University of California at Santa Cruz
Jack Baskin School of Engineering

EE-145L
Properties of Materials Laboratory

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Ali Shakouri, 03/27/2002

Based on the notes by Prof. Emily Allen, San Jose State University and Prof. David Rutledge, California Institute of Technology.
1.0 Learning Objectives

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

1. Generate a potential energy curve from knowledge of the energy function of a bonded system.
2. Determine the bond energy and equilibrium bond length in a solid or molecule from a potential energy curve.
3. Distinguish simple, face-centered, and body-centered elemental cubic crystal structures.
4. Distinguish between crystal structures with an elemental basis and those with more complex bases (alloys or compounds).
5. Identify assigned planes and directions in a cubic solid using the Miller index notation.

2.0 References


3.0 Theory of Atomic Arrangements

3.1 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 which are directional and thus also very hard; metals have metallic bonds which are spherically symmetrical and thus allow easy movement of atoms, or deformation, to occur.

3.2 Metallic Bonding

In metals, the bonds are isotropic or spherical. Metallic bonding can only occur among a large aggregate of atoms, such as in 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 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 or body centered cubic structure, which provides the most dense packing of atoms, thus the highest density solids.

3.3 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 or mixed covalent and ionic. 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 $1s^22s^22p^63s^23p^2$. When the four Si atoms create tetrahedral covalent bonds, the 3s and 3p electrons from a new set of hybrid orbitals called $3sp$. Thus the electronic configuration becomes $1s^22s^22p^6(3sp)^4$. Germanium (Ge) is another covalent semiconductor, with the structure $1s^22s^22p^63s^23p^63d^{10}(4sp)^4$.

Tetrahedral bonds are highly directional and there is little probability of an electron being outside the vicinity of this bond. High temperature or other source or energy is 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.
3.4 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 become 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 deform easily in the solid state. 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 which is simply the sum of the attractive and repulsive forces. The net force between the ions is plotted as a function of $r$, the interionic distance, in Figure 1. When the attractive and repulsive force are equal, the net force is zero, and the ions are said to be at their equilibrium interionic distance. This can be considered to be the bond length in the solid $r_0$, shown in Figure 1.
It is convenient to think about the potential energy between the two ions instead of the forces. Since potential energy \((V)\) is the integral of force \((F)\) over distance:

\[
V_{\text{net}} = \int_{r_{\text{repulsive}}}^{r_{\text{attractive}}} F_{\text{net}} \, dr = \int_{r_{\text{repulsive}}}^{r_{\text{attractive}}} F_{\text{attractive}} \, dr + \int_{r_{\text{repulsive}}}^{r_{\text{attractive}}} F_{\text{repulsive}} \, dr \quad (1)
\]

\[
V_{\text{net}} = V_A + V_R
\]

The potential energy of the pair decreases as they are brought closer together. The attractive energy is considered negative, since decreasing \(r\) (the interionic distance) makes the absolute value of the potential energy larger. Thus the attractive potential can be expressed as:

\[
V_{\text{attractive}} = -\frac{A}{r} \quad (2)
\]

The repulsive energy is considered positive, since decreasing \(r\) makes the repulsive energy larger. It can be expressed as:

\[
V_{\text{repulsive}} = \frac{B}{r^m} \quad (3)
\]

where \(m\) has a value around 8 or 9. The net total potential energy can be written in the form:

\[
V_{\text{total}} = -\frac{A}{r} + \frac{B}{r^m} \quad (4)
\]

Figure 2 shows the plot of potential energy versus interionic distance; this type of energy function is known as “potential well”. The minimum in the curve occurs at \(r_0\), the bond length, and the value of the potential energy at \(r_0\) is the bond energy, \(V_0\). The deeper the “well”, the stronger the bond between the two ions. The larger the value of \(r_0\), the longer the bond length between the ions. Note by comparing Figures 1 and 2, that when the force between the ions is zero, the potential energy is a minimum (not zero).

