### Experiment 4: Simulating X-Ray Diffraction

CH3500: Inorganic Chemistry, Plymouth State University

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**References**


http://www.planewave.de/icp/atoms/atoms.sgml-3.html


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**Introduction:**

Light can reflect off an atom or molecule, if the wavelength is on the order of the size of the particle. Atoms have radii in the range of ~70 – 200 pm (0.7 – 2 Å, or 0.7 – 2 × 10⁻¹⁰ m), which is in the range of X-rays. A number of X-ray diffraction techniques take advantage of this, and the fact that when two X-ray photons reflect off neighboring atoms, they will constructively or destructively interfere according to the angle of their reflection. Figure 1 shows two photons that have reflected at an angle such that the extra distance traveled by the bottom photon is equal to the wavelength of the light. Thus, the photons after reflection are in phase and will constructively interfere. The reflection angle (θ) needed for constructive interference is related to both the wavelength (λ) and the distance between the atoms by Bragg's Law (Equation 1):

\[ n \lambda = 2d \sin \theta \]

'\( n \)' in the equation is any integer number, indicating that many discreet refraction angles are possible (though usually only the first one or two are considered). It follows then that an instrument capable of detecting the intensity of the reflected photons as a function of the reflection angle (see Figure 2) could provide data on the spacing between atoms. In order to perform such an experiment, the atoms in the material must be at a fixed distance from one another, so that the critical angle does not change, and there must be many atoms at that distance, so the reflected beam is intense enough to be detected. In other words, the material must be a crystalline solid, wherein, by definition, the atoms are arranged in an orderly fashion in a regularly repeating pattern. The process by which light (or any wave) passes through a regularly repeating lattice, is reflected, and emerges on the other side in a pattern of constructive and destructive interference is known as “diffraction.” The process of using X-rays to determine structural information (i.e, the distances between atoms) about a material based on those diffraction patterns is known as “X-ray crystallography.”

A unit cell is the smallest arrangement of atoms that can be repeated in all three dimensions to describe the
structure of a crystal. The simplest unit cell is a cube (a six-sided figure with equal sides and all 90° angles), although a more general shape is the parallelepiped (a six-sided figure with sides 'a', 'b', and 'c' that may or may not be equal, and angles α, β, and γ that may or may not be equal, although opposite faces must be parallel). Generally, coordinates of atoms in a unit cell are given as fractions of the axes 'a', 'b', and 'c', and the actual distances of the atoms are stated in angstroms (Å). Thus, an atom at the very center of a unit cell would be at coordinates (½, ½, ½) regardless of whether the length of the 'a' axis is 5 Å or 100 Å, or whether α = 90° or 63°.

Although there are an infinite number of unit cells possible with different values of a, b, c, α, β, and γ, all of these would fit into one of fourteen Bravais lattices (arrays of infinitely repeated points in three dimensions) (Figure 3). These lattices arise from the combination of seven possible crystal/lattice systems (cubic, orthorhombic, tetragonal, hexagonal, trigonal (rhombohedral), monoclinic, and triclinic) and five centering types (see Table 1).

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive</td>
<td>Lattice points on corners only.</td>
<td>P</td>
</tr>
<tr>
<td>Face / Base Centered</td>
<td>Lattice points on corners and centered on 2 faces.</td>
<td>A (face between b, c axes) B (face between a, c axes) C (face between a, b axes)</td>
</tr>
<tr>
<td>All-Face Centered</td>
<td>Lattice points on corners and centered in all faces.</td>
<td>F</td>
</tr>
<tr>
<td>Body-Centered</td>
<td>Lattice points on corners and in the center of the unit</td>
<td>I</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>Lattice points on corners and two interior points equally spaced along a diagonal</td>
<td>R</td>
</tr>
</tbody>
</table>

Figure 3: The 14 Bravais lattices
It is possible for the components of a unit cell (i.e., atoms and molecules) to have various symmetry elements (e.g., rotation, reflection). The combination of potential symmetries in the unit cell with the Bravais lattices results in 230 unique "space groups." A common system for designating three dimensional space groups is the Hermann-Maguin system, which uses two to four symbols to specify the properties of the space group. The first symbol is a single letter (P, I, R, F, A, B or C) referring to the lattice type, and the remaining symbols describe the rotational and/or mirror symmetries of the space group. In addition, all the possible space groups have been given a unique number between 1 and 230, inclusive. Table 2 lists a few common structure types, their Hermann-Maguin designation, and their space group number. (The detailed method of defining a space group and its symmetry elements is beyond the scope of this introduction, and Table 2 is meant to introduce a few symbols only). The determination of a crystal's space group is one of the first steps in the process of solving a structure in crystallography, because once the space group is known, all of the symmetry elements of the crystal are also known. This, in turn, is necessary to interpret a diffraction pattern and solve the structure of a crystal.

