

# X-ray structural analysis: Bragg reflection and Laue diagrams

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The experiment consisted of determining the lattice constants of monocrystals using Bragg reflection. The second part of the experiment was investigating the lattice structure of monocrystals. Using the adjusted Bragg's law for the crystals that have cubic structure (NaCl and LiF), the lattice constant for NaCl has been determined to be  $565.1 \pm 0.7$  pm, which is 0.1% off from calculated value 565.2 pm. The lattice constant for LiF has been determined to be  $402.4 \pm 0.9$  pm, which is 0.1% from calculated value 402.7 pm. In the second part, using obtained Laue diagrams, It has been noted that the Laue spots for NaCl and LiF crystals are highly symmetrical. At the same time it has been noted that if  $\Delta t$  and  $L$  are being varied, the shape of the Laue diagrams is going to remain the same, with constant values for spacing of lattice planes, Bragg angle and wavelength.

## I. INTRODUCTION

The problem of the determining the crystal structure was tackled by numerous English scientists that proposed three-dimensional models of possible structures. But the problem was that the investigations were not systematic and at the time, reality of the atom was still not universally accepted. Furthermore, there was no way how to actually determine a space group and test the theory that the atoms of crystal structures were actually arranged in patterns, that is predicted by space-group theory.[1]

In 1895 Roentgen discovered x-rays. There were different theories of what nature X-ray could be. Wiechert and Stokes believed that the X-rays must be short waves consisting of electromagnetic pulses. At the same time, W. H. Bragg believed in the corpuscular theory of X-rays[1, p. 1-6]. To be able to talk about the actual nature of X-rays we have to understand the phenomenon of diffraction of visible light by gratings. After diffraction experiments were conducted on a fine wedge-shaped slit, it was assumed that the radiation had the same wave properties as light, even though it was of a shorter wavelength. Von Laue came to an idea that the lattice structure could serve as natural three dimensional diffraction grating for a radiation provided that wavelength and cell side were of the same order of magnitude. He also assumed that the lattice points should be occupied by atoms or molecules.

Von Laue's initial experiments failed. After some adjustments, his experiment succeed, he proved the periodic arrangement of atoms in crystals. The wave nature of X-rays, and theory named after him: von Laue's diffraction theory. For his experiment he used a crystal of cubic ZnS, which was placed in the path of a fine beam X-rays. Photographic plate, that was used to record the effects, was placed behind the crystal and normal to the beam. ZnS crystal managed to produce only a specific selection of the diffraction spots. Laue described this by attributing five wavelengths in the radiation. The results of his experiments were published in 1912.[1]

Laue's publication produced a lot of new interest in determining the crystal structure, especially in England.

W. H. Bragg and his son W. L. Bragg shared the interest in Laue's work, and decided to do their own experiments to test Laue's work. W. L. Bragg confirmed that Laue's photographs were due to diffraction, but the explanation for the spots needed to be modified. He observed that the diffracted beam was being reflected by the crystal, which could be explained if the diffraction effect can be seen as a reflection of X-rays from the lattice planes of the crystal. W. L Bragg's tests of this theory showed that all wavelengths over a certain range were represented in the X-ray beam and that the reflection effect was equivalent to a selection from the continuous spectrum of wavelength determined by spacing of the lattice planes parallel to the plate surface of the mica crystal. This lead him to formulation of his famous Bragg's law:

$$n \cdot \lambda = 2 \cdot d \cdot \sin\theta, \quad (1)$$

where  $n$  is an integer,  $\lambda$  is the wavelength of the incident wave,  $d$  is the spacing of the reflecting panes, and  $\theta$  is the angle of reflection.[1]

## II. THEORY

Before we start talking about diffraction patterns of x-rays, we should note two facts: 1) the incident beam and the diffracted beam are always coplanar; 2) the angle between the diffracted beam and the transmitted beam is always  $2 \cdot \theta$ . The condition under the diffraction occurs is that the wavelength of the wave motion is of the same order magnitude as the repeat distance between scattering centers.

