# Materials Science Experimental Laboratories

# MSE Faculty

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This document includes the current laboratories that have been included so far in the digitized portion of our course curriculum.

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# 1 301 Laboratories

# 1.1 Laboratory 1: Crystal Structure, Imperfections, and Diffraction

# Objective

The objectives of this lab are to gain a better understanding of crystal structures, how they are measured and/or identified and the types of defects present in crystalline materials.

# Outcomes

Upon completion of the laboratory, the student will be able to:

- 1. Distinguish FCC, BCC and HCP structures.
- 2. Understand how broadly diffraction enables qualitative identification and quantitative measurement of repeating structures.
- 3. Describe edge and screw dislocations and how they might affect material properties.

**Experimental Details** Tennis balls simulate "metal atoms" formed into different structures. A laser pointer, ruler and tape measure are used to measure spacing of a two-dimensional pattern, simulating the application of x-ray diffraction.

## **Exercise 1: Benchtop Simulation of Crystal Structures**

**A. FCC and HCP space-filling structures** Each group should have a box, several tennis balls, and small wooden balls.

- 1. Arrange the tennis balls in a single close-packed layer in the bottom of the box. Start with a line of balls parallel to the "Start here" arrows along one side of the box.
- 2. Add a second (partial) layer. Identify the three-fold symmetry (six atoms around one) in the first and second planes. Compare this to the HCP model, and you will notice that this hexagonal structure occurs in the basal (base) plane with Miller indices (0001).
- 3. Add a third plane. At this point in building your structure, you must choose between two different sites. What is the difference between picking between one site and another? Which sites correpond to which crystal structure? (FCC vs HCP)
- 4. Identify the three-fold symmetry associated with the close-packed planes in many directions. In all, there are 4 such planes, perpendicular to the 4 different cube diagonals. The Miller indices are (111), (), () and (). There is only one set of close-packed planes in HCP, (0001). What are the consequences of FCC having multiple close-packed planes and HCP having only one? Think about the class discussion of dislocations.
- 5. Identify the FCC unit cell. It isn't easy....it is easier to start with an FCC model and find the close-packed planes. They form the diagonals of the cube! That is, the family of {111} planes. (Look for the half-unit cell styrofoam ball models, which you may put together and take apart – carefully!!!)
- 6. Due to applied stress or deformation of a material, "mistakes" in stacking can occur. These "mistakes" are known as stacking faults. Create a stacking fault in the third plane of tennis balls with one side FCC and the other side HCP.

# **B.** Interstitial Sites

- 1. You will notice gaps, or interstices, between the spherical atoms. These "interstitial" sites leave room for small solute atoms, and reinforce that that atomic packing factor (APF) is less than 1.
- 2. Identify two different interstitial sites: octahedral and tetrahedral. To aid with visualization, you may take the small wooden balls ("solute atoms") and place them in the intersitial sites. What are the coordination numbers for each of these interstitial sites?

**C. Body Centered Cubic Space Filling Model** Build a BCC lattice with tennis balls. Be careful about which balls touch. How do the interstices of BCC compare to that of the close packed structures from Part A?

# Exercise 2: Diffraction (HW is the last part below)

Diffraction occurs when wavelength of the source and obstacle spacing are similar in size. The wavelength of x-rays,  $\lambda = 0.1$ -0.5 nm, is well suited to investigate atoms with d-spacings with the same order of magnitude. Constructive interference occurs when the Bragg law is satisfied:  $n\lambda = 2dsin\theta$ , where n is an integer and diffraction (3-D sample) occurs at an angle  $2\theta$  from the incident direction. The spacing between atom planes is d.



Figure 1.1: Diffraction condition

Visible light with wavelength about a thousand times larger ( $\lambda$  =0.4-0.7 µm) can be diffracted by small dots on a glass plate with a spacing similar to d. Optical diffraction of dot arrays is thus an analogy to crystal structure determination by x-ray diffraction.

Here, for a two-dimensional array,  $n\lambda = dsin\theta$ . This equation applies to the lab HW.



**Figure 1.2:** Figures from: The optical transform: Simulating diffraction experiments in introductory courses George C. Lisensky, Thomas F. Kelly, Donald R. Neu and Arthur B. Ellis J. Chem. Educ., 1991, 68 (2), p 91 DOI: 10.1021/ed068p91 Publication Date: February 1991

Two 35 mm slides are "samples" for this lab. Each slide contains eight patterns as indidated below and are designated A-H. Make sure the ICE text is on the right hand side, facing the laser, as shown below.

- 1. Discovery slide = green
- 2. Unit cell slide = black

**Warm-up exercise:** Label each of the patterns below with its location (a-h) on the slide to the right. You may check your conclusions by looking at the slide under the stereomicroscope. Don't spend too much time here- make sure you proceed to the quantitative measurements, below.



#### Lab Writeup

Due at the beginning of the next lab session.

For the lab writeup you will be using the black unit cell slide. See note about measurement accuracy, above. Record your measurements and calculations with the appropriate number of significant figures. Estimate the uncertainty in each computed value. (Assume your measurement tools are accurate, but with limited precision.)

- 1. Generate the diffraction pattern corresponding to unit cell (B) using a red laser. What wavelength is your laser? (How well do you know this value? How will you account for uncertainty? How might you measure the wavelength? )
- 2. Measure the distance between "sample" and "detector." (Note how changing this distance affects the pattern.)
- 3. Record the diffraction pattern (trace spots) on a sheet of paper, taped to the wall and use the spacing of your "detector" spots applied of the Fraunhaurfer equation to determine the spacing of dots on the slide (the spacing in the "sample"). Is this a reasonable value? Be sure to consider the number of significant figures you should report in your answer.
- 4. Repeat the process to measure the spading for unit Cell (D) based on the corresponding diffraction pattern. Again, pay careful attention to the significance of your answer.
- 5. What if you used a green laser? Qualitatively, how would the diffraction pattern (displayed on the paper) change?
- 6. What type of packing arrangement is observed for Unit Cell (H)?

#### **Models: Visualizing Defects**

Look at the models at the front of the room and identify which model represents

- (a) an edge dislocation
- (b) a screw dislocation
- (c) FCC
- (d) HCP
- (e) BCC

#### DEMO: Atomic Packing illustrated with the "Atomix Raft"

The steel ball raft is a 2-dimensional model of atomic packing. Observe the following features in the demonstration: vacancies, hexagonal-packed grains, square-packed grains, grain and twin boundaries. Similar structures can be seen in (micrographs of) copper and brass samples.

## DEMO: "Atomic Trampoline" Amorphous vs. Polycrystalline Metal

The effect of defects and micro-structure on macroscopic properties:

Stacking the tennis balls provides an example of the ordered crystalline arrays that most metals form. Is it possible for metals to have a completely disordered amorphous structure? Yes. But typically these are many-component alloys.

In this demonstration, one base is aluminum (polycrystalline FCC), the second base has a 1/8" thick disc of amorphous metal alloy (Zr0.42Ti.14Cu.12Ni.10Be.22) glued to the aluminum. As the ball bearing bounces on the aluminum base, it loses kinetic energy to friction, heat and sound generation, and the formation of crystalline defects - slip and dislocation formation. The amorphous metal plate has a highly disordered structure – it is not a regular crystalline array – and these defects do not form. Hence less energy is transferred from the ball to the base. This explains why these alloys are used in state-of-the-art golf clubs.

# 1.2 Laboratory 2: Electrical Conductivity & Optoelectronics

#### Prelab

Before lab, please READ CAREFULLY both the lab handout and Callister Chapter 18, pages 666-689 & 694-695. The relevant concepts are: Ohm's Law, the difference between resistance (R) and resistivity ( $\rho$ ), how conductivity changes with temperature in metals vs. semiconductors, bandgaps, and p-n junctions (pp. 694-695). Come in with questions.

#### Exercise 1

**Conductivity and Resistivity** In this exercise, we will determine resistance as a function of temperature for different materials. This behavior distinguishes semiconductors from metals. If the geometry of the sample is known, you may convert measured **resistance (R)** to the corresponding property, **resistivity (** $\rho$ **)**. **A. Metals** 

- 1. Measure the series resistance of your meter and leads: connect the two leads, then turn the meter to the most sensitive resistance scale, which has a maximum value of 200  $\Omega$ . (Ignore the >+, which indicates the diode test function.) Note: the meter will read 1 if R is greater than the maximum of scale chosen. In that case, turn the dial to the next higher scale.
- 2. Measure the resistance R of the steel wire at room temperature. Record R in the table below.
- 3. Measure R at 77K. With the leads attached, immerse the coil in liquid nitrogen (T = 77 K = -196 °C). Record the value in the table.
- 4. Calculate resistivity and conductivity. The wire has a length of 1 meter and a diameter of 0.203 mm. Remember to subtract the series resistance from the measured value of R!
- 5. Compare your  $\sigma$  to that for "Steel alloy A36" in Table B.9 of the text; some deviation from the "book value" is expected. Why may your result differ from the book's?

	Temperature	$R(\Omega)$	$\rho(\Omega m)$
Series resistance	RT (~298K)		
Steel Wire	RT		
	LN <sub>2</sub> (77K)		
Graphite Composite	RT		
	$LN_2(77K)$		

Table 1.1: Resistance

#### Semiconductor: Thermistor

- 1. Measure the resistance of the metal oxide thermistor at three or more temperatures between  $0^{\circ}$ C and  $\sim 80^{\circ}$ C. Use water baths to expose the thermistor to these temperatures; measure the water bath temperatures with the thermo-couple.
- 2. Plot ln(R) vs. 1/T in Kelvin; the slope = Eg/2k. Note that R  $\alpha$  1/ $\sigma$   $\alpha$  exp(Eg/2kT). What is the effective bandgap, Eg (in eV)? Hint: make sure k is in appropriate units. Typically 0.5 < Eg < 3 eV for semiconductors..

Temperature (K)		
<b>Resistance</b> $(\Omega)$		

Table 1.2: Thermistor Resistance

# B. Graphite Composite of Unknown Composite

- 1. Measure the resistance of the graphite composite pencil "lead" at room temperature. Record in the table on pg. 1.
- 2. Measure the resistance of the graphite composite cooled in liquid nitrogen. Observe what happens immediately when it is dunked into the LN2. If the clips freeze, the measurement will be inaccurate. Record in the table on pg. 1.
- 3. Calculate the resistivity of the graphite composite. The diameter of the rod is 0.7 mm. Measure the length between the leads. Does this material behave like a metal or a semiconductor?

# Exercise 2

**Optoelectronics** In this exercise, we will determine the relationship between the current (I) through and voltage across (V) a light emitting diode (LED) and a photoresistor. We will correlate the I-V behavior with light emission (LED) or absorption (photoresistor).

# A. Light Emitting Diode

A light emitting  $\overline{d}$  iode is an example of a p-n junction. It is based on a solid solution of GaP and GaAs ( $GaAs_xP_{1-x}$ ). The emission wavelength depends on the composition of this solution, as well as any dopants present.

- 1. Set up the measurement apparatus. Attach the voltmeter clips to the alligator clips on the board, so it is in parallel with the diode (p-n junction) that you will also attach there. (Note, red = +) Attach the ammeter in series, across the two bare wire connections on the bottom of the board. (Connect red to red, so you obtain the correct sign for I.)
- Forward Bias (V<sub>bias</sub> >0). Do a quick check that as you turn up the voltage (rotate the post on the potentiometer) the diode eventually emits light. Start with the ammeter on the most sensitive scale (200 μA). Take enough data points (about 10 total) to determine the I-V curve from 0V <V<sub>bias</sub> <+3V. Remember to note the units for both V/I.</li>
- 3. Reverse Bias ( $V_{bias}$  <0) Connect the circuit in reverse bias: take the black lead with the alligator clip and attach it to the opposite side of the potentiometer. Again, measure the I- V response. The magnitude should very small; be sure to use the maximum sensitivity of the ammeter. Please plot the I-V curve based on both forward and reverse bias on one graph (use graphing software). Note that the voltage where the current increases rapidly, and where the light intensity increases, corresponds (approximately) to the bandgap energy. How would the curve change for a green LED? An IR LED?

	Reverse Bias (-V,-I)				I	For	wa	rd	Bia	as (	+V	,+I	)
V				0									
Ι				0									
Light?													

# **B.** Photoresistor

This photoresistor is made of CdS, a II/VI compound intrinsic semiconductor (not doped). The bandgap  $E_g = 2.59$  eV, which means that conduction electron/holes provided by thermal energy (kT) are very rare. However, light with energy  $E(eV) = hc/\lambda = 1.24/\lambda = Eg (\lambda \le 0.48 \mu m)$  will promote valence electrons to create conduction electron/hole pairs. Visible light ranges from 0.4 to 0.7  $\mu m$ . More light will provide more charge carriers (ne = nh), and increasing conductivity  $\sigma$ . A CdS element is the heart of light meters, etc.

- 1. Measure R in the dark. Shield the resistor from ambient light with your hand or a cardboard box. Record the resistance.
- 2. Measure R in ambient light. Take photoresistor out of shadow and record the resistance.
- 3. Observe how R changes with distance from a light source. Move the photoresistor closer to the ceiling lights. What would happen if you illuminated your photoresistor with monochromatic 1µm wavelength light?

	Dark	Light
Resistance $(\Omega)$		

 Table 1.4:
 Photoresistor resistance

#### C. Light Emission vs. Composition

Light emission is possible when charge carriers (electrons and holes) recombine across the bandgap of some semiconductors. The four LED's are solid solutions of GaAs ( $E_g = 1.4\text{eV}$ ) and GaP( $E_g=2.3\text{eV}$ ). Varying the composition of the solid solution allows us to control the bandgap, and thus vary the color of emission.

- 1. Observe light emission from the four LEDs. The LEDs have differing ratios of GaAs and GaP- this ratio varies monotonically along the strip. Given what you know, which LED has the highest ratio of GaAs:GaP?
- 2. Observe the blue LED. This LED is made of a different material. Why might one have to switch to a different material to get the observed light emission? What property would need to be different?

#### Lab Writeup

One writeup per person (not per group) is due at the beginning of the next lab session. Please turn in a full set of data tables, including calculated numbers like resistivity, and answer the questions/do the tasks in italics. The questions are repeated below for your convenience.

- 1. Compare your result for the  $\sigma$  of Steel alloy A36 to that in the book. Why might your value differ?
- 2. For the Thermistor, Plot  $\ln(R)$  vs. 1/T in Kelvin; the slope = Eg/2k. Note that  $R \propto 1/\sigma \propto \exp(Eg/2kT)$ .
- 3. What is the effective bandgap, Eg (in eV)? Hint: make sure k is in appropriate units. Typically 0.5 < Eg < 3 eV for semiconductors.
- 4. Does the graphite composite behave like a metal or a semiconductor?
- 5. Plot the LED I-V curve based on both forward and reverse bias on one graph (use graphing software).
- 6. How would the curve change for a green LED? An IR LED? Note that the voltage where the current increases rapidly, and where the light intensity increases, corresponds (approximately) to the bandgap energy.
- 7. What would happen if you illuminated your photoresistor with monochromatic 1µm wavelength light?
- 8. Given what you know, which LED has the highest ratio of GaAs:GaP?
- 9. Why might one have to switch to a different material to get the observed light emission? What property would need to be different?

# **1.3 Laboratory 3: Mechanical Properties of Metals**

## Objective

The objectives of this lab are to explore how crystal structure and defects affect mechanical properties and to understand how these properties are measured.

## Outcomes

Upon completion of the laboratory, the student will be able to:

- 1. Describe the effects of work-hardening and annealing in metal samples.
- 2. Describe a ductile-to-brittle transition temperature.
- 3. Compute the elastic modulus, yield strength, ultimate tensile strength and strain at fracture from load-displacement (stress-strain) curves.

#### Experiment

Parts A and B are in Room 2068, while parts C and D are in Room 1034. Safety\*\*

**A. Work hardening and annealing in copper - Use caution with torch and hot tubing - see below.\*** You are supplied a length of copper tubing. Grasp it near one end and bend it slightly (through about 20-30°). Now bend it back to straighten the piece. You should feel considerable additional resistance to straightening. Bend and straighten the same place once again, and perhaps a third time. Resistance will continue to grow. Now bend an "original" section near the other end - notice how easy it is to deform the as-received Cu. You are feeling the effect of "work hardening" or "strain hardening". Plastic deformation is accomplished by dislocation motion. The force required to achieve plastic deformation also creates many additional dislocations that were not present initially.

Dislocations move easily through structurally regular crystals. The dislocations created during the first deformation constitute numerous irregularities, and hence make the material more resistant to further deformation, in this case the straightening step. Dislocations are high energy defects that can be removed by annealing the material at Ta ~ 0.5Tm. The melting temperature of Cu is 1360 K, so annealing effects are rapid above 680 K or 407 °C. The propane torch has a flame temperature greater than 1000 °C.

\*\*Keep the propane torch on the table at all times. Holding the Cu tubing with tongs or pliers, heat the "cold worked" region until it is red hot. Cool the entire length of copper and the pliers in water!! Now test the copper for yield force; you should be back to the original "soft" condition.

**B. Rolling of brass** As for copper above, brass is capable of significant work hardening. The purpose of this exercise is to quantify the effect of work hardening that was observed qualitatively with the copper tubing. Resistance to yield is here measured by hardness after different extents of plastic deformation by rolling.

You are provided with a set of brass samples that have been rolled to different thicknesses. For each:

- 1. Measure the thickness of the specimen.
- 2. Measure its hardness. (Use the Rockwell B scale: 1/16" ball indenter, 100 kg load)

Sample	A	B	C	D	Ε
Thickness					
%CW					
Hardness, R <sub>B</sub>					

Table	1.5:	Roll	ling	of	brass
-------	------	------	------	----	-------

**C. Charpy impact testing** Impact tests (also called Charpy tests) induce fracture under conditions of high rates (impact) at an intentional flaw (the notch). This method readily demonstrates the effect of temperature upon the fracture energy of A36 steel (carbon content of not more than 0.30 wt%) and on an Al alloy (2024, 4.4 wt. % Cu). Note: steel is a BCC metal, while Aluminum is FCC. Complete the table below.

