Chapter 1

Crystal Structure

1.0 Learning Objectives

After successfully completing this laboratory workshop, including the assigned reading, the lab worksheets, the lab quizzes, and any required reports, the student will be able to:

- **Draw** a simple atomic model showing the position of electrons, protons, and the nucleus.
- **Describe** ionic, covalent, and metallic bonding.
- **Draw** the lattices for BCC and FCC.
- **Determine** atoms per lattice site and atoms per unit cell for varying crystal structures.
- **Determine** the Miller indices for planes and directions in cubic systems.

2.0 Resources

[1]. Callister, Materials Science and Engineering: An Introduction, (John Wiley and Sons, New York, 2000), pg. 30-91.

[2]. Making Matter: The Atomic Structure of Materials:
http://www.ill.fr/dif/3D-crystals/index.html

[3]. Links on Crystals:
http://www.geocities.com/materialsworldweb/Crystals.html

[4]. More Links…
http://www.uis.edu/~trammell/MaterialsScience/bookmarks.htm#crystal

3.0 Materials Applications

Understanding crystal structure is critically important to understanding why materials behave the way they do and to design processes for specific applications. For example, shape memory alloys are materials that change shape under applied temperature and/or stress and then can return to their original shape when the temperature or stress is removed. These materials are used in applications such as surgical tools that alter shape when inserted in the body and machine parts that can *heal* dents upon heating. The way these materials change and remember their shape is that their crystal structure at one temperature is different than at another temperature. Another example of the importance of crystal structure is in the semiconductor industry. Computer chips are fabricated on single crystal silicon wafers. The electrical reliability of the computer chips relies on the entire wafer having the same unit cell repeated throughout. To ensure this, growth of the wafers is carefully controlled. Properties such as the electron mobility (and thus the end speed of the device) and the rate at which layers on the wafer are deposited or etched depends on the crystal plane that is exposed on the surface.

Understanding what defects are and where they come from is important in understanding why materials fail and how to process them to make them more reliable. An infamous case of atomic defects causing catastrophic failures is dislocation generation and motion resulting in airplane wings falling off after repeated use (watch *Highway in the Sky*, an old movie that glamorizes the search for what was causing these airplane failures).

4.0 Theory of Atomic Arrangements

4.1 Bonding

There are three primary types of bonds in crystalline solids: ionic, covalent, and metallic. The mechanical and electronic properties of solids vary significantly depending on which type of bonding the solid has. Ceramic materials have ionic bonds, which are the strongest type of bonds, producing very hard materials. Semiconductors have covalent and sometimes ionic bonds that are spherically symmetrical and thus allow easy movement of atoms, or deformation, to occur.

4.2 Metallic Bonding

In metals, the bonds are isotropic or spherical. Metallic bonding can only occur among a large aggregate of atoms, such as in a crystal. On the other hand a covalent bond can occur between only two atoms, in an isolated molecule. For example in face-centered cubic and hexagonal close-packed metals, each atom has 12 nearest neighbors and thus is bonded in all directions. In body-centered cubic metals there are 8 nearest neighbors. The valence electrons from each atom are shared throughout the crystal. The valence electrons are very loosely attracted to the nucleus of the atom, and they are spread out so far from the nucleus that they may be closer to another nucleus in the solid. Thus all the metal atoms in the solid are "knitted" together by these free valence electrons. These electrons are hence free to "travel" throughout the crystal, resulting in the large electrical conductivity of metals. The atoms in metals can slide easily by each other, because the bonds are not restricted to one direction or a strict angle, making it easy to deform most metals. This is why we can make so many structural parts from metal. Most metals have a face-centered cubic, hexagonal close-packed, or body-centered cubic structure, which provides the most dense packing of atoms, thus the highest density solids.

4.3 Covalent Bonding

Covalent solids are mainly formed from non-metallic elements. In covalent materials, the bonded atoms share electrons between them. Most semiconductors are covalent. The atom must have a half-filled p-orbital. For example, silicon, with 14 electrons, is covalently bonded. Each silicon atom is bonded to 4 others in a tetrahedral bond, which leads to the diamond cubic crystal structure. The electronic structure of Si is $1s^2 2s^2 2p^6 3s^2\ 3p^2$. When the four Si atoms create tetrahedral covalent bonds, the 3s and 3p electrons form a new set of hybrid orbitals called 3sp. Thus the electronic configuration becomes $1s^2 2s^2 2p^6 (3sp)^4$. Germanium (Ge) is another covalent semiconductor, with the structure $1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^{10} (4sp)^4$.

Tetrahedral bonds are highly directional and there is little probability of an electron being outside the vicinity of this bond. High temperatures or other sources of energy are needed to remove an electron from the strong covalent bond. This is why semiconductors have relatively low electrical conductivities unless they have special impurities added. Because of the directionality of the bond, atoms in a covalent solid cannot be easily displaced from their equilibrium positions, making covalent solids very brittle.

