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Experiment 3.17 X-Ray Structure Analysis with Debye-Scherrer

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Contents

1	Intro	oduction	3
2	The 2.1 2.2	oretical Background X-Ray Radiation	3 3 6
3	Prep	parational Topics	6
	3.1	Structure Factors of bcc and fcc lattices	6
	3.2	Monochromatic beams with a monochromator crystal	7
	3.3	Post-Scatter Filtering	7
	3.4	Atomic form factors of K and Cl	7
	3.5	Error of the lattice parameter	8
	3.6	Error of the grain size	8
4	Exp	eriment	8
	4.1	Preparing the sample	9
	4.2	Lattice parameter and type via calibration sample (Si) \ldots \ldots \ldots	9
	4.3	Lattice parameter and type via $\Delta 2 heta$	10
	4.4	Grain size of a nano-crystalline sample	12
5	Con	cluding Questions	12
	5.1	Shift in the $K_{lpha 2}$ peaks at large angles \ldots \ldots \ldots \ldots \ldots	12
	5.2	X-Ray Analysis of matter with high ΔZ	13
	5.3	Forbidden reflexes	13
	5.4	Analysing Cu samples with Cu anodes \ldots \ldots \ldots \ldots \ldots \ldots	13
	5.5	Grain size weight	13
	5.6	Consequences of inelastic scattering	14

1 Introduction

X-ray scattering is well-tried for analysing an unknown substance. The method of Debye-Scherrer was developed by Peter Debye and Paul Scherrer in 1916. The experiment of Debye and Scherrer is based on a round can. In the middle of this can there is a holder for the substance which has to be analysed. A film, which is fixed on the side of the can, records the interference-structure. The Debye-Scherrer method is different from other methods (as for example the Laue method) in three aspects. It uses monochromatic light, a rotating sample and also a pulverized polycrystalline sample as opposed to a monocrystal.

2 Theoretical Background

2.1 X-Ray Radiation

X-rays are electromagnetic radiation in a wavelength-range of $1 \mathring{A} = 10^{-10}$ m. It was discovered by Wilhelm Conrad Röntgen in 1896.

2.1.1 X-Ray Sources

X-rays can be produced by two different ways. The first one is to use an x-ray tube. It contains a cathode and an anticathode. The electrons are accelerated towards the anticathode by a high voltage (ca. 50 kV). In the anode the electrons are decelerated by the electrical field of the nuclei. In this manner a photon with the wavelength corresponding to the lost energy is created. The radiation which is generated in this process is called bremsstrahlung. The smallest possible wavelength $\lambda_{min}=rac{hc}{eU}$ of the emitted radiation is defined by the tube accelerating voltage U_{\cdot} In our case the minimum wavelength is $\lambda_{min}pprox 1.24 {r A}_{\cdot}$. The accelerated electrons can also eject other electrons from the atom. That way there are gaps in a shell of a given energy. This condition is not stable, so an electron of a higher shell and a smaller energy drops to fill the free place. The excessive energy is emitted as a photon. These x-rays are called the characteristic spectrum. It is composed of sharp lines, because the energy differences between the atomic shells are fixed. For example, the line with greatest intensity is called K_{α} . It is the line which is appropriate to the energy difference between the L shell and the K shell (see fig. 1 for reference). The efficiency of X-Ray tubes is only about 1% and thus alot of excess heat is produced which has to be cooled so that the anode does not melt.

The second way to produce x-rays is within an electron synchrotron. The radiation is emitted by the circling electron because a constant force accelerates the electron towards the center of the synchrotron. Synchrotron radiation has a continuous spectrum and high intensity.



Figure 1: Schematic drawing of the atomic shell model with K and L lines of the characteristic radiation.

