LAB 3: X-RAY CRYSTALLOGRAPHY

Alejandra Rosselli Calderon

November 2020

Contents

1 Abstract

The purpose of this experiment was to use x-ray crystallography to identify different samples. Using x-ray we can learn about the internal structure of crystalline solids. We are looking to learn about the arrangement of atoms within the crystal lattice and the orientation of the crystal. The first method was the powder method, where the sample is fixed in place and the x-ray tube move around to measure the angle at which there are intensity peaks. These angles can then be converted to wavelength to compare with the charts in order to identify the crystal samples. The second method is the Laue back-reflection method. In this method, the sample and x-ray are fixed in place. A photographic film is located in between the sample and the x-ray source. The beam passes through a small pinhole and the reflection pattern from the crystal allows us to observe the intensity peaks. This allows us to compare with charts in order to see the orientation of the crystal and infer the internal arrangement of the atoms in the unit crystal lattice cell. The glass slide shows a non-crystal pattern. The unknown samples were identified as copper, bismuth and tungsten, apart from the know silicon. The silicon sample used during the Laue back reflection method was found to be a face-centered crystal with an orientation of [1,1,1]. This comparison was done by processing the captured image to different arrangement and intensity simulations created with the code given.

2 Introduction & Theory

X-Rays were discovered by German physicist Roentgen in 1895. These rays were invisible but behaved similar to visible light, being affected by photographic film and traveling in straight rays. An important difference that they had is that they are able to pass through opaque objects such as the human body and pieces of metal. This property was very important, as it began to be used to understand the internal structure of these objects. By putting a sheet of photographic paper behind an object and then shinning it with x-rays, scientists observed a shadow called radiograph, in which denser parts of the object blocked more rays than less dense parts. There was little understanding on how x-rays worked until 1912, when x-ray diffraction by crystals was discovered. This discovery allowed to study the finer structure of matter and confirmed the wave nature of x-rays.

Now a days, we know that x-rays are part of the electromagnetic spectrum, with shorter wavelength and higher frequency than visible light. All electromagnetic radiation carries energy. The rate of flow of energy passing through a unit area perpendicular to

the direction of the motion of the wave is called the intensity. The average value of the intensity is proportional to the amplitude squared. Viewing x-rays as waves is the classical approach, but we also have to take into account the quantum effects because of the duality of electromagnetic radiation. In quantum mechanics, electromagnetic radiation travels in quantized packets called photons. Each photon has an associated energy $h\nu$ where h is Planck's constant and ν is the frequency of oscillation.

When the voltage of an x-ray tube shinned at a metal is raised above a critical value, we can observe sharp spikes on the relative intensity. This sharp relative intensity maxima that appear at certain wavelengths are characteristic to the metal and are called characteristic lines. The collection of these lines forms a spectrum called the characteristic spectrum. This will be the spectrum we will analyze in the first part of the experiment to identify the powder samples. We can understand the origins of these lines by thinking about the atoms of the metal sample as a nucleus surrounded by electrons in different quantized energy levels. When an photon from the x-ray hits an electron at the exact wavelength, it knocks it out of the shell, causing the atom to be in an excited state. An electron in a higher energy level goes down to fill the vacancy, and by doing this it emits energy. This emitted energy allows us to know the characteristic wavelength and thus identify the sample. [1]

The second method that was used in order to identify samples was the back reflection Laue method. This method is based on shinning the x-rays into a metal sample and observing the pattern in which they are being diffracted. Diffraction happens when a wave hits an object that has repetitive scattering units. If the wavelength of the wave is of the same order of magnitude of the space in between the scattering units, we can observe diffraction patterns. Physicist had the idea that the wavelength of x-rays was about 1 to 2 Å, and in 1912, von Laue reasoned that it would be possible to diffract them with crystals if that was the case, and if crystals were actually formed by regularly spaced atoms. His experiments proved both the wave nature of the x-rays and the periodic arrangement in the shape of a lattice of crystals.

