CRYSTAL LATTICES AND UNIT CELLS – A WORKSHEET

OBJECTIVES

1. To use macroscopic models to gain an understanding of the microscopic structure of crystal lattices and unit cells.
2. To relate physical properties of metals and ionic compounds to bonding theories.

PRE-LAB READING

Brown & Lemay, Chapter 12 sections 1 to 5.

USEFUL FORMULAS

Area of a square = $(edge\ length)^2 = \ell^2$

Area of a circle = πr^2 where r is the radius

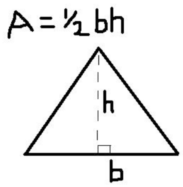
Area of a triangle = $\frac{1}{2}(base\ x\ height) = \frac{1}{2}bh$

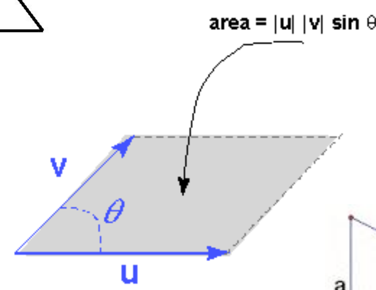
Volume of a cube = ℓ^3

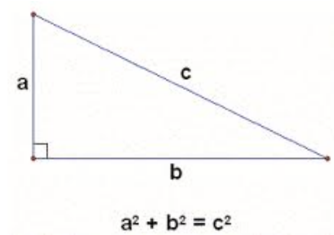
Volume of a sphere = $\frac{4}{3}\pi r^3$

Area of a parallelogram = $u \bullet v\ \sin(\theta)$

Pythagorean theorem: $a^2 + b^2 = c^2$ for a right triangle







BACKGROUND

Macroscopically, we view a crystal as a solid substance having a regular shape with plane surfaces and sharp edges that intersect at fixed angles. For instance, a crystal of sodium chloride is cubic in appearance. We can explain the macroscopic appearance of crystals by understanding their microscopic structure. Microscopically, we view crystals as being composed of atoms, ions or molecules that are arranged in a three-dimensional ordered structure called a **crystal lattice**. The **unit cell** is the smallest part of a crystalline solid which, when repeated in all directions, generates the entire crystal. The unit cell of sodium chloride happens to be cubic which is consistent with the macroscopic outside appearance of a sodium chloride crystal.

Other properties of crystals such as electrical conductivity, hardness and melting point can be explained in terms of the type of forces that hold the crystal together. In this exercise, we will focus on metallic and ionic crystals. A simple theory of metallic bonding, know as the electron sea model, views metallic crystals as being composed of three-dimensional arrays of positive ions (i.e., the metal atom minus their valence electrons) surrounded by a mobile "sea" of valence electrons. The relatively massive metal ions are held in place by the "sea" of valence electrons that can randomly move about. In ionic bonding, the crystal lattice is made up of cations and anions arranged in a three-dimensional array. Ionic crystals are held together by strong electrostatic attractions between the oppositely charged ions. Note that in both metallic and ionic solids, discrete molecules do not exist. Instead, these solids are composed of a continuous array of atoms or ions.

OBJECTIVE

We can view the metal atoms in a metallic solid or the ions in an ionic solid as a collection of spheres packed together. Analogous to the packing of marbles in a box, we cannot pack atoms or ions in such a way that all of the volume is filled. Certain arrangements of packing are more efficient than others. We will explore various arrangements and their packing efficiency as part of this exercise.

LABORATORY EXERCISE – TWO DIMENSIONAL PACKING OF CIRCLES

Before considering the three dimensional structure of crystalline compounds we will do some practice problems on two-dimensional analogs of packing patterns – that is we will consider the arrangement of circles in a single layer. After we practice on simpler two-dimensional systems, we will apply our newly acquired expertise to the modeling of simple crystal lattices as spheres packed in a three-dimensional array.

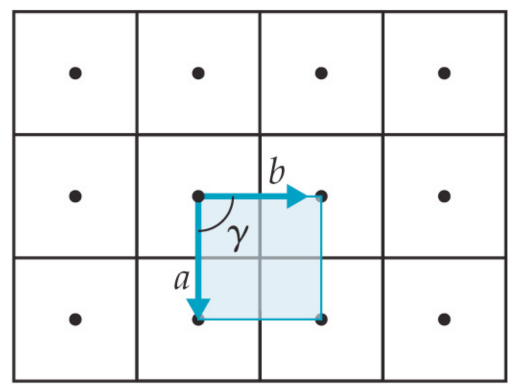
We begin by considering how circles, all of the same size, can most efficiently be arranged in a single 2-D layer. In the 2-D lattices provided, centered in each lattice unit cell, draw circles that completely fill the unit cell.