Sample	Temperature ( $^{\circ}C$ )	Impact Energy (ft-lb)
A36 steel, RT	$25^{\circ}C$	
A36 steel, LN	-196 °C	
2024 Al, RT	25 °C	
2024 Al, LN2	-196 °C	

Table 1	6
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**D. Tensile test of an Al alloy** You will have an opportunity to observe a tensile test on a sample of an Al alloy. Notice inhomogeneous deformation (necking) before failure. The plot below indicates the tensile test results for two 2024 Al samples, one as-received and a second after heat-treatment. 2024 is an aluminum alloy containing small amounts of Cu. Both test samples had the same dimensions: width (w) = 6.35mm, thickness (t) = 1.59mm, and gauge length ( $L_o$ ) = 12.7mm.



Figure 1.3: Tensile test of an Al alloy

#### **Homework Problems**

- 1. (Part A) Copper Work Hardening
  - (a) Given the information in this handout, would you expect to be able to anneal work-hardened copper in boiling water?
  - (b) Would you expect annealing temperatures for molybdenum to be higher or lower? Why?
- 2. (Part C) Charpy Impact testing
  - (a) Why do the high and low temperature steel samples differ in appearance of the fracture region, while they appear similar for the aluminum? Note: this steel is BCC, while the aluminum is FCC.
- 3. (Part D) Tensile Testing: Convert load and displacement values from the graph to stress and strain to calculate the following. Show your work. Use engineering stress and strain (i.e. assume the cross-sectional area remains the same throughout the test).

- (a) Elastic (Young's) modulus for 2024 Al.
- (b) The 0.2% offset field strength for both the as-received sample and the annealed sample.
- (c) The ultimate tensile strength for the both the as-received sample and the annealed sample.
- (d) The amount of strain at fracture for both samples.

# 1.4 Laboratory 4: Phase Diagrams and Transformations

# I. Eutectic salt solidification

Below is part of the phase diagram for the ammonium nitrate-sodium nitrate salt solution. The diagram shows a eutectic reaction at 21wt% *NaNO*<sub>3</sub>.



Figure 1.4: NH<sub>4</sub>NO<sub>3</sub> – NaNO<sub>3</sub>

NOTE: Phase diagrams are determined assuming equilibrium and thus predict equilibrium concentrations and phases. On heating, transitions occur close to equilibrium temperatures. This is not true for cooling (nucleation).

# II. Steel rod

Many useful properties of iron and steel are determined by the crystal structure of the material, which in turn may be altered by heating and cooling. When steel is liquid, carbon dissolves readily in the iron. Even as a solid, carbon dissolves into the iron, forming a solid solution; however, the solubility of carbon in iron is limited by the crystal structure, based on the size of the interstitial sites available for carbon in the crystal structure. FCC gamma iron (austenite) can accommodate carbon at the edges of the crystal cell with little distortion. BCC alpha iron (ferrite) can accommodate carbon at the edge or face center of a cell; however the sites are smaller, and significant distortion of the crystal lattice occurs.

When slow cooled, the carbon has time to diffuse through the iron and form cementite Fe3C at dislocation sites; the steel remains ductile at room temperature.

When quenched, the carbon atoms are not given time to diffuse; they force iron atoms out of the usual places in the unit cell, resulting in a distortion of the crystal. This new structure is called martensite. It results in material that is hard–because dislocations cannot move easily through the distorted lattice, and brittle, for the same reason.

If martensite is tempered, that is, heated to a temperature below the eutectoid transformation (usually this means between  $250 - 600^{\circ}$ C), the material will remain hard, but ductility and toughness will be enhanced. (Getting this right with the torch is a bit tricky – because the temperature is not well-controlled.)

# III. Shape Memory wires (NiTi)

The wire on the table is NiTi (or NiTiNOL, named for the NiTi alloys developed at the Naval Ordinance Lab).

- 1. Start with the wire at room temperature.
- 2. Deform it gently, i.e. curl or bend it.
- 3. Warm it above the austenite transformation temperature, and observe how it recovers.

The low temperature phase (martensite) is deformable, but the alloy "remembers" its shape when it returns to the higher temperature (austenite) phase at T < 100  $^{\circ}$ C.

#### IV. Bi-Cd binary eutectic alloy

We will examine metallographic sections of different compositions in the Bi-Cd system, which exhibits a eutectic at 39.7 wt.% Cd. Note that the Bi-Cd system has negligible solid solubility. Compare this to the binary eutectic Pb-Sn system which does have solid solubility, shown in Fig.5.7 of your text.



Figure 1.5: Bi-Cd Bismuth-Cadmium

#### HOMEWORK PROBLEM

- 1. Sketch each of the three microstructures corresponding to samples A-C.
- 2. Label the composition of the alloy you were shown.
- 3. Label the phases present (indicate which phase is etched dark, which phase is etched light).
- 4. For each sample, use the lever rule to predict amounts (wt%) of primary phase vs. eutectic.

#### V. Steel wire/carburized steel samples



Figure 1.6: Microstructures of hypoeutectoid iron-carbon alloy

**Phase Transformation** When piano (~0.8% carbon steel) wire is heated (in this case by running a current through it) it transforms from BCC alpha iron to FCC gamma iron. The reverse is true on cooling. Why does the wire sag as it is cooled?



Name: \_\_\_\_\_

#### **Homework Problems**

- 1. Identify (circle) the eutectic phase transformation on the NH4NO3-NaNO3 phase diagram and indicate the temperature/composition at which it occurs.
- 2. Explain why steel quenched from high temperature which forms a martensite phase exhibits higher hardness and strength then slow cooled steel which forms a mixture of ferrite/cementite.

3.

- (a) Sketch each of the three microstructures you observed, corresponding to samples A-C.
- (b) Label the composition of the alloy you were shown.
- (c) Label the phases present, which is etched dark and which is etched light?
- (d) For each of the samples use the lever rules to predict the amounts (wt %) of the primary phase vs. the eutectic.
- (e) Are the samples hypo- or hyper eutectic?





Figure 1.9: Part C

4. When piano (~0.8% carbon steel) wire is heated (in this case by running a current through it) it transforms from BCC alpha iron to FCC gamma iron. The reverse is true on cooling. Why does the wire sag as it cools?

# 1.5 Laboratory 5: Mechanical Behavior of Ceramics and Polymers

#### Polymer 1. Crystallization of Isotatic Polypropylene

When cooled from the melt, this isomer, with R = CH3 groups all on the same side of the chain, crystallizes into spherulites. Note that crystallization occurs below Tm = 165 oC (undercooling).

#### Ceramics 1. Three-Point bend test (Bonus)

It is difficult to perform conventional tensile tests on most ceramic materials; they are brittle and break in the grips of the test apparatus. It is easier to test these materials in the bending mode, as illustrated below. Note that when loaded, the top of the material is in compression and the bottom is in tension.

 $F_{12} \xrightarrow{\text{(abraded side down)}}_{L-62 \text{ mm}} \xrightarrow{F}_{12} F_{12} \xrightarrow{\text{(abraded side down)}}_{b-}$ 

Figure 1.10: Three-point bend test

A. Measure the force F (weight of volume of water plus container) to fracture a pristine glass microscope slide.

B. Abrade a second microscope slide with 180 grit ( $a = 80 \mu m$ ) paper. Abrasion should be in center of slide, and in the "b" direction (above). BE SURE YOUR HANDS AND SLIDE ARE DRY. Measure fracture force for slide with flaw dimension a; flaw on bottom (tensile side).

C. If time permits, repeat part b with abraded side up (under compression). This should be close to your answer in part a.

D. Glassblowers often use the trick of scribing a mark, then wetting it, to get the glass to break there. If you notice the maximum load is less when the abraded region of the slide is wet, you have observed stress corrosion cracking. The Si-O-Si network in the glass is broken by formation of Si-O-H bonds at the surface, and the material effectively "unzips."

Container weight = 118 g (Add to obtain total load)	Vol (ml)	Total load (g)
A. Pristine slide: vol. (ml)		
B. Flawed slide: vol. (ml)		
C. Compression: vol. (ml)		
D. Repeat b, but WET abraded region		



## Lab Homework

- 1. Calculate fracture force for experiments A and B.
- 2. Use equation 12.3a in Callister (see addendum) to calculate the "flexural strength" obtained with this three point bend experiment. Sample dimensions are d = 1 mm, b = 25 mm, and L = 62 mm between support points. Your answer should be in MPa, and you will need to convert Ff from g to N.
- 3. Use your result from experiment B and the following equation to calculate  $K_{IC}$  for the microscope glass material:  $K_{IC} = Y \sigma_f \sqrt{\pi a}$ , where a is the flaw size (= 80 $\mu$ ) and Y, dependent on sample & flaw geometry = 1. Compare your  $K_{IC}$  to the range predicted for ceramic materials in Table 8.1.
- 4. Use your *K*<sub>*IC*</sub> and the result from experiment A to calculate flaw size *a* in the pristine glass slide (the slide you did not intentionally scratch).

#### **Ceramics 2. Softening glass**

Hold the glass rod in the flame of the propane torch. When the rod becomes hot enough, that is when the temperature exceeds the "glass transition temperature,"  $T_g$ , the glass will flow and you can easily bend it. **BE CAREFUL NOT TO BURN YOUR FINGERS. Don't touch the HOT glass.** 

## **Polymers 2: Nylon Polymerization**

Nylon is formed by the reaction of two liquid monomers, here dissolved in immiscible liquids. These can react with each other, but not with themselves:

0.5 M hexamethylenediamine  $H_2N - (CH_2)_6 - NH_2$  in 0.5 M NaOH 0.2 M sebacoyl chloride  $Cl - C - (CH_2) - C - Cl$  in hexane

The reaction occurs in a thin layer at the interface between the two liquids. By slowly pulling the film in this region, a long, continuous filament can be pulled from the beaker. NOTE THE BYPRODUCT IS HCl – so use gloves.

#### Polymers 3. Plastic Deformation of Polyethylene

- 1. With thumbs separated by about 0.5 cm, stretch the strip with a slow, steady force. The polyethylene will yield and deform plastically. Here the sliding of planes of atoms (crystals) is accompanied by uncoiling sections of the chain-like polymer molecules (amorphous regions).
- 2. You will notice that a thin portion or "neck" is formed and propagates during stretching. The plastically deformed polymer is anisotropic with different properties in different directions. With many chains or portions of chains in the stretch direction, this chain orientation means that covalent bonds are deformed or break when the film is further loaded in the stretch direction. Relatively weak van der Waals bonds control properties in the transverse directions.
- 3. Grasp a section of the necked polymer and pull in the stretch direction. The oriented film is stiff and strong (no easy yield or failure) in this direction.
- 4. Now grasp the same necked portion in the transverse direction and pull slowly. The materials will yield and "split", as weak secondary bonds are dominant in this direction.



Figure 1.11: Necked polymer

Conclusion: You can "feel" the difference between strong covalent and weak van der Waals bonds when the chains are oriented.

#### Polymers 4. Plastic Deformation of Polyethylene

You are all familiar with "high density" (fc = 0.7) and "low density" (fc = 0.4) polyethylene. As PE at room temperature is a crystal/rubber combination, the elastic modulus of HDPE is larger. As there are more crystals, the yield strength  $\sigma_y$  of HDPE is larger as well.

- With increased yield strength (more crystallinity) comes reduced ductility.
- Somewhat similar to BCC metals, the yield strength of polymers is temperature dependent.
- 1. Test with your fingers the two flexure samples. Which is high density polyethylene? Which is low density polyethylene?
- 2. Cool the tensile samples in liquid nitrogen and repeat. A substantial change in ductility (and likewise an increase in yield stress) will be noticed.

## Polymers 5. Rubber nails (Glass Transition Temperature (a))

Cool a rubber "nail" by holding in liquid nitrogen (with tongs!!). The material is now a glass. Use the glassy nail to join two pieces of (soft) balsa wood. Hints: grasp the nail with the tongs; align the nail with the grain of the wood; use repeated soft taps to avoid shattering your "nail." Have everyone in your group contribute a nail.

## Polymers 6. Rubber band (Glass Transition Temperature (b))

At room temperature, rubber is above its glass transition temperatures  $T_g = -70^{\circ}C$ , but at liquid nitrogen temperature, rubber is below  $T_g$ .

A stretched rubber band is cooled with liquid nitrogen. The shape is conserved as the macro-molecules are "frozen in", and the band is very brittle. As the temperature increases back toward room temperature and  $T_g$  is reached, the band recovers its natural undeformed shape.

## Polymers 7. Happy/ Sad balls (Glass Transition Temperature (c))

Two polymer balls of different compositions are provided, along with hot water and LN2. DO NOT try to FREEZE the balls completely in LN2. Cool them gently, while moving around in a small amount of liquid, for 10-20 seconds. Otherwise, the balls will fracture.

- 1. Drop both balls onto a table at room temperature. Ball 1 is above its Tg and thus bounces back elastically (rubber elasticity). Ball 2 is near its  $T_g$  and dissipates all the kinetic energy without bouncing.
- 2. Heat Ball 2 and repeat the experiment. The ball is now above its  $T_g$  and bounces back elastically (rubber elasticity)
- 3. Cool Ball 2 and repeat the experiment. The ball is now below its  $T_g$  and bounces elastically (glass elasticity).
- 4. Cool Ball 1 and repeat the experiment. The ball will be glass elastic below  $T_g$ , "dead" near  $T_g$  and rubber elastic above  $T_g$ . Very cool!

What practical items are made from such rubbery elastomers? Rubber o-rings, used to seal surfaces – except when they get cold, below  $T_g$ , they become stiff and don't conform – hence resulting in leaks. (The Challenger Disaster was a consequence.)

**E. Viscoelasticity (Stain rate dependence)** Silly Putty is a polymer above its glass transition temperature which is thus viscoelastic at room temp. At high strain rates, it behaves elastically, while at low strain-rates, it is viscous.

#### **Ceramics Demonstrations**

**III. Thermal Shock** If you have ever poured hot water into a cold glass, or vice versa, you may have experienced the effect of the material's low resistance to thermal shock. ( $TSR = \sigma_c k/E\alpha_1$ ). This, in turn, is due to the large thermal expansion coefficient and low thermal conductivity typical of most ceramic materials. These properties may be varied by changing the composition of the glass, as indicated below. (Of course, the cost changes, too.)

	Comp. (wt%)		Thermal expansion	Thermal Shock
GlassSoda-lime		$\begin{array}{c c} \hline & Thermal \\ \hline \hline 70\% SiO_2 \\ \hline 10\% CaO \\ \hline 15\% Na_2O \\ \hline 80\% SiO_2 \\ \hline 15\% B_2O_3 \\ \hline \end{array}$	coefficient (linear),	Resistance
(win-	70% SiO <sub>2</sub>		<i>u</i> <sub>1</sub> ( <i>K</i> )	
dows,bottles)Borosi (Pyrex)	llicate 10% CaO		$8.5 \times 10^{-6}$	84
	15% Na <sub>2</sub> O			
	80% SiO <sub>2</sub>		$4.0  imes 10^{-6}$	280
	$15\% B_2O_3$			
	5% Na <sub>2</sub> O			

Table 1.8: Thermal properties of glass

**IV. Toughening plates** As you will see in the laboratory exercise, ceramics have a high probability of fracturing when a tensile force is applied. This is due to the crack propagation through the material. One way to strengthen ceramics, then, is to introduce compressive forces in the outer portion of the piece, where cracks are likely to initiate. The compressive forces act to close surface cracks, rather than cause them to propagate. An example is tempered glass, which is formed by quickly cooling from above its glass transition temperature: the outside cools faster than the inside, and is put into compression by contraction of the slower cooling core. This technique is used in making car windshields.

A second method for producing ceramics with an outer layer in compression is to use layered materials. In this case, the outside layer has a lower thermal expansion coefficient than the inside, and again is put into compression as the piece forms.

**V. Tough ceramic ball** The material is  $Zr_2/CaO$  "alloy." At room temperature it contains ~10% of nonequilibrium tetragonal phase in a matrix of equilibrium monoclinic phase. Large local tensile stress near a crack tip triggers a tet $\rightarrow$  mono transition with a 4% volume increase. The larger volume of new monoclinic crystals creates compressive stress that "pinches" the crack shut.  $K_{IC}$  is increased to about 10 MPa  $m^{1/2}$ .

**VI. Other Ceramics** Ceramics are refractrory, That is, they maintain structural integrity at high temperature, and may provide thermal and electrical insulation. Some are used as capacitors or resistors on computer motherboards. Some are piezoelectric, that is they may be used to transform mechanical energy into a voltage. Others are magnetic (Hard B  $BaFe_{12}O_{19}$ ,  $SrFe_{12}O_{19}$ , used for small electric motor field magnets, Refrigerator door seals and posting magnets; Soft B  $NiFe_2O_4$ ,  $MnFe_2O_4$ , transformers, inductors) or superconducting.

#### Addendum:

For a sample with a rectangular cross-section tested on a three-point bend apparatus, the tensile breaking stress, termed the flexural strength,  $\sigma_{fs}$ , is:

$$\sigma_{fs} = \frac{3F_bL}{2bd^2}$$

Here Fb is the load at break, L is the distance between supports, b is the width and d is the thickness of the rectangular cross-section.<sup>1</sup>

1. Callister, William D. Jr. Materials Science and Engineering: An Introduction, 6th Edition, ISBN 0-471-13576-3, John Wiley and Sons, Inc., New York, 2003.

