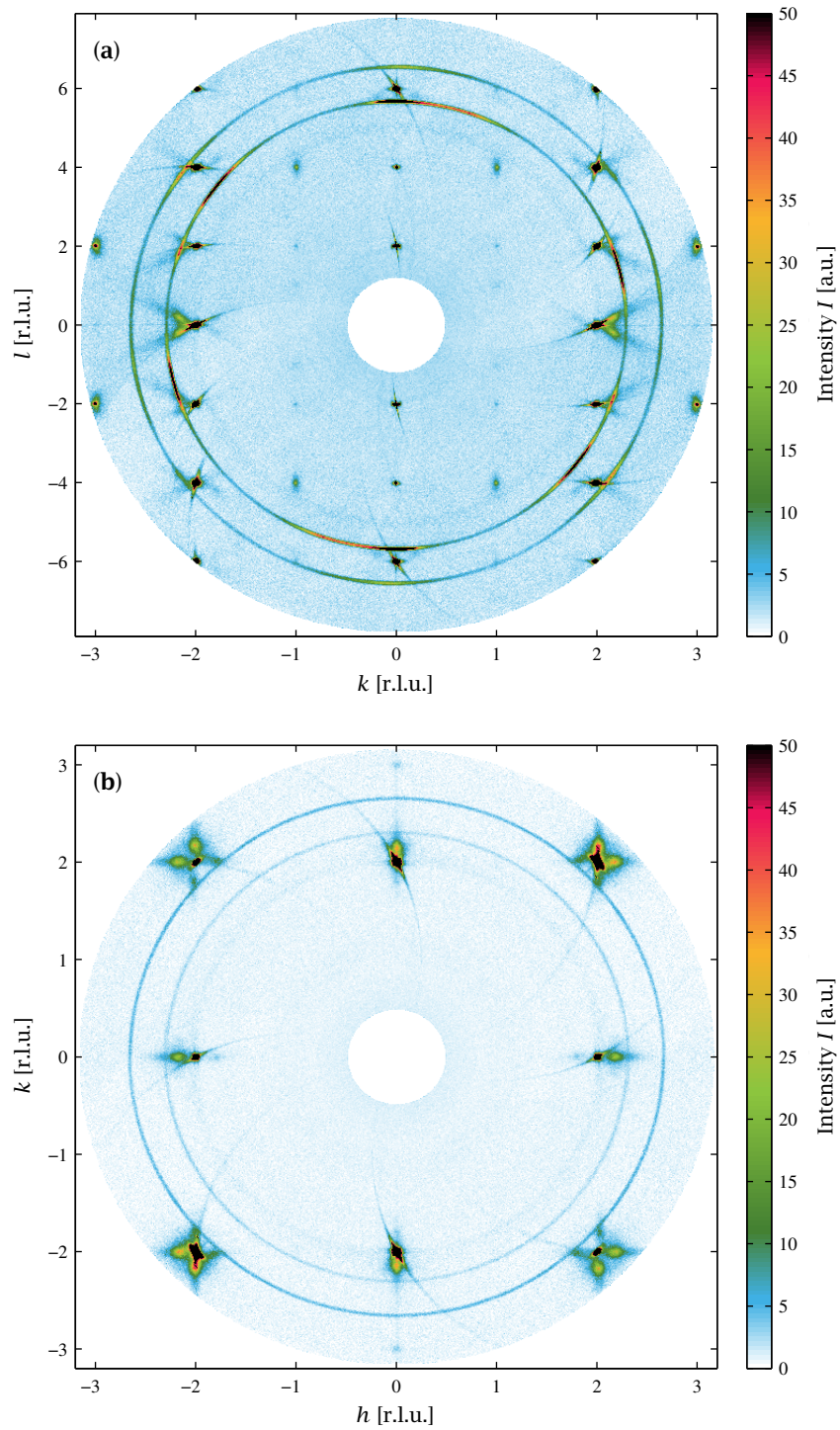


Figure 10.4: Symmetrized reciprocal space maps measured at DMC at low temperatures for the $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$ sample in two different settings; (a) $(0kl)$ plane with temperatures between 100 and 1.5 K (measured while cooling) and (b) $(hk0)$ plane with $T = 2$ K. Measurements at several other temperatures can be found in Appx. E.

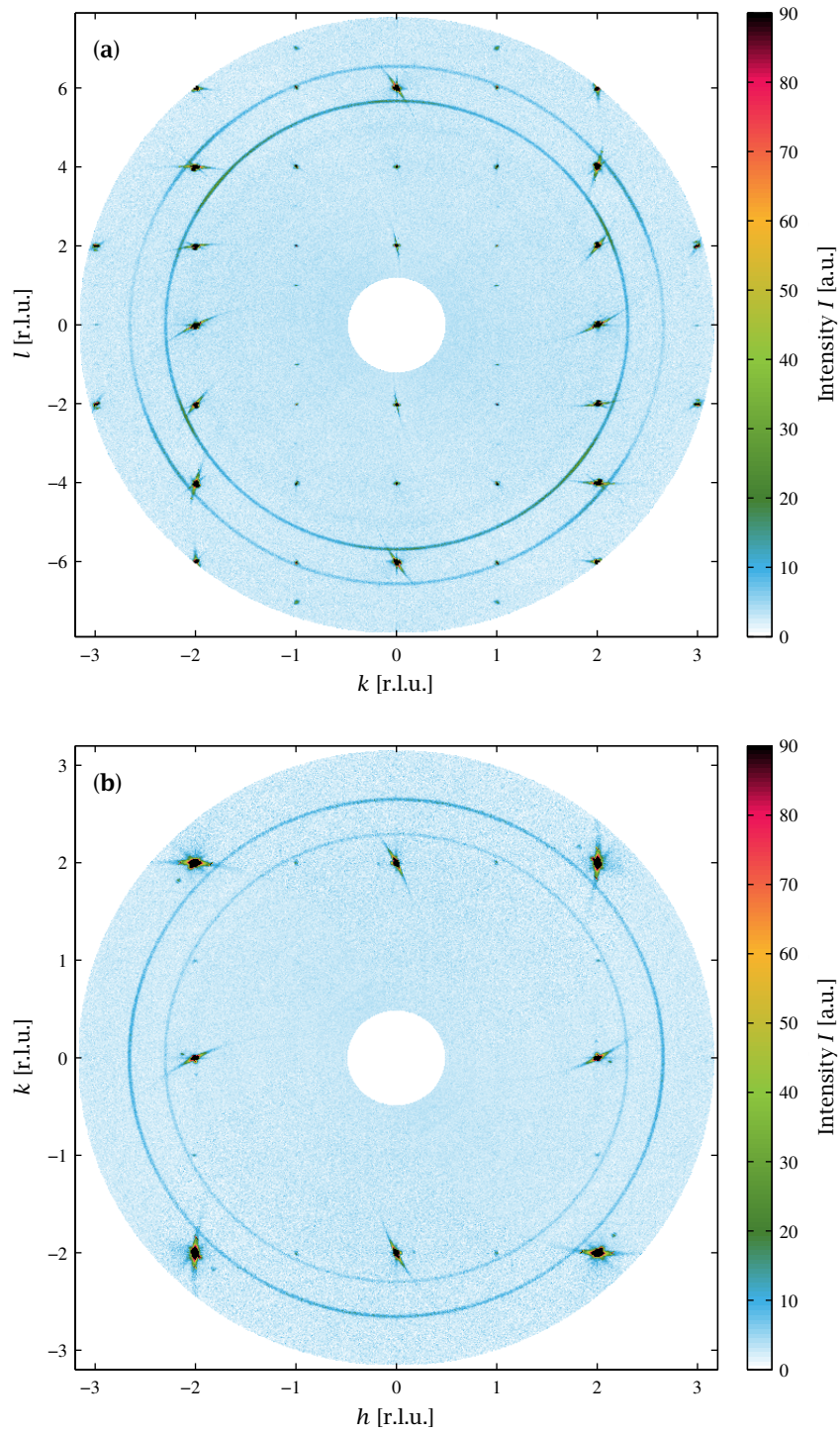


Figure 10.5: Symmetrized reciprocal space maps measured at DMC at $T = 100$ K for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ sample in two different settings; (a) $(0kl)$ plane and (b) $(hk0)$ plane. Measurements at several other temperatures can be found in Appx. E.

10.3 Observations in the reciprocal space maps

Looking at the reciprocal space maps in Figs. 10.3 to 10.5, one thing is apparent: the number of superstructural peaks – especially for the $\text{La}_2\text{CuO}_{4+y}$ sample – is staggering. I will try to give an overview of the reflections in the reciprocal space maps in the following.

10.3.1 Staging

The staging is very visible for the $\text{La}_2\text{CuO}_{4+y}$ sample in Fig. 10.3(a) at positions with even l and odd k , where sets of three or five peaks (depending on the central peak location) are clearly seen along l , possibly with a diffuse background or several smaller peaks hidden underneath.

For the $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$ sample in Fig. 10.4(a) the positions with even l and odd k seem to have more of a diffuse background, with no resolved superstructure peaks.

For the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample in Fig. 10.5(a), there is only a hint of a diffuse background on these positions.

10.3.2 Other superstructures and forbidden reflections

Table 4.2 (on p. 25) give the allowed reflections for the *Bmab* and *Fmmm* space groups. For both *Bmab* and *Fmmm*, a $(hk0)$ plane requires h and k be even for reflection, while they are different in the $(0kl)$ plane: for *Bmab* it is simply required that l is even (and k is even if $l = 0$); while for *Fmmm* it is required that both k and l be even on the whole plane.

For $\text{La}_2\text{CuO}_{4+y}$, the $(0kl)$ plane, apart from the clear staging peaks around the *Bmab* allowed positions at odd k and even l , there are a few similar superstructure peak “chains” along k at $l = \pm 1$ around $k = \pm 2.5$ and $l = \pm 5$ around $k = \pm 1 \pm 0.5$. Single superstructure peaks at odd l for even k (including 0) are also seen. Finally, complicated superstructures appear in “crosses” around the fundamental reflection positions with both k and l even.

In the $(hk0)$ plane there is also a multitude of superstructural peaks, especially concentrated around the fundamental (200), (220), and (020) peaks. The crystal may have been slightly out of alignment for the scan, however, since the (220) peak seems to be very faint and might be out-of-plane, as opposed to the $(2\bar{2}0)$ which ought to have the same intensity because of the symmetry.

For $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$, the $(0kl)$ plane contains peaks at integer positions: the positions with both k and l even are allowed in both *Bmab* and *Fmmm*, while the k odd and l even positions are only allowed in *Bmab*. The small peaks with both k and l odd are not allowed in either space group, and likely related to a commensurately modulated superstructure. Large diffuse backgrounds behind the fundamental peaks with both k and l even are also seen, especially for non-zero k .

In the $(hk0)$ plane there is a hint of a forbidden peak at $k = 3$ for $l = 0$. Incommensurate peaks are also observed close to the fundamental peaks at (200), (220), and (020), although several of these are very smeared.

For $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$, the $(0kl)$ plane seemingly contains only peaks at integer positions. The positions with both k and l even are allowed in both *Bmab* and *Fmmm*, while the k odd and l even positions are only allowed in *Bmab*. The small peaks with both k and l odd are not allowed in either space group, and must be related to a superstructure as for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$.

In the $(hk0)$ plane there are small visible peaks at (210) and (120) (as well as the corresponding peaks in the other quadrants): these are disallowed for both *Bmab* and *Fmmm*. A few small incommensurate peaks are also seen close to the fundamental peaks at (200), (220), and (020).

IV

Discussion of results

11

Discussions

In this chapter I will discuss the results presented in the last two chapters, as well as compare these with results from literature. I will discuss the lattice parameters found for the low temperature X-ray measurements and compare the doping dependence on these with earlier results. I will then comment on the differences in peak intensities between the RITA-II neutron data and the BW5 X-ray results. After this, I will compare the found transition temperatures and critical exponents with similar earlier results, arguing what these results might mean in the context of a few known theoretical models. Finally, I will comment on staging as it has been presented in literature up till now, and discuss a few ways the data analysis could be improved.

11.1 Lattice parameters

The lattice parameters given to the BW5 instrument during the experiments (shown in Tab. 7.1) were mostly off from the real lattice parameters observed while scanning. The calculated c axis lengths found by calibrating the l axis to have data correctly centered around $l = 4$ was shown in Fig. 9.5, with the low temperature values listed in Tab. 9.1. The low temperature values for the lattice constants found from neutron experiments (also shown in Tab. 9.1) did not agree well with the X-ray results, except for the $\text{La}_2\text{CuO}_{4+y}$ sample. The discrepancy – between 0.03 and 0.8% difference in length, with the larger values for the samples with higher Sr content – may be explained by the fact that the neutron measurements to get the lattice parameters were done quickly on the (002) peaks (or similar), according to Udby [154], and might not be as precise as their uncertainties would indicate. What both sets of c lengths could agree on, however, was that they decrease for larger Sr doping.

In the following, I will conclude a little further on the differing lattice constants, as well as calculate the lattice length difference between the seemingly different (at least for some of the samples) structural phases $Bmab$ and $Fmmm$. Finally, I will compare with a few results from literature.

11.1.1 Two different structural phases

The distances in reciprocal space between the $Bmab$ central peak and the mid-point for the staging peaks in the $Fmmm$ phase, δl , were found in Sect. 9.2 and the low temperature results were listed in Tab. 9.2. These distances can be recalculated into units of $\text{\AA}^{-1}$ by using the approximate low temperature lattice parameters for the samples from Tab. 9.1, and

$$\delta l [\text{\AA}^{-1}] = \delta l [\text{r.l.u.}] \frac{2\pi}{c [\text{\AA}]} \quad (11.1.1)$$

Sample	c [Å]	δl [r.l.u.]	δl [Å ⁻¹]	c_{Bmab} [Å]	c_{Fmmm} [Å]
La ₂ CuO _{4+y}	13.2038(11)	0.0094(7)	0.0045(5)	13.2038(11)	13.235(4)
La _{1.96} Sr _{0.04} CuO _{4+y}	13.1367(7)	0.014(2)	0.0067(3)	13.091(3)	13.1367(7)
La _{1.935} Sr _{0.065} CuO _{4+y}	13.0857(2)	0.0017(9)	0.00082(10)	13.0857(2)	13.0801(11)
La _{1.91} Sr _{0.09} CuO _{4+y}	13.0346(1)	0.00039(16)	0.00019(5)	13.0346(1)	13.0333(3)

Table 11.1: Lattice constant length c from the l axis calibration used together with the distance δl between the $Bmab$ peak position and the staging mid-point to find the lattice constant for both the $Bmab$ phase and the $Fmmm$ phase at low temperatures. The greyed out c_{Bmab} and c_{Fmmm} lattice constants are the ones that were found directly (same value as the second column), while the others are calculated with the values in the table using Eq. (11.1.2) as explained in the text.

The results from this calculation are shown in Tab. 11.1.

The two different lattice parameters for the two individual structural phases are also shown in this table – calculated using the one known lattice parameter and the distance between the two in reciprocal space. For La₂CuO_{4+y} this was done by

$$c_{Fmmm} = \frac{2\pi}{c_{Fmmm}^*} = \frac{2\pi}{c_{Bmab}^* - \delta l/4} = \frac{2\pi}{(2\pi)/c_{Bmab} - \delta l/4}, \quad (11.1.2)$$

where the δl is divided by four since the δl value was found at the $l = 4$ position. For La_{1.96}Sr_{0.04}CuO_{4+y} the sign in the denominator is flipped to a plus sign and $Fmmm$ and $Bmab$ switch places (the directly found lattice constant was the one belonging to $Fmmm$ because the mid-point of the staging peaks – as opposed to the $Bmab$ peak – was used for the l axis calibration for this sample). For La_{1.935}Sr_{0.065}CuO_{4+y} and La_{1.91}Sr_{0.09}CuO_{4+y}, the sign is flipped because the $Bmab$ peak was lower in l instead of higher (as also indicated in Tab. 9.2).

As was already mentioned in Sect. 9.2, the differences in apparent lattice parameter for the central $Bmab$ peak, c_{Bmab} , and the mid-point of the staging peaks, c_{Fmmm} , only seem significant for the two first samples, La₂CuO_{4+y} and La_{1.96}Sr_{0.04}CuO_{4+y}, with a difference of 0.24 and 0.35%, respectively – whereas the two parameters are very close (and even have the opposite relation) for La_{1.935}Sr_{0.065}CuO_{4+y} and La_{1.91}Sr_{0.09}CuO_{4+y}, with differences of 0.04 and 0.01%. It is also only these two first mentioned samples that show the staging peaks to be a clear staging with small values of the staging number n , while the La_{1.935}Sr_{0.065}CuO_{4+y} and La_{1.91}Sr_{0.09}CuO_{4+y} samples only had very low intensity staging peaks with higher values of n .

As a final comment it should be noted that the splitting of the structure into two phases with different lengths of the crystal axis c has been seen before for at least La₂CuO_{4+y}, [100]. It was found that the $Bmab$ c axis had a low temperature length of around 13.13 Å, with the axis connected to the staging phase being instead around 13.18 Å, [100, Fig. 5]. This difference in the axis length of about 0.05 Å show a similar relation to what was found for the BW5 X-ray data, although the absolute lengths are lower, with the $Bmab$ value matching other low temperature results from literature well, *e.g.* Radaelli *et al.* [108].

11.1.2 Lattice length as a function of doping

As mentioned, it was found that the lattice parameter length c becomes shorter for increasing Sr doping in co-doped samples, both for the $Bmab$ and $Fmmm$ phase. However, interestingly, Radaelli *et al.* [108] found that the opposite happens when only doping with Sr in oxygen-stoichiometric samples: higher Sr doping meant a longer c axis, as shown in Fig. 11.1 with the gray-scale points. The results from this thesis have been marked in this figure as well (blue diamonds and green triangles for $Bmab$ and $Fmmm$, respectively) along with the earlier neutron experiments (yellow squares).

Since the behavior of the c axis length (for both structural phases) is directly opposite to what was found for only Sr doped samples, the O doping must affect the crystal structure along

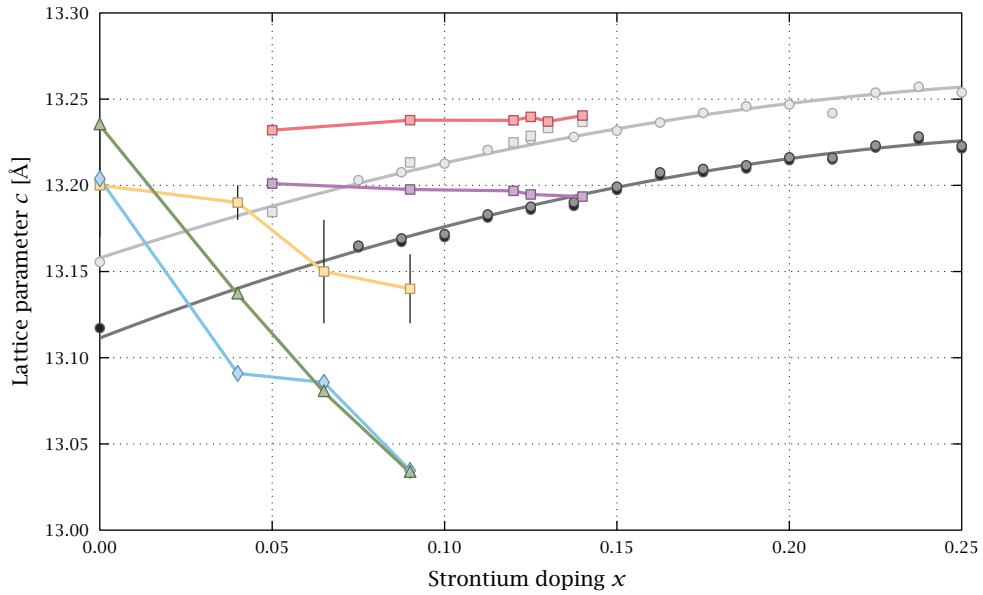


Figure 11.1: Lattice constant c as a function of Sr doping (no oxygenation) for $T = 10$ K (dark gray circles), 70 K (black circles), and 295 K (light gray circles) found with neutron and X-ray powder diffraction by Radaelli *et al.* [108] and for $T = 300$ K (light gray squares) found with neutron powder diffraction by Rial *et al.* [101]. The purple and red squares are measurements on co-doped powder samples at $T = 10$ and 300 K, respectively, by Rial *et al.* [101]. The yellow squares mark the c axis lengths for the four single-crystal samples used in this thesis, found at low temperature with neutrons by Udby [154]. The blue diamonds mark the c axis lengths found for the low temperature BW5 data B_{mab} peaks (see Tab. 9.1), while the green triangles mark the corresponding F_{mmm} values. For points without visible errorbars, the errors are smaller than the marker. Lines through the points are guides to the eye.

c in a way that stops the unit cell from stretching out when adding Sr. This was exactly found by Rial *et al.* [101], who used neutron powder diffraction to investigate a set of samples with several different Sr dopings, before and after superoxygenating them (their structure results are listed in Tab. B.4). They indeed saw the c axis length increasing for increasing Sr content before oxygenation (their investigations were only done at room temperature). These results are also shown in Fig. 11.1, as the light gray squares that match well with the Radaelli *et al.* high temperature data. After oxygenation however, their results were as shown with purple and red squares in the figure, for $T = 10$ and 300 K, respectively. At high temperature, they saw that the c axis length increased less with x for the oxygenated samples, while it was decreasing with x at low temperatures, as we see in our data (although not with as high a slope as seen in the present results).

Replacing some of the small* La^{3+} ions with larger Sr^{2+} ions, electrons are removed from the CuO_2 planes and relieves compressive stress, while tensile stress is released within the (La,Sr)O planes by making the distances La–O and Cu–O in the structure more similar, [123]. Similarly, adding O^{2-} into interstitial positions again reduces the tensile stress in the (La,Sr)O planes and “steals” electrons from the CuO_2 planes, with the same result.

Both of these effects individually cause the unit cell axis length c to increase for Sr-only doped samples ([108], shown in Fig. 11.1 and listed in Tab. B.4), and for O-only doped samples ([98, 100, 104], some results listed in Tab. B.3). In many of these publications the unit cell axis length a instead becomes smaller and b remains constant with O doping, while a seems constant and b decreases towards the value of a with Sr doping.

*Looking up the crystal ionic radii for the constituents of the samples, it is seen that the size of La^{3+} is 1.17 Å, while the size of Sr^{2+} is slightly larger at 1.32 Å, [150].

The present results indicate that when co-doping, these two effects somehow work together to make c decreasing for increasing Sr doping, with the exact value of the O-doping unfortunately unknown. The behavior of the a and b axes were not investigated, however. Rial *et al.* [101] saw the lattice constant a become smaller after oxygenation for all Sr dopings, so it could be interesting to measure values for the other lattice constants more precisely for the present work as well. This would give a better understanding of how these behave with temperature for the different single-crystal samples. Further, it would be very relevant to find the absolute value of the O doping, y , in order to compare more precisely with the results from literature.

11.2 Comparing measured intensities for X-ray and neutron data

The integrated intensities found for the X-ray data from BW5 and the neutron data from RITA-II, as presented in Sects. 9.2 and 9.5, have certain differences in the relations between the central and staging peak values. I will here mention these differences, and discuss what might cause them.

For $\text{La}_2\text{CuO}_{4+y}$ seen with neutrons, the integrated intensity of the central peak is a little smaller than the values for the staging peaks, compared to what is seen in the X-ray data. For the neutron data the integrated intensity of the central peak (at low temperatures) is about the same size as the low l staging peak value (black circles and colored triangles in the third inset of Fig. 9.30(a), respectively), both around 0.6 cts/s, whereas the high l staging peak is significantly higher than this (colored circles in the third inset of Fig. 9.30(a)), at around 1.1 cts/s. For the X-ray data, the low temperature integrated intensities for the two main staging peaks and the central peak are all comparable, as seen in Fig. 9.22(a) and (b), all around 2.3 a.u.*

This small difference might simply be explained by several staging peaks overlapping in the neutron data (due to a larger resolution function), and hence being counted in the main staging peaks, explaining why the high l neutron staging peak is larger (although the low l peak is not, which might go against this explanation).

For $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ seen with neutrons, the integrated intensity of the central peak is significantly larger than the values for the staging peaks, compared to what is seen with X-rays, where the central peak is very small. For the neutron data the integrated intensity of the central peak (low temperatures) is about 4.5 cts/s (black circles in the third inset of Fig. 9.30(b)), whereas the staging peaks lie between 5.5 and 8 cts/s (colored circles and triangles in the third inset of Fig. 9.30(b)). For the X-ray data, however, the low temperature integrated intensity of the central peak lies only around 0.38 a.u. compared to the 2.0 to 2.2 a.u. values for the staging peaks (Fig. 9.10(a) and (b)).

One explanation for the large difference in the central peak to staging ratio as seen with neutrons and X-rays could be that the peak is magnetic in origin: magnetic order is easily seen with neutrons, while the signal from this is orders of magnitude lower when using X-rays. Magnetism in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ tends to disappear very quickly with both x and y , however (as shown in Fig. 6.3), and so far only incommensurate magnetic order has been seen for these compounds at higher dopings, [124]. That is, a magnetic peak at integer (hkl) would be something very unexpected. A second, much simpler, explanation could be the structure factor in the central peak being very dependent on the oxygen scattering length (more so than the staging peaks), in which case the neutrons will see the signal as larger since the oxygen scattering length is larger for neutrons than for X-rays compared to the scattering lengths of the other elements in the compound. A way to investigate this further could be to use polarized neutrons, which make it possible to obtain additional information about magnetic structures in the material.

*Note that the X-ray data integrated intensities are all given with arbitrary units (a.u.), although they are all found in the same way, and normalized to the monitor – so the values are still comparable for the same sample.

