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# X-RAY DIFFRACTION

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# Contents

The	ory	<b>5</b>
2.1	X-ray Sources	5
2.2	Detecting X-rays	7
2.3	Crystal Structures and Notation	7
	2.3.1 Space groups	7
	2.3.2 Bravais Lattices	8
	2.3.3 Crystallographic point groups	9
	2.3.4 Miller Indices	9
2.4	Diffraction	10
	2.4.1 Bragg Formulation	10
	2.4.2 Laue Formulation	11
	2.4.3 Structure Factor and Cancellation	11
2.5	Powder Diffraction	13
2.6	Form factor	13
2.7	Phases of matter	15
2.8	Thermal Expansion	15
	2.8.1 Order parameter	15
$\mathbf{Exp}$	erimental Task	16
3.1	Description of the Experimental Setup	16
3.2	Safety	16
3.3	System startup	18
3.4	System shut down	19
3.5	Sample preparation	20
3.6	Heating Stage	22
	3.6.1 Installation $\ldots$	22
3.7	Pattern acquisition	22
3.8	Estimating the systematic error	23
3.9	Indexing of diffraction patterns	23
3.10	Data analysis	24
3.11	Experimental tasks	25
	The 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 Exp 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 3.10 3.11	Theory         2.1 X-ray Sources         2.2 Detecting X-rays         2.3 Crystal Structures and Notation         2.3.1 Space groups         2.3.2 Bravais Lattices         2.3.3 Crystallographic point groups         2.3.4 Miller Indices         2.4 Diffraction         2.4.1 Bragg Formulation         2.4.2 Laue Formulation         2.4.3 Structure Factor and Cancellation         2.4.3 Structure Factor and Cancellation         2.5 Powder Diffraction         2.6 Form factor         2.7 Phases of matter         2.8.1 Order parameter         2.8.1 Order parameter         2.8.1 Order parameter         3.2 System startup         3.3 System startup         3.4 System shut down         3.5 Sample preparation         3.61 Installation         3.7 Pattern acquisition         3.8 Estimating the systematic error         3.9 Indexing of diffraction patterns         3.10 Data analysis         3.11 Experimental tasks

		3.11.1	The lattice parameter of Silicon	25
		3.11.2	Structure factors: Diffraction Patterns of NaCl and KCl	27
		3.11.3	Single crystal vs. powder diffraction	28
		3.11.4	The Thermal Expansion of Copper	29
		3.11.5	"Melting" of Aluminium Potassium Sulfate dodecahydrate	30
		3.11.6	ASL: The piezoelectric transition in Barium Titanate	31
Α				33
	A.1	Table:	Bravais Lattices in Three Dimensions	33
	A.2	Table:	Visible Reflections for Cubic Lattices	34
	A.3	Table:	Distance between $hkl$ Planes	35
	A.4	Measu	rement Results of Silicon Standard Sample	35

# Chapter 1 Introduction

X-rays are electromagnetic waves with a photon energy  $E = h\nu$  in the range of 5 keV to 100 keV. They were discovered by W. C. Röntgen in 1895, who received the very first Nobel price for this finding. The energy of X-ray photon is more than 3 orders of magnitude higher than the photon energy of visible light and enables X-radiation to permeate materials that are opaque to visible light. Therefore X-rays are commonly used in medical diagnostics or to check the contents of luggage at airports.

The high energy of X-rays brings another advantage: Their wavelength  $\lambda = c \cdot h/E$  is in the range of 0.1 Å to 2 Å. This is in the range of interatomic distances and therefore atomic structures can be resolved using X-rays. As there are only few experimental techniques to access these length scales, X-ray diffration is an important tool to investigate crystal structures of materials with a high accuracy.

In this experiment you will characterize samples that you have prepared yourself. You will investigate the effect of exchanging two atomic species for one another in an otherwise identical crystal structure. In the second part you will compare the diffraction patterns of single crystals and powder samples. You will learn about the strengths and weaknesses of single crystal and powder diffractometry. In the third part you will use powder diffraction to study the structurural properties of thermodynamics phases up to 500 ŰC. This is possible thanks to the curring edge high-intensity powder diffractometer which can be fitted with a high-temperature chamber.

## Chapter 2

## Theory

Understanding the principle of X-ray diffraction and interpreting the results require a basic knowledge about crystal structures and diffraction. The following sections will introduce you to these topics. More detailed explanations and calculations can be found in the excellent book by Ashcroft and Mermin [4].

## 2.1 X-ray Sources

There are two different sources of high energy electromagnetic radiation: Emission of electron transitions with a high energy difference and bremsstrahlung of accelerated charged particles. Both effects occur in an X-ray tube, the most common X-ray source. Figure 2.1(a) shows the schematics of such a tube.



Figure 2.1: (a) Schematic of a water cooled X-ray tube. Electrons (blue) are emitted from the cathode C and accelerated by the acceleration voltage  $U_a$  towards the anode A. X-rays (green) are emitted from the watercooled anode. Image from [2]. (b) Emission intensities as function of wavelength of X-ray tubes with targets of molybdenum and copper, image from [1].

In the X-ray tube, electrons are emitted from a glow cathode K and accelerated by a

voltage  $U_a$  towards the anode A (also called *target*). When hitting the anode, they can eject electrons from the shells of the target material. When electrons from higher orbitals change to those free states at lower energy, a photon with an energy corresponding to the energy difference is released. This emission spectrum is characteristic for the target material. Additionally, the electrons are decelerated by Coulomb interaction in the anode material and emit a continuous bremsstrahlung. Figure 2.1(b) shows total emission spectra of X-ray tubes with continuous bremsstrahlung and peaks from electron transitions. For most applications, a source of radiation with one single frequency is desired. This can be achieved by using the correct filter material that absorbs the unwanted frequencies.

