

361 Laboratories

Laboratory 1: Symmetry in Two Dimensions

Objectives

We will be working with 2-dimensional lattices. You will see how the symmetry of the lattice and not its shape determines to which of the four axial systems it belongs. Parts A and B examine unit cells, translational symmetry, and Miller Planes. Parts C and D add rotational symmetry, mirror, and glide planes. In Part E, we will examine 2-D Si and Ga surface structures grown on a Si (100) substrate.

Laboratory Procedure

Part A1: Lattices and Unit Cells (see worksheet p.4) A unit cell must be able to reproduce the lattice when translated along the axes directions. A primitive unit cell is the simplest case where there is only one lattice point per unit cell. Non-Primitive unit cells contain more than one lattice point per unit cell. All lattice points must have identical surroundings. NOTE: this lattice belongs to the Oblique axial system.

1. You are to locate and outline two different primitive unit cells. Use as your lattice point the angle corner of the triangle. Note that any point would be equally valid as a lattice point but I chose that so everyone would use the same point.
2. Now locate and outline a non-primitive unit cell.
3. Label your unit cells 1,2, and 3. For all unit cells, locate a corner where the angle $\geq 90^\circ$ (γ) and mark it as the origin. Using a right-handed convention, (i) label the axes **a,b** and (ii) measure **a,b**, and γ . In the worksheet margin, calculate the unit cell area:

$$\text{Area} = (ab)\sin\gamma$$

You will note that non-primitive cells have an area that is an integer multiple of the area for a primitive cell.

Part A2: Miller Indices

1. Draw a line parallel to MN and another to OP inside each of your cells; the lines must touch somewhere on the cell axes. Label them MN' and OP'. For convenience, you may want to make these lines intersect a cell axis at: 1, 1/3, 1/10, 3/4 ... etc of the unit length.
2. Using the table at the bottom of the worksheet, calculate the Miller Indices for each line (six total).

Part B: More Lattices Select a printed fabric. Note: all fabrics belong to the Oblique axial system. Choose a feature in the pattern that “stands out to your eye” as a lattice point. Locate a primitive unit cell. Examine it for translational symmetry. Trace the primitive unit cell on 2 the tracing paper provided. Measure and label a, b, γ , and record the pattern number.

Part C: Symmetry, Plane Group, Plane Lattice, and Axial System (worksheets p.5, 6)

1. See the example. Look for symmetry in the pattern #1 and draw the appropriate symbol at all the locations. (e.g. 3-fold ▲, mirror plane , glide plane —)
2. In the blank area to the right of the pattern, make a sketch of the primitive unit cell.
3. Draw the appropriate symbols for all the symmetry you found at the locations where you found them on your sketch. It should match up with a plane group in Hammond p.67. 4) On the work sheet state the: 1) plane group 2) axial system (Symmetry Notes) and 3) plane lattice (Hammond p.62). At home do the same for patterns #2 and #3. These are more difficult.

Part D: Motif (asymmetric) For two Escher drawings:

1. On tracing paper, repeat what you did in Part C.
2. Trace the motif of the pattern.

Part E: Surface Reconstruction (worksheet p.7) The lattice vectors for a surface structure will be different from those of the substrate. This change is known as a surface reconstruction. If we define the lattice vectors of the substrate as \mathbf{a} and \mathbf{b} ; the lattice vectors for a given surface structure can then be expressed in terms relative to the substrate. The unit length of the surface vectors will be

$$\mathbf{a}_{surface} = N\mathbf{a}_{substrate} \quad \mathbf{b}_{surface} = M\mathbf{b}_{substrate}$$

e.g. If $\mathbf{a}_{surface} = 3\mathbf{a}_{substrate}$ and $\mathbf{b}_{surface} = 5\mathbf{b}_{substrate}$, then $N=3$, $M=5$. The surface is then called a 3×5 ($N \times M$).

Now consider the two surface structures on the Si (001) substrate. Here, Ga-ad-dimers have been adsorbed on a surface consisting of Si-dimers on top of a Si (001) bulk. Sketch the primitive lattice of: 1) Si bulk 2) Si-dimer 3) Ga ad-dimer layers with the $N \times M$ for each structure. Ignore the symmetry of the pattern. I am only interested in the primitive unit cells.

Deliverables

Please do everything asked for. Make everything neat and orderly so as to get full credit. Erase all unnecessary lines, marks etc.

Symmetry Notes

I. Periodic structures or patterns in two dimensions belong to one of four axial systems. These are named according to the shape of the unit cell: oblique (parallelogram), rectangular, square, hexagonal (triangular).

There are, however, a total of five two-dimensional plane lattices (Hammond p.62) in which all lattice points have equivalent surroundings; these are analogous to the 14 Bravais lattices in three dimensions. The two-dimensional plane lattices (or nets) are sketched below. Four are primitive and one is non-primitive (rectangular centered/diamond).

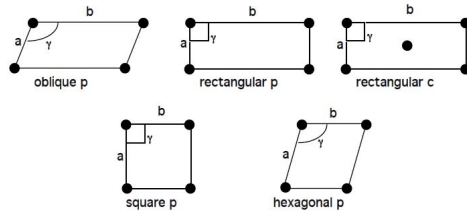


Figure 1: 2-D plane lattices

II. The preceding applies to arrays of featureless points, or, if you prefer, circles, which have "perfect" symmetry. A real pattern is made up of motifs (asymmetric objects, e.g. "7"), which have certain spatial relations. Each lattice point has one or more motifs associated with it. Any pattern can be classified by the symmetry of the collection of motifs at each (or any) lattice point. There are only 17 different patterns in two dimensions; every periodic wallpaper, decorator fabric, etc. conforms to one of these. Such classification is beyond the scope of this course, but a few instructions or conventions are useful. (The summary of the 17 patterns plane groups Hammond p.67).