Table 2: Space group designations of some common structure types

<table>
<thead>
<tr>
<th>Structure</th>
<th>Space Group (Hermann-Maguin notation)</th>
<th>Space Group Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>cubic (primitive)</td>
<td>P m 3 m</td>
<td>221</td>
</tr>
<tr>
<td>body-centered cubic</td>
<td>I m 3 m</td>
<td>229</td>
</tr>
<tr>
<td>face-centered cubic</td>
<td>F m 3 m</td>
<td>225</td>
</tr>
<tr>
<td>halite</td>
<td>F m 3 m</td>
<td>225</td>
</tr>
<tr>
<td>zincblende</td>
<td>F -4 3 m</td>
<td>216</td>
</tr>
<tr>
<td>cesium chloride</td>
<td>P m 3 m</td>
<td>221</td>
</tr>
<tr>
<td>perovskite</td>
<td>P m 3 m</td>
<td>221</td>
</tr>
<tr>
<td>diamond</td>
<td>F d 3 m</td>
<td>227</td>
</tr>
<tr>
<td>hexagonal close pack</td>
<td>P 6/m m c</td>
<td>194</td>
</tr>
<tr>
<td>graphite</td>
<td>P 6/m m c</td>
<td>194</td>
</tr>
</tbody>
</table>

Because X-rays diffract off many atoms in a crystal, it is convenient to consider not just individual atoms, but planes of atoms, chosen such that the distance between parallel planes is the same as that between atoms ('d' from Bragg's law, as discussed above). These planes are described by their intersection points along the axes of the unit cell. For reasons beyond the scope of this introduction, planes are labeled with Miller indices using 'h k l' coordinates, wherein 'h', 'k', and 'l' are the inverse of the intersection points on 'a', 'b', and 'c' respectively (see Figure 4). Miller indices must be integers, so if the process of inverting the unit cell coordinates leaves a fraction, the Miller indices are multiplied by the common denominator.

Figure 4: Cleavage planes in a Unit Cell with their Miller indices
With a little trigonometry and incorporating the concepts of Miller indices just described, it can be shown that distances between planes of atoms in a crystal with any unit cell are given by Equation 2:

\[
\frac{1}{d^2} = \frac{1}{V^2} (S_{11} h^2 + S_{22} k^2 + S_{33} l^2 + 2S_{12} hl + 2S_{13} kl + 2S_{23} hl)
\]

where 'V' is the volume and the 'S' terms are given by Equations 3-8:

\[
S_{11} = b^2 c^2 \sin^2 \alpha \\
S_{22} = a^2 c^2 \sin^2 \beta \\
S_{33} = a^2 b^2 \sin^2 \gamma \\
S_{12} = abc \cos \alpha \cos \beta \cos \gamma \\
S_{23} = a^2 bc \cos \beta \cos \gamma \cos \alpha \\
S_{13} = ab^2 c \cos \gamma \cos \alpha \cos \beta
\]

By consulting Figure 2, you will see that we have just discussed the equations that describe the x-axis positions (angle of reflection) of the peaks in an X-ray diffraction pattern. However, we have not yet described the y-axis: the intensities of peaks (I), which are given by Equation 9:

\[
I_{hkl} = |F_{hkl}|^2
\]

where F is the "structure factor" for the hkl plane of atoms. The structure factor equation is given by Equation 10:

\[
F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}
\]

where 'N' is the total number of atoms in plane hkl, j refers to an individual atom at location x\(yz\), and f is the atomic scattering factor (an empirically derived value related to the number of electrons in an atom). A detailed analysis of this equation is beyond the scope of this lab, but suffice it to say that the location and intensity of a specific peak in an X-ray diffraction pattern depends upon three things:

1. The distance between atoms.
2. The number of electrons in an atom (more electrons means more X-rays will scatter).
3. The number of equivalent atoms in a crystal.

