
BRAGG SCATTERING FROM COLLOIDAL CRYSTALS

In this experiment you have the opportunity to study the structure of microscopic crystals made of polystyrene spheres in water. By measuring the angles at which laser light scattered from the crystals constructively interferes, you can determine the structure of the crystalline lattice. A similar procedure, using x-rays instead of visible light, is commonly used to determine the structure and composition of atomic or molecular crystals for chemical, biological or materials science. From the structure of a crystal, you can determine the size of its spheres, if you know their volume fraction in solution. In fact, by varying the volume fraction and the effective charge on the spheres, it is possible to change the structure of the crystals.

Think! Why are x-rays used instead of visible light for most crystals? Why don't you use x-rays for your crystals?

What you will be studying is, in fact, the classic example of what is known as a *colloidal* crystal, a colloid being any system in which there are two (or more) phases with one (the *dispersed* phase – in this case, polystyrene) distributed in the other (the *continuous* phase – in this case, water). Aside from being of interest for their own sake, colloidal crystals are important in the engineering of many modern materials, including photonic semiconductors, porous catalysts and microfilters. Thus, understanding and controlling their structure and phase behavior has many useful applications.

Although constructive interference occurs at well defined angles from a single crystal, several factors conspire to redistribute the intensity of the scattered light. First, as you will see from just looking at them, your samples will be full of many small crystals oriented at random with respect to one another. (This gives them an opalescent quality in white light. In fact, precious opals are naturally occurring colloidal crystals of similar dimensions, where the dispersed phase consists of the silica skeletons of single-celled animals called diatoms.) So rather than single points, you may see light in a series of rings around the incoming beam. However, since the size of the crystallites can be large compared to the size of the laser beam, the ring may not be continuous but, rather, comprised of dots which brighten and fade as you rotate the sample.

Introduction: Crystal Lattices

Below a certain temperature, atoms or molecules at equilibrium arrange themselves in an organized array known as a *crystal* or *lattice*. Technically, a *lattice* is an infinite coordinate system in space with points at regularly spaced intervals (Fig. 1). A *crystal* is a material in which atoms or molecules are organized on a lattice. Different materials are said to have different crystal structures depending on the spacing and orientation of the intervals in the underlying lattice. A material that is ordered in only one, two, or all three dimensions is referred to as a 1D, 2D, or 3D crystal, respectively. Most of the crystals you have probably dealt with are 3D, however notable exceptions are liquid crystals (2D), the metal films deposited on silicon wafers found in the semiconductor industry (2D), and quantum wires (1D) that may be the future's electrical technology.

STOP! Give one example each of a 1D, 2D and 3D crystal in your notebook. Write a rough estimate of the *lattice spacing* for each.

To specify positions on a lattice, an origin must be chosen. From this origin we may use a vector to describe the location of any lattice site relative to the origin. A vector between lattice sites is called a *translation vector*. Translation vectors which construct the smallest possible building block (the *unit cell* or *primitive cell*) of the lattice are called *primitive translation vectors*. Note that the primitive translation vectors are not necessarily parallel to the Cartesian unit vectors (\hat{i} , \hat{j} , and \hat{k}). an example.)

Figure 1A shows a lattice that does not have any perpendicular primitive translation vectors. There is more than one way to construct the primitive cell for any lattice. (See Figure 5a in Kittel on page 7). Usually the primitive cell will be defined so as to contain only one atom, but some crystal structures are more easily described in terms of a set of nested lattices such that more than one atom is contained in the unit cell. This type of structure is called a *lattice with a basis*. In addition to a set of primitive translation vectors, a lattice with a basis has *basis vectors*, which specify the origins of the nested lattices. Figure 2 gives an example of a two-dimensional lattice with a basis (see also Borchardt-Ott p. 22).

