

X-ray powder diffraction and crystallography

Goals:

- Learn how to operate an x-ray diffractometer.
- Index the diffraction peaks from elements with cubic and hexagonal crystal structures.
- Measure and understand the structure factor of simple crystals.
- Understand statistical uncertainties and systematic errors in a measurement.

Crystallography is the science of the structure (and structure-derived properties) of crystals. X-ray diffraction is the most widely used experimental technique for determining the atomic arrangement of atoms in crystals.

Session #1

I. Background

We describe a crystal structure using the concepts of a lattice and a basis. The lattice is a set of points that is periodic in space. The positions \vec{r} of the lattice points are generated by:

$$\vec{r} = n\vec{a} + m\vec{b} + l\vec{c}, \quad (1)$$

where n , m , and l are integers; the vectors \vec{r} are also known the lattice vectors. The vectors \vec{a} , \vec{b} , and \vec{c} (the base vectors of the primitive lattice) are specified by their lengths (the lattice constants) a , b , c and the three angles between them α , β , γ . For example, the primitive cubic lattice—often referred to as a simple cubic lattice—is described by three perpendicular base vectors of the same length ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$).

A crystal structure is generated by repeating a set of atoms at each lattice point. This set of atoms is called the basis of the crystal structure. The basis is specified by the positions and types of atoms that make up the basis. The positions of the atoms are specified in terms of the base vectors of the lattice:

$$\vec{\rho}_i = u\vec{a} + v\vec{b} + w\vec{c}, \quad 0 \leq u, v, w < 1, \quad (2)$$

where u, v, w are real numbers and ρ_i is the position of atom i .

The description of a crystal structure in terms of a lattice and basis applies equally well to primitive and non-primitive lattices but a crystal structure with a non-primitive Bravais lattice is often described using a primitive lattice in conjunction with a larger basis of atoms. For example, instead of describing the bcc crystal structure as a body-centered cubic Bravais lattice with a basis of one atom located at each lattice point, we often describe the bcc crystal structure as a primitive cubic lattice with a basis of two atoms at locations $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Similarly, instead of describing an fcc crystal structure by a centered cubic Bravais lattice and a basis of one atom, we can, if we find it convenient, use a primitive cubic lattice with a four-atom basis $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$.

Three common cubic crystal structures (NaCl, diamond, and ZnS) are based on the fcc structure and are generated by repeating a two-atom basis at each lattice point of the centered cubic Bravais lattice. The basis for NaCl consists of an atom of type A at $(0, 0, 0)$ and an atom of type B at $(\frac{1}{2}, 0, 0)$. In the diamond structure, the basis is two atoms of the same type A at $(0, 0, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. In the cubic ZnS structure (zinc blend), the basis is two atoms: an atom of type A at $(0, 0, 0)$ and an atom of type B at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

Cubic crystal structures, lattice constant a				
Simple cubic	Body centered	Face centered		
sc	bcc	fcc	Diamond	ZnS
A-(0, 0, 0)	A-(0, 0, 0) A-($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	A-(0, 0, 0) A-(0, $\frac{1}{2}, \frac{1}{2}$) A-($\frac{1}{2}, 0, \frac{1}{2}$) A-($\frac{1}{2}, \frac{1}{2}, 0$)	A-(0, 0, 0) A-($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) A-(0, $\frac{1}{2}, \frac{1}{2}$) A-($\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$) A-($\frac{1}{2}, 0, \frac{1}{2}$) A-($\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$) A-($\frac{1}{2}, \frac{1}{2}, 0$) A-($\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$)	A-(0, 0, 0) B-($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) A-(0, $\frac{1}{2}, \frac{1}{2}$) B-($\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$) A-($\frac{1}{2}, 0, \frac{1}{2}$) B-($\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$) A-($\frac{1}{2}, \frac{1}{2}, 0$) B-($\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$)

Another useful way to think about crystals is as a one-dimensional stacking of two-dimensional planes of atoms. The constructive interference of x-ray reflections from these planes of atoms gives rise to Bragg's law

$$\lambda = 2d_{hkl} \sin(\theta_{hkl}), \quad (3)$$

where, λ is the wavelength of the x-rays, d_{hkl} is the spacing between (hkl) planes, and θ_{hkl} is the Bragg diffraction angle. The order of diffraction is not included in eq. (3) since this can be accounted for by the plane index: (002) is the same as the second-order (001) reflection.