Thus, if the structure of a crystalline material is known, its theoretical diffraction pattern can be calculated. Conversely, if a diffraction pattern is measured experimentally, it should be possible to determine the structure of the material. However, the process of solving a structure from the diffraction data is considerably more complicated. Consider, for example, the peaks in Figure 2. Knowing the x-coordinate (\(\theta\)) for a peak can directly yield 'd' from Equation 1, but when that is related to Equation 2, there are still 9 unknown variables: a, b, c, \(\alpha\), \(\beta\), \(\gamma\), h, k, and l. Further, the y-axis yields intensity (I), but when that is related to Equation 9, there are 7 unknown variables: h, k, l, x, y, z, and f. In other words, it is possible, but it requires a lot of data and computational power!

In this lab, you will develop a spreadsheet that predicts the positions of peaks (diffraction angle) for cubic, orthorhombic, and tetragonal lattice crystals. You will also use a computer program that can predict both diffraction angles and peak intensities for any Bravais lattice to check your spreadsheet and to further explore diffraction patterns.
Safety Considerations:

- This lab does not use any chemicals or other hazardous materials.

Procedure

A. Pre-Lab

Note: You must perform this part of the procedure in your lab notebook before coming to lab.

1. Sketch the cleavage planes from Figure 5 in your notebook. Identify their Miller indices \((hkl)\).

2. Derive a simplified version of Equation 2 for systems when \(\alpha = \beta = \gamma = 90^\circ\).

3. If you did not already do so for your report, calculate the dimensions of the unit cell for your structures b (CsCl) and c (fluorite or zinc blende) from Lab 3.
   a) Look up the radii of the ions. These are available in your book, Resource Section 1: Selected Ionic Radii (pp783-784).
   b) Using the ionic radii and your data on the nearest neighboring atoms (Lab 3, Part B, Analysis question 'c') to calculate the dimensions of the unit cells. These should include the lengths of the unit cell axes and the total volume. Collect these results in a table.

B. Boot and login to computer

- The programs you will be using run on Linux. You will be provided with a bootable USB drive that can be used to run Linux and the programs on just about any 32-bit PC computer. You may use your own computer or those provided in lab.
- You may work with a lab partner or, if computers are available, individually.

1. Boot into the Linux operating system. (Note: These instructions are for the Dell laptops you will be provided in lab. If you are using your own computer, follow the instructors on your computer's screen to get to the Boot Menu and boot from the USB drive).
   a) BEFORE turning the computer on, insert the USB drive into a USB port on the computer.
   b) Turn on the computer and pay close attention. An initial splash screen with the Dell logo will appear. Immediately strike the F12 key a few times to load the Boot Menu. If you are not fast enough, Windows 7 will boot. Allow it to boot fully, then shutdown and try again.
   c) Chose "USB Storage Device."
   d) Another boot menu will appear. Chose the first entry "Ubuntu" or just wait a few seconds and it will be chosen automatically.
   e) Login to the PSU Student account with password "PSUchemistry"
2. Some tips for navigating Ubuntu Linux:
   a) In the far upper-left corner is an icon of a white mouse (Ubuntu) on a blue globe. This is the Applications menu, which you can use to start a number of programs.
   b) To the right of the Applications menu is a Places menu, which lists a number of common directories where you can find files.
   c) In the far upper-right corner will be a button that says "student." Click here to find the Shutdown button.
   d) If you drag the mouse button to the bottom of the page, a Launcher bar will appear, which can be used to launch several different programs.

C. Investigating Crystal Systems
   1. You will be provided with paper templates for constructing three-dimensional representations of the 7 Crystal Systems. Cut these out and construct the three-dimensional shapes. Feel free to use division of labor here—not every group has to do all 7. While one partner works on this, the other may wish to start on Part E.
   2. Use these shapes to determine the rotational and mirror plane symmetries of the 7 Crystal Systems. Make a table in your notebook indicating the types and numbers of each symmetry that appear in all 7 Systems. Make a sketch of one of each type of rotational axis and mirror plane in all the Systems.
      a) If you wish, can also use the program "jmol" to open and view the crystal systems, which are saved as .pdb files in the directory InorgChemLab-04_X-rayDiffraction/CrystalSystems

D. Exploring Bragg's Law
   1. Start a web browser and navigate to the "Bragg's Law Applet" at http://www.eserc.stonybrook.edu/projectjava/bragg/
   2. Click the "details" button to show a simulated detector.
   3. Set Lambda = 2.0 and Distance = 5.0.
   4. Using the arrows, adjust Theta to smaller angles. Notice what happens to the plots of Xray1 and Xray2 waves and the Detector output as you do this. Continue decreasing Theta to the smallest number possible. What value(s) of Theta maximize the Detector output?
   5. Using Equation 1, calculate the Bragg's angle (θ) when λ = 2.0, d = 5, and n=1, 2, and 3.
   6. Plug the Bragg's angles you calculated above into Theta in the Bragg's Law Applet. How do your calculated values compare to those you found in part 'c'?

