

# **An experiment to measure X-ray diffraction in various samples and determine their lattice constants.**

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## **Abstract:**

Using an x-ray diffractometer 4 Bragg angles were recorded at distinct peaks for two samples, NaCl and KCl. These values were then used to find the lattice constants for both samples. From this it could be determined which sample was which. The calculated lattice constant for Sample 1 was  $5.66 \pm 0.044\text{\AA}$  which was found to be consistent with the known value of NaCl. Sample 2 was found to be  $6.37 \pm 0.00763\text{\AA}$  which was not found to be consistent with KCl, however this was due to a small error on the lattice constant. Overall, the experiment can be called a success.

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## **1. Introduction**

X-ray diffraction is an analytical technique based on the diffraction of x-rays by matter [1]. Diffraction occurs from the planes of the matter which are labelled using miller notation (hkl) where h, k and l are all integers. The process of x-ray diffraction by crystals was discovered by Max Von Laue in 1912 when he sent a beam of x-rays through a copper sulphate crystal and recorded the results on a photographic plate [2].

At this point in time x-rays had only been discovered seventeen years prior, so much was still unknown about their nature. Many scientists believed it was some form of electromagnetic radiation but before Max von Laue's experiment there was no evidence of this. Within a year of Laue's experiment William Lawrence Bragg had discovered the rules that govern the diffraction pattern of x-ray crystals and determined them as:

$$2d\sin\theta = n\lambda$$

*Equation 1 – Braggs law.*

Equation 1 became known as Braggs law, both Laue and Bragg were awarded the Nobel prize in 1914 for the discovery of x-ray diffraction and the analysis of crystal structures by x-rays respectively [2]. They are also both credited with the discovery of two new fields of physics, x-ray crystallography and x-ray spectroscopy.

The main purpose of this experiment was to find the lattice constants of 2 samples, NaCl and KCl. Before the experiment began it was not known which sample was which so at the end of the analysis it had to be stated which sample was which, this was another main aim of the experiment.

To determine these values, both samples were ground up into a fine paste using a pestle and mortar. This sample was then placed into a  $^{29}\text{Cu}$  x-ray diffraction machine and rotated across a known angle. This was performed four times for each sample and a mean angle was found. From this the lattice constants could be determined. A more detailed description of how the experiment was conducted can be found in the methodology.

## 2. Theory

Braggs law gives the angles for coherent scattering of waves from a crystal lattice [3].

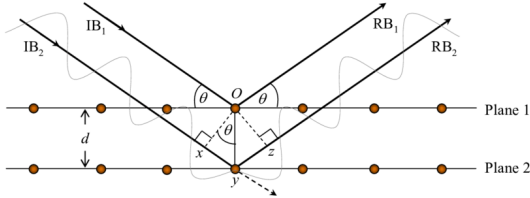


Figure 1 – A diagram showing Bragg's law.

Figure 1 shows a diagram of how Bragg's law applies to hkl planes. The x-rays are fired at the planes of a sample and if Bragg's condition is met then constructive interference begins to take place and x-rays are diffracted off the crystals surface.

The quantity  $\mathbf{q}$  is the vector perpendicular to the hkl planes of atoms diffracting the waves and is defined by  $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ , where  $\mathbf{k}$  is defined as:

$$k = \frac{2\pi}{\lambda}$$

Equation 2 – The wave number equation.

The set of vectors  $\mathbf{q}$  represent the diffraction from a crystal lattice at the position of points which lie on the lattice. These values do not exist in real space but rather in  $\mathbf{k}$  or  $\mathbf{q}$  space, where the magnitude of  $\mathbf{q}$  is proportional to the reciprocals of distances in real space. The magnitude of  $\mathbf{q}$  is given by:

$$q = 2k \sin \theta$$

Equation 3 – The magnitude of  $\mathbf{q}$

The combination of equation 1 and 3 gives Bragg's law for cubic crystals:

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

Equation 4 – Bragg's law for a cubic crystal.

In this equation  $a$  is the lattice constant and  $h$ ,  $k$  and  $l$  are the planes of the crystal (Full

derivation can be found in Appendix B for all equations). When another atom is added to the unit cell a new crystal is created, consider this new atom placed at position vector  $\mathbf{R}$ . When Bragg's law is satisfied for the atoms in the original crystal, the scattered waves are in phase for this atom but not necessary for the new atom at vector  $\mathbf{R}$ . The phase difference of waves scattered from both atoms is as follows:

$$\Delta\phi = \mathbf{q} \cdot \mathbf{R}$$

Equation 5 – The phase difference between 2 atoms in a unit cell.

