

LAB II CRYSTAL STRUCTURE AND CRYSTAL GROWTH

This lab will be divided into two parts. In the first part, you will be growing crystals from a seed crystal in a very visual demonstration of heterogeneous nucleation and epitaxial crystal growth from a supersaturated solution. In the second part, you will be exploring the crystal structures and atomic lattices that we have discussed in class. This lab will be completed within 2 lab periods. Be careful of your time, and make sure to complete the procedural section of Part 1 during your first lab period.

PART 1: CRYSTAL GROWTH

I. Introduction

Heterogeneous crystal nucleation and epitaxial crystal growth from supersaturated solutions are fundamental concepts that permeate all of material science. In particular heterogeneous nucleation of second phase particles is one of the primary strengthening mechanisms used in many metallic alloy systems. In addition, epitaxial growth of seed crystals is used to grow single crystals of silicon for the fabrication of semiconductors used in the electronics industry. Epitaxial crystal growth also explains the microstructure found in weld beads.

As we have learned in class, crystals are atomic lattices in which the atoms of the primary constituent are arranged in repetitive three dimensional arrays. Crystal growth is a slow and careful process since the crystals grow by adding single layers of molecules – one at a time. The crystal shape reflects the basic patterns by which the molecules are organized.

As an example – to grow a sugar crystal, you can start with a super saturated sugar solution. As water evaporates, the solubility of sugar in the water is exceeded and sugar molecules are thermodynamically driven to leave the water solution and crystallize. If there is a seed crystal present in the water, less energy is required to nucleate on this pre-existing surface than would be required to homogeneously nucleate. Therefore the sugar molecules will preferentially crystallize on the seed crystal. Following that, epitaxial crystal growth requires much less energy than either heterogeneous nucleation or homogenous nucleation. Therefore, the pre-existing crystal will continue to grow. As more water evaporates, the sugar crystal grows and grows. If the growth process is

slow enough, a single crystal will grow one layer at a time and take on an interesting geometric shape: the crystal's shape reflects the directions of "slowest growth" of the crystal.

The process of growing a single crystal can be broken down into the following steps:

- Step 1: Creating a super-saturated solution
- Step 2: Introducing a seed crystal
- Step 3: Creating conditions that allow slow growth of a single crystal

Water is a safe and abundant solvent. Anything that dissolves in water can potentially be used to create crystals. Some common materials that can be obtained at stores and pharmacies are: sugar (sugar crystals are also called "rock candy"), salt (Sodium Chloride), Alum (usually aluminum ammonium sulfate), Copper Sulfate, Rochelle Salt (Potassium Sodium Tartrate), Potassium Ferricyanide. Some of these materials are not easy to use. Some will creep up the side of the growth jar while crystals are growing, while others prefer to form clusters of crystals rather than single crystals.

Bellow, we will perform a crystal growth experiment using Copper Sulfate and Potassium Aluminum Sulfate for an extended period of time.

II. Experimental

This experiment will take 2 lab sessions, so you will need to coordinate your time appropriately.

Materials:

Two beakers	Popsicle stick (splint)
Chemical paper	Sandpaper (or emery board)
Balance	Large pan (wide open)
One Hot Plate	Graduated cylinder
Thermometer	Goggles
Water	Apron
Copper Sulfate	Wooden stirring stick for solution
Potassium Aluminum Sulfate	
Thread	

Procedure:

1. Mass out your chemicals. The experiment will require 50 grams of Copper Sulfate and 22 grams of Potassium Aluminum Sulfate. Remember to tare your balance with the chemical paper on it before adding your chemicals to remove the mass of the paper from your calculation.
2. Measure out 100 ml of water with the graduated cylinder and pour it into a beaker.
3. Add both chemicals to the water and heat the mixture until it reaches 50°C. Stir with a non-metal stick as the mixture is being heated.

4. Measure and record both the initial mass of the seed crystal and its initial dimensions.
5. Securely tie the seed crystal onto one end of a piece of thread using a slip-knot. Tie the other end of the thread to the center of your wooden splint.
6. Prepare a warm water bath by heating 150 ml of water in the second beaker to 40 degrees Celsius.
7. When the chemical/ water mixture have been heated to 50°C (step 3), take the beaker off of the heat and let the solution cool on your lab table until it reaches 40 degrees Celsius. Only then, put your seed crystal into the beaker as shown in Figure 1.