2.1.2 Bragg's Law

We need the Bragg equation to determine the size of a cell in the atomic lattice. Therefore we need the relation:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
(1)

But first we need to deduce the Bragg equation: If we have a crystal with the lattice width d and monochromatic radiation which will be reflected on the crystal levels, then the angle of the incoming and the reflected rediation is the same. But between the crystal levels there is a distance. If we look only at the situation of constructive interference, we know that the distance between two partial beams have to be $n \cdot \lambda$ (with n = 0, 1, ...). If we look at figure 2

we see, that the way difference between a partial beam, which is reflected at the first crystal level and one reflected at the second crystal level, is $2d\sin\theta$. These two pieces of information give us the Bragg equation:

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

With equation (1) we get:

$$\sin\theta = \frac{\lambda}{2a}n\sqrt{h^2 + k^2 + l^2} \tag{3}$$

And thus:

$$a = \frac{\lambda}{2\sin\theta} n\sqrt{h^2 + k^2 + l^2} \tag{4}$$



Figure 2: This figure shows the beams of light in Bragg reflexion. Constructive interference only happens when the Bragg law is fulfilled.

2.1.3 Monochromatisation

The Debye-Scherrer experiment needs a monochromatic beam. There are two ways to monochromatise X-ray radiation. The first one is to use an absorption filter, which is rather difficult to set up. The balance between the actual scattered intensity that arrives at the detector and the amount of monochromatisation is hard to find. It is very important that enough X-rays are scattered so that the measurements can be done within a reasonable time frame. To achieve a sufficient scattered intensity the thicknesses of the filters, the crystals and the sample must be well balanced. In this setup we only want to use the K_{α} -line, because it is the one with the highest intensity and also corresponds to the interatomic distances in a crystal. The filter material we use is nickel with the important absorption edge at 1.49Å. The intensity of photons traversing matter is given by:

$$\frac{dI}{dx} = \mu I \tag{5}$$

$$\frac{dI}{I}\mu dx$$
 (6)

$$I = I_0 e^{-\mu x} \text{ with } -\mu x = -\frac{\mu}{\rho} \cdot \rho x \tag{7}$$

$$I = I_0 e^{-\frac{\mu}{\rho} \cdot \rho x} \tag{8}$$

With the empirical law for the mass absorption coefficient along a branch

$$\frac{\mu}{\rho} \propto \lambda^3 \cdot Z^3 \tag{9}$$

we get a connection between the wavelength λ , the atomic number Z and the absorption of the scattered light. Because of this equation, we see that the absorption depends on the wavelength and also on the atomic number and decays with greater photon energies. At the absorption edges, the photon energy is high enough for the photoelectric effect to take place and to elevate an electron from its shell to a higher orbit. The photon with the corresponding energy is absorbed, as can be observed as a steep increase in the absorption coefficient. One of these absorption edges for nickel overlaps with the K_{β} -line of the copper anode, while the K_{α} -line's energy is just below the absorption edge photons of this energy can not cause the photo effect. This way the intensity of the K_{β} -line is greatly reduced in comparison to the intensity of the K_{α} -line.

The second way to get a monochromatic beam, is scattering with a monochromatic crystal. Because of Braggs law (eq. 2) only one wavelength will be reflected at a specified angle.

2.2 X-Ray Scattering

There are two models for describing x-ray scattering.

2.2.1 Compton Scattering

In the Compton theory the scattering between photons and electrons compares to a game of billard. The photon and the electron are seen as hard balls. When the photon hits the electron it transfers some of the motion energy to the electron. So the wavelength of the photon changes dependent on the angle:

$$\Delta \lambda = \frac{h}{m_e c} (1 - \cos \varphi) \tag{10}$$

This type of scattering is inelastic and incoherent, so there is no relation in phase between the incoming and the scattered photon. This model becomes very important in the MeV regime compared to Thomson scattering. In our case (keV) Compton scattering is not as important, so it will only darken the background of the diffractogram.

2.2.2 Thomson Scattering

In Thomson scattering a photon will be absorbed when it interacts with an electron in an atomic lattice. The electrical field of the photon puts the electrons into oscillation and like an antenna the electron emits radiation. The emitted light can only be detected in special directions, because the it is coherent and thus it shows interference patterns. Only at angles with constructive interference the reflected light can be seen as peaks. The Bragg Law follows directly from this consideration. Thomson scattering is an elastic scattering model which is predominant in the keV regime. At these wavelenghts the nuclei provide a very small inhomogeneity due to their size (fm-scale). Scattering by the nuclei can therefore be neglected.