For $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ seen with neutrons, the central peak was simply fitted with one narrow and one underlying wider peak, which makes it more difficult to compare intensities to the X-ray data, where the wider peak was instead split up into two staging peaks, one in each shoulder of the central peak. For the neutron data the narrow central peak, thought of as the *B_{mab}* peak, has a low temperature integrated intensity of around 20 cts/s (black circles in the third inset of Fig. 9.31(a)), whereas the wider peak, thought of as the underlying disorder, has the value 46 cts/s (colored triangles in the third inset of Fig. 9.31(a)). For the X-ray data, on the other hand, the central *B_{mab}* peak has the largest integrated intensity, at 8.3 a.u., whereas the two staging peaks each have values of between 1.0 and 1.7 a.u. (Fig. 9.14(a) and (b)).

The difference in method of analysis on the data from the two methods makes the comparison a little more difficult. It would seem that part of the intensity from the central peak seen with X-rays might be attributed to the underlying peak in the neutron data. In general, though, the peak shapes seem fairly similar. It could be interesting to have both full datasets and do the analysis in the same way for both of them, making a more meaningful comparison possible.

For $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ seen with neutrons, only a simple central peak was observed, whereas a strong asymmetry interpreted as staging was seen in the X-ray data. This can very well be explained by the difference in resolution with the two different methods – with the neutron data showing a much wider peak: around $0.015 \text{ \AA}^{-1}$ for the neutron data (second inset of 9.31(b)) versus around $0.0045 \text{ \AA}^{-1}$ for the X-ray data (as calculated in Subsect. 9.2.3). The staging peaks are simply not resolvable in the neutron data with this resolution.

11.2.1 About absolute scale intensities

In order to be able to compare the measured integrated intensities for each of the measured reflections with calculated structure factors for the different techniques, it is necessary to normalize the values to an absolute scale.

With neutron scattering, it is fairly straight-forward to normalize the intensity data using the mass of the samples, since the incoming beam tends to be large enough to cover the full sample – and at the same time has an interaction small enough to actually see the bulk of the material. For X-rays, however, the beam is very small, and hence all of the sample is not necessarily illuminated, on top of the fact that the interaction is much larger: a typical attenuation length for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ is $\lambda = 0.85 \text{ mm}$ for hard X-rays, following the calculations done in Appx. A.5. Most usual X-ray samples are fairly small, in the order of μm , but the samples used on BW5 had sizes of the order of mm, as listed in Tab. 7.1, which just makes the normalization even more difficult.

It is possible to instead normalize the measured X-ray intensities by normalizing to the size of a fundamental reflection, *e.g.* (200), at the same temperature instead. This might be interesting to do for the results in this thesis, in the case where it is possible to find a reasonable number of fundamental peak measurements with the same attenuation as the reflections I want to normalize. This does, however, also assume that the extinction in the sample is negligible, which could require measurements be done at specific fundamental reflections that have smaller structure factors instead (since extinction is a larger effect for larger reflections, following the description in Subsect. 4.4.1). If this is not possible, it would be necessary to correct for the extinction using the sample geometries – or, in the worst case scenario, instead go back and repeat measurements on smaller samples. A second effect that might make the normalization difficult is if the samples have very inhomogeneous shapes, which is mostly the case, as seen in Fig. 7.1. In this case, absorption correction of the data will be almost impossible, and repeat measurements on samples chosen for their shape will have to be done.

11.3 Discussion of phase transition results

A full overview of the found transition temperatures and critical exponents for the BW5 experiments was shown in Tab. 9.2 and the observed transition temperatures for the RITA-II experiments were shown in Tab. 9.3. Some results from literature are shown in Tab. 11.2, while the theoretically calculated values were shown in Tab. 5.1 (note that the critical exponents are given as β , not 2β , in the table with theoretical values). Some of all these values are compared in Fig. 11.2.

11.3.1 Critical exponents

Starting with the critical exponents shown in Fig. 11.2(a) – which were found for most of the reflections analyzed from the BW5 X-ray data – an actual tendency with Sr doping is not visible for the central *Bmab* reflections, while there is a clear tendency for β to increase with increasing Sr doping for the staging reflections.

There are several publications with investigations of the *Bmab* peak on relevant compounds, as shown in the upper part of Tab. 11.2, with the points shown as green triangles in Fig. 11.2(a). From comparing with these, it is slightly difficult to conclude whether the BW5 X-ray results follow the same behavior as the literature examples, mainly because of the fact that it was not possible to find literature on compounds with Sr dopings comparable to the current work – with or without O doping – that state the critical exponents for their results. The present results seem consistently lower in value, and while both Böni *et al.* [125] and Braden *et al.* [126] concluded that their systems could be modeled by the 3D XY model, the present results more point in the direction of a 2D model like the Ising model marked in the figure with the lowest green line.

The staging in the isostructural compound $\text{La}_2\text{NiO}_{4+y}$ (shown in the lower part of Tab. 11.2) seems to have the same tendency as the staging results from the BW5 X-ray measurements, with a higher doping meaning a higher value of β , even though the actual critical exponents were not mentioned directly in the published work. Note, though, that the dopings investigated by Tranquada *et al.* are *only* with oxygen, so the applicability of this comparison is limited.

However, a comparison between the phase transition seen for the staging in $\text{La}_2\text{NiO}_{4.06}$ with n between 3 and 4, shown in Fig. 11.3, with the phase transition seen for the main staging peaks in the $\text{La}_2\text{CuO}_{4+y}$ sample with n between 4 and 5, shown in Fig. 9.22(b), is especially noteworthy. Both were very rapid, almost approaching first order – something which is difficult to explain with simple models for continuous phase transitions. Evidence for the oxygen ordering in $\text{La}_2\text{NiO}_{4.105}$ being first-order (with the kinetics of the oxygen ordering being understood in terms of nucleation and growth) was actually found, [128], with the shape of the measured transition being dependent on the cooling conditions – indicating that something similar could be happening for the $\text{La}_2\text{CuO}_{4+y}$ sample, which could be very interesting to investigate further.

In general, it is observed that the critical exponent for both the *Bmab* and staging reflections vary widely, from very low values for the staging peaks in $\text{La}_2\text{CuO}_{4+y}$ to values all the way up to $2\beta \approx 0.5$ for the staging peaks in $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$.

Very low values of β could indicate a close to one-dimensional system* or a close to first-order transition, while the higher values – especially seen for the staging – could point in the direction of the conclusions made by Böni and Braden *et al.*, with describing the long-range order in the 3D XY model. There is no ground to rule out the other two shown 3D models, the Ising and Heisenberg models, here, however, which both have critical exponents very close to the 3D XY model. This indicates having to use very different models to describe the long range order in the different samples, while a broader scoped model able to describe all the

*Note however, as was mentioned in Chap. 5, that many pure 1D systems do not show phase transitions – *e.g.* the 1D Ising model, [129].

Sample and peak	Critical temperature [K]	Critical exponent 2β	Reference
Central <i>Bmab</i> peak results		$T_{\text{HTT-LTO}}$	
$\text{La}_2\text{Cu}_{0.95}\text{Li}_{0.05}\text{O}_{4-\delta}$	423(1)	0.55(8)	Böni <i>et al.</i> [125]
La_2CuO_4	507(1)	0.56(2)	Braden <i>et al.</i> [126]
$\text{La}_{1.97}\text{Sr}_{0.13}\text{Cu}_{0.95}\text{Li}_{0.05}\text{O}_{4-\delta}$	351(1)	0.58(8)	Böni <i>et al.</i> [125]
$\text{La}_{1.87}\text{Sr}_{0.13}\text{CuO}_{4+\gamma}$	196.5(5)	0.71(2)	Braden <i>et al.</i> [126]
Staging results		T_{staging}	
$\text{La}_2\text{NiO}_{4.06}$, $n = 3-4$	235(5)	very small	Tranquada <i>et al.</i> [113]
$\text{La}_2\text{NiO}_{4.074}$, $n = 2$	280		Tranquada <i>et al.</i> [113]
$\text{La}_2\text{NiO}_{4.074}$, $n = 3$	245(10)		Tranquada <i>et al.</i> [113]
$\text{La}_2\text{NiO}_{4.105}$, $n \approx 2$	~ 290	large	Tranquada <i>et al.</i> [113]

Table 11.2: Observed critical temperatures and critical exponents from literature. No staging results are available in literature for staging peaks in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, but the isostructural compound $\text{La}_2\text{NiO}_{4+\delta}$ is a common comparison.

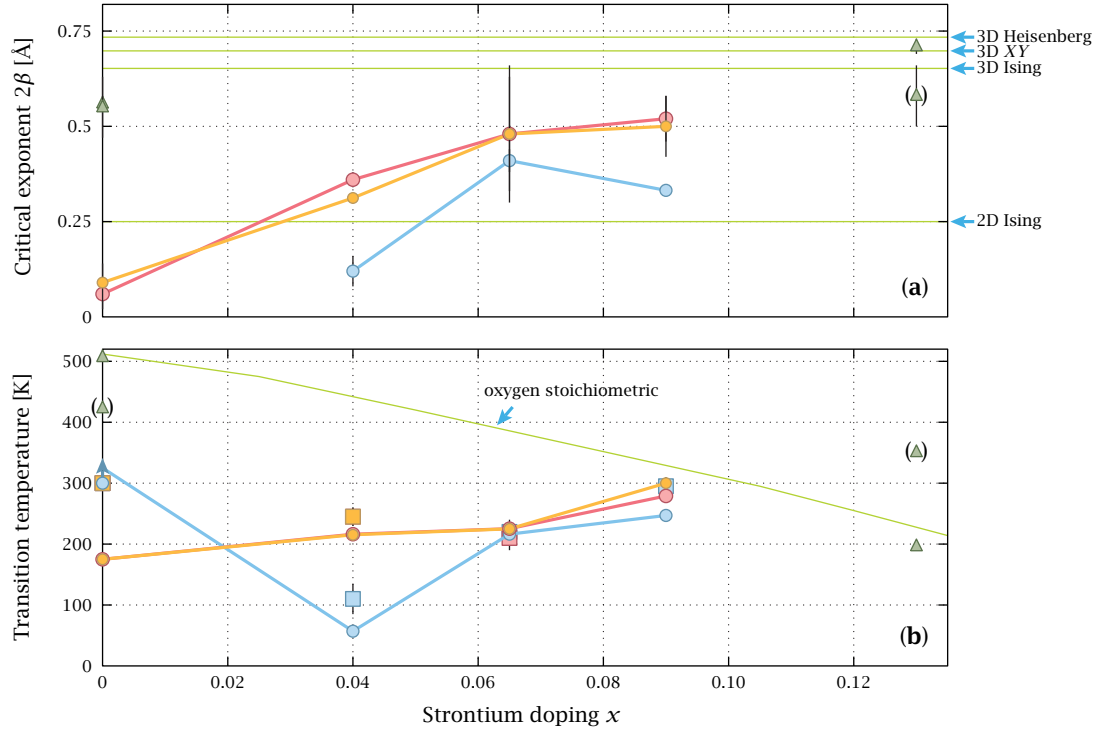


Figure 11.2: (a) Critical exponents 2β and (b) transition temperatures found for the BW5 X-ray measurements (Tab. 9.2), with blue circles marking the central *Bmab* peak and red and yellow circles marking the low and high l staging peaks, respectively. Note the $x = 0.00$ *Bmab* transition temperature, which was only determined to be above $T_{\text{HTT-LTO}} = 300$ K, marked with an arrow. The transition temperatures for the RITA-II neutron measurements (Tab. 9.3) are shown with squares, with colors corresponding to the X-ray points. There is a general tendency for increasing 2β with increasing x for the staging reflections, but no clear tendency seen for the *Bmab* reflections. In the same way, a tendency for increasing T_{staging} with x is observed, while $T_{\text{HTT-LTO}}$ is seen to have a clear minimum at $x = 0.04$, both for neutrons and X-rays. Results from literature (only for the *Bmab* reflection, top part of Tab. 11.2) are marked as green triangles (Li doped samples are shown with parentheses). The critical exponents are compared to theoretical values from Tab. 5.1 (green lines). For comparison, the $T_{\text{HTT-LTO}}$ for only Sr-doped found in *e.g.* Chang [127] are also shown (green line, some values written in Tab. B.1). For points without visible errorbars, the errors are smaller than the marker.

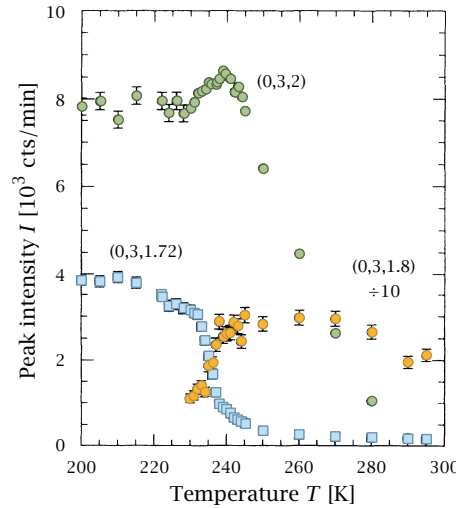


Figure 11.3: Temperature dependence of the scattered intensity for three different peaks measured along l for a $\text{La}_2\text{NiO}_{4.06}$ single crystal with neutron scattering. Especially the $(0,3,1.72)$ peak (blue squares) is relevant for comparison with the $\text{La}_2\text{CuO}_{4+y}$ results in this thesis, with the very rapid change in intensity, just as what was seen for the main staging peaks in the BW5 X-ray data (Fig. 9.22(b)). Figure adapted from [113, Fig. 13].

critical exponents at the same time would be favorable. As a comment to this, the electronic phases and conduction in $\text{La}_2\text{CuO}_{4+y}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have been investigated in the context of percolation theory, which describe networks of conductive regions in the materials, [130–132]. Percolation theory might be interesting to look more into for the structural phases as well, since this might be able to describe the apparent different dimensionalities of the observed order in the samples.

11.3.2 Transition temperatures

The transition temperatures were shown in Fig. 11.2(b), both for the BW5 X-ray measurements (circles) and the RITA-II neutron measurements (squares). The blue points mark the transition temperatures for the central $Bmab$ peaks, and these are seen to have a minimum around the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample. The red and blue points mark the low and high l staging peaks, and the general tendency for both of these seem to be a slightly higher transition temperature with increasing Sr doping.

For the $Bmab$ peaks, the transition temperature $T_{\text{HTT-LTO}}$ is already well known for the Sr-only doped compounds, for which the values are shown in Fig. 11.2(b) as a green line (see also Fig. 6.3(a)). It is expected that the transition temperature will decrease for co-doped samples after oxygenation, as it is seen in Fig. 6.3(b) showing the doping dependence of the O-only doped compounds. The values listed in the top part of Tab. 11.2 from literature do not seem to be in disagreement with the present results, although (again) this comparison is difficult because of the limited number of values found in literature. The minimum at $x = 0.04$ is interesting, but yet unexplained: the very stretched out phase transition seen for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample, shown with blue in Fig. 9.29(b), could be investigated further by taking the critical scattering from the sample into account. Note that the minimum is seen in both the X-ray and neutron data – the small intensity seen with X-rays, and the connected problems with data analysis to this, cannot explain the minimum alone, since the large signal seen with neutrons show the same tendency.

For the staging peaks, the transition temperatures T_{staging} are seen to increase with increasing Sr doping, as mentioned. Again it is interesting to compare with the staging seen in the

isostructural compound $\text{La}_2\text{NiO}_{4+y}$, with results from Tranquada *et al.* [113] shown in the bottom part of Tab. 11.2. The doping is only O-doping, but a slight tendency for larger T_{staging} for larger y is also seen for these compounds.

11.4 Further comments on staging in literature

There has not been any research on the staging in the co-doped compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ outside our research group. However, staging in the oxygen-doped compound, $\text{La}_2\text{CuO}_{4+y}$, was investigated vigorously by Wells *et al.* [100]. They observed stagings between 2 and 6.6 for their samples depending on the oxygenation treatment. This agrees well with the different staging numbers found in the results for the $\text{La}_2\text{CuO}_{4+y}$ sample presented in this thesis, which were between 2 and 6, with a very small intensity of a possible staging peak all the way up to n between 8 and 9.

11.4.1 Phase transition behavior for varying staging number

Apart from the results from Wells *et al.*, the main results in literature on staging stems from the isostructural compound $\text{La}_2\text{NiO}_{4+y}$, as has also been mentioned earlier. Tranquada *et al.* [113] investigated this and characterized the staging for different oxygen dopings. Some results of these investigations were shown in Tab. 11.2, where the staging numbers n observed were also listed. It was, in rough terms, seen that lower staging numbers had higher transition temperatures: the $n = 2$ and close to 2 stagings seen in $\text{La}_2\text{NiO}_{4.074}$ and $\text{La}_2\text{NiO}_{4.105}$ had transition temperatures of 280 and around 290 K, respectively, while the higher $n = 3$ and between 3 and 4 stagings instead had transition temperatures at around 235 and 245 K.

The results in this thesis go directly against this, with the $n = 2, 3.1$, and 4.6 staging peaks for $\text{La}_2\text{CuO}_{4+y}$ having the same transition temperature T_{staging} of around 175 K (see Tab. 9.2); the $n = 5.1$ staging peaks for $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ having $T_{\text{staging}} = 215\text{-}216$ K; the $n = 13.2$ staging peaks for $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ having $T_{\text{staging}} = 225$ K; and finally the $n = 89$ (and larger) staging peaks for $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ having $T_{\text{staging}} = 279\text{-}300$ K. That is, a rising transition temperature for increasing staging number, although not within the same sample, where the transition temperature stays constant (also opposed to the results from Tranquada *et al.*).

From the Tranquada *et al.* results shown in Tab. 11.2, it was also visible how a larger staging number n tended to have a smaller critical exponent 2β . This is also the direct opposite behavior to what is seen in the present work, where increasing n show a clear tendency to an increasing β , although it is difficult to finally conclude on the smaller staging reflections for the $\text{La}_2\text{CuO}_{4+y}$ sample – which seems to be the sample that can easiest be compared with the Tranquada *et al.* results on $\text{La}_2\text{NiO}_{4+y}$.

In the end, based on the present data, it is difficult to finally conclude what determines the transition temperature and critical exponents for the different staging numbers – there might not even be a simple relation. Further investigating this with more doping values and more temperature measurements in the relevant temperature regions could be interesting.

11.5 Other superstructures

Staging was also observed in the reciprocal space maps presented in Chap. 10, especially well for the $\text{La}_2\text{CuO}_{4+y}$ sample. Several other superstructures were also observed, amongst them commensurate peaks indicating that the samples indeed do have at least a fraction of the sample in the *Bmab* phase instead of the *Fmmm* or the tetragonal *I4/mmm* phases.

For $\text{La}_2\text{CuO}_{4+y}$, Fig. 10.3(a), small peaks similar to staging superstructures were seen along k , which might indicate a corresponding (oxygen) ordering along $\mathbf{b}$ (or $\mathbf{a}$ such that the signal is

simply seen due to twinning) in the crystal structure, as was also observed by Wochner *et al.* [115] in $\text{La}_2\text{CuO}_{4+\gamma}$ with $\gamma \approx 0.015$. This could of course be interesting to investigate further in our samples, especially if extending the investigations to the co-doped samples.

Fairly recently, Fratini *et al.* [133], Poccia *et al.* [134] investigated some of the other observed superstructures for $\text{La}_2\text{CuO}_{4+\gamma}$, specifically parts of the “crosses” also observed in the present work. They concluded that the oxygen ordering split into several different real-space regions in the samples, connected in fractal patterns – as opposed to isolated domains – in samples showing optimal superconductivity. This again points in the direction of investigating the present results in connection to percolation theory (as was also mentioned in Sect. 11.3).

11.6 Peak widths and shapes

Through the data analysis, the peak shapes have been fitted with the empirically best matching peak shapes, be it Gaussian, Lorentzian, or a superposition of these. When a peak is very wide, and it fits best with a Gaussian, this might come from the mosaicity in the sample determining the width. This was especially the case with the central peaks for the $\text{La}_2\text{CuO}_{4+\gamma}$ and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ samples (the former though with a low Lorentzian tail).

As was already mentioned once in Sect. 9.2, it could be interesting to fit all of the reflections with Voigts instead of Gaussians and Lorentzians. In this way, it might be possible to follow the peak shapes slightly more accurately, although with the cost of having to fit with more parameters. If the resolution of the instrument is understood, this could result in a better understanding of the mosaicity of the samples.

Another advantage of looking more into the peak widths would be to try to get out a second critical exponent, ν , which is related to the correlation lengths in the sample, and hence related to the inverse of the reflection widths. This could make it possible to easier distinguish between which types of theoretical models might explain the observed phase transitions for the different types of reflections in the samples.

12

Conclusions

In this master's thesis the superoxygenated $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ compound has been investigated as single crystals with four different strontium dopings $x = 0.00, 0.04, 0.065$, and 0.09 , by following the temperature dependence of a specific superstructure. This superstructure is believed to be related to the periodicity of intercalated oxygen along the long axis of the crystal structure, in a similar manner to what has been heavily investigated in the isostructural compound $\text{La}_2\text{NiO}_{4+y}$, where the superstructure is known as staging.

The primary focus of this thesis was on analyzing X-ray data from a total of four different experiments at the BW5 instrument at DESY, Hamburg, Germany. It was found that the crystal structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ does indeed show staging, also for the co-doped samples: samples with higher strontium content showed higher staging numbers with smaller signals than what has previously been observed for the only oxygen-doped compound.

A difference was observed between the c axis length for the structural *Bmab* phase and the corresponding c axis length for the staging peak mid-points, interpreted as belonging to an oxygen-rich *Fmmm* phase. These two structural phases were assumed to divide the samples into different phase fractions. The difference in lattice axes was the most significant for the $x = 0.00$ and 0.04 samples, with a difference of 0.24% and 0.35% , respectively, while the $x = 0.065$ and 0.09 samples showed only a difference of 0.04% and 0.01% .

Both the staging and the *Bmab* phases were investigated as a function of temperature by fitting measured reflections with empirically found Gaussian and Lorentzian peak shapes. The observed phase transitions were investigated by fitting power laws to the found integrated intensities, several times in combination with alternative analysis for finding the transition temperature.

It was found that the critical exponents for the central integer position *Bmab* reflections were in general lower than results from literature, and they did not show a clear tendency with doping for the available data. For the staging reflections, however, the critical exponents for the observed phase transitions showed a clear increase following strontium doping x . This seemed to be consistent with earlier results on $\text{La}_2\text{NiO}_{4+y}$. The $x = 0.00$ sample showed a very sharp transition – consistent with results on $\text{La}_2\text{NiO}_{4.105}$, where the oxygen ordering was found to be first-order, with the shape of the integrated intensity curve being strongly dependent on the cooling conditions.

The transition temperatures found for the *Bmab* reflections showed a minimum for the $x = 0.04$ sample – possibly explained by a very stretched out phase transition with a large

contribution from critical scattering – and were all consistently lower than the corresponding oxygen-stoichiometric values for samples with the same strontium content. This lowering with oxygenation was consistent with earlier results. The transition temperatures for the staging reflections showed a slow increase with strontium doping, which was also consistent with results from $\text{La}_2\text{NiO}_{4+y}$.

Both critical exponents and transition temperatures for the staging reflections, seen as a function of the staging number, seemed to be going against earlier results, or simply not show a direct relation. However, considering how few results are found in both literature and the present work, this will have to be investigated further before a clear conclusion can be made.

Comparisons with earlier analyzed neutron data from the RITA-II instrument (at SINQ, Paul Scherrer Institute, Villigen, Switzerland), as well as newly measured reciprocal space maps also done with neutrons on the DMC instrument (also at SINQ), concluded that the staging is also visible for neutrons. The general behavior of the samples was reproduced between the techniques. The coarser resolution on the neutron instruments did, however, make it difficult to resolve staging for the samples with higher strontium content.

Finally, it was concluded that several other superstructures apart from the staging could be interesting to investigate in further detail. Analyzing the present results as well as further measurements in the context of percolation theory (or other networking mechanisms) and the oxygenated structure being divided into fractal patterns could possibly provide a morphologic explanation for the widely varying phase transitions over the range of doping values. In an average picture, this could also give an understanding of the volume fractions for the different observed superstructures as well as of the superconducting domains. Understanding the morphology and composition of the structure in detail in this way would, hopefully, result in a better understanding of the superconductivity in the compound as a whole.

12.1 Outlook

One of the main challenges of this thesis was the limitation of the analyzed data. More samples with different doping values, a better knowledge of the absolute value of the oxygen content of the samples, as well as further measurements at smaller temperature steps and on different reflections, could make the conclusions on the results more clear – especially in the context of earlier work.

Some preparations have already been made in order to do a full analysis of many more superstructures in especially the $x = 0.00$ compound, where detailed data have been obtained for several different temperatures at the neutron time-of-flight single-crystal diffractometer SXD at ISIS in Harwell, Oxfordshire, England. These data will hopefully result in a full structural model of the 3D oxygen ordering in the compound, which has been sorely missed for a long time.

To this day the mechanisms behind the high-temperature superconductors have not been understood fully. Because of this it is important to investigate even the earliest discovered of these materials with varying experimental techniques, building up a large puzzle that can hopefully – one day – be solved. With this work, I have added a small piece to the collected work, and I hope that I will be able to add many more in the future.

Appendixes



Calculations

In this appendix I will show calculations that are relevant for this thesis, but which I deemed to not be important enough to have in the main text.

A.1 Derivation of the Bragg condition for scattering

To derive the Bragg condition for scattering, consider a crystal made out of parallel planes of ions with a interplanar distance d , as shown in Fig. A.1.