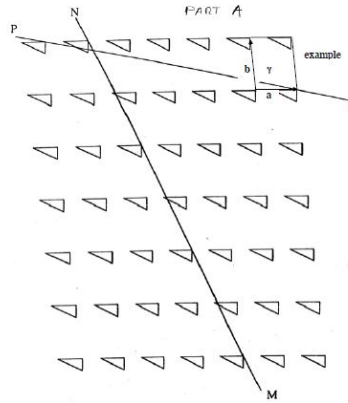


Figure 2: Part A1 example

	Cell 1		Cell 2		Cell 3	
	(MN)'	(OP)'	(MN)'	(OP)'	(MN)'	(OP)'
	a	b	a	b	a	b
Intercept						
Reciprocal						
Miller Indice						

Table 1: Part A2

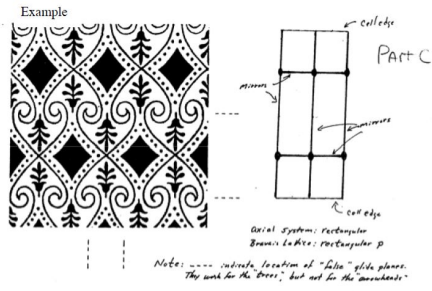


Figure 3: Part C Example

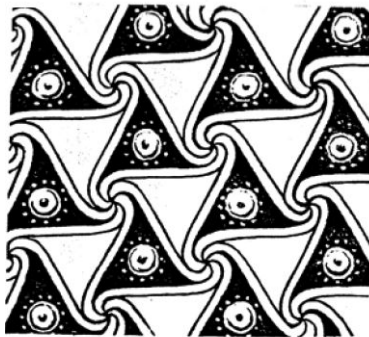


Figure 4: Part C # 1-3

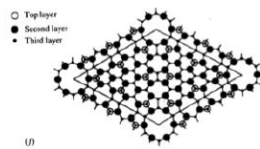
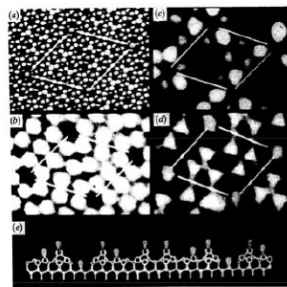
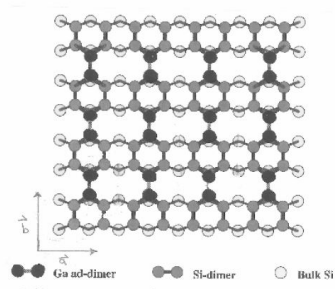


Figure 5: Part E

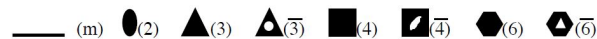
Laboratory 2: Symmetry in Three Dimensions

Reading: Cullity and Stock sec 2.5, 2.6, 2.7, 2.9, 2.10, 2.11, Hammond Sec 12.1, 12.2, 12.3

Part A1: Crystal Shapes and Point Group Symmetry

Inspection of a crystal can provide significant information about its symmetry. One can observe the presence (or absence) of mirror planes, rotation axes, rotoinversion axes and inversion centers. These identify the crystal system and the orientation of the conventional unit cell. One can do even better: the presence of more than the minimum crystal symmetry (C&S table 2.3) specifies the point group symmetry within the crystal system. There are 32 of these: stereographic projections are from the International Tables of Crystallography vol. 1.

You have 5 crystal models; each is from a different crystal axial system (trigonal is combined with hexagonal and orthorhombic will be studied in Part 2). Inspect each for symmetry: mirror planes, rotation axes, roto-inversion axes, and inversion center. Make a stereographic projection of the collection symmetry you found using the symbols below. Next to this, make a perspective sketch of the model indicating which face is at the projection point (center) of your stereographic projection.



Consult the point group symmetry table only after you have thoroughly examined your models to help find any symmetry elements you may have missed. On your worksheet you should have: 1) the identifying number 2) the stereographic projection along with a simple sketch of the model 3) state the axial system 4) state whether the crystal has or does not have a inversion center. **NOTE: Please do not draw on the models and be careful with them; they are very fragile.**

Part A2: Wulff net (orthorhombic)

Use a right-handed coordinate system and make 1) a simple sketch the model, 2) label the axes **a**, **b**, **c** 3) record the axes ratio **a:b:c**, and include the model number.

Now select two faces (only one can be a {100} type) and label these faces “A” and “B” on your sketch. Approximate the angle of the plane-normal between the faces relative to the axes and plot these as **poles** on the provided stereographic (m) (2) (3) (3) (4) (4) (6) (6) 2 projection. Use the **c** axis as the projection point (center).

GRADUATE STUDENTS: (after class) From the three direction cosines for both poles and the axis ratio **a:b:c** , calculate and normalize the ratio of integers $h : k : l$ (C&S p. 82.) These are the Miller Indices of the crystal faces.

Part B: Crystal Models-Cubic

You are provided with open and space filling models of FCC and an open diamond cubic model.

1. Inspect the FCC structure; this can be formed by stacking close packed planes (ABCABC...) which become {111} in the cubic representation. There are octahedral voids (CN=6) at $1/2, 1/2, 1/2 + \text{fct}$ and tetrahedral voids (CN=4) at $1/4, 1/4, 1/4$, etc. (one in each corner).
 - a. After class, calculate the radius of the void(r) in terms of the lattice parameter(a) and radius of the atom(R). Do this for both the octahedral and tetrahedral voids.

- b. GRADUATE STUDENTS (after class): Consider the primitive unit cell of the FCC structure. (Hammond section 5.8.) Write Miller indices for planes in the primitive cell (HKL) in terms of (hkl) in the FCC cell. You can consult Azaroff p. 53-54. The figure 3-19 is incorrect. Switch a_{01} and a_{02} (**a b** in the primitive cell) so the axis system is right handed.
2. Examine the Diamond Cubic structure. Tetrahedral coordination of each atom should be evident. Note the "diamond glide" planes. $\langle 110 \rangle$ 2 per face.
- Give the coordinates of each atom in primitive unit cell.
 - Are all atoms equivalent? Briefly explain your answer with a simple sketch. __
 - Is the three-fold axis along $\langle 111 \rangle$ a 3 or 3? Briefly explain. __
 - Is the four-fold axis along $\langle 100 \rangle$ a 4 or 4? Briefly explain.
 - Identify "diamond glide" planes (2 per face). Note both the plane orientation $\{hkl\}$ and glide direction $\langle uvw \rangle$. Briefly explain.

Part C: Crystal Models - Hexagonal

For the open HCP model, primitive hexagonal, locate the 2 atoms per unit cell. Observe the 6 roto-inversion axis that is present in this structure with 3 inversion centers at $z=0$, $z=1/2$. Identify the 4 tetrahedral voids per cell. The two "internal" ones are easy to see and the others are on vertical edges.