For copper X-ray tubes, usually a nickel filter is used, since it has a minimum of absorption at the  $Cu_{K\alpha}$  energy, but a significant higher absorption at higher energies. Thus  $Cu_{K\beta}$  and most of the continuous bremsstrahlung are efficiently suppressed. The labelling of the X-ray lines come from the name for the inner shell which the electron descended to in the transition. Shells start from K, which is the one nearest to the nucleus and go on alphabetically (K, L, M, etc.). In this case  $K_{\alpha}$  means the electron transitioned to the K shell. The Greek letter, which is found in the subscript, describes the difference in the principle quantum number from the outer most shell from which the electron originally came. In this case  $\alpha$  stands for a difference of 1, so the outer most shell was L,  $\beta$  is a difference of 2 with the outer shell being M and so on.



Figure 2.2: Schematic representation of the energy levels of an atom. One can see the differences between the shells (K, L, M, ...), which are indicated by the principle quantum number. The arrows signify the differences between the energy levels and the K shell.

If a higher X-ray intensity or a tunable frequency is required than it can be created with tubes, the bremsstrahlung from an accelerator ring can be used. The particles are held on their path by magnets to force them on a circular path. Due to this centripetal acceleration they emit bremsstrahlung. Since bremsstrahlung produces a continuous spectrum, a monochromator crystal is often placed before the sample to select a single frequency. An example of such a storage ring X-ray source is the *Swiss Light Source SLS* at Paul Scherrer Institute in Villigen AG. Due to the high costs of building and maintaining an acceleration ring, only few such X-ray sources exist.

## 2.2 Detecting X-rays

X-rays are electromagnetic waves, therefore the detection mechanisms are based on similar principles as detectors for optical photons. The most common detectors are

- photomultiplier
- semiconductor detectors
- scintillators

The first one, the photomultiplier, enables a quantitative measurement of the photon count, but it is restricted to the detection area of the counter. It aims to take a very weak signal, often only comprised of one photon, and make it into a detectable signal by knocking out more and more electrons in a chain reaction. To obtain spatial information of the X-ray intensity, the detector has to be moved in space. Reducing the detection area improves the spatial resolution of the detector, but lowers the number of counts per time and therefore increases the required measurement time.

The second detector type measures the electric current created by absorption of a photon in a semiconductor diode (same working principle as a solar cell). Having a chip with an array of such diodes results in a semiconductor detector with spatial resolution. Other advantages include for example time efficiency.

Both these detection principles are capable of measuring both X-ray photons and optical photons. Therefore the detection rate can be increased by adding a photoluminescent material between the X-rays and the detector. Such a material that converts an X-ray photon to multiple low-energy photons is called a scintillator and increases the sensitivity of the detector.

## 2.3 Crystal Structures and Notation

The following sections explain how to describe the microscopic structure of an atomic lattice and its orientation in the environment. A material which has an infinite periodic arrangement of atoms is called a crystal. Of course this is not true for "real life" structures, but for most practical purposes one can treats all ordered structures, as if they were infinitely periodic.

#### 2.3.1 Space groups

A space group is a symmetry group of a configuration in space. In three dimensions there are 230 distinct space groups. They are made up from 32 crystallographic point groups with the 14 Bravais lattices. This results in a space group being some combination of the translational symmetry of a unit cell including lattice centering, the point group symmetry operations and the screw axis and glide plane symmetry operations. The combination of

all these symmetry operations results in a total of 230 different space groups describing all the possible crystal symmetries.

#### 2.3.2 Bravais Lattices

The microscopic structure of most solid materials is a periodic arrangement of atoms. The size of the regions with strict periodicity can vary from micrometers to the size of the entire crystal. For the following discussion a perfect translational periodicity without crystal defects is assumed. Based on their translational symmetries and centering crystal structures can be classified into 14 Bravais lattices. The centering defines the locations of the atoms in the unit cell as follows:

- P primitive: Atoms are located at the cell corners only (this is sometimes called simple centering).
- I body centered (from the German Innenzentriert): Atoms are positioned at the cell corners, with one additional point at the center of the unit cell.
- F face centered (from the German Flächenzentriert): Atoms are located at the cell corners and at one additional point at the center of each of the faces of the cell.
- Base-centered A,B or C: Atoms at the cell corners. In addition, one additional point at the center of a pair of parallel faces. C stands for top and bottom face having an additonal point at the center of the face.

There are two equivalent definitions of a Bravais lattice [4]:

- A Bravais lattice is an infinite array of discrete points with an arrangement and orientation the appears *exactly* the same, from whichever of the points the array is viewed.
- A (three-dimensional) Bravais lattice consists of all points at the position vectors  $\vec{R}$  of the form  $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$  with  $\vec{a}_i$  being linear independent vectors and  $n_i$  integer numbers.

The volume spanned by the basis vectors  $\vec{a}_i$  is the *unit cell*. In three dimensions, there are 14 different Bravais lattices fulfilling the definitions above. Their unit cells are listed in table A.1 in appendix A.1.

For a set of vectors  $\vec{R}$  forming a Bravais lattice, a set of vectors  $\vec{K}$  can be found such that

$$e^{i\vec{R}\cdot\vec{K}} = 1 \tag{2.1}$$

is fulfilled for all  $\vec{R}$  and  $\vec{K}$ . Each  $\vec{K}$  can be expressed in the yet unknown basis  $\vec{g}_i$ 

$$K = K_{hkl} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$$

From (2.1) follows a condition for the basis  $\vec{g}_i$ , that can be used to construct  $\vec{g}_i$  from  $\vec{a}_i$ :

$$\vec{g}_i \cdot \vec{a}_j = 2\pi \cdot \delta_{ij}$$

The vectors  $\vec{K}_{hkl}$  also form a Bravais lattice, which is called the *reciprocal lattice* of  $\vec{R}$ .

Real crystal lattice are not always Bravais lattices, but can have a reduced symmetry. Such lattices are describes by adding a *basis* to each lattice point of the Bravais lattice. This will be discussed using the example of the face-centered cubic Bravais lattice.