# 1.6 Discovery Lab 1: Cholesteryl Ester Liquid Crystals

## Pre-lab

Important: Be sure that you are wearing long pants and closed -toed shoes for this lab. Lab coats, safety glasses, and gloves will be provided.

**Goal** To investigate the relationship between temperature, composition, and reflected/trans-mitted colors of a cholesteryl ester liquid crystal.

**Background** Liquid crystals are organic compounds that are in a state between liquid and solid forms. They are viscous, jelly-like materials that resemble liquids in certain respects (viscosity) and crystals in other properties (light scattering and reflection). Liquid crystals must be geometrically highly anisotropic, as opposed to an isotropic liquid. Such properties, however, can be altered through thermal action (heat) or by the influence of a solvent.

Common liquid crystals are composed of derivatives of cholesterol, C27H46O. Materials that will be used in this lab for making the cholesteryl ester liquid crystals are cholesteryl benzoate, C34H50O2, cholesteryl pelargonate, C36H62O2, and cholesteryl oleyl carbonate, C46H80O3.

Cholesteric-phase liquid crystals contain molecules aligned in layers rotated with respect to one another, resembling helix structures (Figure 1.12). The distance between layers that have the same orientation is known as the pitch, p. At high temperature, the rotation angle from one layer to the next increases, hence the pitch is smaller. A color will be reflected when the pitch is approximately equal to the color's wavelength of light.



Figure 1.12: Cholesteric-phase liquid crystals (Figure courtesy of George Lindsey)

## **Pre-lab Questions**

- 1. What are the safety concerns with each of the chemicals? What is the proper way to handle the chemical waste? Please read the Materials Safety Data Sheets (MSDS) for each chemical used in this lab beforehand.
- 2. Liquid crystals have anisotropic structures. In your own words, explain the term "anisotropy" and how will this affect the material properties of liquid crystals.
- 3. If the reflected color is green and changes to red, chemically/physically explain what has happened to the liquid crystal. Be specific. Does this correspond to a temperature increase or decrease? Why?

# Lab Part 1

**Objective** Build a cholesteryl ester liquid crystals thermometer that covers the temperature range between 17-40°C.

# Laboratory Procedure

- 1. Based on Table 1, select 5 ratio combinations of the cholesteryl oleyl carbonate, the cholesteryl pelargonate, and the cholesteryl benzoate.
- 2. Measure out the alloted amounts of each of the cholesterol components and place them in a 10 ml vial.
- 3. Melt the solid in a smaple vial using a hair drier or heat gun. (Make sure the vial lid is off during the melting process because it can ruin the seal on the vial.)
- 4. Cut one piece of clear packing tape and lay the sticky side up on a table.
- 5. Take the vial of teh cholesteryl ester mixture, open it and transfer a small amount of the gel paste to the tape with a spatula. Spread the gel uniformly in the middle of the tape. Be sure to leave a centimeter clearance from the edge of the tape. Take the other piece of packing tape and place the sticky sides together. Smooth the paste evenly so there are no air bubbles.
- 6. Submerge the liquid crystal sandwich in a beaker of water and gently heat the water with a hot plate.
- 7. Measure and record the temperature at which the liquid crystals first change color. What color do you see first?
- 8. Measure and record the temperature at which the liquid crystals become colorless. What color do you see last?
- 9. Cool the sample by removing it from the water. Repeat steps 2-3 as necessary to list the order of colors observed.

Cholesteryl oleyl carbonate	Cholesteryl pelargonate	Cholesteryl benzoate	Transition range, $^{\circ}C$
0.65 g	0.25 g	0.10 g	
0.70 g	0.10 g	0.20 g	
0.45 g	0.45 g	0.10 g	
0.43 g	0.47 g	0.10 g	
0.44 g	0.46 g	0.10 g	
0.42 g	0.48 g	0.10 g	
0.40 g	0.50 g	0.10 g	
0.38 g	0.52 g	0.10 g	
0.36 g	0.54 g	0.10 g	
0.34 g	0.56 g	0.10 g	
0.32 g	0.58 g	0.10 g	
0.30 g	0.60 g	0.10 g	

**Table 1.9:** Cholesteryl liquid crystal mixtures and their transition temperatures. Different compositions give different color patterns over different temperature ranges.

# Lab Writeup

- 1. Upon heating, when the liquid crystal sandwich undergoes a color change, what color do you see first (i.e., at coolest temperature)? What color do you see last (warmest)? What is the order of colors you see going from coolest to warmest? Explain what happens to the liquid crystal during this transition at molecular level.
- 2. What is the relationship between the mass of cholesteryl oleyl carbonate in the mixture and the transition temperature? What do you think might be the reason for this?
- 3. As the liquid crystal changes temperature it reflects different colors. Is the color change better observed over a black background or a white background? Why?
- 4. What are some of the applications you can think of with the temperature sensitive cholesteryl ester liquid crystals?
- 5. What happens if you heat 0.30 g of Cholesteryl oleyl carbonate, Cholesteryl pelargonate, Cholesteryl benzoate by themselves, will you observe the same behavior?

# References

- 1. Lisensky, G (2007). Preparation of cholesteryl ester liquid crystals. Interdisciplinary Education Group, Retrieved May 26, 2008.
- 2. Lisensky, G, & Boatman, E (2005). Colors in liquid crystals. Journal of Chemical Education, 82, 1360A, Retrieved June 4, 2008.

#### Lab Part 2

Liquid crystal display (http://www.microscopyu.com/articles/polarized/polarizedlightintro.html)

One of the most common and practical applications of polarization is the liquid crystal display (LCD) used in numerous devices including wristwatches, computer screens, timers, clocks, and a host of others. These display systems are based upon the interaction of rod-like liquid crystalline molecules with an electric field and polarized light waves. The liquid crystalline phase exists in a ground state that is termed cholesteric, in which the molecules are oriented in layers, and each successive layer is slightly twisted to form a spiral pattern (Figure 1.13). When polarized light waves interact with the liquid crystalline phase the wave is "twisted" by an angle of approximately 90 degrees with respect to the incident wave. The exact magnitude of this angle is a function of the helical pitch of the cholesteric liquid crystalline phase, which is dependent upon the chemical composition of the molecules (it can be fine-tuned by small changes to the molecular structure).



Figure 1.13: Liquid crystal display

An excellent example of the basic application of liquid crystals to display devices can be found in the seven- segment liquid crystal numerical display (illustrated in Figure 1.13). Here, the liquid crystalline phase is sandwiched between two glass plates that have electrodes attached, similar to those depicted in the illustration. In Figure 2, the glass plates are configured with seven black electrodes that can be individually charged (these electrodes are transparent to light in real devices). Light passing through polarizer 1 is polarized in the vertical direction and, when no current is applied to the electrodes, the liquid crystalline phase induces a 90 degree "twist" of the light that enables it to pass through polarizer 2, which is polarized horizontally and is oriented perpendicular to polarizer 1. This light can then form one of the seven segments on the display.

When current is applied to the electrodes, the liquid crystalline phase aligns with the current and loses the cholesteric spiral pattern. Light passing through a charged electrode is not twisted and is blocked by polarizer 2. By coordinating the voltage on the seven positive and negative electrodes, the display is capable of rendering the numbers 0 through 9. In this example the upper right and lower left electrodes are charged and block light passing through them, allowing formation of the number "2" by the display device (seen reversed in the figure).

Procedure Liquid Crystal Transition Temperature Measurement by Optical Characterization

- 1. Heat the liquid crystal mixtures prepared in last lab
- 2. Prepare sample slides for the 5 compositions of liquid crystals (LC) prepared in Lab 1
  - (a) It will be helpful if you heat up your slide so that the LC mixture is still liquid when you carefully put a coverslip on top of it
  - (b) While placing coverslip try to avoid trapping as many bubble as possible in your sample
- 3. TA/instructor will provide instructions on how to operate the optical microscope and record your data
  - (a) The polarized light microscope is designed to observe and photograph specimens that are visible primarily due to their optically anisotropic character. In order to accomplish this task, the microscope must be equipped with both a polarizer, positioned in the light path somewhere before the specimen, and an analyzer (a second polarizer; see Figure 1.14), placed in the optical pathway between the objective rear aperture and the observation tubes or camera port. It is a contrast-enhancing technique exploits the optical properties specific to

anisotropy and reveals detailed information concerning the structure and composition of materials that are invaluable for identification and diagnostic purposes.

- (b) The liquid crystalline phase exists in a ground state that is termed cholesteric where the molecules are oriented in layers where each successive layer is slightly twisted to form a spiral pattern. When polarized light waves interact with the liquid crystalline phase the wave is "twisted" by an angle of approximately 90 degrees with respect to the incident wave. This angle is a function of the helical pitch of the cholesteric liquid crystalline phase, which is dependent upon the chemical composition of the molecules (it can be fine-tuned by small changes to the molecules).
- (c) References: Useful resources are the Nikon web page describing polarized light microscopy and the Olympus page on polarization of light.



Figure 1.14: Polarized light microscope

You will generate movies of transitions observed in the liquid crystals with changing temperatures. For the report please record observations of transition in structures from the different samples.

# 2 315 Labs

#### 315 lab schedule WQ2020

Week of Jan 13<sup>th</sup> – Worksheet #1 (temp measurements) due at beginning of lab; in-lab, measure BiSn cooling curves and mount samples.

Week of Jan. 20<sup>th</sup> – Worksheet #2 (thermocalc free-energy) due at beginning of lab; in-lab, polish, etch, examine mounted samples.

Week of Jan. 30<sup>th</sup> – Lab #1 due. In-lab, complete microscopy/ stereology on BiSn samples

Week of Feb. 7<sup>th</sup> - Worksheet #3 (ternarys) due.

Week of Feb. 14<sup>th</sup> – Lab #2 due. In-lab, mount and polish carburized steel samples.

Week of Feb. 21<sup>st</sup> – Worksheet #4 (carburization) due. Hardness profiles and microscopy of polished samples. Work on Worksheet #5 (DICTRA) in lab.

Week of Feb. 29<sup>th</sup> – Worksheet #5 due. In-lab, complete hardness testing and microscopy.

Week of Mar. 3<sup>rd</sup> – Lab#3 due. In-lab quiz/ practicum.

## Metlab (MATCI facility) Safety Guidelines

#### THINK FIRST!

Be alert. Act cautiously. Don't rush. Ask.

## Use Proper Equipment:

Safety glasses or goggles are mandatory.

**Hoods** should be used when handling chemicals. Use them properly. Use the sash for shielding; keep the sash open only the minimal amount.

Gloves must be used when handling chemicals.

- Latex- OK for sample preparation, light etching (nital, methanol or ethanol). NOT OK for strong acids or anything containing HF.
- Nitrile gloves more chemically resistant than latex. But thin gloves offer limited protection.
- Silver Shield gloves recommended for HF.

**Heat resistant gloves** should be used when handling hot samples or working with furnaces (room 2028).

**Tools** – Use the right one for the job.

**Clothing** – Lab coats are available in the lab. Use them. Note: open-toed shoes and shorts do not provide adequate protection against spills. Dress appropriately (pants, closed-toe shoes) for lab.

# Use Common Sense

Do not eat in the laboratory.

Use caution: hot items might not look hot; be careful what you touch; use PPE. Use proper techniques: properly mounted samples, wheels and pads will avoid finger/ hand injuries during grinding or polishing.

Sharp blades should be moved in a direction away from body parts.

Ask - check with the lab instructor or manager if you have questions.

# *Be Considerate*

Clean up incidental spills immediately to avoid further contamination. Dispose of cleaning materials properly – not in the general waste.

Notify lab manager (or Research Safety) immediately about large spills.

Dispose of chemicals properly. There are separate solvent, acid, base waste containers. There are also separate waste containers for HF based solns. & nital. Dispose of sharps properly. There are separate containers provided for broken glass and metal sharps.

Do NOT dispose of chemicals down the drain.

Do NOT leave unlabelled chemicals in the hood or elsewhere in the lab. Label containers with chemical names, quantities, date, your name.

Do NOT track chemicals from etching hood to microscope (or elsewhere).

Remove gloves before using scopes or other equipment outside the etching area. Do NOT add other solvents to the nital container (see below).

# Metlab particulars

- Consult MSDS sheets, available on the reference table in 2008.
- DO NOT bring chemicals into the lab without discussing details with lab manager. You must provide an MSDS sheet with your proposed use.
- Nitric acid. Strong oxidizer. Do NOT mix with organics or solvents. The only exception to this is nital: 2% nitric acid in methanol. Do not exceed this concentration. Do not use another solvent. Dispose of separately from acid or solvent waste.
- HF consult lab manager prior to use. Latex gloves are not sufficient. Do not store in glass. Make sure calcium gluconate is available before use.
- Please notify the lab manager of any accidents, spills, equipment malfunctions.

Be aware of the j	following h	hazards, and u	se appropriate	e equipmen	t and steps to	avoid
problems:						

Activity	Location	Safety issues	Safety equipment provided
Heat treatment	2028	Burns (carelessness). Dust from	Heat-resistant gloves, tongs,
		refractory materials. Proper use	refractory bricks. Face shields.
		of gas tanks on tube furnaces	
		(see below).	
Gas Cylinders	2028	High pressure venting.	Dual stage regulators to be used on
(with furnaces)			each tank when in use.
			Tank caps must in place for any
			transport. Tank belts must be used
			to secure tanks in lab.
Sawing	2086	Disposal of residual scarf and	All saws in the lab are enclosed.
		cutting fluids/ coolants.	Disposal containers are provided.
Mounting	2086	Noxious smell, acrylic irritant.	Use of hood for acrylic or epoxy
			mounting
Grinding/	2084	Spinning wheels.	Safety glasses.
polishing		Clogged drains and overflow	Мор
		sometimes leads to wet floor.	Proper sample/wheel/pad
		Concern about materials in	mounting. Caution when using
		drain. Eye protection for	spinning/motorized equipment:
		samples and debris off wheels.	keep hands free of wheels.
Polishing	2084	Same as grinding	Same as grinding
Chemical	2084	Improper mixing of chemicals	Goggles and safety glasses, face
Etching		and solvents.	shields. Rubber aprons. Gloves
			(rubber, latex, nitrile and silver
		Spills.	shield). Labeled waste containers
			are provided in hood.
		Transport of chemicals outside	Undergraduate students should ask
		of hood. (Remove gloves before	for help mixing etchants.
		using other equipment	Calcium gluconate is provided.
		(microscopes, etc.) and before	Cautions against mixing particular
		exiting lab.	chemicals are highlighted.
			Additional reference material is
			provided in 2008.
			Spill trays are provided.
			Spill kits are supplied in lab.

NAME:\_\_

## MATSCI 315: Phase Equilibria and Diffusion in Materials Laboratory Instructor: Dr. Kathleen Stair, Cook 2039, <u>kstair@northwestern.edu</u> Lab Worsheet#1: Binary Alloy Phase Diagrams

DUE at the beginning of lab week of Jan 9th. Please write neatly.

In the first lab of 315, we'll experimentally determine the phase diagram for a binary alloy (BiSn) and then look at the corresponding microstructure. To measure temperature in the range of room temperature to ~ 300 degrees Celsius, we'll use thermocouples.

Before coming to lab, please answer the following questions (you may include sketches) and bring these to lab:

1) What is a thermocouple?

2) How does it work? (What is actually measured?)

3) What type of thermocouple would you choose for the measurements we will make? Why? (What are your design criteria?)

4) Name and describe at least two other methods of measuring temperature, excluding thermometers.

#### 2 315 LABS

#### NAME:

# Lab Worksheet#2: BiSn Alloys – phase diagram generation from free energy curves in Thermocalc – do this on your own. Due at the beginning of lab week of January 16<sup>th</sup>.

# Thermocalc (TCW5) is found on the computers in Bodeen (Tech C115).

Instructions to generate free energy curves to plot Bi-Sn phase diagram:

Open Thermo-Calc for Windows (TCW5)

Click on the icon for a binary phase diagram (center of the top tab) – this opens the "TCW Binary Phase Diagram "window.

Within the new window, select Bi and Sn

Choose Phase Diagram. This will display the binary phase diagram – note that you may redefine the axes. **Choose weight percent Bi to be consistent with the experimental plot you will generate.** 

NOW – the question is – how was this generated? (A review of 314!)

Click on G-curves

Enter a temperature (in Kelvin); begin at a temperature above 573K

Click on Apply. This will generate a series of free energy curves at that temperature.

Note: you can normalize to 1 mole or 1 gram; to find wt% choose the latter.

Generate enough free energy curves to map out the BiSn phase diagram on the blank sheet. You are also provided with some hardcopies. Show your work on these - draw in how your determined compositions corresponding to transitions at any given temperature.

Summary Instructions:

Use the set of free energy curves that follow to draw the Bi-Sn phase diagram into the empty graph, above. First, draw vertical lines indicating phase boundaries on the free energy curves. Then draw the

corresponding isotherm and add the range of phases to the phase diagram.

Use Thermocalc to access additional free energy curves. Label phases.





THERMO-CALC (2008.01.22:11.38) :BI SN Temperature: 570 K DATABASE:BIN

THERMO-CALC (2008.01.22:11.40) :BI SN Temperature: 470 K DATABASE:BIN





THERMO-CALC (2008.01.22:11.41) :BI SN Temperature: 420 K DATABASE:BIN

THERMO-CALC (2008.01.25:09.28) :BI SN Temperature: 400 K DATABASE:BIN





THERMO-CALC (2008.01.22:11.42) :BI SN Temperature: 370 K DATABASE:BIN

#### MATSCI 315: Phase Equilibria and Diffusion in Materials Laboratory Instructor: Dr. Kathleen Stair, Cook 2039, <u>kstair@northwestern.edu</u> Lab#1: Binary Alloy Phase Diagrams

REMINDER: Laboratory Notebook: You should be prepared to take notes in a notebook (not on loose paper) during lab. Keep notes and lab handouts in order. You will need to refer to these when writing your lab reports.