Diffraction occurs when there is a phase relation between two or more waves. Most of the interference between these waves is destructive, but at some points it is constructive and it creates this points with higher light intensity that can help decode the internal structure of the crystal. These phenomenon can be explained using Bragg diffraction law.

$$\lambda = 2dsin(\theta) \tag{1}$$

where λ is the wavelength in Å, d is the distance between atoms in the crystal lattice

and θ is the angle of incidence of the x-ray beam. Bragg's Law illustrates that diffraction will occur when there is a spacing between atoms and rays that hit an atom will be reflected while rays that do not will pass straight through. This is illustrated in Figure 1.

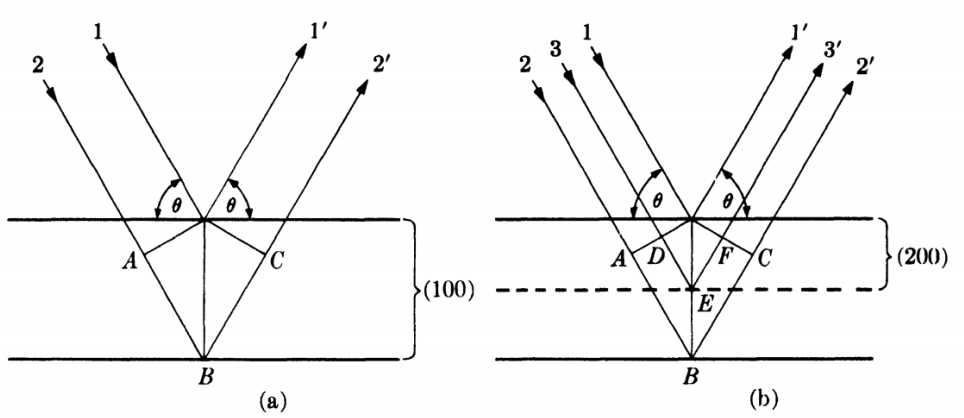


Figure 1: Bragg angle diagrams for a **a)** second order 100 diffraction and a **b)** first order 200 diffraction. We can see how rays get reflected when they hit the specific points of the lattice where there is an atom. [1]

The Laue back reflection method that we used during the lab is very similar to von Laue's original experiment, where we have a beam of x-rays to hit a fixed crystal target. In the back reflection method, the photographic film is placed in between the x-ray source and the crystal sample. The film has a small hole, similar to a pinhole camera, where the rays pass. An schematic of the setup can be seen in Figure 2.

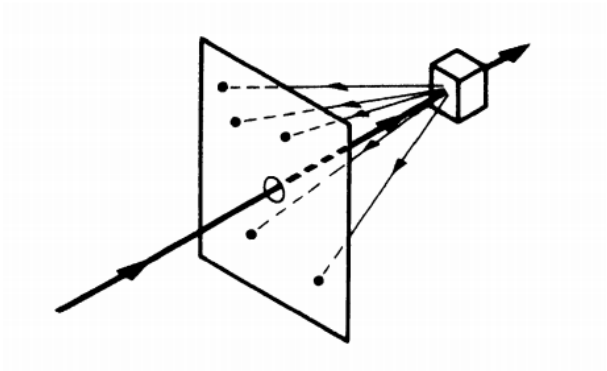


Figure 2: Schematic of Laue back reflection method. Incident ray comes from the left and the sample is on the right. [1]

The points that appear on the screen are called a pattern, and in the case of the Laue back reflection, they have the shape of hyperbolas. It is important to understand crystal structures to understand these lines of bright spots. Crystals are solids arranged

in periodic, three dimensional patterns. Glass, for example, does not have a periodic arrangement and therefore will not have these diffraction patterns. The types of pattern that we analyzed during the experiment, and the ones we worked to simulate, were simple. The three main types are simple cubic, body-centered cubic (BCC) and face-centered cubic (FCC). The shape of these three structures can be seen in Figure 3. The orientation of the crystals is also important to note. The convention is that the orientation is given by the location of a point of a vector starting at the origin. The vector goes from the origin to one of the points of the lattice. These directions are represented on Figure 4. Because we are interested on the orientation of the vector and not the magnitude, multiplying it by a constant does not affect our calculations (ie vector [1,0,0] is equivalent to vector [3,0,0]). We will use these naming and direction conventions throughout the lab report and simulations. [1]

