

# Powder Pattern Simulation

by

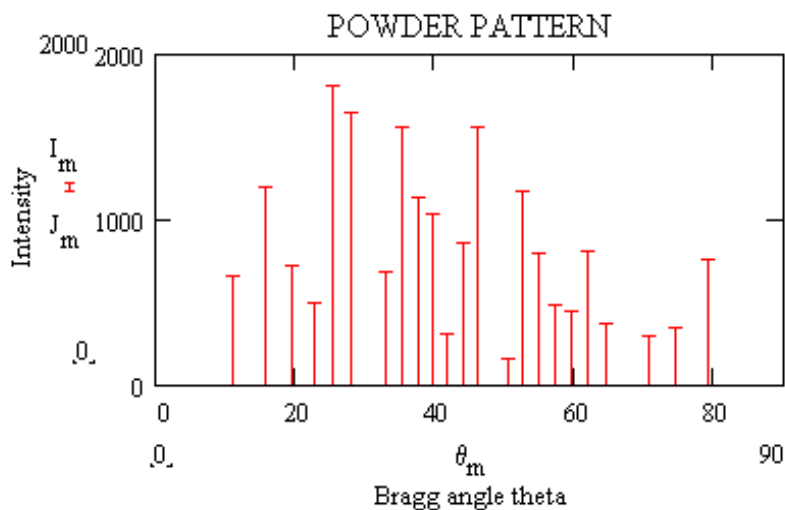
George Hardgrove  
Chemistry Department  
St. Olaf College  
Northfield, MN 55057

hardgrov@lars.acc.stolaf.edu

© Copyright George Hardgrove 1996. All rights reserved. You are welcome to use this document in your own classes but commercial use is not allowed without the permission of the author.

## STUDENT INSTRUCTION DOCUMENT

This document is designed to help you understand the powder diffraction method in X-ray crystallography. This is a very useful analytical method for materials research, industrial analysis, and in crime laboratories. Powder patterns are produced experimentally when a powdered solid sample in a glass capillary is placed in the X-ray beam and the scattered radiation recorded on a photographic film. Other apparatus may use a radiation detector which moves through the different angles  $\theta$  recording the intensity of scattered X-rays at different angles. A simulated diffraction pattern is shown here.



An experimental diffraction pattern shows rather sharp peaks at various angles  $\theta$ . From the pattern it is possible to learn something about the structure of the material. For example, in industrial laboratories an unknown compound may be identified by comparing the observed angles and intensities with many thousands of tabulated patterns by means of a computer search program.

#### Learning Objectives:

- To identify lattice types for cubic unit cells
- To describe a crystal structure by giving the fractional coordinates of the atoms in the unit cell.
- To describe the various crystal planes with indices hkl.
- To calculate the  $\theta$  values of the reflections
- To calculate the intensities of the reflections
- To display the calculated diffraction pattern
- To recognize the lattice type from the diffraction pattern
- To determine the unit cell dimension from a diffraction pattern.

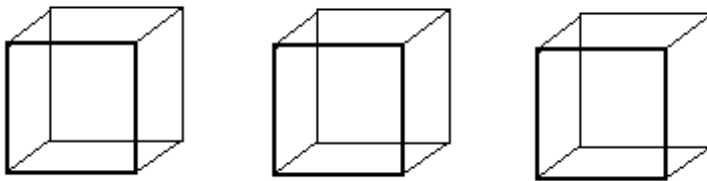
A crystalline material has a repeating pattern of atoms or molecules which extends in three dimensions. It is a lattice if we can pick out points in three dimensional space whose surroundings are alike by translation operations. These are called lattice points. Unit cells are constructed by building three-dimensional boxes which have lattice points at all eight corners. Unit cells come in a variety of shapes, but for this exercise we will consider only cubic unit cells where the angles between edges are all  $90^\circ$  and the length of the edges are all alike. We will call this length  $a$ .

