UNIVERSITY OF DELAWARE
Department of Materials Science and Engineering
MSEG 367 Spring 2004

Lab 1: Crystal Models (2/23-2/27)

Introduction

The properties of materials are determined by the types of bonding between constituent atoms and the spatial arrangement of those atoms. Atoms may be arranged in a regular, repeating (periodic) assembly to form crystals or may be arranged with only local structure (*i.e.* without regular repeating units) to form amorphous (or glassy) materials. Crystalline solids are far more common than amorphous ones among the metals and ceramics, whereas polymers are most often amorphous. The focus of this laboratory exercise is on crystalline materials.

There are many ways of arranging atoms in three-dimensional space to form crystals, particularly in the case of ceramic materials where there are multiple elements with different character. In the case of metals and alloys the structures tend to be rather simple, namely, face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP). Most pure metals and metal alloys crystallize with one of these simple structures.

The aim of this exercise is to familiarize the student with the FCC, BCC, and HCP crystal structures, as well as a few of the simplest ceramic structures. The structures will then be studied to determine important crystallographic parameters relating to crystal symmetry, density of atomic packing, and the location and size of the holes within the crystal.

The first part of the exercise is focused on simple two-dimensional arrangements of spheres and will serve to clarify some of the terminology used and provide practice in the calculation of the parameters mentioned above. The second part of the exercise will entail the construction of three-dimensional models of the FCC, BCC, and HCP crystal structures. Part three will involve construction of two of the simplest ceramic structure types, NaCl and CsCl. In part four, the voids within the crystal will be examined in detail for the case of the FCC structure.

SINCE THIS EXERCISE MUST BE COMPLETED IN THE ALLOTTED LABORATORY PERIOD, PART 1 MUST BE DONE BEFORE COMING TO LABORATORY.

Procedure

Bring to the laboratory: paper and drawing equipment – pencils, erasers, rulers, drafting triangles, and circle templates. Show your work where necessary! Answer the questions on your own paper, except for Part 1, where you will use Figures 1 and 2 on page 4.

Part 1 - Planes of Atoms

1.1 Close-Packed Planes and Planar Density

Consider the circles in Figures 1 and 2 to represent infinite arrays of spherical atoms. The array which produces the closest packing of atoms in a plane is shown in Figure 2. Planes with this array of atoms are called CLOSED-PACKED PLANES.

Calculate the planar density in Figures 1 and 2 in terms of "a", the distance between atom centers.

Planar Density = Number of Atoms/Unit Area

1.2 Close-Packed Directions.

When applied to crystal planes and directions, the adjective "close" really means "closest possible." The close-packed directions are those crystal directions along which the atoms touch.

Draw all the non-parallel close-packed directions on Figures 1 and 2.

1.3 Indexing Directions.

Since the spacing between atoms varies along different directions, the properties of the crystal will also vary with direction, and thus a method of numbering or indexing directions will be useful in discussing crystal structure. The method is very similar to the concept of vectors in mathematics and is as follows:

1. Place an origin at the center of an atom and establish a coordinate system, which is not necessarily an orthogonal system. (In Figures 1 and 2, use the axis shown. The *z*-axis is perpendicular to the paper.)

2. Draw a direction from the origin to the center of another (any) atom.

3. Determine the *x*, *y*, and *z* components of the direction.

4. Divide by the highest common factor. Negative values are indicated as follows: $\underline{x}$. Do not use commas between numbers. Square brackets indicate directions, *e. g*. [100], [$1\underline{2}3$].

5. Draw and label the following directions on Figures 1 and 2: [100], [010], [$\underline{1}00$], [$0\underline{1}0$], [110], [$\underline{1}10$], [$\underline{1}\underline{1}0$], [120], [$\underline{1}20$], [130], [$\underline{1}30$].