E. Develop your own diffraction pattern predictor
   1. On the Desktop, you will see the folder "InorgChemLab-04_X-rayDiffraction." Open it. In this folder, open the file "04-X-rayPowderPrediction.ods" with LibreOffice Calc (double clicking the file will probably work, and if not, right-click and use the "Open with" option).
   2. A few lines down on the left you will see the columns 'h', 'k', and 'l'. In the cells under these, enter the hkl values for all the planes using values from 0 to 3. Notes:
      a) There is no 0 0 0 plane.
b) There are $4^3 - 1 = 63$ possibilities. *Take a moment to think about how you can arrange these so you do not miss any, do not duplicate any, and do not take hours to fill them in!*

3. Using your simplified version of Equation 2 (Part A2), enter the formula to find $1/d^2$ in the appropriate cell.

4. With reference to the cell you used above, enter a formula to find $d$.

5. With reference to the cell you used above, and assuming $n = 1$, use Bragg's law to enter a formula for "2theta." *Notes:*
   a) This should be 2 times the $\theta$ value in Bragg's law.
   b) The built-in spreadsheet formula for arcsine is "asin()".
   c) The "asin()" function outputs an angle in terms of radians. Convert it to degrees with the function "degrees()". Thus, a portion of your equation will be "degrees(asin(XXX))."

6. Copy and paste the formulas you just entered down the columns next to all your values of $hkl$.

7. In the "Cell Parameters" area:
   a) Enter a formula to calculate volume in the cell next to "V"
   b) Enter the value for the wavelength of Cu K-\(\alpha\) X-rays in the cell next to "lambda"
   c) Enter the cell parameters you calculated (Part A3) for CsCl structure from Lab 03.

8. At this point, you should see a pattern appear in the spreadsheet's pre-existing figure. Make a table with headings as shown below in your notebook to record how many peaks there are and their 2theta positions. You will see that many of these hkl planes have the value "#VALUE!" under "2theta." These planes would result in a diffraction angle greater than 180°, which is nonsensical, so you may ignore them. You will also note that many of the hkl planes result in the same 2theta value. Rather than write down each plane, note the plane with the smallest values of hkl and how many planes total result in this 2theta.

Table XX: Appropriately number and label table

<table>
<thead>
<tr>
<th>Structure</th>
<th>My Diffraction Prediction</th>
<th>GDIS prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl plane</td>
<td>20 angles (deg)</td>
<td>Number of planes with 20</td>
</tr>
</tbody>
</table>

9. Use GDIS to verify your program:
   a) Open your .cif for CsCl from Lab 3 using Gnome Crystal Structure Viewer
   b) Use "Save as" to give your file a new name, so you do not overwrite your original
   c) In "Crystal -> Lattice":
      • select Lattice = "Simple Cubic"
      • Enter your cell parameter for 'a'. *Note: 100 pm = 1Å.*
   d) Save the file and open it with GDIS.
   e) Calculate the diffraction patterns
      • "Tools -> Diffraction" or the "Diffraction button"
      • Change "2Theta max" to 170
      • Before you can calculate the pattern, you need to select the choice in the left menu that displays the 3-D unit cell, not the text file

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• Click "execute"
• Your diffraction pattern will output as a graphic in the "X-Ray" tab and as a text file in "spectrum_x.txt." The displays on some laptops may render the graphic in a fuzzy way, but you can read the exact angles, intensities, and hkl values in the file.

f) If the GDIS values for 2θ and the number of peaks do not closely resemble yours, go back and try to fix the problem. Are the formulas in your prediction correct? Are both predictors using the same \( \lambda \) value for the X-ray? Are the unit cell parameters the same? Is the 2θ range the same?

g) Once your two predictions are the same, record the values for hkl planes, 2θ, and intensity from the GDIS prediction. Do NOT record any planes with any hkl values that are negative or greater than 4. Observe any differences in the way GDIS does its prediction versus yours, as well as any similar patterns in the data.

10. Return to your spreadsheet predictor. By right-clicking on the "Sheet1" tab at the bottom, you can rename and copy this sheet. Rename this to "CsCl" and make a copy.