3 Preparational Topics

3.1 Structure Factors of bcc and fcc lattices

BCC The structure factor of the bcc lattice is same as the structure factor of an sc lattice with a two atomic basis: (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The structure factor of an sc lattice is 1, and

$$S_{bcc} = S_{sc} + e^{2\pi i \left(\frac{h}{2} + \frac{k}{2} + \frac{l}{2}\right)} = 1 + e^{\pi i (h+k+l)}$$
(11)

$$S_{bcc} = \begin{cases} 2 & (h+k+l) \text{ even} \\ 0 & (h+k+l) \text{ odd} \end{cases}$$
(12)

This shows that we can only see the reflexes with even sums of h,k and l.

FCC This lattice can be described as four simple cubic lattices put inside each other with base atoms at: (0,0,0), $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$. The structure factor computes similar to the above to:

$$S_{fcc} = 1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)}$$
(13)

$$S_{fcc} = \begin{cases} 4 & \text{h,k and l either even or odd} \\ 0 & \text{else} \end{cases}$$
(14)

Here only reflexes like (3,1,1) or (2,2,4) are allowed, but others like (0,1,1) or (3,2,1) are forbidden.

3.2 Monochromatic beams with a monochromator crystal

You can create monochromatic light with a crystal using the Bragg law. In a setup with a fixed angle θ and a broad spectrum of light with the wavelengths $\lambda \pm \Delta \lambda$ the Bragg law will only be fulfilled for one special λ . The partial beam of this special wavelength is scattered on the crystal and can be detected at the scattering angle. The rest of the light is reflected in other directions.

3.3 Post-Scatter Filtering

Several effects like fluorescence in the crystal or momentum transfer between photons and phonons can alter the wavelength of the incident light in the scattering process. In case the beam passes a monochromator before scattering, the quality of the beam decreases due to these effects. Monochromation after scattering suppresses this effect.

3.4 Atomic form factors of K and Cl

The atomic form factor is the fourier transform of the electron distribution in the orbitals. If the form factors of K and Cl in the KCl molecule are the same, then the electron distribution must be similar. Potassium has one valence electron, while chlorine needs only one electron to fill the valence orbital. In the ionic bond chlorine receives one electron from potassium and thus the electron waveforms assume the same structure. This leads to very similar form factors.

$$Z_{K^+} + Z_{Cl^-} = Z_{Ar} (15)$$

3.5 Error of the lattice parameter

Using gaussian error propagation on equation (4) for lattice parameter a we get an error for Δa :

$$a = \frac{\lambda}{2\sin\theta}\sqrt{h^2 + k^2 + l^2} \tag{16}$$

$$\frac{da}{d\theta} = \frac{\lambda \cos \theta}{2 \sin^2 \theta} \sqrt{h^2 + k^2 + l^2}$$
(17)

$$\frac{da}{d\theta} = \frac{a}{\tan\theta} \tag{18}$$

$$\frac{da}{a} = \frac{d\theta}{\tan\theta} \tag{19}$$

We see that at large angles $\theta \to \frac{\pi}{2}$ the error vanishes, while at small angles $\theta \to 0$ the error becomes infinity. This shows that large angles should be used to calculate a.

3.6 Error of the grain size

Using the same method on the Scherrer equation:

$$B = \frac{0.89 \cdot \lambda}{\cos \theta \cdot \Delta 2\theta} \tag{20}$$

we get from the derivative of B in respect to θ

$$\frac{dB}{d\theta} = \frac{0.89\lambda}{2\cos^2\theta \cdot \Delta 2\theta}\sin\theta \tag{21}$$

$$\frac{dB}{d\theta} = \frac{B}{2} \tan \theta \tag{22}$$

$$\frac{dB}{B} = \frac{d\theta}{2} \tan \theta \tag{23}$$

We see that at large angles $\theta \to \frac{\pi}{2}$ the error grows to infinity, and at small angles $\theta \to 0$ the error vanishes this time. Consequently the grain size can best be determined at small angles.