Bragg's law gives the angular positions of the diffracted beams, but gives no information about the diffracted intensity. For a perfectly random powder—i.e., a powder in which all grain orientations are present with equal probability—the diffracted intensity is proportional to

$$I_{hkl} \propto m |F_{hkl}|^2, \quad (4)$$

where m is the multiplicity factor which indicates the number of equivalent planes (e.g., (100), (010), etc.) contributing to diffraction at a given angle, and F_{hkl} (in general a complex number) is the structure factor, defined as the sum of the scattering factors f_n of all the atoms in the unit cell

$$F_{hkl} = \sum_{n=0}^N f_n e^{2\pi i(hu_n + kv_n + lw_n)}. \quad (5)$$

If the atomic positions is described in term of a cell basis and an atomic basis (e.g. ZnS is fcc + two atom basis), the structure factor can be expressed as the product

$$F_{hkl} = F_{hkl}^{\text{cell}} \cdot F_{hkl}^{\text{atomic}} = \left(\sum_{n=0}^{N_{\text{cell}}} e^{2\pi i(hu_n + kv_n + lw_n)} \right) \left(\sum_{m=0}^{N_{\text{basis}}} f_m e^{2\pi i(hu_m + kv_m + lw_m)} \right). \quad (6)$$

(A discussion of scattering factors can be found in C. Hammond, *The Basics of Crystallography and Diffraction*, Chapter 9)

* In this lab, you will use the Cu K_α line, $\lambda = 1.5406 \text{ \AA}$.

The following table lists reflections in the cubic system; the corresponding plane spacing (in units of the lattice constant), multiplicity factor, and scattering factors for the bcc and fcc lattices.

(hkl)	d_{hkl} / a	m_{hkl}	F_{bcc}	F_{fcc}
(100)	1	6	0	0
(110)	0.7071	12	2	0
(111)	0.5774	8	0	4
(200)	0.5	6	2	4
(210)	0.4472	24	0	0
(211)	0.4082	24	2	0
(220)	0.3536	12	2	4
(310)	0.3162	24	2	0
(311)	0.3015	24	0	4
(222)	0.2887	8	2	4
(321)	0.2673	48	2	0
(400)	0.25	6	2	4
(330)	0.2357	12	2	0
(331)	0.2294	24	0	4
(420)	0.2236	24	2	4
(332)	0.2132	24	2	0
(422)	0.2041	24	2	4
(431)	0.1961	72	2	0

(511)	0.1925	32	0	4
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II. Shot noise, statistical errors, and data acquisition time

Comment: Use the time needed to acquire the x-ray diffraction data to analyze data you acquired in previous scans. This will save time and allow you to detect errors and repeat measurements if needed.

The detector in the x-ray diffractometer counts the number of x-ray photons incident on the detector. The efficiency of this counting, i.e., the fraction of x-rays that are actually detected, is called the quantum efficiency of the detector. Therefore, inherently, the x-ray diffraction signal has statistical noise: the number of counts that are detected within in some time interval (typically referred to as the *acquisition time* or the *dwell time*) has a Poisson distribution and the standard deviation of the signal will be given by the $N^{1/2}$, where N is the total number of x-rays detected (i.e., the total number of *counts*). This type of noise is often referred to as *shot noise*.

In almost any experiment that involves counting, we have to decide what acquisition time is sufficient to reduce the shot noise to an acceptable level. Note that the noise scales as $N^{1/2}$ and the signal scales as N so the signal-to-noise scales as $N^{1/2}$. Also, there is not much point in reducing the errors in the measurement produced by shot noise much below the errors the *systematic errors*. (Systematic errors are discussed in more detail below.)

1. Load a Cu powder sample (fcc) into the diffractometer and collect a diffraction spectrum $20^\circ \leq 2\theta \leq 100^\circ$ at a high scan rate of $24^\circ/\text{min}$ and step size of 0.05° . (The acquisition time per point is then $60/24 \cdot 0.05 = 0.125$ sec.) Refer to the written procedure for operating the diffractometer at your station.
2. Open the raw data file with *Jade MDI* and save the data as a text file.
3. Open *MatLab* and import the *Intensity* and *2 theta* data in the text file as two separate vectors. Plot the intensity versus 2θ and print a copy for your report.
4. Repeat the scan using a scan rate of $6^\circ/\text{min}$ and a step size of 0.05 and repeat steps 2 and 3. (The acquisition time per point is then $60/6 \cdot 0.05 = 0.5$ sec.)
5. For your report, analyze the standard deviation in the number of counts in some region of the diffraction pattern that is far removed from the diffraction peaks. Is the standard deviation what you expect?
6. Below, you will try to determine if the longer acquisition time of the second scan is actually helpful in determining the lattice constant of Cu.

III. Indexing and structure factors for fcc, bcc, and hcp crystals

7. Collect the diffraction pattern for a bcc crystal, Mo, using an acquisition speed of 24°/min and step size 0.02°. While you are collecting data for Mo, start analyzing the Cu data according to the procedure outlined in Section IV.
8. Repeat the measurement for a diamond structure crystal, Si. While you are collecting data for Si, analyze the Mo data.
9. Repeat the measurement for ZnS.
10. Repeat the measurement for an hcp metal, Ti. The basis of atoms for the hcp structure is two atoms of the same type at (0, 0, 0) and (2/3, 1/3, 1/2).