Equation 5 is important as it allows for the calculation of the amplitude of the scattered waves in the crystal. The combination of these waves plus the number of atoms in the crystal ( $n$  atoms) will give us the structure factor:

$$A_{hkl} = \sum A_i e^{i\mathbf{q} \cdot \mathbf{R}_i} = \sum A_i [\cos(\mathbf{q} \cdot \mathbf{R}_i) + i \sin(\mathbf{q} \cdot \mathbf{R}_i)]$$

Equation 6 – The structure factor

The structure factor shows the intensities of x-rays diffracted by the crystal. The actual intensity for each hkl plane can be calculated using the following equation:

$$I_{hkl} = A_{hkl}^2$$

Equation 7 – The intensity of each hkl plane.

Before the main experiment began models of various cubic crystal structures were made including our samples of NaCl and KCl.

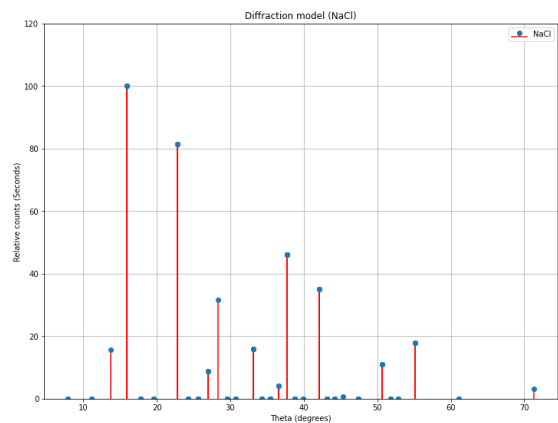


Figure 2 – A model of NaCl's cubic structure

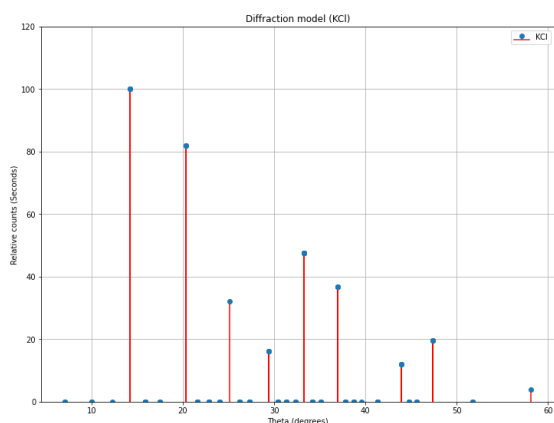


Figure 3 – A model of KCl's cubic structure

Both figures 2 and 3 show models of the samples used in the experiment. As it was not known which sample was which when the experiment began both these figures were used as a reference point to determine which angles to measure over and approximately figure out which sample was which. Although the main method of determining the samples was through finding out the lattice constants, the peaks in the data could also be compared to the peaks in the model to ascertain which sample was NaCl and which was KCl.

### 3. Methodology

Before the experiment could begin the x-ray machine had to be calibrated.

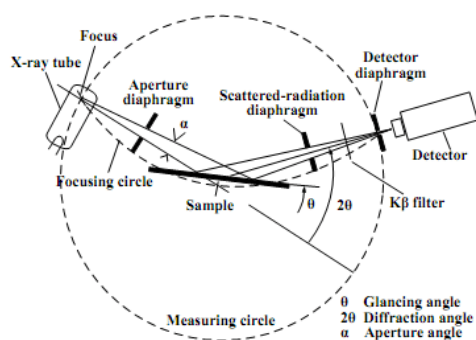


Figure 4 – A diagram to show the inner workings of the x-ray diffraction machine.

The machine used in this experiment was a Cu x-ray diffractometer. Two apertures could be placed into the machine, a 2mm aperture and a Ni foil aperture (0.01mm), the diffractometer was calibrated for both. The 2mm aperture was calibrated first, it was placed into the

diffractometer as well as a Lithium Fluoride crystal. The LiF crystal was used as it will diffract the x-rays according to Bragg's law. It was also good for checking the calibration was a success as it gives two distinct peaks.

Once everything was in place the diffractometer doors were shut and the detector was rotated from  $0^\circ$  to  $45^\circ$ . This outputted two clear distinct peaks showing that the calibration was a success. The process was then repeated for the Ni aperture. The only difference between the two calibrations was that the 2mm aperture showed two distinct peaks whereas the Ni foil only showed one. This is because the 2mm aperture shows the beta peaks of the samples whereas the Ni only shows the alpha.

The next step was to perform a rocking curve. This is a process where the detector angle is kept constant at  $2\theta$  where  $2\theta$  is found by Bragg's law. The crystal was then rotated from  $0^\circ$  to  $45^\circ$  giving 1 distinct peak for both apertures at  $22.5^\circ$  ( $2\theta$  at  $45.5^\circ$ ) showing the quality of the crystal was good (All calibration data in Appendix B).