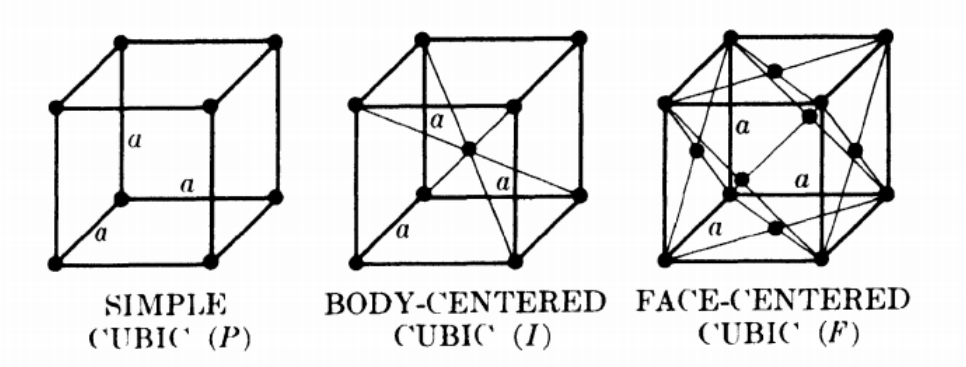


Figure 3: Simple cubic, body-centered cubic and face-centered cubic lattice unit cells. [1]

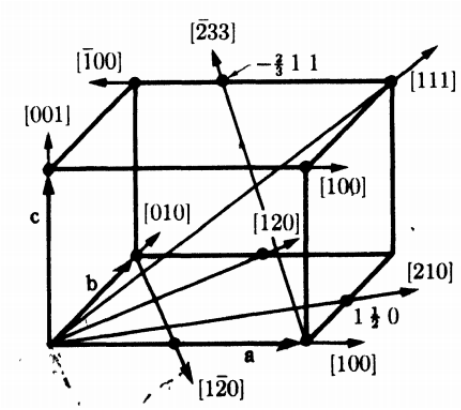


Figure 4: Convention of direction of crystal lattice orientation [1]

The lines in a Laue back reflection image correspond to points on the lattice that are part of the same zone. Prominent diffraction patterns usually correspond to low-level

zones, so we focused on the brighter pattern lines.

Based on this theoretical background, I am hoping to find that the samples in the lab will have a crystal lattice structure. The glass slide should not show this type of diffraction pattern. I am hoping to see a pattern with high intensity peaks for the powder diffraction method that will allow me to infer the nature of each mystery sample. I am also looking to be able to get an image with hyperbolas for the Laue back reflection method. This will allow me to see the nature of the crystal lattice and its orientation.

3 Experiment

One very important part of working with x-rays is having previous training in order to know the risks and how to mitigate them. We took an online training but we would have appreciated an in-person component, maybe during the startup of the lab. The main important takeaway of x-ray safety is to avoid getting radiated by a powerful ray.

Figure 5: X-ray crystallography machine

We can see the machine that we used during the experiment on Figure 5. The red light inside of the hood means that the x-ray tube is on and it is running. The x-ray we used was a Cu X-ray Tube. The machine has sliding doors that offer protection from the

x-rays. The machine does not operate unless all of the doors are shut, which is a good safety measure. The x-ray tube can get very hot while working with it, so it is important to have the water running and the cooling system on during the whole experiment.

i Powder Diffraction Method

The first part of the experiment was the analysis of the samples by using the powder method. First we put the silicon sample in the machine. We closed the lid of the sample holder and closed all of the doors of the x-ray machine. The values on the machine had already been calibrated at 30 kV for the accelerating voltage and 30 mA for the filament current. We made sure the water supply was on in order to cool down the x-ray tube. We opened the Datascan program and set the angle to be swept to be from 20° to 140°. We set the step size to 0.02° so that the scan would take approximately 30 minutes. After putting the silicon sample, we repeated this process another three times with unknown samples and once with the glass slide.