1.4 Atomic Spacing along Crystal Directions.

Calculate the distances between atom centers in the following directions: [100], [010], $[\bar{1}\,00]$, $[0\bar{1}\,0]$, [110], $[\bar{1}\bar{1}\,0]$, in terms of "a" and record the results as follows:

Direction	Distance between atom centers	
	Figure 1	Figure 2
[1 0 0]	-------	-------
[0 1 0]	-------	-------
$[\underline{1}\ 0\ 0]$	-------	-------
$[0\ \underline{1}\ 0]$	-------	-------
[1 1 0]	-------	-------
$[\underline{1}\ \underline{1}\ 0]$	-------	-------

1.5 Crystallographically Equivalent Directions.

Because of the symmetry of crystal structures, there will be directions with different indices but with the same pattern and spacing of atoms, *e.g.* the [100] and [010] directions in Figure 1. These directions are termed crystallographically equivalent directions.

For the directions listed in Section 1.3 determine all the sets of equivalent directions in Figure 1. Repeat for Figure 2.

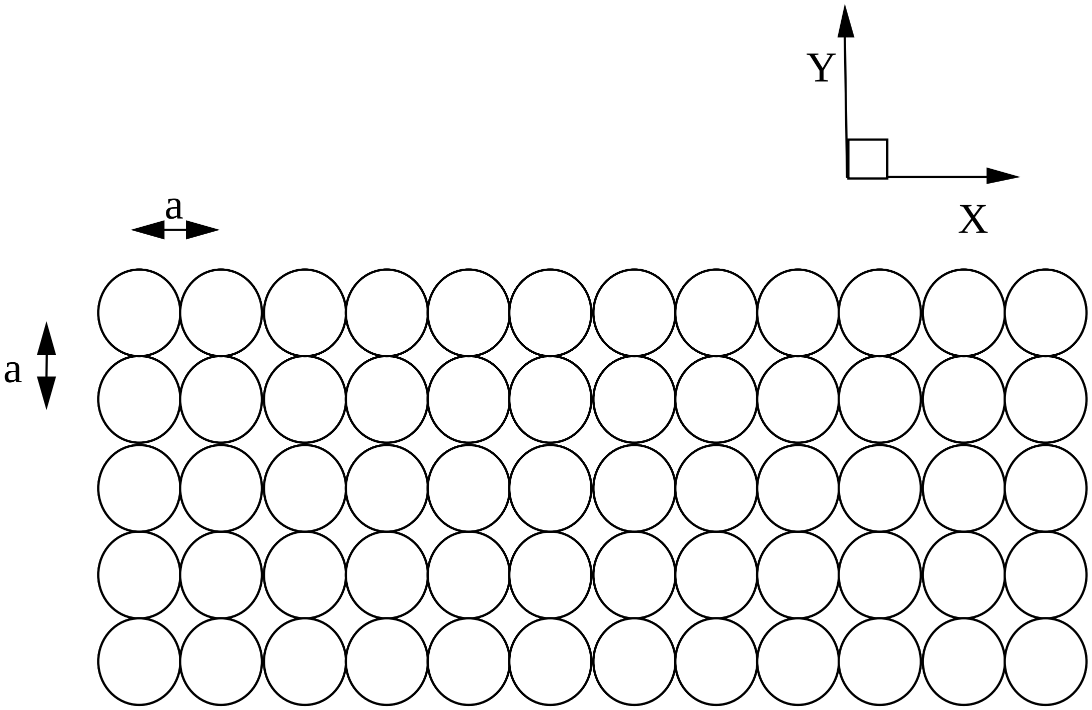


Figure 1

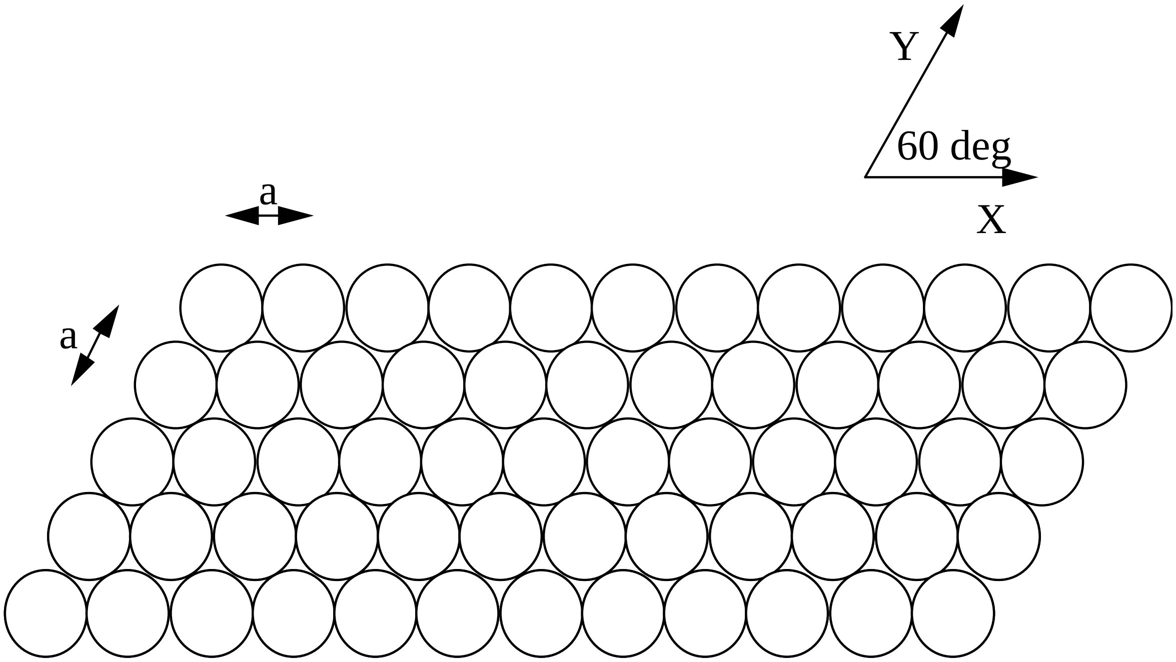


Figure 2

Part 2 - The BCC, FCC, and HCP Crystal Structures

2.0 Convention. The following notations are used to remind you about the specific activities required for the different questions. The lack of these signs for a question **does not** mean that you can ignore the question; it only means the question requires no building, drawing or calculation.

[Building] a model or models is a part of the required task.

[Calculation] is a part of the required task.

[Drawing] or sketching a graph, or labeling an existing graph is a part of the required task.

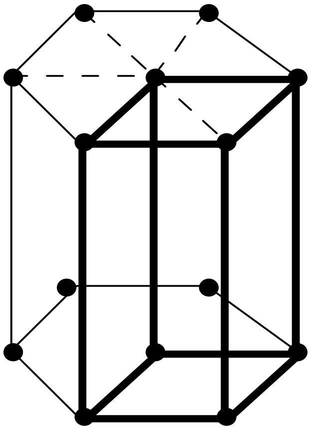
2.1 Construction of the Unit Cells. Using the crystal model set, stack the balls on the templates and construct models for BCC, FCC and HCP.