Figure 2.3: Schematic of the diamond lattice unit cell. Adding a two-atomic basis (a) to the points of a face-centered cubic lattice (b) gives the diamond lattice (c).

Figure 2.3(b) shows a unit cell of the face-centerd cubic Bravais lattice. But the crystal structure of diamond looks different (figure 2.3(c)), it has additional atoms on the points marked with an empty circle. To get a descripton of all atomic positions, one adds a *two-atomic basis* (a full and a neigboring empty circle) to each (black) fcc lattice point. For a diamond lattice, both atoms in the basis are of the same kind. But a basis can also consist of different atoms, for example a Na and Cl to describe the lattice structure of table salt.

#### 2.3.3 Crystallographic point groups

In crystallography, a crystallographic point group is a set of symmetry operations e.g. rotations or reflections, that leave a central point fixed while moving other directions and faces of the crystal equivalent positions in the crystal. For a periodic crystal, the group must also be consistent with maintenance of the three-dimensional translational symmetry that defines crystallinity. The macroscopic properties of a crystal will look identical before and after any of the operations in its point group.

#### 2.3.4 Miller Indices

This paragraph shows how to describe the orientation of a crystal plane with respect to the basis vectors  $\vec{a}_i$ . The shaded area in figure 2.4(a) is the plane of interest, it intersects the axes (defined by the basis vectors) at the points  $x_i \cdot \vec{a}_i$ . The *Miller indices* h, k, l are defined by the inverse values of  $x_i$ 

$$h, k, l = \frac{1}{x_1}, \frac{1}{x_2}, \frac{1}{x_3}$$
(2.2)

The values of h, k, l are reduced to the smalles possible integer values. The set of h, k, l uniquely defines the orientation of a crystal plane, but not its position. Note: to faciliate labeling, the commas are often left away and negative values are replaced by a bar, e.g. the plane (1, -2, 0) is noted as  $(1\overline{2}0)$ . Examples for the most basic indices are shown in figures 2.4(b)-(d).



Figure 2.4: (a) The grey shaded plane hkl intersects the axis at the points  $x_i a_i$ . (b)-(c) Examples of planes with their Miller indices. Images modified from [4].

## 2.4 Diffraction

The phenomena of diffraction can be explained by the Bragg and the Laue formulation, both will be outlined briefly in the following paragraphs.

#### 2.4.1 Bragg Formulation

The Bragg formulation describes the crystal lattice by parallel planes, on which the atoms are located. Figure 2.5 shows an X-ray hitting these planes under an angle  $\theta$ .



Figure 2.5: X-ray hits Bragg planes under an angle  $\theta$ . Image from [4].

The ray hitting the second plane has a path that is  $2d \cdot \sin \theta$  longer than the path of the ray reflected at the top plane. To see the reflex of the X-ray, the reflected rays must

interfere constructively. This is fulfilled when the path differences are an integer multiple of the wavelength:

$$n \cdot \lambda = 2d \cdot \sin \theta \tag{2.3}$$

This is the celebrated *Bragg condition* for constructive interference of the reflected beams. The idea of describing the scattering process in terms of parallel planes reduces the complexity of the scattering problem from a three-dimensional problem to a two-dimensional problem.

#### 2.4.2 Laue Formulation

The Bragg formalism above gives an intuitive explanation why reflection is only observed under certain angles. But it assumes the existence of distinct crystal planes, on which a specular reflection happens (reflection with light in a single outward direction). In contrast, the *Laue formulation* does not require these assumptions to come to the same results.

The Laue approach assumes that identical microscopical objects (atoms, ions) are places at the sites  $\vec{R}$  of a Bravais lattice. Then an incident X-ray with wave vector  $\vec{k}$  is sent to this ensemble. The condition of constructive interference for the reflected ray with wavevector  $\vec{k'}$  leads to the expression

$$\vec{R} \cdot (\vec{k} - \vec{k'}) = m \cdot 2\pi$$

with m an integer number. This is equivalent to the *Laue condition* stating that for constructive interference the difference of the wave vectors must equal a vector of the reciprocal lattice:

$$(\vec{k} - \vec{k'}) = \vec{K}_{hkl} \tag{2.4}$$

This condition is depicted geometrically by the *Ewald construction* in figure 2.6. The direction and energy of the incident beam is represented by drawing the wave vector  $\vec{k}$ , then the crystal orientation is added by drawing the points  $\vec{K}$  of the reciprocal lattice. To find the direction in which a reflection can be observed, draw a circle of radius  $|\vec{k}| = |\vec{k'}|$  around  $\vec{k}$ . Wherever the circle hits a point of the reciprocal lattice, the Laue condition is fulfilled and in the direction of  $\vec{k'}$  a reflection can be observed.

#### 2.4.3 Structure Factor and Cancellation

So far we only cared about the direction of the reflections and neglected their intensity. Here we will discuss the basic aspects since *cancellation* will play an important role in the analysis of the data.

We choose a reciprocal lattice vector  $\vec{K}_{hkl}$  and discuss the intensity of the reflection that is attributed to  $\vec{K}_{hkl}$  by (2.4). The vectors  $\vec{r}_{\alpha} = n_i \vec{a}_i$  ( $n_i$  in [0,1]) shall describe the position of the atoms  $\alpha$  in the unit cell of the lattice, that is spanned by the basic vectors  $\vec{a}_i$ .



Figure 2.6: Two-dimensional visualization of Ewald construction including the incident wave vector  $\vec{k}$ , the circle indicating all possible detector directions and the points of the reciprocal lattice. Image from [4].