**Note:** Since this is the instructional document the equations are toggled off.

## PRIMITIVE, BODY-CENTERED AND FACE-CENTERED LATTICES

For cubic crystals there are 3 types of lattices:

- P or primitive lattice has lattice points only at the corners of the cell.
- I or body-centered lattice has lattice points at the corners and middle of the cell.
- F or face-centered lattice has lattice points at the corners and the centers of all six faces of the cell.



For the P (and I and F) lattices there is  $1/8$  of a lattice point at each corner coordinates  $0,0,0$ ;  $1,0,0$ ; etc, but crystallographers simplify this by listing only one lattice point at the origin of the cell  $0,0,0$ . Note that for face-centered cubic you have six extra lattice points which are each shared with a neighboring unit cell. The list is usually shortened to include only the three lattice points nearest the origin. If you should want a paper copy of this page, click on the printer icon, then click on current page, then click on ok on the dialog screen.

### EXERCISE 1

Using the three cubes above draw small circles at the locations of the lattice points for the P, I, and F lattices.

List the coordinates (fractions of a unit cell) for the extra lattice points in the I and F lattices.

The body-centered and face-centered lattices can be thought of as symmetry operations in the sense that they tell us the equivalent positions of other atoms related to some atom at  $x, y, z$ . The body-centering operation adds  $0.5, 0.5, 0.5$  to the fractional coordinates  $x, y, z$ . Thus if we have an atom at  $x, y, z$  position  $0.13, 0.23, 0.05$  the body-centering operation will generate another one at  $0.63, 0.73, 0.55$ .

## EXERCISE 2

The NaCl structure is face-centered cubic. It has a Na<sup>+</sup> ion at fractional coordinates 0, 0, 0. Considering the three face-centered lattice points nearest the origin calculate the positions of the other three Na<sup>+</sup> ions. The Cl<sup>-</sup> ion is at position 0.5, 0.5, 0.5. Calculate the positions of the other three Cl<sup>-</sup> ions.

## Describing a Structure to the Computer Program

The computer program cub2run.mcd is found on your Crystallography with MATHCAD disk or at the WWW url given to you by your instructor. Open this file.

We will show how to set up the calculation for the diffraction pattern for NaCl. Refer to the computational document page 2. We need to put in values for natoms, symno, the matrix ASYM and values of  $\lambda$ , a, and B.

**natoms** This number is the least number of atoms which are not replicated by any symmetry operations. For NaCl this number is 2. If we describe the locations of one Na<sup>+</sup> ion and one Cl<sup>-</sup> ion, the symmetry operations for face-centered cubic will generate the positions of the rest.

**symno** This number tells the computer which type of lattice we have according to the following scheme:

- 1 if the structure is simple cubic (P lattice)
- 2 if the structure is body-centered cubic (I lattice)
- 4 if the structure is face-centered (F lattice)

Since NaCl is face-centered cubic we assign symno=4.

## ASYM

This matrix tells the computer the number of electrons and the x,y,z coordinates for each atom in the asymmetric unit. The matrix has four rows: the top row contains the numbers of electrons for the atom or ion, the lower three contain the coordinates x, y, z. There is one column for each atom. For NaCl with a Na<sup>+</sup> ion at 0,0,0 and a Cl<sup>-</sup> ion at 0.5,0.5,0.5 this matrix becomes

$$\text{ASYM} := \begin{bmatrix} 10 & 18 \\ 0 & 0.5 \\ 0 & 0.5 \\ 0 & 0.5 \end{bmatrix}$$

- a This is the cell dimension in A units. (1A = 10<sup>-8</sup> cm.)  
For NaCl the value is 5.64. The symbol for Angstrom is not available in Mathcad 6.0+
- $\lambda$  The wavelength of the X-rays in A. Let us assume  $\lambda = 1.5418$ .
- B This is the amplitude of vibration of the atoms. Atoms in a crystal are always vibrating, and these motions have an effect on the diffraction pattern which we will investigate later. We will start out with a value of 3.