4 Experiment

The experiment took place in a closed system X-Ray scattering setup layed out after Bragg-Brentano. The wavelength of the installed X-Ray source is $\lambda = 1.541838 \mathring{A}$. This wavelength results from averaging over the wavelengths of the K_{α_1} and the K_{α_2} line from the copper anode. The relative intensity of the lines is about 2:1, so the K_{α_1} -line has double weight. All lines of higher order have progressively less intensity, so their impact on the final wavelength can be neglected. Using the data from Table 1 in the instruction sheet ($\lambda K_{\alpha_1} = 1.5405\mathring{A}$ and $\lambda K_{\alpha_2} = 1.5443\mathring{A}$) we obtain $\lambda = \frac{2}{3} \cdot \lambda K_{\alpha_1} + \frac{1}{3} \cdot \lambda K_{\alpha_2} = 1.541838\mathring{A}$. The two different wavelengths can not be resolved at small angles, but at greater angles two peaks are visible.

4.1 Preparing the sample

We prepared the sample consisting of silicon and an unknown substance by grinding them up in a mortar. Then we applied the ground mixture to the sample holder and fit it into the setup. It is important that the surface of the sample is flat and parallel to the edges of the holder in order to minimize side effects.

4.2 Lattice parameter and type via calibration sample (Si)

Using the well known properties of silicon we can calibrate the measured diffractogram and pinpoint the exact angles of the unknown substance. This enables us to determine its lattice parameter and the lattice type.

At first we calculated the difference $\Delta 2\theta_{Si}$ of seven different silicon peaks in the diffractogram compared to their literature values.

(h,k,l)	$\Delta 2 heta_{Si}$ in $^\circ$	$2 heta_{Si}$ in $^\circ$
1, 1, 1	0.031	27.276
2,2,0	0.053	31.631
3,1,1	0.064	42.186
2,2,2	0.069	45.373
4,0,0	0.084	53.689
3,3,1	0.096	75.227
4,2,2	0.118	83.940

Using the plot of $\Delta 2\theta_{Si}$ over $2\theta_{Si}$ (fig 3) we determined the experimental relative error $\left(\frac{\Delta 2\theta}{2\theta}\right)_{Sustem}$.

Steepness:
$$\left(\frac{\Delta 2\theta}{2\theta}\right)_{System} = \frac{(115-30)\cdot 10^{-3}}{90-31.5} = \frac{85.5\cdot 10^{-3}}{58.5} = 1.45\cdot 10^{-3}$$
 (24)

The steepness of the graph in fig 3 gives us the relative error of the system. This relative error is the same for the unknown substance, so we can correct the values for 2θ .

$$(2\theta)_{Si} \cdot \left(\frac{\Delta 2\theta}{2\theta}\right)_{System} = (\Delta 2\theta)_{Unknown}$$
(25)

This produces the following values. The table also shows $\sin^2(\theta)$, $(h^2+k^2+l^2)$ and (h,k,l) which help calculating the lattice parameter a.

$(\Delta 2\theta)_{Unknown}$	$\sin^2(\theta)$	$(h^2 + k^2 + l^2)$	(h,k,l)
0.040	0.0556	3	(1, 1, 1)
0.046	0.0743	4	(2,0,0)
0.061	0.1295	7	
0.066	0.1488	8	(2,2,0)
0.078	0.2039	11	(3,1,1)
0.199	0.3725	20	(4,2,0)
0.122	0.4472	24	(4,2,2)



Figure 3: Relative system error is gained from the steepness of the red line. Values in degrees.

We knew that the current lattice type forbids scattering on planes with mixed (h, k, l), so the lowest possible combination was (1, 1, 1). We calculated the other values for $(h^2 + k^2 + l^2)$ using this iteration:

$$(h^{2} + k^{2} + l^{2})_{n+1} = \frac{\sin^{2}(\theta)_{n+1}}{\sin^{2}(\theta)_{n}} (h^{2} + k^{2} + l^{2})_{n}$$
(26)

The value for a and its error were derived from a least squares fit with gnuplot. $\sin(\theta)$ was plotted over $\frac{\lambda}{2}\sqrt{h^2 + k^2 + l^2}$ (see fig. 4). The steepness m (see equ. (27)) of the red graph gives us the inverse lattice parameter $\frac{1}{a}$. The error computes as follows: $\Delta a = \left|\frac{1}{m^2}\right|$.

$$\sin(\theta) = m \frac{\lambda}{2} \sqrt{h^2 + k^2 + l^2}$$

$$a[\mathring{A}] \quad \Delta a[\mathring{A}] \quad 5.65 \quad 4 \cdot 10^{-2}$$
(27)

The literature value of a is 5.62779 and the unknown substance we analysed was NaCl which is ordinary cooking salt. Its lattice type is sc.