- Locate the octahedral interstices (voids) and give the coordinates; 2 per unit cell.
- All the octahedral sites could be occupied in a compound. Alumina, Al_2O_3 , presents an interesting variation. The O-2 form an HCP structure however; the Al+3's occupy only 2/3 of the available octahedral sites. Note the pattern of occupation varies from layer to layer.
 - How many layers are required for the structure to repeat? Hint: Start counting at the midpoint of the bottom most HCP structure.
- The crystal system is actually rhombohedral (trigonal), but the model and structure are most easily visualized in a hexagonal setting. To determine the proper symmetry, show the following:
 - A 6 fold is not present along c.
 - A 3 fold is present along c. __
 - A 6 is not present along c (this is trickier; consider both O and Al atoms).

Laboratory 3: Laue Diffraction Patterns

Reading: Cullity sec. 16-1, 16-2, 2-13, Hammond sec 12.1, 12.2, 12.3

Lab Summary

You will use the Laue Back Scattering technique to determine the crystallographic orientation of a single crystal. Then you will re-orientate the crystal to a different plane.

Introduction

The Laue method records the x-ray diffraction pattern on a CCD camera, image plate or photographic film. The Back Reflection Laue technique is for high x-ray absorbing samples at diffraction angles (2θ) between 120° and 180° . The Front Reflection Laue method is used for $0^\circ < 2\theta < 60^\circ$ but is suitable only with low absorbing samples like polymers.

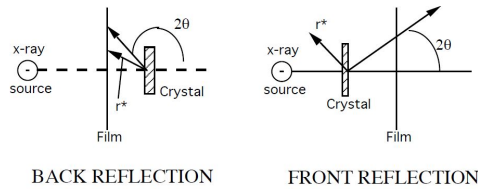


Figure 6: Back Reflection and Front Reflection Laue

While Laue methods are used for several purposes, one of the most important is to determine the orientation of single crystals. Well-grown crystals have habits (shapes or facets) that indicate the symmetry possessed by the lattice on which the crystal was "constructed". But if a crystal is poorly formed or was made in such a way that facet development is prevented, xrays can be used to determine the presence and orientation of planes within a crystal using Bragg Diffraction. Bragg Diffraction or Bragg Scattering only occurs when:

- i) the Bragg condition is satisfied, $n\lambda = 2d_{hkl}\sin\theta$
- ii) r_{hkl}^* the normal to a plane(hkl), bisects the incident and diffracted x-rays. This is shown in the figure above.

Crystals have many planes of atoms with different values of d_{hkl} . To ensure that the Bragg condition will be satisfied for many of these, a large range of λ 's are supplied by the white or Bremsstrahlung radiation of the x-ray tube. Generally Mo or W anode x-ray tubes are used for Laue because of the greater white component to their spectrum at lower operating voltages but any target material (e.g. Cu, Cr, etc.) is suitable.

The incident x-rays are collimated into a beam, pass through a hole in the film holder and strike the sample. X-rays backscatter onto the film where the pattern is recorded. The sample is mounted on a goniostat, a device that permits the rotation of the sample about its horizontal and vertical axes (see figure page 3). The position of a diffraction spot enables us to determine the direction of r_{hkl}^* , if we remember that r_{hkl}^* bisects So the incident beam direction and S the scattered beam direction.

Experimental Procedure

With both goniostat axes set to 0.0° , record a back reflection Laue pattern of the MgO crystal. Your instructor will give you recommended voltage, current, and exposure times. Note the symmetry apparent in the diffraction pattern. Given that MgO has the sodium chloride crystal structure, which pole (plane normal) is nearly parallel to the x-ray beam?

With the assistance of your instructor, locate six zones and label them as 1,2,3 etc. Measure the position of each zone using the Greninger Chart. The Greninger Chart is a device that saves tedious trigonometric calculations, allowing you to read directly the latitude (γ°) and longitude (δ°) of individual poles. We will further simplify the work by measuring $\tilde{\alpha}^\circ$ for an entire zone of poles simply by rotating ε° (the Greninger Chart) and aligning γ° . Make a table of ε° , its direction (CW/CCW), and γ° . For accuracy, read all angles to the nearest $1/2^\circ$.

To Plot: Orientate the Wulff Net with NS axis **horizontal** to make tracing easier. You need to rotate the Wulff Net the same direction as the Greninger Chart to plot the zones. However, the Wulff Net will be remaining stationary and you will be rotating the tracing paper. Therefore, you need to rotate the tracing paper in the **opposite** direction that you rotated the Greninger Chart. Plot zones as great circles.

Now measure the interplaner angles between zones simply by placing two poles (intersecting zones) on the same great circle and measuring the angle between them. Index all intersecting zones with this technique referring to the table of inter-axial angles for cubic crystals provided in lab. Note: If you cannot match a pole, label it with a "?". Bad guesses will be graded as incorrect. When you finish, you should find at least one pole to be a $\{111\}$ or $\{110\}$. Reorientate the sample to one of these reflections by adjusting the goniostat arcs. Record the diffraction pattern and note the symmetry.

Report:

Provide the experimental conditions: x-ray tube anode material, voltage, current, exposure times, beam size, and sample to film distance. Attach both photographs, table of zones with γ , ε , CW/CCW, and goniostat setting for the second photo. Lastly, *index* your stereographic projection using a standard projection (Cullity fig 2-40.)

Laboratory 4: X-Ray Diffractometer Part I

Lab Summary

Labs IV and V examine the principle of operation of the X-ray Diffractometer system. The instrument you will be using is a Rigaku Dmax. Note that both labs will be combined into one report. This week you will investigate the details of: 1) the X-ray spectrum emitted from the X-ray tube, 2) absorption of X-rays by materials.

Experimental Procedure

The instrument is equipped with a Cu anode X-ray tube. The source is a line, 10mm high x 0.4mm wide at a 6° “take-off angle”. The apparent source size therefore is 0.04mm or 0.01° at a sample distance of 185mm, the “radius of the diffractometer.” With your instructors assistance and X-rays off

: 1) Inspect the X-ray generator and X-ray shutter operation to be certain how they work together with the indicator lights.

2) Note the X-ray collimating system with the incident beam slit “Divergence Slit” (DS), and the scattered beam slits, “Receiving Slit” (RS) and “Scatter Slit” (SS). These are used to define the incident and scattered beam directions S_o and S.