The computer then selects the appropriate matrix for the lattice type to generate the complete list of atoms. This list is called ATOMS.

$$\text{SYMP} := \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad \text{SYMI} := \begin{bmatrix} 0 & 0 \\ 0 & .5 \\ 0 & .5 \\ 0 & .5 \end{bmatrix} \quad \text{SYMF} := \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & .5 & .5 \\ 0 & .5 & 0 & .5 \\ 0 & .5 & .5 & 0 \end{bmatrix}$$

The SYMP matrix refers to simple cubic, the SYMI matrix to body-centered and the SYMF matrix to face-centered cubic.

### EXERCISE 3

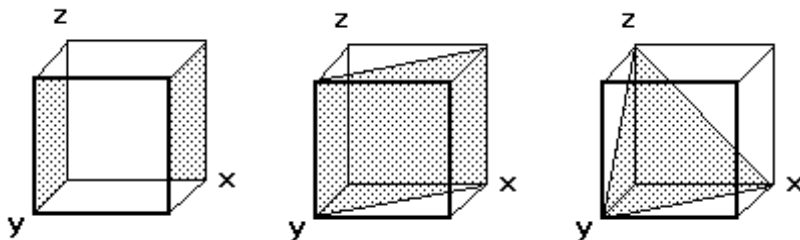
Explain the form of the matrices SYMP, SYMI, SYMF. Refer to exercise 1 above.

### EXERCISE 4

In the computational document make the necessary entries (natoms, symno, and ASYM to describe the NaCl structure. The easiest way to change the ASYM matrix is to move the cursor towards it until a dotted line surrounds it and then press the delete key on the keyboard. Then enter the new matrix. Press function key F9 to obtain the atoms list and compare it to the one you found in exercise 2.

### Diffraction from Bragg Planes - Miller Indices

W. L. Bragg and his son Lawrence pictured X-ray diffraction as mirror reflection from sets of parallel planes. You may need to review crystal hkl planes in your text as well as the derivation of Bragg's Law. A crystallographic plane is described in terms of Miller indices which are the inverses of the intercepts where the plane cuts the crystallographic axes.



1 0 0

In the figure on the left above the marked plane on the right cuts the x axis at 1.00 (fractional coordinates) and since it is parallel to the y and z axes the intercepts are  $\infty$ . The inverse intercepts are 1 0 0. Where is the origin here?

**EXERCISE 5** For the middle and right hand figure above find the intercepts and obtain the Miller indices.

Analysis of the geometry for a cubic crystal shows that the perpendicular spacing between planes  $d_{hkl}$  can be calculated as follows where  $a$  is the length of the edge of the unit cell.

$$d_{hkl} := \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

For diffraction to occur the waves from successive planes must be in phase. This leads to the Bragg relation where we assume 1st order diffraction.

$$\lambda := 2 \cdot d \cdot \sin(\theta) \quad (2)$$

Combining equations 1 and 2:

$$\sin(\theta)^2 := (h^2 + k^2 + l^2) \cdot \frac{\lambda^2}{4 \cdot a^2} \quad \text{or} \quad \sin(\theta)^2 := M \cdot \frac{\lambda^2}{4 \cdot a^2} \quad (3)$$

where  $M = h^2 + k^2 + l^2$  and where  $\sin(\theta)^2$  means  $\sin^2(\theta)$ .

We note that since  $h$ ,  $k$ , and  $l$  are integers, then  $M$  is an integer. So the values of  $\sin^2\theta$  must be multiples of a common factor  $\lambda^2/4a^2$ .

#### EXERCISE 6

Combine equations 1 and 2 to get equation 3.

#### EXERCISE 7

For NaCl with a unit cell dimension  $a = 5.63 \text{ \AA}$  calculate the spacing between the following planes: 1 0 0 and 1 1 1.

## Relation of M Values to Lattice Type

The diffraction pattern of a simple cubic lattice will exhibit all possible hkl planes. The body-centered and face-centered diffraction patterns exhibit some missing reflections. These are useful for identifying the lattice type. The following reflections appear for various lattice types:

For a P lattice  $M = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16$  etc.  
but note that  $M = 7$  and  $M = 15$  are not present because no set of integers  $h k l$  can be found such that  $h^2 + k^2 + l^2 = 7$  or  $15$  etc.