4.3 Lattice parameter and type via $\Delta 2\theta$

In the next experiment we investigated anatase which is TiO. We tried to calculate the lattice parameters a and c of this substance comparing two peaks of a relative intensity greater than 20% with each other. With equation 28 we can calculate the parameters a and c.



Figure 4: Plot of $\sin(\theta)$ over $\frac{\lambda}{2}\sqrt{h^2 + k^2 + l^2}$ to find a and Δa . The errorbars have been derived from $\sin\left(\frac{(\Delta 2\theta)}{2}\right)$ via gaussian error propagation.

$$\Delta \sin^2 \theta = \frac{\lambda^2}{4} \left[\left(\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{c^2} \right)_{\text{large angle}} - \left(\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{c^2} \right)_{\text{small angle}} \right]$$
(28)

As the large angle peak we chose the one with 15.62% intensity at an angle of 82.679° . With the help of an excel spreadsheet we calculated the following data for anatase:

	2θ [°]	(h,k,l)	$a[{A}]$	$c[\mathring{A}]$
Large angle peak	82.679	(2,2,4)		
Smaller angle peaks	25.304	(1,0,1)	3.7842	9.5084
	37.819	(0,0,4)	4.3101	10.8297
	48.031	(2,0,0)	3.7841	9.5079
	53.915	(1,0,5)	3.7850	9.5103
	55.055	(2, 1, 1)	3.7840	9.5077
	62.698	(2,0,4)	3.7847	3.5094
	75.065	(2,1,5)	3.7859	9.5127
Mean			3.86 ± 0.2 (5%)	9.70 ± 0.5 (5%)
Literature			3.7840	9.5118

We can see that even without a calibration sample we can determine the lattice constants to a precision of 5%. The structure of TiO_2 is bcc.

4.4 Grain size of a nano-crystalline sample

In this last part of our experiment we want to measure the grain size of the crystallites in our sample. To do this we compare the full width at half maximum (FWHM) of the peaks in the diffractogram of a nano-crystalline sample and of a sample with macroscopic grains. As a sample we use platinum both times and do not change anything else in the setup. We know that platinum has an fcc structure. This way the change in the FWHM results only from a difference in grain size. We looked at two specific peaks and compared their widths:

2θ [°]	FWHM macro [°]	FWHM nano [°]	$\Delta 2\theta$ [°]
39.961	0.249	1.325	1.032
67.680	0.311	2.034	1.672

Using the Scherrer-formula

$$B = \frac{0.89 \cdot \lambda}{\cos \theta \cdot \Delta 2\theta} \tag{29}$$

we gain values for B and the number N of unit cells per grain:

2θ [°]	В	Ν
39.961	81.065	21
67.680	56.614	14

We can see that our values are not very precise and we only looked at two different peaks, but we can gain a good estimate for the grain size with this simple method.

5 Concluding Questions

5.1 Shift in the $K_{\alpha 2}$ peaks at large angles

The distance between the $K_{\alpha 1}$ and the $K_{\alpha 2}$ peaks are bigger at large angles than the distance between the peaks at small angles, because of Bragg's law. If we have a look at the total differential:

$$d\lambda = 2d\cos\theta d\theta \tag{30}$$

With $\Delta \lambda = \lambda_{K_{\alpha 1}} - \lambda_{K_{\alpha 2}}$ we get:

$$\Delta \lambda = 2d\cos\theta \Delta \theta \tag{31}$$

Now we see that

$$\Delta\theta \propto \cos^{-1}\theta \tag{32}$$

Thus the peak splitting becomes more and more visible towards larger angles.