To get constructive interference of a beam scattered by two consecutive layers, the difference in distance traveled by either beam must be an integer number, n , of wavelengths λ . This assumes elastic scattering so $\lambda = \lambda_i = \lambda_f$ (equivalent to $k = |\mathbf{k}_i| = |\mathbf{k}_f|$). Looking at the figure, the extra distance traveled by the lower of the two shown beams is $2d \sin \theta$, and hence the condition for constructive interference is

$$n\lambda = 2d \sin \theta, \quad (\text{A.1.1})$$

also known as Bragg's law. The Laue condition further states that $\mathbf{q} = \boldsymbol{\tau}$, such that q must equal $\tau = 2\pi n/d$. Further applying that $k = 2\pi/\lambda$, Bragg's law can be rewritten to

$$q = 2k \sin \theta, \quad (\text{A.1.2})$$

which is very useful when working with reciprocal space instead of real space.

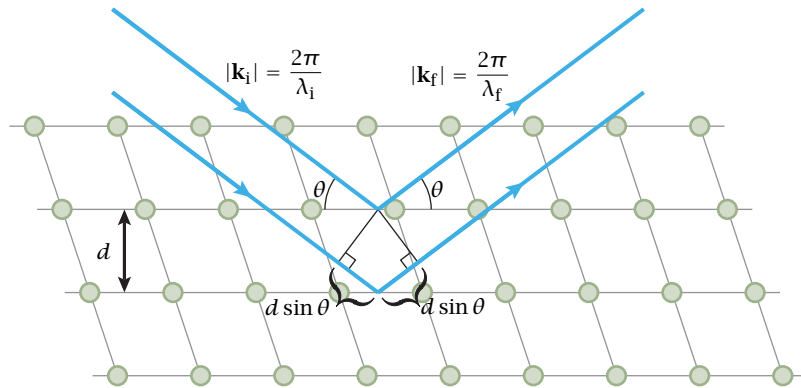


Figure A.1: Illustration to derive the Bragg law, showing the ingoing and outgoing beams being scattered elastically at an angle of 2θ on crystal planes with interplanar distance d .

A.2 Proof that the Bragg and Laue conditions are equivalent

Suppose the incident and scattered wave vectors $\mathbf{k}_i$ and $\mathbf{k}_f$ satisfy the Laue condition, such that $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is a reciprocal lattice vector $\boldsymbol{\tau}$. The scattering vector must hence be a normal vector to the scattering planes defined by $\boldsymbol{\tau}$.

Assuming elastic scattering, $|\mathbf{k}_i| = |\mathbf{k}_f|$, it follows that $\mathbf{k}_i$ and $\mathbf{k}_f$ must make the same angle θ with the plane perpendicular to $\mathbf{q}$. Hence, as seen on Fig. A.2, the scattering can be seen as a Bragg reflection from the family of real space lattice planes perpendicular to the reciprocal lattice vector $\boldsymbol{\tau}$, with Bragg angle θ .

From the figure, it is geometrically visible that

$$|\mathbf{q}| = 2k \sin \theta, \quad (\text{A.2.1})$$

and hence we come directly back to Bragg's law in the form of Eq. (A.1.2).

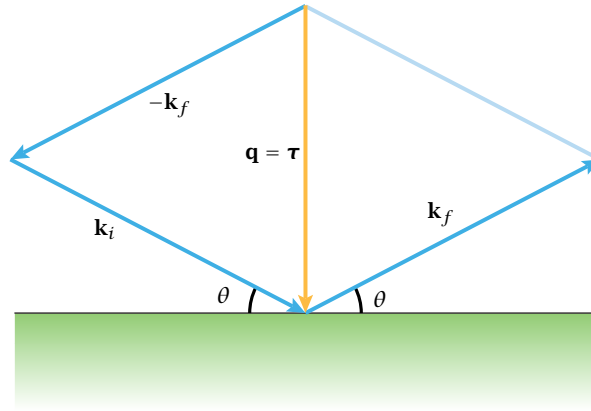


Figure A.2: Illustration to show how $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ being perpendicular to a lattice plane means that $\mathbf{k}_i$ and $\mathbf{k}_f$ must have the same angle θ to the plane for elastic scattering with $|\mathbf{k}_i| = |\mathbf{k}_f|$.

A similar way to see the equivalence of the Laue and Bragg conditions is to look at the vectors in reciprocal space as in Fig. A.3. Again assuming elastic scattering $|\mathbf{k}_i| = |\mathbf{k}_f|$, and defining the angle between $\mathbf{k}_i$ and $\mathbf{k}_f$ to be 2θ , it is simple to see trigonometrically that

$$\sin \theta = \frac{q/2}{k}, \quad (\text{A.2.2})$$

which once more leads to Bragg's law in the form of Eq. (A.1.2).

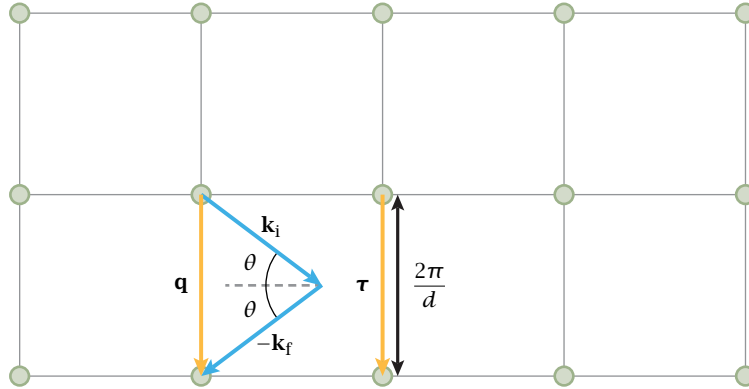


Figure A.3: Illustration to show how the length of $\mathbf{q}$ can be expressed as a function of k and θ for elastic scattering $|\mathbf{k}_i| = |\mathbf{k}_f|$.

A.3 Loss of flux due to typical sample environments on BW5

A typical cooling sample environment on the BW5 instrument, such as a displer cryostat or an ILL “Orange” cryostat, has in total 3 mm aluminium in the beam, divided into two times 1 mm vacuum shielding and two times 0.5 mm thermal radiation shielding, [168].

Assuming an X-ray energy of 100 keV, it is possible to look up the absorption coefficient to be $\mu = 0.45887708 \text{ cm}^{-1}$, [151]. Through the total length of aluminium in the beam, it is then possible to calculate the remaining flux by

$$\Psi(z = 3 \text{ mm}) = \Psi_0 \exp(-\mu z) = \Psi_0 \exp(-0.45887708 \text{ cm}^{-1} \cdot 0.3 \text{ cm}) = 0.87139 \Psi_0. \quad (\text{A.3.1})$$

In Fig. A.4 this calculation has been done for several more thicknesses and X-ray energies, as an overview.

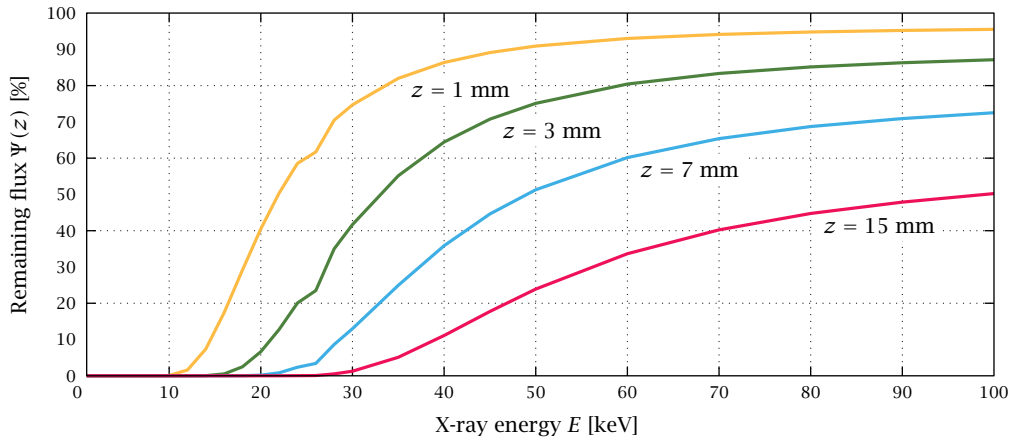


Figure A.4: Remaining flux after sending varying energies of X-rays through several different thicknesses of aluminium. The curves have been calculated as in Eq. (A.3.1) using absorption coefficients from Bandyopadhyay *et al.* [151].

A.4 Typical twinning separation

Using Eq. (6.3.2), it is possible to calculate typical angular separations between measured peaks in the hk plane. The low temperature lattice constants were given in Tab. 7.1, and from this I get

$$\text{La}_2\text{CuO}_{4+y}: \quad \Delta = 90^\circ - 2 \tan^{-1} \left(\frac{a}{b} \right) = 90^\circ - 2 \tan^{-1} \left(\frac{5.30 \text{ \AA}}{5.37 \text{ \AA}} \right) = 0.75^\circ, \quad (\text{A.4.1})$$

$$\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}: \quad \Delta = 90^\circ - 2 \tan^{-1} \left(\frac{a}{b} \right) = 90^\circ - 2 \tan^{-1} \left(\frac{5.32 \text{ \AA}}{5.38 \text{ \AA}} \right) = 0.64^\circ, \quad (\text{A.4.2})$$

$$\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}: \quad \Delta = 90^\circ - 2 \tan^{-1} \left(\frac{a}{b} \right) = 90^\circ - 2 \tan^{-1} \left(\frac{5.32 \text{ \AA}}{5.36 \text{ \AA}} \right) = 0.43^\circ, \quad (\text{A.4.3})$$

$$\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}: \quad \Delta = 90^\circ - 2 \tan^{-1} \left(\frac{a}{b} \right) = 90^\circ - 2 \tan^{-1} \left(\frac{5.33 \text{ \AA}}{5.34 \text{ \AA}} \right) = 0.11^\circ. \quad (\text{A.4.4})$$

A.5 X-ray attenuation lengths

In order to find the X-ray attenuation coefficient for a sample material, it is necessary to first know the density of the material. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, this is calculated by

$$\rho = 4 \frac{(2-x)m_{\text{La}} + xm_{\text{Sr}} + m_{\text{Cu}} + (4+y)m_{\text{O}}}{V_0}, \quad (\text{A.5.1})$$

where $V_0 = abc$ is the unit cell volume, and the 4 comes from the fact that there are four chemical units in each crystallographic unit cell. The crystal lattice parameters for the four samples can be found in Tab. 7.1, and the values for the atomic masses are $m_{\text{La}} = 138.9055$ amu, $m_{\text{Sr}} = 87.62$ amu, $m_{\text{Cu}} = 63.546$ amu, and $m_{\text{O}} = 15.9994$ amu. Setting $y = 0.055$ for simplicity, this results in

$$\text{La}_2\text{CuO}_{4+y}: \quad \rho = 7.182 \text{ g/cm}^3, \quad (\text{A.5.2})$$

$$\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}: \quad \rho = 7.112 \text{ g/cm}^3, \quad (\text{A.5.3})$$

$$\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}: \quad \rho = 7.137 \text{ g/cm}^3, \quad (\text{A.5.4})$$

$$\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}: \quad \rho = 7.133 \text{ g/cm}^3. \quad (\text{A.5.5})$$

With the densities known, it is possible to look up the X-ray attenuation length λ for the material using the NIST database *X-ray Form Factor, Attenuation, and Scattering Tables*, [152]. The result for a lookup with density 7.1 g/cm^3 is plotted in Fig. A.5 both on a linear and logarithmic scale for a large range of energies. For an energy of $E \approx 100 \text{ keV}$, the attenuation length is $\lambda \approx 0.85 \text{ mm}$.

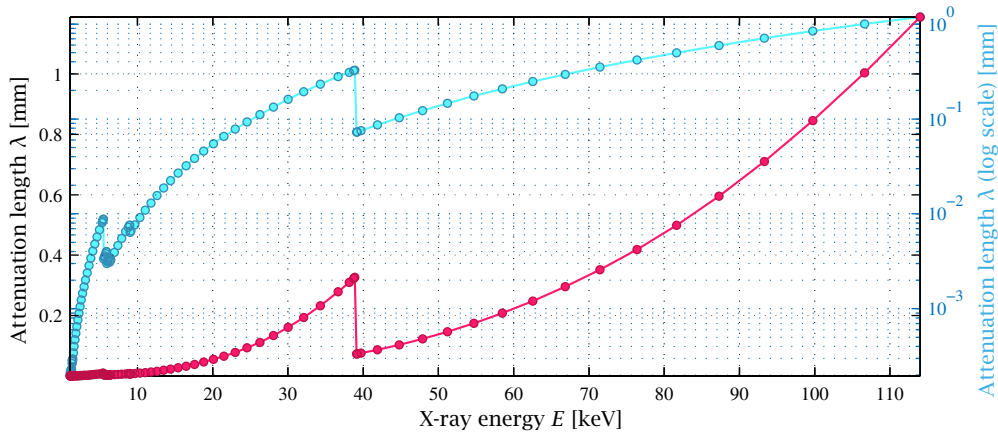


Figure A.5: X-ray attenuation lengths plotted linearly (left axis, red points) and logarithmic (right axis, blue points). Data from table lookup, [152]. Lines are a guide to the eye.



Additional crystallographic information

B.1 Overview of space group investigations

An overview of a few of the more extensive studies on the space group/space groups of differently doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ is shown in Tab. B.1.

B.2 Examples of crystal refinement results

There are many refinement results of the average structure for different Sr and O dopings of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ in literature, both using powder and single crystal samples with neutrons and X-rays. I have tried to collect a few of these results in the following tables.

Grande *et al.* [90] were the first to solve the un-doped structure, using X-rays on powder samples to solve the average structure at room temperature ($T = 300$ K) for La_2CuO_4 as shown in Tab. B.2. These data were also visualized in Fig. 6.1.

Rial *et al.* [104] used neutrons on powder samples to solve the average structure at room temperature for La_2CuO_4 and $\text{La}_2\text{CuO}_{4+y}$, as shown in Tab. B.3. Note that the un-doped structure matches well with the old results from Tab. B.2, even with the O(2) 8f position, which for the y value is simply chosen below the unit cell instead of in the top (the large value in Tab. B.2 versus the negative value in Tab. B.3).

Rial *et al.* [101] also used neutrons on powder samples to solve the average structure at room temperature for a set of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples, then oxygenated them and solved the structure similarly for both room temperature and low temperature, as shown in Tab. B.4.

Sr doping x	O doping y	$Fmmm$	$Bmab$	$I4/mmm$	Ref.
Un-doped					
0	0		$T < 533 \text{ K}$	$533 \text{ K} < T$	[89, 90]
Only strontium doped					
0.025	0		$T \lesssim 475 \text{ K}$	$475 \text{ K} \gtrsim T$	[127]
0.05	0		$T \lesssim 420 \text{ K}$	$420 \text{ K} \gtrsim T$	[127]
0.105	0		$T \lesssim 295 \text{ K}$	$295 \text{ K} \gtrsim T$	[127]
0.12	0		$T \lesssim 255 \text{ K}$	$255 \text{ K} \gtrsim T$	[127]
0.145	0		$T \lesssim 195 \text{ K}$	$195 \text{ K} \gtrsim T$	[127]
0.17	0		$T \lesssim 140 \text{ K}$	$140 \text{ K} \gtrsim T$	[127]
Only oxygen doped					
0	0.018	$T < 315 \text{ K}$	$T < 520 \text{ K}$	$520 \text{ K} < T$	[99]
0	0.03	$T < 320 \text{ K}$	$T < 430 \text{ K}$	$430 \text{ K} < T$	[105]
0	0.032	$T < 415 \text{ K}$ $a = b$ for $380 \text{ K} < T$	$T < 415 \text{ K}$	$415 \text{ K} < T$	[99]
0	0.044	$T < 340 \text{ K}$	$T < 275 \text{ K}$	$340 \text{ K} < T$	[99]
Co-doped					
Several oxygen annealed samples with $0 \geq (x, y) \geq 0.03$ showed phase separation into oxygen-rich and oxygen-stoichiometric domains, possibly $Fmmm$ and $Bmab$ (although not solved directly):					
0.004	0.03	$T \lesssim 280 \text{ K}$	$T \lesssim 520 \text{ K}$	$520 \text{ K} \gtrsim T$	[135]
0.016	0.03	$T \lesssim 130 \text{ K}$	$T \lesssim 500 \text{ K}$	$500 \text{ K} \gtrsim T$	[135]
0.03	0.03		$T \lesssim 460 \text{ K}$	$460 \text{ K} \gtrsim T$	[135]

Table B.1: Overview of space group results from investigations where refinements were done for a large number of temperatures to obtain accurate transition temperatures. Many more experiments have been done exclusively at, say, 10-20 K and then again at 280-320 K. There is a distinct lack of investigations for $\text{La}_2\text{CuO}_{4+y}$ samples with large y , while the investigations on co-doped materials mentioned here (shown in grey, with the values being very roughly read from a graph) did not actually solve the structure, but simply conclude on phase separation.

Atom	Site	x [a]	y [b]	z [c]	Occ
La	8f (m...)	0.00	0.007	0.362	2
Cu	4a (2/m...)	0.00	0.000	0.000	1
O(1)	8e (..2)	0.25	0.25	0.007	2
O(2)	8f (m..)	0.00	0.969	0.187	2

Table B.2: Room temperature ($T = 300 \text{ K}$) structure from Grande *et al.* [90, Tab. 1] for La_2CuO_4 in space group $Bmab$ (changed from their used space group $Abma$, where the a and b directions are exchanged) with $a = 5.370 \text{ \AA}$, $b = 5.406 \text{ \AA}$, $c = 13.15 \text{ \AA}$. Occ is the occupation factor, which is simply here for comparison with other results (the occupation was not changed from the chemical content in their structure solution).

Atom	Site	$x [a]$	$y [b]$	$z [c]$	Occ	$B [\text{\AA}^2]$
La ₂ CuO ₄ with $a = 5.3562(2) \text{ \AA}$, $b = 5.4024(2) \text{ \AA}$, $c = 13.1494(6) \text{ \AA}$						
La	8f (m..)	0	0.0060(6)	0.3610(1)	2	0.33(3)
Cu	4a (2/m..)	0	0	0	1	0.12(3)
O(1)	8e (..2)	0.25	0.25	0.0081(3)	1.99(2)	0.43(5)
O(2)	8f (m..)	0	-0.0332(6)	0.1839(3)	2.01(2)	0.98(6)
La ₂ CuO _{4+y} with $a = 5.3427(3) \text{ \AA}$, $b = 5.4040(3) \text{ \AA}$, $c = 13.2124(7) \text{ \AA}$						
La	8f (m...)	0	-0.002(1)	0.3597(2)	2	0.49(4)
Cu	4a (2/m..)	0	0	0	1	0.20(7)
O(1)	8e (..2)	0.25	0.25	0.0043(6)	1.99(3)	0.60(7)
O(2)	8f (m..)	0	-0.019(1)	0.1825(4)	1.69(1)	0.93(7)
O(3)	16g (1)	0.029(7)	0.093(5)	0.179(3)	0.31(1)	0.93(7)
O(4)	8e (..2)	0.25	0.25	0.238(6)	0.105(14)	0.93(7)

Table B.3: Room temperature ($T = 300 \text{ K}$) structures from Rial *et al.* [104, Tab. 1] for La₂CuO₄ and La₂CuO_{4+y} in space group *Bmab*. Occ is the occupation factor, while B is the equivalent isotropic thermal parameter.

Sr doping x	a [Å]	b [Å]	c [Å]	γ (La/Sr)	z (La/Sr)	z (O(1))	y (O(2))	z (O(2))	x (O(3))	y (O(3))	z (O(3))	z (O(4))
La_{2-x}Sr_xCuO₄ at $T = 300$ K												
0.05	5.3541(4)	5.3866(4)	13.1846(8)	0.0047(9)	0.3612(2)	0.0067(5)	-0.0279(8)	0.1823(3)				
0.09	5.3510(5)	5.3633(5)	13.2133(8)	0.004(1)	0.3608(2)	0.0051(6)	-0.021(1)	0.1817(3)				
0.12	5.3539(2)		13.2249(7)	0	0.3610(1)	0	0	0.1813(3)				
0.125	5.3518(2)		13.2287(7)	0	0.3609(1)	0	0	0.1814(3)				
0.13	5.3502(2)		13.2333(7)	0	0.3609(1)	0	0	0.1813(3)				
0.14	5.3493(2)		13.2368(7)	0	0.3609(1)	0	0	0.1815(3)				
La_{2-x}Sr_xCuO_{4+y} at $T = 300$ K												
0.05	5.3545(4)	5.3856(5)	13.232(1)	-0.001(2)	0.3602(2)	-0.003(1)	-0.016(2)	0.1815(5)	0.02(1)	0.089(5)	0.177(3)	0.218(5)
0.09	5.3468(5)	5.3663(5)	13.2378(9)	0.003(2)	0.3603(2)	-0.002(1)	-0.021(2)	0.1813(6)	0.02(1)	0.078(7)	0.179(4)	0.216(5)
0.12	5.3496(3)		13.2377(9)	0	0.3602(2)	0	0	0.1812(6)	0.056(5)	0.056(5)	0.181(4)	0.226(7)
0.125	5.3499(3)		13.2397(9)	0	0.3605(2)	0	0	0.1809(6)	0.056(5)	0.056(5)	0.181(4)	0.217(7)
0.13	5.3486(3)		13.2370(8)	0	0.3602(2)	0	0	0.1812(6)	0.055(6)	0.055(6)	0.182(5)	0.222(8)
0.14	5.3476(3)		13.2405(8)	0	0.3605(2)	0	0	0.1813(6)	0.052(3)	0.052(3)	0.182(4)	0.216(7)
La_{2-x}Sr_xCuO_{4+y} at $T = 10$ K												
0.05	5.3312(4)	5.3793(5)	13.201(1)	0.005(2)	0.3603(2)	0.004(1)	-0.014(3)	0.1819(6)	-0.01(1)	0.087(6)	0.179(3)	0.224(5)
0.09	5.3333(4)	5.3548(5)	13.1976(9)	0.009(1)	0.3604(2)	0.003(1)	-0.016(2)	0.1814(6)	-0.02(1)	0.077(7)	0.179(3)	0.219(5)
0.12	5.3274(5)	5.3505(5)	13.1968(9)	0.009(1)	0.3602(2)	-0.0047(8)	-0.022(2)	0.1818(5)	0.033(9)	0.074(9)	0.179(4)	0.225(7)
0.125	5.3301(4)	5.3482(5)	13.1947(8)	0.007(1)	0.3604(2)	-0.0033(9)	-0.026(2)	0.1818(7)	0.04(1)	0.03(1)	0.179(6)	0.213(7)
0.14	5.3245(4)	5.3473(9)	13.1935(8)	0.009(1)	0.3604(2)	-0.0033(9)	-0.025(2)	0.1819(6)	0.04(1)	0.05(1)	0.181(6)	0.216(7)

Table B.4: Room temperature and low temperature structures from Rial *et al.* [101, Tab. 2, 3, and 4] for La_{2-x}Sr_xCuO₄ and La_{2-x}Sr_xCuO_{4+y} in space group *Bmab* and *F4/mmm* (when $a = b$). The site positions refer to the same naming convention as used in Tab. B.3, with the site-forced 0 and 0.25 positions omitted here.



Mathematical functions

C.1 Gaussian

The Gaussian function is the classical bell shaped function with amplitude I_0 , center μ , and width σ ,

$$I(x) = I_0 \exp\left(-\frac{1}{2} \left(\frac{x - \mu}{\sigma}\right)^2\right), \quad (\text{C.1.1})$$

as shown in Fig. C.1(a). The area of the curve is found by

$$A = I_0 \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} \left(\frac{x - \mu}{\sigma}\right)^2\right) dx \quad (\text{C.1.2})$$

$$= I_0 \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} \left(\frac{y}{\sigma}\right)^2\right) dy \quad (\text{C.1.3})$$

$$= \sqrt{2} I_0 \sigma \int_{-\infty}^{\infty} \exp(-z^2) dz \quad (\text{C.1.4})$$

$$= \sqrt{2\pi} I_0 \sigma, \quad (\text{C.1.5})$$

where the variable of integration was first changed from x to $y = x - \mu$ and then to $z = y/\sqrt{2}\sigma$, and finally recognizing the Gaussian integral identity of $\sqrt{\pi}$.

Using the law of combinations of errors [11, Eq. (4.14)] (assuming uncorrelated uncertainties), it is possible to find the error on the area, δA , following the error on the amplitude and width, δI_0 and $\delta \sigma$,

$$\delta A^2 = \left(\frac{dA}{dI_0}\right)^2 \delta I_0^2 + \left(\frac{dA}{d\sigma}\right)^2 \delta \sigma^2 \quad (\text{C.1.6})$$

$$= 2\pi\sigma^2 \delta I_0^2 + 2\pi I_0^2 \delta \sigma^2 \quad (\text{C.1.7})$$

$$= A^2 \left(\frac{\delta I_0^2}{I_0^2} + \frac{\delta \sigma^2}{\sigma^2}\right), \quad (\text{C.1.8})$$

inserting the expression for the area from Eq. (C.1.5) in the last line.

The parameter σ controls the width of the peak, but not in a simple way: About 68.2% of the area of the peak lie within $\mu \pm \sigma$.