We can see from Figure 1 that the second wave travels longer distance  $A'B'$  and  $B'C'$ , then the first wave. We can have constructive interference only if  $\Delta = A'B' + B'C'$  is a multiple of  $n \lambda$ , where  $n$  can have integer values of 1 and bigger. This gives us:

$$\Delta = n \cdot \lambda. \quad (2)$$

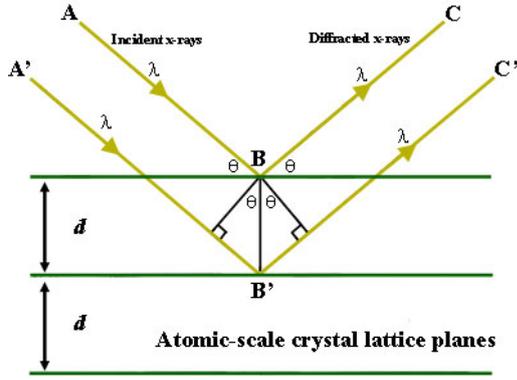


FIG. 1: Geometry behind Bragg scattering. The figure comes from [2].

Looking at the Figure 1, we can also note using geometry that :

$$\Delta = 2 \cdot d \cdot \sin\theta, \quad (3)$$

where  $d$  is the spacing between parallel lattices, and  $\theta$  is the angle of reflection. If we equate Equations 2 and 3 we get Equation 1, which is Bragg's law [3].

From Bragg's law, we can see that since  $\sin\theta$  has to be less than 1 (cause the max value sine function has is 1) :

$$\frac{n \cdot \lambda}{2d} = \sin\theta, \quad (4)$$

then  $n \cdot \lambda$  has to be less than  $2d$ . Since  $n=0$  means that the diffracted beam is in the same direction as transmitted beam, the lowest value that  $n$  can have is 1, which implies that:

$$\lambda < 2 \cdot d'. \quad (5)$$

Since for most crystals  $d < 3 \cdot 10^{-10}$  m, that implies that the biggest value that  $\lambda$  can have is  $6 \cdot 10^{-10}$  m [4, p. 95].

In the experiment only crystals with cubic structure are being used. The cubic structure is specific, because the lattice planes run parallel to the surfaces of the crystal's unit cells, which implies that spacing  $d$  is one half of the lattice constant:

$$d = \frac{a_0}{2}. \quad (6)$$

This can be seen graphically in Figure 2. From where it follows that:

$$n \cdot \lambda = a_0 \cdot \sin\theta, \quad (7)$$

where  $a_0$  is lattice constant. From here we can calculate the lattice constant for each of the crystals, NaCl and LiF. In this experiment x-rays that are used are the molybdenum x-rays. These x-rays have two lines, with corresponding wavelengths [5]:

$$K_\alpha = 71.08 \text{ pm}, K_\beta = 63.09 \text{ pm}. \quad (8)$$

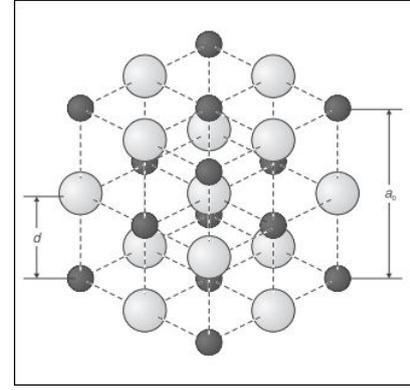


FIG. 2: Three-dimensional representation of the structure of NaCl. Picture taken from [5].

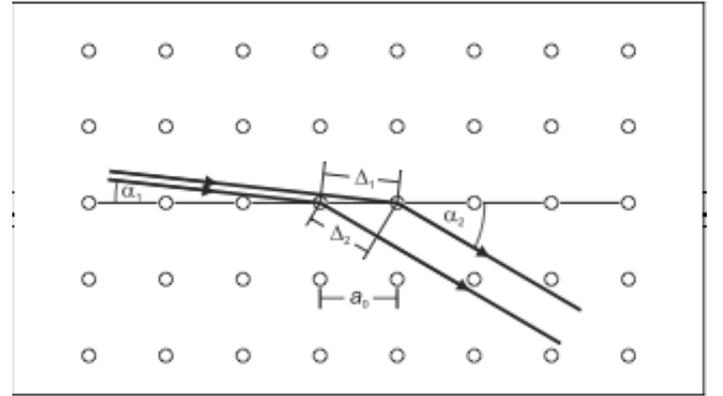


FIG. 3: Two dimensional representation of Laue condition of two neighbouring x-rays. Picture taken from [6].

The cubic structure of the crystals is also neat for determining the Laue condition for constructive interference, because the rows of the points associated with the three spatial directions are perpendicular to each other, with the distance between the points,  $a_0$ , always being the same.