Even though not all solids are ionically bonded, we can use this idea of a potential well to describe loosely the potential energy distribution between atoms as well as the equilibrium interatomic distance in all types of solids.
3.5 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 or motif.
The smallest group of lattice points that displays the full symmetry of the crystal structure is called the unit cell (see Fig. 1.37, p. 46 text). 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 $\alpha$, $\beta$, and $\gamma$. 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 $\alpha = \beta = \gamma = 90^\circ$. Therefore, the lattice parameter is referred to as $a$ and the angles are ignored. The three Bravais lattices associated the cubic system are simple cubic (SC-sometimes called primitive cubic), body centered cubic (BCC), and face centered cubic (FCC) (see Figs. 1.28, 1.29, pp. 40-41 text). 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 also 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 depends on the basis or motif. 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.

A quick calculation can help determine the basis.

Number of atoms in the basis = \( \frac{\text{number of atoms in the unit cell}}{\text{number of lattice points in the unit cell}} \)
This can be a trial and error process if you do not know the crystal lattice. However there are only 14 Bravais lattices and x-ray diffraction data can limit some of the choices.

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 it 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 atoms 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.

Atomic Packing Factor = (# of atoms) x (atom volume)/unit cell volume

This is the amount of space that is occupied by atoms in the unit cell. Knowing the atomic weight of the element and the crystal structure, one can calculate the density of a material. An example of how the crystal structure can affect density is by comparing Ca and Rb.

The element Ca has a FCC crystal structure and an atomic weight of 40.078. The element Rb has a BCC crystal structure and an atomic weight of 85.4678. The density of Ca is 1.4 g/cm³. The unit cell volumes for Ca and Rb are $1.72 \times 10^{-22} \text{ cm}^3$ and $1.85 \times 10^{-22} \text{ cm}^3$ respectively. The difference is that there are only 2 Rb atoms per unit cell, while there are 4 atoms per unit cell in Ca.
3.6 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.

3.6a Identifying Crystalline Planes

Miller indices are commonly accepted method of identifying specific planes within a crystal. To find 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 we 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 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 4.

4. If the plane is not parallel to an axis, but does not intersect it, move the origin until step 2 is fulfilled.

5. Record the value of each coordinate intercept, in fractional from. 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.

**3.6b 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 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.
4.0 Prelab Exercises

4.1 Identifying Planes

Try identifying the planes shown below, then check your answers with the bottom of the page.

For plane (a), notice where the plane intersects x, y, and z-axis. In case (a) it is necessary to move the origin to the front left corner. Then the intercepts are $-1$, $\infty$, and $1$.

We take the reciprocal of each intercept, resulting in the plane named: (101).
4.2 Identifying Crystalline Directions

Try the exercise (a)-(e). Look at the direction represented by (a). The x-, y-, and z-axis projections are $\frac{1}{2}$, $\frac{1}{2}$, 1. We multiply by the lowest common denominator 2, then surround 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 [101].

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

(a) [112]  (b) [011]  (c) [121]  (d) [110]  (e) [201]  
(f) [011]  (g) [111]  (h) [011]
Lab Section 1

Coordination Number

Using the Solid State Model Kits:

Helpful Hints:

1. The two plastic bases have marks on them, one is 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°.

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 bases 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.

Good Luck!

Coordination Number (CN):

Build the model 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?

3. How many nearest neighbors do an octahedral and tetrahedral atom have?
Lab Section 2a

Crystal Directions

Exercise 1

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

(A) [100] [010] [001] (all in the same unit cell)

(B) [111] [111] [111] (all in the same unit cell)

(C) [121] [112] [211] (all in the same unit cell)
Exercise 2

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

(A) (100) (010) (001)
(B) (110) (101) (011)
(C) (121) (211) (321)
# Lab Section 3

**Crystal Systems and Bravais Lattices:**

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

<table>
<thead>
<tr>
<th></th>
<th>Simple Cubic</th>
<th>Body Centered Cubic</th>
<th>Face Centered Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td># of atoms in the unit cell?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td># of lattice points in the unit cell?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td># of atoms per basis?</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Coordination Number?</td>
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<tr>
<td>Lattice Parameter a?</td>
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<tr>
<td>Atomic Packing Factor?</td>
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<tr>
<td># of atoms in the [111] direction</td>
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</tr>
<tr>
<td># of atoms on the (110) plane?</td>
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<td></td>
</tr>
<tr>
<td>Which plane has the highest atom density?</td>
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</tbody>
</table>