3) Note the Specular Reflection geometry of the diffractometer with the sample axis θ and detector axis 2θ as they change simultaneously. The X-ray detector is a scintillation type and uses an electronic device called a Pulse Height Analyzer (PHA). We will need to re-adjust the PHA for this weeks lab. Record the initial PHA settings: Baseline (BL) and Window (W) voltages. Adjust the BL to 0.5V and the W to 5.0V.

Part A: X-ray Tube Emission Spectrum

Energize the X-ray tube to -20kV and 2mA. X-rays will irradiate a LiF (100) single crystal that acts like a diffraction grating scattering X-rays. LiF has the FCC NaCl crystal structure. Scan 2θ from 15° to 50° , Appendix L4A1. Ignoring the absorption effects of: 1) the X-ray tube Be window, 2) the detector Be window, 3) air, and 4) the Al absorber foil, you have recorded the emission spectrum of the Cu anode X-ray tube.

Note that the most intense peak in the spectrum is from the Cu $K_{\alpha 1}$ emission line, $\lambda = 1.54056\text{\AA}$. You will now determine a more precise 2θ position for the line by scanning with a smaller step size, L4A2. Now having an accurate value for the Cu $K_{\alpha 1}$ position, calculate the exact value for $LiF d_{200}$. For your report, using Bragg’s Law and d_{200} of LiF, calculate λ for all the notable lines and features present in the spectrum i.e. the Bremsstrahlung radiation, short wavelength limit (SWL), and **all** emission lines. Identify the element(s) responsible for each noted emission line, see Cullity app 7. (Hint: What impurity metal is present inside the X-ray tube?) Also include in your report, the comparison between your measured λ_{SWL} wavelength and the calculated value using the X-ray tube operating voltage (kV).

Part B: Scattering from LiF (400)

Calculate the 2θ position for the LiF (004) $CuK_{\alpha 1}$ line. Scan 2θ from 99° to 101° (L4B) to determine the exact angles for $CuK_{\alpha 1}$ and $K_{\alpha 2}$ wavelengths. Compare measured and calculated positions.

Part C: Absorption of X-rays by Al

Move the detector to the Cu $K_{\alpha 1}$ line. Use the Ratemeter to count the X-ray intensity for ten one-second measurements, average these values (I_0), and record. CLOSE THE SHUTTER, insert two sheets of Al foil in front of the detector, open the shutter and average 10 more one-second measurements. Repeat, adding two foils at a time until $I = 0.1 I_0$. For your report plot $\ln I$ vs. t (t = foil thickness in cm). If the detector response is linear, this will be a straight line. From the slope of this line you can calculate the absorption coefficient μ . Calculate the Al foil thickness given the density = 2.70 g/cm^3 and the weight of 100 cm^2 of foil = 0.439 g . Compare your value of μ to that found in the *International Tables for X-ray Crystallography (SEL)*.

Part D: Absorption of X-rays by Ni

Insert the Ni filter. Scan 2θ from 39° to 46° to include the Cu K_{β} and Cu K_{α} emission lines (L4D). Note the differences in the spectrum, especially the relative intensities of the K_{β} and K_{α} lines by comparing to L4A1. Re-plot the region between the K_{β} and K_{α} peaks to experimentally locate the K absorption edge of Ni. For your report, calculate the thickness of the Ni filter using the data from the Cu K_{β} absorption. You will need to look up the $\frac{\mu}{\rho}$ and ρ values for Ni. Calculate the wavelength of the Ni K absorption edge and compare this to the value in the International Tables. Close the shutter, turn off the X-rays, and return the PHA to the original settings.

APPENDIX

File Name	Start ($2\theta^\circ$)	Stop ($2\theta^\circ$)	Step Size ($2\theta^\circ$)	Dwell (s)	Axis
L4A1	15	50	0.05	1	$2\theta/\theta$
L4A2	44.5	45.5	0.02	1	$2\theta/\theta$
L4B	99	101	0.02	1	$2\theta/\theta$
L4D	39	46	0.05	1	$2\theta/\theta$

Laboratory 5: X-Ray Diffractometer Part 2

Reading, Cullity and Stock: sec 6-7, 6-9, 6-11, and p.201-202

Lab Summary

This week you will study the details of the X-ray detector system. You will: 1) perform measurements to determine the energy resolution of the NaI scintillation detector 2) select filters and make adjustments to the PHA to produce a monochromatic X-ray beam from the polychromatic X-ray source suitable for Powder X-ray Diffraction (PXR) experiments.

Part A: Energy resolution of the NaI detector

When a single X-ray photon enters a scintillation detector, it produces a voltage pulse whose amplitude (in volts) is linearly proportional to the X-ray energy. However, there is a limit (resolution) where a small change in λ produces no change in voltage.

Procedure Adjust the PHA, slits, and the X-ray tube power to that used last week. Scan the LiF (200) crystal (L5) to locate the Cu $K_{\alpha 1}$ emission line and move the detector to the position.

1. Open the shutter so X-rays from the $CuK_{\alpha 1}$ emission line enter the detector. (Note: $\Delta\lambda/\lambda$ is $\sim 0.1\%$)
2. Adjust the PHA: Baseline = 0.4V, Window = 0.2V. Lock the Window setting, as it must remain constant throughout the entire measurement!
3. Use the Ratemeter function and average ten one-second readings and record: i) Intensity (counts), ii) $V_{detectoroutput} = V_{Baseline} + 1/2V_{Window}$
4. Increase the V_{BL} by 0.5V and repeat step 3.
5. Keep repeating until the upper limit of V_{BL} is reached.
6. Collect additional data around the maxima by stepping V_{BL} at 0.2V intervals. A plot of I vs. $V_{detector}$ is the differential voltage curve for the detector. Measuring the Full Width Half Maximum (FWHM) of the curve yields the resolution:

$$Resolution\% = 100 \times \frac{FWHM}{V_{det}(maxima)}$$

More useful plots are of I vs. $\lambda(\text{\AA})$ and especially I vs. E (keV) as

$$\Delta V/V = \Delta\lambda/\lambda = \Delta E/E$$

To plot I vs. E:

$$E(ke) = (V_{BL} + 0.1V) \times \frac{8.05keV}{V_{det}(maxima)}$$

To plot I vs. λ :

$$\lambda(\text{\AA}) = \frac{12.4}{E(\text{keV})}$$

You have now calibrated the PHA for Energy (keV), Wavelength (\AA) and Voltage (V).

