

X-ray diffraction: Introduction to the θ - 2θ method

Objectives:

1. To become familiar with the Siemens θ - 2θ x-ray diffractometer.
2. To obtain θ - 2θ x-ray scans from samples of known elemental content, and to identify the crystal structure.
3. To identify an unknown sample.

Background Preparation:

Obtain a good introductory x-ray book such as
Elements of X-ray Diffraction (Cullity and Stock) Prentice-Hall, 3rd edition

Visit an interactive web site such as:
<http://www.matter.org.uk/diffraction/geometry/default.htm> and play with some of the java applications.

In your reading, pay particular attention to the following concepts:

- crystal structures and crystal planes
- Bragg diffraction
- reciprocal space
- structure factor
- experimental arrangements for computerized θ - 2θ method

Suggested Procedure:

Identify and document the various experimental components in the x-ray diffraction system from the goniometer to the detector to the computer interface.

A pencil dosimeter will be provided which must be worn while using the x-ray generator. These register whether you were exposed to x-rays during the lab. Each student must choose one and sign in the starting value before the lab and sign out the ending value when the lab is done. If there is a change in the level please notify your instructor as soon as possible.

The x-ray generator is an expensive piece of equipment that can easily be damaged. Follow startup and shutdown procedures carefully to avoid damaging the equipment.

To turn on the x-ray generator:

1. Make sure that the voltage (kV) and current (mA) knobs are at their lowest settings.
2. Turn the key clockwise by 45°.
3. Push the orange button.

4. Push the green button.
5. Wait a few seconds to ensure that ON is stabilized.
6. SLOWLY turn the kV knob to set the voltage to 35 kV.
7. SLOWLY turn the mA knob to set the current to 30 mA.

To turn off the x-ray generator:

1. Turn the current down to its lowest setting.
2. Turn the voltage down to its lowest setting.
3. Push the orange button.
4. Turn the key counter-clockwise by 45°.

Load the standard polycrystalline Si sample (the gray colored disc). Place the sample in the sample holder of the diffractometer and raise the pressure unit to hold it in place. Close the main door to the x-ray generator before starting a run.

A PC controls the operation of the diffractometer through a windows based program called XRD Commander, shown below in figure 1.

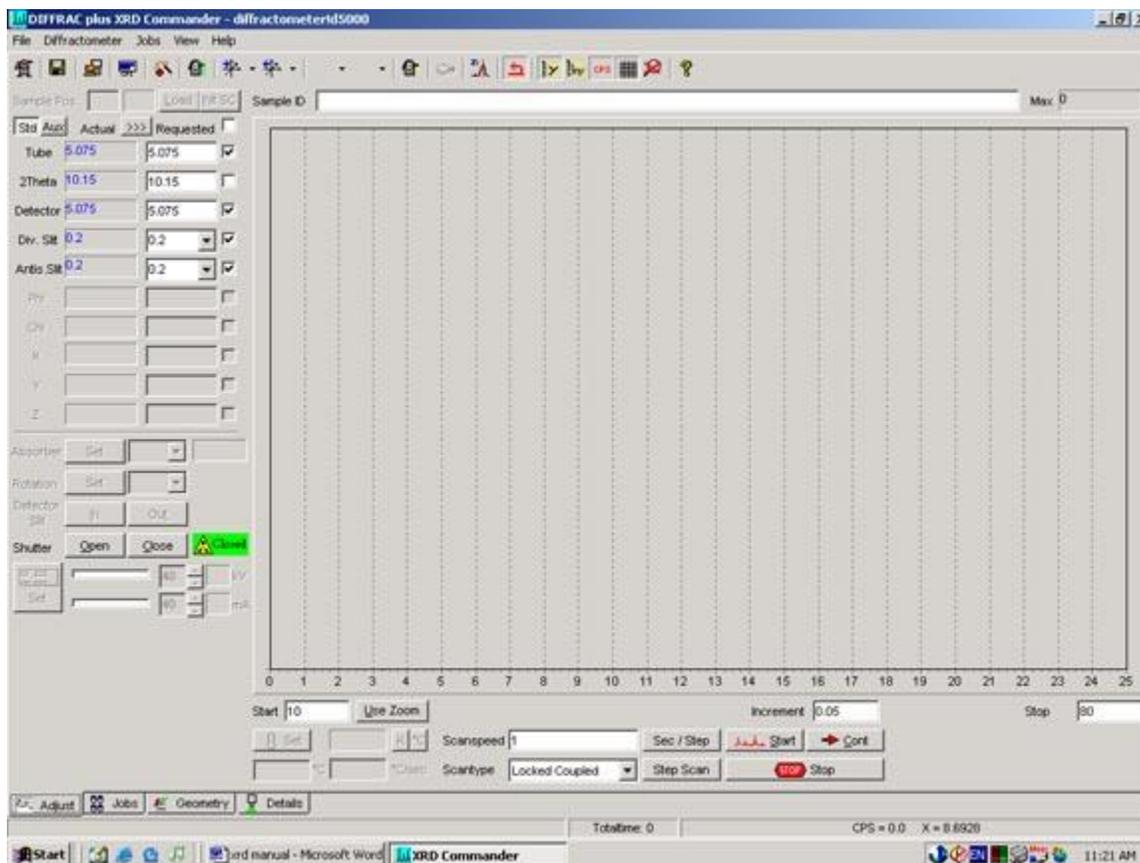


Figure 1: The XRD Commander Program

Depending on where the system was left you may have to restart the XRD Commander program by double clicking the XRD Commander icon on the desktop. The XRD