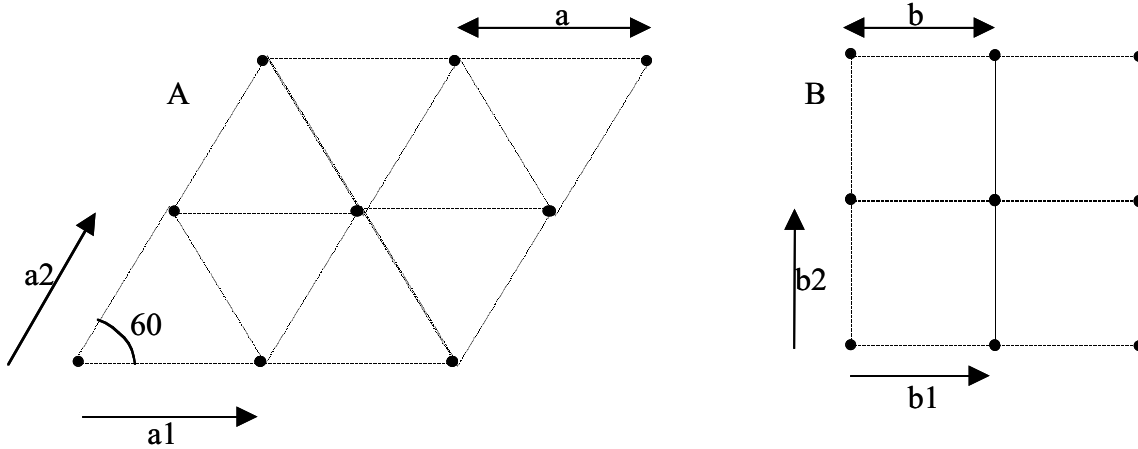


Figure 1. A) a hexagonal lattice with lattice spacing $a_1 = a_2 = a$ and basis vectors $\mathbf{a}_1 = a\mathbf{i}$ and $\mathbf{a}_2 = \frac{a}{2}\mathbf{i} + \frac{a\sqrt{3}}{2}\mathbf{j}$; B) a square lattice with lattice spacing $b_1 = b_2 = b$ and basis vectors $\mathbf{b}_1 = b\mathbf{i}$ and $\mathbf{b}_2 = b\mathbf{j}$.

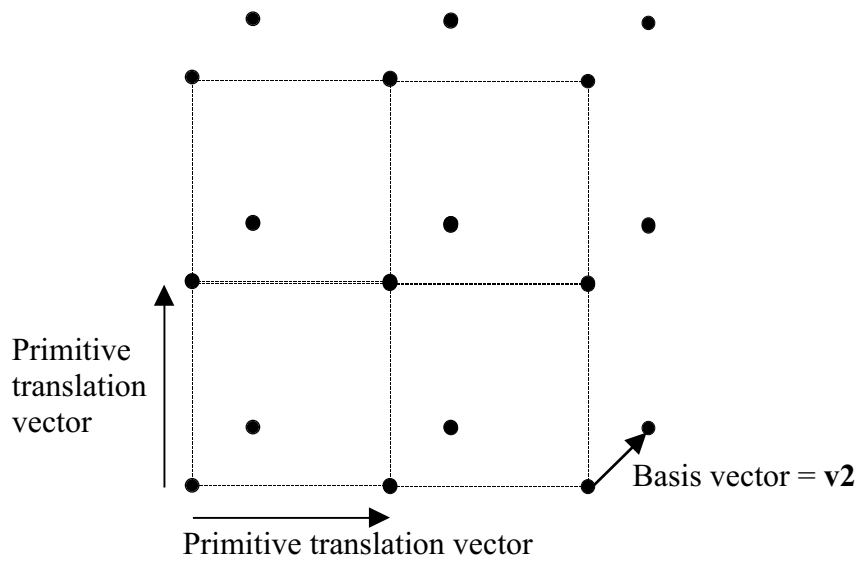


Figure 2. Diagram of a 2D square lattice with a basis. The primitive translation vectors are the same as those for a square lattice. There are two atoms per lattice site, one located on the lattice site and the other translated from the lattice site by vector \mathbf{v}_2 . The *basis vectors* for this lattice are then $\mathbf{v}_1 = 0\mathbf{i} + 0\mathbf{j} + 0\mathbf{k}$ and \mathbf{v}_2

For a thorough introduction to the concept of lattices see Kittel Chapter 1. In particular you should read the discussion on pp. 10-13 about 3D lattices. Specifically of interest to this lab are Figures 10, 12 and 13 showing the *simple cubic*(SC), the *body centered cubic*(BCC), and the *face centered cubic*(FCC) lattices.

Introduction: Lattice Planes and Miller Indices

If you look at a model lattice while rotating it slowly in front of you, you will quickly notice that from certain perspectives you can see clear through the structure since the atoms fall into well-spaced planes. While any three non-colinear lattice points define a *lattice plane*, the planes that are defined by points that are closest together are easiest to see because they present the greatest density of obstacles to your line of sight. For much the same reason, these are the principle planes that interact with a beam of collimated light that is incident on a crystal.