We found that using the step method worked best for us. A way that we tested our setup was to do some quick runs at the beginning instead of waiting 30 minutes to realize that the setup was not working. We originally did not know where and how to load the samples into the machine because no one explained that to us and there was no reference to it on the lab manual. Then after figuring that out we did not know that there was an additional switch that we had to turn on on the machine in order for the data collection to work. This set us back for a long time because we just had no clue why by doing everything as stated on the manual we were not getting any good results.

ii Laue Back Reflection Method

For the Laue back reflection method, we first checked that the sample was correctly placed perpendicularly to the x-ray beam, and about 2 to 3 cm away from it. We were advised not to touch any of the settings on the x-ray machine, so we left them as we had for the previous part of the experiment. We used the program Artemis Capture in order to control the setup and capture the image. We followed the lab manual to set up the capture rate and number of bins. While we were doing this alignment we used a loop exposure of 0.05 second. This allowed us to see if the image was changing, since at this short exposure we were only observing noise. We changed the setting on the main x-ray machine and made sure the left capture was on. The manual on the lab said to cool down the system to -15°C and the lab manual said 5°C. When we set it down to -15°C we had

very foggy images that we could not analyze. We therefore set it to 0°C, and at that temperature we were able to capture images that were clear enough. When we had set the setup, we changed the exposure to last 5 minutes and set it to a single exposure instead of a loop.

One thing that we did not know was that the image on Artemis Capture looks quite different to the image given by the lab report and the type of image we thought we were supposed to get. In the raw image we cannot see the intensity patterns dots. Those appear only after processing the image. Knowing this beforehand would have saved us some confusion. After obtaining the raw image, we processed it. To do this, we reduced the noise by using the "Despeckle" function and then we normalized the contrast. We were originally told to make the image a binary. This gave us an image with a lot of black and some white, but no scales of grays. These part was very confusing but I think it was due to the fact that none of the TAs had done this lab before and it seemed like we were all learning as we were going. The original image was a .tif file while the processed image was a .png.

4 Data Analysis

The data was collected with Data Scan software and Artemis Capture software. The data processing and analysis was done with Google Colab. The notebooks can be found on the shared Google Drive and attached at the end of this report. Parts of the simulation code was borrowed for the given python notebooks for the course.

The x-ray tube that we used throughout the experiment was a Copper tube with a wavelength $\lambda = 0.154\ 059\ 29$ nm.

i Powder Diffraction Method

The first thing we checked to make sure that our data scans were working was just a scan of an empty glass slide. Since glass does not have a crystal lattice structure, we were expecting a very noisy curve. The curve that we got can be seen in Figure 6.

We can see that this is a very noisy arrangement. The relative intensity is greater at the beginning of the scan and then flattens out. There are no prominent peaks.

The next measurement we made was for silicon powder. The angles at which we would have peaks are known, so this allowed us to know what the uncertainty in our measurements was. In figure 7 we can see the comparison between the obtained values

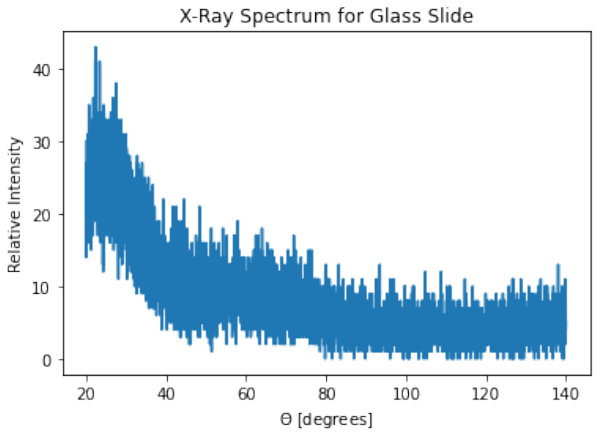


Figure 6: Convention of direction of crystal lattice orientation

and the theoretically accepted ones. The two graphs are very similar in shape and have the peaks at close locations. In order to know what the uncertainty was, I found the absolute value of the difference between the location of the peaks in degrees. In this case, the mean uncertainty in our measurements was 0.055 degrees.

