

# 1 361 Problems

**Homework Policy:** You may consult with other class members when preparing your homework answers; indicate clearly on your paper the names of the students with whom you worked. The solutions you submit should, nevertheless, be your own and in your own hand.

**Reading Assignments:** See the Syllabus, which is published on the NU Blackboard for this course.

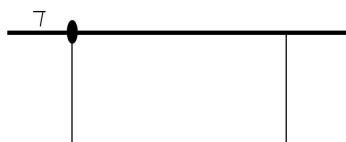
1) By operating on a "7" in the plane of the paper, show that an inversion center is equivalent to a 2-fold rotation axis (perpendicular to the plane of the paper) in two dimensions. Show that the inversion center and 2-fold rotation axis are not equivalent in three dimensions by doing the same type of operation on a 3D asymmetrical unit "7".

2) Below are sketched a 2-fold axis parallel to a mirror and two perpendicular mirrors. Operate on the "7" with the indicated symmetry elements and show that a third symmetry element is present in each case and that the two cases are equivalent. Which point group does this pattern of 7's belong to?



3) For the following 2D primitive rectangular unit cell:

- Fill in the pattern of 7's based on the indicated unit cell and symmetry elements.
- Draw in the additional symmetry elements that are present.
- Indicate which 2D space group this pattern belongs to.



4) From Azaroff 1-7

Examine the crystal on page 22 of Week 1 notes (Azaroff Fig. 1-29) and list all the symmetry elements that you find present. Determine the correct crystal class and system.

5) From Azaroff 1-8

Consider the tetragonal crystal shown on page 21 of Week 1 notes (Azaroff Fig. 1-24). Using the axis labeled  $a_1$ ,  $a_2$ , and  $c$  in that figure, what are the indices of the four faces visible? What is the form?

6) C&S Prob. 2-6

7) Hammond Prob. 2-3

8) C&S Prob. 2-10

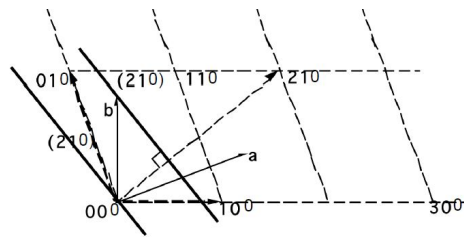
9) C&S Problem 2-13 (Use tracing paper on top of a Wulff net for this problem, in addition to the following two).

10) C&S Problem 2-14

11) C&S Problem 2-15

12) Prepare a drawing of the  $hk0$  layer in the reciprocal lattice of a monoclinic crystal for which  $a = 2.5 \text{ \AA}$ ,  $b = 3.0 \text{ \AA}$ ,  $c = 5.12 \text{ \AA}$ , and  $\gamma = 120^\circ$ . Note that  $\gamma^* = 180^\circ - \gamma = 60^\circ$ .

13) Using the figure from lecture notes Week 2 slide 11, draw two lines that represent the edge-on view of the (010), (110) and (210) hkl planes. Draw the corresponding reciprocal lattice vectors, noting that they are perpendicular to the hkl planes. This is already done below for the (210) plane. Using a ruler, measure the interplanar spacing,  $d_{hkl}$ , and the length of the reciprocal lattice vector  $r_{hkl}^*$ . Verify that the product  $d_{hkl} \cdot r_{hkl}^*$  is the same for each set of planes, thus demonstrating that reciprocal lattice vector lengths are inversely proportional to d-spacings in direct space.



14) Using the general definition of the reciprocal lattice vector (see Week 2 Lecture Notes), derive the relation for  $d_{hkl}$  for the tetragonal, orthorhombic, and monoclinic systems in terms of the unit cell parameters  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$  and the Miller indices  $h$ ,  $k$ ,  $l$ . Check answer with C&S A3-1.

15)

- Determine the lattice constant "a" in terms of R for a BCC (body centered cubic) structure with spheres of radius R at each lattice point packed as closely as possible.
- repeat part (a) for an FCC lattice.

16) GaAs is a zinc blende structure, which has Ga atoms at FCC positions and As atoms at FCC + (1/4, 1/4, 1/4) positions. Write out the 4 coordinates for Ga and the 4 coordinates for As for a unit cell. Make a sketch of this unit cell with the 8 atoms or use Crystal Maker.

17) Hammond Prob. 5.6. Plus use MatLab to perform the matrix transformations between cubic-I (HKL) and rhombohedral (hkl) for  $HKL = \{100, 111, 110\}$  and  $hkl = \{100, 111, 110\}$ .