Lattice planes are indexed (hkl) according to their location within a unit cell. The indices are chosen such that the plane intersects the unit cell at three points a/h , b/k , and c/l . The indices $[h\ k\ l]$ are known as the *Miller indices*. To calculate the Miller indices corresponding to a set of crystal planes:

1. Use the basis vectors as a coordinate system.
2. Find the intercepts of the plane with the above coordinate system
3. Take the reciprocal of the intercepts. If there is no intercept then the reciprocal is 0.
4. Multiply by the lowest common denominator. The result is written in standard notation as (hkl) which is called the index of the plane.

Figure 3 provides an example. (See also pg. 14 in ref Kittel.)

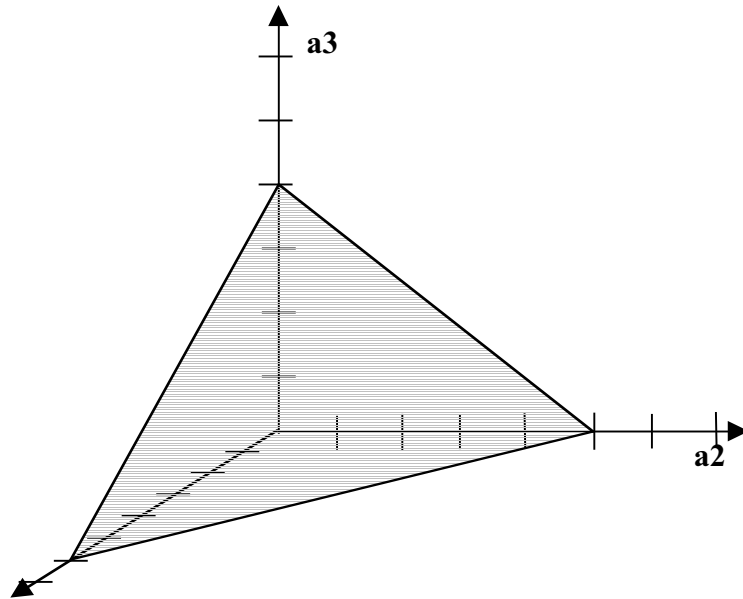


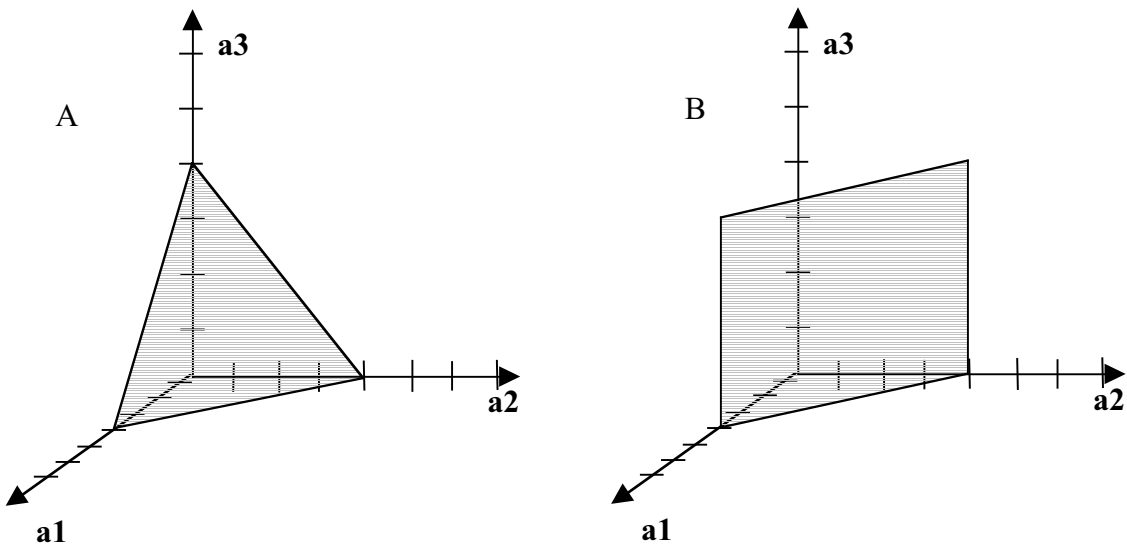
Figure 3. A plane made by three non collinear lattice points. Here the basis vectors are indicated by \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . The lattice points intersected are at $6\mathbf{a}_1$, $5\mathbf{a}_2$, and $4\mathbf{a}_3$. The reciprocals of these numbers are $1/6$, $1/5$, and $1/4$. The smallest integers sharing the same ratio as the reciprocals are 10, 12, 15. Therefore the indices of the plane are written (10 12 15).

