X-ray Diffraction
Rochester Institute of Technology

Goals

You must have read through the Background material and have a basic understanding of X-ray diffraction before beginning.

In this lab, X-ray production in this apparatus will be measured. An unknown powder material and an evaporation boat will both be characterized, and their structure and lattice constant measured. Two highly-crystalline materials will be investigated, and their Miller indices determined.

It is recommended that you analyze previously collected data while you are waiting for the long data collection runs to complete, later in the experiment.

Apparatus

The X-ray diffractometer uses an arrangement of sample and detector mounts called a goniometer. The goniometer can rotate the sample to adjust the angle θ; it can also adjust the detector angle. For Bragg scattering, a $\theta - 2\theta$ scan is used; that is, the sample makes an angle θ with respect to the beam of X-rays, while the detector makes an angle 2θ. The goniometer provides this coupled rotation.

Examine the Phywe diffractometer with the **power off**. The glass sliding door is operated by pushing in the red button, twisting, and then opening the door by sliding it to the left. The X-ray source is a Cu anode bombarded by electrons accelerated across a few tens of kV. **This door absolutely must never be opened while the X-ray tube is on.** It is interlocked (with the red button) but care should be exercised not to thoughtlessly try to force it open while the tube is on. **Before trying to turn on the xrays, you must close the sliding door then push and release the red button again to enable the power's interlock.**

The goniometer is rather delicate; do not push it around or it will lose its $\theta - 2\theta$ angular

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button for door   aperture for pinhole   sample or crystal   detector
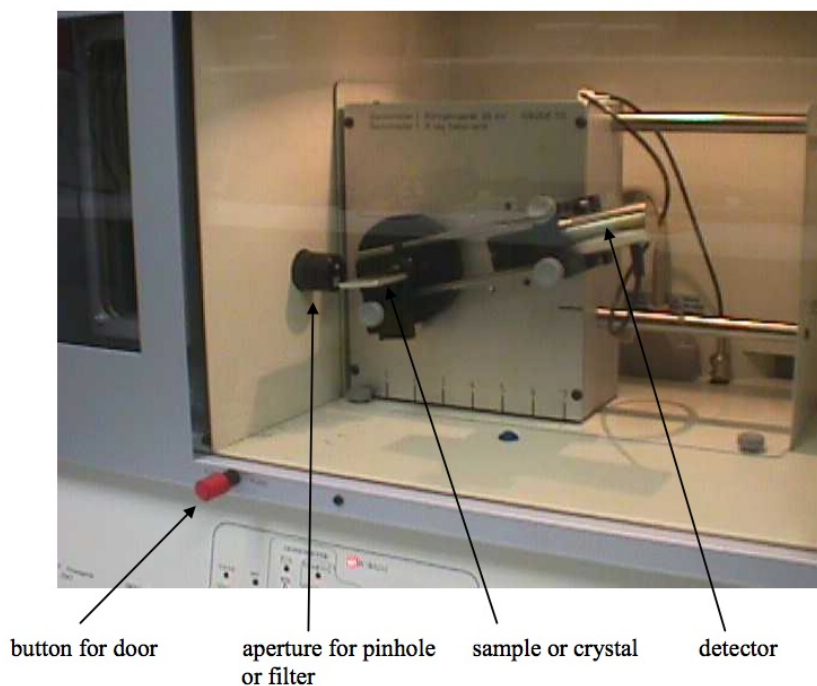   or filter

Figure 1: Diagram of table-top X-ray machine.

alignment. The sample mounts in the center of the goniometer. To the left is a place where a pinhole aperture or a filter can be mounted. The detector is a Geiger-Muller tube, which is mounted on the 2θ arm of the goniometer, to the right.

Make sure you understand where the pinhole mounts. Find the various pinholes, and the Nickel filter covered 2-mm pinhole.

Software

The PHYWE diffractometer is fully computer controlled, using a program called *Measure*. There is an icon on the desktop for the *Measure* program. Make sure the power to the Xray unit is on before you invoke the software. The power switch is on the lower right, back of the unit (reach behind - you'll feel the toggle switch). As you run the *Measure* software, it will open many sub-windows. These do not "tile" very nicely with this system. Feel free to move these windows around on the display so you can see what you need to see.

Direct printing of the data from within the *Measure* program does not work. Instead, choose the Measurement tab on the top, and within it, you must export the data to a text file for later analysis purposes. Additionally, you may choose to save the native file format, in case you want to return to the data on this computer at a later point. Finally, you should save a screenshot or export a .bmp file to represent your raw data in your notebook (don't print and paste thousands of data points).