Lab 1 Objectives:

To understand the experimental generation of phase diagrams. To understand the relationship between phase diagrams and free energy curves. To measure, analyze and interpret data.

There are three parts to Lab1:

Lab Worksheet #1 – pre-lab on temperature measurement. Due at beginning of lab week of January 9.

Lab Worksheet #2 - Generating a BiSn phase diagram using free energy curves in Thermocalc. Outside of class – generate the phase diagram using TCW5 found on computers in the Bodeen lab.Tech C115. (Start in lab, if time permits.) Due in lab week of Jan.  $18^{\rm h}$ .

Lab1 – In lab exercise week of Jan. 9<sup>th</sup>: generate a BiSn phase diagram from experimental cooling curves. Individual write-up based on pooled class data. Due at the beginning of lab, week of Jan. 23.

## Lab #1: BiSn Alloys – phase diagram generation from Cooling Curves

**Checking calibration:** We will be using type K thermocouples and data-logging devices to measure temperature in the range of 100-300°C as a function of time for Bi, Sn and a series of binary alloys of BiSn. The change in the rate of change in temperature as a function of time indicates changes in phases, as described by the Gibbs Phase Rule (also see <a href="http://www.doitpoms.ac.uk/tlplib/phase-diagrams/cooling.php">http://www.doitpoms.ac.uk/tlplib/phase-diagrams/cooling.php</a>) How accurate and precise is your measurement device? Think about how you might check this and anticipate that you will discuss this in your report.

## Part i: Endpoints

Start by measuring a cooling curve of either Bi or Sn. Plan to pool group data.

- Use the Easy-Log program to setup a data-logger.
  - Use a ring-stand and clamp to secure a data-logger and thermocouple near your hotplate. You don't want the data logger too close to the heat; you do want the thermocouple to "spring-load" into the melt. Make sure the thermocouple leads are not touching anywhere along the length, except at the join.
  - Heat the crucible on a hotplate until the endpoint metal has melted. (This might not be obvious if there is an oxide on the surface. You can remove surface oxides by skimming the melt with a stirring rod.)
  - Make sure the thermocouple is in the melt and double-check that it is not shorted along its length.
  - Turn off the power to the hotplate and use the data-logger to record temperature down to ~ 100°C. Re-heat your sample, again measuring temperature vs. time to remove your thermocouple.

- Download your data to a common group folder using the EasyLog software. You may save the curves in Excel for export. Use a logically formatted filename for easy identification, .eg. Sn\_Mon3\_KS or 40Bi\_Thurs1\_KS
- Determine the transition temperatures and record these.

## Part ii: Alloys

Repeat the procedure, above, for an alloy. These are designated by wt% Bi. Determine the changes in slope that correspond to phase transitions. Record these on the pooled data sheets.

## Lab 1 Write-up

- 1) Write a short paragraph describing the theory behind cooling curve measurements. Include relevant equation(s).
- 2) Write a second short paragraph describing what was measured and how and include some mention of measurement uncertainty.
- 3) Using a plotting program (Excel or Matlab...or other) plot your endpoint (Bi or Sn) and alloy cooling curves. Indicate what phases are present in what temperature ranges by labeling the two curves with phase and temperature information.
- 4) Use the tabulated data, as well as the posted raw data, to determine all phase transition temperatures that can be determined for alloys in the Bi-Sn system. Again, using a plotting program, plot these transition temperatures as a function of wt% Bismuth, to determine the phase diagram. You will need to decide which points form a set corresponding to the same phase transition, i.e. a given liquidus line, for instance. Add appropriate fit(s), label phases, label axes, etc....in order to generate a neat, complete, self-explanatory phase diagram.
- 5) Write a paragraph discussing the results. Also discuss what assumptions were made and how your plot does/doesn't agree with theory and other experimentally-determined Bi-Sn phase diagrams. (Be especially aware of what assumptions you make in compositional ranges where no measurements were made.) You will find a calculated Bi-Sn plot at: http://www.metallurgy.nist.gov/phase/solder/bisn.html. Note that the temperature and composition that correspond to the invariant reaction (that is the eutectic temperature and composition) are listed in a table below this figure.

## **Notes on graphing:**

i) You are gathering discrete *data points*, hence plot the data as such. (In Excel, choose a scatter-plot, without additional lines.) When you *fit the data* (i.e. by adding a trendline) use a *line*. Always consider your options: which points should you include or not include when fitting a given line? Should you let the program find the best regressive fit? Or should you fix the slope? Is the fit linear? Non-linear? Can you use data to determine all the liquidus, solidus and solvus lines in the system? Are there any you cannot determine? (You could indicate an approximation as dashed lines.) The details should be discussed in paragraph II of your text.

ii) Represent data with the appropriate number of significant figures. If you are averaging 321 °C, 323 °C, 324 °C the average value is 323 °C. (Do not add false significance when computing an average value.) If there is uncertainty in determination of a transition temperature, it is OK to indicate this as a range. Likewise, if you have
several data points for a single value, i.e. the melting temperatures of the endpoints, then you could plot *all* the points, or plot the average but indicate the range which was measured. Assuming a normal (Gaussian) distribution of these values, you can find the uncertainty of the mean to within a 95% confidence level by determining *2X the standard error of the mean*: 2x the standard deviation (STDEV in Exel) divided by the square root of the number of points measured. Indicate these values on your plots by adding error bars: left click the data set and choose Format data series > Y error bars.

iii) Label axes appropriately AND label all phases present in different regimes.

#### MSc 750-315: Applications of Thermodynamics Worksheet #3 - Ternary diagrams using Thermo-Calc

You will find the TCW5 program and the NIST\_solder database installed on the computers in the Bodeen lab (Tech C115). You can login using your netid and password – though you may need to change your password.

#### For the Bi-Sn-Pb system:

Part 1, draw isotherms/ label temps on the liquidus projection. Label invariant points. Part 2, apply the lever rule on the isotherm at 423 K to determine quantities and compositions of phases at that temperature for two specific alloy compositions.

Open TCW5; click on the ternary phase diagram icon (upper right). Choose Database: User. Find TDB NIST\_solder.TBD file Choose Bi Sn Pb Choose liquidus projection or isothermal section (in this case, choose a temperature). Note that you can redefine the axes.

On the liquidus projection below, use the isothermal sections to draw in the isotherms – labeling temperatures. Label all (binary and ternary) invariant points.







**Tie lines.** - Use the lever rule to determine the following (show work on figure, above).

150°C (423K): 80wt% Bi, 5wt% Pb: How much liquid? Composition of liquid? How much solid? Composition of solid? 150°C (423K): 70wt% Bi, 15wt% Pb: How much liquid? Composition of liquid? How much solid? Composition of solid?

### 315 Lab #2 BiSn alloys: Metallographic preparation and microstructural examination

Recall that we determined the phase diagram of Bi-Sn using cooling curves. In this lab we will examine microstructures of the alloys. Part of the learning objective is to become familiar with metallographic preparation procedures and use of the optical microscope, as well as correlating microstructure to the phase diagram. Read through all steps before starting.

- 1. **Put on safety glasses.** Choose a sectioned sample of Bi-Sn; make sure each group (every subgroup of 2-3) in the lab section selects a different composition. Record the composition. Each of these samples contains saw-cut damage. Your objective is to reveal the true microstructure of the sample by removing this damage, as well as sequentially removing damage from the initial grinding steps.
- 2. The samples will be mounted in acrylic using 1 <sup>1</sup>/<sub>4</sub>" diameter molds. Make a label for your sample (composition, your initials) that will fit in the mold, under the surface of the acrylic, before it hardens. A small piece of paper stuck just under the surface will suffice.
- 3. Gloves are located in the two drawers to the left of the hood in 2084. Set the side of the sample to be examined face down in a Sampl Kup (blue) mold. Measure two parts acrylic powder into a small paper cup. Add one part acrylic resin. Mix (or more appropriately, "fold" to avoid mixing in too many air bubbles) the powder and liquid (it should have a consistency of honey or syrup), then pour the mixture over the sample in a Sampl Kup. Add a label to the back of your mount before the acrylic solidifies. The acrylic will harden in about 15 minutes.
- 4. Round the sharp edge of the sample by rotating the edge on a piece of grit paper. This helps keep the samples from "grabbing" the paper or cloths on the autopolisher. Use the autopolisher to sequentially grind with SiC grit (~ 1-2 minutes for each size), then polish diamond suspension. (Note that this is slightly modified from the recommended "universal" autopolishing sequence; the diamond suspensions tend to become embedded in the soft metals you are polishing, and the surfaces become gummy and discolored when using the normally-recommended 0.05 micron alumina final step. Also you can use lower force 4 or 5 lbs and shorter times than are recommended for harder materials.) It is critical that you wash and ultrasonically clean the samples between each polishing step (but not each grinding step) to avoid contaminating the polishing pad with larger sized grit or sample debris.
- 5. Before looking at samples on the light microscope, make sure they are clean and DRY. Use ethanol as a final rinse, and then dry the samples under the hand dryer. Please be careful. Moisture or solvents will ruin the objective lenses. Set the samples face down on a piece of paper to make sure water does not seep from between the sample and mount. Microscope instructions are attached.
- 6. Use the autopolisher to sequentially grind and polish the samples to a final grit size of 1 micron diamond.
- 7. Etch (using the assigned etchant) to reveal microstructure. The etchant for this lab is 5% HCl in methanol, by volume prepared by your TA or lab instructor. Make sure you are wearing your safety glasses and add gloves rubber gloves or latex gloves are OK before working with the etchant. The etchant should remain in the hood. (You should remain entirely outside the hood.) You are etching until you rinse the sample. Use tongs to dip the sample in the etchant for ~ 5 seconds; rinse; examine the surface by eye. It will become slightly cloudy as etching occurs.
- 8. Record images that are representative of your sample, to be included in your lab report. Be sure to mark each micrograph with a micron bar.
- 9. Share images of all the final polished, etched samples between all members of your lab group.
- 10. Analyze the volume fraction of the different phases present using a point grid. Note: you could measure the relative amount of each phase or the relative amount of primary phase vs. eutectic (remember, the eutectic is a two-phase micro-constituent). Make a careful note of what you measured and why.

## Lab#2: WRITE\_UP: Due beginning of lab week of Feb 6<sup>th</sup> – groups of two or three.

### Metallographic preparation and microstructure of BiSn alloys

This (short memo-style) report will be a truncated version of a formal lab report. The intent is to document your sample preparation and relate the final microstructures to the phase diagram.

## Title, authors

**Methods and Materials:** Describe your samples and how you prepared them. Include any images that show the progression of grinding, polishing, etching steps. Include details about grit size, diamond suspension size, loads, etchant and etching times. Label images as figure 1, etc. and include captions. Note that figure captions are placed below a figure. (The convention for tables is that the title is above the table.)

**Results & Discussion:** (Begin this section with text.) Discuss the alloys that were prepared by your group. Show corresponding images. Include figure numbers and captions and *label the phases present*. Include a discussion of the volume fraction analysis and conversion to weight percent and how it agrees (or doesn't) with the known composition of your alloy.

# Using Stereology to measure Volume Fraction (for more details, see ASTM E562 – 83)

Often, when viewing cross-section of metallography (or ceramic, etc) samples under a microscope, it is desirable to make quantitative measurements of such values as the grain size and volume fraction of particular phases.

The latter is easily accomplished using point-counting techniques. In this case, a test grid is superimposed upon the image of the sample and the number of points falling within the microstructural constituent of interest is counted. This, divided by the total number of points in the grid, provide an estimate of the volume fraction of the constituent of interest.

$$V_V = P(alpha)/P_T$$

# Size of grid/ Number of Measurements

The size of the test gird is typically 4x4 or 5x5 points. In order to lower the uncertainty in the measurements, one should count approximately 100 points *on the constituent of interest*, P (alpha). This means overlaying the grid many times, on different areas of the sample. Often, an eyepiece reticle is used to facilitate this counting.

# Magnification

The magnification should be high enough to avoid adjacent grid points falling on the same microconstituent feature. Choose a magnification giving an average constituent size of  $\sim \frac{1}{2}$  the grid spacing.

# Counting

Count and record the number of points on the microconstituent in each application of the grid. Count points falling on a boundary between constituents as  $\frac{1}{2}$ .

# Uncertainty in measurement

You can easily determine the standard deviation, standard error of the mean and confidence levels by tabulating all the values measured. In theory, the value of the coefficient of variation (the standard deviation / mean) is:

$$\frac{\sigma(V_v)}{V_v} = \sqrt{\frac{1 - V_v}{P_a}}$$

Comparison to mass fraction

Note that the volume fraction and mass fraction are not equivalent, but one may convert from one to the other using the densities of the respective phases (see Callister, chapter 9):

$$W_{\alpha} = \frac{V_{\alpha}\rho_{\alpha}}{V_{\alpha}\rho_{\alpha} + V_{\beta}\rho_{\beta}}$$

# Materials Science and Engineering Dept. 315 - Phase Equilibria and Diffusion Worksheet #4 Diffusion of Carbon into 1018 steel using pack-carburization

# These are questions to answer during lab and after – and include in your final report. These answers will be due in the beginning of lab, week of Feb. 13th

- 1. What equations (solutions to the diffusion equations) describe diffusion from a plane source, i.e. carburization? That is, equations that describe the concentration profile (concentration vs. distance) as a function of time, temperature and diffusivity?
- 2. Re-write these equations to describe the change in hardness. What assumptions are made in our experiment?
- 3. <u>Briefly</u> describe the following hardness measurements:

Rockwell

Vickers

Knoop.

4. What are the units for Vickers and Knoop testing? Assuming a ductile material, hardness  $\sim 3$  x yield strength. What units will you use for the comparison between hardness and yield strength? Explain the conversion.

5. You will be experimentally determining the diffusivity of carbon in steel at 940 and 960°C, the temperatures at which class samples were prepared. Find some comparison values or an equation you can solve – that is values from the literature to which you will be able to compare your results:

## Dictra – Carburization simulation (www.thermocalc.com)

#### 1 Introduction

DICTRA is a general software package for simulation of DIffusion Controlled TRAnsformations in multicomponent alloys. The DICTRA software is based on a numerical solution of the multicomponent diffusion equations. DICTRA is interfaced with Thermo-Calc, which handles all necessary thermodynamic calculations. The diffusion simulations are based on assessed kinetic and thermodynamic data, which have been stored in databases. Up to 10 components may be treated simultaneously in a simulation, provided that the necessary kinetic and thermodynamic data is available.

In the development of DICTRA, emphasis has been placed on linking fundamental methods to critically assessed thermodynamic and kinetic data, allowing simulations to be performed with realistic conditions on alloys of practical importance. The simulations are one-dimensional and three different geometries, cylindrical, spherical and planar can be used. This is sufficient to model many cases of interest. The cylindrical geometry can e.g. be used both for modelling of diffusion in a tube wall as well as the dissolution of a rod-shaped precipitate.

#### 2.1 Applications

The DICTRA software has been applied to several problems of scientific and practical interest such as:

- · Solidification and microsegregation in steels
- · Gradient sintering of cemented carbides
- Coarsening of '-precipitates in nickel base alloys
- Carburization and decarburization of steels
- Carburization of High-Temperature alloys
- · Nitriding and Nitrocarburizing of steels
- Austenite/ferrite diffusional transformations in steels
- Generate input for construction of TTT- and CCT-diagrams
- Interdiffusion in coating/substrate compounds
- · Growth of pearlite in alloyed steels

In a DICTRA simulation, the multicomponent diffusion equations:

$$\mathbf{J}_{k} = -\sum_{j=1}^{n-1} \widetilde{\mathbf{D}}_{kj}^{n} \frac{\partial \mathbf{c}_{j}}{\partial \mathbf{z}}$$

are solved, using a complete, (n-1)x(n-1) temperature and concentration dependent diffusivity matrix  $\vec{D}_{kj}^n$ . The diffusivity matrix is calculated from parameters stored in a mobility database and a thermodynamic database. The thermodynamic databases are the same as used by Thermo-Calc.

The mobility databases are created through an assessment procedure similar to the one for thermodynamic databases. Experimental data are collected and selected from the literature. Parameters in the mobility models are optimised to give the best possible description of the experimental data. The optimised parameters are then stored in a mobility database.

DICTRA contains a module for optimisation of mobility data, PARROT. This module enables the user to expand existing databases as well as creating own databases. Demonstration examples and documentation for this is available in the DICTRA User's Guide and Calculation Examples.

Using the mobility databases it is possible to calculate e.g. tracer-, self-, intrinsic- and interdiffusivities. The diffusivities are normally temperature and concentration dependent as shown below.



Logarithm of the interdiffusion coefficient ( $\vec{D}$ ) in the FCC-phase of the Ni-Al system as a function of x<sub>Al</sub> for different temperatures (1273,1323,1373,1423,1473,1523and 1573K). Solid lines are calculated using DICTRA and the symbols are experimental measurements.





# Materials Science and Engineering Dept. 315 - Phase Equilibria and Diffusion Diffusion of Carbon into 1018 steel using pack-carburization

Samples of 1018 steel were packed in a mixture of 85wt% activated charcoal and 15wt% calcium carbonate in steel bags. Samples were subsequently pack-carburized for three times at three temperatures (915°C, 940°C and 960°C). Each lab group will examine three samples from a single carburization temperature.

**Part I:** Mount the samples in thermo-setting resin and label. Grind (320, 400, 600, 800 girt SiC) then polish with  $3\mu$  and  $1\mu$  diamond suspension on a microcloth pad. Briefly (1-3 seconds) etch with nital (2% nitric acid in methanol). You might swab the etchant on the surface with a cotton-tipped swab. Rinse with water, then with solvent; dry. Examine the microstructure across the sample. Gather images that you can relate to the change in composition from center-to-edge of the samples.