Then the intensity of the reflection hkl can be shown [4] to be proportional to the structure factor

$$S_{hkl} = \sum_{\alpha} f_{\alpha,hkl} e^{i\vec{K}_{hkl}\cdot\vec{r}_{\alpha}}$$
(2.5)

where  $f_{\alpha}$  is the atomic form factor. Lets discuss this on the example of body-centered cubic lattice: There are two atoms per unit cell, one at the corner and one in the center. Therefore the vectors  $\vec{r}_{\alpha}$  are

$$\vec{r}_1 = 0 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 0 \cdot \vec{a}_3$$
  $\vec{r}_2 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3$ 

Plugging the  $\vec{r}_{\alpha}$  into (2.5) and setting  $f_1 = f_2 = f$  since the atoms are equal leads to

$$S_{hkl} = f(e^{1 \cdot 0} + e^{i\pi(h+k+l)}) = \begin{cases} 0 & \text{if } (h+k+l) \text{ odd} \\ 2f & \text{if } (h+k+l) \text{ even} \end{cases}$$

Therefore the intensity of the (hkl) = (100) reflection is zero because the ray reflected at all the atoms 1 *interferes destructively* with the ray reflected at all the atoms 2. Repeating this calculation for the most common lattices gives the following general conditions for a non-zero intensity of reflection hkl:

- primitive(simple) cubic (sc): all reflections visible
- body-centered cubic (bcc): (h + k + l) must be even
- face-centered cubic (fcc): h, k, l must be either all even or all odd
- diamond lattice (fcc with two-atomic basis): either (h, k, l all even and h+k+l=4n)or  $(h, k, l \text{ all odd and } h \neq 0, k \neq 0, l \neq 0)$

The table A.1 in the appendix section A.2 gives an overview which reflections are visible for the lattices above and for different values of h, k, l. For different lattices, the structure factor and thus the reflection intensity can be calculated using (2.5).

## 2.5 Powder Diffraction

As we have discussed in section 2.4, X-ray reflection from a single crystal can only be observed if the geometric arrangement of X-ray source, sample and detector is correct. This is also visible in the Ewald construction in figure 2.6 which shows that reflections are only observed in the directions the circle coincides with points of the reciprocal lattice.

The technique of *powder diffraction* solves this problem by replacing the single crystal sample by a sample that consists of a powder of the same material. Each grain of the powder is a crystalline piece that is large enough to have the diffraction properties of a large crystal. But since the powder sample consists of crystal grains which are placed in every possible orientation, rotating it will not change the diffraction pattern (whereas the rotation of a single crystal sample would also rotate the directions of the observed reflections). The same effect is achieved if the sample is not a single crystal, but an ensemble of microscopic crystallites (polycristalline sample).

The effect of a powder sample can be visualized in the Ewald construction by replacing the points of the reciprocal lattice by circles around the origin, which represent the sum of the reciprocal lattices of all possible crystal orientations. This construction is shown in figure 2.7.

Using a powder sample it is sufficient to measure the reflections in any plane containing the incident beam (due to symmetry of the sample). A technique that makes use of this is the *Debye-Scherrer method*. It works by placing a strip of photographic paper around the sample, on which the reflections appear as lines. This method is suitable to determine under which angles the reflections are found, but for information about the reflection intensities a photon counting detector is required.

A photon counting detector measures the number of X-ray photons arriving on a small area and has to be moved around the sample to determine the intensity as function of the angle. Figure 2.8 shows the schematics of such a setup, where the X-ray source is fixed, the sample rotates and the goniometer moves the detector around the sample with double the sample rotation speed. A setup of this kind will be used in this VP experiment.

#### 2.6 Form factor

The form factor describes the momentum transfer dependence of the scattering amplitude from a single scattering centre. Because of this form factor the intensity drops dramatically for very large momentum transfers. It depends on the type of radiation that is used to determine the structure. The form factors for Xray scattering are tabulated values which can be found in lookup tables. In the simplest dipole approximation the form factor is



Figure 2.7: Two-dimensional visualization of Ewald construction for a powder sample. The points indicate the reciprocal lattice for a single crystal, the circles the added reciprocal lattice points for all possible lattice orientations. Image from [4].



Figure 2.8: Schematic of a  $\theta - 2\theta$  measurement setup and a typical measurement result.

angle-independent and can be seen as a simple prefactor for structure factor calculations. (Intensity of diffracted intensities, P. J. Brown, A. G. Fox, E. N. Maslen, M. A. O'Keefec and B. T. M. Willisd International Tables for Crystallography (2006). Vol. C, ch. 6.1, pp. 554-595) **Exercise:** Repeat the calculation of the structure factor for the structure

of NaCl. It can be seen as a face-centered cubic (fcc) lattice with a two-atom basis. If you compare the atomic form factors of  $Na^+$ ,  $K^+$  and  $Cl^-$ , which differences between the diffraction patterns of NaCl and KCl do you expect?

## 2.7 Phases of matter

The term "phase" refers to a homogeneous state of thermodynamic equilibrium for an infinite system. Every phase is characterized by a set of observable quantities such as density, compressibility, refractive index etc. which are obtained by averaging over the whole infinite system. So if we speak of a phase we always think of collective behaviour rather than the individual constituents. The observable quantities will depend on the external conditions, such as pressure or temperature, under which they are measured. Typically, these observable will be smooth functions of these parameters. However, sometimes this will not be the case and some of the observables or their derivatives will exhibit a discontinuous change as one of the external parameters changes (Example: The density of water changes discontinuously when it is boiling). This sudden change in properties of a material is called a phase transition. In this experiment you will investigate both the smooth linear expansion of the lattice parameter of copper, as well as two phase transitions.

## 2.8 Thermal Expansion

Over small temperature ranges, the thermal expansion of materials can be regarded as linear. This leads to expansion relationships for length in terms of the linear expansion coefficient:

$$\frac{\Delta l}{l_0} = \alpha \Delta T \tag{2.6}$$

#### 2.8.1 Order parameter

# Chapter 3 Experimental Task

The Experiment consists of three parts and for each, you will have to prepare the samples that you will characterize yourself.