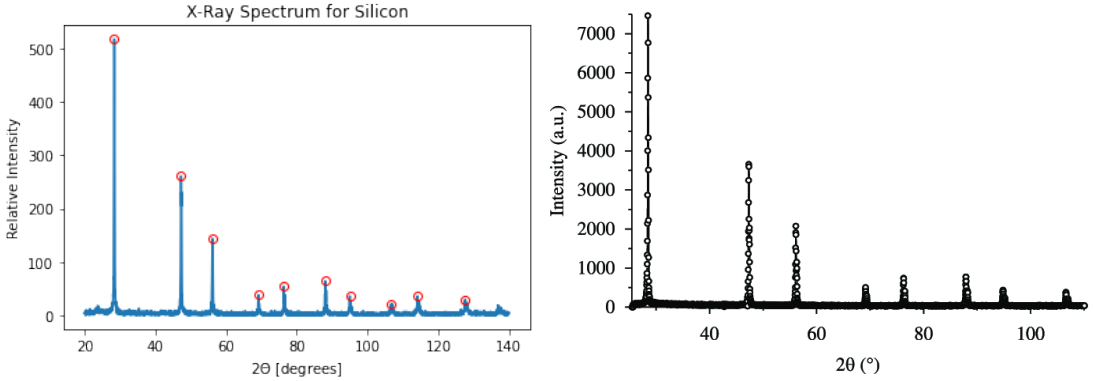
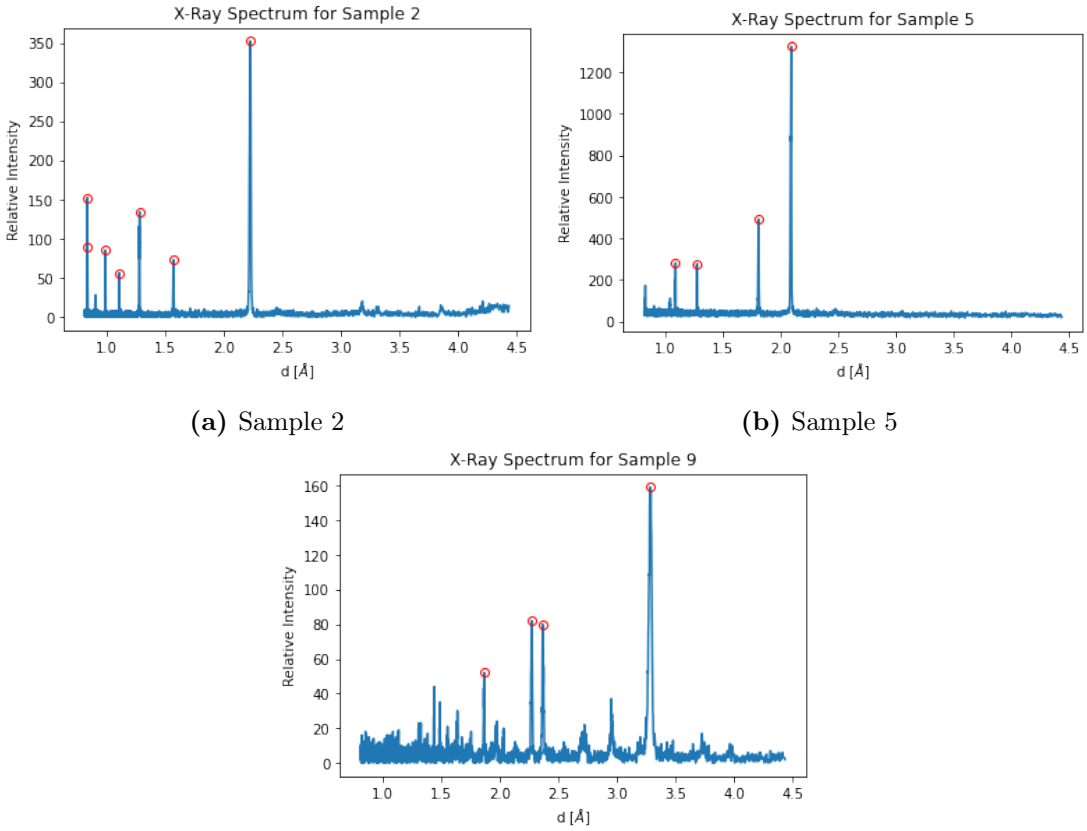


Figure 7: Left: Experimental spectrum for silicon powder **Right:** Accepted spectrum for silicon powder [2]

Using equation 1, we converted the values in angles to values of distance in Åbetween the planes of the lattice as following:

$$d = \lambda/2sin(\theta) \tag{2}$$

We plotted relative intensity vs d (in Å) and found the peak intensities for these values. Using this values, we matched the peaks in our intensities with the given values on the index books in the lab. [3].