2.1a The BCC Unit Cell (Page 18 on the Instruction Manual). *(These are already built)* The square-patterned template yields the BCC structure. The construction is straightforward, note, however, that there are NO CLOSE-PACKED PLANES. ***[Building]*** After building the BCC unit cell answer the Questions from 2.2 to 2.9 pertaining to the BCC crystal lattice before moving onto 2.1b.

2.1b The FCC Unit Cell. (Page 27 on the Instruction Manual) *(These are already built)* The unit cell is built by using the hexagonal patterned template and stacking close-packed planes. The ABCABC sequence results in a close-packed structure with cubic symmetry, namely the FCC structure. If you have problems with the stacking sequences, try the following procedure. ***[Building]*** After building the FCC unit cell answer the Questions from 2.2 to 2.9 pertaining to the FCC crystal lattice

2.1c The HCP unit cell: (Pg 24 on the Instruction manual.) *(These are already built)* The unit cell is built by using the hexagonal patterned template and stacking close-packed planes. There are two stacking sequences. The ABAB sequence results in a close-packed structure with hexagonal symmetry, namely the HCP structure. After building the HCP unit cell answer the Questions from 2.2 to 2.9 pertaining to the HCP crystal lattice

2.2 *Draw* a ball and stick sketches of the FCC, BCC, and HCP unit cells (see Callister). Your figure should be at least 3" across. The drawing below illustrates the two choices of unit cell for the HCP structure. By convention most unit cells are parallelepipeds but for the HCP structure a larger, hexagonal prism is often used because it emphasizes the symmetry (the C_6 rotation axis). Either is correct. Pick one and use it throughout the lab. ***[Drawing]***



2.3 <u>Close-Packed Directions.</u> ***[Drawing]***

For each of the three unit cells (FCC, BCC and HCP), please show a close-packed **direction** in your sketches for 2.2.