The interplanar distance for cubic lattices, d , is given by

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

where a is the cubic lattice spacing. This works for the SC, BCC, and FCC lattices. A more general formula and derivation is given in Borchardt-Ott on pg. 251.

Exercise 1: Give the Miller indices for the planes drawn below.



Exercise 2a: Find the interplanar distances for (111), (200), (110), and (101). The first two will be the scattering planes of interest in the FCC crystal and the latter two for the BCC crystal.

Exercise 2b: Using the dot product determine the angles between the (111) and the (200) planes. Do the same for the (101) and the (110) planes.

BRAGG REFLECTIONS

Bragg reflection is the simplest model used to explain crystals diffracting light. From the previous discussion you know that the crystal has many different planes. One can think of these planes acting as mirrors to incoming light. Since some of the planes will be at different angles to the incoming light, the outgoing light is reflected at an angle relative to the transmitted beams. If the angle between the normal to the plane and the incoming light is ψ then the diffraction angle will be 2ψ . (See Fig. 4).

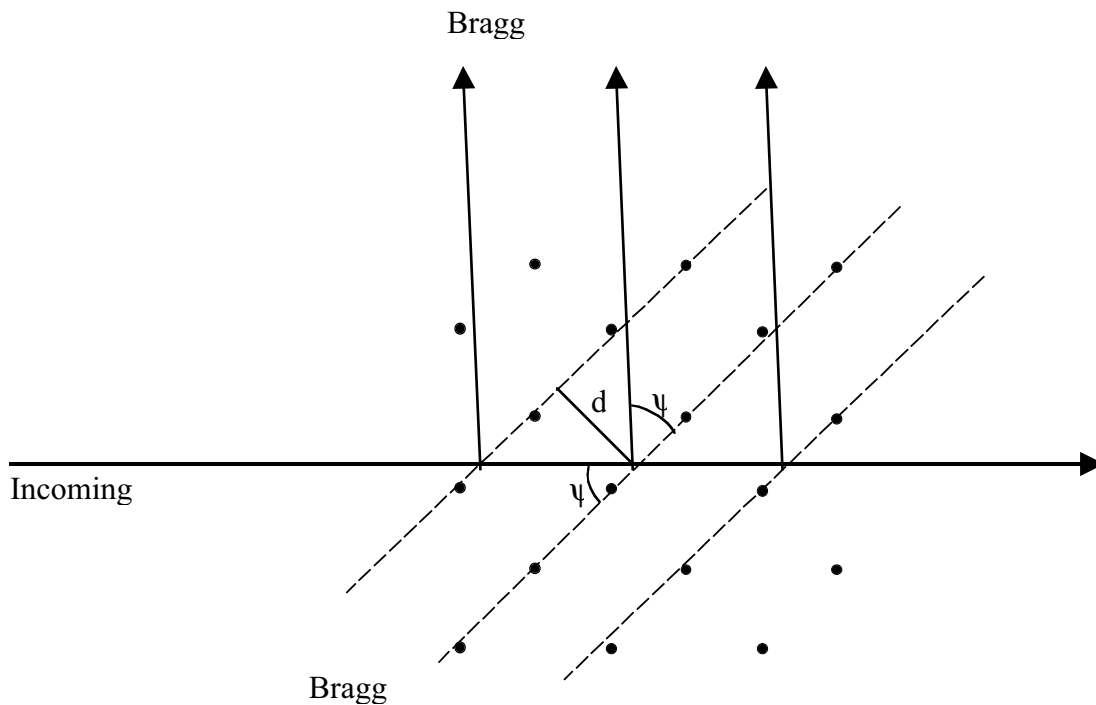


Figure 4. Here incoming light is diffracted off a lattice. The Bragg planes which are reflecting the light are the diagonal dashed lines. Notice that the incoming light is diffracted by an angle of 2ψ where ψ is the angle between the normal to the plane and the incoming light.

Since light can be reflected from multiple planes there will be interference. The path length difference between beams reflecting off adjacent planes will depend on the angle of the plane, ψ , and the interplanar distance, d . Also the index of refraction, n , of the medium in which the crystal sits will affect the wavelength, λ , of the light (the crystals grown in this lab are immersed in water with $n=1.33$). These factors combine to give the Bragg constructive interference condition

$$\delta = 2d \sin \psi = m \frac{\lambda}{n} \quad (2)$$

where m is an integer. In this lab you will only consider lowest order reflections or those with $m=1$.

Since different planes have different angles we should see light reflected constructively at different angles as well. However, not all planes will contribute constructively. Since $\sin \psi \leq 1$ there is a restriction on the interplanar distance for constructive interference.