(a) Sample 2

(b) Sample 5

(c) Sample 9

Figure 8: X-Ray spectrum peaks for unknown samples vs distance d

For sample 2, the 3 main peaks were 2.09, 1.81, 1.28. Based on the index, we think this element is Copper. The accepted values for copper are 2.09, 1.81 and 1.28. The mean of the difference between the accepted values and the experimental values was 0. The mean uncertainty, based on our calibration with the measurements of silicon, was 0.00091.

For sample 5, the 3 main peaks were 2.23, 1.58, 1.29. Based on the index, we think this element is tungsten. The accepted values for tungsten are 2.24, 1.29 and 1.58. The mean of the difference between the accepted values and the experimental values was 0.003. The mean uncertainty, based on our calibration with the measurements of silicon, was 0.00143.

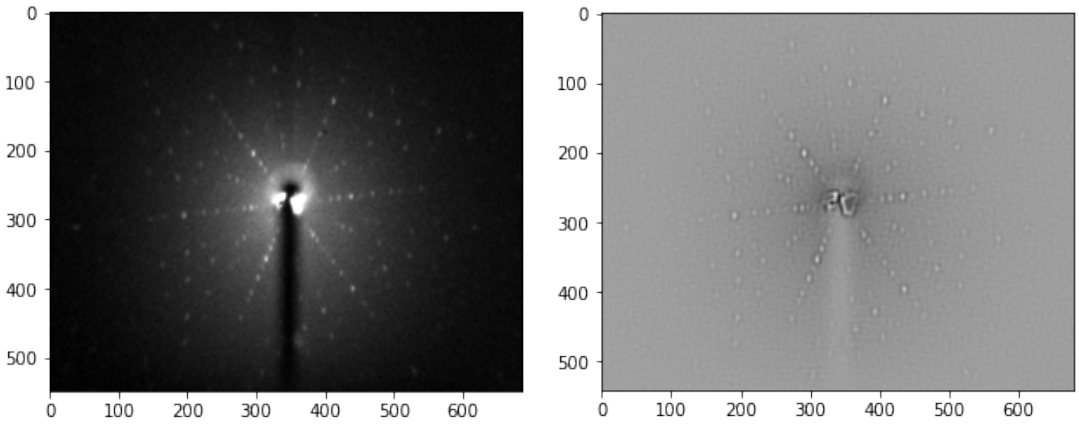
For sample 9, the 3 main peaks were 3.28, 2.37, 2.27. Based on the index, we think this element is bismuth. The accepted values for bismuth are 3.28, 2.27, 2.37. The mean of the difference between the accepted values and the experimental values was 0. The mean uncertainty, based on our calibration with the measurements of silicon, was 0.00371.

The average uncertainty for this part of the experiment was 0.00202.

ii Laue Back Reflection Method

My approach for the Laue back reflection method analysis was to process the image to find the intensity and pattern of the brighter spots in order to run a simulation with those parameters. This way, I would be able to figure out the shape of the lattice's unit cell and the orientation of the crystal.

The first step I did for the image processing on python was to use a convolution filter in order to smooth down the background of the image and highlight the bright spots that the right shape and brightness. I used a round 10x10 convolution filter, with a bright middle, mid tone ring and dark edges.



(a) Original **(b)** Convoluted

Figure 9: Original and processed Laue back reflection images.

We can see that the background and pinhole have significantly faded. After this, I made the image a binary, so that all the bright spots would become white and everything else black. This binary image can be seen in Figure 10. The hyperbolas and straight lines formed by the reflections of the different zones can be more clearly observed. I was having a little trouble with the edges that have a lot of dots, so I proceeded to crop the image and work with the area that was more important.

From here, I identified the brighter spots on the image using a tensor and the python cv library. Some of the smaller dots along the lines that intercept at the center were lost during this process but it did show me what the brightest spots were according to the pixel intensity. I thing this is a source of error, as it is removing some of the information, but I still think it is a good approximation.