For the BCC and FCC cells, index these directions.

2.4 <u>Close-Packed Planes</u> ***[Drawing]***

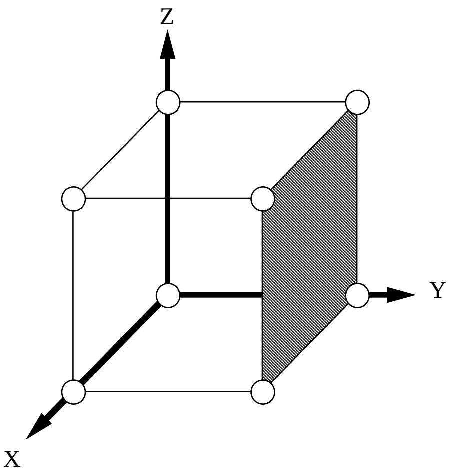
For each of the two unit cells (FCC and HCP), please show a close-packed **plane** in your sketches for 2.2. and also index the planes. As there is no close-packed plane for BCC, draw and index the densest plane. Draw the actual plane using circles to represent the atoms, do <u>not</u> use a "ball and stick" representation for this question.

2.5 Indexing Planes - Miller Indices. ***[Calculation]***

Index the densest packed planes in the BCC and FCC unit cells. The method is explained below.

1. Choose your origin and establish the axes. The plane of interest must not go through the origin.

Example:
Simple Cubic
Unit Cell



2. Write down the coordinates of the intersection of the plane with the axes. The coordinates are in terms of the length of the sides of the unit cell. Note that when an axis is parallel to the plane, the intercept is at infinity.

x intercept = ∞
y intercept = 1
z intercept = ∞

3. Take the inverse of the intercepts.

$1/\infty = 0 \;\; ; \;\; 1/1 = 1 \;\; ; \;\; 1/\infty = 0$

4. Divide through by the largest common factor. Use a bar above the number to denote a negative quantity and place parentheses around the numbers, (010). These numbers are termed the Miller indices of the plane.

2.6 Crystallographically Equivalent Planes. ***[Calculation] [Drawing]***

Because of symmetry, there will be planes with different indices, but the same pattern of atoms. These planes will be crystallographic equivalents. For example, in any cubic unit cell all the face planes of the cube will be equivalent, thus (100) + (010) + (001) + $(\underline{1}00)$ + $(0\underline{1}0)$ + $(00\underline{1})$

A family of equivalent planes is denoted by pointed parenthesis { }; therefore the family of cubic face planes is shown as {100}.

→ For each of the three structures draw a plane which is crystallographically equivalent to the densest plane you drew in Section 2.4. Redraw the unit cell if necessary. ***[Drawing]***

→ For the BCC and FCC unit cells index the equivalent plane you have drawn. ***[Drawing]***

2.7 Number of Nearest Neighbors. The nearest neighbors are the neighboring atoms which make contact with a given atom (this is in three dimensions, not just in the plane). ***[Calculation]***

→ The number of nearest neighbors is called the coordination number. What is the coordination number in each of the three structures (FCC, BCC and HCP)?

2.8 Number of Atoms per Unit Cell. Only the part of the atom contained within the parallelepiped unit cell is counted. An atom which has its center on the face of a cubic cell is shared equally between 2 unit cells; an atom which has its center at a corner is shared equally between 8 unit cells, etc. ***[Calculation]***

→ What is the number of atoms per unit cell for each of the three structures?

2.9 Packing Density (or Packing Efficiency). The packing density is defined here as the fraction of *occupied* space assuming spherical atoms. ***[Calculation]***

→ For the BCC and FCC unit cells calculate the packing density as follows:

(1) Determine the number of atoms per unit cell as in Section 2.8.

(2) Calculate the volume of the unit cell in terms of "a", the lattice parameter.

(3) Calculate the volume of an atom by determining the close packed direction and hence, the relation between the atom radius, *r*, and the lattice parameter, a.

