

Experiment #12
X-Ray Diffraction Laboratory

Introduction:

To determine crystal lattice spacings, as well as identify unknown substances, a x-ray diffractometer is used to replace the traditional Debye-Scherrer camera. A powdered (or metallic wire) sample is exposed to a monochromatic x-ray beam that is diffracted by the crystal planes in the randomly oriented crystallites that make up the powder (or wire). When the crystal planes are oriented properly with respect to the incident beam of x-rays (of wavelength λ) a diffracted beam is produced. The correct orientation of this diffracted beam is given the Bragg law: $\lambda = 2d\sin\theta$ where λ is the x-ray wavelength, d is the spacing between the crystal planes and θ is the diffraction angle. The crystallites in the sample can be assumed to be present in all possible orientations, so for any given set of crystal planes, the diffracted beam will trace out a continuous cone that is coaxial with the incident beam. The detector of the diffractometer (or the filmstrip in the case of the Debye-Scherrer camera) intercepts the cone and records the angle, 2θ , of the diffracted cone with respect to the incident beam. From the angular position of the diffraction peaks it is possible to deduce with high accuracy the d values (plane spacings) and the lattice parameter of the crystals if the crystal type is known (or can be determined).

Operating the X-Ray Diffractometer

- 1) Turn on the apparatus:
 - a) Turn on water supply (enables interlock 1).
 - b) On the large power supply below the experiment cage, make sure both of the (large) kilovolts and milliampere dials are at zero (fully ccw). Then press the **Control Power ON** (orange button) and then the '**X-RAY ON**' (red button). Bring up the voltage to -30 kV FIRST and then increase the current to 8 mA
 - c) There are a couple of power supplies mounted in the rack that is located to the right of the experiment area. Check that the one at the top left of the rack installation (the detector) high voltage supply is set to approximately 0.70kV. Do Not adjust any controls on the channel analyzer or the other power supply.
 - d) The stepper motor power supply is also located in the middle of the rack. It does not have any adjustments.

- e) In the bottom area of the rack, is a Step Pak motor control model MCU-2. The display could be reading any angle depending on the current position of the detector arm. Do not make any adjustments here either.
- f) On the top of the rack assembly is the x-ray shutter control box. Turn the key switch on the lower left of the shutter control to the Power position and toggle the large switch from the Closed to the ON position. The Timed switch should be left at the lower (∞) position. The momentary switch at the top right opens the X-Ray shutter. DO NOT yet open the shutter until you are ready to perform the experiment.
- g) Open doors to the experimental setup, and Place the sample on the goniometer making sure not to hit anything to avoid altering the alignment. The sample is to be placed in the sample holder located on a circular disc between the x-ray generator (square box on the right) and the detector (cylinder on the left). There is a 'C' shaped piece of metal that has holes in it to hold the sample capillary (or metallic wire) in position. Gently place the sample in the holder. Again, make sure not to hit any of the equipment. Close the doors making sure that the magnetic safety latches are contacting (enables interlock #2).

2) Turn on the computer if it is not already turned on. Use the username and password:

Username: **user**

Password: **teaching**

- I. After you have logged in open up a command terminal. This can be done by clicking on the icon on the bottom of the screen that looks something like a monitor. Once the terminal is open, you want to start the experiment program. This is done by running the program: "**twoc**". Simply type in the program name (without the quotes) at the command prompt. The program may ask you if you want to update the motor, typically just accept the default answer by pressing the Enter key.
- II. You should now see a command prompt for the program, this is where you enter in all commands required to perform the experiment. Move the detector to a position at 10 degrees or so to avoid directing the detector directly into the source beam, which will cause damage to the detector. This is done by typing the following command: "**mv tth 10**" (without the quotes) this moves the two-theta motor (detector) to a position 10° away from beam axis which is at 0° .
- III. In the **twoc** program type "**startup**" and press the enter to set all of the experimental settings. Typically you will simply accept all the default settings. However you will want to make sure to specify a new name for the data file in which the recorded data to be stored.
- IV. Now we want to start the scan. This is done with the "**ascan**" command. The proper syntax for this command is as follows: If we wanted to perform a scan from 10 to 120 degrees using 1100 data points (i.e. in 0.1° steps) using an

exposure time of 4 seconds for each data point (step) we would use the command: **ascan tth 10 120 1100 4**. When you type in such a command and press enter, the apparatus will quickly move the motor to 10 degrees and then start the slow scan. The data will automatically be displayed on the screen and a graph will pop-up showing the data as it is gathered. You will know that the experiment is done when the you see the command prompt for the “**twoc**” program appear.

When the scan is complete, close the shutter by moving the large switch on the shutter power supply to the Closed (down) position. The red light located on the far side of the X-Ray source should go out, indicating the beam has been shuttered off, and it is now safe to open the cabinet. Open the doors, remove the powder sample and replace it with the metal wire. Repeat the scan using the same parameters as previously.