Looking at Figure 3, we can see that the x-ray can be diffracted at different lattice planes. This implies that:

$$\Delta = \Delta_1 - \Delta_2 = a_0 \cdot \cos\alpha_1 - a_0 \cos\alpha_2, \quad (9)$$

where  $\alpha_1$  is an angle between the incoming x-ray and the row of points,  $\alpha_2$  is angle between the diffracted x-ray and the row of points. Now that we know this fact we can construct the Laue condition for constructive interference in three dimensions [6]:

$$a_0 \cdot \cos\alpha_1 - a_0 \cos\alpha_2 = h \times \lambda$$

$$a_0 \cdot \cos\beta_1 - a_0 \cos\beta_2 = k \times \lambda$$

$$a_0 \cdot \cos\gamma_1 - a_0 \cos\gamma_2 = k \times \lambda. \quad (10)$$

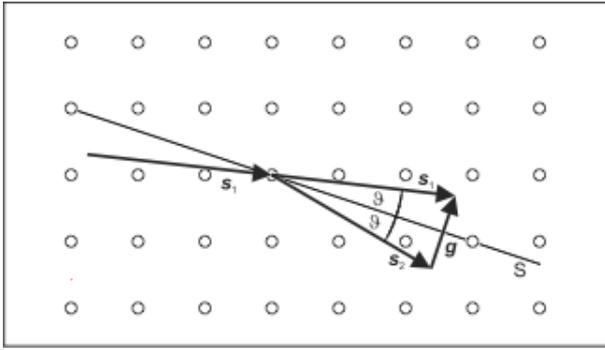


FIG. 4: Unit vectors  $s_1$  and  $s_2$ , and their connection with vector  $g = \lambda \cdot G$ . This comes from [6]

The quantities  $h, k, l$  are integer numbers and they are called Miller indices. In order to simplify our understanding of the theory let us introduce unit vectors, as seen in Figure 4.:

$$\begin{aligned} s_1 &= (\cos\alpha_1, \cos\beta_1, \cos\gamma_1) \\ s_2 &= (\cos\alpha_2, \cos\beta_2, \cos\gamma_2). \end{aligned} \quad (11)$$

Taking into consideration our new unit vectors we can rewrite Laue condition as:

$$s_1 - s_2 = \lambda \cdot G, \quad (12)$$

where  $B$  is vector of the reciprocal lattice, and is equal to  $B = (h, k, l) \cdot (1/a_0)$ . Since  $s_1$  and  $s_2$  are unit vectors, they have equal magnitudes, which implies that vector  $G$  is perpendicular to bisectrix  $S$  between the incoming and the diffracted x-ray. This implies, if we plug in the magnitude of vector  $G$ , that we get Bragg's law [6]:

$$\lambda = 2 \cdot \sin\theta \cdot \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}, \quad (13)$$

where:

$$d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}. \quad (14)$$

### III. PROCEDURE

The experiment consisted of two parts. First part was determining the lattice constants of monocrystals, NaCl and LiF, using Bragg's reflection. Second part of the experiment was investigating the lattice structure of monocrystals, NaCl and LiF, by analyzing Laue diagrams.

**Bragg Reflection:** The experimental apparatus consisted of X-ray apparatus Leybold 554 811 and NaCl

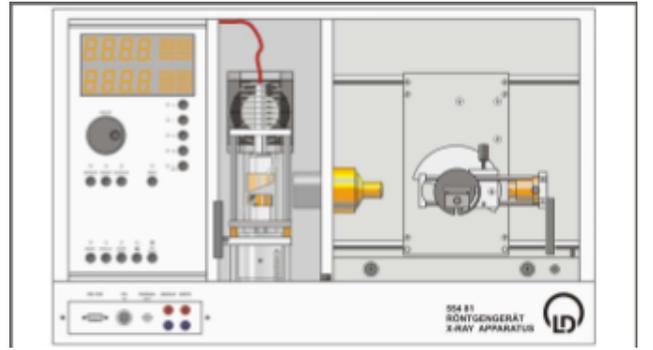


FIG. 5: X-ray apparatus (554 811) with goniometer.

and LiF crystals. The apparatus can be seen in Figure 5.