In the first part you will investigate the effect of exchanging two atomic species for one another in an otherwise identical crystal structure on the diffraction patterns. In the second part you will compare the diffraction patterns of single crystals and powder samples of Silicon. You will learn about the strengths and weaknesses of single crystal and powder diffractometry. In the third part you will use powder diffraction to study physical properties of thermodynamics phases and how they depend on temperature. You will investigate the thermal expansion of copper, the physical changes happening in KAlSO<sub>4</sub>.  $12H_2O$  when heated up and the temperature dependence of the diffraction pattern of the piezoelectric compound BaTiO<sub>3</sub>. This will allow you to determine the structural changes which make single crystals of BaTiO<sub>3</sub> a piezoelectric, used for example in microphones.

## 3.1 Description of the Experimental Setup

The experimental equipment is a commercial X-ray powder diffractometer as shown in figure 3.2(Rigaku MiniFlex). The tube is usually operated with an acceleration voltage of 30 kV and a current of 30 mA. A nickel filter is suited to use the  $Cu_{K\alpha}$  emission line with a wavelength  $\lambda = 1.5406$  Å. In front of the shutter there are the  $\theta$ -stage for the sample and the  $2\theta$ -stage with the counting detector.

## 3.2 Safety

**Safety Measures** X-rays are carcinogenic and therefore exposure to high doses must be avoided. The Rigaku MiniFlex X-ray source provides a high level of safety since there is a fail-safe radiation enclosure. Additionally, the beam shutter can only be opened if all the safety features are in place. The assistant of this experiment will discuss the safety measures and precautions with you.



Figure 3.1: The experimental setup consists of the high voltage source at the bottom, the X-ray tube in the center and the detector, which is mounted on the goniometer around the sample stage.

Since technical failure can occur at any time, it is recommended that you perform a radiation survey of the device at the beginning of every measurement day. The assistant will instruct you on how to do this.

For your own safety it is highly recommended to wear gloves at all time when handling any chemicals whilst preparing samples. These will be provided in appropriate sizes. If they run out please contact your assistant.

**Taking Measurements over Night** Some parts of this experiment will take longer than you will be able to stay in the facilities. In this case you can always do a measurement over night or over the weekend, but you will have to take extra precautions.

Do not leave anything lying around that could be harmful (this applies generally, but especially for over-night experiments). Make sure the measurement has been put into execution before you leave the room. You will also require a so called "Nachttafel". This will let others know that the machine is meant to be left on, if you do not leave such a Nachttafel your experiment will be terminated and may lead to other consequences. The Nachttafel can be sought out in HPP J14, there are multiple versions, be sure to choose the correct one.



Figure 3.2: Gloves will be provided in different sizes. Be careful to wear gloves when handling chemicals.

## 3.3 System startup

#### Hardware start up

- 1. Turn on the water cooler by pressing the highlighted button
- 2. Make sure the temperature is stable at around 20 Celsius as shown in the picture.
- 3. Pick up the key located at the wall just behind the PC.

- 4. Insert this key into the diffractometer as shown in the figure below at rotate it clockwise for 90 degrees.
- 5. Push the green button, the yellow lights turn on



Figure 3.3: Left: Cooling Pump set to 20°, Right: General workspace with Rigaku Mini-Flex, computer and dosimeter, key in the background

#### Software start up

- 1. Upon starting MiniFlexGuidance the following login screen appears. In order to get rights for running the diffractometer a login user1 must be used. NO PASSWORD is required.
- 2. To start X-ray production the following steps must be carried out.

Click the start up icon.

Choose option not used for 1-3 weeks (see figure 3.5). Press execute and await until the hardware control window allows for other steps. There is a countdown clock shown in Hardware control window.

## 3.4 System shut down

To shut down the system proceed in the reverse order to the startup.

- Turn off the X-ray production in the MiniFlex guidance software (see figure 3.7).
- Power off the xray tube by pressing the white button on the front panel.
- Disable the high voltage by turning the key on the front panel and place it at the designated hook on the wall.
- Switch off the cooling water pump.



Figure 3.4: Left: Key to use Rigaku MiniFlex, Right: Control panel on Rigaku MiniFlex, (from left to right) door lock, indicator lamp, lock, off button, on button, emergency shutdown

Startup	×
Timer	
● Start ○ End	
11/29/2018 💷 01:0	)1:01 🚔
Estimated BE: 2018/11/29	01:08:24
Generator usage: Not use	ed for 2 days-1 week $\sim$
XG set: Hold	~
Voltage(kV) ; 20 Cu	rrrent(mA) : 2
Execute	OK Cancel

Figure 3.5: Start up window

## 3.5 Sample preparation

For your own safety, wear protective gloves at all stages of sample preparation. To obtain nice powder diffraction spectra, the samples need to be as homogeneous and as flat as possible. Therefore, preparing the samples for measurement is a crucial part for the success of the experiment. Try to grind the powder as fine as possible using the provided mortars. Use sample the sample holder in figure 3.8 for all powder diffraction measurements. To flatten the surface use a glass plate or a second sample holder to produce a flat surface of the powder in the sample holder. Please label the samples, others will not know their composition!

To prepare the copper sample cut our a piece of copper from the plate provided and



Figure 3.6: The experimental set up consists of the high voltage source at the bottom, the X-ray tube in the center and the detector, which is mounted on the goniometer around the sample stage.

Shutdown			×							
Execute										
Shutdown conditions										
XG set:	XG Off		~							
	10	minutes be	efore Power Off							
Voltage(kV)	40	Current	(mA): 15							
Execute		ОК	Cancel							

Figure 3.7: Shut down window

fit it into the other type of sample holder (see figure 3.9).

**Samples for high-temperature measurements** Since many adhesives decompose at elevated temperatures, please do not use any grease or glue to prepare your samples to be used in the heating stage.



Figure 3.8: Sample holder for ambient temperature measurements.



Figure 3.9: Sample holder for temperature dependent studies in the heating stage.

## 3.6 Heating Stage

The BTS 500 Heating Stage allows for measurements between room temperature and 500 °C. Samples are heated by a resistance heater and a Platinum Pt100 thermometer is located close to the sample. It can be used to study e.g. phase transitions, thermal expansion or chemical processes through structural analysis. All manipulations are only to be performed when the heating stage is at room temperature!