**Part II:** Measure a hardness profile from edge toward the center of the sample. (Note that this might work best on an unetched sample. If you have already etched, return to the 1 micron diamond wheel to remove the etched layer from the surface.) Use the Struers semi-automated microhardness tester to measure Vickers hardness from the carburized surface toward the center of the specimen in increments of ~50-100 microns for the first ~2 mm, then ~200 microns until the values clearly plateau. Use the 10X objective to focus; use the 40X objective to measure the indent. Rotating between objectives and indenter is best done using the automated program (Duramin5). To avoid interference between indentations, spacing should be about 3x the indent size -- but zig-zagging is allowed. You want to obtain 10-20 points to define your hardness profile. In addition, you should measure ~ 10 points near the center (undiffused region of the sample) to determine what uncertainty is associated with the measurement on these samples, independent of the change in hardness.

# Write-up (groups of 2 or 3):

**Introduction** – brief background on pack-carburization of steel and literature values of the diffusivities which you will solve for experimentally.

**Methods** – how did you prepare and characterize samples? Well-written and concise, with enough detail to repeat the experiments.

**Results** - Your results will include micrographs with appropriate captions that describe the effect of carburization on the steel microstructure. You will need images from both the center and the edge of your sample(s). Label phases/ microconstituents, add micron bars, etc. on these. Estimate the carbon content at the surface, and explain your rationale.

**Results, cont'd** - Your results will also include experimental hardness profiles along with a fit from which you estimate the diffusivity of carbon in steel. The experimental data should be represented as points; the fit should be represented as a smooth curve. (Note that this curve will NOT be a polynomial; you know the functionality based on the solutions to planar diffusion -see in-lab handout from week 1 of this lab. USE THESE, *NOT* a polynomial, which will give a very poor fit. ERF and ERFC functions are available in Excel and Matlab.

**Discussion** – place your results in the context of literature values and those determined from the Dictra plots. Clearly state any assumptions you made in your analysis. (Use the DICTRA solutions (in-lab handout week 2 of this lab) as a starting point to determine D and also for

comparison. Also include values of D based on other sources (Porter & Easterling, Callister, etc.). Show the comparison graphically.)

**Conclusions** – provide a summary of the main points/ values determined in the lab, how well they matched expected values and some assessment about the agreement or lack thereof.

# **Quick Microhardness Instructions: Vickers (Knoop)**

Turn on microhardness tester (rear) and restart computer.

Insert specimen into holder.

VERY IMPORTANT: THE SAMPLE MUST BE FLUSH WITH THE TOP OF THE HOLDER. Note that the tip clearance is very small. IF the sample is at all recessed, when you focus you will be below the tip clearance level. If the tip runs into the sample holder this is a VERY COSTLY and TIME-CONSUMING repair. (The equipment must be shipped back to Struers for repair.)

Inspect with 10X objective to focus and find the test area. Also, focus the eyepeice. Set the load to 300gm. (Note on load selection -- you want a large enough indent to measure accurately; but use a load that does not cause excessive damage to your sample, such as deformation or cracking at the indent tips.)

Vickers is chosen, and the processor load is set to 300gm; objective to 40X

Select "indent." Do NOT move the indentor with the start button illuminated. Note that for a Vickers test the indent should be an equiaxed pyramid.

Change to the 40X objective.

You may use (or over-ride as necessary) the Automeasure feature.

Make sure you record both hardness and distance from the edge of the sample.

NOTE: Use the Struers semi-automated microhardness tester to measure Vickers hardness from the carburized surface toward the center of the specimen in increments of  $\sim$ 50-100 microns for the first  $\sim$ 2 mm, then  $\sim$ 200 microns until the values clearly plateau. Use the 10X objective to focus; use the 40X objective to measure the indent. Rotating between objectives and indenter is best done using the automated program (Duramin5). To avoid interference between indentations, spacing should be about 3x the indent size -- but zig-zagging is allowed. You want to obtain 10-20 points to define your hardness profile. In addition, you should measure  $\sim$  10 points near the center (undiffused region of the sample) to determine what uncertainty is associated with the measurement on these samples, independent of the change in hardness.

# 3 316-1 Labs

# 3.1 Laboratory 1: Diffusion in Substitutional Cu-Ni Alloys

## Objectives

- To observe diffusion in a Cu-Ni diffusion couple.
- To determine if these observations are consistent with a composition-dependent interdiffusion coefficient, expected for diffusion in substitutional alloys.
- To begin to model the diffusion process using MATLAB.

## Introduction

In the case of pack-carburization, we were able to make the assumption that diffusivity of carbon in iron was independent of composition. For substitutional alloys, this is not the case. The interdiffusion coefficient in this case is composition dependent and related to the intrinsic diffusion coefficients as follows:

$$\tilde{D} = X_a D_b + X_b D_a$$

In addition, in situations where  $D_a$  and  $D_b$  differ from one another, there will be a net vacancy flux in the material, giving rise to the motion of an inert set of markers that can be observed experimentally.

## Samples

Samples have been prepared using two techniques:

- 1. electroplating of nickel layers onto copper, and
- 2. welding Ni-Cu sandwich layers.

In both cases, Mo wires were placed at the interface, to mark the position of the original interface; however in the case of the electroplated samples, these wires sometimes shifted away from the surface during plating. After electroplating/ welding, the samples were sealed in evacuated quartz tubes to prevent oxidation, and annealed at 1000°C for 4, 16, and 72 hours.

**Laboratory Procedure** Refer to the class notes in addition to the paper describing the background and history of the Kirkendall effect [?]. Look at the Cu-Ni samples (annealed at 4, 16 and 72 hours at 1000 °C) under the optical microscope. Note that there are two types of sample: 1) copper strips wound with Mo wire which were nickel-electroplated and 2) a welded "sandwich" of nickel with outer copper layers and rolled molybdenum "marker wires" at the interface. Note that in (1) the Mo was not secured to the copper strip well-enough to mark the original interface (this will be obvious in your observations). In (2) you will find enough pairs of wires that are nearly across from each other to measure the distance between markers as a function of time at elevated temperature. (Unfortunately, the weld broke on the unannealed (time = 0) samples; but you should be able to assess the three remaining samples quantitatively or at least semi-quantitatively. Include these measurements with your other observations, as well as a discussion of what you expected. Discuss whether or not your observations and measurements are consistent with the Kirkendall effect. In future exercises we will be comparing these diffusion profiles to what we would expect from published values of the relevant diffusion coefficients. For now document your in-class observations, including well labeled sketches and micrographs.

# 3.2 Laboratory 2: Recovery, Recrystallization and Grain Growth in Cold Worked 70/30 Brass

### Objectives

To observe the phenomena of recovery, recrystallization and grain growth. To understand the effect of processing on microstructure, specifically the effect of amount of cold-work on recrystallization and final grain size. To understand the time dependence of grain growth. To understand the predictions of the Hall-Petch relationship.

### **General Procedure: Week 1**

You will be provided with brass (70%Cu, 30% Zn) that has been heated to  $700^{\circ}$  C for six hours, from the as-received state and then rolled to reductions of ~ 15% and ~ 30%, as well as some brass that has not yet been rolled. Your groups will cold-roll samples to similar reductions for the next group. The specified amount of cold-work will be introduced using the rolling mill.

- 1. Measure the thickness and the Rockwell hardness of your as-received and rolled samples. Choose an appropriate Rockwell scale over which you can anticipate measuring your sample after it is rolled then subsequently annealed. Always check to make sure the load and indenter size correspond to the correct scale. Use a standard to check the tester.
- 2. As a group, roll two samples, using the rolling mill, one to a reduction of ~ 30-40%, a second to a lesser reduction, e.g. 15-20%. Anticipate the target thickness before you begin rolling. Calculate target thicknesses for each reduction, assuming width does not change with rolling. Percent reduction (or percent coldwork) is defined as:

$$%CW = \frac{A_0 - A_d}{A_d} \times 100$$
(3.1)

which may be re-written for this lab:

$$%CW = \frac{t_0 - t_d}{t_d} \times 100$$
(3.2)

where  $t_0$  is the starting thickness and  $t_d$  is the final thickness. Set aside for the next group.

- 1. Re-measure hardness after rolling. (Make sure to measure a flat region. The sample should not deflect when the indenter is applied.)
- 2. Section the rolled samples into about 8 pieces (~ 1cm long). Note that we will be interested in observing the transverse sections, defined in the figure below. Set aside a time = 0 sample; each of the other 1 cm long "coupons" will be annealed at a specified time at the temperature assigned to your group



- 3. Record the temperature assigned to your group. T=\_\_\_ degrees C.
- 4. samples that have been annealed from 2 minutes, 8 minutes, 32 minutes....up to a week. You will be measuring and recording Rockwell hardness on each of these samples, then mounting them for polishing and etching.
- 5. After reserving the time = 0 sample, place the remaining samples in the furnace assigned to your lab group. (All samples of both reductions, except t=0, should be annealed at the SAME TEMPERATURE

\*\*\*Suggest (the entire group's) annealing conditions by reviewing information available in the Metals Handbook, and by discussion with your lab mates & instructor. You want to achieve conditions under which you will observe partial to total recrystallization. Consider how you will need to vary the conditions to test the Johnson-Avrami-Mehl equation.

## **General Procedure: Week 2**

- 1. Make sure you have measured the Rockwell hardness of each annealed sample. Note that you should try to take all your hardness readings on the same scale.
- 2. Mount transverse cross-sections of each of the annealed samples, along with an unannealed piece in an acrylic mount for polishing. Follow the instructions for the auto-polisher. Wash your sample carefully and ultrasonic between each step to avoid contaminating the wheels. (These are soft samples; it will be difficult to remove the scratches that are introduced by such contamination!)
- 3. Etch to reveal grains. (Be careful; the different reductions and different temperatures of annealing may result in different etch rates.) Record a photomicrograph of each sample at an appropriate magnification.
- 4. From your micrographs, calculate the volume fraction of recrystallized material, and the grain size of samples that are completely recrystallized.
- 5. Measure the Vickers hardness of each sample (three indents, minimum, on each sample.)

## In-Lab Questions DUE at the Beginning of Week 2:

Rolling, hardness testing and cutting will take some time. If you are waiting you may use time in lab to answer the following. Make sure you define all terms and cite sources:

- 1. What equation describes the rate of grain growth?
- 2. Refer to Chapter 3 of Shewmon and summarize the "Engineering Laws of Recrystallization" relevant to this experiment. (You may summarize all then determine which you might be able to test vs. not able to test.)
- 3. What equation describes the volume fraction of material recrystallized with time?
- 4. How can the rate of recrystallization at a given temperature be determined?
- 5. What is the Hall-Petch equation? Discuss the equation and any limitations.

#### Final Deliverable - Group PowerPoint Presentation

Your presentation will be judged on content, delivery (presentation style), neatness, completeness. You must submit a hardcopy of your presentation slides. Imagine you are presenting this to Prof. Voorhees and other MSE students who were not in lab; they are familiar with terms like grain size and hardness, but do not know the details of your sample preparation and what you are testing (i.e. which of the Engineering laws of Recrystallization you were able to test.) Length: 12 minutes. Each group member must participate.

Due: one week after completing in-class measurements.

- 1. Refer to Chapter 3 of Shewmon; discuss whether or not the class data substantiates the "Engineering Laws of Recrystallization," i.e. how do hardness, grain size, volume fraction of recrystallized material vary with the amount of cold-rolling, and time of anneal? Plot hardness (Rockwell is OK, here) as a function of annealing time for both reductions, including time = 0 values. Explain changes in hardness by comparison with micrographs.
- 2. Estimate the recrystallization rate for your group's annealing temperature: Rate = 1/(time for volume fraction transformed = 0.5).

Note: We will try to use the information from different groups to compare recrystallization as a function of temperature. If you have enough points (this is unlikely), you may be able to fit the Avrami (JMAK) equation:

$$y (fraction recrystallized) = 1 - \exp(-kt^n)$$
(3.3)

- 3. Make sure you use actual not target reductions when discussing your results. Double-check that the reduction is, for example, 40%, not 70%.
- 4. For samples in which complete recrystallization was observed does the Hall-Petch relationship hold? Assume that hardness is proportional to yield strength (see next page). The Hall Petch equation states that the yield stress,  $\sigma_y$ , is increases linearly with  $d^{-1/2}$ , where *d* is the average grain size:

$$\sigma_y = \sigma_0 + \frac{k_y}{d^{1/2}} \tag{3.4}$$

where  $\sigma_0$  and  $k_y$  are constants for a given material. Note that you do not have to confine comparisons to a single recrystallization; use all the samples available that have recrystallized. (It tends not to be valid for very large or very small grains.)

5. For completely recrystallized samples, is normal grain growth observed? Measure grain sizes for recrystallized material at a given reduction and determine the exponent for grain growth as a function of annealing time at a given temperature:

$$d^n - d_0^n = Kt \tag{3.5}$$

Solve to see if *n* is greater than or equal to 2, as expected. Note that at the start of recrystallization, the grain size is infinitesimally small.

#### Heyn Procedure for counting lineal intercept length:[?]

- 1. Estimate the average grain size by counting, on a micrograph, screen or the specimen itself, the number of grains intercepted by one or more straight lines sufficiently long to yield at least 50 intercepts. Select the magnification such that this can be done in a single field.
- 2. Make counts on 3-5 blindly selected, widely separated fields.
- 3. Use a factor of 1.5 to determine the average grain size from the lineal intercept length.

#### Hall–Petch determination:

- 1. Measure Vickers hardness.
- 2. Use hardness and grain size to determine if the Hall-Petch relationship holds true for your data. (Plot HV vs.  $1/\sqrt{d}$ )
- 3. You can use Vickers hardness to calculate the Yield strength of brass. Assume 1/3 of the applied load in a Vickers Hardness test plastically deforms the sample and use the appropriate conversion factor (*CF*) to convert to MPa:

$$\sigma_y = \frac{HV \,(\mathrm{kg}/\mathrm{mm}^3)}{3} \times CF$$

Q – Are your values of yield strength within a reasonable range? Compare to typical values (Metals Handbook)

**Empirical relationship between Rockwell B and Vickers hardness (kg/mm<sup>2</sup>).** Note that it is best to measure the Vickers hardness directly. The following relationship between the Vickers hardness (HV) and Rockwell B hardness ( $R_b$ ) is obtained from ASTM Standard E140 (table 4, Conversion data for Cartridge brass), Annual Book of ASTM Standards, volume 3.01, 1989:

$$HV = 0.002R_h^3 - 0.0092R_h^2 + 0.8163R_b + 52.865$$
(3.6)

# 3.3 Laboratory 3: Surface Energy and Contact Angles

# Objectives

- To understand what aspects of liquid behavior are determined by surface and interfacial energies.
- To understand how contact angles are used to characterize material surfaces.

#### Introduction

The properties of solid surfaces are often probed by measuring the ability of liquids to spread over the surface of a material. The relevant property is the contact angle,  $\theta$ , illustrated in Figure 3.1a. If the droplet is small enough so that it is not affected by gravity, the radius of curvature, R, of the droplet is uniform, and shape of the droplet is a spherical cap, *i.e.*, the portion of a sphere that exists above a specified plane. The relationship between the droplet height, h, the basal radius of the droplet, r, and the contact angle in this situation is as follows:

$$\tan\left(\frac{\theta}{2}\right) = h/r \tag{3.7}$$

At equilibrium, a horizontal force balance at the periphery of the object gives the following expression for the equilibrium contact angle,  $\theta_e$  and the relevant surface and interfacial energies (Figure 3.1b):

$$\gamma_s = \gamma_{s\ell} + \gamma_\ell \cos \theta_e \tag{3.8}$$



**Figure 3.1:** a) Geometric parameters characterizing the shape of a small liquid droplet on a solid surface. The b) Force equilibrium illustrating the origins of Eq. 3.8.

It is often useful to rewrite Eq. 3.8 in terms of the thermodynamic work of adhesion,  $W_{adh}$ , which describes the energy required to remove the liquid from the solid surface, replacing the solid/liquid interface with a liquid/air interface and a air/solid interface (see Figure 3.2):

$$W_{adh} = \gamma_s + \gamma_\ell - \gamma_{s\ell} \tag{3.9}$$

Here  $\gamma_s$  is the solid surface free energy,  $\gamma_\ell$  is the liquid surface free energy and  $\gamma_{s\ell}$  is the solid/liquid interfacial free energy. Note that for liquids, the surface tension and the surface free energy are identical to one another, so we refer to  $\gamma_\ell$  as either the liquid surface tension or surface free energy.



**Figure 3.2:** Separation of a liquid and a solid, illustrating the meaning of the work of adhesion,  $W_{adh}$ , as the change in total free energy of the system when a solid/liquid interface is replaced by a liquid/air and air/solid interfaces.

Combination of Eqs. 3.8 and 3.9 gives the following:

$$W_{adh} = \gamma_{\ell} \left( 1 + \cos \theta_e \right) \tag{3.10}$$

Equation 3.10 indicates that we can know the quantitative interaction between the liquid and the solid if we are able to measure the liquid surface energy,  $\gamma_{\ell}$  and the equilibrium contact angle,  $\theta_e$ . This purpose of this lab is to measure both of these quantities in some model systems and to show how these quantities can be easily modified. Before we do that, we need to talk about two important issues:

- The actual contact angle you will measure is almost certainly not going to be the equilibrium contact angle.
- Liquid surface energies are often measured by understanding the effect of gravity on a relatively small drop.

**Non-equilibrium effects:** In reality, the situation is more complicated than is implied by Eq. 3.8, and the contact angles you will measure depend on a whole bunch of factors, in addition to the surface and interfacial energies. Factors like surface roughness and surface inhomogeneities on the nanometer scale cause the measured contact angles differ from the  $\theta_e$ , and to depend on the details of the way the experiment is done. When a droplet is originally applied to the materials surface and the droplet volume is increasing with time, the contact angle is referred to an advancing contact angle,  $\theta_a$ . The receding contact angle,  $\theta_r$ , corresponds to the opposite situation, where the droplet size is shrinking. The advancing contact angle is larger than  $\theta_e$  and the receding contact angle will be less than  $\theta_e$ :

$$\theta_r < \theta_e < \theta_a \tag{3.11}$$

Generally you'll want to report both advancing and receding angles in your work. The difference between  $\theta_a$  and  $\theta_r$  is an important parameter referred to as the contact angle hysteresis, and controls the tendency of droplets to stick to an inclined surface.