IV. Indexing diffraction patterns

11. For each of the elements Cu, Mo, Si, and Ti:
 - a. Make a table listing the allowed diffractions (hkl), d-spacing, expected diffraction angle θ_{hkl} , and $2\theta_{hkl}$.
 - b. For Si and Ti, list also the structure factor due to the two-atom basis.Use the information provided in Section I and the lattice constants listed in the periodic table provided by the TAs. For Ti, use the following formula to calculate the d-spacings for planes with $0 \leq h \leq 2$, $0 \leq k \leq h$, and $0 \leq l \leq 4$.

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}. \quad (7)$$

12. Open the raw data files with *Jade MDI*
13. For each material, use your calculated values of the diffraction angles to index (identify) the peaks in your experimental spectra. Save the data as a text file
14. Open *MatLab* and import the *Intensity* and *2 theta* data in the text file as two separate vectors. Plot the intensity versus 2θ using MatLab. With your report, turn in a printout of the x-ray diffraction spectra with (hkl) labels indexing the peaks. How do the experimental angles compare to the observed ones? Are there any absent or extra lines in the spectra?

Session #2

V. Systematic errors and precise determination of lattice constants

15. For Cu, Mo, and Si pick the 4 most intense diffraction peaks and use your experimental $2\theta_{hkl}$ values and Bragg's law to calculate the lattice constant a for each peak. For your report make a plot of the measured value of a versus 2θ . Include both the slow-scan and fast-scan data for Cu. Approximately, how large is the spread in the value of a (the uncertainty in a) for each material? Did the slow-scan (longer data acquisition time) help for Cu?
16. In most measurements in materials science, statistical errors are not the dominant source of uncertainty. The dominant sources of uncertainty are what are called *systematic errors*, e.g., errors in how the encoders report the angles in the diffractometer or the fact that the surface of the powder sample is either above or below the plane of the sample holder. (In other experiments in the MSE 405 lab, possible systematic errors are errors in the calibration of the spectrograph used for Raman spectroscopy; errors in the positions of lenses used in the optics experiments; or errors introduced by inaccurate pulse durations in the NMR experiment.)
17. For our XRD experiments, the dominant systematic errors in a are probably created by errors in θ_{hkl} . Differentiating Eq 3, we find

$$\frac{\partial a}{a} = \frac{\partial d_{hkl}}{d_{hkl}} = -\frac{\cos(\theta_{hkl})}{\sin(\theta_{hkl})} \partial\theta_{hkl}. \quad (8)$$

18. Inspection of Eq. 8 tells us that we might be able to minimize systematic errors in a by extrapolating measurements to high diffraction angles, $2\theta = 180^\circ$. A common source of systematic error in a powder diffraction experiment is the position of the plane of the sample surface (sometimes called a *defocusing error*). We can minimize defocusing errors by using the following method of extrapolation: plot the measured values of a derived from each peak as a function of $\cos^2 \theta / \sin \theta$ and then linearly extrapolate the data to find the intercept with the y-axis. (That will happen when $2\theta = 180^\circ$ so that $\cos \theta = 0$.) Use MatLab to do this analysis. Does this procedure give you a better value for a ?

VI. Characterization of the Cu K_α doublet

19. Acquire more detailed XRD spectra of the two Si peaks at high diffraction angles ($85^\circ \leq 2\theta \leq 100^\circ$). Change the step size to 0.005° , decrease the scan speed, and pick adequate start and stop angles for each peak. You will want to make sure that you scan the whole peak while

minimizing the amount of time wasted scanning far away from the peak where the only signal is background.

20. Looking carefully at these more detailed Si spectra, you will see that the diffraction peaks are doubled. The reason is that you are resolving two separate diffraction peaks created by the two Cu-K α x-ray lines ($\lambda_1 = 1.54056 \text{ \AA}$ and $\lambda_2 = 1.54439 \text{ \AA}$).
21. Measure the angular position of the two sub-peaks for each reflection and use Bragg's law to determine the ratio λ_1/λ_2 of the wavelengths of the two lines. How does this ratio compare with the theoretical one?
22. Use the experimental sub-peak intensities (maximum values) to estimate the intensity ratio of the two Cu-K α lines. Note that you may need to do a linear background subtraction to get accurate intensity values.

VII. Analysis of structure factors

23. What are the differences (in terms of reflections present or absent) between the Si, Cu, and ZnS spectra? Explain qualitatively why some reflections are present in Cu but not in Si. Are these reflections present in ZnS? Why?
24. Use the measured intensities of the (220) and (222) ZnS peaks to estimate the ratio

$$\frac{|f_A + f_B|^2}{|f_A - f_B|^2}. \text{ Use this value to calculate } \frac{f_A}{f_B}. \text{ Which atom (Zn or S) would you expect to have}$$

a higher atomic scattering factor? Why? (See, *The Basics of Crystallography and Diffraction*, Chapter 9 for a discussion of atomic scattering factors).