#### 3.6.1 Installation

To install and remove the heating stage, always get in touch with your assistants. They will modify the set-up for you!

## 3.7 Pattern acquisition

To determine the lattice parameters reliably it is crucial to be able to fit the Bragg peaks with high precision. In order to correctly assign the Miller indices of the Bragg peaks, one needs several peaks to check whether the lattice parameters and the reflection conditions really work out. Try to find a good compromise between speed and data quality. **Room temperature** Choose the macro "General Measurement" and define the measurement parameters in the pop-up window. Make sure to set the unit to "counts". Otherwise a sensible error estimate will not be possible. You run a set of scans in sequence if you want to carefully measure a particularly weak feature. It is here where you can define where the data will be stored.

**High-temperature** Choose the macro "High\_temperature\_scan" and define the temperatures at which you want to obtain the Xray patterns. Make sure to check all the boxes, otherwise no patterns will be obtained. Inside the loop, click on "General Measurement" to choose the measurement conditions for the patterns to be obtained. Do not heat the sealed sample of  $BaTiO_3$  above 200 degree Celsius for your own safety!s

## 3.8 Estimating the systematic error

Silicon is available at a high purity and its lattice parameters are precisely known. Therefore we use a silicon sample to calibrate our device. Measure the intensity  $I(\theta)$  profile and compare it to the expected reflection positions.

The angles, under which reflections are expected, are calculated the following way: find the visible values for hkl (cancellation!) and calculate the distance  $d_{hkl}$  between the (hkl) planes. For cubic lattices it is calculated with

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

with  $a_{\rm Si} = 5.43088$  Å being the lattice parameter of silicon. For non-cubic lattices the  $d_{hkl}$  are listed in table A.2. From the Bragg condition (2.3) we know the angle  $\theta_{hkl}$  under which the hkl reflex is visible

$$\theta_{hkl} = \arcsin(\frac{\lambda}{2d_{hkl}})$$

Use the data from the Si standard sample to correct for errors in the detector position. For checking your results, reference data of a Si standard sample are attached in the appendix section A.4.

## 3.9 Indexing of diffraction patterns

The main task of this experiment is to measure your samples and determine the indices hkl responsible for each peak. First, start by measuring the  $I(\theta)$  of your sample. Choose the measurement parameters in a way to get a sufficient signal-to-noise ratio.

From the peaks *i* and their angles  $\theta_i$  in the measured date we calculate  $d_{hkl}$  using the Bragg condition (2.3). Since we don't know which hkl belong to which reflection, it is useful to calculate the ratios  $Q_i$ 

$$Q_i := \frac{\sin^2 \theta_i}{\sin^2 \theta_1} = \frac{d_1}{d_i} \stackrel{\text{cubic}}{=} \frac{h_i^2 + k_i^2 + l_i^2}{h_1^2 + k_1^2 + l_1^2}$$
(3.1)

Since the values of  $h_i^2 + k_i^2 + l_i^2$  are integer numbers, the values of  $Q_i$  can be used to determine the value of  $h_1^2 + k_1^2 + l_1^2$ . From the appearance and not-appearance of certain values of  $Q_i$  you will know the type of crystal lattice and the indicies hkl of each peak. For non-cubic lattices the last equility in (3.1) is not correct. In this case, find the correct expression using table A.2.

## 3.10 Data analysis

In order to extract the peak positions, widths and intensities of your diffraction pattern, you need to perform a fit to your data. For diffraction patterns, a Gaussian has proven a useful approximation to the peakshape. At small scattering angles, a single Gaussian can be used to approximate the peak shape. At larger scattering angles you will always observe two peaks due to the  $K_{\alpha 2}$  contamination. To extract the correct peak positions it is imperative to use a sum of two Gaussians.

Example

```
import math
import random
import numpy as np
import matplotlib.pyplot as plt
from scipy import optimize
# define the Gaussian peak shape
def g(x, A, \hat{1}\frac{1}{4}, \ddot{I}f):
    return A / (If * math.sqrt(2 * math.pi)) * np.exp(-(x-I\frac{1}{4})**2 / (2*If**2))
# Generate the sample data as a sum of two Gaussians with superimposed random noise
g_0 = [20.0, 7.0, 1.5]
g_1 = [20.0, 3.0, 0.8]
n = 150
x = np.linspace(0, 15, n)
y = g(x, *g_0) + g(x, *g_1) + np.random.randn(n)
fig, ax = plt.subplots()
ax.scatter(x, y, s=1)
#uncomment to plot the functions used to generate the data
#ax.plot(x, g(x, *g_0))
#ax.plot(x, g(x, *g_1))
#ax.plot(x, g(x, *g_0) + g(x, *g_1))
def cost(parameters):
    g_0 = parameters[:3]
    g_1 = parameters[3:6]
    return np.sum(np.power(g(x, *g_0) + g(x, *g_1) - y, 2)) / len(x)
```

```
initial_guess = [2, 3, 1, 2, 7, 1]
result = optimize.minimize(cost, initial_guess)
print('steps', result.nit, result.fun)
print(f'g_0: amplitude: {result.x[0]:3.3f} mean: {result.x[1]:3.3f} sigma: {result.x[2]
print(f'g_1: amplitude: {result.x[3]:3.3f} mean: {result.x[4]:3.3f} sigma: {result.x[4]
ax.plot(x, g(x, *result.x[:3]))
ax.plot(x, g(x, *result.x[3:6]))
ax.plot(x, g(x, *result.x[:3]) + g(x, *result.x[3:6]))
```



Figure 3.10: Output of the code snippet.

## 3.11 Experimental tasks

#### 3.11.1 The lattice parameter of Silicon

The goal is to estimate the systematic error made in the experiment by comparing your measurement of the lattice parameter of silicon to the international standard. This is done by preparing a sample of silicon as described in section 3.5.