F. Investigate diffraction patterns

1. In the new, copied tab, enter the cell parameters for your structure 'c' (fluorite or zinc blende) from Lab 3. Record the first 6 peaks (6 smallest values of 2θ) in your table from Step E8. Rename this tab.

2. Find a group that did the other structure 'c', get their cell parameters, and create a new, appropriately named tab in your spreadsheet to find the diffraction pattern for this structure.

3. Obtain .cif files for the minerals:
   a) In a web browser, navigate to http://rruff.geo.arizona.edu/AMS/amcsd.php
   b) Search for the minerals "fluorite" and "sphalerite" (zinc blende) and download their CIF data files.

4. One at a time, load the .cif files for the fluorite and sphalerite and run their diffraction patterns. Compare them to your prediction. If NONE of the 2θ values are the same, double check that both predictors are using the same cell parameters. Record the first 6 peaks (6 smallest values of 2θ). Do NOT record any planes with any hkl values that are negative or greater than 4.

5. Investigate effects on diffraction patterns using your spreadsheet in the following way:
   a) In your spreadsheet, make four copies of the CsCl tab. Label them "Mo-Ka," "Larger," "Tetragonal," and "Orthorhombic."
   b) In the Mo-Ka tab, change "lambda" to the wavelength for Mo K\( \alpha \). Record the total number of peaks and values for the first 6 peaks in your table from Step E8.
   c) In the Larger tab, increase all three cell axes by 1 unit. Record the total number of peaks and values for the first 6 peaks in your table from Step E8.
   d) In the Tetragonal tab, increase the length of the 'b' axis by 1. Record the total number of peaks and values for the first 6 peaks in your table from Step E8.
   e) In the Orthorhombic tab, increase the length of the 'b' axis by 1 and the 'c' axis by 2. Record the total number of peaks and values for the first 6 peaks in your table from Step E8.

6. Investigate the effects on diffraction patterns using GDIS in the following way:
a) Make a copy of your CsCl CIF file used to verify your diffraction patterns in Step E9. Label the file "Monoclinic.cif"

b) Open the Monoclinic.cif file in Gnome Crystal Viewer. Edit the lattice in "Crystal -> Lattice" to:
   • Lattice = Monoclinic
   • a, b, and c axes equal to your parameters in the Orthorhombic tab
   • $\beta = 70^\circ$

c) Save the file and open it in GDIS. Run the diffraction patterns. Record the total number of peaks and values for the first 6 peaks in your table from Step E8. Do NOT record any planes with any hkl values that are negative or greater than 4.

d) In a web browser, navigate to http://www.rcsb.org/pdb Search for the structure 1MBN and download the .pdb file.
   • Little historical note: You have just downloaded the structure of the myoglobin protein from the sperm whale. This was the first protein to be structurally characterized by X-ray crystallography! You can view the protein structure using the program Jmol. Right-click and select "Style -> Scheme -> Cartoon"

e) Load the 1MBN.pdb file into GDIS. Set the 2Theta max = 45 and run the diffraction pattern. Note: This may take several minutes!
   • It is likely GDIS will complain that the resulting "spectrum_x.txt" is too large to display. Open this file with Leafpad and count the number of reflections.

Analysis (Lab Notebook)
The following must be completed in your lab notebook before you can turn in your Notebook Report:

1. Determine the effects on the number of reflections seen in the predicted diffraction patterns upon making the following changes:
   a) Decreasing the wavelength of the X-rays used.
   b) Decreasing the symmetry of the space group by making the axes unequal.
   c) Decreasing the symmetry of the space group by changing one of the angles away from 90°.

Analysis and Conclusions (Lab Report)
Your lab report is due by lecture a week from Friday. Your report must be handed in BOTH electronically (via Moodle) and in hard copy form. See the document "InorgChem-LabReportGuide.pdf" on the course website for guidelines on writing your report.

1. Increasing the symmetry of a cell, for example by moving from a primitive to a face-centered cube, often results in the disappearance of some of the reflections. These are known as "systematic absences." Compare your predicted patterns for fluorite and sphalerite to those produced by GDIS. What evidence do you see for the occurrence of systematic absences?

2. Mo-Kα radiation is preferred to Cu-Kα under some circumstances, because the smaller wavelength allows for more precise location of atoms and the location of smaller atoms, such as hydrogen. Explain this preference with reference to Bragg’s Law.

3. Protein crystallography almost always uses Cu-Kα radiation instead of Mo-Kα. With reference to your findings in this lab, explain why.