Part 3 - Some Simple Ceramic Crystal Structures

3.1a The NaCl Unit Cell (Page 33 on the Instruction Manual): The sodium chloride structure is often referred to as "interpenetrated face centered cubic" since the sodium ions and the chloride ions each reside on individual FCC sublattices; however, one sublattice is translated by half of the unit cell length along (any) one axis. Make ball and stick sketches of the NaCl unit cell. Your figure should be at least 3" across. ***[Drawing]***

3.1b The CsCl Unit Cell (Page 11on the Instruction Manual): The CsCl structure consists again of two cubic sublattices with the same geometry. This time they are each simple cubic and are interpenetrated by placing the "displaced origin" of one sublattice at coordinates (0.5,0.5,0.5) relative the other with proper origin designated as (0,0,0). Note that coordinates are always measured in units of the lattice constant along the corresponding direction, x-axis associated with lattice constant a, y-axis associated with lattice constant b, z-axis associated with lattice constant c. Make ball and stick sketches of the CsCl unit cell. Your figure should be at least 3" across. ***[Drawing]***

3.1c The word lattice actually refers to a grid of points periodically arranged in space onto which atoms are placed. A crystal is generated by superimposing atoms or clusters of atoms onto the lattice. The set of atoms which must be placed on each lattice point is called the basis. Thus,

Lattice + Basis = Crystal

- A body-centered lattice, designated by "I-centered" (note: I is for inversion), is one for which there are equivalent atoms at coordinates:

"I" $(x,y,z) \equiv (x+0.5,y+0.5,z+0.5)$.

- A face-centered lattice, designated as "F-centered" has equivalent atoms at coordinates:

"F" $(x,y,z),\equiv (x+0.5,y+0.5,z)$, $(x+0.5,y,z+0.5)$ and $(x,y+0.5,z+0.5)$.

- A lattice may also have centering on a single face, designated by "A", "B", or "C", such that the equivalent coordinates are:

"A" $(x,y,z) \equiv (x,y+0.5,z+0.5)$

"B" $(x,y,z) \equiv (x+0.5,y,z+0.5)$

"C" $(x,y,z) \equiv (x+0.5,y+0.5,z)$

- A primitive lattice, designated as "P", has no centering of any kind.

→ The simple cubic (SC) structure has a P lattice, the FCC structure has an F-centered lattice, and the BCC structure has an I-centered lattice. How many atoms comprise the basis for SC, FCC, BCC, NaCl, and CsCl? ***[Calculation]***

Part 4 - Interstitial Sites

It is clear by observation of the models and from Question 2.9, that there are "empty" regions within the unit cell. These regions are termed interstitial sites (from the Latin "intersistere," meaning "to stand in the middle of"). Foreign atoms in these sites can significantly change the properties of the material.

The FCC, BCC, and HCP structures contain two types of interstitial sites: TETRAHEDRAL and OCTAHEDRAL. The tetrahedral site has four nearest neighbors. Connecting the centers of the four neighboring atoms forms a tetrahedron. The octahedral site has <u>six</u> nearest neighbors which, when connected, form an eight-sided solid called an octahedron, hence the terminology.

YOU WILL EXAMINE THE SIZE, NUMBER, AND POSITION OF BOTH TYPES OF SITES IN THE FCC UNIT CELL.

You are not asked to find the interstitial sites in the HCP unit cell. But since both the FCC and HCP structures are close-packed, the interstitial sites are similar in each. For example, the size calculations in Section 3.3 apply to the interstitial sites in both structures.

The octahedral and tetrahedral sites are also present in the BCC unit cell, but are distorted (their sizes are different from the FCC structure because the BCC structure is not close-packed) and are more difficult to see.

4.1 <u>Build the FCC crystal structure with tetrahedral and octahedral interstitial sites occupied.</u>

Place the interstitial atoms in their sites. Two different sized spheres are provided to represent interstitial atoms in your models. The larger ones are for the octahedral sites. If you have difficulty locating the sites try the following: ***[Building]***

1. Construct just the first layer on the template. Place the interstitial atoms in the valleys around each sphere, alternating small and large interstitial atoms.

2. Place the second layer over the small interstitial atoms. These have four nearest neighbors and thus are tetrahedral sites. There are also tetrahedral sites at the top of every atom in the first layer. Place small interstitial atoms in these sites.