From here, I did some simulation for the different unit cell lattice configurations. I did first some for the shape that the dots would have along each of the orientations. I chose to

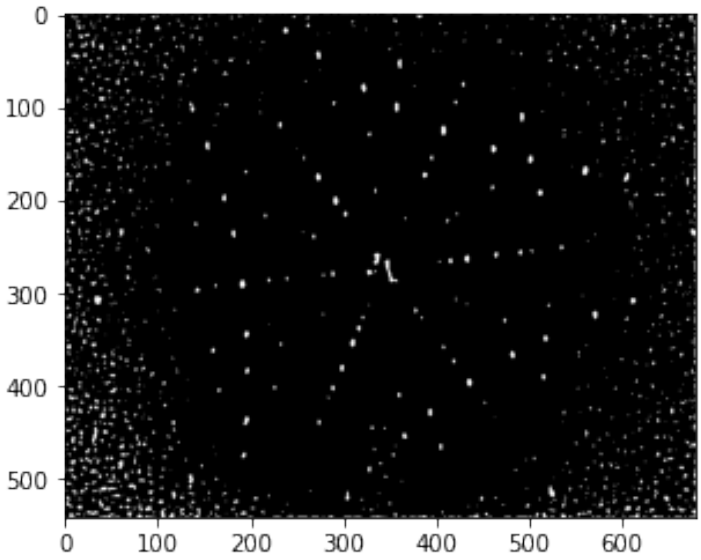


Figure 10: Binary image of the Laue back reflection method.

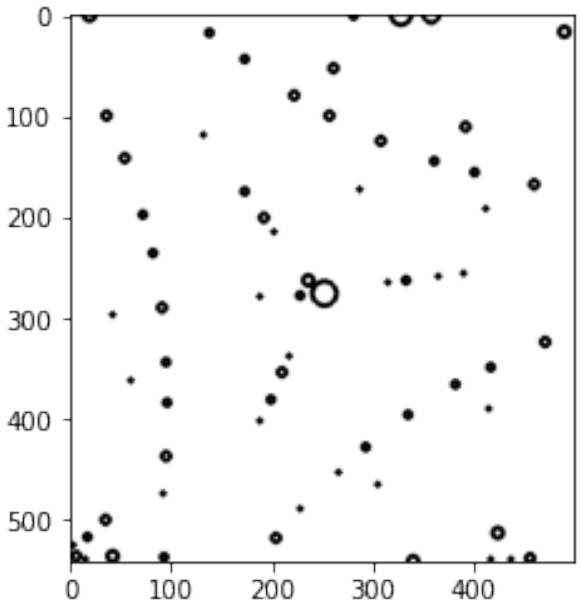


Figure 11: Computer identified brighter spots.

do these first as they were easier and faster. By comparing these ones to the image that I experimentally obtained, I concluded that I was looking at a face centered cubic (FCC) crystal in a [1,1,1] orientation. The shape simulation for this particular configuration can be seen in Figure 12. The characteristics that stood out to me most were the three hyperbolas and how the straight lines coming out from the middle seem to intercept at

the points where each of the hyperbolas intercept with the others. The shape seems to be the same, but with a rotation about the center of the plane.

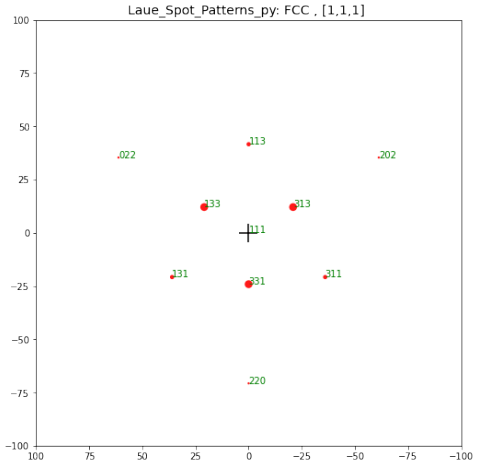


Figure 12: Computer simulation for a FCC [1,1,1] configuration

The next simulation that I did was to observe the intensities of this particular configuration, to see if they match with the ones on the experimental image. This computer simulated image can be seen in Figure 13. We can see how the overall pattern remains, and the intensity have some resemblance. It is clear here that the hyperbolas are the brighter spots on the image. We can also see that the straight lines coming from the center are next in brightness.