The apparatus already came setup, but the instructions on how to setup the Bragg configuration can be found in [5]. The first step that was done was to make sure that the apparatus is aligned properly according to the instruction sheet. There were some modifications done, the distance between slit diaphragm of the collimator and the target arm was set to 5 cm. The distance between the target arm and the slit diaphragm of the sensor was set to 6 cm. The apparatus was manually aligned to the zeroth position. Apparatus was also connected to PC using an USB cable. The program, X-ray Apparatus, needed to operate the apparatus and perform the data measurements was pre installed on the PC.

The first data run was performed using LiF. The crystal was placed on the appropriate holder on goniometer, and tightened with the knurled screw. The voltage of the tube was set to  $U = 35$  kV, while the current emission was set to  $I = 1$  mA. Maximum counting rate for the sensor mode was found at the angle  $19.7^\circ$ , and for the target mode it was at the angle  $10.3^\circ$ . After the system has been aligned the data measurement has been taken with the following configuration:  $U = 35$  kV,  $I = 1$  mA,  $\Delta\beta = 0.1^\circ$ ,  $\Delta t = 10s$ , and  $\beta$  going from  $4^\circ$  to  $34^\circ$ , where  $\Delta\beta$  is angular step. The data has been measured and transferred to the PC by pressing the SCAN key. Using the command "Calculate Peak Center" the width of each peak has been measured in order to find the glancing angle. The value of the angles have been recorded and the data has been analyzed, which will be discussed in the following section.

The second data run was performed using NaCl crystal. LiF crystal has been replaced with the NaCl crystal. Maximum counting rate for the sensor mode was found at the angle  $14.2^\circ$ , and for the target mode it was at the angle  $8.7^\circ$ . The data measurements have been taken with the same configuration, as in the previous part:  $U = 35$  kV,  $I = 1$  mA,  $\Delta\beta = 0.1^\circ$ ,  $\Delta t = 10s$ , and  $\beta$  going from  $4^\circ$  to  $24^\circ$ . The values for glancing angle have been found using the same way as for the previous part

for LiF. Data will be analyzed in the following section.

### Laue diagrams:

In order to perform this part of the experiment, the apparatus needed to be adjusted. The goniometer was removed. First part to removing the goniometer was to remove the sensor from its seat, and then the knurled screws of the bottom guide groove were removed. Goniometer was then slid to the left in the experiment chamber, and the cable was unplugged. The sensor arm was moved to position  $0^\circ$  and the goniometer was finally removed. Next step was placing the film holder inside the apparatus. The mounting plugs of the film holder were placed into the mounting sockets in the experiment chamber. Experiment was conducted with NaCl and LiF crystals [6].

First NaCl crystal was placed on the pinhole diaphragm of the collimator. Agfa Dentus M2 Comfort x-ray film was placed on the holder, aligned so that the center of the film matched the marked center of the film holder. The film was placed on the front side of the film holder (first data gathering was done with the film on the backside of the film holder, as gathered data wasn't as good as when the film was placed in front). The distance,  $L$ , between film holder and collimator was varied, between 15 and 11 mm. The data measurements were taken with  $U = 35$  kV,  $I = 1$  mA,  $\Delta\beta = 0.0^\circ$ ,  $\Delta t = 1800$ s. Third data run has been done with  $\Delta t = 2100$ s. After the film has been exposed to x-rays, next step was developing the film. This was done under the dark room conditions. Mixture for developing and fixing were first prepared. For developing three parts of water (300 ml) and 1 part of the developer (100 ml) were mixed in a tray. For fixing three parts of water (300 ml) and 1 part of the fixer (100 ml) were mixed in a tray. Film was first placed in the developer for approximately 2 minutes and 20 seconds. After that the film was washed under the running water for 15 s. Then the film was soaked into the fixer for 2 minutes. After that the film was again washed under the running water for 4 minutes in order to ensure radiograph quality required. After that films were scanned on a Epson scanner with a resolution of 1600 dpi. Next step was analyzing the scans using Canvas X. Scans were imported into Canvas, and the size of the films was set to 5.7 cm by 7.5 cm. The center of the coordinate system was set into the center of the Laue diagram, and the x and y coordinates were determined.