5.2 X-Ray Analysis of matter with high ΔZ

If we have a bond of elements with different atomic numbers, the structure factor is

$$F = f_1 \sum_{r_1} e^{2\pi i (u_{r_1} \cdot h + v_{r_1} \cdot k + w_{r_1} \cdot l)} + f_2 \sum_{r_2} e^{2\pi i (u_{r_2} \cdot h + v_{r_2} \cdot k + w_{r_2} \cdot l)}$$
(33)

The problem to detect reflexes of molecules with a high ΔZ lies in the atomic form factor f (= amplitude of the scattered wave by one electron). For $\theta = 0$ we have f = Z and with varying $\theta f \propto \sin \theta$ is valid for all the elements. So from highly different Z follow very different form factors. It follows that the intensity scattered by heavy elements is larger as the intensity scattered by light elements. The different intensities are hard to detect in the diffractogram.

5.3 Forbidden reflexes

The intensity of Bragg reflexes is given by:

$$I(h,k,l) = I_0 \cdot |F(h,k,l)|^2 \cdot p \cdot \left(\frac{1+\cos^2 2\theta}{2\sin^2 \theta \cdot \cos \theta}\right)$$
(34)

 $F(h,k,l) = \sum_r f_r \cdot e^{2\pi i (hu_r + kv_r + lw_r)}$ is called structure factor. If the atomic numbers are equal, we can pull the atomic form factor out of the sum

$$F(h,k,l) = \sum_{r} f_r \cdot e^{2\pi i(hu_r + kv_r + lw_r)}$$
(35)

$$\Rightarrow F(h,k,l) = f \cdot \sum_{r} e^{2\pi i (hu_r + kv_r + lw_r)}$$
(36)

$$\Rightarrow F(h,k,l) = f \cdot S(h,k,l) \tag{37}$$

S(h,k,l) is called geometrical structure factor. If it is equal to zero there are forbidden reflexes, even if the Bragg equation says that a reflex exists. Forbidden reflexes are not visible in the diffractogram.

5.4 Analysing Cu samples with Cu anodes

You can analyse a copper sample with the x-ray radiation of a copper anode, because the $K_{\alpha 1}$ -line belongs to the energy difference between the K- and the L-shell. So the radiation can only hit electrons out of the higher orbitals of a copper atom, because the energy is not high enough to fully eject electrons from the innermost shells of the atom. The radiation which is emitted (so called fluorescence-x-ray-radiation) can be identified in the diffractogram.

5.5 Grain size weight

The Scherrer equation reads:

$$\Delta 2\theta = \frac{0,89 \cdot \lambda}{B \cdot \cos \theta} \tag{38}$$

 $\Delta 2\theta$ is the widening of the Bragg reflexes, because of the limited grain size. B is the grain size. In this case $\Delta 2\theta$ is the full with at half maximum of the peaks (FHWM). Small values for $B \ (B \ll 1 \text{\AA})$ result in large values for the FHWM, whereas large values for B result in small values for the FHWM. This means that small values for B must have a greater weight in the average than larger values for B.

5.6 Consequences of inelastic scattering

The physical size which is responsible for this is the Debye-Waller factor. It describes the intensity of the peaks in relation to the temperature:

$$I = I_0 e^{-\frac{1}{3}|\vec{G}|^2 \langle u^2 \rangle} \tag{39}$$

The size $\langle u^2 \rangle$ is the root mean square of the deviation of the position of the atoms in the lattice and \vec{G} is a reciprocal lattice vektor. If the temperature increases, the atoms in the lattice oszillate more and u gets larger. We see that the intensity decreases, because the argument of the exponential in the Debye-Waller factor is negative. Therefore the peaks shrink with increasing temperature.

U does also depends on the elastic constants of our sample. There are two effects:

- The thermal agitation causes the planes to deviate from the mathematical planes used by the Bragg law. The reinforcement of the scattered waves is not really perfect. Therefore the intensity of the peaks is lower.
- Temperature causes diffuse scattering: the vibration of the atoms causes general coherent scattering in all directions thus increasing the background of the diffractogramm.