X-ray Production

Power on the PHYWE device using the rocker power switch in the rear lower right corner. Run the *Measure* program. Make sure that Gauge is set to *X-ray device*.

Bremsstrahlung

Push the red door button in and turn clockwise to unlock the door. Place the LiF single crystal sample in the diffractometer. Place the 2-mm pinhole aperture between the source tube and the sample.

Press the red *New Measurement* button, then enter the following configuration settings:

Spectra	
Constant Voltage	20 kV
Crystal	LiF
Emission Current	1 mA
Integration time	1 s
2:1 coupled mode	
Starting Angle	3.5 degrees
Stopping Angle	25 degrees
Angle Increment	0.1 degrees

The next screen will come up with various displays. In order to actually start the measurement, you must do two things:

- Close the sliding door and rotate the red button counter-clockwise. Press the red button firmly and release it - this is one more level of interlock to make sure you really are ready. You only need to do this if the door has been opened since the last time you ran the software.

- Click on the *Start Measurement* button on the controller screen - make sure this window isn't lost on your display!

The tube should light, and glow faintly blue (X-rays and UV) as well as the normal filament light.

Data will appear on the screen as it is taken. You will see the goniometer arm move every second. It will stop taking data when the angle is no longer stepping up. Then click on *Stop Measurement*.

You must export the data as a text file for use with external plotting or analysis software. Save the data in the native file format. Print a screenshot of the data for your lab notebook.

Repeat the scan with voltages of 8 kV, 10 kV, 12 kV, 15 kV, 25 kV, 30 kV, and 35 kV. Save, print, and export each.

Characteristic Spectra: Nickel Filter and Alignment

Note the appearance of the characteristic spectrum (the two sharp lines) as the accelerating voltage increases above threshold. Do they appear above the voltage you would expect, given the required excitation energy?

The $K_{\alpha 1}$ and $K_{\alpha 2}$ lines are a "doublet" that is difficult to resolve, similar to some of the Mercury emission lines studied in the Photoelectric Effect experiment. Calculate the difference in scattering angle between these two lines based upon their known wavelengths (review the Background Material) and the lattice spacing for a LiF crystal. What is the smallest angle increment that our device can resolve? Comment upon whether we expect to resolve this doublet with our goniometer.

The presence of the K_β line complicates things; instead of having a nearly monochromatic source, there are two predominant wavelengths being produced by the tube. Fortunately, Nickel absorbs X-rays with a sharp absorption edge; it filters out most of the K_β line but leaves the K_α lines mostly unchanged.

Make sure the tube is OFF; that is, zero accelerating voltage. Visually verify this; the tube should be **not** lit. Open the door. Remove the 2-mm pinhole and insert the 2-mm pinhole with Ni filter. Close everything up.

Take another scan at 35 kV, with the Ni filter in. Compare to the unfiltered scan you just did. Compare the ratio of the peak intensities K_α/K_β with and without the filter.

The characteristic K_α line, when scattered from a LiF crystal, should be at 22.5 degrees. Verify this by looking at the data in a numerical table and ascertaining the location of the peak. It must be at EXACTLY 22.5 degrees or the rest of these experiments will not work!!! If it is not, please ask your instructor to realign the goniometer.

The Ni filter allows us to use the tube as a nearly monochromatic source of X-rays. We used the LiF crystal as a "diffraction grating" to learn about the radiation from the tube. We now remove the LiF crystal, and use our X-ray tube as a source of nearly ideally monochromatic radiation with which to study other structures.

Xray Production - Analysis

The higher accelerating voltages produce bremsstrahlung at lower angles = smaller wavelengths = higher energies. Tabulate the lowest angle at which you see bremsstrahlung for each of the accelerating voltages you measured. Convert angle to wavelength using Bragg's law and d=2.014 Å. Combine Equations 1 and 2 from the Background material to get a relationship between λ_{min} and the accelerating voltage V. Plot λ_{min} as a function of $1/V$. Does your measured slope agree with theory within uncertainty? Using the relation between energy and wavelength, what ratio of physical constants did you just measure, and what is your value?

Compute the wavelength of the Cu K_α line from your data. Compare to the known value of 1.5418 Angstroms.

At the start of each new day of experiments...

You should quickly verify at the beginning of each day that the LiF crystal is producing a diffraction peak at or near (within 0.1 degree) of $\theta = 22.5$ and $2\theta = 45$ degrees. Simply mount the LiF crystal and the Ni filter, set the voltage to 35 kV, and collect data over a small range surrounding that peak. If it's very close, then you're good to proceed. If it is off substantially (more than a tenth of a degree) then have your instructor reset the calibration on the machine manually.