Once calibration was over the samples could be prepared. Sample one was a fine salt like compound and sample 2 was a bulkier mixture. Both samples were ground up in a pestle and mortar for appropriately 20 minutes until they were a fine powder. The samples were then transferred into a receptacle using a spatula and flattened out using a fine piece of glass. This was to ensure the sample was completely smooth.

For sample 1 the diffractometer had an angle range of  $0^\circ$  to  $60^\circ$  with an integration time of 1 second. This was to obtain a full spectrum of the sample and see where the peaks were. The integration time is how long the machine takes one measurement for. Using the full spectrum scan and figures 2 and 3 as a reference the four biggest peaks were taken for each sample.

The integration time was increased depending on how small the peak was. For example, the

first 2 peaks for sample one used an integration time of 20 seconds, however this was not accurate enough for the smaller peaks, so the integration time was increased to 30 seconds. Once it was clear where the peaks were for each sample the angle range was dramatically decreased to only a few degrees either side of where the peak was. For instance, the first peak of sample one was taken between  $14^{\circ}$  to  $18^{\circ}$ .

The four biggest peaks were taken in total for each sample, this was determined to be enough data to work out a lattice constant for each sample. More peaks would have been taken, however, given the resolution of the x-ray diffractometers this was not possible as it was incredibly difficult to distinguish the peaks from the background data. For sample 1 the 2mm aperture was used, this was changed to the Ni foil aperture for sample 2 to avoid any beta peaks.

#### 4. Results and analysis

The four peaks from each sample clearly fit a gaussian distribution (gaussian fits not included in the main report will be Appendix B).

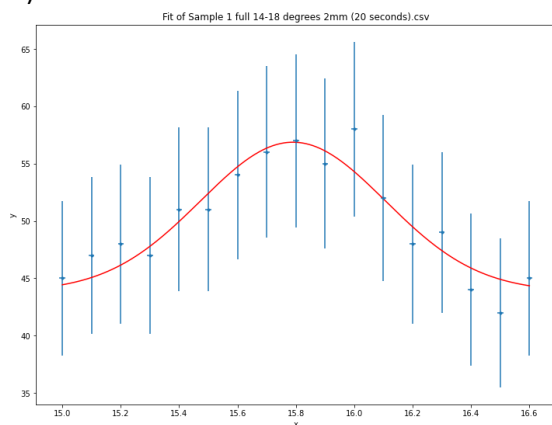


Figure 5 – Gaussian distribution for Sample 1 peak 1.

Figure 5 shows the first peak from sample 1 following a gaussian distribution between  $14^{\circ}$  and  $18^{\circ}$ . This was the biggest peak detected in this sample, as a result it was very clear between what range the gaussian should be measured from ( $15^{\circ}$  and  $16.6^{\circ}$  in this case) leading to a good fit for the data. This is further supported by the chi square value of 0.07 proving the expected results are a good fit for our calculated values.

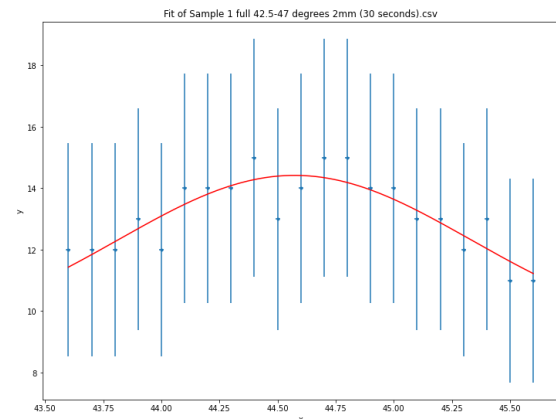


Figure 6 – Gaussian distribution for Sample 1 peak 4

Figure 6 shows the gaussian distribution for the 4<sup>th</sup> peak taken from sample 1. The chi squared value for this graph was 0.03 which shows the fit is an excellent match for the data. However, looking at figure 6 the distribution is clearly not as good as figure 5. The reason for this poor fit is because as the relative counts of the peaks got smaller, it became harder to determine a clear peak from the data.

For example, with figure 6 it was evident there was a peak between the angle range, however the peak was so small compared to the background data that the background data points either side of the peak had as many relative counts as the peak itself. This is due to the resolution of the x-ray diffractometer being used, as it was not high enough to properly distinguish these peaks. This explains why the chi squared value is so good despite the final graph being so poor.

Figure 6 was taken between an angle range of  $42.5^{\circ}$  and  $47^{\circ}$ , looking at figures 2 and 3 it can be estimated that sample 1 is NaCl based on where the peaks occurred.