1. Make a qualitative observation about which of the two patterns gives the most efficient packing arrangement of the circles. In other words, which arrangement looks likes the greatest area of the unit cell is occupied by a circle, i.e., less empty space around the circle.
   a) Mathematically determine the percent of the unit cell occupied by the circle.

      Percent unit cell occupied the circle = $\frac{\textbf{Area covered by circle in unit cell}}{\textbf{Area of unit cell}}$ x100%

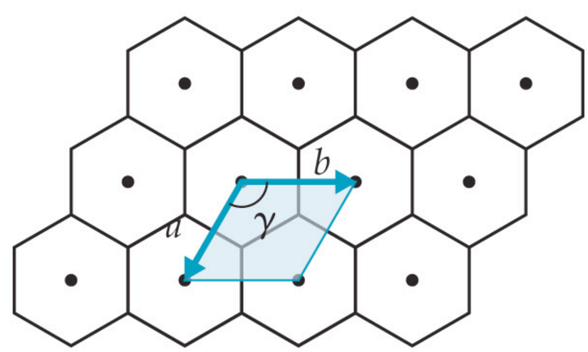
      Square lattice:

      Hexagonal lattice:



Square lattice ($a = b$, $\gamma = 90°$)

2. Which of the two arrangements had the greatest packing efficiency, that is which had the highest percent of the unit cell occupied? This arrangement is called a **closest packed** structure.

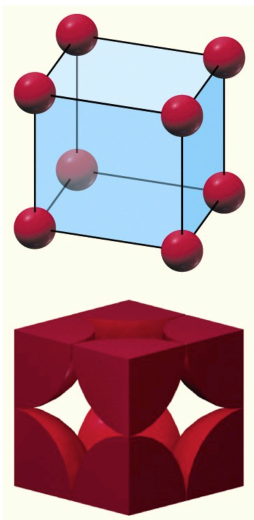
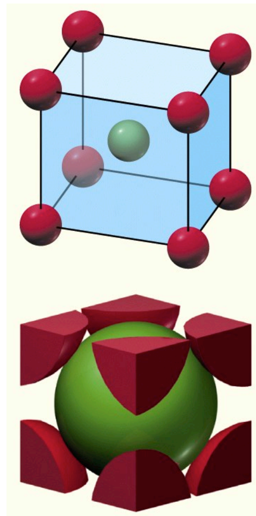
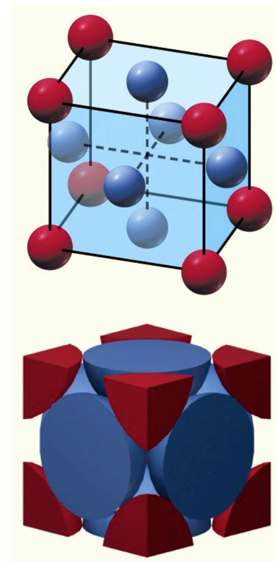


Hexagonal lattice ($a = b$, $\gamma = 120°$)

3. Will the percent of unit cell occupied by the circle for each pattern remain the same if the lattice and circles used were microscopic in size? That is, does the percent occupancy depend on the radius of the circle? Why or why not?

LABORATORY EXERCISE – UNIT CELLS AND THREE-DIMENSIONAL PACKED STRUCTURES

We now apply what we learned in our two-dimensional analysis to the packing of spheres in three dimensions. **We will limit our discussion to cubic unit cells, that is, cells with edges that are of equal length and meet at 90° angles.**
In a sample of a pure metal, only one type of atom is present. Therefore, when modeling the structure of metallic crystals we can view them as being composed of spheres that are all the same size.
There are three types of cubic unit cells: 1) Primitive or simple cubic (SC), 2) Body-centered cubic (BCC), and 3) Face-centered cubic (FCC). Each is shown below.

These unit cells have some important similarities and differences. Examine each cell above to complete the table that follows.