When you are through with the second scan, it is time to completely shut down the apparatus. Do this by first closing the shutter, and then turning off the shutter control power supply using the key switch. Then, ramp down (to zero) the amperage then the voltage to controls on the X-Ray power supply and then press the ‘**X-RAY OFF**’ button.

All of the other power supplies (in the rack) are to be left on.

The water supply should be left on for at least one hour to let it cool down. The demonstrator will look after shutting this off for you.

useful “twoc” commands

- ascan** Proper syntax: **ascan** {motor} {start} {finish} {intervals} {time}
- The ‘motor’ condition requires you to enter in the motor name, the two motors in the experiment are ‘**th**’ (theta, moves sample) and ‘**tth**’ (two theta, moves detector) respectively. We will only use the tth (detector) motor. ‘start’ and ‘finish’ refer to the start and finish positions for the detector you should typically perform the experiment in the positive direction only. ‘intervals’ sets the number of data points within the interval and ‘time’ refers to the exposure time of each interval.
- mv** Proper syntax: **mv** {motor} {position}
- This command moves the desired motor to any position (given in degrees).
- umv** Proper syntax: **umv** {motor} {position}
- This command is identical to ‘**mv**’ with the exception that the program displays the current position of the detector as it is being moved.
- wa** This command displays the current position of the motors.
- startup** This command allows the user to set up all of the program settings, which includes the name of the file where the experiment data is to be stored.
- newfile** creates a file to store data and can be imported to excel for analysis.

Your data is saved to plain text file. It contains a few lines header information and then actual data from the scans. The header will occur at the beginning of each scan you attempted while the data file you specified was open.

You can edit out the header data and simply import the (space delimited) file into a spreadsheet program such as Excel. The columns of primary interest to this experiment are the first one (the angle in degrees) and the last one (the # of counts recorded by the detector)

If the user account does not show a floppy drive icon on the desktop, use System > Disk Management to mount the floppy drive. Copy your data file from the User's home folder to the floppy. Un-mount the drive and eject the disk.

Report: In your introduction explain how x-rays are generated and how filters provide monochromatic x-rays. Next you should certainly include a sketch of the apparatus showing the positions of the incident and diffracted x-ray beams, the sample and the detector. Finally, all calculations, graphs and the indexed diffractometer x-ray spectra should appear in your report, together with a discussion of the experimental errors.

Experiment - 1) Determining the Lattice Spacing of a Metal

Method: You are provided with a sample of a metallic wire which you can insert directly into the sample holder in the diffractometer.

Using the crystal chart in 'Cullity', identify each diffracted (Bragg) peak with the appropriated reflecting plane (hkl) and verify using your experimental $\sin^2\theta$ values from the Bragg law in conjunction with the cubic crystal relation: $d_{hkl} = a_0 / (\mathbf{h}^2 + \mathbf{k}^2 + \mathbf{l}^2)$ to determine the lattice constant a_0 for every peak in the sample. Note that the x-ray consists of two Cu-K_α wavelengths (0.154051 nm and 0.154433 nm) and if these two lines are not resolved (typical at most angles) a weighted average of 0.154178 nm should be used. Use the extrapolation technique illustrated in Fig. 11.4 of Cullity to determine your best value lattice parameter as well as your margin of error. Use this lattice parameter and the crystal type information to identify the metal.

Experiment - 2) Identification of Unknown Substances

The identification of a completely unknown sample (or one within a limited range of possibilities) can often be handled with x-ray techniques. Both the 'Hanwalt' and a graphical method are used to index the powder pattern. Refer to Cullity's "Elements of X-ray Diffraction" Ch's. 10 and 14 for more details.

Method: You are provided with a thin capillary tube with the sample powder. It is a metallic oxide of the form M_xO_y (where x, y are ≥ 1) where M is a base metal (one type) and O is oxygen. Obtain a diffraction pattern by exposing to radiation from a Cu target. The lines and intensities will have a certain pattern that defines the crystal's symmetry (see Ch. 10 for details). The three strongest lines (d-spacings) can be referenced using the ASTM powder diffraction files and a reasonable guess can be made about the material's identity (Cullity, Ch.14.3, 4, 5); be careful about the possibility of preferred orientations. Do use additional lines and their intensities as a means to further limit your choices.

Report: Include your calculations along with a table of observed d-spacings and relative intensities (eg. using vs, s, m, w, vw) along with the corresponding values found in the card files for this 'unknown' sample. Conclude with a brief discussion of the certainty of your identification and possible concerns. Show your calculations for the cell constants and discuss the accuracy of your results. You may want to do a $\sin^2\theta$ plot (Ch. 11.1) and extrapolate your d-spacing data to get the best possible lattice parameter(s).

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