Often it is preferable to know the full width at half maximum (FWHM), or half width at half maximum (HWHM), instead. For a Gaussian curve this can be found by letting $x = w$ at half the

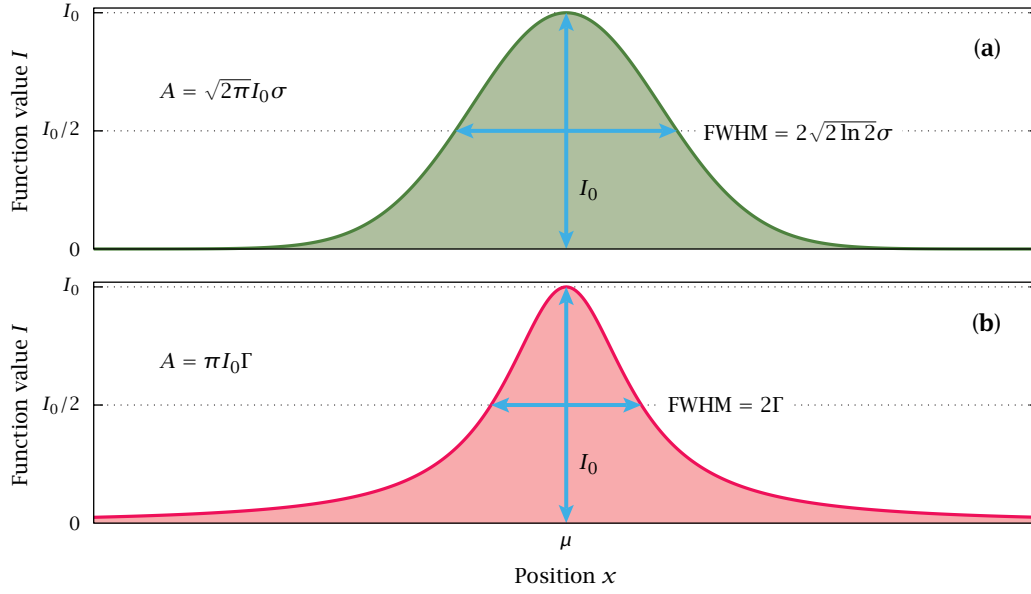


Figure C.1: A Gaussian (a) and a Lorentzian (b) normalized to have the same height and area. Note how much more of the area is hidden in the long tails in the Lorentzian.

maximum height, keeping the center of the curve in zero ($\mu = 0$), which means that

$$\frac{1}{2}I_0 = I_0 \exp\left(-\frac{1}{2}\left(\frac{w}{\sigma}\right)^2\right) \Rightarrow w = \sqrt{2\ln 2}\sigma, \quad (\text{C.1.9})$$

so $\text{FWHM} = 2w = 2\sqrt{2\ln 2}\sigma \approx 2.355\sigma$ and $\text{HWHM} = w = \sqrt{2\ln 2}\sigma \approx 1.177\sigma$.

C.2 Lorentzian

The Lorentzian function is another typical peak shape, which has larger tails than the Gaussian, and a sharper middle part. It is given by the amplitude I_0 , center μ , and width Γ ,

$$I(x) = I_0 \frac{\Gamma^2}{\Gamma^2 + (x - \mu)^2}, \quad (\text{C.2.1})$$

as shown in Fig. C.1(b). The area of this curve is found by

$$A = I_0\Gamma^2 \int_{-\infty}^{\infty} \frac{1}{\Gamma^2 + (x - \mu)^2} dx \quad (\text{C.2.2})$$

$$= I_0\Gamma^2 \int_{-\infty}^{\infty} \frac{1}{\Gamma^2 + y^2} dy \quad (\text{C.2.3})$$

$$= I_0\Gamma^2 \left[\frac{1}{\Gamma} \tan^{-1}\left(\frac{y}{\Gamma}\right) \right]_{-\infty}^{\infty} \quad (\text{C.2.4})$$

$$= I_0\Gamma \left(\frac{\pi}{2} + \frac{\pi}{2} \right) \quad (\text{C.2.5})$$

$$= \pi I_0\Gamma, \quad (\text{C.2.6})$$

where the variable of integration was changed from x to $y = x - \mu$ in the first step.

The error on the area, δA , is found with the law of combinations of errors from the errors on the amplitude and width, δI_0 and $\delta \Gamma$,

$$\delta A^2 = \left(\frac{dA}{dI_0} \right)^2 \delta I_0^2 + \left(\frac{dA}{d\Gamma} \right)^2 \delta \Gamma^2 \quad (\text{C.2.7})$$

$$= \pi^2 \Gamma^2 \delta I_0^2 + \pi^2 I_0^2 \delta \Gamma^2 \quad (\text{C.2.8})$$

$$= A^2 \left(\frac{\delta I_0^2}{I_0^2} + \frac{\delta \Gamma^2}{\Gamma^2} \right), \quad (\text{C.2.9})$$

inserting the expression for the area from Eq. (C.2.6) in the last line.

Setting $\mu = 0$, it is easy to see that the width Γ is defined simply by being the half width at half maximum, so HWHM = Γ and FWHM = 2Γ for the Lorentzian.

C.3 Voigt

The Voigt is a third peak shape, which I could have used for some of my data analysis, but chose not to because of it having more parameters. The Voigt is a convolution of a Gaussian and a Lorentzian peak shape,

$$I(x) = I_0 \int_{-\infty}^{\infty} G(x', \sigma) L(x - x', \Gamma) dx', \quad (\text{C.3.1})$$

where $G(x', \sigma)$ is a Gaussian with center μ_G and width σ as defined in Sect. C.1, and $L(x - x', \Gamma)$ is a Lorentzian with center μ_L and width Γ as defined in Sect. C.2, giving the center of the Voigt as $\mu = \mu_G + \mu_L$.

Often a pseudo-Voigt is defined as a linear combination of a Gaussian and a Lorentzian at the same center μ instead, as

$$I(x) = \eta L(x, \Gamma) + (1 - \eta) G(x, \sigma) \quad (\text{C.3.2})$$

with $0 < \eta < 1$. This function is simpler to use for fitting peak shapes, compared to the full convolution necessary for each fit step if using the original definition.

The Voigt is often used for peak shape analysis, where the peak shape is a combination of a Gaussian and a Lorentzian because of *e.g.* resolution effects, [136].

C.4 Power law

The classical power law used to fit transition curves as a function of temperature T , is given with the following expression.

$$f(T) = \begin{cases} I_0 |T - T_c|^\beta + I_b & \text{for } T \leq T_c, \\ I_b & \text{for } T \geq T_c, \end{cases} \quad (\text{C.4.1})$$

where I_0 is the amplitude, T_c is the critical temperature for the transition, β is the critical exponent, and I_b is the background.



Additional staging figures

D.1 All raw BW5 staging measurements

As explained in Chap. 7, measurements over the (014) peak along l were done on the BW5 instrument for four different samples, $\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ (see Tab. 7.2 on p. 51 for an overview of the experiments). An overview of the different datafiles – showing the temperature and the l interval they were measured for, is shown in Fig. D.1.

The raw data from the measurements are shown in Figs. D.2 to D.13, first showing the plots on a linear scale,

- ▶ Figure D.2; $\text{La}_2\text{CuO}_{4+y}$,
- ▶ Figure D.3 and D.4; $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$,
- ▶ Figure D.5; $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$,
- ▶ Figure D.6 and D.7; $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$,

and then on a logarithmic scale,

- ▶ Figure D.8; $\text{La}_2\text{CuO}_{4+y}$,
- ▶ Figure D.9 and D.10; $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$,
- ▶ Figure D.11; $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$,
- ▶ Figure D.12 and D.13; $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$.

A few overview figures have been plotted with the same l axes above each other, to make comparison of peak sizes easier. For the uncorrected data in Fig. 9.1 (p. 60) and the logarithmic scale plot in Fig. 9.2 (p. 61), these are Fig. D.14 and Fig. D.15. For the corrected data in Fig. 9.6 (p. 65) and the logarithmic scale plot in Fig. 9.7 (p. 66), these are Fig. D.16 and Fig. D.17.

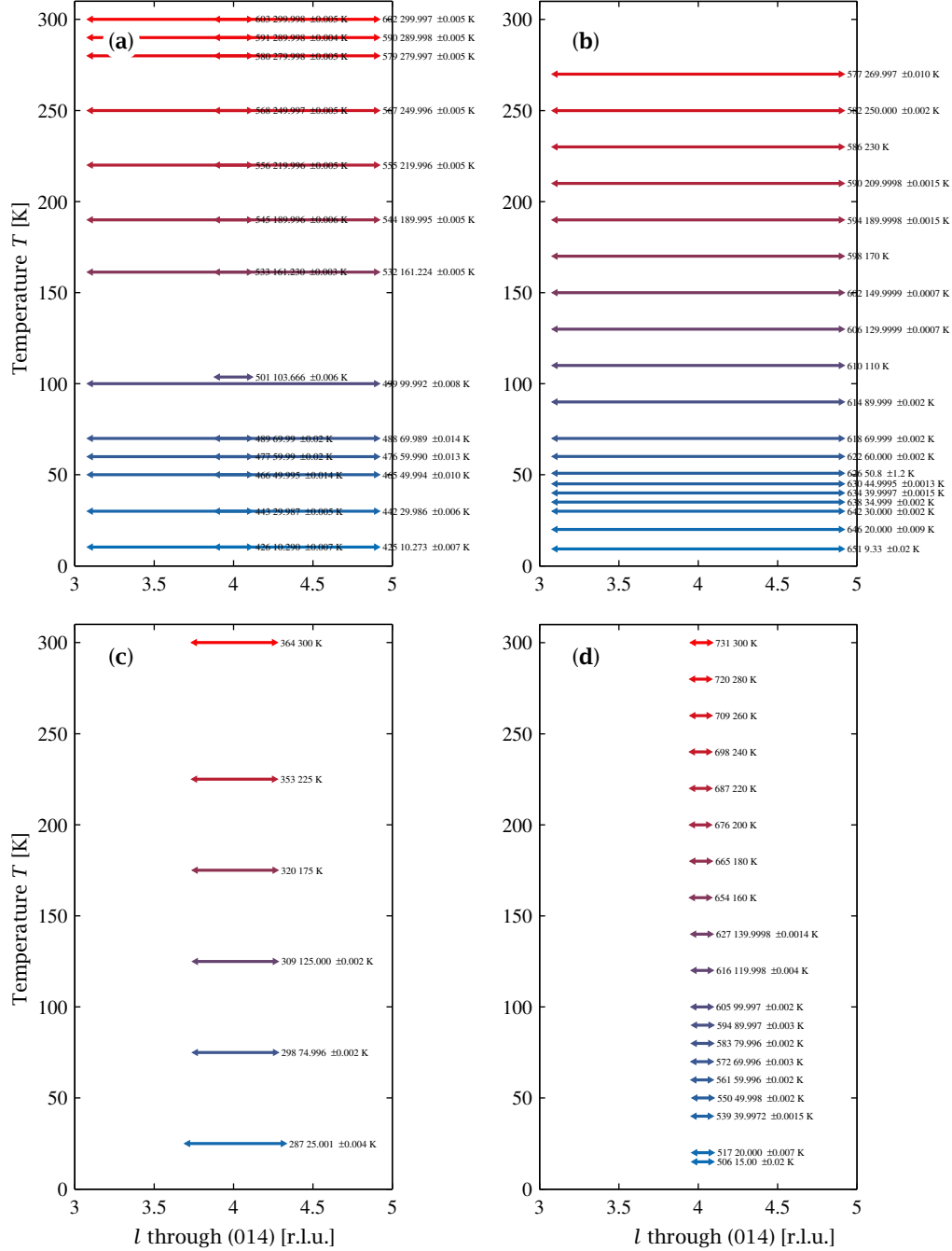


Figure D.1: Overview of the BW5 staging scans on the (a) $\text{La}_2\text{CuO}_{4+y}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ samples, with file numbers and corresponding average temperatures. The errors given on the temperatures are the standard deviation values.

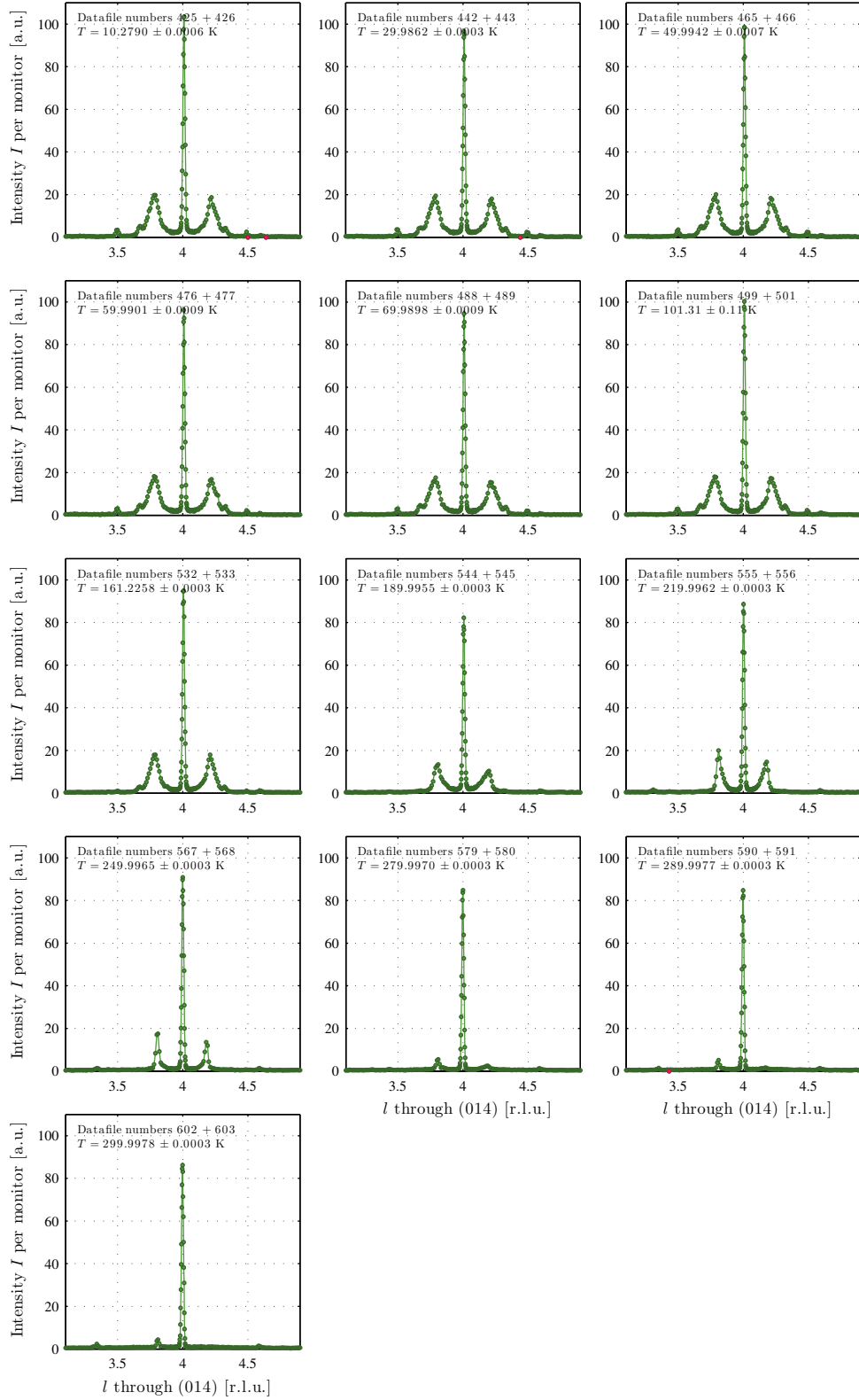


Figure D.2: Raw BW5 staging scans for the $\text{La}_2\text{CuO}_{4+y}$ sample (see Fig. D.1(a) for an overall view). The narrow scans around $l = 4$, as seen on Fig. D.1(a), have been combined with the wider scans at the same temperature, to form one single dataset. These are shown on a logarithmic scale in Fig. D.8.

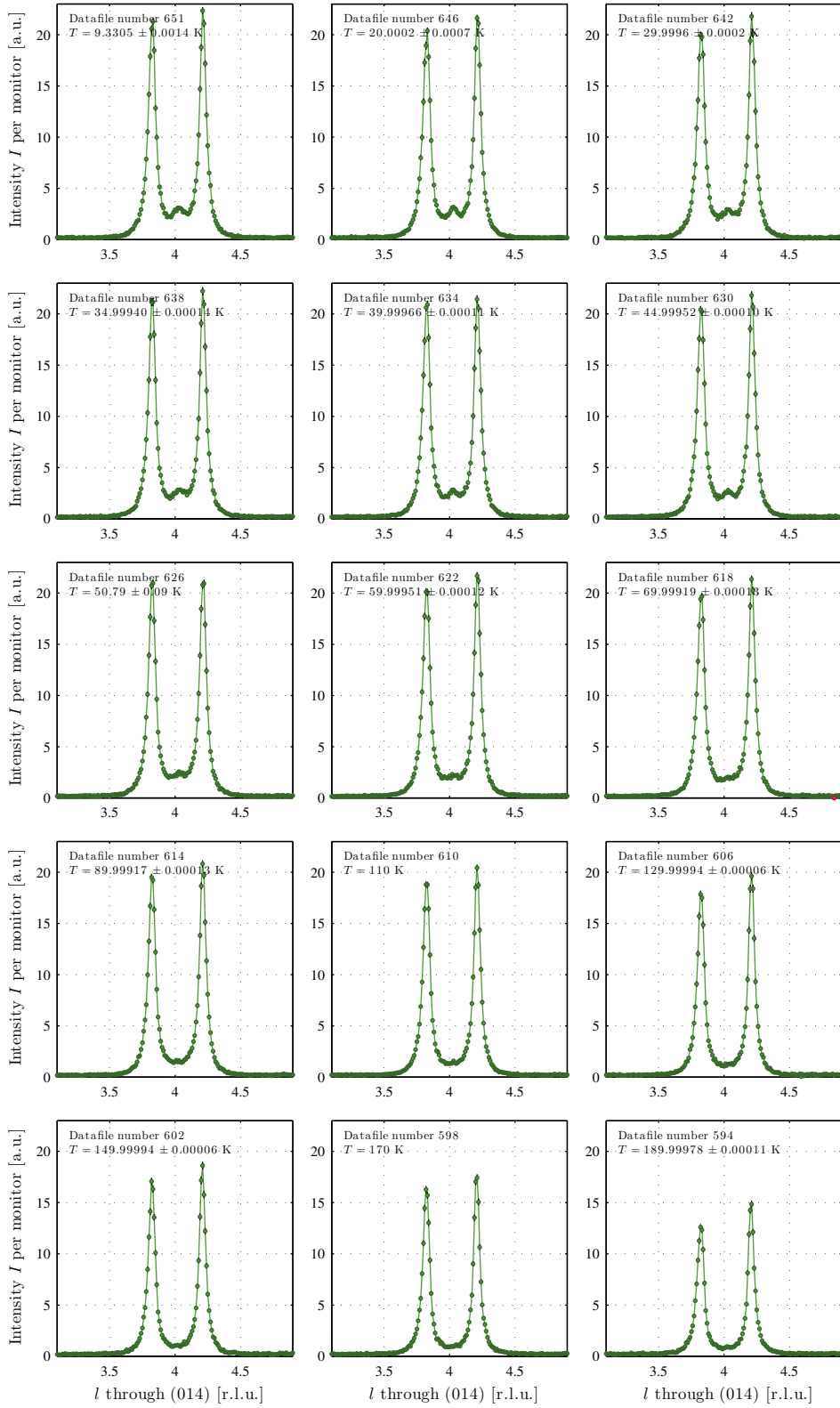


Figure D.3: Raw BW5 staging scans for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample (see Fig. D.1(b) for an overall view). Continued in Fig. D.4. These are shown on a logarithmic scale in Fig. D.9.

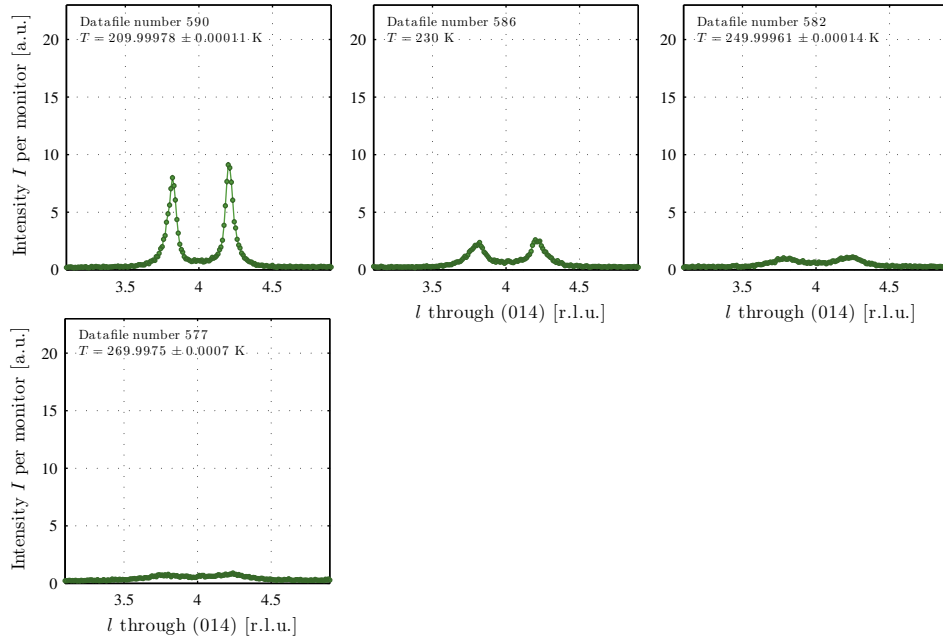


Figure D.4: Raw BW5 staging scans for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample (see Fig. D.1(b) for an overall view). Continued from Fig. D.3. These are shown on a logarithmic scale in Fig. D.10.

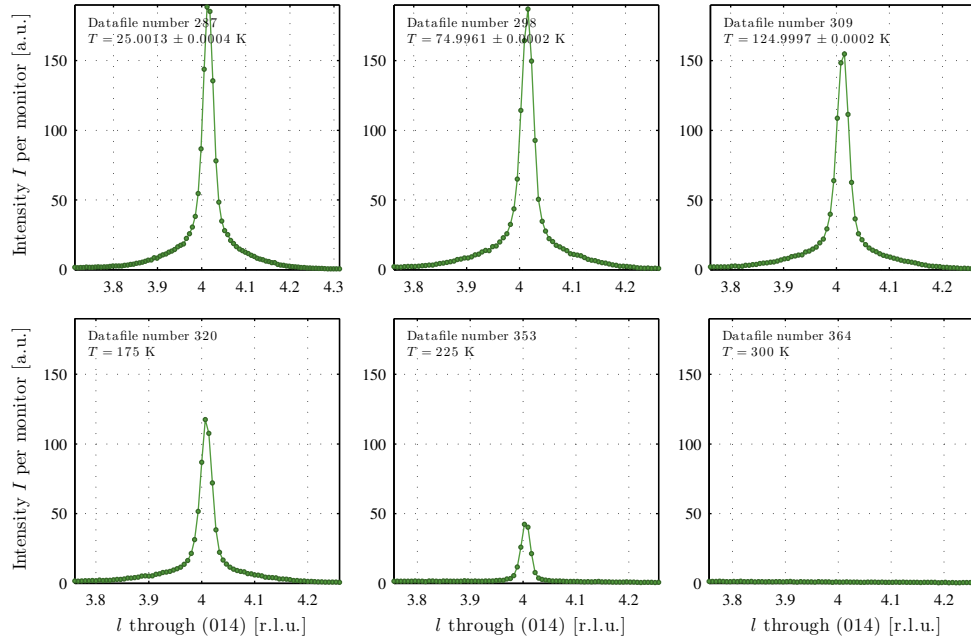


Figure D.5: Raw BW5 staging scans for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample (see Fig. D.1(c) for an overall view). These are shown on a logarithmic scale in Fig. D.11.

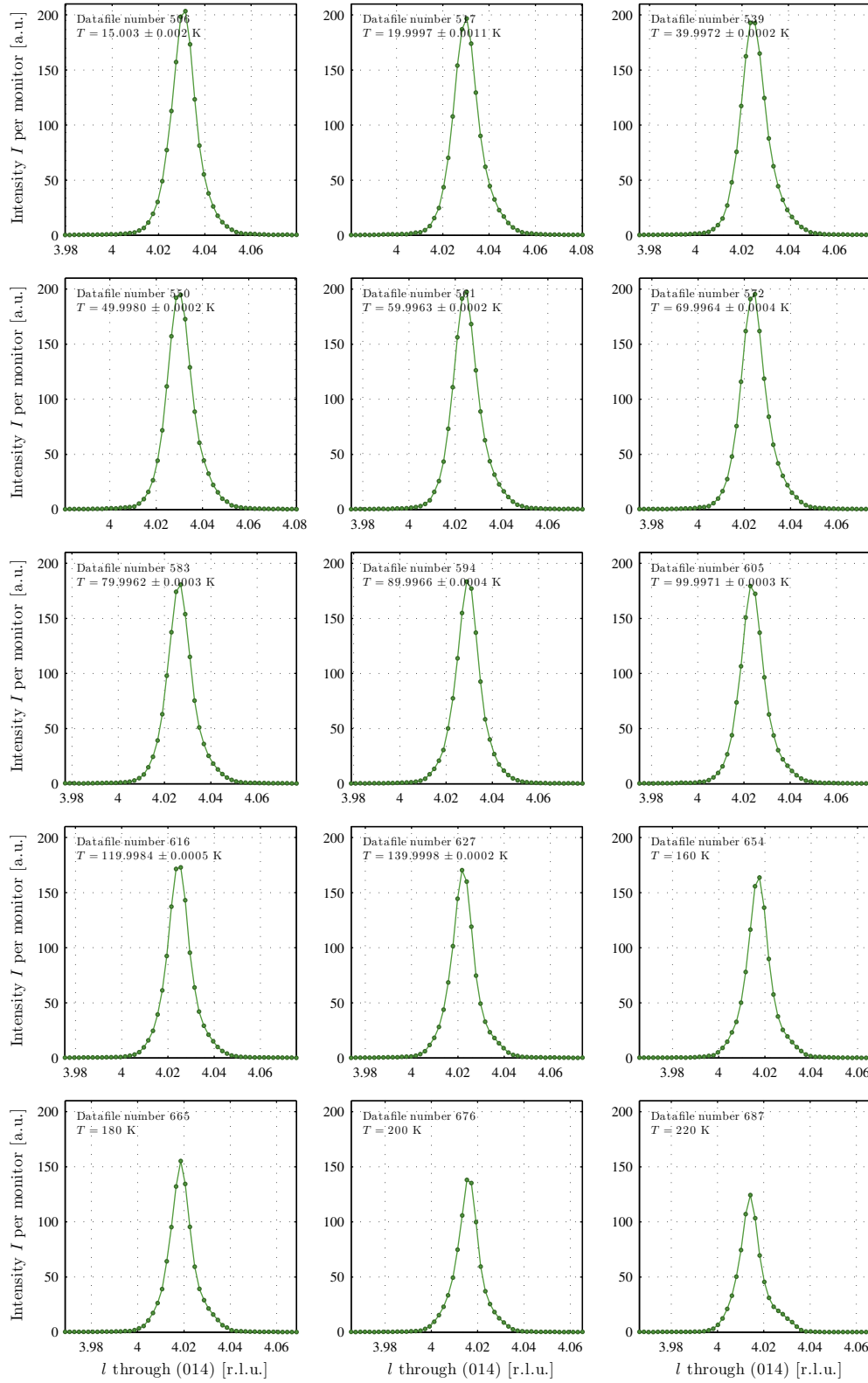


Figure D.6: Raw BW5 staging scans for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample (see Fig. D.1(d) for an overall view). Continued in Fig. D.7. These are shown on a logarithmic scale in Fig. D.12.