Commander program allows you to control all aspect of your scan. In particular, you will need to change 6 parameters over the course of this lab:

- **The Div. Slit (divergence slit):** this slit is located between the x-ray tube and the sample. It is measured in degrees.
- **The Antis. Slit (antiscatter slit):** this slit is located between the sample and the detector. It is measured in degrees.
- **The Start Angle:** the angle at which you begin your scan. It is measured in degrees.
- **The Increment:** the angle traveled in each step. A lower increment increases the overall amount of data, but also increases run time. It is measured in degrees/step. The minimum increment is .005 degrees/step.
- **The Stop Angle:** the angle at which you finish your scan. It is measured in degrees.
- **The Scan Speed:** the scan speed determines how many seconds the computer will accumulate data for at each step. A longer scan speed decreases statistical error, but increases run time. It is measured in seconds.

When you have set the parameters for your scan, select the **Start** button. The run will start and the x-ray shutter will open automatically. When your run has finished, select the **Close** button in the **Shutter** section to close the shutter.

Warning: Always ensure the shutter is closed before opening the door to the x-ray diffractometer.

Save your data by selecting the save icon  on the top menu of XRD Commander. Create a folder on the desktop and title it with your name and the course number. Save all your data there.

Run a full scan (from 10-80 degrees) for all your samples to find peak positions. Once you are finished, run smaller, more detailed scans for all peaks.

Suggestions for analysis

Compare your reference peak results to the expected values and therefore, determine whether the peak positions are shifted or distorted over the 10 to 80 degree range. Use these corrections to correct the sample spectra. Measure the peak positions, full width at half maximum (FWHM), and areas accurately. Tabulate the experimental 2θ peak positions and the FWHM for the reference and lab sample spectra. Do the intensities of the reference sample agree with those expected for a randomly oriented powder sample? See Cullity for a discussion of calculation of x-ray intensities. You will need to obtain the structure factors, multiplicities and scattering factors for each of the lines.

Intensities are given by $I = |F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)$ Additional corrections for absorption

can be added.

Measure the rocking curves for a single crystal (001) Si sample. Why is the observed spectrum so much simpler than the polycrystalline sample? Identify all possible peaks and artifacts. The peaks are much narrower. Try and measure the intrinsic linewidth by using the narrowest possible entrance and exit slits. What is the maximum instrument resolution?

Compare the diffraction for single crystal Si with that of a compound semiconductor with the zincblende structure (e.g. GaAs, InP or GaSb). Identify the observed peaks and obtain a best estimate for the lattice constant. Explain any observed differences in the x-ray diffraction scans with those of Si single crystal.

Measure the diffraction pattern of another polycrystalline sample of the cubic family such as Cu, Al, Pb etc. Identify the principle peaks and obtain accurate values for the lattice constants of these materials to compare with literature values. Index the sample peaks based on the known structure. Compare the peak's FWHM to the reference sample

results. Calculate $\frac{\sin^2(\theta)}{(h^2 + k^2 + l^2)}$ for your assumed values of the structure. Use the data to confirm or reject your proposed crystal structure.

Compare the observed intensities with those predicted from the method you used in the above analysis for at least one of the samples. Do you see evidence of preferred orientation of the crystallites (the single crystal Si specimen is an extreme example of preferred (i.e. nonrandom) orientation).

Measure an unknown sample and determine its crystal structure. Compile a table of corrected peaks assuming calibration from Si (note that some Si peaks are not as listed, this implies a systematic correction to all your data)

Compare the linewidth obtained for the single crystal with that of the Si powder reference sample. Can you estimate the grain size of the Si reference sample from the observed linewidth (See Cullity) What about the other polycrystalline sample?

Safety Warning: (X-rays can kill you)

It is better to not put any part of your body in front of the shutter even if you think it is closed. Pay close attention to the operation of the safety interlocks, but they can fail. You will need to use a temporary pencil-shaped, x-ray dosimeter to be worn anytime you are using the diffractometer. This is a safety device that measures any exposure to x-rays. (It does not prevent errors or unwanted exposure but is a way to limit future exposure.)

References:

1. Joint Committee on Powder Diffraction Files (JCPDF) in the SFU library QC 482 D5 J64 Bennett Reference. Companion search manual next to it on the shelf (QC 482 D5 J642). These references lists materials by name, telling you the crystal space group, the expected d-spacings and intensities of each peak, and other information. This data has been collected from powder specimens assuming completely random crystal orientations.
2. SFU Library Online Inorganic Crystal Structure Database. This scans the literature for given elemental content or crystal structure to find possible matches, then listing the phase, space groups, calculated expected x-ray lines giving you a crystal drawing, x-ray spectrum, atomic positions, lists of d-spacings, hkl, etc.