LiF crystals were also used to create Laue diagrams. NaCl crystal was removed, and LiF crystal was placed instead of it on the collimator. The data measurements were taken with  $U = 35$  kV,  $I = 1$  mA,  $\Delta\beta = 0.0^\circ$ ,  $\Delta t = 1200$ s. The distance  $L$  was varied from 11 to 15 mm. The film has been developed and the data has been analyzed in the same way as previously explained for the NaCl crystal. The purpose of this experiment is to evaluate Laue diagrams for NaCl and LiF. The experiment and coordinate system is setup as described in Figure 6.

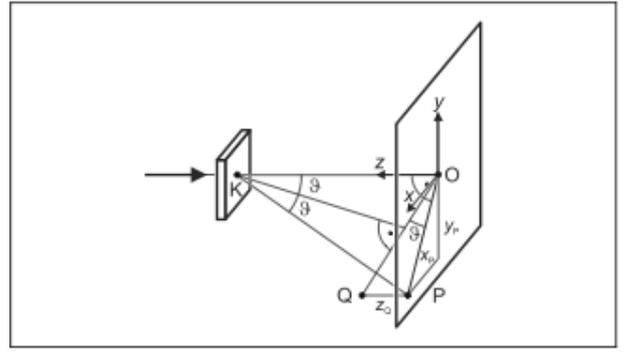


FIG. 6: Diagram of x-ray that is diffracted on the crystal at point K and hits the film at point P. Picture taken from [6].

The angle,  $2\theta$ , at which diffracted ray leaves the crystal can be represented from looking at Figure 4 as:

$$\tan 2\theta = \frac{\sqrt{x_p^2 + y_p^2}}{L}, \quad (15)$$

where  $L$  is the distance between the crystal and x-ray film. The coordinate  $z_Q$  can be calculated from the formula :

$$z_Q = \sqrt{x_Q^2 + y_Q^2 + L^2} - L. \quad (16)$$

NaCl and LiF crystals, that are used in this experiment, have been cut parallel to the plane (1 0 0). From here it follows that:

$$h : k : l = x_Q : y_Q : z_Q, \quad (17)$$

where  $h, k, l$  are smallest triple of integers that fulfill Equation 17. The spacing of lattice planes can be calculated from the Equation 14, and the wavelength can be calculated from Equation 14, and the Bragg angle can be calculated from [6]:

$$\theta = \arctan\left(\frac{l}{\sqrt{h^2 + k^2}}\right). \quad (18)$$

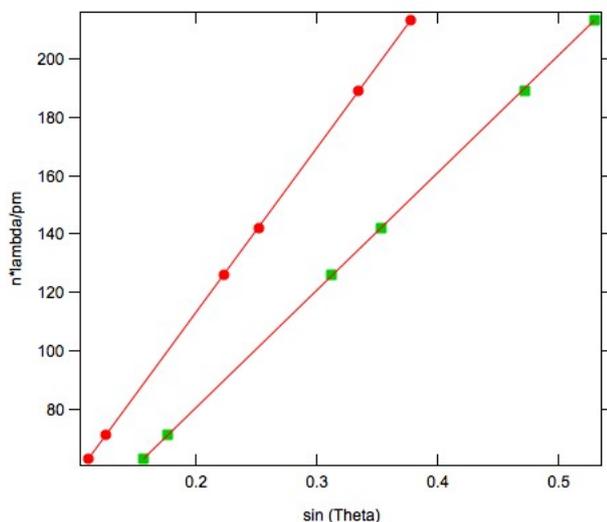
## IV. RESULTS & ANALYSIS

The goal of the first part of the experiment was determining the lattice constants of monocrystals using Bragg reflection. This was done using Equation 7 where values for  $\lambda$  have been represented by wavelengths for  $K_\alpha$  and  $K_\beta$ , as given in Equation 8. Values for glancing angle have been measured as described in procedure section. Values for  $n$  ran from 1 to 3, where each index had a two values, one for  $K_\alpha$  and other for  $K_\beta$ . The values for each valuable can be seen in Figure 7 and 8. In order to calculate lattice constant  $a_0$  for both crystals Equation 7 has been used, where  $a_0$  represents the slope of  $n/\lambda$  versus  $\sin\theta$ . The graph representation of this

$\Theta(\text{LiF})$	$\sin \Theta(\text{LiF})$	$N\lambda(\text{pm}) (\text{LiF})$	$n$	Line (pm)
9.03	0.1569	63.09	1	63.06
10.19	0.1769	71.08	1	71.08
18.22	0.3126	126.18	2	63.06
20.66	0.3528	142.16	2	71.08
28.12	0.4713	169.27	3	63.06
31.97	0.5294	213.24	3	71.08

FIG. 7: Table 1: Glancing angle  $\theta$  of the LiF crystal.