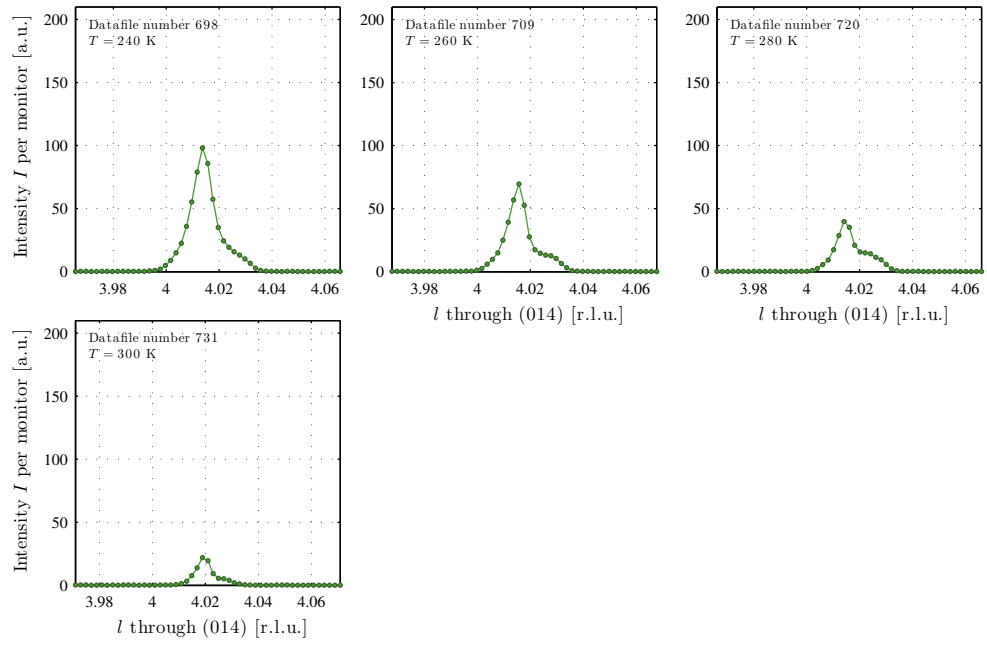


Figure D.7: Raw BW5 staging scans for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ sample (see Fig. D.1(d) for an overall view). Continued from Fig. D.6. These are shown on a logarithmic scale in Fig. D.13.

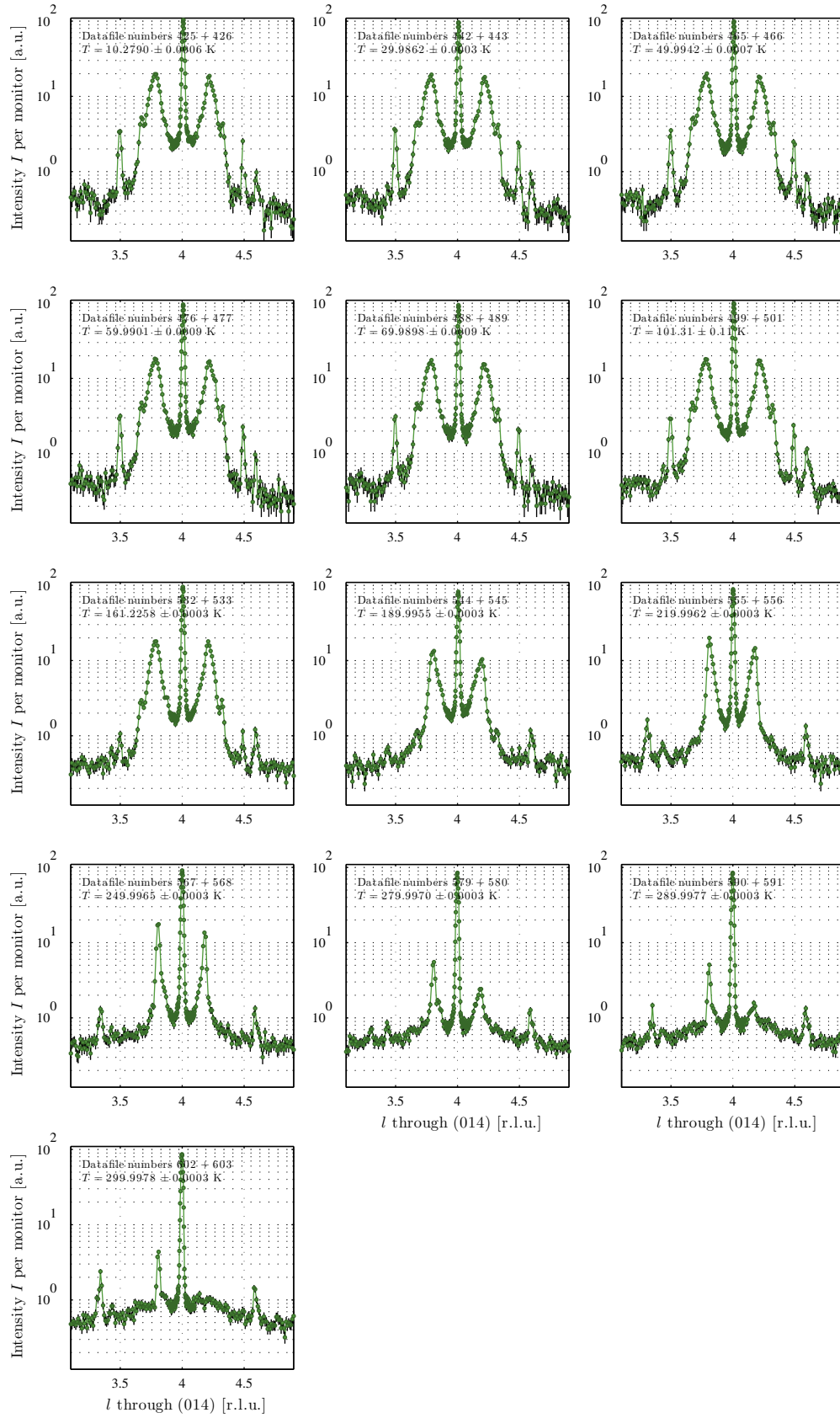


Figure D.8: Raw BW5 staging scans for the $\text{La}_2\text{CuO}_{4+y}$ sample (see Fig. D.1(a) for an overall view). These are shown on a linear scale in Fig. D.2.

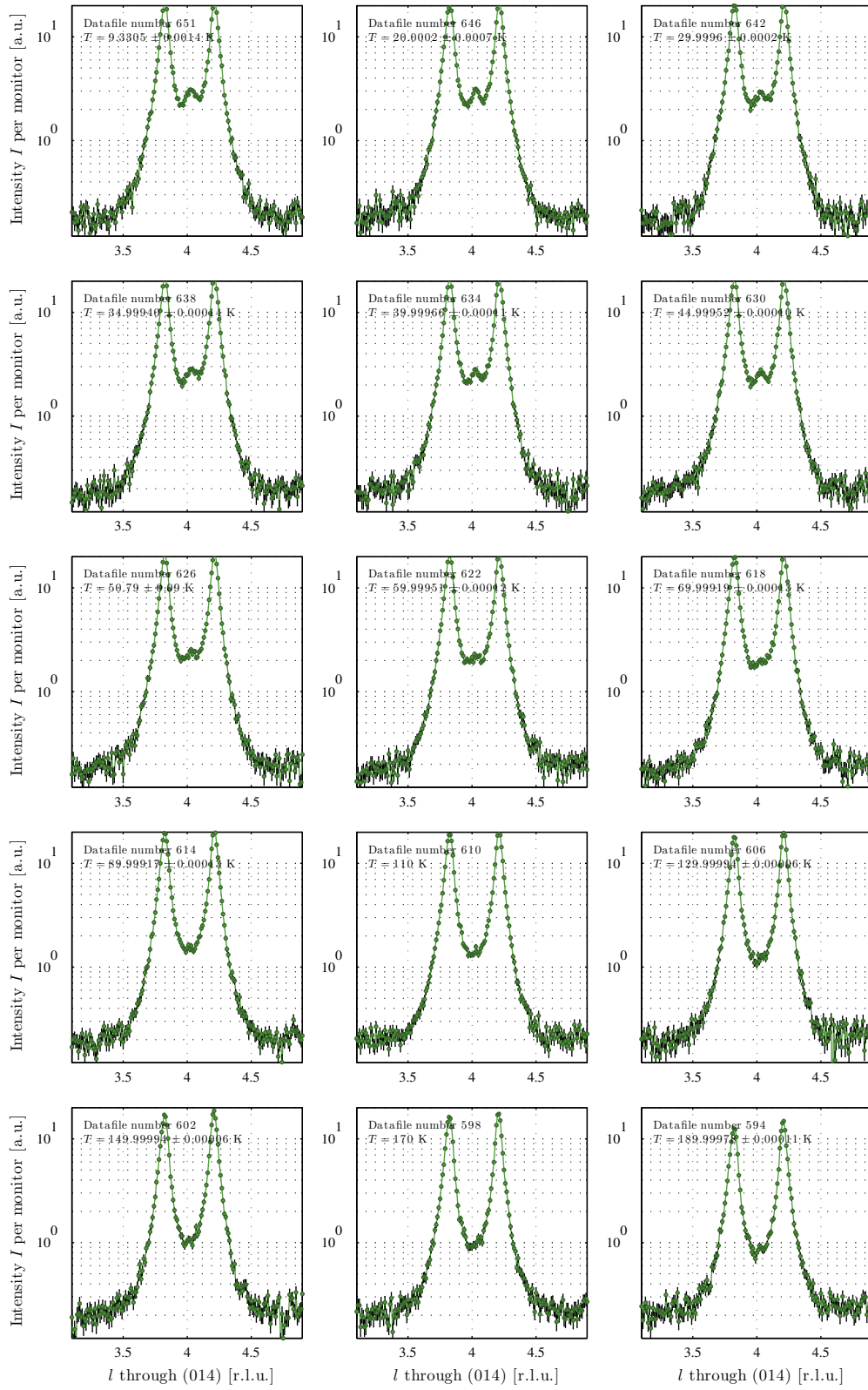


Figure D.9: Raw BW5 staging scans for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ sample (see Fig. D.1(b) for an overall view). Continued in Fig. D.4. These are shown on a linear scale in Fig. D.3.

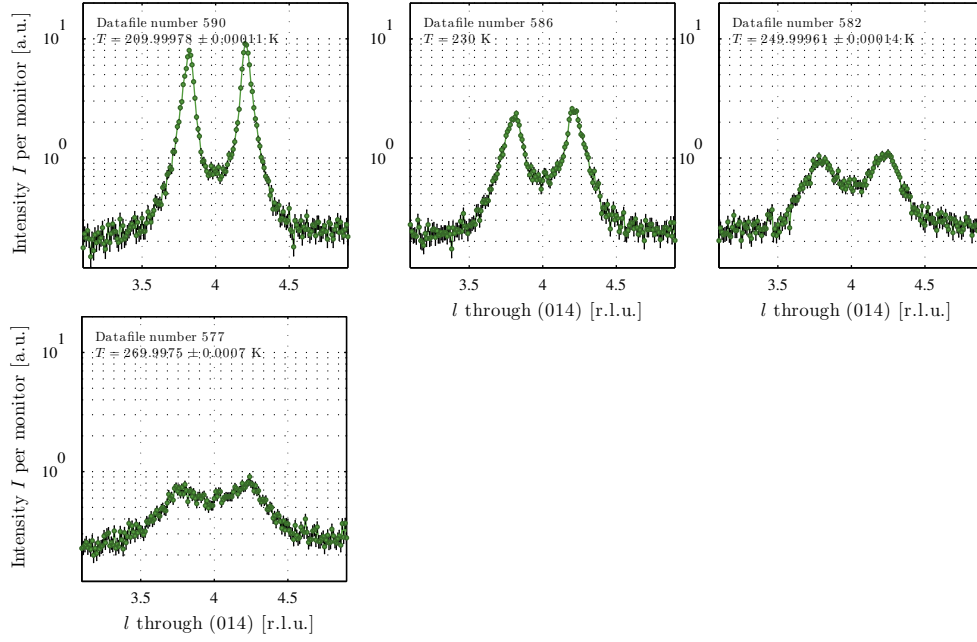


Figure D.10: Raw BW5 staging scans for $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ (see Fig. D.1(b) for an overall view). Continued from Fig. D.3. These are shown on a linear scale in Fig. D.4.

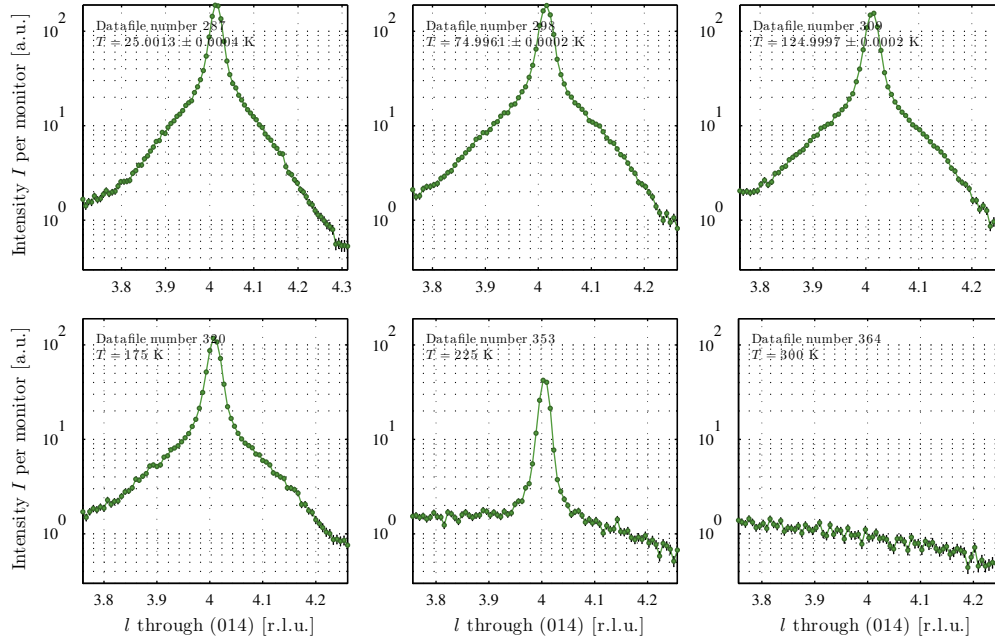


Figure D.11: Raw BW5 staging scans for the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ sample (see Fig. D.1(c) for an overall view). These are shown on a linear scale in Fig. D.5.

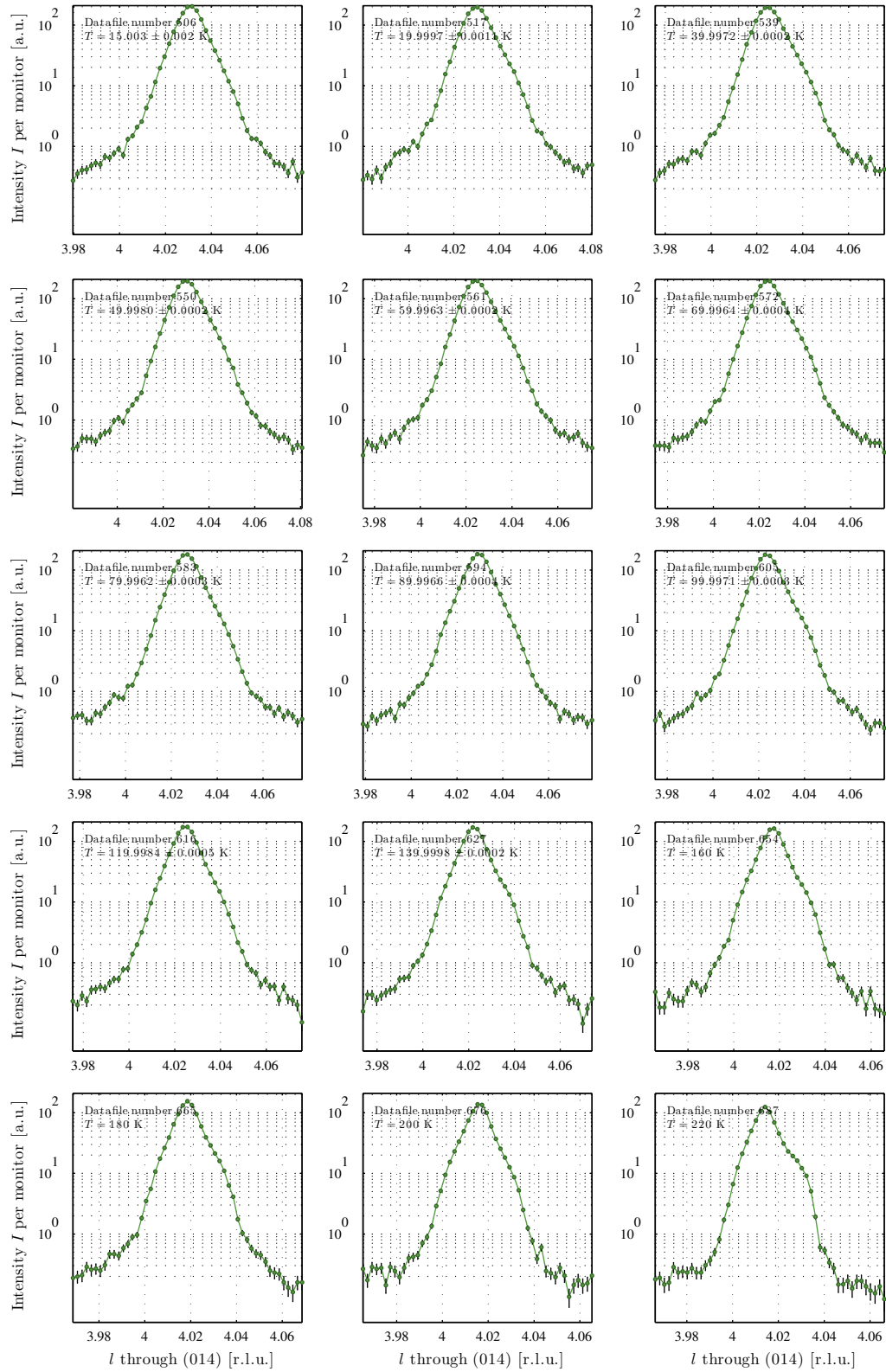


Figure D.12: Raw BW5 staging scans for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample (see Fig. D.1(d) for an overall view). Continued in Fig. D.7. These are shown on a linear scale in Fig. D.6.

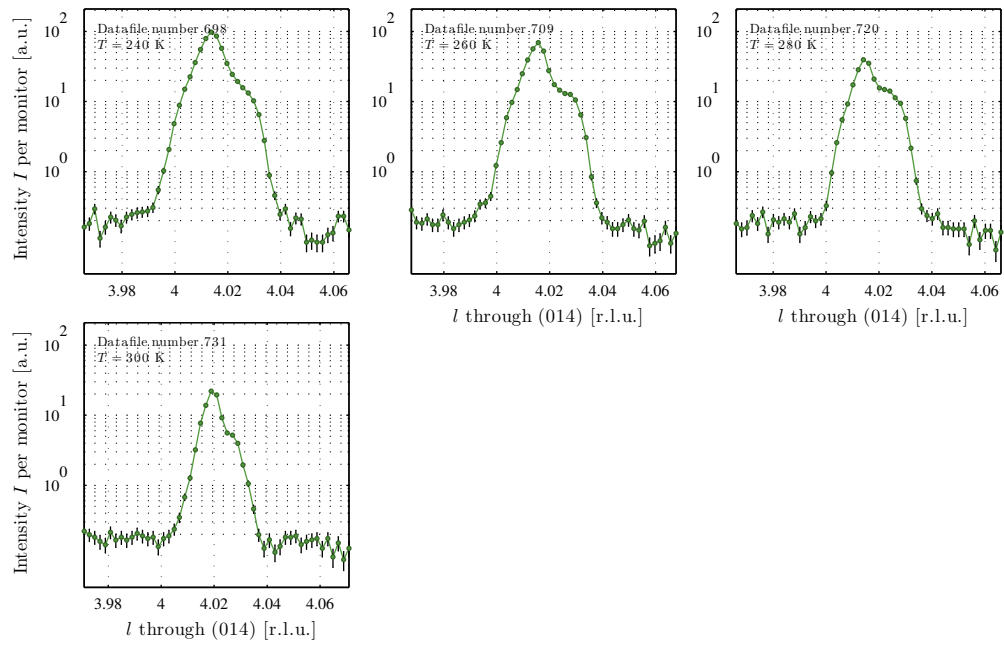


Figure D.13: Raw BW5 staging scans for the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ sample (see Fig. D.1(d) for an overall view). Continued from Fig. D.6. These are shown on a linear scale in Fig. D.7.

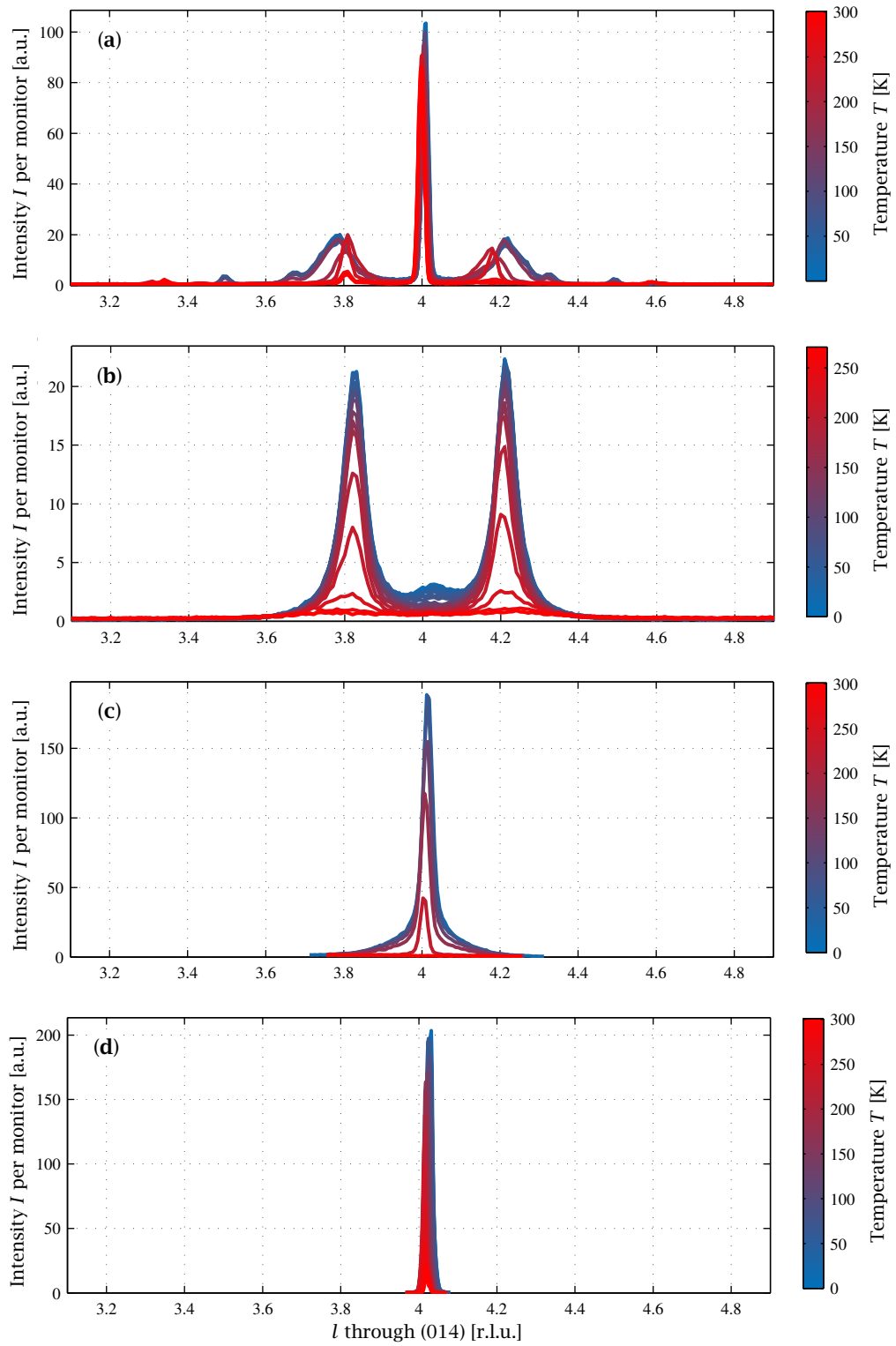


Figure D.14: Measurement on the (a) $\text{La}_2\text{CuO}_{4+\gamma}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ crystals along l over the (014) peak on BW5 before any correction of the first-axis. Here the data are plotted such that the l axes are the same, to compare better – a more zoomed in version can be seen in Fig. 9.1 (p. 60).