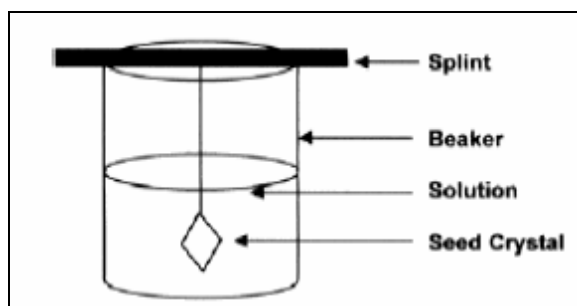


Figure 1: Schematic of seed crystal assembly

8. Pour the water for your water bath into a pan. Check to make sure that its temperature is 40 degrees Celsius or less. **MAKE SURE THAT YOUR WATER BATH IS COOLER THAN YOUR SOLUTION.**
9. Put your beaker with the solution and seed crystal into your water bath as shown in Figure 2 below:

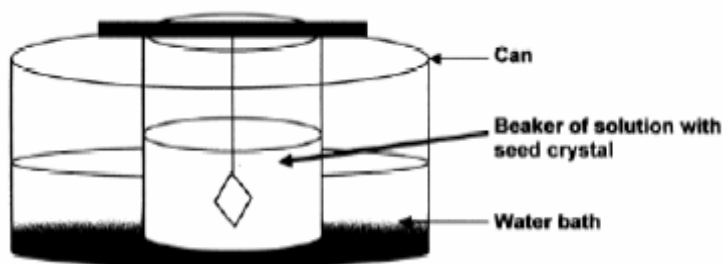


Figure 2: Schematic of seed crystal assembly and water bath

9. Crystal growth takes days, so use the following schedule:
 - On Day 1 you prepare the crystal growth assembly.

- On Day 3 (this will not be a standard lab day, so somebody from your group will have to coordinate with your lab TA to get access for the following procedure) remove the crystal from the beaker and dry it off. If there are bumps on it, file them off with your emery board (or sandpaper). Remember that the bumps will get larger but holes will fill in over time. Spill out the water bath water and put the crystal back into its solution until the next time it is checked. Measure the mass and length of your crystal.
 - On Day 6 perform the same procedure.
10. Log all the events that you observe during your recording days. Keep a chart of the date, size and mass of your crystal. Sketch the shape and size of the crystal.
 11. During the period of the second laboratory (Day 8), check your crystal. Measure its length and find its mass.
 12. On Day 8 (2nd lab period) pour out the solution and donate the seed crystals on the bottom of your beaker for future crystal growers.

Analysis:

1. Draw a graph showing how the mass of the crystal changed during time.
2. Draw a second graph showing how the size changed during time.
3. Discuss the following questions.
 - a. What problems did you have during the project? How did you solve them?
 - b. Why was the water bath needed only on the day the crystal solution was heated?
4. What is a supersaturated solution? How did the solubility of your chemicals in the water solution change as the water was heated and then cooled?
5. What is heterogenous nucleation? What is homogenous nucleation? How do the two processes differ?
6. What is epitaxial growth? Why is epitaxial growth the preferred mechanism in our experiment? What would be the alternative?
7. Under which conditions could your crystal become smaller while in the beaker of solution? Explain why each would happen and how you could "fix" each problem.
8. How would you improve what you have done in this project to produce a better crystal?