Part B: Adjusting the PHA for a 90% Window

The PHA can be adjusted to prevent the scattering from unwanted wavelengths from being recorded in an X-ray pattern. That is desirable in kinematic scattering experiments like PXRD. Also, to keep the intensity high, you will set a “90% window” as it allows 90% of the intensity to pass to the counter and rejects 10%.

Procedure Open the shutter to allow Cu $K_{\alpha 1}$ radiation to enter the detector

1. Set $V_{BL} = 0.5V$ and $V_W = 5.0V$.
2. Start the Ratemeter and record I0 (average ten one-second readings.) Note this is the integrated intensity (100%) of the differential curve: I vs. V_{det}
3. Increase V_{BL} and reduce I0 by 5%, record V_{BL} 4) Without changing V_{BL} , decrease V_W to reduce I by another 5%, record V_W .

You have now set the PHA to pass 90% of the intensity. Consequently, x-rays whose energy is lower than V_{BL} or higher than $(V_{BL} + V_W)$ will be rejected and not be counted.

For your report on each plot I vs. E, I vs. λ , and I vs. V, indicate the positions of:

- 1) Cu $K_{\alpha 1}$ 2) Cu K_{β} 3) V_{BL} 4) $V_{BL} + V_W$.

For your report answer the following questions: With the PHA set to pass 90% of the Cu $K_{\alpha 1}$:

- 1) What range of wavelengths are: i) passed and ii) eliminated by the 90% window?
- 2) What energies are: i) passed and ii) eliminated?
- 3) Is Cu K_{β} eliminated by the 90% window?

Part C: Powder X-ray Diffraction (PXRD)

With instructor’s assistance, replace the LiF single crystal with a polycrystalline LiF sample. Scan the sample with the same conditions as L5, (L5C1). Note the difference. With your instructor’s assistance, remove Al absorber, increase the tube power, and change slits to increase the diffracted intensity. Scan 2θ from 35° to 70° (L5C2).

For your report, 1) discuss why the intensity is lower (L5C1) 2) identify all the diffraction peaks present in L5C2

Part D: Determining the best condition for PXRD

For a PXRD experiment, you want to have monochromatic radiation in order to simplify interpretation of the diffraction pattern. You also would like high peak intensities and a low background. We will investigate various combinations of PHA settings and the Ni filter to determine the optimum conditions for recording a diffraction pattern. The best condition will result with a high-diffracted

intensity (I_p) for only one wavelength λ and a low background level (I_b). Note: Do not use the Jade peak finder.

1. Set the PHA, BL = 0.5V, W= 5.0V, and scan the K_β and K_α peaks for LiF (200) (L5D1).
2. Close the shutter, insert the Ni filter and scan the same region (L5D2).
3. Set the PHA for a 90% window determined in Part B. Scan again (L5D3).
4. Close the shutter, remove the Ni filter and scan again. (L5D4).

In your report, calculate $(I_p - I_b)$ and $(I_p - I_b)/I_b$ for the K_α peak for each of the four conditions. Also calculate $\sigma = \sqrt{N}/N$ for $N = (I_p - I_b)$ and the ratio $(I_p)K_\alpha/(I_p)K_\beta$ in each case. This data should be presented in a table. The best condition is a large value of $(I_p - I_b)/I_b$ for K_α , subject to a small σ for $(I_p - I_b)$ and a relatively small K_β peak. In other words, we want a large peak-to-background ratio and a high intensity for only one peak. (We cannot eliminate the $K_{\alpha 2}$ radiation.) Your report should identify the best condition for obtaining the powder diffraction pattern.

APPENDIX

File Name	Start ($2\theta^\circ$)	Stop ($2\theta^\circ$)	Step Size ($2\theta^\circ$)	Dwell (s)
L5	44.5	45.5	0.02	1
L5C1	44.5	45.5	0.02	1
L5C2	35	70	0.1	0.5
L5D1	39	46	0.1	1
L5D2	39	46	0.1	1
L5D3	39	46	0.1	1
L5D4	39	46	0.1	1

Laboratory 6: Quantitative Analysis of a Mixture

Reading: Cullity and Stock. sec 6-1,2,3, 9-1,2,3,7, 10-1,2,3 Supplement for Lab VI at the end of this handout.

Lab Summary

You are supplied with a mixture of two unknown powdered materials. One has a cubic structure and the other is non-cubic. We will collect a powder diffraction pattern for the mixture and use Search/Match software to identify the unknowns. After class, you will get information online or from the SEL library and calculate the volume fraction for each phase in the mixture.

Experimental Procedure

Prepare a powder xrd sample holder with the unknowns as instructed in lab. Slit sizes to use are 1°DS/SS and 0.3mm RS 0.1°, Ni filter. Adjust the x-ray tube power to 40kV and 20mA. Perform a $2\theta/\theta$ scan from 2θ from 20° to 115°, 0.05 step size, and 1s count time (L6A). Note the $CuK_{\alpha 1,2}$ peak splitting at the higher angles. Examine the data to see that for all peaks there are least three data points within the FWHM. Check that the receiving slit has an angular size that is smaller than the FWHM. Also, the peak height for the six most intense peaks should have adequate counts to better define the peak shape ($\sigma = .03\sim 1000$ counts.)

Identify the diffraction lines using Jade. With the instructor's assistance, use the diffraction analysis software to identify peaks. Check the pattern carefully that Jade did not miss any peaks or incorrectly chooses a peak from CuK_{β} or a tungsten L line. Use the peak editor tool to correct peak finder. Print the peak list, as you will need the info for the Volume % calculation you do at home.

Search Match using Jade. Per instructor's assistance, perform a Search/Match for your unknowns. Overlay the many results of the search on your data to solve the unknowns.

GRADUATE STUDENTS: Texture can be a problem in this type of analysis. The theory assumes that each phase is randomly oriented, which may not be the case. You can check this assumption by comparing the calculated and observed intensity ratios for more than one pair of peaks. Check for random orientation by comparing the ratios for a second set of using different (hkl 's). Do not try to correct your derived volume fraction for any texture effect you may have. Simple knowledge of how close your intensities are to those with random orientation is adequate for this laboratory.