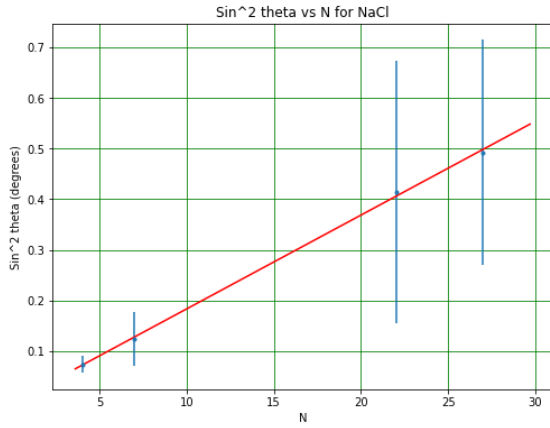


Figure 7 – A graph of  $\sin^2\theta$  vs N for Sample 1

Figure 7 shows the graph used to calculate the lattice constant for sample 1. The  $\theta$  values in this graph are obtained from the mean each gaussian graph. The value of N is calculated as follows:

$$N = \frac{\sin\theta^2}{\sin\theta^2[0]} (\text{Multiplied Ratio})$$

Equation 8 – The N value

In equation 8, the denominator in the fraction was the first value in the array and the multiplied ratio was the number which got each value closed to an integer. It should be noted that through the combination of equation 1 and 4 it can be found that N is also equal to:

$$N = h^2 + k^2 + l^2$$

Equation 9 – Alternative equation for N.

The chi squared value for figure 7 was 0.0082791 shown the expected values were a good fit for the known values. The errors on N were negligible but the errors on  $\sin\theta^2$  were calculated using the following equation:

$$\sin\theta_{err}^2 = 2\sin\theta\cos\theta\theta_{err}$$

Equation 10 – The error on  $\sin\theta^2$

Looking at figure 7 the errors increase massively with the N value. This is because the  $\theta_{err}$  got large as the relative counts increased. This was due to the poor gaussian peaks as  $\theta$  increased.

To calculate the lattice constant the gradient of the graph was taken and used in the following equation:

$$a = \frac{\lambda^2}{4m}$$

Equation 11 – Lattice constant from gradient

The lattice constant obtained for sample 1 was  $5.66 \pm 0.044\text{\AA}$ . Comparing this too the known lattice constant of  $5.64\text{\AA}$ [4] for NaCl the calculated values error falls within the known error. The error on this value was calculated as follows:

$$a_{err} = \frac{1}{2} \frac{m_{err}}{0.024} a$$

Equation 12 – The error on the lattice constant

The standard error on the known value for the NaCl lattice constant was  $\pm 0.01\text{\AA}$ . To check the calculated value was consistent with the known a consistency check was performed:

$$x_1 - x_2 < 3\sqrt{\Delta x_1^2 + \Delta x_2^2}$$

Equation 13 – The consistency check

The consistency check output was that there was consistency between the two values. This proves definitively that Sample 1 was NaCl.

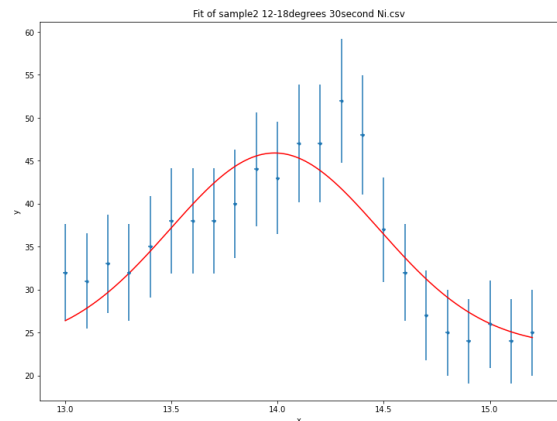


Figure 8 – Gaussian distribution for Sample 2 peak 1

Figure 8 shows the gaussian fit for the first peak of sample 2. The chi squared for this plot was 0.47, while this is a very good chi squared value it was not as good as the sample 1 values.

This is because the peak was uneven, this can be observed in figure 8 as the gaussian fit does not perfectly match the data.

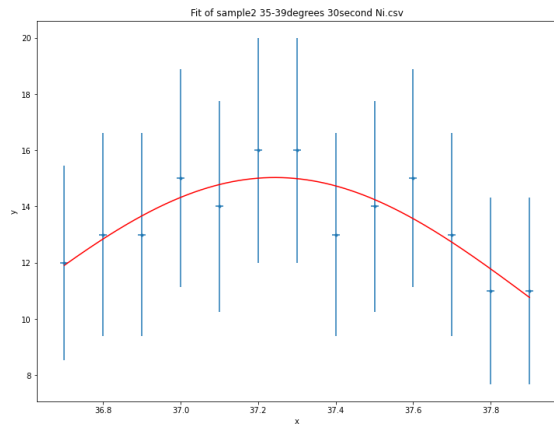


Figure 9 – Gaussian distribution for Sample 2 peak 4

Figure 9 shows the gaussian fit for the 4<sup>th</sup> peak. The chi squared for this fit was 0.07. while this is an excellent chi squared value this plot suffers from the same problem as peak 4 of sample one, that being the poor resolution of the detector making this fit less accurate than the previous fits. Comparing figures 5 and 6 to figures 8 and 9 the gaussian fits for Sample 1 were much more accurate than Sample 2. This means that less accurate average  $\theta$  values were obtained for Sample 2 as a result.