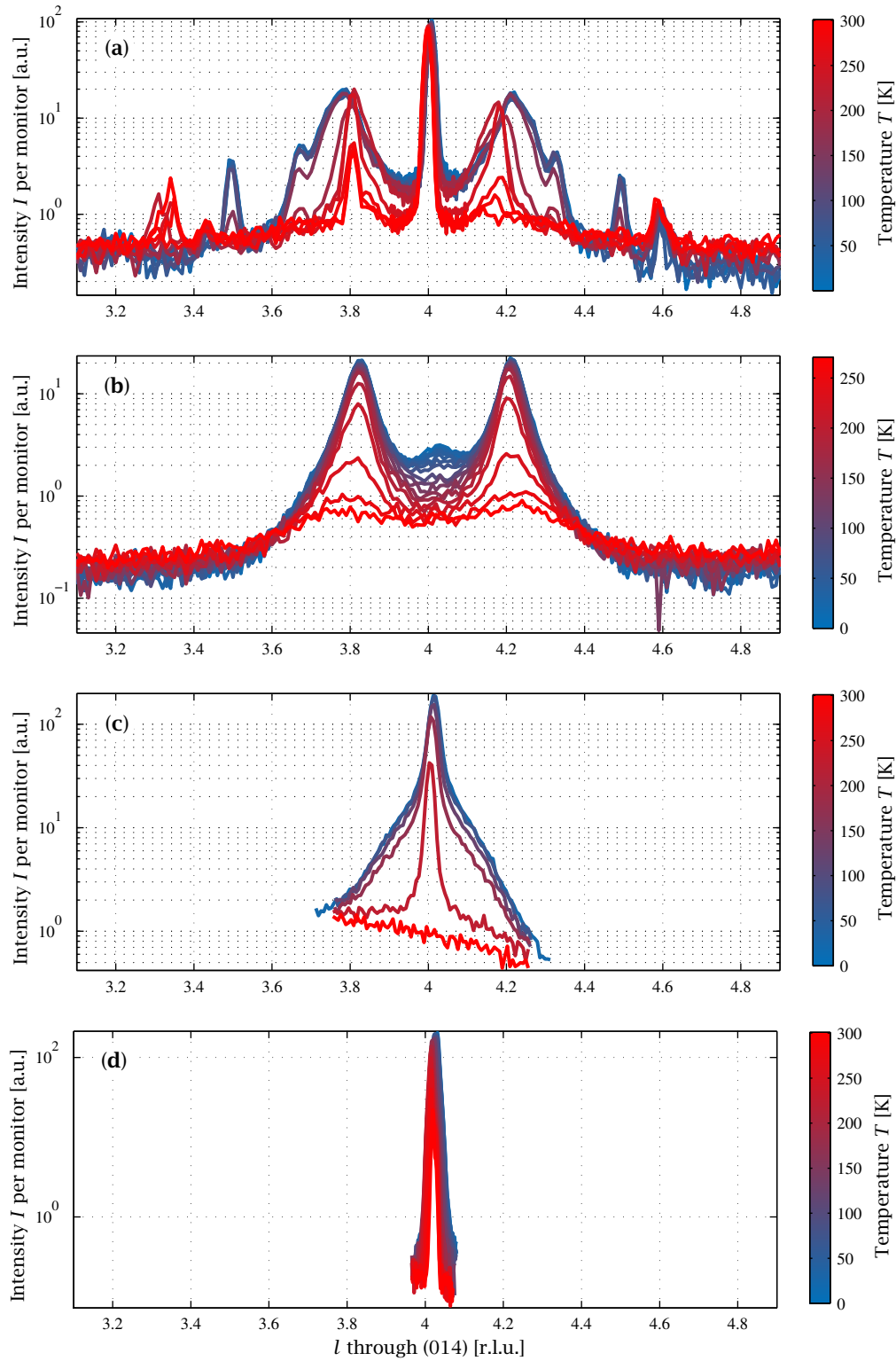


Figure D.15: As figure Fig. D.14, but with the intensity on a logarithmic scale. (a) $\text{La}_2\text{CuO}_{4+y}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$. Here the data are plotted such that the l axes are the same, to compare better – a more zoomed in version can be seen in Fig. 9.2 (p. 61).

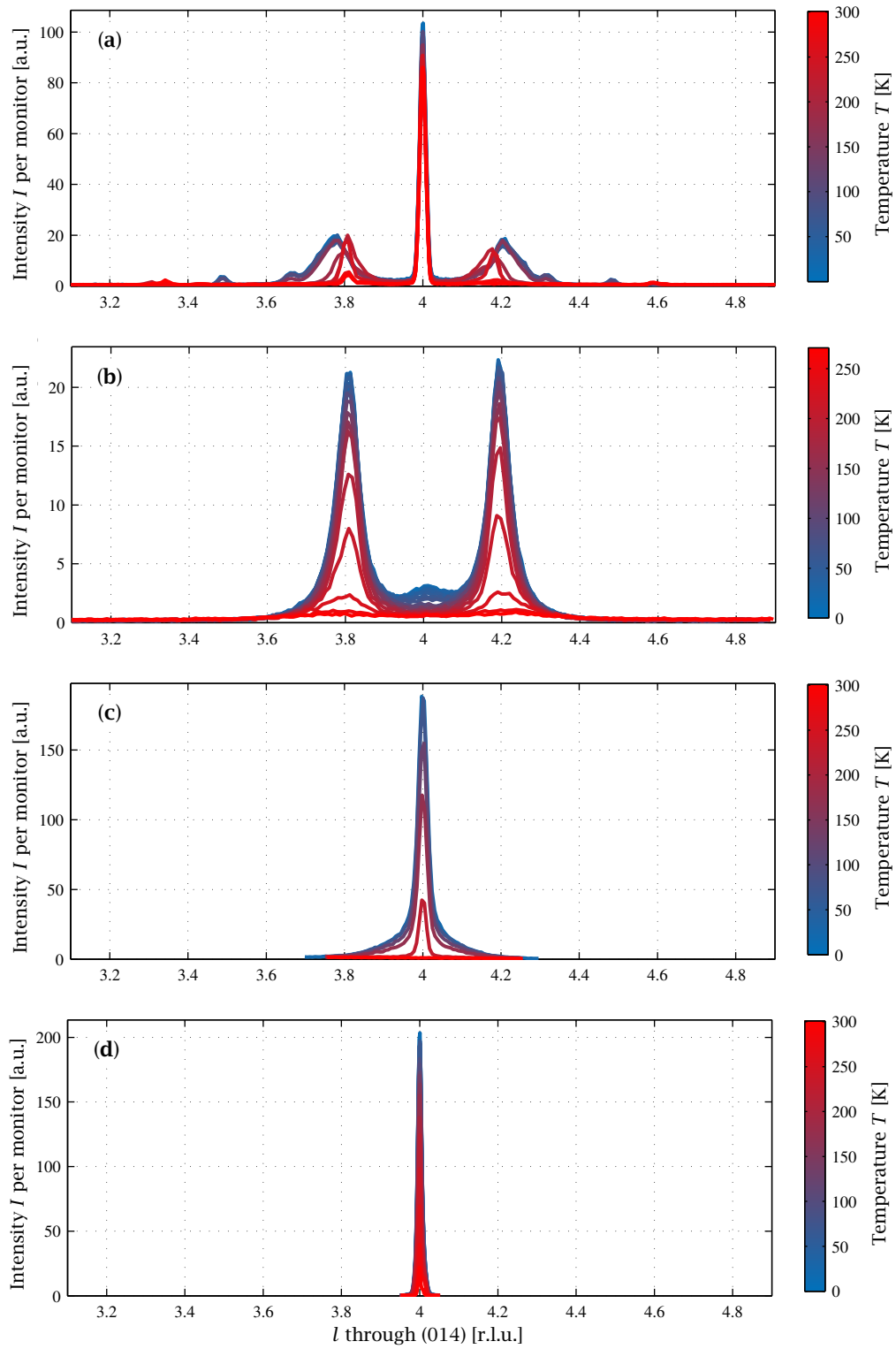


Figure D.16: Measurement on the (a) $\text{La}_2\text{CuO}_{4+\gamma}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$ crystals along l over the (014) peak on BW5 after correction of the first-axis. Here the data are plotted such that the l axes are the same, to compare better – a more zoomed in version can be seen in Fig. 9.6 (p. 65).

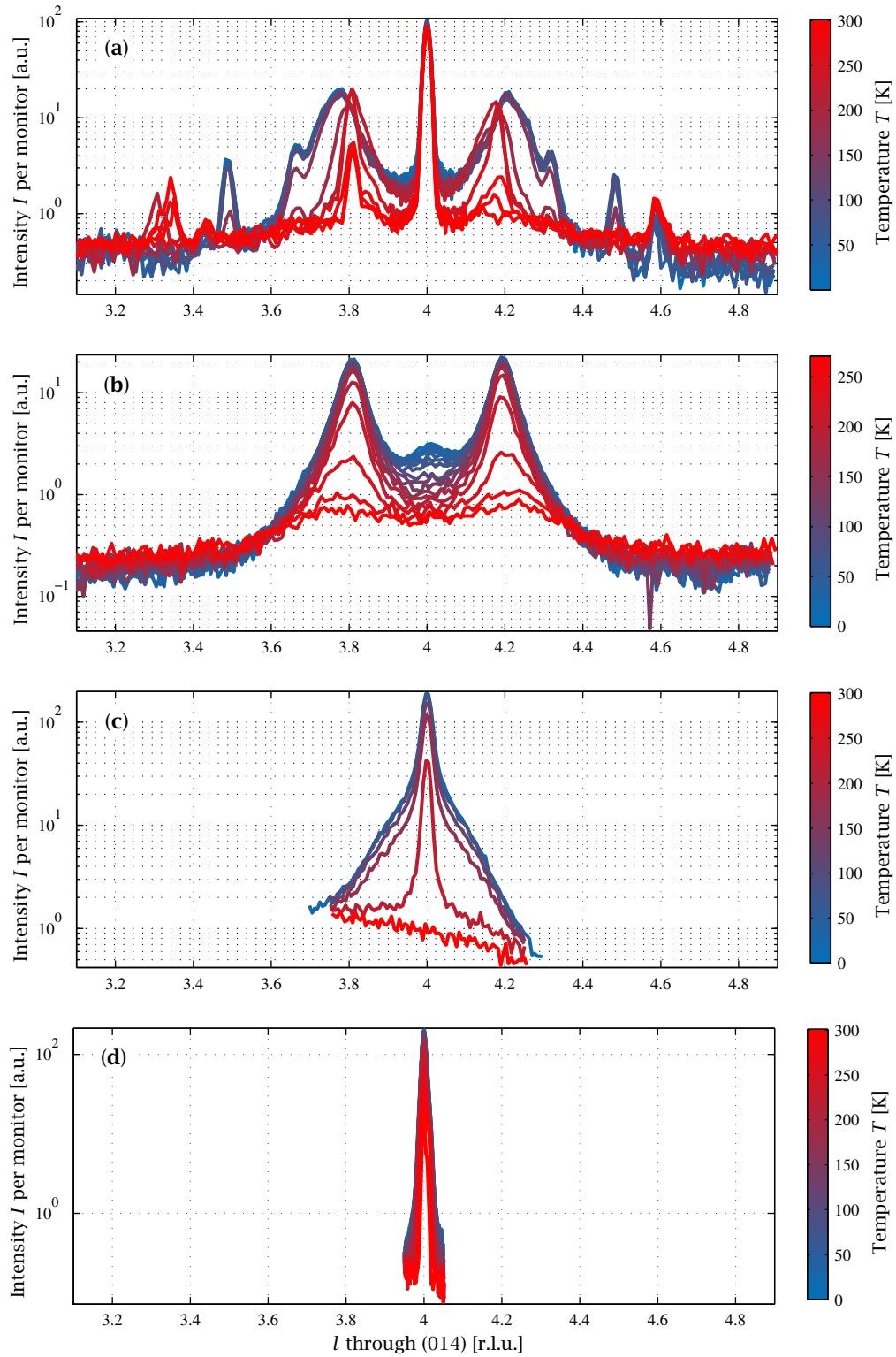


Figure D.17: As figure Fig. D.16, but with the intensity on a logarithmic scale. (a) $\text{La}_2\text{CuO}_{4+y}$, (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, (c) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and (d) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$. Here the data are plotted such that the l axes are the same, to compare better – a more zoomed in version can be seen in Fig. 9.7 (p. 66).

D.2 Extra BW5 data analysis figures

In Figs. D.18 to D.21 the central regions of the data is shown before and after the scaling of the l axis, to see the change in the data as clearly as possible. These figures were referred to in Subsect. 9.1.1.

In Fig. D.22, extra measurements over the (004) and (022) peaks for the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$, $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$, and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ samples are shown. These figures were referred to in Subsect. 9.3.1.

In Fig. D.23, the slope analysis of integrated intensities not shown in Figs. 9.27 and 9.28 (p. 84) are shown. This figure was referred to in Subsect. 9.3.2.

In Fig. D.24 the fitted points, along with the fitted curve, from Fig. 9.29 (p. 86) are shown individually in double logarithmic plots, to give an overview of the validity of the fits.

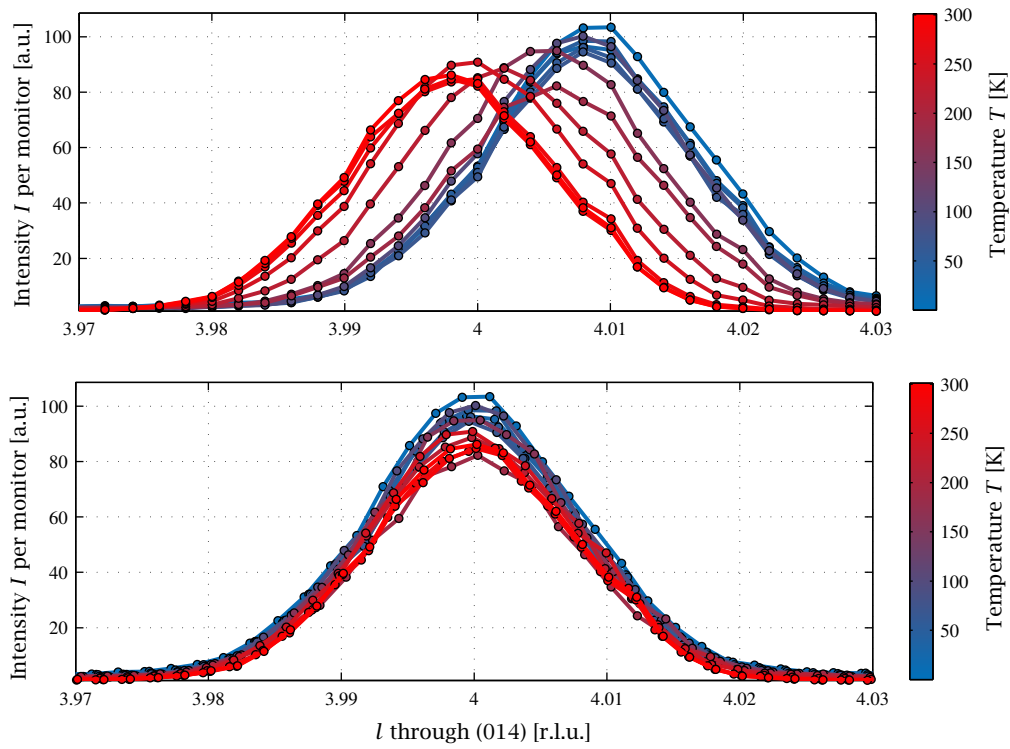


Figure D.18: Measurement on the $\text{La}_2\text{CuO}_{4+y}$ crystal along l over the (014) peak on BW5 (**top**) before and (**bottom**) after correction of the first-axis.

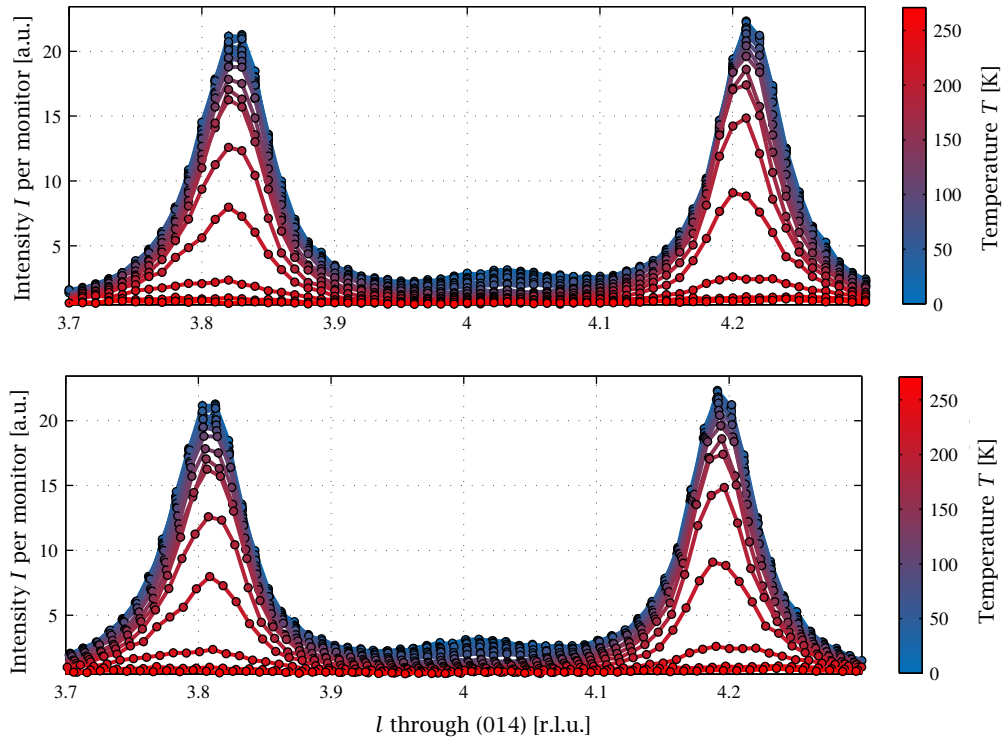


Figure D.19: Measurement on the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ crystal along l over the (014) peak on BW5 (**top**) before and (**bottom**) after correction of the first-axis.

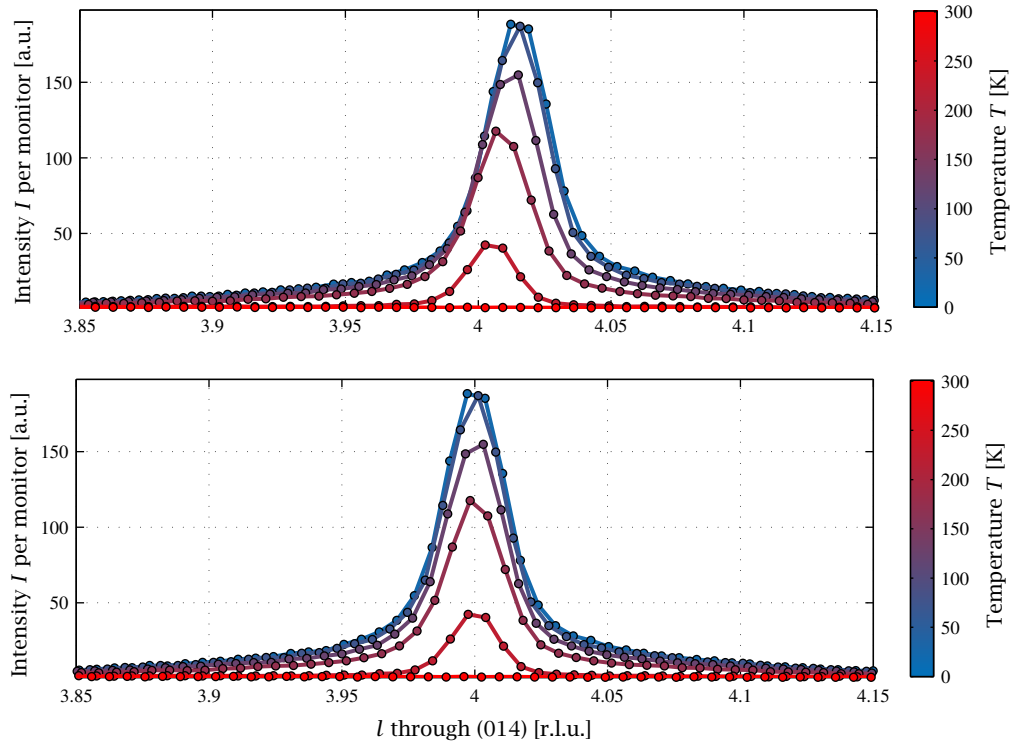


Figure D.20: Measurement on the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ crystal along l over the (014) peak on BW5 (**top**) before and (**bottom**) after correction of the first-axis.

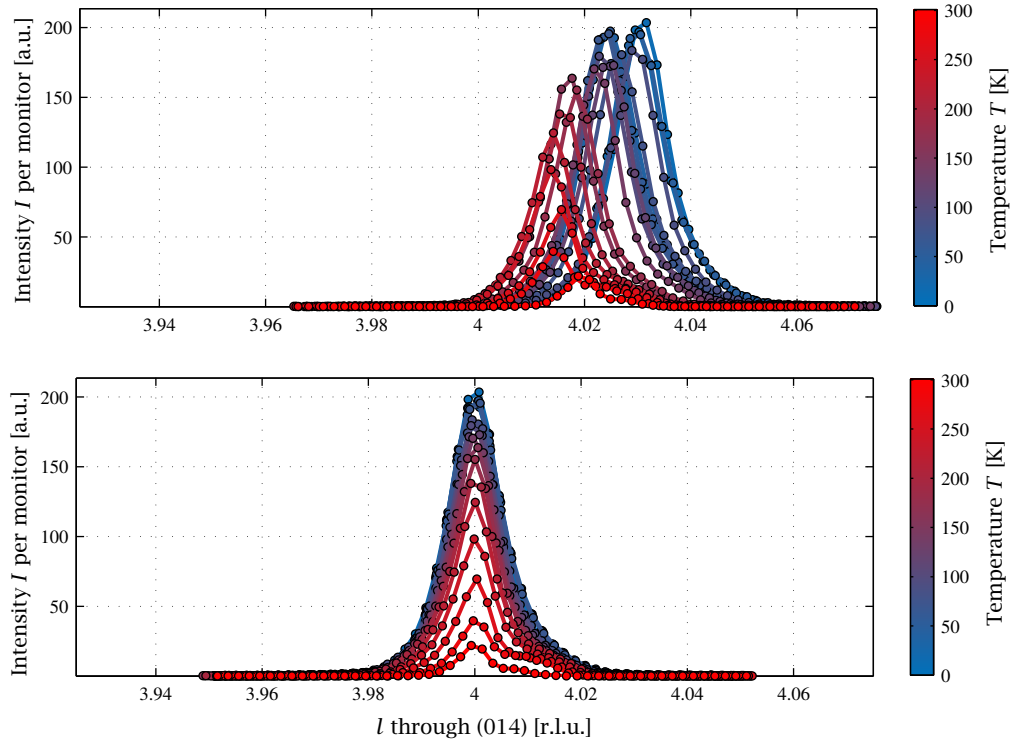


Figure D.21: Measurement on the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ crystal along l over the (014) peak on BW5 (**top**) before and (**bottom**) after correction of the first-axis.

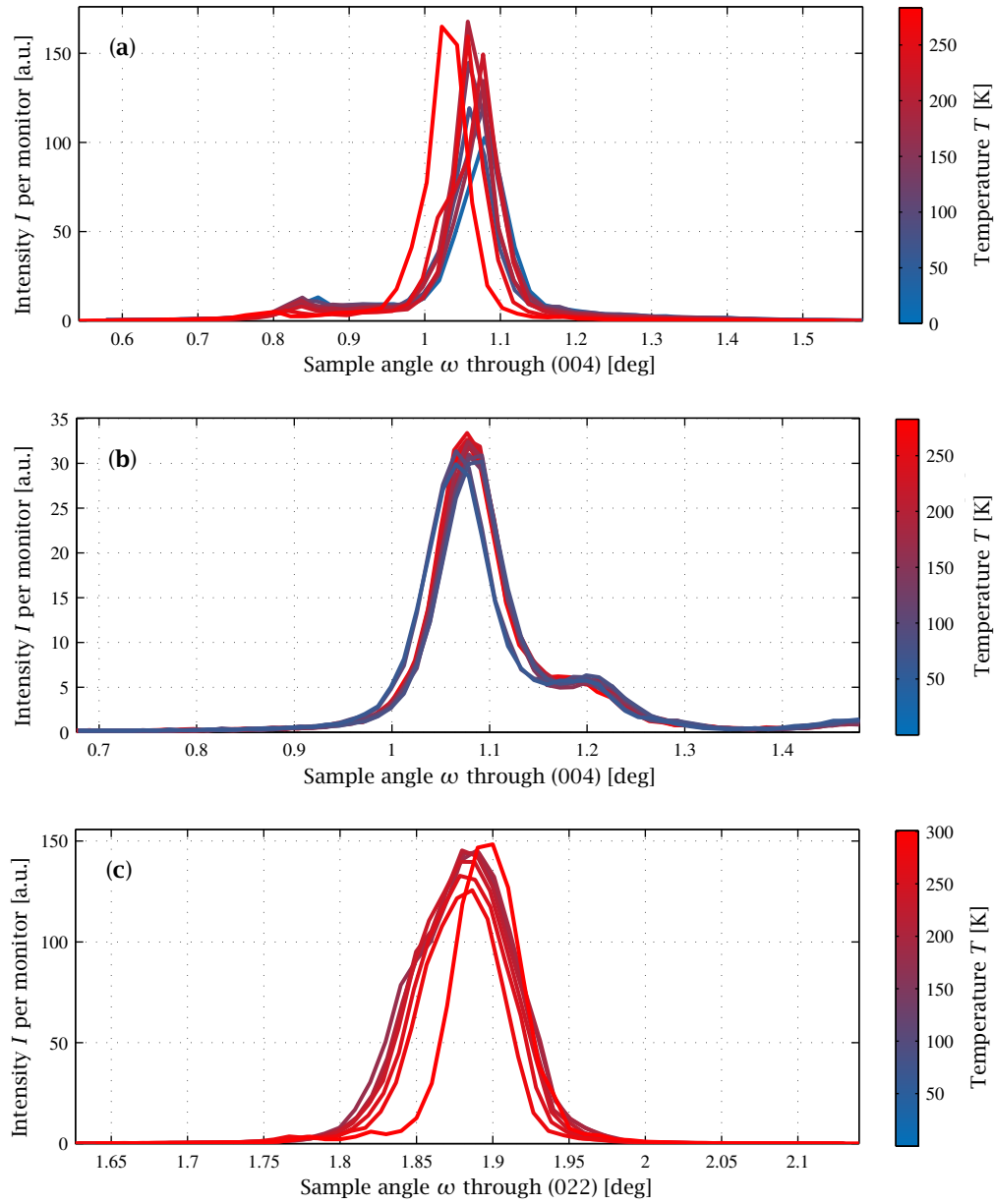


Figure D.22: Measurement of ω over a peak on BW5. (a) The $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ (004) peak, (b) the $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ (004) peak, and (c) the $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ (022) peak.