Deliverables (non-formal report):

- 1) Experimental conditions: tube target and power, slit sizes, sample ID number, survey-scan, other scans and peak reports.
- 2) A table of: The unknowns, hkl , f , F^*F (show work), multiplicity, LP factor, unit cell volume and measured integrated intensities. You will use one peak for each phase (undergraduates) or two peaks for each phase (graduates). The instructor will tell you which peaks you should use for this.
- 3) Calculation of volume fractions of phases from XRD. See Supplement for Lab IV

To calculate F , you will need to look up the x_n, y_n, z_n atom positions for the given structure:

- 1) Use ICDD tables to determine structure space group number, lattice constants and z, the number of atoms per unit cell.
- 2) Online databases or the R.W.G. Wyckoff (SEL library ref. section)"Crystal Structures, 2nd., ed., Wiley (1963) to obtain x_n, y_n, z_n .

Supplement for Lab IV

The following is to clarify the ideas and procedure of Laboratory IV from Azaroff Ch 19. We start with the result of the powder diffraction theorem (Azaroff eq.19-5):

$$I_{hkl} = I_o C \frac{F_{hkl}^2 mLP}{V_c^2} V_s$$

Here C is a constant (involving λ , electron characteristics and diffractometer geometry), V_c is the unit cell volume and V_s is the effective diffracting volume of the sample (which depends on sample absorption coefficient μ). This is for one material. If you have a two-component mixture, with material A present with volume fraction v_A , the intensity of a reflection from that material is given by:

$$\frac{I_{hkl}^A}{I_{hkl}^B} = \frac{[F_{hkl}^2 mLP/V_c^2]_A v_A}{[F_{hkl}^2 mLP/V_c^2] v_B}$$

The left hand side is from the experimental data. The first ratio on the right hand side is calculated. This gives you v_A/v_B , or v_A since $v_B = 1 - v_A$. Azaroff is incorrect in omitting from the denominators in eqs: 19-5, 19-7 and 19-9 of the text.

To use this you must be able to evaluate F_{hkl}^2 for the two materials. An example will be worked here. Take the case of antimony (Sb). You must know its crystal structure. The JCPDS file says that the crystal system is "Rhombohedral (Hex)". That means that the primitive unit cell is rhombohedral, but that the pattern is indexed (hkl) with the larger (more convenient) hexagonal cell ($a = b, \gamma = 120^\circ$). There are three lattice points in the hexagonal cell at 000; $2/3 \ 1/3 \ 1/3$; $1/3 \ 2/3 \ 2/3$ (Azaroff, pp. 49 ff; Cullity, Appendix 4). You must look up the crystal structure of Sb (it is not HCP!). A good reference is: R.W.G. Wyckoff, *Crystal Structures*, 2nd. edn., Wiley (1963). This multivolume set is in the reference section of SEL. There you find that there are two Sb per lattice point with displacements $\pm z = 0.233$. This information locates the 6 Sb atoms per hexagonal unit cell. In writing down structure factors, it is convenient to factor the positions of lattice points and the atom displacements from the lattice points (you have done this with FCC structures such as diamond/silicon or NaCl):

$$F_{hkl} = f \left[1 + e^{\frac{2\pi i}{3}(2h+k+l)} + e^{\frac{2\pi i}{3}(h+2k+l)} \right] \left[e^{2\pi i z l} + e^{-2\pi i z l} \right]$$

Recalling that $e^{ix} + e^{-ix} = 2\cos x$ and that $F^2 = FF^*$, straightforward algebra yields:

$$F_{hkl}^2 = 4f^2 \left[3 + 2\cos\frac{2\pi}{3}(2h + k + l) + 2\cos\frac{2\pi}{3}(h + 2k + 2l) + 2\cos\frac{2\pi}{3}(h - k - l) \right] \cos^2 2\pi zl$$

Remember that the arguments of the trigonometric functions are in radians. An easy check on F^2 is to see that it gives $Z^2 f^2$ when $h = k = l = 0$; here $Z = 6$ is the number of atoms per unit cell.

Multiplicity m is looked up or derived for each reflection, and LP factor and f depend on 2θ (or $\sin\theta/\theta$). The remaining factor to be calculated is $V_c = a \cdot b \times c = abcc\cos 30^\circ$ ($\neq abc$ in hexagonal systems!). Do the same calculations for the other material and solve for v_A .

Laboratory 7: Rotating Crystal Method (et al.)

Reading: Lecture notes: “Rotating Crystal Method”(bring to lab), Cullity pp. 111-113, sec 5-2, 5-6, Hammond App. 6 Table A6.1, “Correction Term For Powder Diffractometry” (attached), and Digital Image Plates (Lab Documents Folder).

Lab Summary

Polyethylene (CH_2)- crystallizes into an orthorhombic unit cell. One sample has been heated and drawn causing it to have a strong **c**-axis orientation along the draw direction but random in the **a-b** plane. The other is an isotropic polycrystalline sheet.

A) This week you will perform a rotating crystal experiment using the Cylindrical Camera to determine lattice parameter and Miller Indices for an orientated polyethylene sample.

B) For isotropic polyethylene, you will perform PXR to measure, 1) the average crystallite size, 2) the percent of the crystalline and amorphous phases, and 3) the 2θ peak shift due to sample displacement for the Bragg/Brentano diffractometer geometry.

Part A: Determine Lattice Parameter and Index Sample

With your instructor’s assistance, mount the sample in the cylindrical camera with the sample draw direction along the axis of the camera and insert the Image Plate (IP, a film like image recording media). Mount the camera to a point focus port of a Ni filtered Cu x-ray tube (monochromatic radiation, $\lambda=1.5418\text{\AA}$). Record a diffraction pattern for 5min at 40 kV, 11 mA. Process the IP.

Use the image analysis program “Image Quant” to process your data. You will observe two “layer lines” corresponding to $l = 0$ and $l = 1$. With the software, convert the image to an *Intensity vs. Distance* plot and with the peak finder function, locate peak positions. Print data.

After lab:

Use the data from the layer line $l = 0$ and r_H^2 for each of the first two diffraction lines and solve for **a*** and **b***. You will have two equations and four unknowns. Start by guessing values for h and k . (Hint: h and k are not (10) or (01)). Understand that h and k can only be integers and start with numerically low values. Once **a*** and **b*** are known, you can now index all other diffraction lines (use a spreadsheet program) for both the $l=0$ and $l=1$. Do this for six line pairs for each the $l = 0$ and $l = 1$ layer lines (12 total). Make a table of the measured r_H^2 and compare with calculated $r_{H_{calc}}^2$ (using the **a*** and **b*** from above) to check accuracy.