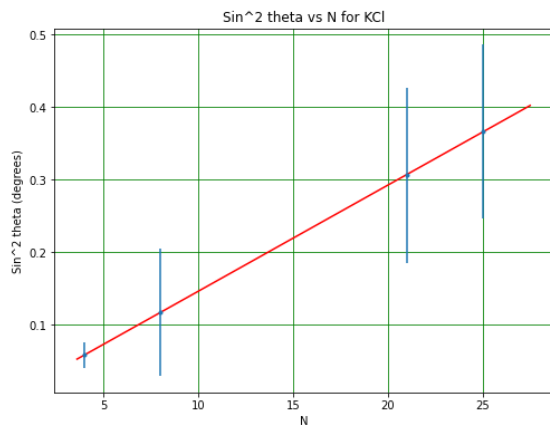


Figure 10 -- A graph of  $\sin^2\theta$  vs N for Sample 2

Figure 10 shows the graph to calculate the lattice constant for sample 2. The chi squared values for this graph was 0.000129 showing the linear fit was a good approximation for the data points. Finding the lattice constant for this plot using the same method as sample 1, a value of  $6.37 \pm 0.00763\text{\AA}$  was calculated. The

known value for KCl is  $6.36\text{\AA}$ [5] This technically falls outside the calculated error showing that this part of the experiment was not a success, this is further supported by the consistency check not being consistent.

Despite this result, it can still be concluded that this sample is KCl. The accepted value was only 0.01 away from the calculated value, the reason the sample was not consistent was because the error was so small. The error reason for this is that the  $m_{err}$  on figure 10's gradient is so small leading to the modest error on the result.

As well as the lattice constant, the mean crystal size was also calculated for each gaussian peak. This involved taking the full width half maximum of the peak, done using the following equation:

$$\beta = 2\sqrt{2\ln(2)}\sigma$$

Equation 14 – The full width half maximum

In equation 14  $\sigma$  is the full width of the gaussian. After this value was determined the Scherrer equation was used to find the crystal size:

$$L = \frac{0.9\lambda}{2\beta\cos\theta}$$

Equation 15 – The Scherrer equation

Using equation 15 the mean crystal size for figure 5 was found to be  $54.75 \pm 13.45\text{\AA}$ . This is above the lattice constant for NaCl showing it is a feasible answer for the mean crystal size, however the error on this value is relatively large. This gets worse for less accurate gaussians as figure 6's mean crystal size was  $31.14 \pm 21.90\text{\AA}$ . This error is 70% of the calculated value which is incredibly high. The equation to calculate these errors was:

$$L_{err} = \sqrt{\beta_{final\ err}^2 + \theta_{final\ err}^2}$$

Equation 16 – The error on meal crystal size

The reason for these extremely large errors are a result of the poor gaussian fits. The error on

the widths of the gaussians were very high often being either the same size of the width or even higher. The most extreme case of this was on figure 6 where the width was 0.76 and the width error was 2.48. This leads to a substantial error on  $\beta_{err}$  causing the large error on  $L_{err}$ .

## **5. Discussion**

Only sample 1's lattice constant was found to be consistent with the known value whereas sample 2 was not. However, despite sample 2 not being definitively proven as KCl it can still be confidently stated that sample 2 was KCl so overall the experiment can be called a success. The main reason why sample 2 was not consistent was because of the exceptionally small error of  $\pm 0.00763\text{\AA}$ . As there was marginal room for error with this sample it would have been very unlikely that a consistent lattice constant would have been obtained using the same method and equipment.

The reason for this small error comes down to drawbacks in the resolution of the x-ray diffractometers and as a result the produced gaussian plots. As can be seen in figures 6 and 9 the gaussian fits are very poor. Although the plots fit the data well, they do not represent a true gaussian fit but rather just the curve of the gaussian and not the "tails" that are often seen either side of a typical gaussian. This causes a massive error on the width giving a skewed final Bragg angle for that for that gaussian peak. Resulting in a poor final error for the lattice constant.

The reason the gaussian peaks appear inferior as the angle increases is due to the poor resolution on the x-ray diffractometers. The relative intensity of the low angle peaks was large, this resulted in easy distinguishable peaks from the background data. As the angle increased these peaks became harder to detect. To compensate for this, the integration time was increased to help highlight the peaks more.