Identification of an Unknown Powder with Unknown Cubic Structure

Powder samples can be measured and analyzed with this instrument. The idea is that if a material is pulverized to a very fine powder, and the powder is placed in the goniometer, there will be a completely random arrangement of small crystallites. Some small piece is apt to be arranged at any given angle with respect to the incident beam. If that angle corresponds to an allowed diffraction peak, according to the Bragg condition, there will be diffraction. Intensities are typically very low, however, since only a small fraction of the powder happens to be at the correct orientation.

Powders are typically ground until they pass through a 350 mesh screen; this is a size of 44 microns or less. This is very fine powder! (drugstore talcum powder is about this size). In order to immobilize the powder long enough to measure it, it is mixed with a very small amount of Vaseline to form a gummy amalgam. This is packed into a shallow sample holder that can be mounted in the diffractometer.

Identify the Aluminum sample holder (there are two samples on each side) that has a dark gray rectangular patch (the amalgam set in place) and mount this to the goniometer. **Make sure the Nickel filter is in place for the rest of the experiment!**

Since the intensities are low, you will need to take a very slow, time consuming, scan. Set up the software for:

Spectra	
Constant Voltage	35 kV
Crystal	(doesn't matter, no crystal is in)
Emission Current	1 mA
Integration time	10 s, note this long integration time!
2:1 coupled mode	
Starting Angle	20 degrees
Stopping Angle	52 degrees
Angle Increment	0.1 degrees

This is θ varying from 20 to 52 degrees at 0.1 degree steps and 10 seconds integration per step, which is 3200 seconds long (54 minutes)! Start the scan and continue with the practice analysis below.

The analysis of this data is somewhat tricky. While the instrument is scanning, **practice** the analysis, while you have an instructor here to help you, using the data for a different material provided in Figure 2.
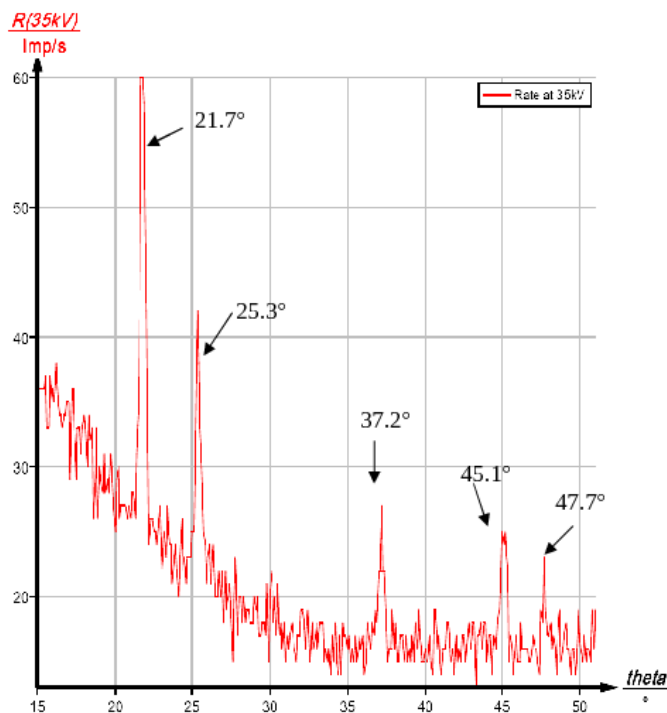

Figure 2: Sample data to practice identification of a transition metal powder. Peak position angles are marked.

You will be using a more robust version of Bragg's law (found in the background reference material):

$$\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \tag{1}$$

Rearranging this a bit gives:

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

First, deterimine if the material is simple-cubic (sc), face-centered-cubic (fcc), or body-centered-cubic (bcc). Thus if the **correct** hkl are assigned to each angle, the result (left side of Equation 2) should be the same for all five peaks. Thus you know the structure. Then, that constant easily gives the lattice parameter of the material since the wavelength is known to be λ=1.5418 Å.

Analyze the data using the table below. That is, compute the left side of Equation 2 as if it were sc, as if it were fcc, and as if it were bcc. One of these structures gives a constant for all peaks (one column in the table), while the others do not. That tells you the structure! The allowed diffraction peaks for each structure are given in the table in Appendix A.

angle θ	$\sin^2\theta$	hkl if sc	hkl if fcc	hkl if bcc	$\sin^2\theta/(h^2+k^2+l^2)$ if sc	$\sin^2\theta/(h^2+k^2+l^2)$ if fcc	$\sin^2\theta/(h^2+k^2+l^2)$ if bcc

Figure 3: Data table for practice analysis. Use the peak position angles θ as marked in Figure 2.