The Effect of Gravity and the Measurement of  $\gamma_{\ell}$ : We know from experience that Eq. 3.7 can't work for very large droplets. Eventually, gravity flattens the droplet and the drop height, *h*, no longer continues to increase as *r* gets larger and larger. This situation is as shown in the left part of Figure 3.3, where we show the behavior of small and large droplets sitting on a surface (sessile drops). The obvious question to ask here is 'how small is small'? and what controls the maximum value of *h* that can be obtained? The answer to this question is the capillary length,  $\lambda_c$ , which can be viewed as the radius of the spherical droplet for which the Laplace pressure inside the drop  $(2\gamma/R)$  is equal to the gravitational hydrostatic pressure at the bottom of the drop  $(2\rho gR$ , where *g* is the gravitational acceleration and  $\rho$  is the liquid density). These pressures are equal to one another for  $R = \lambda_c$ , where  $\lambda_c$  is given by the following:



Figure 3.3: 'Small' and 'Large' sessile drops (left) and a pendant drop (right) used for the quantitative determination of the liquid surface energy.

The capillary length determines the degree to which gravity distorts the droplet the droplet from a spherical cap, with no noticeable distortion observed for  $R \ll \lambda_c$ . The measurement can done sessile drops like those in the left part of Figure 3.3, but it is generally more accurately done for the pendant drop geometry at the right of Figure 3.3. The pendant drop geometry is used in this laboratory. The software automatically measures the shape of the droplet and determines the capillary length from the shape, which is then converted to a surface energy using Eq. 3.3 and a known value of the

liquid density. (Note that the experiment can also be used to measure the interfacial free energy between two immiscible liquids, in which case  $\rho$  is replaced with the density difference between the liquids).

A reasonable estimate of the surface free energy can be obtained by continuously injecting liquid through the syringe needle with the pendant drop geometry and measuring the critical droplet volume,  $V_c$ , where a droplet detaches and a new one is formed. Droplet detachment happens when the force corresponding to the surface tension around the perimeter of the droplet ( $2\pi R_m \gamma_\ell$ , where  $R_m$  is the inner radius of the capillary) is equal to the gravitational force exerted by the droplet ( $\rho_g V_c$ ). By equating these two forces we get the following approximate expression for  $\gamma_\ell$ :

$$\gamma_{\ell} \approx \frac{\rho g V_c}{2\pi R_m} \tag{3.13}$$

If you are interested in a more complete treatment of the entire problem, take a look at the first few pages of reference [?].

## Samples

The following materials will be provided:

- Clean water
- A soap solution that can be added to the water to reduce it's surface energy
- A variety of materials expected to have different contact angles with water
- Access to a UV-ozone cleaner for surface modification

## Laboratory Procedure and Write-up

- First of all, answer the following questions and include a brief discussion the following points in your lab report:
  - 1. Look up the surface energy of pure water and write down the value of this quantity.
  - 2. Draw the shape of a sessile drop for  $\theta = 90^{\circ}$  and for  $\theta = 180^{\circ}$ , and show that Eq. 3.7 is correct in these two limits.
  - 3. What is the capillary length for water? Is this consistent with your own experience with how water behaves? Give a couple examples.
- Measure the interfacial tension of pure water and of a soap solution, using the full drop shape analysis.
- Measure the interfacial tension for one of the solutions from the previous experiment using the critical volume method, comparing the result you get with drop shape analysis with the value you get from Eq. 3.13
- Measure the advancing and receding contact angles for at least 5 solid surfaces, making an attempt to obtain the following:
  - 1. What surface/liquid combination gives the maximum value of  $\theta_a$ ?
  - 2. What surface/liquid combination gives the minimum value of  $\theta_a$ ?
  - 3. What surface/liquid combination gives the minimum contact angle hysteresis, expressed as  $\cos \theta_r \cos \theta_a$ ?

In your writeup, describe potential applications where each of these surfaces would be useful.

• In your writeup, describe the experimental protocol for measuring the surface tension and contact angles in sufficient detail so that the experiments could be repeated by other students, just be reading your procedures.

# 4 316-2 Laboratories

# 4.1 Laboratory 1: Nucleation and Solidification in a Binary Eutectic Salt System

# Laboratory Objectives:

To observe phase transformations in a binary eutectic system and the formation and subsequent coarsening of dendrites.

# Learning Outcomes:

Upon completing the lab exercise, students should be able to:

- Explain the observation of birefringence.
- Discuss undercooling and observations related to cooling rate.
- Quantify coarsening using measured secondary arm spacing and surface area to volume ratios. Predict how  $S_v$  will change with coarsening.
- Estimate uncertainty in measured values (temperature and dimension).

## **General Instructions:**

Read through the lab before you begin. It is possible to acquire data for parts II and III during the same runs, but you must anticipate when to pause the temperature on the hotstage and when to acquire images on the printer. Parts I and II are measurements of phase transitions and dendrite growth rates and initial secondary arm spacing at a constant cooling rate. Part III is a measure of dendrite evolution as a function of time at a constant temperature. Therefore, you could pause the temperature of the system as soon as dendrites appear. The initial progression of the dendrite across the screen will provide you with the rate for part II; the subsequent evolution of the structure at a constant temperature will provide the data for part III. Note: setup a video file and record time / temperature / scale bar on the images.



Figure 4.1: Phase diagram for the ammonium nitrate/sodium nitrate system.

**Part I: Solidification** Use the hotstage and transmission microscope to observe melting and solidification of ~10wt% NaNO3 in the above salt system. Record transition temperatures on heating and cooling, and carefully note which transitions they correspond to. Fill in the table, below.

Table 4.1: Tempeartures of phase transformations at different cooling rates.

Rate		T(eut)	$\mathbf{T}(\delta - \varepsilon)$	T(liq)
	Heating			
	Cooling			
	Heating			
	Cooling			
	Heating			
	Cooling			

Birefringence: Are any of the phases observed during heating and cooling birefringent? Which? Label the phase diagram.

**Part II: Observing the Microstructure as a Function of Constant Cooling Rate:** A. Cool the sample from the melt at a rate between 1 deg/ minute and 15 degrees per minute. Watch the melt (from the microscope – it has a larger area of view than the camera) until you observe the primary solidification begin, then "hold" the temperature and start recording the video image. The actual distance can be scaled based on the magnification, and the dendrite growth velocity calculated from these results. The information for Part III may be obtained by continuing to record as the microstructure evolves with time at constant temperature.

B. Repeat (A) for two additional cooling rates.

**Table 4.2:** Data collection table for constant cooling rate.

Rate	T (dendrite formation)	Dendrite growth rate*	Initial secondary arm spacing *		

\* Correct for magnification. Magnification : \_\_\_\_\_

**Part III: Observing the Microstructure as a Function of Time at Constant Temperature (Isothermal Experiments)** Repeat (A), but when solidification begins, pause the hotstage. Note the temperature. Capture images as a function of time (isothermal this time). Note: We will pause the temperature when we observe the dendrite formation. So the initial dendrite velocity, as well as the initial dendrite secondary arm spacing is a function of constant cooling rate; subsequent dendrite coarsening (secondary arm spacing) is a function of time at a constant temperature.

Table 4.3: Measured dendrite properties for isothermal experiments. Paused temperature =

Time	Secondary Arm Spacing	Surface Area to Volume Counts

<b>Fable 4.4:</b> Measured dendrite	properties for isothermal e	xperiments. Paused temp	oerature =

Time	Secondary Arm Spacing	Surface Area to Volume Counts

#### Lab Write Up:

Answer the following questions, using appropriate discussion of results, tables and plots. Neatness counts.

- 1. Describe what equipment was used in this lab and what measurements were made.
- 2. Make a table of your temperature results.
- 3. Is the temperature of the hotstage reliable? Why or why not? Be quantitative. Use your observations to substantiate your answer.
- 4. Did you observe birefringent phases? Which? Did you observe phases that were not birefringent? Which? What are the corresponding crystal structures?
- 5. Is there a relationship between the transition temperatures and the rate of cooling? What is it?
- 6. Does dendrite growth velocity depend on the cooling rate? What trend to you observe? Discuss.
- 7. From the constant cooling rate data, plot (initial) secondary arm spacing vs. cooling rate. Discuss.
- 8. Quantitatively, the secondary arm spacing is predicted to increase as a function of time to the 1/3 power. Plot the secondary arm spacing vs. time to determine if your data exhibits this behavior. Use the isothermal data.
- 9. The quantitative behavior of the surface area to volume ratio is predicted to change as time to the -1/3 power. What do your results indicate about coarsening? You can use overlays to determine the surface area per unit volume (# intersection of curved lines with phase / # points on overlay).
- 10. Choose a set of images, one taken at the initial dendrite formation, a second after some time has elapsed. Estimate the radius of curvature in each case. Assume that you had a uniform distribution of spheres, first with radius 1, coarsening to radius 2, using the two values above. Calculate the change in surface area to volume of such a change in radii. Show your work. If you didn't measure these, try to choose reasonable values. Approximate the radius of curvature of the tip by half the distance across a secondary dendrite arm.

# 4.2 Laboratory 2: Age Hardening in Al Alloys

### **Objective:**

To determine the hardness and conductivity versus aging time of 2024 (1" wide x 1/8" thick), 6061 (1/2" wide x 1/8" thick) and 7075 (1" wide x  $\frac{1}{4}$ " thick) aluminum alloys aged at temperatures of 25°C, 125°C, 225°C. Each lab section will be responsible for a single alloy. Aging will be conducted over the course of the week; team members should plan to make measurements throughout the week.

### Final write-up:

Data from the three lab sections will be pooled. This must be submitted by the end of week 2. Group reports will need to include (discuss) ALL class data.

#### **Procedure:**

1. Measure as-received, un-solutionized samples.

Alloy	Hardness Scale	Hardness (5 values)	Conductivity

- 2. Solution-treat~ a set samples of each alloy at 500C for one hour. Quench in ice water.
- 3. Measure the hardness of each solutionized sample (5 measurements on each!); discard outliers. Record.
- 4. Measure conductivity. Note: the sample MUST be at room temp. (do this after hardness) Record. Store samples in ice water.

Table	4.5:	Hardness	and	Condi	activitv	of	Various	Same	oles
Invie	1.0.	1 Iai ai ieoo	unu	contai	activity	01	( ario ao	Cump	100

Sample #	Hardness (5 values)	Conductivity

- 5. Anneal at:
  - (a) room temperature
  - (b) 125 °C
  - (c) 225°C

for times ranging from 10 minutes, ½ hour, 1 hour, 2 hours....64, 128, 264 hours....Note that data will be plotted on a logarithmic scale. Use this information to plan your measurements.

Sample #	Т	Date in	Time in	Date out	Time out	Anneal	Hardness	$\sigma$
_	(°C)					time	(5 meas)	5 meas)
						(min)		

#### Table 4.6

#### Group report (informal)

First describe each alloy. (What do the 2XXX, 6XXX, and 7XXX designations indicate?) Give some examples of applications in each case. Indicate what the normal thermo-mechanical heat-treatments (tempers) would be for each alloy. Discuss your results in the context of these heat-treatments. (Include references.)

- 1. Plot hardness versus log-time for each of the temperatures measured using the pooled data.
- 2. Discuss the curves and their relative magnitudes and relative position on the time axis of any peaks observed, and label appropriately. In your own words, discuss in terms of the theory of precipitation hardening.
- 3. Plot conductivity vs. log-time. Correlate with hardness measurements. Why does the conductivity change?
- 4. Discuss uncertainties in your data. Include error bars on your figures. Use the correct number of significant figures. Assuming a normal (Gaussian) distribution of these values, you can find the uncertainty of the mean to within a 95% confidence level ,by determining 2X the standard error of the mean: 2x the standard deviation (STDEV in Excel) divided by the square root of the number of points measured (COUNT in Excel). There is a single command to do this: CONFIDENCE (.05, STDEV, COUNT). Indicate these values on your plots by adding error bars: left click the data set and choose Format data series > Y error bars. Note that you can use the Custom error bar command to add different values for each data point (i.e. each mean value of hardness for each individual sample).

#### Be sure to include the following:

- 1. Data from all alloys not just the one measured by your group.
- 2. error bars on plots see the handout.
- 3. results on as-received samples (Note that the 2024 samples had a **T4 temper**. The 6061 and 7075 samples had a **T6 temper**. Your discussion should define these, and indicate if they make sense, based on your aging results.)
- 4. results on solutionized samples.

**References** Porter and Easterling [?], pages 291-308. Matter program (on Macs). Rosen paper posted on Bb, others you might find.

# 4.3 Laboratory 3: Al-Si Alloy Solidification and Modification (not currently used)

# **Experiment:**

Each lab group (2-3 individuals) will prepare a castable alloy of AlSi using Al and a "Master Alloy" of 50wt% Al/Si. One group in each section should choose a hypoeutectic composition, another the hypereutectic composition, a third, if there is one, the eutectic composition. Consult the Al-Si phase diagram. Total alloy mass should be~ 25 grams. Once cast, we will cut a portion of this sample to polish, and a portion to re-cast with a 10%Sr, 90%Al alloy to achieve Sr compositions between .05 and .2 wt% Sr. We will examine the microstructures of the polished alloys.

# Write-up (memo style):

- Project objectives brief summary. Why are Al-Si alloys of interest?
- Methods briefly summarize procedures.
- Results and Discussion
  - Micrographs:
    - \* Hypo, hyper and (if done) eutectic unmodified samples
    - \* Modified samples compare to unmodified.
  - Stereology
    - \* How do Image J results compare to predictions from phase diagram?
  - Details of microscopy is Jackson criteria valid?
  - Other observations: porosity? Differences from center-to-edge of samples? What? Why?

# **Experimental details (record here):**

- Mass Al:
- Mass Al(50wt%)Si(50wt%) master alloy:
- Alloy composition (wt% Si):
- Mass of alloy used for modification:
- Mass of Al(90wt%)Sr(10wt%): Note: Target amount = .05 .2 wt% Sr
- Other details, i.e furnace temperatures, materials, procedures used.

# Short Answer Questions: due at the beginning of lab, week 2

- 1. We will be using the casting process in lab. What limitations or potential difficulties can you anticipate using this technique?
- 2. You have already used the AlSi phase diagram to predict the microstructure for each alloy. Can further detail be added? Can you predict any differences in primary phase formation? Use the Jackson criteria, discussed in P&E in section 3.4.6 (p. 170) to predict in detail what the shape of the primary phase in the hypo and hyper-eutectic alloys might be. Show your work. Lv, Si = 1788 kJ/kg; Lv, Al = 397 kJ/kg. Q will the microstructures look like figure 3.65 (a) or (b) or neither?
- 3. How might the microstructure be further controlled by solidification conditions?
- 4. What might be the technological importance of Al-Si alloys?
- 5. What effect do modifiers (careful "grain refiners" and "modifiers" play different roles) have on the microstructure?
- 6. Why is the modification in (6) desired?
- 7. A recent research summary by Napolitano *et al.* attributes the differences in morphology between un-modified and modified AlSi alloys to a variety of factors. Describe these factors.

# 5 332 Laboratories

# 5.1 L1-C: Finite Element Modeling of a Uniformaly Loaded Cantilever Beam

The embodiment of stresses and strains in a cantilever beam is well known from solid mechanics. A simple but powerful theory used to explain this behavior is Euler-Bernoulli beam theory, or E-B theory, a model that, while extremely useful, is limited. For example, it does not account for large or plastic deformation, transverse shear strain, or Poisson contraction. You have likely encounted this theory in CIV\_ENG 216, if you've taken the course.

In this exercise, you will use the finite element method (FEM) to model a rectangular cantilever beam under load. You will use COMSOL explore the stresses and strains present in the beam, compare your model to E-B theory, and use engineering principles to optimize the cantilever design under operational constraint.

# Outcomes

- Develop basic FEM models (defining geometries, loads, boundary conditions, and meshes) using COMSOL.
- Use computational solvers to calculate and subsequently visualize stress and displacement fields.
- Compare computational and analytical results, noting the strengths and weaknesses of each model.
- Use your results to adapt the cantilever design to achieve a performance tolerance using reasonable constraints.

## Directions

Use COMSOL model a cantilever beam loaded on its top surface by a load  $P_z$ , as shown in Figure 5.1, below. Step-by-step directions are supplied in the walk-through handout.



Figure 5.1: A cantilever beam with a uniform load on the top surface. Dimensions not to scale.

The beam is made of a solid, linear-elastic material with various mechanical properties: elastic modulus, Poisson's ratio, and yield strength. Its dimensions are length *L*, height *h* and base *b*. The beam is loaded with a uniform pressure of  $P_z$  on the surface. We will model the cantilever beam to be affixed to the wall at one end (displacements of nodes at x = 0 are u = v = w = 0). We define our origin (point 0) as the point at the beam's centroid and the interface with the wall. Using COMSOL, we'll first use linear hexahedral elements with "normal" resolution) to solve for, visualize, and interpret the displacement and stress fields within the beam. We'll then compare these values to E-B theory. Finally, you will use parametric design techniques to design a stiff, lightweight composite beam.

Refer to the walk-through provided in class to construct your model and perform the computational analysis. Don't hesitate to ask questions if you get stuck.

#### **Exploration of the Model**

Work in groups to compose a coherent, narrative, journal-style report of your results. Work throug the following **Parts** to guide your investigation of the model.