3. The other interstitial atoms will have six nearest neighbors and hence are in octahedral sites.

4.2 Location and Number of Interstitial Sites. ***[Calculation] [Drawing]***

→ Using your template and unit cell for the FCC cell, make two sketches of this unit cell. On one sketch show the location of each tetrahedral site. Use the other sketch to show each octahedral site.

In order to receive credit for this question, the coordinates of representative interstitial sites must be given.

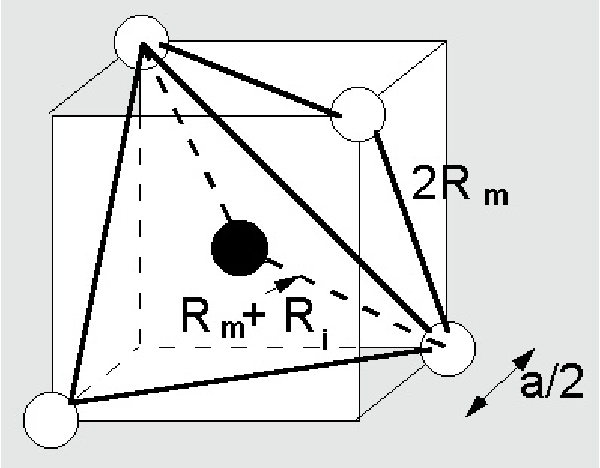
→ Calculate the total number of octahedral and tetrahedral sites per unit cell for the FCC structure. The same rules apply for "shared" sites as discussed in 2.9 for lattice sites.

4.3 Size of the Interstitial Sites. ***[Calculation]***

→ Calculate (and show your working to receive credit) the maximum size of the foreign atom that can be placed in the octahedral site without causing distortion of the lattice. Express your answer as the ratio of the radius of the interstitial atom to the radius of the matrix atom.

The general method is first to determine the direction along which the interstitial and matrix atoms touch. Express the distance along this direction as the sum of both radii. Next express the distance as a function of the radius of the matrix atom. Equate the two expressions and solve.

The calculation for the tetrahedral site is given below. Good quality, clear sketches will help you solve for the octahedral case.



"Ball and stick" representation. Matrix atoms actually touch each other along the solid lines, such that:

$\sqrt{2}\,(a/2) = 2R_m$ or $a/2 = \sqrt{2}\;R_m$

1. The center of the cube is also the center of the tetrahedron, so the matrix and interstitial atoms touch along the body diagonal.

2. The distance from the center of the matrix atom to the center of the interstitial atom is $R_i + R_m$.

3. This distance also equals half the length of the cube body diagonal.

1/2 (cube body diagonal) = 1/2 ($\sqrt{3}$ x length of cube edge) = 1/2 ($\sqrt{3}$ x $\sqrt{2}$ R_m)

4. Equating and solving.

$$R_i + R_m = 1/2\,(\sqrt{6}\;\; R_m)$$

$$R_i/R_m \approx 0.225$$

Glossary

A variety of terms from solid geometry and crystallography are used in this laboratory. Some useful definitions and descriptions are given below:

POLYHEDRON	-	A solid bounded by polygons.
PRISM	-	A Shape generated by moving a line (the generator) parallel to itself so that the ends generate a polygon.
PARALLELEPIPED	-	A prism whose bases are parallelograms.
TETRAHEDRON	-	A regular polyhedron with four surfaces.
OCTAHEDRON	-	A regular polyhedron with eight surfaces.
BRAVAIS LATTICE	-	A three dimensional array of points (lattice points) each of which has identical surrounding: also called a <u>space lattice</u>. There are 14 distinct Bravais lattices. If one atom or a group of atoms (called a <u>basis</u>) is placed at each lattice point a <u>crystal structure</u> is formed. Lattice + Basis = Crystal Structure
UNIT CELL	-	A repeating unit of both the Bravais lattice and the crystal structure. Identical unit cells of a particular Bravais lattice will fill space and generate the Bravais lattice when packed face-to-face. One Bravais lattice can have a number different unit cells but conventionally, unit cells are chosen which have a simple geometry and contain only a few lattice points. Most unit cells form parallelepipeds when the centers of the atoms are connected (e.g., a cube), but for the HCP unit cell a hexagonal prism is frequently chosen because it emphasizes the symmetry.