From this, which structure is consistent with our practice data? In other words, which of the last three columns is most constant?

Extract the lattice constant a, with uncertainty.

Compare to common transition metals in the periodic table. Lattice constants and crystal types for elements are given at

http://www.periodictable.com/

This sample data is from one of the top-row transition metals. Look at the Full Technical Data.

Which do you think it is? You will do exactly the same analysis for your unknown powder sample, as well as the unknown evaporation boat later in the experiment.

When your scan is done, save the data, print a screenshot, and export it to a text file. Do you see five clear peaks, as in the practice data? If you do not, you can likely complete the analysis and identfy the powder using only four peaks.

In order to find the fifth peak, you need to re-scan a subset of the angles for a much longer integration time. First, complete your data collection for the next three materials (Copper, Silicon, and the unknown evaporation boat). This will take more than one day.

Only if you have time remaining after all other data has been collected, return to this powder sample. Scan from 48 to 51 degrees in 0.1 degree increments for at least 50 seconds each to locate the fifth peak.

Perform the same analysis. Your sample is a different top-row transition metal. Again, what structure is it, what lattice constant does it have with uncertainty, and what element do you think it is?

angle θ	sin²θ	hkl if sc	hkl if fcc	hkl if bcc	sin²θ/(h²+k²+l²) if sc	sin²θ/(h²+k²+l²) if fcc	sin²θ/(h²+k²+l²) if bcc

Figure 4: Table for the unknown powder data you collect and analyze.

Highly crystalline materials: Copper Foil and Silicon Crystal

Single crystals (or semi-ordered materials), will have some "agreement" about the orientation of a majority of the unit cells within the material. As such, simple powder scans will usually not suffice to obtain a signal. However, when the lattice planes are aligned appropriately, there will be a strong signal. Ask yourself why a single crystal, in the appropriate orientation, will have a much, much stronger signal than a corresponding signal for a powder material.

We will investigate this a bit further with two materials: Cu and then Si. Mount the sample holder so that the copper foil is the intended target. Take a scan using, 2 second integration time, with a θ starting angle of 15 degrees, ending angle 50, and Ni filter in.

Can you explain both peaks? What crystalline planes form the surface of this foil? Foils like this are made by a hot rolling process; apparently it strongly orients the material. From what you know about Copper, determine the Miller indices of the rolled foil surface.

Next we will examine the signal from a small piece of Si. A high purity Silicon wafer was smashed with a hammer. Mount the sample holder so the Silicon shards are the intended target. Scan it using 2 second integration time, with a θ starting angle of 20 degrees, ending angle of 40 degrees, and the Ni filter in.

From what you know about Silicon, determine the Miller indices of the face cut for the wafer.

Identification of an Unknown Metal with Unknown Cubic Structure

Evaporation boats used for thin film production are typically made of Tantalum or Tungsten. Both are dark, relatively dense materials that are highly resistant to corrosion at room temperatures. You will determine which metal is used in this sample.

Mount a cut piece of the polycrystalline evaporation boat. Scan a large range of angles for this sample. Use the same high-power settings as before. You'll want to scan θ from 15° up

to 50°, with the Ni filter in. You can either attempt a quick scan to identify the approximate peak locations, followed by close-up detailed scans, or you may take a single long scan (an hour or more) that has decent resolution and statistics. You should find five peaks in this range.

How you wish to determine the actual peak positions from the data is up to you. What are some of the alternatives? The position of each peak is very important to your calculation and hence choosing the "most intense data point" will limit your accuracy significantly.

Determine the lattice type and the value of the lattice parameter using a similar methodology to what you did last week with the mystery powder sample. If you have two possible lattice types, consider the fact that almost nothing (elemental) in this world is simple cubic. Google to find the ONE element which is simple cubic? Would we expose you to this element in this course?

angle θ	$\sin^2\theta$	hkl if sc	hkl if fcc	hkl if bcc	$\sin^2\theta/(h^2+k^2+l^2)$ if sc	$\sin^2\theta/(h^2+k^2+l^2)$ if fcc	$\sin^2\theta/(h^2+k^2+l^2)$ if bcc

Figure 5: Table for the unknown evaporation boat data you collect and analyze.