4.4 Ionic Bonding

Solids with more than one type of atom often possess ionic bonds. This includes ceramic materials, such as oxides and silicates, as well as salts. In an ionic bond an electron is “given” by the cation to the anion; this then creates an electrostatic attraction between them, creating a very strong ionic bond. Electronegative atoms are those that have a few empty p-orbitals; they tend to acquire electrons and become negative anions. Electropositive atoms have only a few electrons in an outer shell, and tend to give up electrons, becoming cations. Thus none of the atoms in an ionic solid are neutral; all atoms in the crystal are ions with either a plus charge (cation) or a minus charge (anion). The electron swapping lowers the energy of the crystal by providing each ion with an electron configuration closer to a filled outer shell. For example, in NaCl, when the Na gives up one electron (and becomes Na^+), it has a filled 3s shell and becomes more stable. When the Cl accepts the electron from the Na (becoming Cl^-), it now has a filled 3p shell and is more stable. Not all combinations of elements can form ionic bonds; only pairs which complement each other can combine.

It is difficult to deform ionic solids because of the strong electrostatic force between the ions. Thus ceramic materials are very brittle and cannot be deformed easily. The electrical conductivity in general is very low because there are no free electrons to conduct current. However, some ionic solids have ionic conductivity, in which small mobile ions can conduct current.

Once the cation and anion have formed, there is an electrostatic attraction between them. This attractive force increases as the ions come closer to each other. However when the ions get too close to each other, their electronic clouds start to overlap and a repulsive force arises. At any given distance apart, there is a net force between the ions that is simply the sum of the attractive and repulsive forces.

5.0 Crystalline Solids

When atoms come together to form solids they may be arranged in many different ways. In a crystalline solid the atoms are arranged in a periodic fashion and have long range order. By translating an atom or group of atoms in three dimensions a crystal structure is formed. The crystal structure of a material is based on the crystal lattice which is an array of imaginary points in space. This array of points is not arbitrary but follows a set of rotational and translational rules. Each lattice point may have one or more atoms, ions or molecules associated with it, called a basis.

The smallest group of lattice points that displays the full symmetry of the crystal structure is called the unit cell. The unit cell has all the properties found in the bulk crystal. The geometry and the arrangement of lattice points define the unit cell. By translating the unit cell in three dimensions the entire crystal structure is formed.

The geometry of a unit cell can be represented by a parallelepiped with lattice parameters a, b, and c and angles α, β, and γ. By varying the lattice parameters and angles, seven distinct crystal systems can be formed. The seven crystal systems are cubic, tetragonal, orthorhombic, hexagonal, rhombohedral, monoclinic, and triclinic. There are 14 ways to place the lattice points in these systems to create Bravais lattices. Most of the metals, ionic salts, and semiconductors studied in this course are members of the cubic crystal system.

The cubic crystal system has lattice parameters $a = b = c$ and angles $\alpha = \beta = \gamma = 90^o$. Therefore, the lattice parameter is referred to as a and the angles are ignored. The three Bravais lattices associated with the cubic system are simple cubic (SC - sometimes called primitive cubic), body centered cubic (BCC), and face centered cubic (FCC). The distinction between the Bravais lattices is in the number and position of the lattice points. SC has a lattice point at each of the cube corners. BCC has lattice points at its corners and one in the center of the cube. FCC has lattice points at the corners and one point on each of the cube faces.

The different crystal structures that can be formed from these lattices depend on the basis. The basis is the smallest number of atoms that can be placed at the lattice points to build the crystal structure. Every lattice point has the exact same basis. Many of the metallic elements form solids that are BCC and FCC. The basis in the metal lattice is typically one atom centered at each lattice point. Some structures have more than one atom or ion associated with a lattice point.

The number of atoms bonded to one particular atom is called the coordination number. These are the nearest neighbor atoms and are assumed to be "touching" each other. This is a good assumption for building models of metals and ionic compounds but is not the case for covalently bonded materials. By using x-ray diffraction data the bond lengths can be determined and the unit cell parameters calculated. The coordination number gives information about the environment around a particular atom (i.e. electron energy states and physical properties).

One property that can be calculated from knowing the arrangements of atoms in the crystal structure and the radius of the atom is the atomic packing factor (APF). The APF is the number of atoms in the unit cell multiplied by the volume of the atom and divided by the volume of the unit cell.

$$APF = \frac{V_{atoms}}{V_{cell}}$$

(1)

where V_{atoms} is the volume of the atoms in the unit cell, and V_{cell} is the volume of the unit cell.

5.1 Identifying Planes and Directions in Crystals

To understand the properties of crystalline materials, we need a common way of discussing the symmetry properties of the crystal. Since the atoms or molecules are arranged the same way throughout the crystal, we can use certain planes of atoms, which are two-dimensional slices through the crystal, to describe the crystal. Sometimes we also need to discuss certain directions through the crystal, because properties may be anisotropic, or different in different directions.

5.1.1 Identifying Crystalline Planes

Miller indices are the commonly accepted method of identifying specific planes within a crystal. To find the Miller indices, first visualize or sketch the crystal structure of interest. If the basis is a single atom, then drawing only the lattice points arranged on a coordinate axis will be sufficient.