Part B: Perform a PXR scan

Cu K_α , 40kV, 5mA, DS/SS=2/3°, RS=0.1°(0.6mm), Ni filter, 2θ from 10°-50°, step= 0.05°, dwell=1s (L7B).

1) **Determine crystallite size.** Measure the FWHM (convert to radians) for each of the first eight peaks. Use the Scherrer equation to average the results to calculate the apparent average crystallite size D .

2) **Determine percent crystallinity.** Some materials are not totally crystalline or totally amorphous like glass, but a mix of both. In the diffraction pattern, a distinct amorphous halo will be seen mixed with the crystalline diffraction peaks. The percentage of each is determined

by the ratio of the integrated intensities after subtracting background i.e. $\%crystallinity = I_{crystalline} / (I_{crystalline} + I_{amorphous})$. Use the peaks in the range of 2θ from 10° to 28° .

3) **Peak shift due to sample displacement.** To simulate the error produced by an off-center sample, the instructor will displace the sample holder with the spacer. Rescan 2θ from 20° - 23° (L7B3). Note the peak shift and calculate the thickness of the spacer using the attached handout: "Correction term for Powder Diffractometry." The radius (R) of the Rigaku Ultima diffractometer is 285mm.

Report

Part A 1) Make a table of the peaks #1-6 for both layer lines $l=0, l=1$ with: x, y , measured r_H^* , $hkl, \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$, calculated r_H^* , and Miller Indices. Include the multiple (ambiguous) indexing as appropriate.

2) Make another table with $\mathbf{a}, \mathbf{b}, \mathbf{c}, V_c$ (unit cell volume).

3) Based on your unit cell parameters and a density of 1 g/cm^3 , how many $-CH_2-$ units are there per unit cell?

4) Look for the systematic absences of Miller Indices to determine the Bravais lattice (Hammond Table A6.1).

Part B 1) Calculate percent crystallinity, include calculations for background and integrated intensities and L7B plot.

2) The crystallite size calculation with a table of peak widths (degrees, radians) for the first six peaks, and the averaged grain size. Check that the angular size of the RS ($0.6\text{mm}=0.1^\circ$) $<$ FWHM in order to make a valid measurement.

3) For the displaced sample, include plot (L7B3) for the shifted 2θ peak. Referring to the attached handout, calculate (show work) the spacer thickness (δ) from the $\Delta 2\theta$ peak shifts. Explain how sample absorption (the depth that x-rays penetrate the sample) can cause shifting of peaks.

APPENDIX

Correction Term For Powder Diffractometry If the sample is displaced from the center of the powder camera or diffractometer of radius R by a distance of δ (δ may be due to misalignment and/or sample absorption), the following diagram applies:

Using $\frac{\sin(\text{angle})}{\text{side opposite}} = \text{constant}$, $\frac{\sin(\Delta 2\theta)}{\delta/\sin\theta} = \frac{\sin(180-2\theta)}{R} = \frac{\sin 2\theta}{R}$

For small errors, $\sin(\Delta 2\theta) \approx \Delta 2\theta = \frac{-\delta \sin 2\theta}{R \sin\theta} = \frac{-\delta 2 \sin\theta \cos\theta}{R \sin\theta} = -\frac{2\delta \cos\theta}{R}$

To determine effect on d , use $d = \lambda / (2 \sin\theta)$

$$\Delta d = \frac{-\lambda}{2} (\sin\theta)^{-2} \Delta \sin\theta = \frac{-\lambda}{2 \sin^2\theta} \cos\theta \Delta\theta = \frac{-\lambda \Delta\theta}{2 \tan\theta \sin\theta}$$

then

$$\frac{\Delta d}{d_o} = \frac{-\lambda \Delta\theta / (2 \tan\theta \sin\theta)}{\lambda / (2 \sin\theta)} = \frac{-\Delta\theta}{\tan\theta} = \frac{\delta \cos\theta}{R \tan\theta}$$

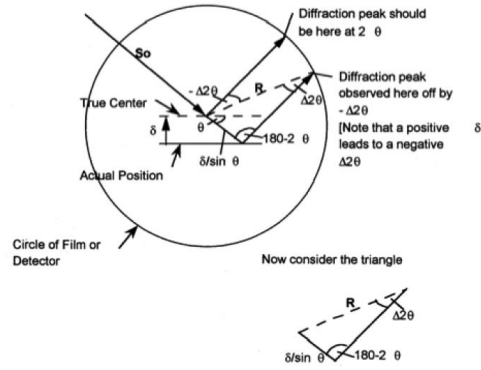


Figure 7: Powder diffractometry geometry

$$\frac{\Delta d}{d_o} = \frac{\delta \cos^2 \theta}{R \sin \theta}$$

Complete Nelson-Riley function also corrects for vertical divergence of beam, leading to additional term of $\cos^2 \theta / \theta$; see Cullity, p. 356.

Laboratory 8: Single Crystal Epitaxial Thin Film

Reading: C.R.Wie, Introduction sec1,2,3, sec2.1, 3.1, 3.2

Lab Summary

The sample to be studied is a PTO ($PbTiO_3$) (001) single crystal thin film grown epitaxially by MOCVD on a STO ($SrTiO_3$) (001) single crystal substrate. Several things will be examined: 1) Measure the thickness of the PTO film. 2) Determine the quality (how single crystal it is) of the PTO single crystal film. 3) Generate a simulated data set to compare with raw data to better refine measured parameters. 4) Determine the angular resolution limit of the x-ray diffraction system using the “perfect crystal” STO substrate as a standard.

Note you will be using an instrument that has been optimized for thin film diffraction studies. That is: 1) the radiation source is $CuK_{\alpha 1}$ having $CuK_{\alpha 2}$ removed by using a monochromator and slit, 2) the incident beam divergence is $\sim 0.02^\circ$.