$\Theta(\text{NaCl})$	$\sin \Theta(\text{NaCl})$	$N\lambda/\text{pm} (\text{LiF})$	$n$	Line (pm)
6.41	0.1116	63.09	1	63.06
7.23	0.1258	71.08	1	71.08
12.93	0.2237	126.18	2	63.06
14.6	0.252	142.16	2	71.08
19.55	0.3346	189.27	3	63.06
22.18	0.3775	213.24	3	71.08

FIG. 8: Table 2: Glancing angle  $\theta$  of the NaCl crystal.FIG. 9: Graph of  $n/\lambda$  versus  $\sin\theta$ , where NaCl is represented by circles, and LiF is represented by squares.

relationship can be seen in Figure 9.

From the slopes it has been determined that lattice constant for NaCl is equal to  $565.1 \pm 0.7$  pm, which is 0.1% off from calculated value 565.2 pm. Lattice constant for LiF has been measured to be  $402.4 \pm 0.9$  pm, which is 0.1% from calculated value 402.7 pm.

The second part of the experiment consisted of investigating the lattice structure of monocrystals using Laue diagrams. Five different diagrams have been made. The data runs have been represented in Figure 10:

As it can be seen two variables have been varied,  $\Delta t$  and L. From the obtained results that have been performed on NaCl crystals, it has been determined that varying

Run:	U (kV)	I (mA)	$\Delta t$ (s)	L (mm)	Crystal
1	35	1	1800	15	NaCl
2	35	1	1800	11	NaCl
3	35	1	2100	15	NaCl
4	35	1	1200	11	LiF
5	35	1	1200	15	LiF

FIG. 10: Tabular representation of data runs performed in the second part of the experiment.

$h(\text{NaCl})$	$k(\text{NaCl})$	$l(\text{NaCl})$	$d/\text{pm} (\text{NaCl})$	$\Theta(\text{NaCl})$	$\lambda/\text{pm}(\text{NaCl})$
4	2	2	115.1	24.1	94
6	0	2	89.2	18.4	56.3
6	2	2	85	17.5	51.1
4	4	2	94	19.5	62.8
6	4	2	75.4	15.5	40.3
3	3	1	129.4	13.3	59.5
5	1	1	108.5	11.1	41.8
0	6	2	89.1	18.4	56.3

FIG. 11: Spacing of lattice planes  $d$ , Bragg angle and wavelength associated with the sets of lattice planes of NaCl

$\Delta t$  while keeping L constant, does not actually affect the corresponding Miller indices, Bragg angle, wavelengths or the shape of Laue diagrams(it just makes them more clear, if the exposure time is increased). This actually makes sense because none of the equations that are used to calculate Miller indices, or any other variable are dependent on  $\Delta t$ . This can be seen by looking at the values for certain Miller indices, and corresponding Bragg angle, wavelengths, in Figure 11. Like it has been already said, the values are the same for both runs, so only one generic table has been created for both cases.

In Figure 12, we can see an example of obtained Laue diagram for third run on NaCl crystal, with some of the Miller indices labeled.

From the obtained results that have been performed on LiF crystals, it has been determined that varying L while keeping  $\Delta t$  constant, does not actually affect the corresponding Miller indices, Bragg angle, wavelengths or the shape of Laue diagrams (in case when the distance l is increased we just get more clear and more spread out Laue spots, take into consideration that we have a big enough x-ray film). This actually makes sense because the equation that is used to calculate Miller indices does include L, but increasing L implies that x and y coordinates are going to increase, as z coordinate (increase is proportional to increase in z coordinate). Since Miller indices are determined from the ratio of x,y and z coordinates, it means that they are going to remain basically the same, which gives us the same values for Miller indices, Bragg angle, wavelengths and the shape of Laue diagrams. This can be seen by looking at the values for certain Miller indices, and corresponding Bragg angle, wavelengths, in Figure 13.