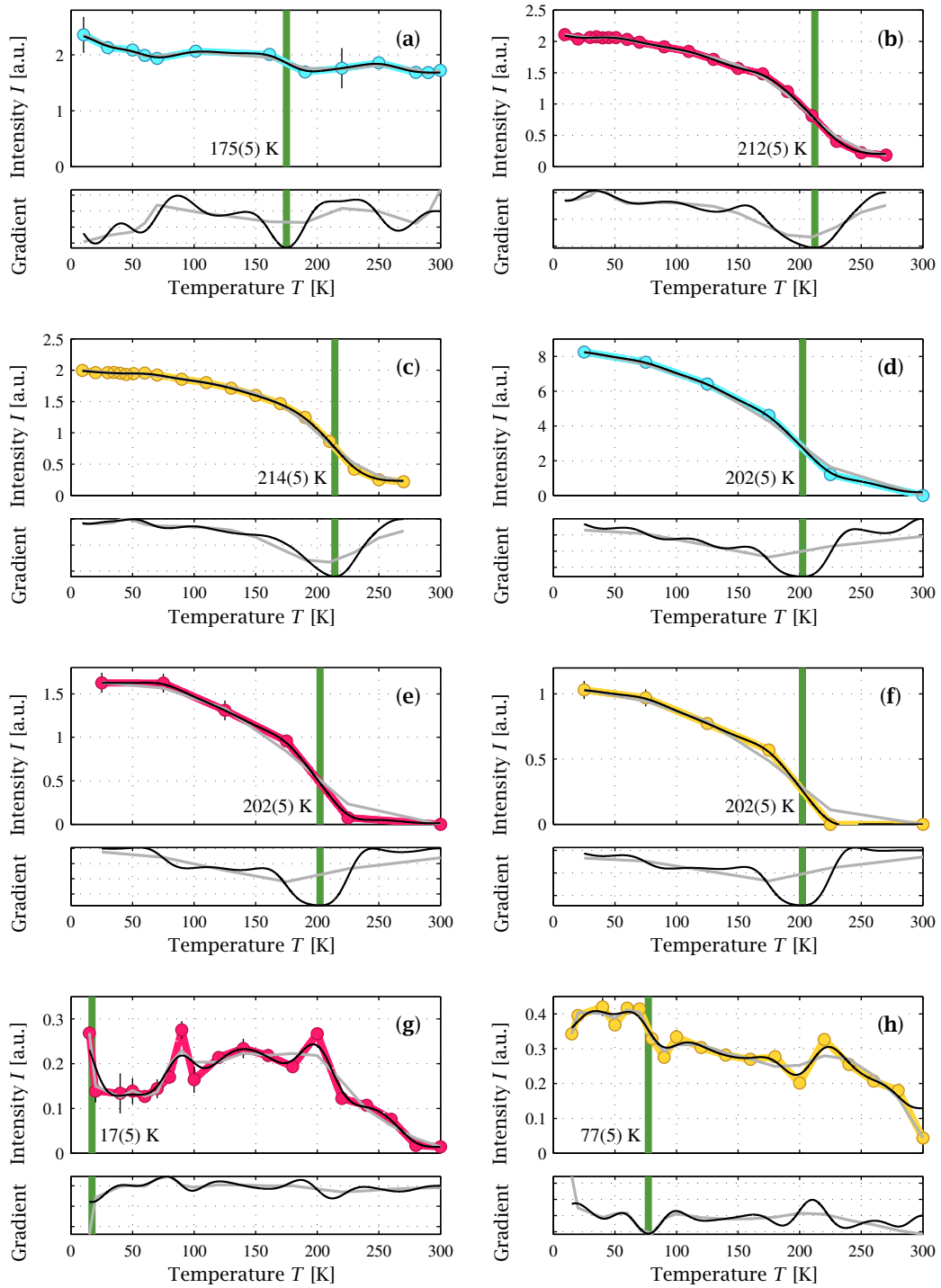


Figure D.23: Additional slope analysis done on the integrated intensities for the following peaks: (a) $\text{La}_2\text{CuO}_{4+y}$ central $Bmab$ peak (does not show a phase transition). (b) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ low l staging peak. (c) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+y}$ high l staging peak. (d) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ central $Bmab$ peak. (e) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ low l staging peak. (f) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+y}$ high l staging peak. (g) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ low l staging peak (result should probably be around room temperature, if analysing by eye). (h) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ high l staging peak (around room temperature as for the low l). The integrated intensity points are plotted directly, while the linearly interpolated points are shown as a colored line underneath these. A smoothing filter has been applied to both the actual data (grey) and the interpolated data (black), resulting in the gradients shown in the bottom parts of each plot. The gradient minimum for the smoothed data is marked with a green line. This is in addition to the graphs in Figs. 9.27 and 9.28 (p. 84).

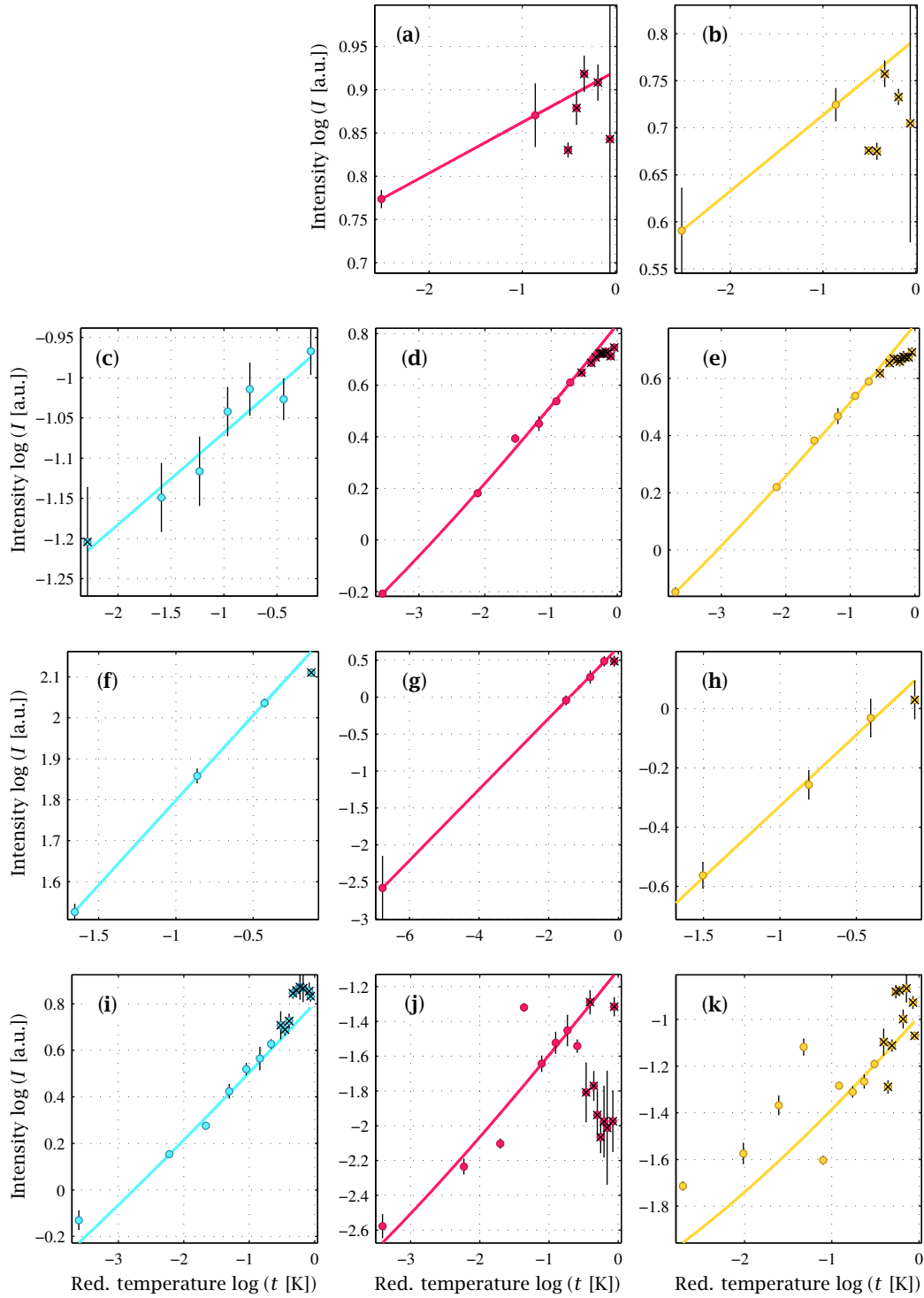


Figure D.24: Double logarithmic plots of the integrated intensities versus the reduced temperature $t = (T_c - T)/T_c$ for temperature points below the found critical temperature T_c from the individual fits shown in Fig. 9.29 (p. 86) (the shown lines are the fitted curves from this figure as well). Blue points are for the central B_{mab} peak while red and yellow points are the low and high l staging peaks, respectively, for (a-b) $\text{La}_2\text{CuO}_{4+\gamma}$, (c-e) $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_{4+\gamma}$, (f-h) $\text{La}_{1.935}\text{Sr}_{0.065}\text{CuO}_{4+\gamma}$, and (i-k) $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+\gamma}$. Crossmarks indicate points that were not used for the fit. Note how saturation causes the points at high t to fall below the fitted line, as expected – with exception of (i), where there are signs of a second phase transition.



Additional reciprocal space figures

E.1 All DMC maps

As explained in Chap. 8, measurements were done on the DMC instrument for four different samples, $\text{La}_2\text{CuO}_{4+y}$, $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$, and $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ (see Tab. 8.1 on p. 56 for an overview of the experiments). In this appendix I show all of these data. They are as follows:

- For $\text{La}_2\text{CuO}_{4+y}$
 - $(0kl)$ plane at $T = 10, 100$, and 300 K in Figs. E.1 to E.3
 - $(hk0)$ plane at $T = 10$ and 300 K in Figs. E.4 and E.5
 - $(0kl)$ plane for different sample with same doping at $T = 5$ K in Fig. E.6
- For $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$
 - $(0kl)$ plane with temperature between $T = 100$ and 1.5 K (cooling during measurement) and at $T = 100$ and 300 K in Figs. E.7 to E.9
 - $(hk0)$ plane at $T = 2$ and 300 K in Figs. E.10 and E.11
- For $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$
 - $(0kl)$ plane at $T = 100$ and 300 K in Figs. E.12 and E.13
 - $(hk0)$ plane at $T = 100$ K in Fig. E.14

All the data have been symmetrized to make it easier to look at the reciprocal space patterns. The actual non-symmetrized data are shown in small insets of each figure. The process of going from measured 2θ spectra to the reciprocal space planes has been explained in Chap. 10.

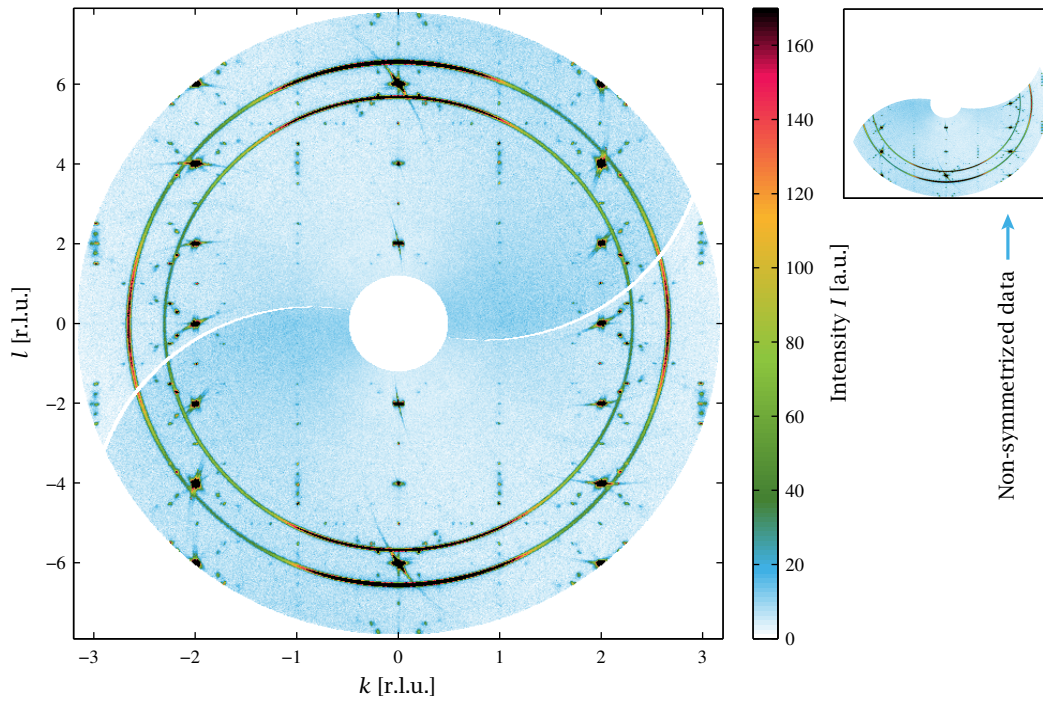


Figure E.1: Reciprocal kl plane for $\text{La}_2\text{CuO}_{4+y}$ at $T = 10$ K with lattice constants $b = 5.3567$ Å and $c = 13.1953$ Å. Data taken during November 2012. Measurement time was ~ 10 hr and 10 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 20. Measurements were done at angles $\omega \in [70.1^\circ; 249.9^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$), and $\omega \in [70.0^\circ; 249.8^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.1^\circ$). The last of the two sample angles was stopped early, and hence the full space is not filled – as opposed to in all of the the following plots.

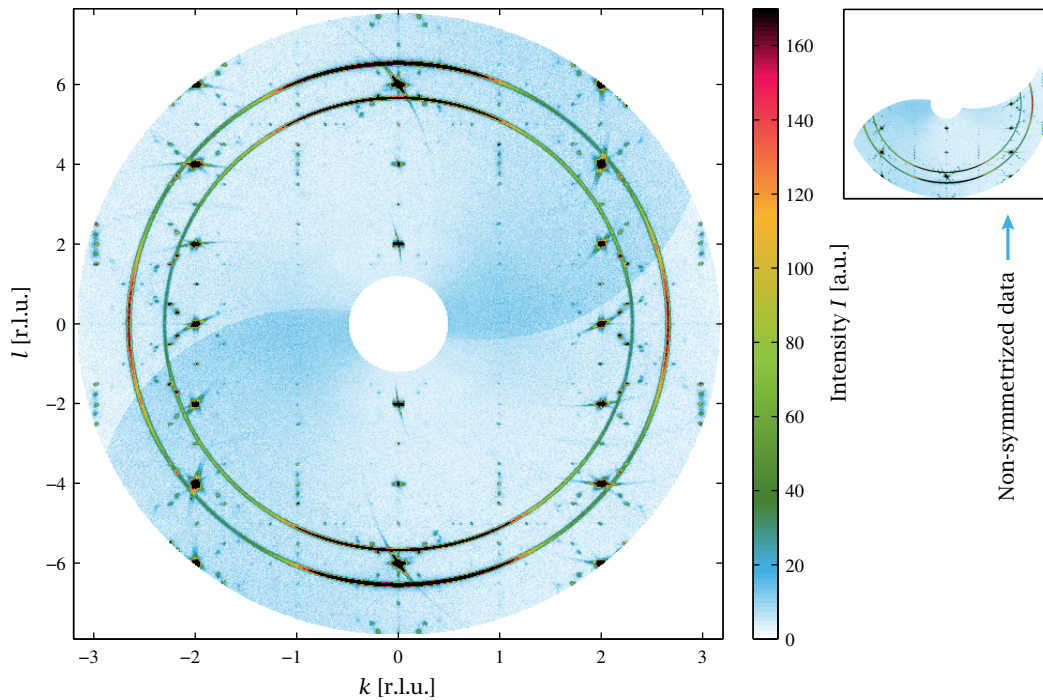


Figure E.2: Reciprocal kl plane for $\text{La}_2\text{CuO}_{4+y}$ at $T = 100$ K with lattice constants $b = 5.358$ Å and $c = 13.1997$ Å. Data taken during November 2012. Measurement time was ~ 10 hr and 50 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 20. Measurements were done at angles $\omega \in [70.1^\circ; 249.9^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$).

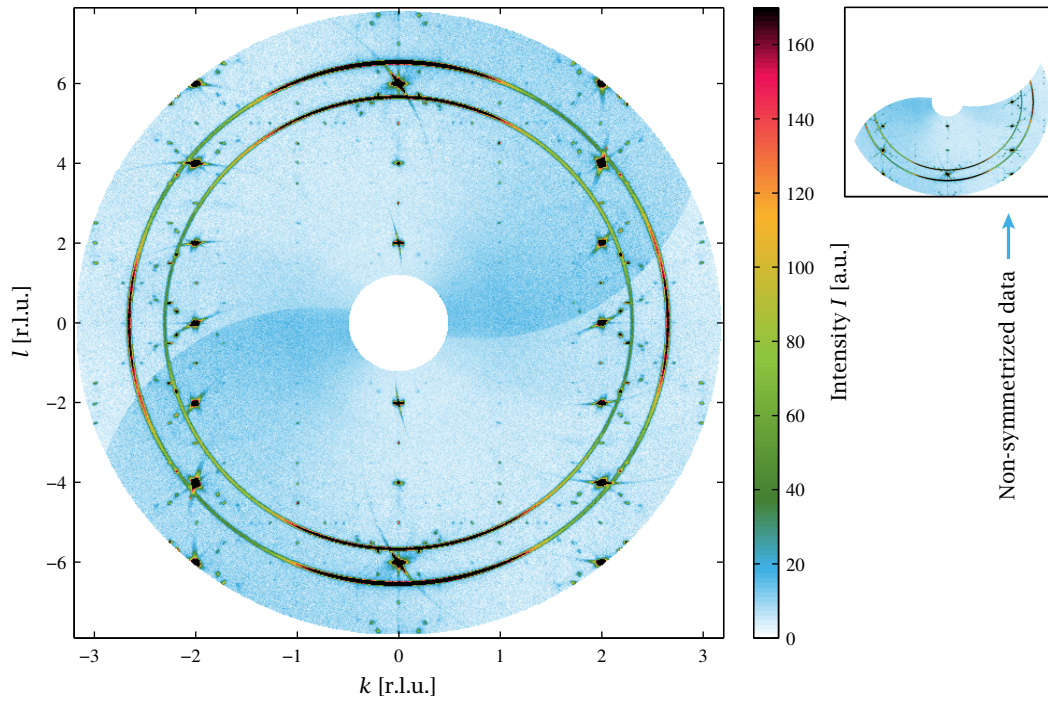


Figure E.3: Reciprocal kl plane for $\text{La}_2\text{CuO}_{4+y}$ at $T = 300$ K with lattice constants $b = 5.3771$ Å and $c = 13.2352$ Å. Data taken during November 2012. Measurement time was ~ 12 hr and 50 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 20. Measurements were done at angles $\omega \in [70.1^\circ; 249.9^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$).

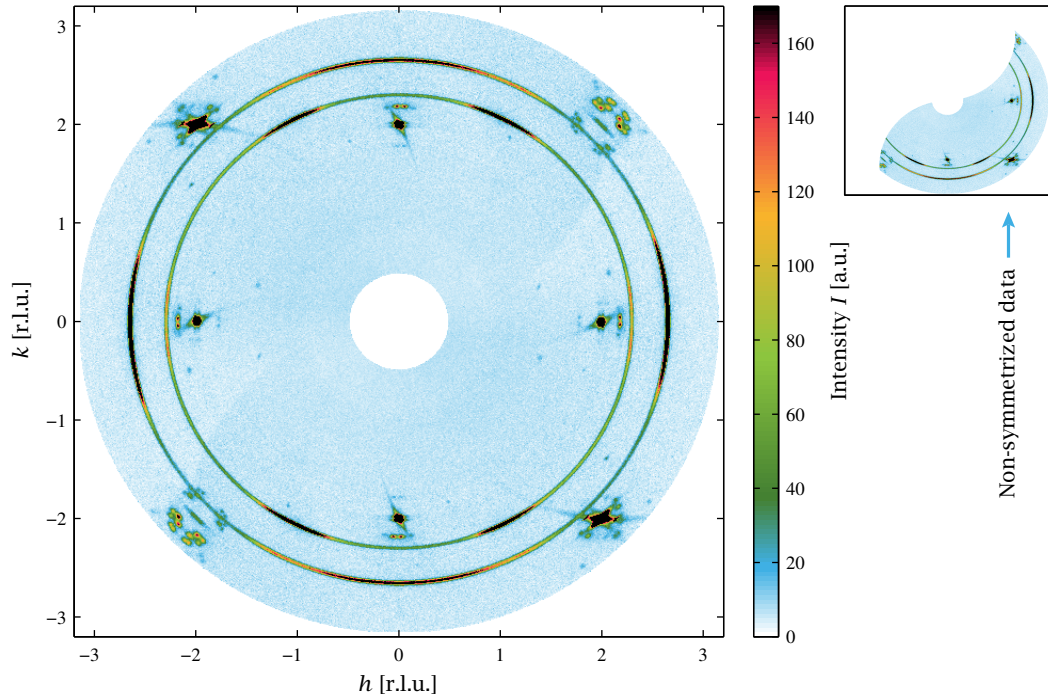


Figure E.4: Reciprocal hk plane for $\text{La}_2\text{CuO}_{4+y}$ at $T = 10$ K with lattice constants $a = 5.3417$ Å and $b = 5.3442$ Å. Data taken during November 2012. Measurement time was ~ 9 hr and 30 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 20. Measurements were done at angles $\omega \in [90.0^\circ; 270^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$).

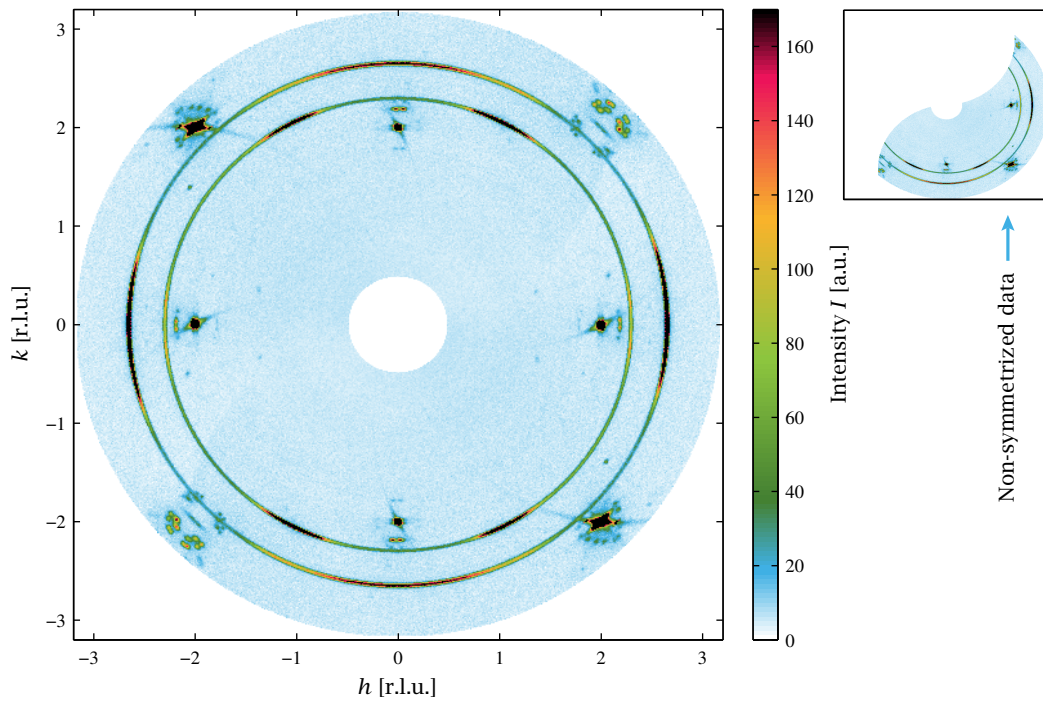


Figure E.5: Reciprocal hk plane for $\text{La}_2\text{CuO}_{4+y}$ at $T = 300$ K with lattice constants $a = 5.3678$ Å and $b = 5.3682$ Å. Data taken during November 2012. Measurement time was ~ 9 hr, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 20. Measurements were done at angles $\omega \in [90.0^\circ; 270^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$).