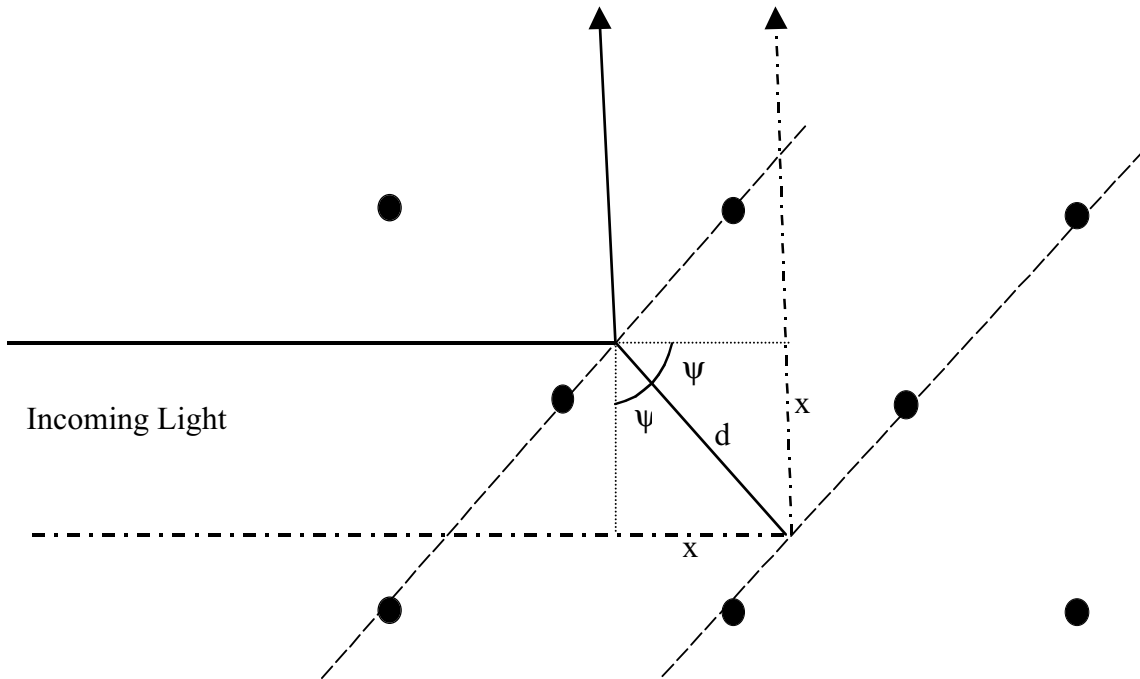


Figure 5. The path length difference between beams scattering off of adjacent planes is $\delta = 2x = 2d \sin \psi$ where d is the interplanar distance.

- Exercise 3a:** Find the constraint on the interplanar spacing for constructive interference using equation (2). What is the constraint on h , k , and l ? Remember to consider only lowest order reflections.
- Exercise 3b:** In this lab you will use a HeNe laser of wavelength 632.8 nm and the crystals will be immersed in water. Again considering only lowest order reflections, give a numerical constraint on the size of the interplanar spacing.
- Exercise 3c:** For the largest crystals in this experiment the lattice spacing will be about 700 nm for the FCC and 555 nm for the BCC. List all possible h , k , and l which will satisfy the constraint of interplanar spacing. Hint: h , k , and l are each no greater than 2.

FCC VERSUS BCC

There are several important similarities and distinctions between the FCC and BCC lattices. Both the FCC and the BCC lattices have primitive cells which are smaller than the SC lattice (see pg. 13 in Kittel for a diagram). Both the FCC and BCC can be thought of as a SC lattice with basis.

Think! How many atoms per unit cell are present in a BCC lattice? How many in an FCC lattice?

The intensity of light scattered from a crystal will be affected by the crystal's *structure factor*. The *structure factor*, S , determines which planes will reflect light constructively or destructively in a lattice with a basis. The addition of basis atoms will often double the number of planes in a certain direction. For example, in both the FCC and BCC in the (100) direction the number of planes is twice that of the SC. This essentially changes the wavelength in the Bragg condition by a factor of 2. Just as in thin film interference, this will change some constructive interference reflections to destructive interference reflections. For the BCC lattice

- Destructive interference occurs when $h + k + l = \text{odd}$
- Constructive interference occurs when $h + k + l = \text{even}$.

For the FCC one finds

- Destructive interference when h , k , and l not all even or not all odd
- Constructive interference when h , k , and l all even or all odd.