Part 1: Describe (using both words and figures) the u, v, and w (these are expressions u, y, and w in COMSOL) displacement fields present in the deformed beam. Explain the sources of the features of these fields and their pertinent features.

- Part 2: Describe (using both words and figures) the  $\sigma_{yy}$  (solid.sy) and von Mises ( $\sigma_v$ , solid.mises) stress fields present in the deformed beam. Explain the similarities and differences between these fields. Do you expect this beam to yield?<sup>1</sup>
- Part 3: Plot and discuss the FEM-computed and the Euler-Bernoulli displacement as a function of distance from the fixed end (*y*-direction). The beam deflection in the *z*-direction as a function of distance is

$$w(y) = \frac{\omega y^2}{24EI} (y^2 + 6\ell^2 - 4\ell y)$$
(5.1)

where  $\omega = F/\ell$  in this equation is the applied force divided by the length of the beam  $\ell$ . The beam and  $I = \frac{bh^3}{12}$  is the second moment of inertia. Run this model for both linear shape functions and quadratic Lagrange shape functions. What do you observe in each case compared to the analytical result?

Part 4: Plot and discuss the FEM-computed and the Euler-Bernoulli axial stresses ( $\sigma_{yy}$ , or solid.sy in COMSOL) in the tensile region of the beam in the *y*-direction. Use quadratic Lagrange elements. The analytical expression for the axial stress,  $\sigma_{yy}$ , at the topmost *xy*-face of the beam is:

$$\sigma_{yy}(y) = \frac{\omega(\ell - y)^2}{2Z},\tag{5.2}$$

where  $Z = \frac{bh^2}{6}$  is the section modulus.

- Part 5: Referring to your results in Parts 3 and 4, identify any major deviations between the FEM results and the results from Euler-Bernoulli theory. Identify two possible sources reasons for any derivations you may see. Hint: Both E-B theory *and* your FEM model may have shortcomings. Consider them both.
- Part 6: You are charged designing this beam for a use in an engineering application and you want to reduce its weight as much as possible without resulting in yield (while accounting for a safety factor) and limiting overall displacement. You decide to replace a portion of the beam with a more compliant material. Based on your earlier results, design a new composite beam which compiles to these restrictions. Describe your engineering approach and your final design, as well as how much you reduced the weight of the component.

## • Part 6 Hints:

- 1. Use Quadratic Lagrange elements. Find this under Solid Mechanics  $\rightarrow$ Discretization  $\rightarrow$ Quadratic Lagrange
- 2. Remember the *layers* option you encountered during geometrical construction this is a great area to explore. You are, of course, free to consider other geometries.
- 3. Look at the von Mises stress field. Where can you tolerate a more compliant material?
- 4. You may have to remesh or re-apply boundary conditions.
- 5. Parametrization studies (Study → Parametric Sweep) are the best way to approach this problem. Figuring out a good optimization algorithm may save you time and may provide you with the best answer. Google is your friend here.
- 6. You can analyze values from a parameter sweep in the Results tab.
- 7. It is very easy to copy and modify an COMSOL model!

# MAT SCI 332 FEM Report Guidelines

Your formal report should contain:

- 1. A brief introduction describing your work and providing context for your study.
- 2. A methods section including all information necessary for the reader (assume they know how to operate COMSOL).
- 3. A results/discussion section in which you describe *relavent* results, analyze the strengths and shortcomings of your FEM results and how they compare to E-B theory, and present your newly designed composite beam.
- 4. A brief conclusion summarizing results and generalize the importance of your study.

<sup>&</sup>lt;sup>1</sup>It's my understand that you'll be seeing yield criterion in later lectures. To determine whether the beam will yield, find if the maximum von Mises stress ( $\sigma_v > \sigma_y$ ). This will shift you into the plastic regime of the stress-strain curve.

I am looking for accuracy and deliberation in your modeling and thoughtful consideration of the results. I am not particaularly concerned the length of your report, but about 5 pages of text (not including figures) is typically sufficient. As is true for any report you turn in, your work should be concise, readable, well cited, possess clear, informative figures. For technical writing, I strongly recommend the use LATEX for good typesetting, figure presentation, and equation writing. Overleaf is a powerful online LATEXeditor that you can use for co-authoring in small groups.

# 5.2 L3-C: FEM of a Stress Concentrator

In this assignment, you'll assess the stress fields in a simulated section of the of an aluminum (Young's modulus E = 70 GPa, Poisson's ratio v = 0.2) ASTM tensile specimen. Here we investigate the stress concentration effects of a 5 mm diameter (*d*) hole.

You will construct the finite element problem in Fig 5.2, below. In COMSOL, define your origin to be center of the stress concentrator (the hole). The experimental sample can be adequately approximated by approximating the specimen as a 2D plate of length length  $(l) \times \text{width } (w) \times \text{thickness } (t)$  of 60 mm  $\times$  20 mm  $\times$  3.2 mm. We will take advantage of specimen symmetry and Saint-Venant's Principle and further reduce our model to a single quadrant of the rectangular section of the gauge (dimensions shown in Fig. 5.2). We will assume a plane-stress condition and operate in 2D. We'll investigate the stress distribution near the hole during ramping a load of  $\sigma_{App} = 0$ MPa to 135MPa and back to 0 MPa.



**Figure 5.2:** (Top) The ASTM dogbone specimen with a d = 5 mm hole drilled through the center of the gauge. (Bottom) The finite element model limits the calculation to the center of the gauge and takes advantage of mirror symmetries.

#### Part I

Use COMSOL and the walk-through to formulate the model in Fig. 5.2 using a 2D representation. Note that plane stress conditions (the principle stress in the z-direction is zero) applies when the plate thickness is small compared to the other plate dimensions, as is the case here. We seek to find the stress distribution, and in particular, the magnitudes and positions of the maximum and minimum normal stresses,  $\sigma_{xx(max)}$  and  $\sigma_{yy(min)}$  respectively.

- 1. Initially, mesh the model using linear, free triangular elements and predefined "normal size" elements (minimum element size should be ~0.01 mm by default). Solve the problem. At the maximum applied load: t = 1.1 and  $\sigma_{Avv} = 135$  MPa briefly describe in figures and words the:
  - (a) Overall displacement field (solid.disp)
  - (b)  $\sigma_{xx}$  stress field (solid.sx)
  - (c)  $\sigma_{yy}$  stress field (solid.sy)

If you smooth or scale your result for presentation purposes, be clear about this in your report. Be sure to consider:

- (a) Where does the maximum value of  $\sigma_{xx(max)}$  occur? Report the ratio  $\sigma_{xx(max)}/\sigma_{App}$ .
- (b) Where does the minimum (largest negative/compressive) value of  $\sigma_{yy(min)}$  occur? Report the ratio  $\sigma_{yy(min)}/\sigma_{App}$ .

(c) Our specimen is a decent approximation of a stress concentrator in an thin, infinite plate under uniaxial far-field tension. In an ideal "infinite plate", maximum  $\sigma_{xx(max)} = 3\sigma_{App}$  and  $\sigma_{yy(min)} = -1\sigma_{App}$ . How does our FEM analysis compare?

2. In addition to the meshing parameters employed in Part 1(a), explore the parameters listed below:

- (a) Total number of elements
- (b) the estimated time and virtual memory required to complete the job
- (c)  $\sigma_{xx(max)}$
- (d)  $\sigma_{yy(min)}$ .
- (a.) Element type: linear triangular Min/max element size: 4/5
- (b.) Element type: linear triangular Min/max element size: 1/2
- (d.) Element type: linear triangular Min/max element size: 0.4/0.5
- (e.) Element type: linear triangular Min/max element size: 0.1/0.2
- (c.) Element type: linear triangular Min/max element size: 0.8/0.9
  - (f.) Element type: linear triangular Min/max element size: 0.04/0.05<sup>2</sup>

In your report, provide two plots, one of  $\sigma_{xx(max)}/\sigma_{App} vs.$  total number of elements and one of  $\sigma_{yy(min)}/\sigma_{App} vs.$  total number of elements. Comment on the trends.

3. For a finite-width plate of some thickness, *t*, the empirical solution for the maximum stress (Roark's Formulas for Stress and Strain, 8th Ed.), $\sigma_{xx(max)}$  is

$$\sigma_{xx(max)} = K_t \sigma_{nom}$$

where

$$K_t = 3.000 - 3.140(\frac{d}{w}) + 3.667(\frac{d}{w})^2 - 1.527(\frac{d}{w})^3$$

is the stress concentration factor and

$$\sigma_{nom} = \frac{\sigma_{App}w}{(w-d)}$$

is the nominal stress due to the reduced cross-sectional area that arises from the defect.

- (a) Using these equations, find the analytical value for the maximum stress,  $\sigma_{xx(max)}$ .
- (b) Now, create an efficient mesh (i.e., as few domain elements as possible) using the knowledge gained from your preliminary meshes and mesh refinement techniques to converge your solution to within 1.5% of the analytical solution.

Challenge Details: Turn in your .mph file for this mesh.

- Use your coarse result to inform your meshing. There are numerous tactics. Explore:
  - **Partitioning**: creating sub-domains with different element densities. To do this, navigate to the Geometry tab and create new shapes and use Partition Object to create sub-domains.
  - Change Mesh Sizes: you can define the size of the mesh in various sub-domains by adding different sizes in each domain. Add Sizes under Mesh 1 to try this.
  - Meshing Algorithms: you can control mesh densities by employing various meshing algorithms such as free-quad, mapping, or boundary layers. To do this, navigate to the Mesh tab and explore these possibilities.
  - Mesh Distribution: you can define nodal density functions using Distribution controls. Add these to a
    meshed domain and control Number of Elements to define node distributions. Press F1 when hovering
    above the Distribution button for full descriptions
- Meshes must be convergent. It is possible to get a result for an unconverged mesh that is in the 1.5% of the target value without being converges.
- You must use linear shape functions: i.e. Solid Mechanics →Discretization (you will need to activate this, like you did in the previous lab) → Displacement Field → Linear.
- Algorithmic mesh refining is not allowed.
- The group with the most efficient mesh (fewest elements) will receive 2 *e.c. points on their assignment.*
- If you beat my mesh, you get 4 *e.c.* (I'm undefeated, but some students have come close!).

# Part II

The analysis in Part 1 yields stress concentrations higher than the yield strength of our material (~243MPa). This makes a linear-elastic model insufficient to correctly describe the stress and strain state.

- 1. Enable plasticity. Rerun the model using linear triangular elements and 0.09/0.1 mm min/max size for your elements.
- 2. Show plots of  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and effective plastic stain (solid.epe) a measure of permanent plastic deformation at relevant time steps.
- 3. What do you conclude about the effect plasticity has on stress concentrations after yielding occurs?

# 5.3 L3-E: Mechanical Testing of Materials - Lab and Final Project

# Overview

# Description

Testing of materials to acquire mechanical properties is a critical skill for the materials scientist or engineer. Assessing the mechanical properties of a material is a necessary tool in determining whether a material is suitable for its expected application. Since this lab will be the basis for your final project, it will be treated as a structured research assignment, consisting of a white paper proposal, material testing, data analysis, and presentation of your results (both written and oral).

# Objectives

- Research and identify the test protocols necessary to investigate your material.
- Gain experience with mechanical testing of a material or set of materials.
- Determine mechanical properties from the analysis of tensile, compression, indentation, bending, and/or impact experiments.
- Assess if the results from experiments to answer the question proposed in your white paper.
- Present your results through both written and verbal communication.

# Materials

Each lab group (3 students per group) is requested to source their own materials. These can be everyday materials (coins, cellphone components, automotive components, earplugs, food items etc.), or materials from your research groups. However, if you do not have samples available through a research group or are finding selection of another material challenging, there are some options available from groups in the MSE department. These specimens are limited, so let us know as soon as possible of your interest in using a sample set by emailing Gwen to claim that sample.\*

- Epoxy samples Shull group
- Thin film coatings Chung group
- Bio-inspired samples Joester group
- Bioreasorbable polymer specimens Rogers group
- Metal Foams (McMaster)\*\*
- Porous Conductive Carbon (McMaster)\*\*
- Miscellaneous tensile or bending samples from CLAMMP (metals, polymers, and wood being the most common).\*\*\* Please contact Carla Shute for more details.

\*If your entire group is unable to participate in the in-person component of labs, please email Gwen and Dr. Shull as soon as possible to discuss potential options for a virtual final project.

\*\*These samples need to be purchased and require as much lead time as possible.

\*\*\*If you would like to use these samples, please let Gwen and Carla know with the material class you're interested in.

# Instrumentation

In order to help us prepare the in person component of the lab, you are expected to propose which tests and ASTM standard(s) would be most useful to probe the mechanical properties of your material. The Sintech 20G instrument in CLAMMP can perform tensile, bending and compression measurements. Charpy impact tests will be performed in CLAMMP, but require a specific sample geometry for the experiment. Indentation tests will be performed in MatCI using the Struers Duramin 5. Depending on the type of material and sample geometry, you will need to use between 1 and 3 different instruments to fully investigate your material. If you have specific questions about a test or an ASTM standard, please reach out to Carla Shute.

# **Timeline and Assignment Expectations**

# White Paper

The white paper is due Jan. 29th, 2021 at 11:59 pm as a *Canvas* submission. The white paper should provide the following information:

- Who is in your lab group
- What sample you are planning to test
- Significance of the material (i.e., what is its application)
- What research project do you propose (material property, variation between samples, effect of solvent, characterization of unknown samples)
- What instrumentation you will need to determine the mechanical properties
- ASTM standard(s) that you will need for your instrumentation
- Availability for testing over the data collection period (February 8-19)

Your white paper should be between 1/2 and 1 page in length.

# Lab Data Collection

In person data collection will occur from Feb. 8-19. Due to Covid safety protocols, only 1-2 students will be able to participate in a lab session at a time. Please be prepared to take detailed notes about your experimental setup, data collection, and any preliminary findings from the tests. These will be important to share with your other group members and for your final report.

# Status Update

To help track progress on your final projects and provide guidance for your data analysis, a **Status Update** is due on February 26<sup>th</sup>, 2021 at 11:59 pm as a *Canvas* submission. The status update should include:

- Your sample material
- The experiments you ran on your material (instrumentation and relevant protocol information)
- Preliminary data analysis (i.e., stress-strain curves for tensile testing, hardness and modulus data for indentation tests)
  - All figures and tables shown in this section should be labeled with proper units and axes!
- Any questions you may have about your data

This portion of the final project is an informal write up to ensure that you are on track for finishing your project by the end of the quarter and should be between 1 and 5 pages in length, depending on how many figures you need to include for your data analysis.

#### **Final Report**

The final report is due on March 19<sup>th</sup> by 9 am as a *Canvas* submission. The report should be a formal report 5-10 pages in length and include the following sections:

- Background what is your material, how is it used, and why is it important? Include citations in this section.
- Experimental methods What instrumentation did you use to test your material? What were the experimental parameters and protocols used? Provide enough detail so that a knowledgeable researcher could reproduce your work.
- Data analysis Present the data from your experiments, providing the mechanical properties of interest for your sample.

- Discussion What were significant findings from your data? Did you have to make any assumptions in your data analysis (i.e., account for compliance of the instrument)? How complete is your dataset? Is there another test that could be performed and provide more information about the mechanical properties of the material?
- Conclusion based on your results, is your material well suited for its given application? Are there any improvements that can be made to the material? If you were working with unknowns, were you able to successfully identify your samples?

## **Final Presentation**

The final presentations will take place on **Friday**, **March 19<sup>th</sup>**, **2021 from 9-11 am**. Presentations should be between 10 and 12 minutes in length and cover the following information:

- Your material and the projected application of the material
- How you investigated your material instrumentation and ASTM standard(s)
- Overview of results were they what you expected?
- Significance of the results summarize your conclusion

Everyone in the group must present during the course of the presentation. Please ensure your labels and text on figures and tables are legible and that any information not directly from your results is cited.

# Assessment

Each portion of the final project will be assessed for completeness (addressing all components for each section) and connection to the course material. Towards the end of the quarter, self assessments will be distributed to allow you to each provide feedback about your and your partners' contributions to the project during the quarter.

#### **Best-practices Reminders**

- Please use SI units.
- Appropriately caption and label all figures and tables.
- Please cite any sources.
- Upload your reports to *Canvas* as a .pdf.



Figure 6.1: Part 7; B is uniform throughout the area of interest

# 6 351-2 Laboratories

# 6.1 Laboratory 1: Measurement of Charge Carrier Transport Parameters Using the Hall Effect

# Objective

The purpose of this lab is to measure the electronic transport properties of semiconductors and semiconducting thin films using the ECOPIA Hall apparatus.

# Outcomes

Upon completion of the laboratory, the student will be able to:

- 1. Use a Hall effect apparatus to measure the mobility and carrier concentration in a semiconductor.
- 2. Derive the equations that enable the extraction of fundamental materials parameters using the Hall effect.
- 3. Describe the dependence of mobility on carrier concentration and temperature, and explain the origins of differences in mobilities between different semiconductors.

## References

- (1) M. Ali Omar, Elementary Solid State Physics;
- (2) Solymar & Walsh, Electrical Properties of Materials;
- (3) MSE 351-1 Lecture Notes; and
- (4) the NIST web page: http://www.nist.gov/pml/div683/hall.cfm

# **Pre-Lab Questions**

- 1. What is the Lorentz Force?
- 2. What is the Hall effect and when was it discovered?
- 3. Write the equation describing the force, FM, on a particle of charge q and with velocity v in a uniform magnetic field, B.
- 4. Does the velocity of a charged particle (with non-zero initial velocity) in a uniform magnetic field change as a result of that field? If so, how? Does its speed change?
- 5. What is the right-hand-rule?
- 6. For a particle with negative charge, q, in the situation below, in what direction will the particle be deflected?