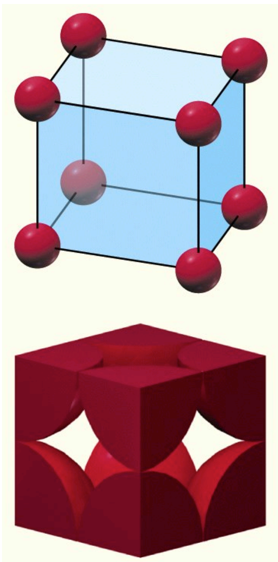
TABLE I. CUBIC UNIT CELL SIMILARITIES AND DIFFERENCES.

Similarities	SC	BCC	FCC
How many different unit cells, when stacked together, share one corner?			
What fraction of each sphere lies within a corner of one unit cell?			
1. How many complete spheres make up the corners of each unit cell?			
Differences	SC	BCC	FCC
2. How many complete spheres occupy ONLY the center of the unit cell?			
3. How many complete spheres occupy ONLY the faces of the unit cell?			
How many complete spheres in each unit cell? Add 1, 2, and 3 from above.			

DETAILED CALCULATIONS OF PERCENT VOLUME OCCUPIED FOR EACH UNIT CELL

PRIMITIVE OR SIMPLE CUBIC (SC) UNIT CELL

Determine the percentage of volume occupied in a SC structure mathematically. Show your work in the spaces provided. Refer to Table I. All distances need to be written in terms of r, the radius of a sphere.



$$\text{Percentage of volume occupied} = \frac{\text{volume occupied by spheres in unit cell}}{\text{total volume of unit cell}} \text{x}100\%$$

1. Express the edge length of the unit cell, ℓ, in terms of r. Enter in Table II.

2. Calculate the volume of the unit cell in terms of r.

3. Calculate the volume occupied by the sphere(s) in the unit cell.

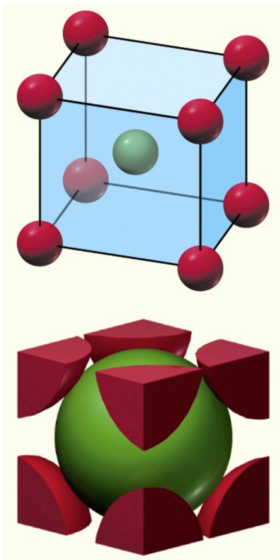
4. Determine the percentage of the unit cell occupied by the spheres. Enter in Table II.

Crystal Lattices.doc **Report Sheet** Name ______________________________

Circle Lab Section: MW or TTh Partner ______________________________

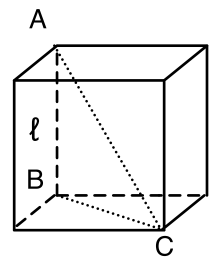
BODY-CENTERED CUBIC (BCC) UNIT CELL

Determine the percentage of volume occupied in a BCC structure mathematically. Show your work in the spaces provided. Refer to Table I. All distances need to be written in terms of r, the radius of a sphere.



$$\text{Percentage of volume occupied} = \frac{\text{volume occupied by spheres in unit cell}}{\text{total volume of unit cell}} \text{x}100\%$$

1. What is the length of the body diagonal of the cube, AC, in terms of the radius of the sphere, r (i.e. the diagonal can be represented as a multiple of r)?



2. Using the Pythagorean theorem, write the length of the diagonal AC in terms of the diagonal BC and the cube edge length, AB.

3. Again using the Pythagorean theorem, write the length of the diagonal BC in terms of only the edge length, AB = .

4. Now, express the diagonal AC in terms of only the edge length, ℓ = AB.

5. Now express the edge length, ℓ, in terms of r. Enter in Table II.

6. Calculate the volume of the unit cell in terms of r.

7. Calculate the volume occupied by the sphere(s) in the unit cell.

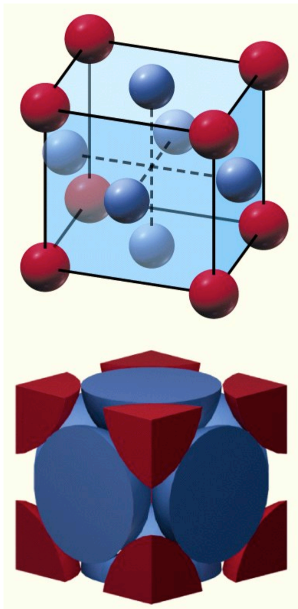
8. Determine the percentage of the unit cell occupied by the spheres. Enter in Table II.