Make sure you do several measurements with different silicon samples. Does the surface condition affect the measurement? Be sure to grind the powder as described, otherwise powder may shift or even fall during a measurement.



Figure 3.11: Simple sample holder



Figure 3.12: Interface in MiniFlex Guidance

To start a measurement using the software "MiniFlex Guidance" start up the system as referred to section 3.3. You will use the sidebar "Package/Macro Measurement" (see figure 3.12), there are multiple options you can choose from in the drop down menu, in this case you will choose "General Measurement". For these options the settings have already been set for you. Now click on the yellow button "1 General Measurement". A window will open, allowing you to set the execution parameters and conditions for your next measurement.

In figure 3.13 one can see the new window. Depending on how many iterations will be

Gener	al Me	asurement							-			×
A	Automatic generation of data file names											
No.	Exec	c. Folder	File name		Sample name	Memo 🔽	Conditi	on	Analysis condition	Spin	Sar	nple
1	$\checkmark$	C:\MiniFlex Data\tests\test1\	test1.ras				No1	~	Set		1	
2	$\checkmark$	C:\MiniFlex Data\tests\test2\	test2.ras				No1	~	Set		1	
3							No1		Set		1	
4							No1		Set		1	
5							No1		Set		1	
5							Nol		Set		1	
6							No1		Set		1	
9							No1		Set		1	
10						1	No1		Set		1	
XG t	XB termination condition Optical devices confirmation message Set Meas. Conditions											
() T	The status quo Stop the X-Ray Show Don't show      Run      OK      Cancel											

Figure 3.13: Screen shot of the general measurement file window

taken, the appropriate amount of boxes should be selected on the left hand side. **Important:** Always give thought to your file names. It will be easier if you describe your measurement as detailed as possible, so you do not have a problem figuring out which file was for which measurement later on.

To set the measurement conditions one clicks on the button "Set Meas. Conditions...", which again opens a new window (see figure 3.14). Here one can define the intermediate steps for each general measurement. "Scan Axis", "Mode" and "Unit" should be selected as in the screen shot. The panel allows the conditions for each step to be specified. One can make several versions of conditions (labelled No1, No2, etc.), which can then be preselected in the drop down menu "Condition" in the first window (see figure 3.13).

When the measurement conditions are set and all files have been named the window can be closed by clicking "OK". To start the experiment the button "Execute" in the original side bar should be selected.

To use the files which were created you can save the .ras files on a USB stick. If you open these in your text editor the .ras file gives you all the information you require to create graphs. It also includes the x and f(x) points of your measurement.

#### 3.11.2 Structure factors: Diffraction Patterns of NaCl and KCl

Measure the diffraction patterns of NaCl and KCl. What differences do you observe in the diffraction patterns of these very closely related compounds? Plot the peaks relative to the value of the highest measured peak. Make a table including the hkl-value,  $2\theta$  and the intensity.



Figure 3.14: Setting the measurement conditions for a general measurement. Make sure to set the unit to "counts". Otherwise a sensible error estimate will not be possible.

After the measurement the samples of NaCl and KCl have undergone a change in physical appearance. Find an explanation for this phenomenon.

#### 3.11.3 Single crystal vs. powder diffraction

Measure the diffraction patterns of silicon (111) and (100) single crystals. Make sure to stick the crystals on in an area of the sample holder which is irradiated. You will have realised from the changes in NaCl and KCl that the scanning area is larger than the provided single crystals, so that the sample holder will also be sampled. To be able to determine which peaks are from the crystal and which from the aluminium sample holder, one should first measure the sample holder by itself. One will then be able to subtract the signal produced by the sample holder in the actual single crystal measurement.

What differences do you observe when you compare each of the crystal patterns to the powder pattern? Explain them and index the peaks correctly. Which groups of peaks are possible to distinguish in a single crystal experiment which are degenerate in a powder spectrum?



#### 3.11.4 The Thermal Expansion of Copper

Figure 3.15: Set up for thermal expansion measurements

Measure the thermal expansion of the unit cell of copper and compare it to the literature value. For this your assistant will have to install another module in the Rigaku MiniFlex (see figure 3.15).

This new attachment will have to be added to the software as well. For this select "Options" and select "Hardware Configuration". The button "Attachment" will then open a small window where you can select "BTS150/500" (see figure ??).



Figure 3.16: Adding the heating unit to the software

To then take a measurement select "Temperature\_loop\_measurement" in the drop down menu in the side panel. Instead of just having a general measurement button there



Figure 3.17: Selecting Temperature\_loop\_measurement

will now also be a startloop and an endloop (see figure 3.17). The settings for the start loop and the general measurement have to be specified. Figure ?? shows the window to change the settings for the startloop. Here one selects the temperatures at which ones wants to measure. If both boxes are ticked then the software will automatically add the temperature at which it measured to the end of your general measurement file name, the right box selects the temperature measurement.

After the measurement you will realise that the surface of the copper sample has also undergone a slight change. Can you determine what happened and at which temperature the transformation took place? Think of a way to stop such a transformation from happening for future measurements of copper.

What do you observe when comparing your measured thermal expansion with the literature value? How does the linear expansion coefficient itself depend on temperature?

#### 3.11.5 "Melting" of Aluminium Potassium Sulfate dodecahydrate

When heating Aluminium Potassium Sulfate dodecahydrate up to 500 °C, the diffraction pattern will change dramatically on two instances. Can you find an explanation for this unusual behaviour. What do you observe when you let the sample cool back to room temperature?

Be careful to measure the patterns with enough accuracy. In this case a speed of 1 °per minute should suffice.