The structure factor is discussed in more detail in Kittel pgs. 42-45. To understand his discussion it may be useful to read the later section in this lab on reciprocal lattices.

The structure factor combines with the *atomic form factor* to determine the brightness of Bragg reflections. The atomic form factor is discussed in Kittel pgs. 45-48, but you will not use it in this experiment.

Exercise 4: List the planes from **Exercise 3c** which will contribute to scattering for FCC and BCC lattices based on structure factor considerations. These are then the only possible planes you will see in your experiment.

POLYSTYRENE MICROSPHERES

To make crystals, we will use a solution of charged polystyrene microspheres in water. The spheres carry a negative charge, which is usually screened by counterions (*e.g.*, Na⁺) in solution. The screening length is greatly increased by placing deionizing resin (*aka* REXYN) in solution. The resin binds counterions and releases hydrogen (H⁺) and hydroxyl (OH⁻). The high motility of hydrogen and hydroxyl ions in water makes them less effective at screening the charge of the spheres. For a high concentration of spheres in deionized water, electrostatic repulsion between spheres will cause them to arrange in a lattice or crystal. A convenient measure of the concentration is the volume fraction, γ , defined by

$$\gamma = \frac{\text{total volume of spheres}}{\text{total volume of solution}} \quad (3)$$

This can also be described by the unit cell as

$$\gamma = \frac{(\# \text{ of spheres per unit cell}) \times (\text{volume of a sphere})}{\text{volume of a unit cell}} \quad (4)$$

The concentration of solution will determine both the lattice spacing and the lattice type (FCC or BCC). Recalling that the number of points per unit cell is 2 for BCC and 4 for FCC (see FCC versus BCC) we find

$$\gamma_{bcc} = \frac{(2) \times \left(\frac{4\pi r^3}{3}\right)}{a^3} \quad (5)$$

and

$$\gamma_{fcc} = \frac{(4) \times \left(\frac{4\pi r^3}{3}\right)}{a^3} \quad (6)$$

where a is the lattice spacing and r is the radius of a microsphere. Knowing the sphere diameter, $d = 2r$, and solving for the lattice spacing we find

$$a_{bcc} = d(\pi/3\gamma)^{1/3} \quad (7)$$

and

$$a_{fcc} = d(2\pi/3\gamma)^{1/3}. \quad (8)$$

Therefore, for a known γ , determined by the preparation conditions, one can calculate a .

- Exercise 5a:** Derive equations (7) and (8) from (5) and (6).
- Exercise 5b:** The smallest concentrations used in this experiment is 0.5% and the largest is 1.5%. Determine the range of lattice spacings.
- Exercise 5c:** What effect will this have on **Q4** and **Q3c**? Will you see more or fewer planes? Which planes will likely be added or lost?
- Exercise 5d:** The diameter of the microspheres used in this experiment is 0.093 μm . Will the spheres be touching in the crystal?
- Exercise 5e:** What material takes up the rest of the space in the crystal? What will be the index of refraction for light hitting the crystal planes?

Materials and Methods: Overview

Since individual atoms (or microspheres) are diffracting instead of planes reflecting certain experimental problems arise. To get constructive interference (and thus the bright spots of a diffraction pattern) the light must directly hit an atom while simultaneously satisfying the Bragg condition. For any random position of a crystal this occurrence is rare. This means one will not see the entire diffraction pattern for any one position of the crystal with monochromatic light.

To remedy the above situation, several methods have been employed. By using many wavelengths of light at the same time the Bragg condition is likely to be satisfied when an atom is hit. This method, called the *Laue method*, is the oldest crystallographic technique. Another method is the *powder method*

(sometimes called the Debye-Scherrer method). A powder form of the material to be studied is illuminated with monochromatic light. In the powder there are many different crystals randomly oriented, which ensures that some will meet the Bragg condition for the wavelength used. However, the diffraction pattern will not show a distinct spot from a single atom but rather a ring from the many different atoms of the different randomly oriented crystals.

In the *rotating crystal method* a monochromatic light shines on a rotating crystal (or a rotating light shines on a fixed crystal). As the crystal is rotated the light will eventually hit all possible atoms which meet the Bragg condition for the specific wavelength used. Each time a spot appears its location can be marked and the entire diffraction pattern can later be reconstructed. This is the method you will use in this experiment.