This experiment was limited by time so the integration time could only be set so high to account for all the data to be collected within a reasonable time frame. As a result, some of these high Bragg angle gaussians intensity were not that much higher than the background data. This is what caused the lack of "tails" on the gaussian resulting in the poor gaussians fits.

Comparing the positions of the gaussians on figures 5, 6, 8 and 9 to the models in figures 2 and 3. It can be observed that the low Bragg angle peaks match up with the model well, whereas the high angle peaks do not. This can be attributed to the diffractometer being uncalibrated. The first two peaks for NaCl and KCl were taken all on the same day after the diffractometer had undergone a full calibration. However, the second two peaks for both samples were done on a different day, although a calibration was performed on this day it is possible it may not have been done correctly leading to inaccurate Bragg angles for these peaks.

Overall, if the experiment was to be repeated it could be improved by using a higher resolution diffractometer that could produce more defined peaks without the need to increase the integration time by a substantial amount. Only 4 peaks from each sample were taken during this experiment, so to improve the accuracy of the lattice constant more peaks could be taken for each sample. To do this more time could go to collecting the results.

## **6. Conclusion**

To conclude, x-ray diffractometer can be used to find peaks where constructive interference occurs. Gaussian distributions can be plotted to these peaks, 4 peaks for both NaCl and KCl were plotted, and the average Bragg angle was found. From this these values could then be plotted against  $N$  to obtain a value for the lattice constant.

Despite sample 2 not being found consistent with KCl the experiment was a success. If this

experiment was to be repeated higher resolution diffractometers would have to be used and more time would have to be given to collect more than 4 peaks from each Sample.

## 7. References

- [1] - Sima, F., Ristoscu, C., Duta, L., Gallet, O., Anselme, K. and Mihailescu, I.N. (2016). *Laser thin films deposition and characterization for biomedical applications*. [online] Available at: [https://www.sciencedirect.com/topics/materials-science/x-ray-diffraction#:~:text=X%2Dray%20diffraction%20\(XRD\)%20is%20an%20analytical%20technique%20based](https://www.sciencedirect.com/topics/materials-science/x-ray-diffraction#:~:text=X%2Dray%20diffraction%20(XRD)%20is%20an%20analytical%20technique%20based) [Accessed 19 Dec. 2021].
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- [5] - Schwabegger, G., Djuric, T., Sitter, H., Resel, R. and Simbrunner, C. (2013). Morphological and Structural Investigation of Sexithiophene Growth on KCl (100). *Crystal Growth & Design*, [online] 13(2), pp.536–542. Available at: <https://www.ncbi.nlm.nih.gov/pmc/articles/P>

MC3567699/#:~:text=KCl%20exhibits%20a%20face%20centered [Accessed 19 Dec. 2021].

## 8. Appendix A – Error calculation

Error on  $\sin\theta^2$ :

$$\frac{\sin\theta^2}{\frac{d}{d\theta}\sin\theta^2}$$

$$\sin\theta_{err}^2 = \sin\theta\cos\theta\theta_{err}$$

Error on lattice constant:

$$a_{err} = \frac{1}{2} \frac{m_{err}}{0.024} a$$

Error on mean crystal size:

$$L = \frac{0.9\lambda}{2\beta\cos\theta}$$

$$\frac{d\beta}{dL} = \frac{0.9\lambda}{2\cos\theta} \frac{1}{-\beta^2} \beta_{err} = \beta_{final\ err}$$

$$\frac{d\theta}{dL} = \frac{0.9\lambda}{2\beta} \frac{\sin\theta^2}{\cos\theta}$$

$$\frac{d\theta}{dL} = \frac{0.9\lambda}{2\beta} \tan\theta^2 \theta_{err} = \theta_{final\ err}$$

$$L_{err} = \sqrt{\beta_{final\ err}^2 + \theta_{final\ err}^2}$$

## 9. Appendix B – Other relevant information

Derivation of equations

Equation 4:

$$q = 2k\sin\theta$$

$$2d_{(hkl)}\sin\theta = \lambda = \frac{2\pi}{k}$$

$$2d_{(hkl)}k\sin\theta = 2\pi$$

$$q = \frac{2\pi}{d_{(hkl)}}$$

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

Equation 5:

$$\Delta r = R[\cos(\pi - \theta - \alpha) + \cos(\theta - \alpha)]$$

$$\Delta r = R[\cos(\theta + \alpha) + \cos(\theta - \alpha)]$$



$$\Delta r = R[-\cos\theta\cos\alpha + \sin\theta\sin\alpha + \cos\theta\cos\alpha + \sin\theta\sin\alpha]$$

$$\Delta r = 2R\sin\theta\sin\alpha$$

$$\Delta\phi = \frac{\Delta r}{\lambda} 2\pi = k\Delta r = 2kR\sin\theta\sin\alpha$$