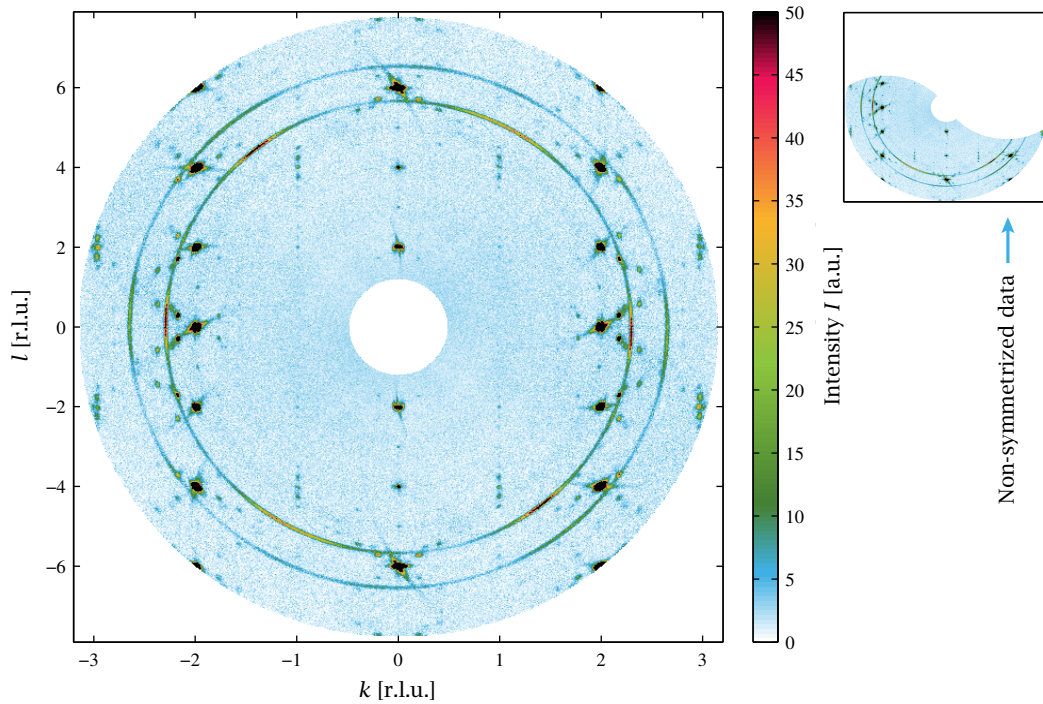


Figure E.6: Reciprocal kl plane for $\text{La}_2\text{CuO}_{4+y}$ (other sample) at $T = 5$ K with lattice constants $b = 5.3107$ Å and $c = 13.1171$ Å. Data taken during July 2013. Measurement time was ~ 22 hr and 8 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 1.0. Measurements were done at angles $\omega \in [0^\circ; 180^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13^\circ$). I am unsure about sample rotations, since it was not written in a logbook.

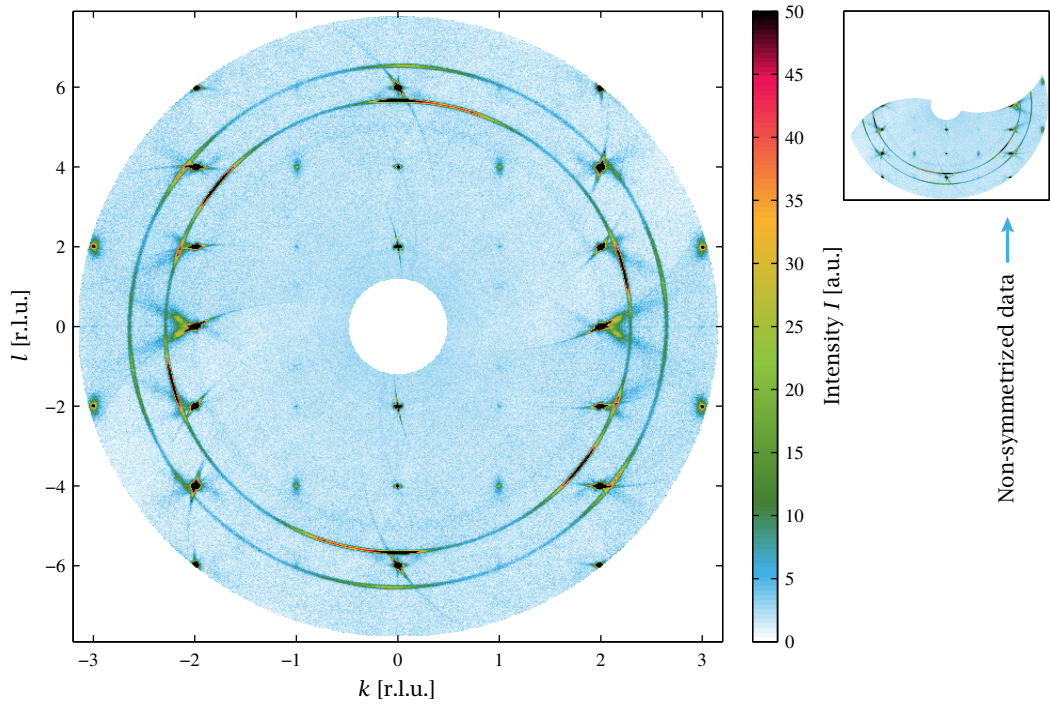


Figure E.7: Reciprocal kl plane for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$ at $T = 1.5\text{-}100$ K with lattice constants $b = 5.3171$ Å and $c = 13.1268$ Å. Data taken during July 2013. Measurement time was ~ 12 hr and 50 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 1.0. Measurements were done at angles $\omega \in [180.0^\circ; 360.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$), and $\omega \in [180.1^\circ; 360.0^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.1^\circ$). I am unsure about sample rotations, since it was not written in a logbook.

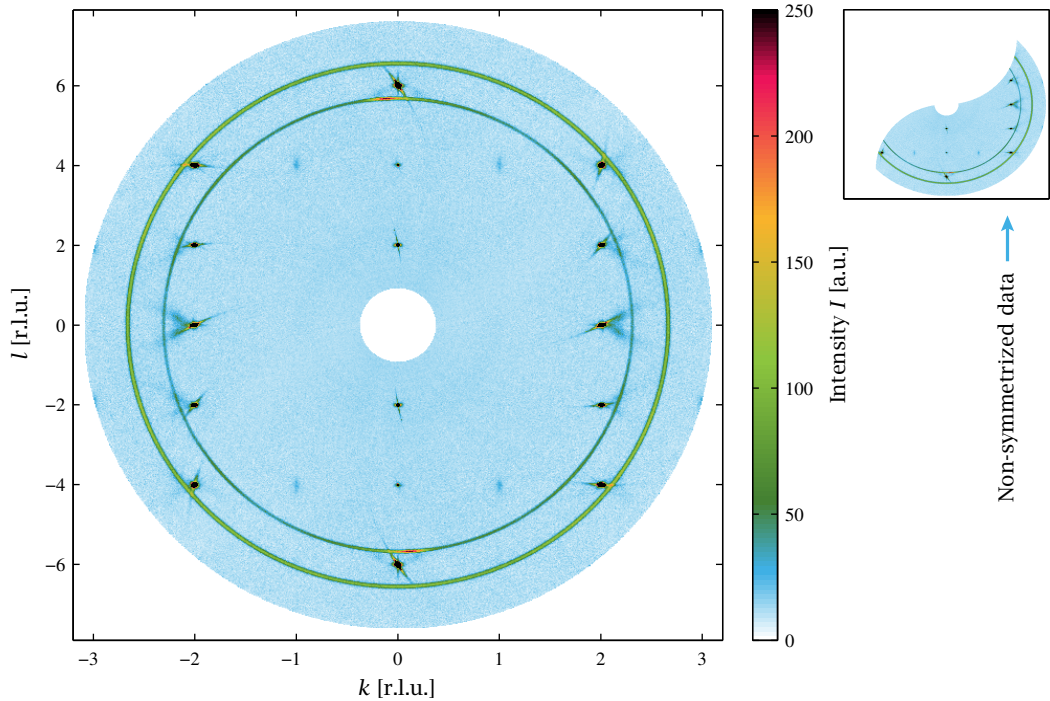


Figure E.8: Reciprocal kl plane for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$ at $T = 100$ K with lattice constants $b = 5.3413$ Å and $c = 13.1533$ Å. Data taken during November 2013. Measurement time was ~ 9 hr and 20 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 0.79 (1.58 initially). Measurements were done at angles $\omega \in [90.0^\circ; 270.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 10.0^\circ$), and $\omega \in [90.1^\circ; 270.2^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 10.1^\circ$). Statistics was lowered from 1.58 to 0.79 part way through.

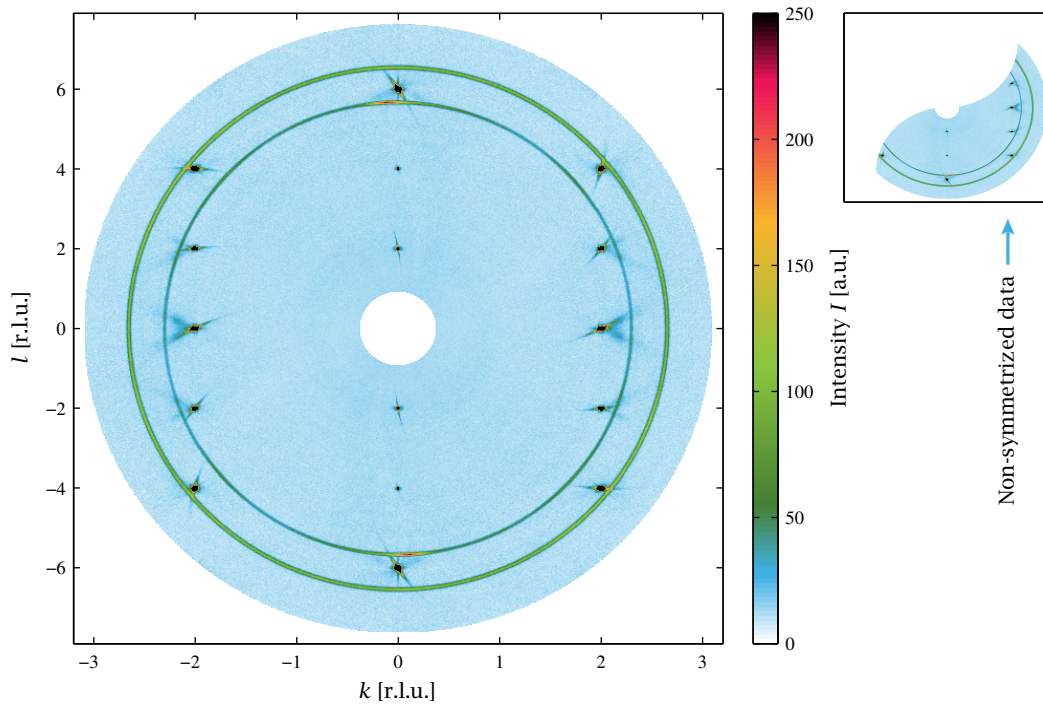


Figure E.9: Reciprocal kl plane for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$ at $T = 300$ K with lattice constants $b = 5.3501$ Å and $c = 13.1889$ Å. Data taken during November 2013. Measurement time was ~ 16 hr and 55 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 1.58. Measurements were done at angles $\omega \in [90.0^\circ; 270.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 10.0^\circ$), and $\omega \in [90.1^\circ; 270.2^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 10.1^\circ$).

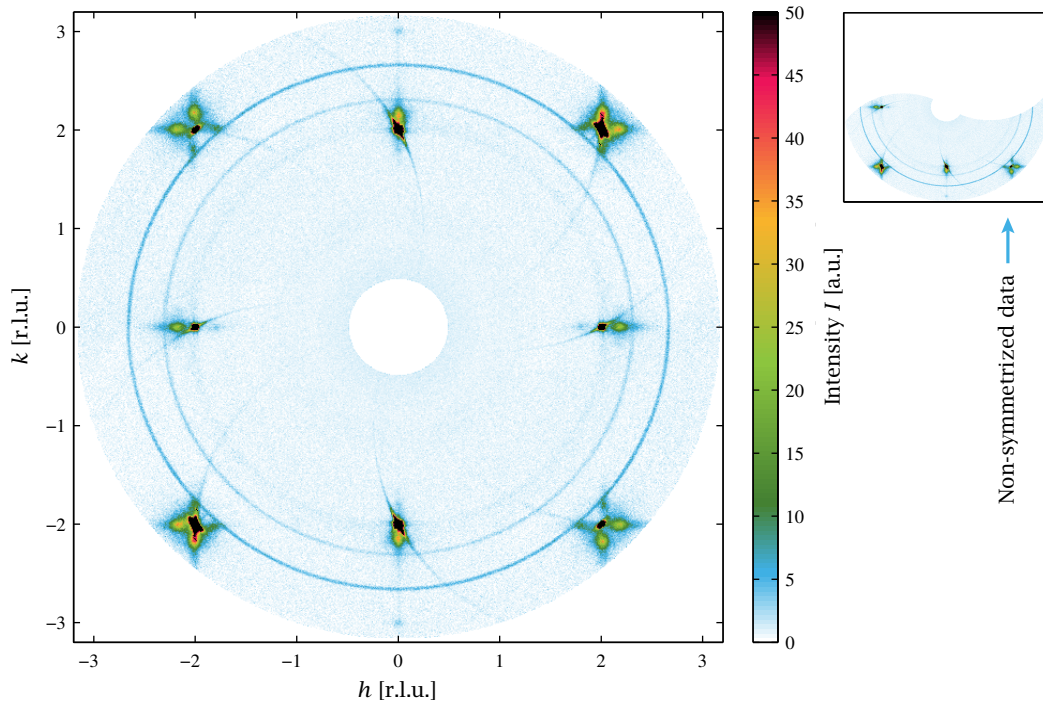


Figure E.10: Reciprocal hk plane for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$ at $T = 2$ K with lattice constants $a = 5.3349$ Å and $b = 5.3291$ Å. Data taken during July 2013. Measurement time was ~ 11 hr and 50 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 1.12. Measurements were done at angles $\omega \in [180.0^\circ; 360.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$), and $\omega \in [180.1^\circ; 360.0^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.1^\circ$).

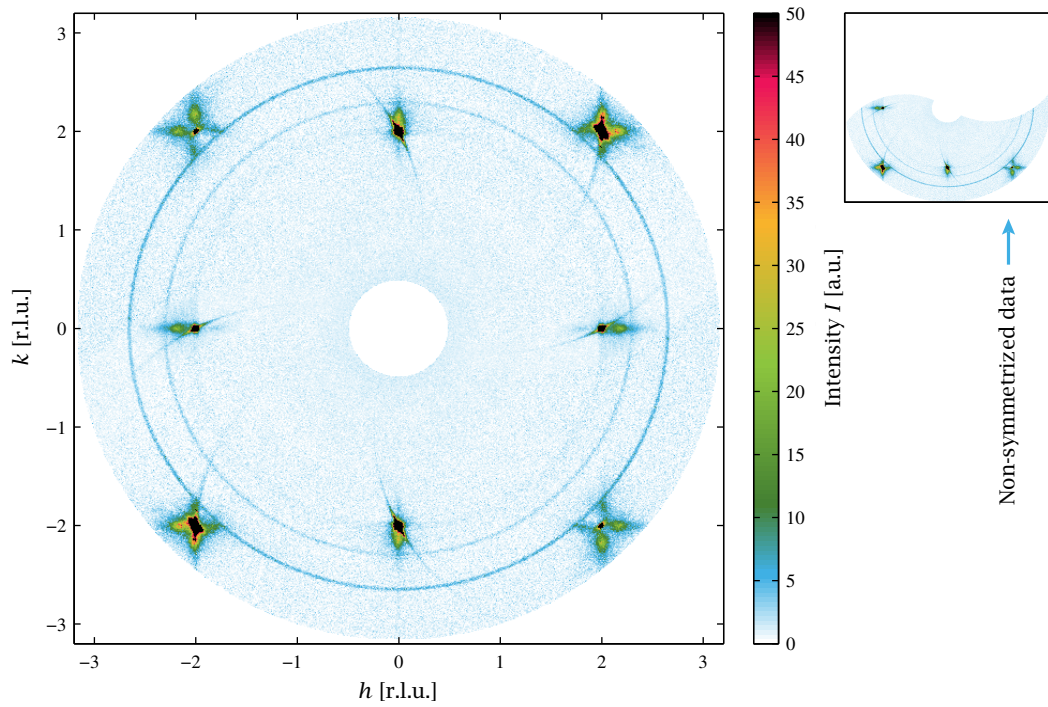


Figure E.11: Reciprocal hk plane for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_{4+y}$ at $T = 300$ K with lattice constants $a = 5.3413$ Å and $b = 5.3361$ Å. Data taken during July 2013. Measurement time was ~ 7 hr and 30 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 1.12. Measurements were done at angles $\omega \in [180.0^\circ; 360.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$), and $\omega \in [180.1^\circ; 360.0^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.1^\circ$). Stopped quite shortly into the second scan part with the detector moved 0.1° .

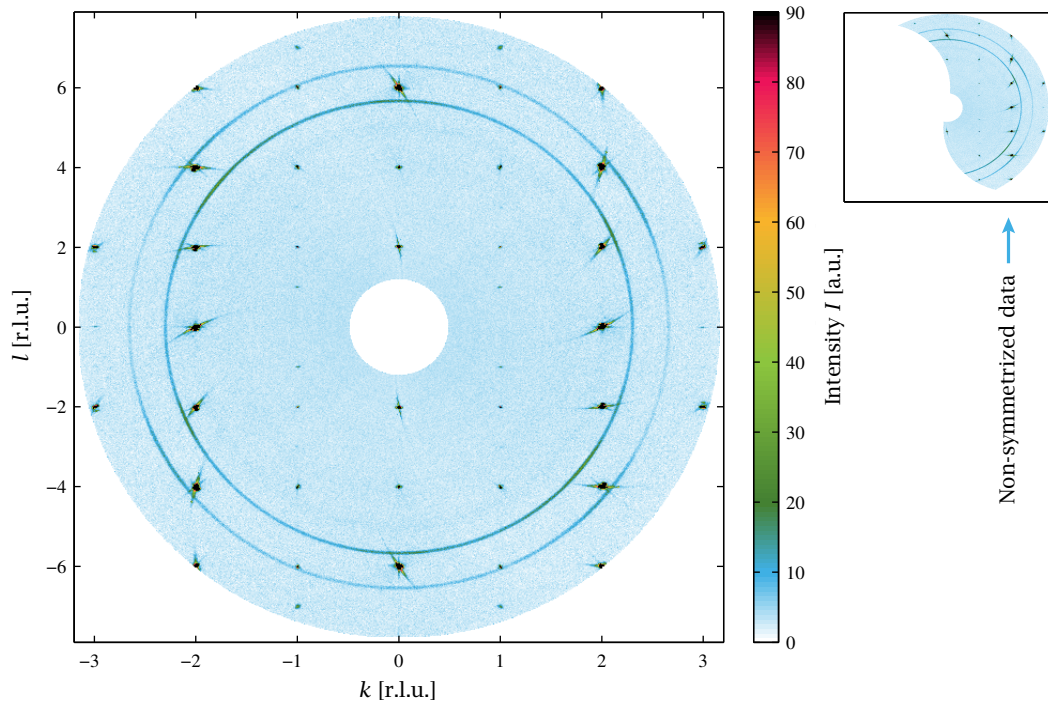


Figure E.12: Reciprocal kl plane for $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ at $T = 100$ K with lattice constants $b = 5.3288$ Å and $c = 13.138$ Å. Data taken during November 2013. Measurement time was ~ 33 hr and 15 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 0.79. Measurements were done at angles $\omega \in [90.0^\circ; 270.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$), and $\omega \in [90.1^\circ; 270.2^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.1^\circ$). The time is longer than usual because the neutron beam was down for part of it.

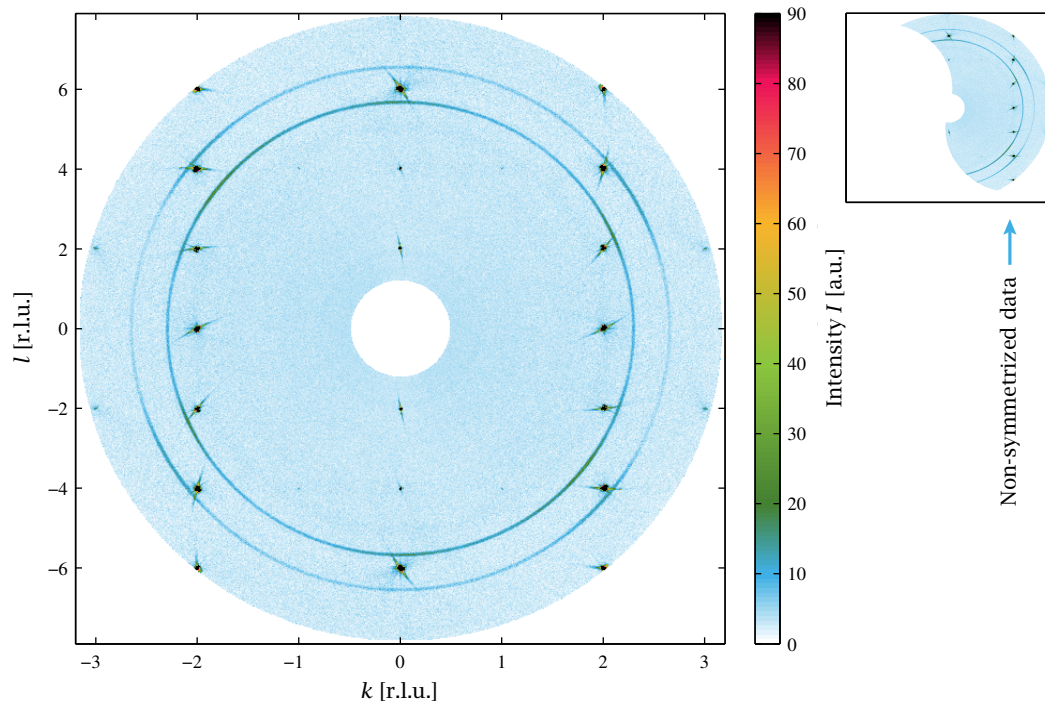


Figure E.13: Reciprocal kl plane for $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ at $T = 300$ K with lattice constants $b = 5.3322$ Å and $c = 13.183$ Å. Data taken during November 2013. Measurement time was ~ 38 hr and 47 min, the instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 0.79. Measurements were done at angles $\omega \in [90.0^\circ; 270.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$), and $\omega \in [90.1^\circ; 270.2^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.1^\circ$).

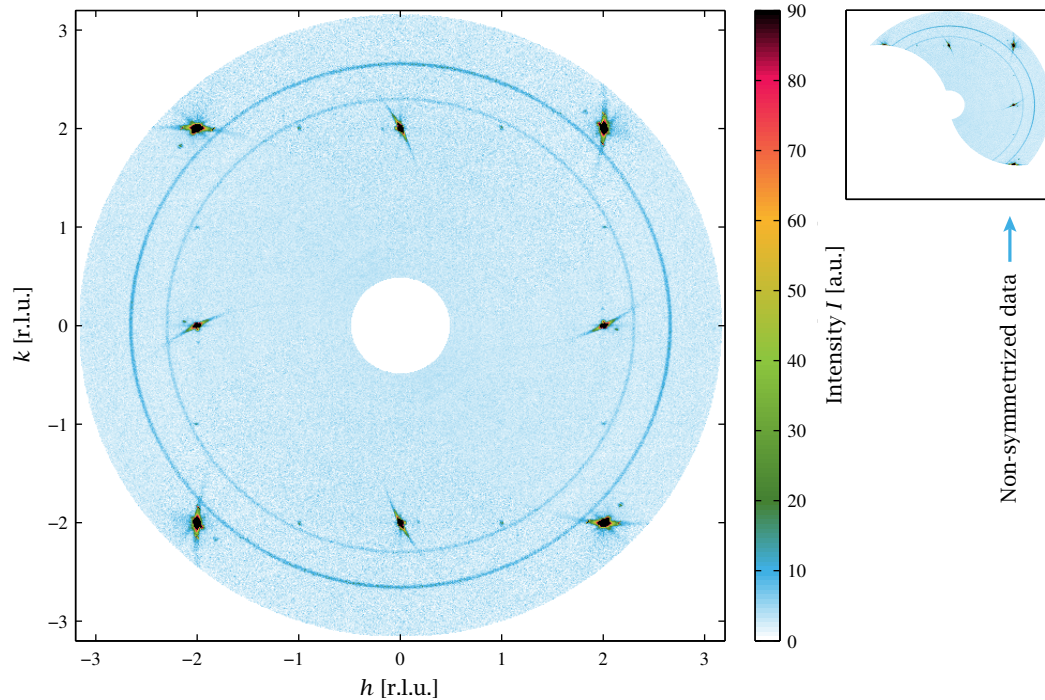


Figure E.14: Reciprocal hk plane for $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{4+y}$ at $T = 100$ K with lattice constants $a = 5.3375$ Å and $b = 5.3264$ Å. Data taken during November 2013. The instrument wavelength was $\lambda = 2.45$ Å, and the monitor preset was 0.79. Measurements were done at angles $\omega \in [90.0^\circ; 270.1^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.0^\circ$), and $\omega \in [90.1^\circ; 270.2^\circ]$, $\Delta\omega = 0.2^\circ$ (detector at $2\theta = 13.1^\circ$).

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