18) C&S Problem 2-7

19) C&S Problem 2-8

20) Hammond Exercise 5.2

21) One formula weight of NiO equals 74.69 amu, and the density of a NiO crystal is  $6.67 \text{ g/cm}^3$ . (a) Calculate the length of the unit cell edge,  $a$ . (b) Using  $\lambda = 1.54 \text{ \AA}$  prepare a list of the first 6 allowed reflections (hkl) and the corresponding Bragg angles,  $\theta_{hkl}$ . Refer to CS Appendix 9 which lists the allowed reflections for various Bravais direct-space lattices.

22) Prepare a 3-d drawing of the reciprocal lattice for a body-centered-cubic direct space lattice. Show and label all reciprocal lattice points for  $0 \leq h, k, l \leq 2$ . Show and label the reciprocal space axes,  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ , and  $\mathbf{c}^*$ . Identify the Bravais lattice type for this reciprocal space lattice.

23)

- (a) What are the (hkl) Rhombohedral unit cell Miller indices for the three nonparallel faces of the Rhombohedral unit cell?
- (b) Read Hammond Section 5.9, make sure you understand how the transformation matrices were generated for trigonal crystals with rhombohedral lattices. Using the transformation matrix derived in Sec. 5.9, what are the (HKL) Hexagonal unit cell Miller indices for the three nonparallel faces of the Rhombohedral unit cell?
- (c) Now list these as (hkil) Miller- Bravais indices.
- (d) What is the [uvw] direction in the Rhombohedral unit cell for the hexagonal c-axis direction [001]?
- (e) EXTRA CREDIT: Hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has a rhombohedral crystal structure with  $a=5.43\text{\AA}$  and  $\alpha = 55.3^\circ$ . What is the angle between the hexagonal c-axis and the rhombohedral c-axis? What is the angle between the hexagonal c-face and the rhombohedral c-face?

24) Find Azaroff Chapters 6 and 8 on BlackBoard, Read Azaroff Ch 6. pp 86-113, an Azaroff Ch. 8 pp. 155-165

25) [Azaroff 6-1]

26) Refer to Azaroff Fig. 6-2 on page 88. This experiment is with continuous radiation.

- (a) The x ray beam from the x-ray tube is traveling along y. Is this x ray beam:
  - i preferentially polarized along x ?
  - ii preferentially polarized along y ?
  - iii preferentially polarized along z ?
  - iv not preferentially polarized ? Explain your answer.
- (b) Is radiation scattered by the block stronger in detector 1 (along x) or in detector 2 (along z)? Again explain your answer.

27) [Azaroff 6-2]

28) [Azaroff 6-3]

29) [Azaroff 8-1] **Hint** : According to the Bohr model, the radius  $r_n$  of the  $n$ th orbit is proportional to  $n^2/Z$ , where  $Z$  is the atomic number. Plot the scattering-factor curves  $f_K, f_L$  and  $f$  as functions of  $kr_K$ .

$$f = 2 \frac{\sin kr_K}{kr_K} + 8 \frac{\sin kr_L}{kr_L}$$

Note that there is a typo in the text book. "a missing factor of 8".

30) [Azaroff 8-2] (see Cullity & Stock Appendix 10)

31) [Azaroff 8-9]

32) The one dimensional interference function is:

$$\frac{\sin^2 \pi Q \cdot a M}{\sin^2 \pi Q \cdot a} = \frac{\sin^2 \beta M}{\sin^2 \beta}$$

$\mathbf{Q} = (\mathbf{S} - \mathbf{S}_0)/\lambda$  is the scattering vector.  $\mathbf{S}$  and  $\mathbf{S}_0$  are unit vectors in the scattered and incident directions where  $\beta = \pi Q \cdot a$  is one-half the phase angle difference (in radians) for rays scattered by planes separated by  $a$ . The crystal contains  $M$  planes separated by  $a$ .