PART 2: CRYSTAL STRUCTURE

Study Questions:

1. What properties of a strongly bonded covalent solid like diamond can be attributed to its bond type?
2. Explain why covalent bonds are directional but ionic bonds are not.
3. Show the electron notation of Cu, Cu⁺¹, and Cu⁺².
4. Explain why a simple ionic crystal like CsCl cannot crystallize into a BCC structure.
5. Graphite is very anisotropic; that is, its properties are dependent on crystallographic direction. Given a cross-section of graphite, try to explain why

- the electrical conductivity of graphite is 100 times greater in the horizontal direction than in the vertical.
6. Consider an FCC unit cell with the lattice parameter 'a'. Calculate the diameter of the atoms making up this unit cell.
 7. For a cubic crystal system, how many $_110_$ directions are contained in the (111) plane?
 8. For a cubic crystal system, label the following: [100], (112), [123], and (123).
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I. Crystal Structure

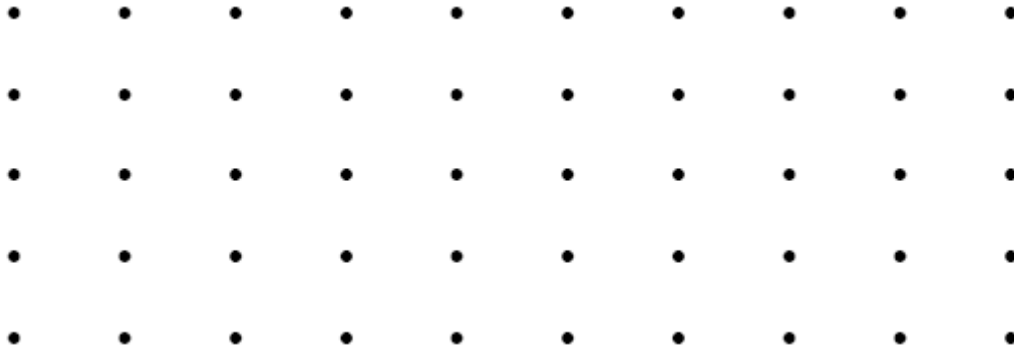
A lattice is a regular array of points repeated through space. The Bravais lattices are the 14 different unique lattices possible in 3-dimensional space. A crystal structure is a three dimensional arrangement of atoms or groups of atoms in space that can follow any of the 14 Bravais lattices. A primary unit cell is the smallest repeating unit of a crystal structure. Unit cells are parallelograms in two dimensions and parallelepipeds in three dimensions.

The size and shape of a unit cell is described, in three dimensions, by the lengths of the three edges (a, b, and c) and the angles between the edges (α , β , and γ). These quantities are referred to as the lattice parameters of the unit cell. For a cubic unit cell, $a=b=c$ and $\alpha=\beta=\gamma=90^\circ$. Note that although different materials may have the same unit cell and crystal structure, they will not have the same lattice parameters.

I.1 What would explain the difference in lattice parameters between materials with the same crystal structure (e.g., BCC)?

The selection of a unit cell is not unique; the corners of a unit cell may actually be anywhere within the space of the lattice, provided that repeated translations of this chosen cell will fill all of the space of the lattice. Conventional practice is to choose the smallest, simplest, most expressive and symmetric unit cell for the lattice.

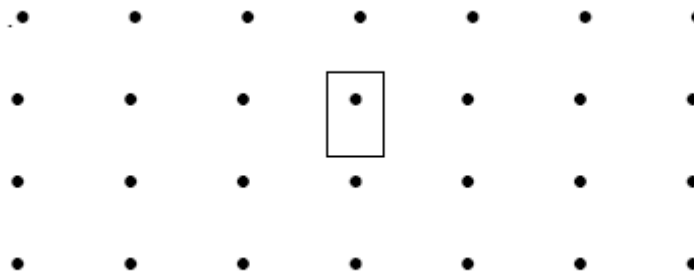
I.2 Here is a two-dimensional grid of dots. Draw 3 unique unit cells on this grid, with cell corners on dots, labeling the unit cells as A, B, and C, respectively. Next, determine each cell's lattice parameters a , b , and α (here, the smallest angle between any a and b). Finally, give the number of dots in each cell (assuming that any lines intersect the exact middle of dots, so a dot on a line will *not* be a whole dot!).



The horizontal distance between adjacent dots is 'x' and the vertical distance between adjacent dots is 'y'. Express 'a', 'b', and ' α ' (if necessary) in terms of these.

Unit Cell	a	b	α	# dots in unit cell
A				
B				
C				

I.3 Other than not having its corners on dots, would the following cell be a valid unit cell? If not, why not?



II. 2-Dimensional Packing (2D)

Use pennies to represent a two dimensional array of atoms. There are two basic configurations: square packing and close packing.