$$\Delta\phi = q \cdot R$$

Equation 6:

$$A_1 e^{i(k \cdot r - \omega t)}$$

And

$$A_2 e^{i(k \cdot r - \omega t + \Delta\phi)}$$

$$A_{sum} = A_1 e^{i(k \cdot r - \omega t)} + A_2 e^{i(k \cdot r - \omega t + \Delta\phi)}$$

$$A_{sum} = [A_1 + A_2 e^{i\Delta\phi}] e^{i(k \cdot r - \omega t)}$$

$$A_{sum} = [A_1 + A_2 e^{i(q \cdot r)}] e^{i(k \cdot r - \omega t)}$$

$$A_{sum} = A_1 + A_2 e^{i(q \cdot R)}$$

$$A_{sum} = \sum A_i e^{i(q \cdot R_i)}$$

$$A_{hkl} = \sum A_i e^{i q \cdot R_i} = \sum A_i [\cos(q \cdot R_i) + i \sin(q \cdot R_i)]$$

### Calibration data

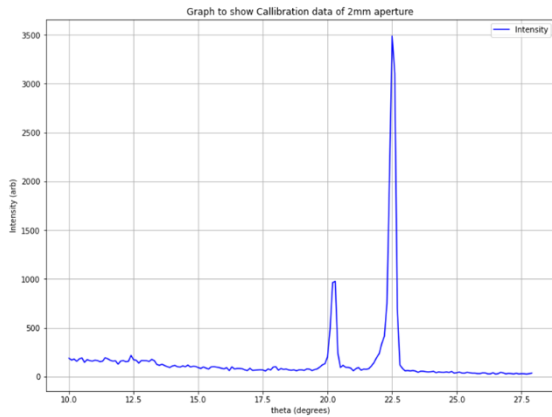


Figure 11 – 2mm aperture calibration

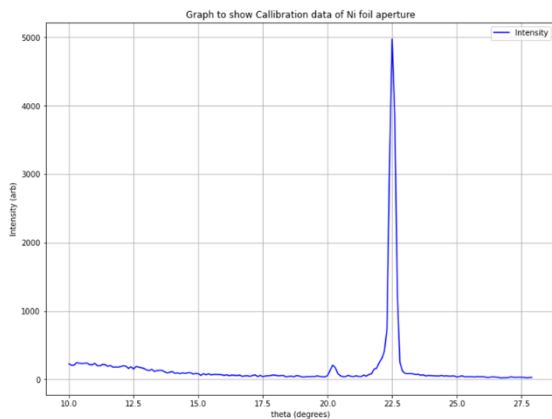


Figure 12 – Ni foil calibration

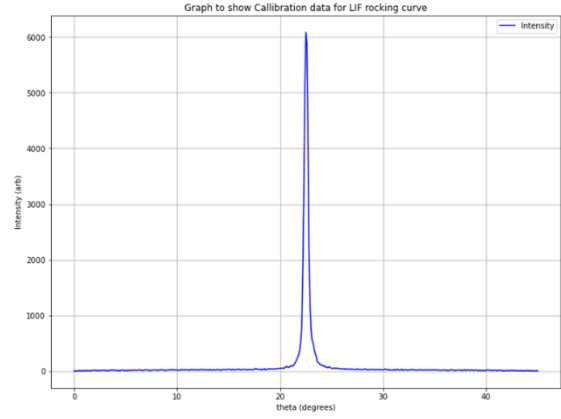