- Use a computer with a suitable program or spreadsheet and plotting program (MSE Ugrads must use MatLab) to plot this function over the domain  $0 \leq \beta \leq \pi$ . Note that this is a periodic function repeated every  $\pi$  radians. Make separate plots of the function for the cases of  $M = 2, 4,$  and  $16$ . You will have to appropriately adjust the evaluation interval  $\Delta\beta$  to accommodate the sharpness of the function that varies with  $M$ .
  - For each  $M$  above, tabulate the height of the primary maxima, the height of the first subsidiary maxima, and the ratio of the height of the first subsidiary maxima to the height of the primary maxima. This demonstrates how the subsidiary maxima become less significant as  $M$  increases.
  - By numerical integration determine the area under the  $\beta = 0$  primary diffraction peak between the first intensity minima (nulls) for each  $M$  above. How does this vary with  $M$ ?
  - The integral breadth of a peak is the quotient of the area over the height. This represents the full width of a rectangle that has the same height and area as the peak in question. Calculate the integral breadth of the primary maximum for the three cases, and consider its relation to  $M$ .
- 33) Consider powder diffraction from CsCl ( $a = 4.11 \text{ \AA}$ ) with Cu  $K\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ). This is a simple cubic structure with  $\text{Cs}^+$  at  $0,0,0$  and  $\text{Cl}^-$  at  $1/2,1/2,1/2$ . (Note: CsCl is not BCC.)

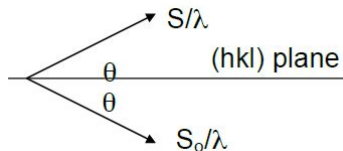
- What are the  $hkl$  indices for the first 7 observed reflections from CsCl?
- For the first four of these calculate and tabulate  $\sin\theta/\lambda, f_{\text{Cs}^+}, f_{\text{Cl}^-}, F_{hkl}, 2\theta,$  and LP.
- Look up multiplicities  $m_{hkl}$  (Cullity & Stock Appendix 11). Combine these with your results from part B to calculate the relative intensities of the four peaks in question. Assign the value of 100 to the most intense peak.

34) The relation of multiplicity factors  $m_{hkl}$  to powder diffraction intensities can be appreciated with the reciprocal lattice.

- Sketch the  $hk0$  plane of the reciprocal lattice for an HCP crystal, using solid dots ( $\bullet$ ) to indicate nonzero  $|F_{hkl}|^2$ . Cover the range from  $-2a^*$  to  $+2a^*$  and  $-2b^*$  to  $+2b^*$ .
- Show that there are 6 reciprocal lattice vectors of the same length  $r_{hkl}^* = a^* = b^*$ . Give the  $hkl$  indices for these six vectors. In a powder sample, these will all diffract at the same value of (scalar)  $Q$  (or in the same  $2\theta$  direction).
- The six planes responsible for this diffraction are of the form  $\{100\}$ , though this is seen more clearly in the 4 axis Bravais-Miller system  $hkil$ , where  $i = -(h+k)$ . Write the indices  $hkil$  for these six planes.

35) Write the structure factor for a crystal with two atoms of the same type per unit cell at  $x, y, z$  and  $x + 1/2, y + 1/2, z + 1/2$ . This conforms to a body centered (I) unit cell with an arbitrarily displaced origin at  $x, y, z$ .

Now evaluate the product  $FF^*$  for all possible values of  $h, k,$  and  $l$ . You should see that the result is independent of  $x, y, z$ . Therefore, the intensity ( $FF^*$ ) depends only on the separation between atoms; absolute positions are not relevant.

Figure 1:  $S/\lambda$  and  $S_o/\lambda$ 

Make a perspective sketch of the reciprocal lattice for an orthorhombic I crystal,  $a = 3\text{Å}$ ,  $b = 4\text{Å}$  and  $c = 5\text{Å}$ . Include 8 reciprocal lattice unit cells (from origin to  $2a^*$ ,  $2b^*$ ,  $2c^*$ ). Indicate nonzero values of  $FF^*$  by dots ( $\bullet$ ).

You should notice two things: the "missing" reciprocal lattice points result from the choice of the nonprimitive unit cell; the pattern of nonzero points forms a face centered (F) array in reciprocal space. The same is true for cubic I and tetragonal I Bravais lattices, the reciprocal lattices of which are face centered.

36) (Cullity & Stock Prob. 4-4) Derive simplified expressions for  $F$  and  $F^2$  for diamond, including the rules governing observed reflections. This crystal is FCC and contains 8 atoms per unit cell located at: FCC and FCC +  $1/4\ 1/4\ 1/4$ . Note, silicon and germanium are diamond structure.

37) Construct a diagram that illustrates the  $hkl$  Bragg condition, showing  $S/\lambda$ ,  $S_o/\lambda$  and an  $(hkl)$  reflecting plane such that the two unit vectors originate from the same point as shown below. Continue the diagram and show that the vector  $\mathbf{Q} = (S_o/\lambda - S/\lambda)$  must be perpendicular to the  $hkl$  plane. From the construction derive Bragg's Law recalling that  $\mathbf{Q}$  must be the same as a reciprocal lattice vector.