STARTLOOP (w/temp. control)											
File save condition											
Suffix : Consecutive +Temp											
Temp. condition											
remp, condition											
Temp. control :	Hold	ling meas.	Y Temp. unit :		deg	~					
Target temp.(de	eg) <b>20</b>				30						
End temp. cond	: Targ	jet temp	~								
End temp. (de	g) 30										
Temp. control	Meas.	Start temp.	Ramp rate	Holding	time						
		(deg)	(deg/min)	min	$\sim$						
1 🗹		25	10	15		^					
2 🗹		30	10	40							
3 🗹		25	30	40							
4 🗹		25	30	40							
5 🔽		25	30	40							
6 🗌		25	30	40							
7		25	30	40							
8 🗌		25	30	40							
9 🗌		25	30	40							
10 🗌		25	30	40		Υ.					
If the measure	ment is int	errupted in bet	ween the runs								
Hold     O Set 25 C deg											
						?					
			ОК		Canc	el					

Figure 3.18: Settings for the startloop of the temperature measurement

#### 3.11.6 ASL: The piezoelectric transition in Barium Titanate

Heat the sealed sample of  $BaTiO_3$  slowly through the piezoelectric transition which is expected at approximately 120 degrees. Before every measurement wait for at least 30 minutes to let the sample thermalize. Describe the changes you observe. The high temperature phase is cubic and allows you to determine the lattice parameter. What is your guess for the low-temperature phase?

As the seal in which the sample is encased is not stable at high temperatures you should think of a measuring strategy and discuss it with your assistant first. Do not heat the sealed sample of  $BaTiO_3$  above 200 degree Celsius for your own safety!

This measurement sequence is difficult because the signal is very weak and the splitting of the peaks in the low temperature phase is small. Measure the peaks located between 43.9 °and 46.5 °with a step size of 0.005 °and a speed of 0.005 °per minute. This will require you to do a measurement overnight. For any experiments in progress overnight you require a "Nachttafel" (see section 3.2). Determine the peak width and lattice parameters in the cubic high-temperature phase. Below the transition, the peak splitting is very small. It therefore may help your fit robustness if you fix the peak width below the transition to the value you observed above the transition. This is justified since the material is far away from its melting point of 1620° C, where peaks might become broadened. Plot the lattice parameters as a function of temperature. What could be an appropriate order parameter of this transition? Is the phase transition continuous or discontinuous?

# Appendix A

## A.1 Table: Bravais Lattices in Three Dimensions



Figure A.1: Geometric properties and unit cells of all 14 Bravais lattices that exist in three dimensions. The length of the basis vectors  $(\vec{a}_1, \vec{a}_2, \text{ and } \vec{a}_3)$  are labelled a, b, and c. Image from [3].

## A.2 Table: Visible Reflections for Cubic Lattices

hkl	$h^2 + k^2 + l^2$	sc	bcc	fcc	diamond
100	1	$\checkmark$			
110	2	$\checkmark$	$\checkmark$		
111	3	$\checkmark$		$\checkmark$	$\checkmark$
200	4	$\checkmark$	$\checkmark$	$\checkmark$	
210	5	$\checkmark$			
211	6	$\checkmark$	$\checkmark$		
220	8	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
300, 221	9	$\checkmark$			
310	10	$\checkmark$	$\checkmark$		
311	11	$\checkmark$		$\checkmark$	$\checkmark$
222	12	$\checkmark$	$\checkmark$	$\checkmark$	
320	13	$\checkmark$			
321	14	$\checkmark$	$\checkmark$		
400	16	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
410	17	$\checkmark$			
330, 411	18	$\checkmark$	$\checkmark$		
331	19	$\checkmark$		$\checkmark$	$\checkmark$
420	20	$\checkmark$	$\checkmark$	$\checkmark$	
421	21	$\checkmark$			
332	22	$\checkmark$	$\checkmark$		
422	24	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
500	25	$\checkmark$			
510	26	$\checkmark$	$\checkmark$		
511, 333	27	$\checkmark$		$\checkmark$	$\checkmark$

Table A.1: Visible reflections of simple cubic (sc), body-centerd cubic (bcc), face-centered cubic (fcc), and diamond lattice.

## A.3 Table: Distance between *hkl* Planes

The following table gives the distances  $d_{hkl}$  between the Bragg planes (hkl). The length of the basis vectors  $(\vec{a}_1, \vec{a}_2, \text{ and } \vec{a}_3)$  of the corresponding Bravais lattice are labelled a, b, and c. This is the same notation as used in table A.1.

Bravais lattice	distance $d_{hkl}$	angle $\theta_{hkl}$ of reflection
cubic	$rac{1}{d_{hkl}^2} = rac{h^2 + k^2 + l^2}{a^2}$	$\sin^2 \theta_{hkl} = \lambda^2 \frac{h^2 + k^2 + l^2}{4a^2}$
tetragonal	$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$	$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \left( \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right)$
orthorombic	$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$	$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$
hexagonal	$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$	$\sin^2(\theta_{hkl}) = \frac{\lambda^2}{4} \left( \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)$

Table A.2: Interplanar distance and angles under which reflections are observed for the four classes of Bravais lattices in three dimensions.

## A.4 Measurement Results of Silicon Standard Sample

27-1402									Wav	elen	gth= 1.540	56	1 A .
Si						2.	Int	Þ	k	1			
Silicon Silicon. syn				1		28.442 47.302 56.121 69.130	100 55 30 6	1234	1210	1010			
Rad.: CuKal Cut off: Ref: Natl. Bur	1.540598 Int.: Diffra Stand. (U.S. )	Filter: Mono et. l/ ) Monogr. 25, 13	d-sp Icor.: 4.70 . 35 (1976)	Diff.	-	88.026 94.948 106.715 114.087 127.541	12 6 3 7 8	345456	32-4320	2 1 0 1 0			
Sys.: Cubic		S.G.: Fd3n	n (227)			136.890	3	5	3	3			
a: 5.43088(4) a:	b: β:	с: 7	A: 2:8	mp:	C:							2	
Ref: Ibid. Dx: 2.329	Dm:	SS/FOM	F11 = 409(	0021 .	13)								
Color: Gray						· · ·							

Figure A.2: Measurement results for a Si standard sample including the peak positions and the relative peak intensity.

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