Figure 13 – Rocking curve calibration

### Gaussian data not included in main report

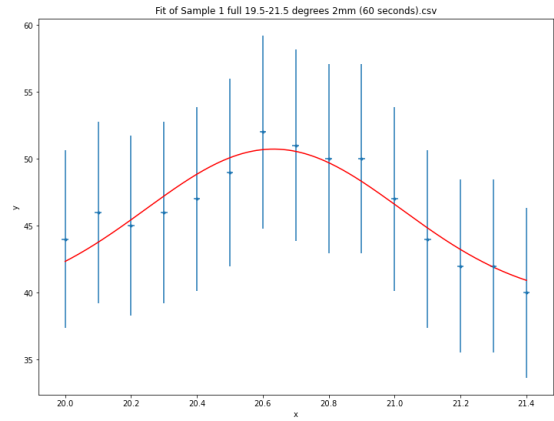


Figure 14 – Gaussian fit of sample 1 peak 2

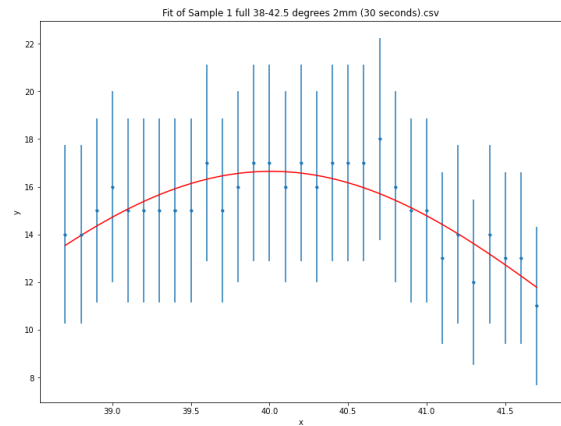


Figure 15 – Gaussian fit of sample 1 peak 3

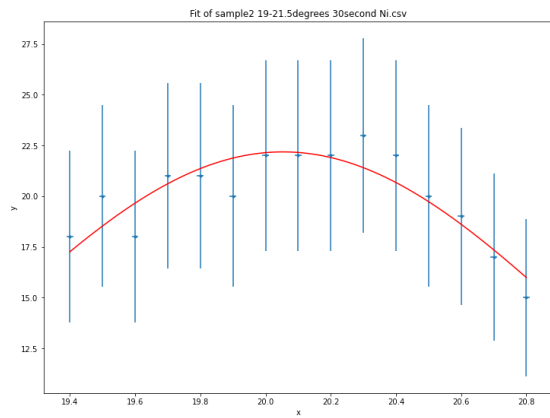


Figure 15 – Gaussian fit of Sample 2 peak 2

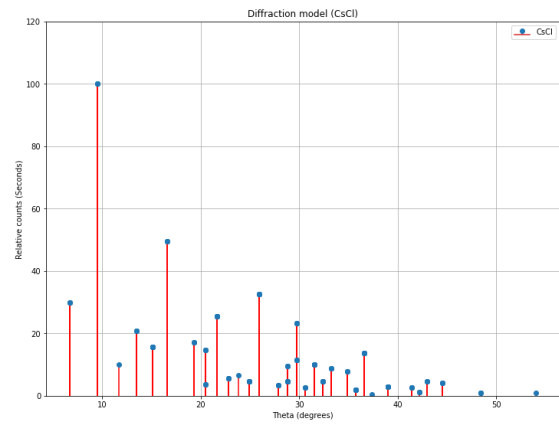


Figure 18 – A model of a CsCl crystal structure

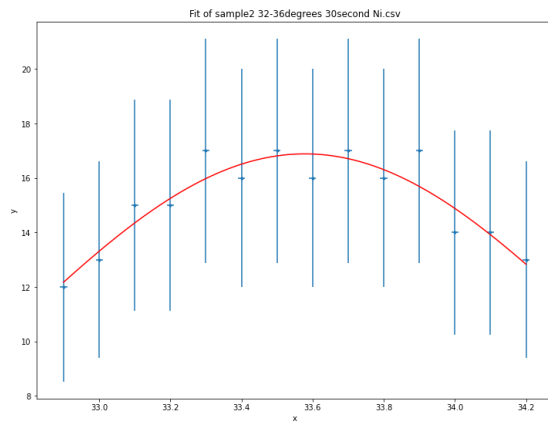


Figure 16 – Gaussian fit of Sample 2 peak 3

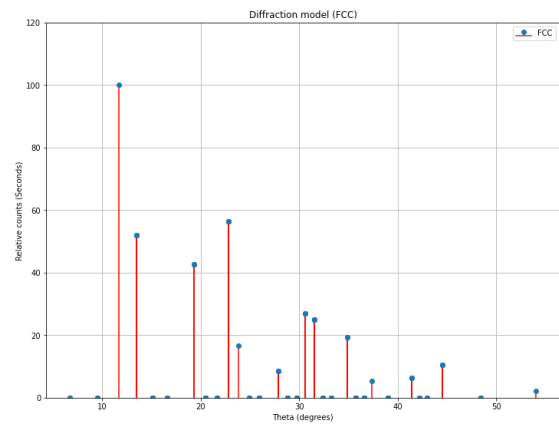


Figure 19 – A model of an FCC crystal structure

### Models not included in main report

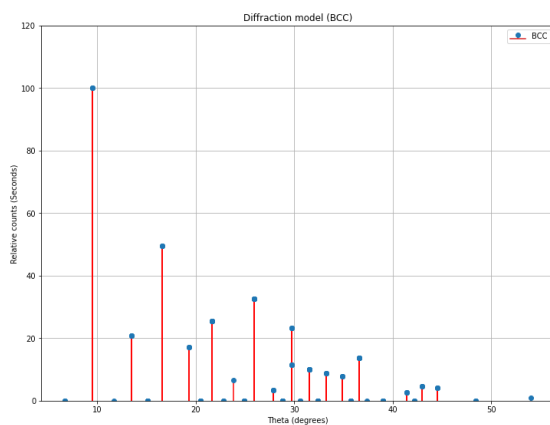


Figure 17 – A model of a BCC crystal structure