The placement of the origin in a coordinate system is arbitrary, as long as you use the right-hand rule. To determine the indices of a specific plane, follow these steps:

1. Sketch the crystal lattice and mark the plane of interest.
2. Assign an origin and mark the x, y, and z axes.
3. If the plane either intersects all three axes, or is parallel to one or more of the axes, go on to step 5.
4. If the plane is not parallel to an axis, but does not intersect it, move the origin until step 3 is fulfilled.
5. Record the value of each coordinate intercept, in fractional form. A plane which is parallel to an axis has an intercept of infinity.
6. Take the reciprocal of the intercepts and place them in parentheses. Negative intercepts have a bar over the numeral.
7. Clear fractions by multiplying by the least common denominator.

8. A plane is thus described by the indices h, k and l, as (hkl). These are called the Miller indices of the plane.
9. In a cubic crystal, a family of planes is a set with the same three indices, in any order, and regardless of sign. Thus the group or family of planes with the indices (hkl) may be generalized and written {hkl}. Such a family will have the same measurable properties on every plane of that family.

5.1.2 Identifying Crystalline Directions

To identify a crystallographic direction, follow these steps:

1. Sketch the crystal lattice and mark the direction of interest; it should be considered a vector with a specific direction.
2. Assign an origin and mark the x, y, and z axes.
3. Move the vector (parallel to itself) so that its tail is at the origin; or move the origin.
4. Record the value of the projection of the vector onto each coordinate axis. If the vector is normal to an axis, its projection is zero.
5. Multiply through by the least common denominator and reduce to integers.
6. Place the reduced numerals in square brackets. Negative intercepts have a bar over the numeral.
7. A direction is thus described by the indices [uvw].
8. In a cubic crystal, a family of directions is a set with the same three indices, regardless of sign, and in any order. Thus the family of directions with the indices [uvw] may be generalized and written <uvw>. Such a family will have the same measurable properties in every direction of that family.

6.0 Practice Exercises

6.1 Identifying Planes

Try identifying the planes shown on the next page, then check your answers at the bottom of the page.

6.2 Identifying Crystalline Directions

Try exercises (a)-(e). Look at the direction represented by (a). The x-,y-, and z-axis projections are 1/2, 1/2, 1. We multiply by the lowest common denominator 2, then surround by square brackets, resulting in the direction named [112]. Try the other directions yourself, then compare to the answers below.

In the next exercises (f)-(h), some of the directions are negative and some do not begin at the origin of our coordinate system. For example, look at the direction represented by (f). First we need to move our origin to the corner where the tail of the vector is. Then the x-,y-, and z-axis projections are –1, 0, -1. This results in the direction named $\left[\bar{1}0\bar{1}\right]$.

Try the other directions yourself, then compare to the answers below.

(a) [112] (b) [011] (c) [121] (d) [110] (e) [201]

(f) $\left[\bar{1}0\bar{1}\right]$ (g) $\left[\bar{1}\bar{1}\bar{1}\right]$ (h) $\left[0\bar{1}1\right]$

Lab Worksheet: 1.1
Crystal Systems

Build the models for simple cubic (SC) pg. 9, Body-Centered Cubic pg. 18, and Face-Centered Cubic pg. 27 and answer questions in table below.

	Simple Cubic	**Body Centered Cubic**	**Face Centered Cubic**
# of atoms in the unit cell?			
# of lattice points in the unit cell?			
# of atoms per basis?			
Coordination Number?			
Lattice Parameter a?			
Atomic Packing Factor?			
# of atoms in the [111] direction			
# of atoms on the (110) plane?			
Which plane has the highest atom density?			

Worksheet: 1.2

Coordination Number

Using the Solid State Model Kits:

Helpful Hints:

1. The two plastic bases have marks on them, one is a yellow semicircle and the other is a green circle. These symbols match the symbols on the lettered templates.
2. If the holes on the template do not match up, turn the template 90^o.
3. If you tried hint 2 and they still don't line up try the other base.
4. Do not force the rods into the base holes. They should slide in easily.
5. Do not force the balls down the rods.
6. The color of the balls used for each model is displayed at the bottom of each page.
7. The numbers for each layer of the model correspond to the balls at the bottom of each page.
8. At the top of the page there are instructions for building each model and the template you should use.

Coordination Number (CN):

Build the models for CN 8, 6, and 4 on page 93 of the Model Kit Manual.

Build the model for CN 8 pg. 100.

Build the model for CN 4 on pg. 103.

Answer these questions about coordination numbers:

1. Which set of structures that you just built represent compounds and why?

2. What is the maximum number of nearest neighbors you can have for a structure with a single element?

Worksheet 1.3

Crystal Directions

Draw the following directions in the cubic unit cells shown below:

(a) [100] [010] [001]

(b) [111] $[1\bar{1}1]$ $[\bar{1}\bar{1}1]$

(c) [121] $[11\bar{2}]$ [211]

Worksheet 1.4

Crystal Planes

Draw the following planes in the cubic unit cells shown below:

(a) (100) (010) (001)

(b) (110) (101) (011)

(c) (121) $(2\bar{1}1)$ (321)