First, arrange the pennies into square packing and answer the following questions:

II.1 What is the coordination number (number of nearest neighbors or pennies touching) of one penny in this arrangement? _____

II.2 Draw the simplest unit cell (must be more than one penny!) for this packing configuration and indicate all close packed directions.

II.3 What is its value for α ? _____

II.4 Give an expression for the unit cell lattice parameter 'a' in terms of penny radius 'r'.

a =

II.5 Find the packing fraction (i.e., packing efficiency) for your unit cell: _____
(defined as area of the atoms divided by the area of the unit cell).

Now arrange the pennies into close packing and answer the following questions:

II.6 What is the coordination number (number of nearest neighbors or pennies touching) of one penny in this arrangement? _____

II.2 Draw the simplest unit cell (must be more than one penny!) for this packing configuration and indicate all close packed directions.

II.8 What is its value for α ? _____

II.9 Give an expression for the unit cell lattice parameter 'a' in terms of penny radius 'r'.

a =

II.10 Find the packing fraction (i.e., packing efficiency) for your unit cell: _____
(defined as area of the atoms divided by the area of the unit cell)

III. 3-Dimensional Packing (3-D)

The four most basic crystal structures are:

- Simple cubic (SC)
- Body centered cubic (BCC)
- Face centered cubic (FCC)
- Hexagonal close packed (HCP)

You should develop a complete understanding of the geometry and atomic arrangement of each of these structures. Make a sketch of each of these structures below.

III.1 Simple Cubic

III.2 Body Centered Cubic

III.3 Face Centered Cubic

III.4 Hexagonal Close Packed

Now construct each of these four crystal structures using Styrofoam balls and toothpicks. You should strive to completely understand the atomic packing and geometry of each of these structures. Begin by creating the individual layers, and then stack each layer together to compose the structure. To test your understanding you should discuss the similarities and differences between the structures in your team. Be sure that you can completely visualize each structure.

III.5 For each structure determine the following:

Structure	Atoms/cell	Coordination #	APF	$a = f(r)$
SC				
BCC				
FCC				
HCP				

Which two structures show the greatest similarities? _____ and _____

Consider the BCC and FCC structures you have built:

III.6 Which crystal has the largest interstitial site? _____

III.7 Does the size of the interstitial sites in each crystal type correlate with APF? (i.e., does a higher APF mean smaller interstitial sites?) _____

III.8 There are 2 different types of interstitial sites for BCC crystals. How many of each type are there? Indicate in a sketch where each is.

III.9 There are 2 different types of interstitial sites for FCC crystals. How many of each type are there? Indicate in a sketch where each is.

III.10 If material properties (tensile strength, conductivity, etc) are a function of crystal structure, will the measured properties of some materials vary with crystal orientation? How can you explain this?

IV. Ionic Structure

Although we have been examining single element crystal structures, the same principles apply to ionic structures composed of two or more elements. In this case we find the bonding to be predominately ionic, rather than metallic or covalent, which has several implications.

In your textbook, there is a discussion of coordination numbers and geometries that are dependent on the cation-anion radius ratio in the ionic compound: r_c/r_a . Stable ceramic crystal structures form when anions that surround a cation are all in direct contact with the cation, and the coordination of that cation is related to the cation-anion radius ratio.

IV.1 Given an ionic radius for Na^+ ion = 0.95\AA and for Cl^- = 1.81\AA , what is the cation to anion radius ratio for NaCl?

$$r_c/r_a =$$

IV.2 Referring to the range of radius ratios to coordination numbers (in Callister), what is the coordination number of the Na^+ ions in the NaCl structure?

$$C\# =$$

IV.3 Make a three dimensional sketch of the NaCl structure below, indicating which are the Na^+ and Cl^- ions. The ions should be roughly in scale relative to one another: that is, they should not be drawn having the same size.

IV.4 How many Na^+ ions are present within the cell? _____ How many Cl^- ions are present? _____ Is there charge neutrality within the cell? _____

IV.5 How might you explain the brittle nature of ceramics? Consider that ceramic materials are composed of two or more ionic species, while metals are not. They both form similar crystal structures, why is one so much more brittle than the other?