For an I lattice  $M = 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22$ , etc.  
with no missing blanks as observed for the P lattice.

For an F lattice  $M = 3, 4, 8, 11, 12, 16, 19, 20$  etc. - a more irregular pattern.

In order to simulate a diffraction pattern we need three things:

1. A list of all possible hkl for cubic crystals
2. A calculation of the Bragg angle  $\theta$  for each reflection
3. A calculation of the intensity of diffracted X-rays for each reflection.

These three tasks are done in the computational document.



Later on in the computational document the computer will read a list of the first 63 hkl reflections from a file called HKLPM that is on your disk or available from the WWW site where you got this document.

For each reflection it gives h, k, l, Q, and M. The value of Q is the number of possible reflections which will diffract at this same value of  $\theta$ . For example the reflection 1 1 0 will diffract at the same angle as  $\bar{1}$  0 1 and 0 1 1. We must also consider reflections with negative indices so we must include -1 1 0, 1  $\bar{1}$  0, -1  $\bar{1}$  0 and all of their permutations as listed for 1 1 0. So  $Q = 12$  for this reflection. The value of  $M = h^2 + k^2 + l^2 = 2$  for this reflection.

#### EXERCISE 8

Calculate Q and M for the 2 0 0 reflection.

#### EXERCISE 9

In the computational document press F9 (or toggle automatic recalculate to on) to get the listings of h, k, l, Q, and M. Verify your calculation in the previous exercise.

Next we calculate the Bragg angle  $\theta$  for the reflections until  $\sin^2\theta > 1$  which is physically impossible. The number of reflections which fit this condition will depend on  $\lambda$  and the cell dimension 'a.'

#### EXERCISE 10

Get a listing of the  $\sin^2\theta$  values by typing 'ssq $\theta$ = ' and pressing F9. Looking at these results and those for EXERCISE 9 tell what lattice type is consistent with these data.

## THE AMPLITUDES AND INTENSITIES OF X-RAY REFLECTIONS

Finally we need to calculate the intensities of the diffraction peaks. When an X-ray beam hits a crystal it causes the electrons in the unit cell to oscillate at the frequency  $\nu$  of the X-rays. This oscillating charge then radiates X-rays in all directions. The diffraction peaks are at particular angles where the scattering from the atoms is in phase.

Each hkl plane scatters X-rays with a certain amplitude  $F$  and its associated intensity  $F^2$ . The amplitudes are calculated using the structure factor formula

$$F_{\text{calc}}(h, k, l) := \sum_{j=1}^{na} f_j \cdot \exp\left[2 \cdot \pi \cdot (h \cdot x_j + k \cdot y_j + l \cdot z_j)\right] \quad \square$$

where  $F_{\text{calc}}$  is the calculated scattering amplitude for the reflection hkl, and the summation (index = j) is carried out over all the atoms in the unit cell. The positions  $x_j$ ,  $y_j$ ,  $z_j$  refer to the coordinates of the jth atom, and  $f_j$  is the scattering factor. The scattering factors  $f$  are the effective numbers of electrons, and they are tabulated from the results of quantum mechanical calculations. Thermal vibrations reduce the effective scattering of the atoms especially at high  $\theta$  angles. To simplify things the following approximation will be made

$$f_j := z_j \cdot \exp\left[-B \cdot \left(\frac{\sin\theta}{\lambda}\right)^2\right] \quad \square$$

where  $z_j$  is the atomic number of the jth atom or ion,  $B$  a thermal parameter giving the amplitude of vibration for all the atoms, and  $\theta$  the diffraction angle and  $\lambda$  the wavelength of the X-rays.