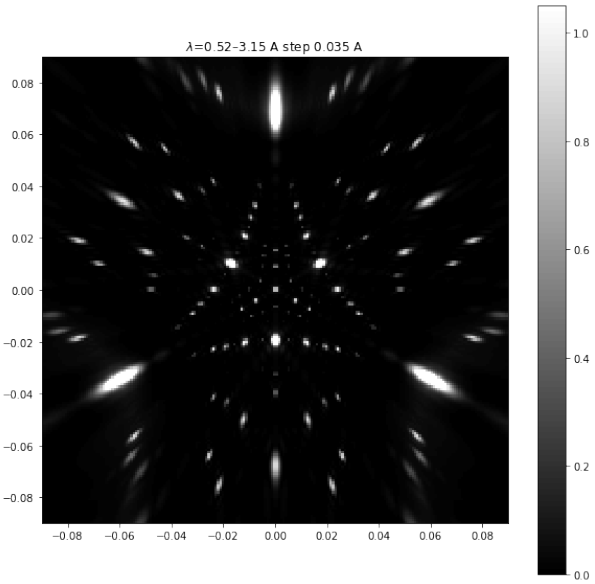


Figure 13: Computer simulation for a FCC [1,1,1] configuration

I think that the shape and brightness pattern simulations match the image enough to conclude it is a FCC [1,1,1] crystal. The image is rotated compared to these simulations so I would have wanted to have more time in order to work the simulations rotated. These findings show that it is possible to get diffraction of x-rays with crystals, while non crystals such as glass do not have this ability. This pattern prove to be unique, which allowed us to make a guess about the powder samples and about the structure and orientation of the Silicon sample in the Laue back-reflection method.

5 Conclusion

The results from this experiment show that the behavior of x-rays is similar to that of visible light, so they can get diffracted by objects that have a spacing of the order of angstroms. The observed diffraction patterns found with the powder method allowed me to see intensity peaks to match with accepted values in order to identify the different crystals. By knowing the incident angle of the ray, I was able to calculate the crystal lattice spacing with equation $d = \lambda/2sin(\theta)$. This allows us to know what the internal arrangement of atoms in the lattice looks like. This was a pretty accurate method, as the value barely differed from the values found in the Data File. Using the know values of silicon, I was able to calculate the average uncertainty of our calculations. This is a systematic error that would be seen throughout all of the experiment, as it is a calibration offset. Doing the Laue back reflection method allowed to see how we can learn even more about a crystal's internal structure and orientation. The analysis of these images was done by comparing them to simulations, but I could have done a more thorough job. I have no previous knowledge of solid state physics, so all of the things in the lab report and during the experiments were what I had read from the references. Because of this, the second analysis is more qualitative and I focused more on the image processing to pick out the more important features of the image.

I think it would be beneficial to have all of the lab manuals around the lab and on the web page up to date. The fact that the temperatures did not match and the manual on the lab had information that was not correct set us back a lot of hours. I think it would also be useful for the TAs to get training with this specific machine, as it seemed like we were all figuring out at the same time. It was very confusing when neither the TAs nor us knew how to load a sample. This makes the lab really frustrating because there is no progress and it is only because we didn't know how to make the simplest things. The TAs gave us wrong information about the image processing which made things really

confusing as well. One of them opened the machine's door while the x-rays were on and the light was on. Thankfully it automatically shuts down but the fact that they did not have the precaution to look if the x-rays were running makes me believe that they also were unfamiliar with the equipment. I do not think this is something to blame on them, they spend several hours with us in the lab making sure we understood everything and helping us figure out how to take the data.

Bibliography

[1] B. D. Cullity. *Elements of X-ray diffraction.* Addison-Wesley, 1956.

[2] Swapan Kumar Pradhan Soumitra Patra, Partha Mitra. Preparation of nanodimensional cds by chemical dipping technique and their characterization. *Material Research*, 14, 2011.

[3] A.S.T.M. (American Society for Testing Materials). *X-ray Powder Diffraction Data File.* 1967.