Crystal Lattices.doc **Report Sheet** Name ____________________

Circle Lab Section: MW or TTh Partner ____________________

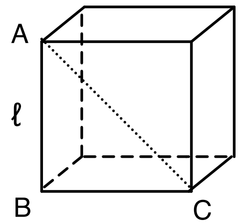
FACE-CENTERED CUBIC (FCC) UNIT CELL

Determine the percentage of volume occupied in a FCC structure mathematically. Show your work in the spaces provided. Refer to Table I. All distances need to be written in terms of r, the radius of a sphere.



$$\text{Percentage of volume occupied} = \frac{\text{volume occupied by spheres in unit cell}}{\text{total volume of unit cell}} \text{x}100\%$$

1. What is the length of the diagonal of the cube face (AC in the figure) in terms of the radius of the sphere, r (i.e. the diagonal can be represented as a multiple of r)?



2. Now, using the Pythagorean theorem, write the length of the diagonal AC in terms of only the edge length, ℓ = AB.

3. Now express the edge length, ℓ, in terms of r. Enter in Table II.

4. Calculate the volume of the unit cell in terms of r.

5. Calculate the volume occupied by the sphere(s) in the unit cell.

6. Determine the percentage of the unit cell occupied by the spheres. Enter in Table II.

1. Summarize all your calculations in the table that follows.

TABLE II. CUBIC UNIT CELL SUMMARY OF CALCULATIONS.

Summary of Calculations	SC	BCC	FCC
Edge length in terms of the radius, r			
Percent volume of cell occupied by spherical atoms			

FOLLOW-UP QUESTIONS – SHOW YOUR WORK WITH UNITS AND CORRECT SIGNIFICANT FIGURES FOR ALL MATHEMATICAL PROBLEMS.

1. Which packing arrangement, SC, BCC or FCC, is most efficient?

2. Copper crystallizes in a FCC arrangement. The atomic radius of a copper atom is 127.8 pm.
   a) What is the edge length of a unit cell of copper in pm? (see your summary of calculations.)

   b) What is the volume of a unit cell of copper in cm^3?

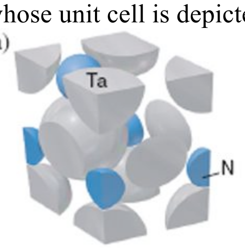
   c) Calculate the density of copper in g/cm^3. Note: How many atoms of Cu in an FCC unit cell?

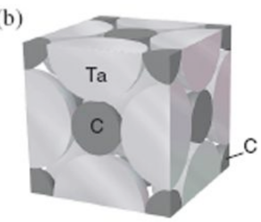
   d) Look up the density of copper online. Write this literature value below. Is your calculated value consistent with the literature value? Determine a percent error.

   Literature Value:________________ Source: ____

   Percent Error:_________________________

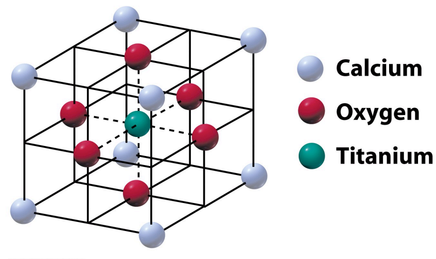
3. Like most transition metals, tantalum (Ta) exhibits several oxidation states. Give the formula of each titanium compound whose unit cell is depicted below.

(a)


(b)


4. An element crystalizes in a BCC unit cell and has a density of 19.3 g/cm^3. The atomic radius is 321 pm. Calculate an approximate molar mass for this element.

Perovskite, a mineral composed of Ca, O, and Ti, has the cubic unit cell shown in the drawing (Ca at the corners, O on the faces, Ti in the center). What is the chemical formula of this mineral?



5. An element crystallizes in a body-centered cubic lattice. The edge of the unit cell is 2.86 Å, and the density of the crystal is 7.92 g/cm^3. Calculate the molar mass of the element.

6. Spinel is a mineral that contains 37.9% Al, 17.1% Mg, and 45.0% O by mass, and has a density of 3.57g cm^{-3}. The unit cell is cubic with an edge length of 8.09 Å. How many atoms of each type are in the unit cell?