The crystals will be placed in a spherical flask with lines indicating longitude (α) and latitude (β). Longitude is the same as the angle from the x-axis in spherical coordinates, ϕ , and runs from -180 to 180 . Latitude is the angle upwards towards the z-axis and is therefore $90-\theta$ which runs from -90 to 90 . If one assumes a beam of moving towards the origin along the positive x-axis ($-\hat{\mathbf{i}}$) and the diffracted beam coming off at an angle of 2ψ then the dot product gives $\cos 2\psi$. Working out the dot product component by component gives $-\sin\theta\cos\phi = -\cos\beta\cos\alpha$ where the minus sign comes from the beam going in the negative direction (see Figure 7). Equating the two gives

$$\cos 2\psi = -\cos\beta\cos\alpha \quad (9)$$

Thus by knowing the latitude and longitude of Bragg spots one can determine the diffraction angle 2ψ .

The experiment is summarized briefly as follows:

- Prepare microsphere solutions of different concentrations
- Observe the diffraction patterns for each solution
- Determine lattice type, lattice spacing, and concentration for each solution
- Compare experimental values of the lattice spacing and concentration to calculated values

Materials and Methods: Procedure

PREPARE SOLUTIONS

- A. Determine the stock solution concentration of microspheres in units of % by volume. Use the % by weight value on the bottle and the density of polystyrene found on the spec sheet.
- B. Determine the amount of fluid in μL required to fill a glass sample tube (6x50 mm) to within 10 μL using the pipettor and a small bottle filled with deionized water. **NOTE: EVERY TIME YOU USE THE PIPETTOR YOU SHOULD CHANGE THE TIP.** This is to prevent previous solutions from affecting the concentration of the next solution to be used. **ALSO: THE PIPETTE BUTTON HAS TWO STOPS, THE FIRST FOR TAKING IN SOLUTION AND THE SECOND FOR EXPELLING IT. DO NOT DEPRESS THE BUTTON TO THE SECOND STAGE WHEN TAKING IN FLUID. THIS CAN CAUSE FLUID TO BE DRAWN INTO THE BODY OF THE PIPETTOR AND ADVERSELY AFFECT SOLUTION QUANTITIES AND PURITY.**
- C. Determine how much deionized (DI) water and stock solution you will need to make concentrations of 0.5%, 0.6%, ..., 1.4% by volume. You will need a total amount of fluid equal to the volume of the sample tube you measured in step B, above. Write the quantities of DI water and stock solution for each concentration in table in your notebook.
- D. Place the bottle of polyspheres in the sonic tank for 30 seconds. **DO NOT SHAKE THE BOTTLE OF MICROSPHERES.**
- E. Fill 10 glass sample tubes (6x50 mm) about 1/4 full or REXYN. Use the scoopula to put the REXYN into the tubes.
- F. Determine the total amount of stock solution required. Write the value in your notebook and put this amount into one of the hexagonal plastic weigh dishes. Don't put too much in the dish or it will go to waste. Extra can be added later if needed. Since you won't be able to measure it out as you deliver, you can get an idea for the size of the drop you'd like to create by first putting that amount of water in another dish using the pipettor.

- G. Get out 10 more plastic weigh dishes out for each of the 10 solutions to be made. Label the dishes so that you don't get them confused. Add the appropriate amount of stock solution to each dish using the pipettor (REMEMBER TO USE A CLEAN TIP - and look carefully to be sure you deliver the full amount each time. There shouldn't be drops left behind in the tip.)
- H. Add the appropriate amounts of DI water to each dish using the pipettor (new tip!). Mix each solution by gently agitating the petri dish. Be sure you know which solution is which. You may want to indicate which dish is for which solution by placing a strip of masking tape on the tabletop and writing the different concentrations.
- I. Add the 0.5% solution to the a glass sample tube(6x50 mm) containing REXYN (use a new tip). First fill the glass tube about half full. Slightly agitate the tube to let the REXYN settle to the bottom. You can do this by covering the tube with parafin and inverting it a few times. Then proceed to fill the tube so that it has a positive meniscus at the top.
- J. Seal the tube by covering it with a small piece of parafilm (use the side which was protected by paper against the tube). Stretch it taut and wrap the excess around the top of the tube. It is important to not allow any air bubbles since these will prevent ionization of the spheres. Use masking tape to cover the parafilm and immediately write down the concentration on the masking tape. If you have trouble writing on the tape once it is on the tube you should write on the tape before placing it on the tube and tape it again.
- K. Repeat steps 9 and 10 for the 0.6-1.4% solutions. Be sure to label them correctly since they will be difficult to distinguish later.
- L. Once all 10 tubes are prepared and labeled you may put them in the tumbler. Watch the tubes to be sure the REXYN flows smoothly. You may have to thump the tubes to break up any clumps.
- M. Allow to tumble for several hours or overnight if possible. Remove your samples from the tumbler and place in a storage tray. The lower concentrations are delicate and will take longer to crystallize. If possible, after removing the tubes from the tumbler, allow the

solutions to settle overnight or over the weekend. The quality of the crystals will improve with time.