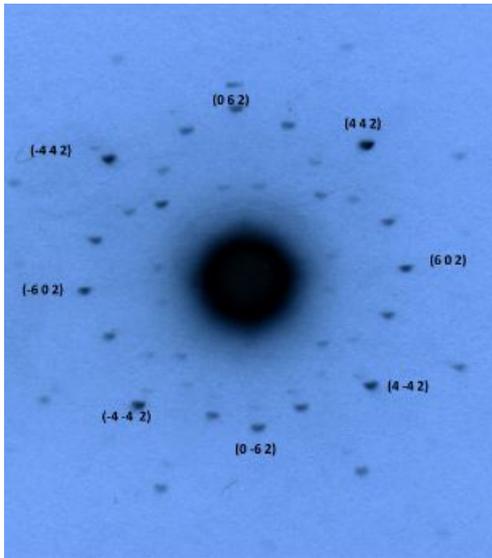


FIG. 12: Laue diagram at NaCl.

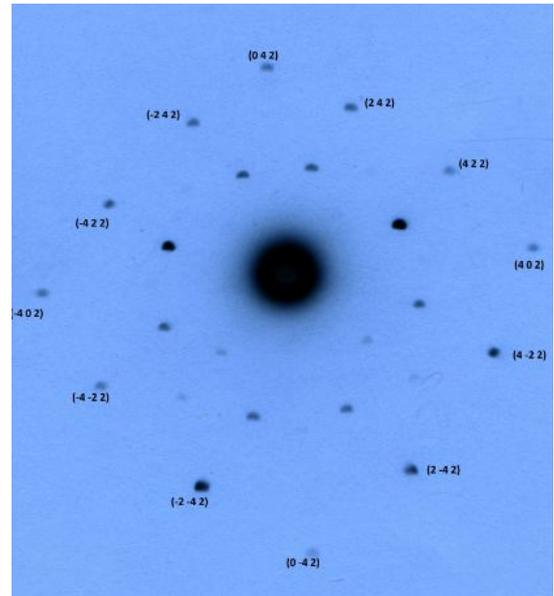


FIG. 14: Laue diagram at LiF.

$h(\text{LiF})$	$k(\text{LiF})$	$l(\text{LiF})$	$d/\text{pm}(\text{LiF})$	$\Theta(\text{LiF})$	$\lambda/\text{pm}(\text{LiF})$
4	0	2	90.1	26.6	80.6
4	2	2	82.2	24.1	67.1
6	0	2	63.7	18.4	40.3
6	2	2	60.7	17.5	36.5
4	4	2	67.1	19.5	44.8
3	3	1	92.4	13.3	42.5

FIG. 13: Spacing of lattice planes  $d$ , Bragg angle and wavelength associated with the sets of lattice planes of LiF

Like it has been already said, the values are the same for both runs, so only one generic table has been created for both cases.

In Figure 14, we can see an example of obtained Laue diagram for the second run on LiF crystal, with some of the miller indices labeled.

When looking at the both Laue diagrams, it is easy to note that is a high symmetry among the Laue spots. Each Laue spot has its own symmetrical pair. Some of the spots might not be showing. There are some errors. These errors might be due not proper alignment of the x-ray film on the film holder. Some of the errors might be due to not long enough exposing the film to x-rays. Another source of the error might be due to improper determination of Miller indices. This error seems as the most probable one, cause if the x-ray film was misaligned during the exposure time, then we would have wrong x,y and z coordinates, which makes the determination of Miller indices almost impossible.

Some of the future work can consists of performing Back-Reflection Laue method, instead of Transmission Laue method that has been used for this experiment.

## V. CONCLUSION

The experiment consisted of determining the lattice constants of monocrystals using Bragg reflection. The second part of the experiment was investigating the lattice structure of monocrystals. Using the adjusted Bragg's law for the crystals that have cubic structure (NaCl and LiF), the lattice constant for NaCl has been determined to be  $565.1 \pm 0.7$  pm, which is 0.1% off from calculated value 565.2 pm. The lattice constant for LiF has been determined to be  $402.4 \pm 0.9$  pm, which is 0.1% from calculated value 402.7 pm. In the second part, using obtained Laue diagrams, It has been noted that the Laue spots for NaCl and LiF crystals are highly symmetrical. At the same time it has been noted that if  $\Delta t$  and  $L$  are being varied, the shape of the Laue diagrams is going to remain the same, with constant values for spacing of lattice planes, Bragg angle and wavelength.

## VI. ACKNOWLEDGMENTS

I would like to thank to Professor Lehman for helping me understand the experiment better. I also want to thank the College of Wooster for providing the necessary equipment needed for conducting the experiment.

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