38) Figure P2 is a  $c$ -axis-rotation photograph of an orthorhombic crystal which has  $\mathbf{a}^* = 0.25\text{Å}^{-1}$ ,  $\mathbf{b}^* = 0.15\text{Å}^{-1}$  and  $\mathbf{c}^* = 0.36\text{Å}^{-1}$ . The radius of the cylindrical camera used for taking this photograph is 50 mm and the x-ray wavelength is  $1.542\text{Å}$ . Construct the appropriate reciprocal lattice nets ( $l=0$  and  $l=1$ ) to index all the reflections shown. What is the lattice type of this crystal?

39) Use the Scherrer equation ( $\delta(2\theta) = 2\varepsilon_{1/2} = 0.94\lambda/D\cos\theta$ ) to evaluate the FWHM peak width  $\delta(2\theta)$  (in degrees) for crystallite sizes  $D = 25, 75, 125, 450,$  and  $900\text{Å}$ . Assume that  $\lambda = 1.542\text{Å}$  and that the peak in this  $\theta - 2\theta$  scan whose width we are considering occurs at  $2\theta = 80^\circ$ .

The ability to measure small peak widths is hampered by instrumental broadening. Even if the incident and diffracted beams were perfectly collimated, the peaks would still be broadened by the  $K_{\alpha 1} - K_{\alpha 2}$  splitting. Differentiate Bragg's law to obtain an expression for  $d\theta$  as a function of  $\theta$ ,  $\lambda$ , and  $d\lambda$ . Using this expression, calculate  $d\theta$  for the  $K_{\alpha 1} - K_{\alpha 2}$  splitting of Cu radiation at  $2\theta = 90^\circ$ .

$$\lambda(K_{\alpha 1}) = 1.5405\text{Å}$$

$$\lambda(K_{\alpha 2}) = 1.5433\text{Å}$$

From this you should appreciate that it is difficult to measure  $D$  values greater than about  $500\text{Å}$  when using the Cu  $K_{\alpha}$  doublet as a radiation source. Note that the wavelength resolution  $\lambda/d\lambda$  can be improved by an order of magnitude by using a single crystal monochromator to select out the Cu  $K_{\alpha 1}$ , whose width is approximately 2 eV in comparison to the 20 eV energy separation between the  $K_{\alpha 1}$  and  $K_{\alpha 2}$ .

40) Identical powder diffraction scans are made of a diamond powder sample and a germanium powder sample with Cu  $K_{\alpha}$  radiation. Each has "diamond cubic" crystal structure with 8 atoms per unit cell. Other pertinent information for this problem is as follows:

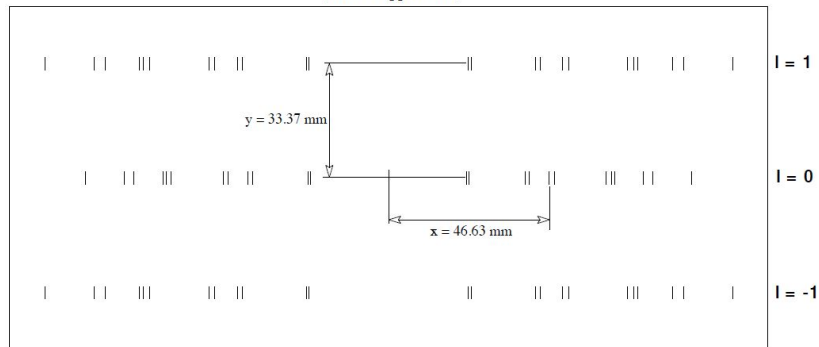
Sample	Z	$a[\text{Å}]$	$\mu/\rho [cm^2/g]$	$\rho [g/cm^3]$
Carbon	6	3.5671	4.22	3.51
Germanium	32	5.6577	67.9	5.91

The scans were done in symmetric reflection. One might think that the ratio of observed intensities would be given by the ratio of the quantities

$$K_x = \frac{|F_{hkl}|^2 m_{hkl} L P}{V_C^2}$$

where x is C or Ge. However, the observed intensity of diamond, relative to that of germanium, was 25 times larger than that calculated from the ratio  $K_C / K_{Ge}$ . Explain where this factor of 25 comes from.

Figure P2 C-axis-rotation photograph for 361 HW  
(scale is approx 1:1)



Radius of the cylindrical camera = 50 mm  
x-ray wavelength  $\lambda = 1.542 \text{ \AA}$   
 $a^* = 0.25 \text{ \AA}^{-1}$ ,  $b^* = 0.15 \text{ \AA}^{-1}$ ,  $c^* = 0.36 \text{ \AA}^{-1}$