OBSERVE DIFFRACTION

- A. Align the laser. Be careful not to look directly at the beam or its reflections. You will know the laser is NOT aligned if you see two spots on the front of the spherical flask. Keep adjusting until there is only one spot and that spot is centered on the crosshairs of the spherical flask. You may also have to adjust the spherical flask so the laser is hitting the crosshairs properly.
- B. Remove the sample support rod from the top of the spherical flask. You should find small o-ring fastened to the bottom of the support rod. Use this to attach a glass sample tube containing crystals. NOTE: The blue and yellow spheres at the bottom of your tubes are the REXYN. They are not the crystals you are looking for. Your crystals will form just above the REXYN layer and will be a faint reflective pink color.
- C. Replace the sample support rod with sample into the spherical flask. Lower the the rod so that the crystals (and not the REXYN) are in the laser beam.
- D. Turn out the lights and observe the latitude (β) and longitude (α) of spots on the surface of the flask. You may be able to see more spots by rotating the sample tube or moving it slightly up and down. To mark spots you may find it easier to cover small parts of the sphere with masking tape and mark the spots and perform the measurements later with the lights on.

DETERMINE CRYSTAL STRUCTURE

- Use equation (9) to determine the diffraction angle 2ψ for several spots.
- Use ψ to determine the interplanar spacing d . You may have more than one ψ and d .
- Use d to determine (hkl) if possible.

- For samples which have more than one angle ψ , take the ratio of interplanar spacings.
- Compare steps 3 and 4 with what you know from the FCC and BCC lattices. Determine if one of the two types can be ruled out.
- For those crystals with determined lattice type you may use the scattering planes mentioned in **Exercise 2a** to determine the lattice spacing a . Be sure to use the correct plane for each angle.
- Calculate the sphere diameter using equation (7) or (8).
- Calculate the concentration γ using equation (5) or (6).

QUESTIONS

- What is your error in measuring α and β ? How will this propagate to ψ ? You may want to consult Bevington section 3.2. Give propagated errors for all quantities calculated in the DETERMINE STRUCTURE section. Are your errors acceptable? What are your main sources of error? Average the values of ψ and d for Bragg spots which are fairly close to each other. Calculate how this modifies the above error calculations. You may want to consult Bevington Chapter 4.
- What is the material which makes up the microspheres?
- What is the index of refraction of the microspheres and for what wavelength(s) is that number valid? Will this produce a strong reflection (hint: consider the equation for the reflection coefficient in normal incidence in Hecht p. 80)?
- What material makes up the bulk of the crystals? What is its index of refraction? Why is the spherical flask filled with water (hint: how would not doing this affect the diffraction pattern)?
- What is the typical size of the microspheres? What is the uncertainty in that size?
- Suppose you had ignored the difference between 10% by *weight* solutions and 10% by *volume* solutions. What percent by volume will the 10% by weight solution be? What is the percent difference between

this solution and one which is truly 10% by volume? If this error is ignored will it be a random error or a systematic error? In light of question 3 would this have a large effect?

RECIPROCAL LATTICE

The vectors which point normal to different planes of a lattice are known as *reciprocal lattice vectors*. A reciprocal lattice vector, \mathbf{G} , for a plane points perpendicular to the plane. From geometry it can be determined that $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ where \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 are primitive translation vectors of a reciprocal lattice. They are defined by $\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$ and cyclic permutations thereof (notice the units are 1/length). For the simple cubic lattice with $\mathbf{a}_1 = a\mathbf{i}$, $\mathbf{a}_2 = a\mathbf{j}$, and $\mathbf{a}_3 = a\mathbf{k}$ the reciprocal lattice vectors become just $\mathbf{a}_1 = 2\pi/a\mathbf{i}$, $\mathbf{a}_2 = 2\pi/a\mathbf{j}$, and $\mathbf{a}_3 = 2\pi/a\mathbf{k}$. It is interesting to note that the reciprocal lattice of an FCC lattice is a BCC and vice versa. Also, switching between the lattice and reciprocal lattice is the discrete version of doing a Fourier transform (going from position space to momentum space). For more information see Kittel pgs. 33 and 40-42. His discussion uses the primitive vectors for FCC and BCC given on pg. 13.