Introduction

Both materials have the perovskite crystal structures, with the STO substrate forming a cubic perovskite and the PTO forming a tetragonal perovskite structure at RT (room temperature.) The current interest in PTO thin films arises from its ferroelectric properties; under an applied electric field, the O^{2-} anion sublattice can shift in position with respect to the Pb^{2+} and Ti^{4+} cation sub-lattices, resulting a net dipole moment along the c axis. This shift is depicted in Figure 8 below, which shows an a axis projection of the PTO perovskite at its two different stable polarization states. Investigating this ferroelectric behavior in thin films requires very high crystalline perfection. Since the cubic a -axis lattice constant ($a=3.905 \text{ \AA}$ at RT) of bulk STO matches closely with the a -axis lattice constant of bulk PTO ($a=3.905 \text{ \AA}$ at RT), the PTO film grows in the c -axis direction (for film thicknesses less than a critical thickness of 600 \AA). The bulk PTO at RT is tetragonal with a c/a ratio of 1.063 ($c = 4.151 \text{ \AA}$.)

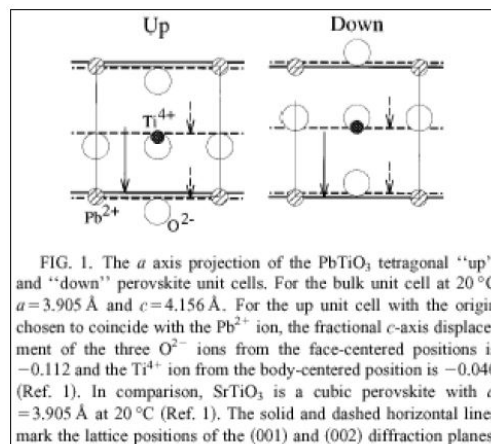


Figure 8: $PbTiO_3$ perovskite unit cells

Experimental Procedure

1. Perform the “Half Beam Alignment” sample alignment procedure with the aid of lab instructor, to align the sample with the x-ray beam.
2. Calculate 2θ for Bragg peaks of both the substrate and film (001) reflections, given that the xray source is Cu $K_{\alpha 1}$ $\lambda = 1.54056 \text{ \AA}$ and move $2\theta/\theta$ the STO (001) peak. Located and maximize the scattering intensity by making small positional corrections to 2θ , θ and χ to better align the substrate scattering vector to the scatter plane. Perform a “ ω or Rocking Scan” of the STO (001) peak and record the peak width. Rocking scans measure the distribution of plane-normals of the domains within the sample. The smaller the angle, the more “single crystal” it is. Because the STO is a “perfect” crystal, the value will be the minimum angular divergence of the instrument.
3. Perform a $2\theta/\theta$ scan along a path in reciprocal space that passes through the (001) peaks for both the PTO film and STO substrate peaks. Thus you will be able to determine the c lattice constants for both the film and substrate from their respective 2θ peak positions. Compare these to the bulk values. Depending on the amount of perpendicular strain on the film due to any lattice mismatch, the peak separation can vary from the amount predicted by the bulk lattice constants of PTO. With the data plotted on a log scale, you will also note the kinematic thickness fringe peaks about the film peak maxima. From the $2\theta/\theta$ scan it is possible to calculate the film thicknesses from the width of the diffraction peaks by understanding the one dimensional interference function,

$I(s) = K \frac{\sin^2(M\pi s \cdot c)}{\sin^2(\pi s \cdot c)}$ where the scattering vector magnitude is $s = 2\sin\theta/\lambda$ and M= number of unit cells. Note that the film thickness is $t = Mc$. This interference function, which is based on simple kinematical diffraction theory, can describe the $2\theta/\theta$ scan scattered intensity from a thin epitaxial film such as the PTO. This measured intensity $I(s)$ will consist of the primary diffraction peaks from the film and the substrate. It will also show the thickness fringes from the film. From the numerator of the interference function it can be seen that the fringe periodicity (angular spacing) is directly related to the thickness of the film by: $\Delta s = \frac{1}{t \cos\theta}$.

4. Move $2\theta/\theta$ to the PTO (001) and locate the peak position. Optimize 2θ , θ and χ again. Perform a rocking scan of the PTO (001) peak and record the peak width. This angular width quantifies the film quality. You can then determine if the film is epitaxial as depicted in Fig. 1. For example, if the film were polycrystalline with no preferred growth direction an ω -scan of the PTO peak position would be rather flat and featureless. If on the other hand the ω -scan shows a sharp peak then there is a preferred growth direction.

Simulation of kinematical diffraction Once c (PTO (001)) and the film thickness t are known, use a spreadsheet program and plot the diffraction pattern from the PTO (001) film using the one dimensional interference function described above plotting $\log I$ vs. $q(\text{\AA}^{-1})$. Over-lay the simulation output on your $2\theta/\theta$ data (convert 2θ to $q(\text{\AA}^{-1})$) and re-scale the intensity if necessary. Refine the values of t (M(t)) and c so the simulation will best match your data.

Deliverables

For your report:

1. Include the instrument parameter information: slits, target, scan parameters etc,
2. Rocking scans plots for STO and PTO with width measured and discuss the significance of each plot.
3. A log plot of the $2\theta/\theta$ scan over the film and substrate peaks show thickness fringes and calculation of the film thickness.
4. A simulation plot with t and c refined for the best match to your raw data (overlaid.) Report the refined values you found for c (PTO (001)) and t . (see example below).

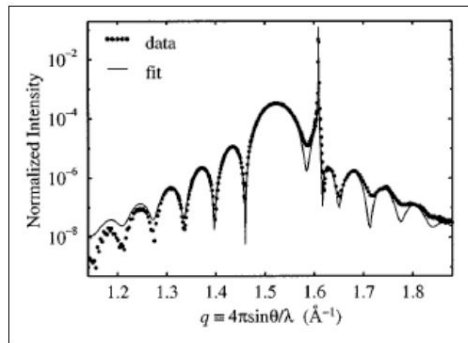


Figure 9: Simulation plot example

Simulation example: A $2\theta/\theta$ scan at $\lambda = 1.540 \text{ \AA}$ of $t \sim 103 \text{ \AA}$ thick PTO (001) film grown by MOCVD on a (001) STO substrate. Note the thickness fringes about the broad PTO (001) peak. The solid line is a fit to the experimental data using the interference function corrected for absorption from the film and substrate. (From C. Thompson, C. Foster, J.A. Eastman, and G. B. Stephenson, Appl. Phys. Lett. 71, 3516 (1997).)