## EXERCISE 11

Return the variables in the worksheet to their original values. The easiest way to do this is to use 'File Close' and do not save. Then reopen cub2run and it should reappear with the original values for the constants. These constants describe simple cubic sodium (if it should exist). On page 6 press F9 for calculation and label this pattern by putting the cursor at the top and pressing " to get into the text mode. Type in your label. Print this page by clicking on the printer icon, choose 'current page' and finally 'ok' to print. Now go back to page 2 and increase 'a' the length of the unit cell. Return to page 6 and press F9 to recalculate. What effect does this have on the pattern? If you wish to print this pattern (page 6) change the label to avoid confusion.

## EXERCISE 12

Increase the wavelength  $\lambda$  of the xrays. Recalculate. What effect does this have on the diffraction pattern? Would you prefer long or short  $\lambda$  values for displaying patterns with large unit cells?

## EXERCISE 13

Increase the value of B to 5 and recalculate. B is a measure of the amplitude of thermal vibrations of the atoms. At higher temperatures the atoms will vibrate with a higher amplitude. What effect does this have on the intensities? Does it have the same effect at all values of  $\theta$ ? What are the advantages of taking diffraction data at low temperatures?

## EXERCISE 14

Return the constants on page 2 to their standard values of  $a=4.00$   $\lambda=1.5418$   $B=3.0$   $n_{atoms} = 1$   $symno=1$ . Get a printed copy of the diffraction pattern for a P lattice. Consult the table on page 8 of the instructional document and write the M values on your diffraction pattern. Change the symno to 2 for a body-centered (I) lattice and recalculate. Label and print out the graph. Note the atom lists on page 3 in matrix ATOMS and tell how the structure has been changed. What is the effect of changing lattice type on the pattern? If you saw diffraction patterns of the P and I types, how could you tell them apart?

## EXERCISE 15

Change the symno to 4 for an F lattice. Recalculate. How has the diffraction pattern changed? Look on page 3 and tell how the structure has changed. How can you identify a face-centered diffraction pattern when you see one? It may help to consult the output list on page 6 of the computational document.

## EXERCISE 16

The structure of CsCl has  $\text{Cs}^+$  ions at the origin and  $\text{Cl}^-$  ions at the position 0.5, 0.5, 0.5. What lattice type does this arrangement have? How many electrons does each ion have? Set up the coordinates and numbers of electrons in the ASYM matrix and choose values for symno and noatoms. Calculate the diffraction pattern. Determine if the pattern is different if you switch the  $\text{Cs}^+$  and  $\text{Cl}^-$  ions.

## EXERCISE 17

The structure of NaCl has an F lattice with  $\text{Na}^+$  at the origin and  $\text{Cl}^-$  at 0.5, 0.5, 0.5. Set up the structure by adjusting the ASYM matrix on page 2 and by adjusting the other variables. Calculate the pattern. Do the atoms in the matrix ATOMS form a face-centered lattice? Look at the output on page 6. How do the intensities of the even even even hkl (such as 2 0 0) differ from the odd odd odd hkl such as 1 1 3? This pattern is characteristic of the alkali halide structures.

## EXERCISE 18

Without changing the cell dimension a, change the NaCl structure above into KCl. Recalculate the pattern. What lattice type does this pattern appear to be? Explain how this occurs.

## EXERCISE 19

The structure of ZnS is face-centered cubic with Zn at the origin and the S atoms in tetrahedral holes at x, y, z of 0.25, 0.25, 0.25 respectively. The face centering operation will generate the rest. From the atom list on page 3 tell where the others belong. Note the structure factor list on page 6. Are the structure factors real or complex numbers? This occurs when the structure lacks a center of symmetry.

## EXERCISE 20

The crystal structure of  $\text{CaF}_2$  is face-centered cubic and has  $\text{Ca}^{++}$  at the face centers and  $\text{F}^-$  atoms in all of the tetrahedral holes. Put them at 0.25, 0.25, 0.25 and -0.25, -0.25, -0.25, and then verify from the atom list page 3 that all the tetrahedral holes are filled. Calculate the pattern. Compare this pattern to the others you obtained in this series of exercises. Write your observations in you note book.