(a)

7. For the example below, what will be the sign of the charge built up on the surfaces (M) and (N) if the particle P is charged (+)? if it is (-)? (**B** is into the page and uniform throughout the specimen.)

(a)

- 8. By convention, current is defined as the flow of what sign of charge carrier?
- 9. What is the electric field, E, in the situation below? What is the electrostatic force,  $F_E$  on the particle if it has a charge q?







Figure 6.3: Part 9

(a)

10. Why are both a resistivity measurement and a Hall measurement needed in order to extract fundamental material parameters?

### **Experimental Details**

The samples to be characterized include:

- 1. "bulk" Si, GaAs, InAs (i.e. substrates ~ 400 microns thick)
- 2. "thin films" of InAs and doped GaAs, grown on semi-insulating GaAs substrates
- 3. Indium tin oxide (ITO) on glass.

You may have the opportunity to make additional samples. For contacts on n-type GaAs, use In-Sn solder; for contacts on p-type GaAs, use In-Zn solder. Most samples are mounted on mini-circuit boards for easy insertion into the apparatus.

#### Instructions/Methods

See Instructor

# Link to Google Form for Data Entry

https://docs.google.com/forms/d/1lrAokPI1vIJ-a8pmLx4FVCqHh80PKgGr8oDD6eVzx\_w/viewform

#### Lab Report Template

- 1. Balance the forces (magnetic and electric) acting on a charged particle in a Hall apparatus to derive the equation that describes the Hall Coefficient in terms of the applied current and magnetic field and measured Hall voltage. Show your work. See hints at the end.
- 2. Apply data from a sample measurement to test the equation derived in (1). Show your work.
- 3. How is the carrier concentration related to the Hall Coefficient? What is the difference between bulk and sheet concentration?


Figure 6.4: Example

- 4. Calculate the carrier concentration (bulk and sheet) using the sample data and the equations derived above. Show your work.
- 5. Does the mobility exhibit any dependence on the carrier concentration? Discuss briefly; include observations from lab for the same material & type (e.g. n-GaAs).
- 6. What is the origin of the difference in mobilities between the n-type and p-type samples, assuming that the doping levels are similar?
- 7. How do carrier mobilities compare for different materials? Use the pooled data to compare mobility as a function of material (as well as carrier type). Explain your observations.
- 8. When the magnetic field, current, and sample thickness are known, the carrier concentration and type may be determined. Conversely, if the current, sample thickness and carrier concentration are known, the magnetic field may be determined. A device that measures these parameters, known as a Hall Probe, provides a way to measure magnetic fields. Write an expression that relates these parameters. Which is the more sensitive (higher ratio of mV/Tesla) Hall probe the bulk InAs or bulk GaAs sample? Show your work. (Note you should have recorded average Hall voltage for a given current. How do these compare?)

### Hints for derivation

- 1. For the example below, what VH would you need to apply to make the particle continue on in a straight line throughout the sample? (B is uniform throughout the specimen. Hint: Balance the magnetic and electric forces on the particle.)
- 2. The current density, *J*, can be expressed in two ways: J=i/(A), and J=nqv, where i is the total current passing through a cross-sectional area A, n is the concentration of carriers per unit volume in the material passing the current, q is the charge on each carrier, and v is the drift velocity of the carriers. If you knew i, A, VH, d, B, and q from the situation illustrated above, what expression tells you n?
- 3. The "Hall coefficient" of a material,  $R_H$ , is defined as the Hall electric field,  $E_H$ , per current density, per magnetic field,  $R_H = E_H / (J^*B)$  Using the equations given and derived thus far, express the Hall coefficient in terms of just q and n.

# 6.2 Laboratory 2: Diodes

# Objective

The purpose of this lab is to explore the I-V characteristics of semiconductor diodes (including light emitting diodes (LEDs) and solar cells), and the spectral response of LEDs and lasers.

# Outcomes

Upon completion of the laboratory, the student will be able to:

- 1. Measure diode I-V characteristics and relate them to band diagrams.
- 2. Fit I-V data to the diode equation, extract relevant parameters, and relate these to materials constants.
- 3. Determine the open circuit voltage and short-circuit current of the solar cell.
- 4. Describe the dependence of emission wavelength on bandgap and describe origins of spectral broadening.
- 5. Describe how lasers differ from LEDs in design and performance.

# **Pre-lab Questions**

- 1. What expression describes the I-V characteristics of a diode?
- 2. Sketch the I-V characteristics of a diode and label the sections of the curve corresponding to zero bias (1), forward bias (beyond the built-in voltage) (2), and reverse bias(3), and then sketch the corresponding band diagrams for 1, 2, and 3.
- 3. Sketch the I-V characteristics of a Zener diode and the corresponding band-diagram for reverse bias.
- 4. Sketch the I-V characteristics of a p-n junction with and without illumination. Label  $V_{OC}$  and  $I_{SC}$ .
- 5. Take pictures (use your phone) of lights around campus; try to get pictures of LEDs. Which do you think are LEDs (why?)?
- 6. Why are fluorescent lights "white?" How white are they?

# **Experimental Details**

The devices to be characterized include:

- 1. Si diode
- 2. Zener diode
- 3. LEDs (different colors)
- 4. Si solar cell

# References

MSE 351-2 Lecture Notes, Omar Chapter 7, Solymar & Walsh Chapter 9, 12, 13.

# Instructions/Methods

Use multimeters and the Tektronix curve tracer for I-V measurements. Use the Ocean Optics spectrometer to obtain spectral responses.

### Station 1 - CURVE TRACER

### p-n junction diode

Attach diode to "diode" slot on Curve Tracer. Measure both forward and reverse bias characteristics.

- 1. (In lab) Measure and record the I-V (current-voltage) characteristics of the silicon diode over the current range 2μA to 50 mA in the forward bias condition. Pay particular attention to the region from 200 to 800 mV.
- 2. (In lab) Measure the I-V characteristics of the diode in the reverse bias condition.
- 3. (Post-lab) The ideal diode equation is:  $I = I_{sat}[\exp(qV/kT) 1]$ . Note that for V>>kT/q,  $I = I_{sat}\exp(qV/kT)$ ; however recombination of carriers in the space charge region leads to a departure from ideality by a factor m, where  $I = I_0[\exp(qV/mkT) 1]$ .
  - (a) Plot the data using ln(I) vs. *V* plot to determine *m*.
  - (b) Use the value of the applied voltage corresponding to ~ 1mA to solve for *I*<sub>0</sub> (which is too small to measure in our case.)
- 4. (In lab) Repeat the forward bias measurement using "Store." Now cool the diode and repeat. Sketch the two curves. (Post-lab) Explain what you observe.
- 5. Test red and green LEDs. Record the color and the turn-on voltage.
- 6. (Post-lab) Compare the I-V characteristics for the silicon diode and LEDs. Why would you choose Si over Ge for a rectifier? (Omar 7.21)
- 7. (In-Lab) Test the Zener diode. Sketch. (Post-lab) Compare to figure 9.28 (S&W).

### Station 2: Solar Cells

- 1. Use the potentiometer, an ammeter and voltmeter to determine the I-V characteristics of a solar cell at different light levels. Determine the values of  $V_{oc}$  (the open circuit voltage) and  $I_{sc}$  (the short-circuit current) under ambient light, then use the potentiometer to determine additional points on the I-V curve. Record the results.
- 2. Repeat the I-V measurements for a higher light level. Record the light intensity measured with the photodiode meter. Area~1 cm2 : \_\_\_\_\_ Measure the area of the solar cell:\_\_\_\_\_
- 3. (Post-Lab) Estimate the fill factor and the conversion efficiency of the solar cell.

### Station 3: Spectrometer and Power Supply

### **Light Emitting Diodes**

- 1. Measure the spectral response (intensity vs. wavelength) of the light emitting diodes using the spectrometer.
- 2. Cool the LEDs and observe the response. Qualitatively, what do the results suggest about the change in Eg vs. temperature? About emission efficiency vs. temperature? How do these results compare to the I-V response of the cooled silicon diode?
- 3. Record the peak-wavelength and the full-width-half-maximum (FWHM) for each diode.
- 4. Calculate the bandgap that would correspond to the peak wavelength.

### Semiconductor Lasers

- 1. Attach the laser to the power meter and setup the power meter to measure intensity from the device. Slowly increase the voltage and record the I-V characteristics vs. power output for the laser.
- 2. Measure the spectral response of the laser: i) below threshold, and ii) above threshold. Note the FWHM of the peaks. How do they differ? How do they correspond to the I-V-power data?
- 3. Plot the light output (intensity) as a function of current. What is the threshold current? Label the regions of spontaneous and stimulated emission.
- 4. Calculate the efficiency of the laser.
- 5. Determine the bandgap of the laser material.
- 6. Explain the change in the width of the spectral emission.

LED Color	Peak wavelength	$E_g$ (in eV, from peak	Intensity	FW (left)	FW (right)	FWHM
	Ũ	wavelength)				
Laser						

Table 6.1: Spectrometer and Power Supply

### **Station 4: Stereomicroscope**

- 1. Sketch the structure of the LED observed under the stereomicroscope. Note the color of the chip when the device is off and the color of emission when the device is on. Sketch what the device structure might look like.
- 2. Sketch the structure of the laser observed under the stereomicroscope. Sketch what the device structure might look like.

# 6.3 Laboratory 3: Transistors

# Objective

The purpose of this lab is explore the input/output characteristics of transistors and understand how they are used in common technologies.

# Outcomes

Upon completion of the laboratory, the student will be able to:

- 1. Measure the output characteristics of a few important transistors using a "curve tracer."
- 2. Qualitatively relate the characteristics to the p-n junctions in the devices.
- 3. Describe transistor function and performance in terms of appropriate gains.
- 4. Identify applications of these devices in common technologies.

# **Pre-lab** questions

# **Bipolar Transistor**

- 1. Sketch and label the band-diagrams for npn and pnp transitors.
- 2. Sketch I-V characteristics for this device as a function of base current.
- 3. In what technologies are these devices used?

# MOSFETS

- 4. Sketch and label a MOSFET structure.
- 1. Sketch I-V characteristic for this device as a function of gate voltage. In your sketch of the *I*<sub>Source-Drain</sub>-*V*<sub>Source-Drain</sub> characteristics vs. gate voltage, *V*<sub>gate</sub>, label the linear and saturated regions.
- 2. What is threshold voltage? What structural and materials properties determine the threshold voltage?
- 3. In what technologies are these devices used?

# "Current Events"

- 1. What materials developments have changed transistor technology in the past decade? (Hint: Search Intel high-k; Intel transistors)
- 2. What new types of devices are on the horizon? Hint: search IBM nanotubes graphene

# **Experimental Details**

The devices to be characterized include the following

- 1. pnp and npn bi-polar junction transistors
- 2. phototransistor
- 3. metal oxide semiconductor field effect transistor (MOSFET).

References MSE 351-2 Lecture Notes, Omar Chapter 7; Solymar and Walsh Chapter 9



Figure 6.5: n-Channel MOFSET.

Instructions/Methods Use the Tektronix curve tracer for I-V measurements.

- 1. Bipolar Transistors (npn and pnp)
  - (a) Attach an npn transistor to the T-shaped Transistor slot on the Curve Tracer (making sure that E, B, & C all connect as indicated on the instrument). Set the menu parameters to generate a family of I-V curves. Keep the collector-emitter voltage  $V_{CE}$  below 30V to avoid damaging the device.
  - (b) Sketch how E,B,C are configured in the device.
  - (c) Measure  $I_{collector}$  (output current) for  $V_{CE} > V_{saturation}$  as a function of base (input) current,  $I_{base}$ .
  - (d) Post-Lab: determine the transistor gains,  $\alpha = -I_{collector}/I_{emitter}$  and  $\beta = I_{collector}/I_{base}$ .
  - (e) Repeat for a pnp transistor.

#### 2. Phototransistor

- (a) Measure the I-V characteristics of the phototransistor under varying illumination intensity (using the microscope light source). Compare qualitatively to what you observed for the pnp and npn transistors.
- (b) Post-lab: discuss the mechanism by which the light influences the device current, and compare with the bipolar transistor operation.

#### 3. MOSFETS

- (a) Attach MOSFET Device to the linear FET slot on the Curve Tracer, making sure that S,G,D are connected appropriately. Observe both the linear and saturated regions for *I*<sub>Source-Drain</sub>*vs*.*V*<sub>Source-Drain</sub>.
- (b) Vary the gate voltage step size and offset to estimate the threshold value of the gate voltage (the voltage at which the device turns on).
- (c) Measure the  $V_{Source-Drain}$  and  $I_{Source-Drain}$  to extract  $R_{Source-Drain}$  in the linear region as a function of  $V_{Gate}$ . You should take at least 4 measurements.
- (d) Post-lab, using the data from B, plot the conductance of the channel,  $G_{Source-Drain} = 1/R_{Source-Drain}$ , vs.  $V_{Gate}$ . You should observe a linear relationship following the equation ,

$$G_{SD} = \left(\frac{\mu_n W}{L}\right) \left(\frac{C_{OX}}{A}\right) \left(V_G - V_T\right)$$

where  $\mu_n$  is the electron mobility and W, L, and A are the width, length and area of the gate respectively (A = W x L).  $C_{OX}$  is the capacitance of the oxide, which can be measured using an impedance analyzer as a function of gate voltage. A plot is shown in Figure 6.5.

- (e) Using  $\mu_n = 1500 \text{ cm}^2/\text{V-sec}$ , C =  $4.8x10^{-10}F$  (from the attached plot), plot of conductance vs.  $V_{Gate}$ , calculate L, the length of the gate.
- (f) Determine *V*<sub>threshold</sub> from the above values. Compare with your observations from the curve tracer (part a).



Figure 6.6: Capacitor.

# 6.4 Laboratory 4: Dielectric Materials

### Objective

The objectives of this lab are to measure capacitance and understand the dependence on geometry and the dielectric constant, which may vary with temperature and frequency.

### Outcomes

Upon completion of the laboratory, the student will be able to:

- 1. Use an impedance analyzer to measure capacitance.
- 2. Given the capacitance of a parallel plate capacitor, calculate the dielectric constant.
- 3. For a known material, explain the microscopic origins of the temperature dependence of the dielectric constant.
- 4. Understand how the dielectric constant and the index of refraction are related. Use the reflectance spectroscopy to fit the thickness, index of refraction and extinction coefficient of several thin films. Explore how the index of refraction is affected by composition and how this informs design of heterostructure devices.

# **Pre-lab** questions

- 1. What distinctions can you make between capacitance and the dielectric constant? What are the units of each?
- 2. What is the relationship between the dielectric constant and the 'relative' dielectric constant?
- 3. What is the dielectric constant (or permittivity) of 'free space' (or vacuum)?
- 4. What is the relative dielectric constant of air? Water? Glass? SiO<sub>2</sub>? Explain their relative magnitudes.
- 5. For the capacitor shown in Figure 6.6, what is the expression that relates the capacitance and relative dielectric constant?
- 6. What relationship determines the amount of charge stored on the plates of a capacitor when a specific voltage is applied to it?
- 7. With the above answer in mind how could you measure the capacitance of a structure?
- 8. Name two materials for which the capacitance (charge per unit voltage) is fixed. Name a material type or structure for which the capacitance is dependent on V.
- 9. What is the relationship that gives the amount of energy stored on a capacitor?
- 10. Why are batteries the primary storage medium for electric vehicles, rather than capacitors?
- 11. Intel and their competitors are interested in both "low-k" and "high-k" dielectrics.
  - (a) What defines the boundary between "low" and "high?"
  - (b) What drives the need for "high-k" dielectrics? What other properties besides the dielectric constant are important characteristics of these materials?

Material	Area	Thickness	Capacitanc	$e\varepsilon_r(lab)$	$\varepsilon_r(lit)$
Glass slide					
(sample 1)					
Lithium					
niobate					
$(LiNbO_3)$					
Glass sheet					
(sample 2)					
Plexiglass					

#### Table 6.2: Dielectric Constants

LED=		LE	D=	LED=		
Bias	Capacitanc	e Bias	Capacitanc	e Bias	Capacitanc	

Table 6.3: Capacitance

- (c) What drives the need for "low-k" dielectrics?
- 12. Find one or two additional examples of technologies/devices that incorporate capacitors, and explain the function of the capacitor in that context.

### **Experimental Details**

The dielectric constant of a number of different materials will be probed through measurements of parallel plate capacitance. Capacitors of solid inorganic dielectrics (in thin slabs) is accomplished through the evaporation of metal contacts on either side of the material. The total capacitance of a p-n junction diode is measured through the device contacts. The capacitance of liquids is determined by filling a rectangular container between two electrodes, and neglecting the contributions of the container.

### References

Solymar and Walsh Chapter 10, Omar Chapter 8, Kittel Chapter 16

### Instructions/Methods

Use the HP Impedance analyzer to measure the materials provided in lab. Note the sample dimensions and the measured capacitance values on the attached table.

### Lab Report Template

#### Part I - Dielectric constants; Measuring capacitance with Impedance Analyzer

- 1. Using the default frequency of 100kHz and zero bias voltage, measure capacitance and contact dimensions and then calculate the relative dielectric constant of the following materials:
- 2. Using the default frequency of 100 kHz, measure capacitance vs. voltage for several LEDs

Determine the built-in voltage of the corresponding p-n junction,  $\varphi_0$ , for each diode, and discuss the difference. See equation 7.64, pg. 362, Omar. Note that the equation may be re-written as follows:

$$\frac{1}{C^2} = 2\frac{(\varphi_0 - V_0)(N_a - N_d)}{\varepsilon e N_a N_d}$$

Plot  $1/C^2$  vs.  $V_0$ , and extrapolate the linear region (reverse bias) to the x-intercept to determine the value of interest. Note that the slope depends on the doping concentration.

- 3. Calculate the relative dielectric constant, based on capacitance measured in lab for:
  - (a) air (4.0inch x 3.5 inch plates, separated by \_\_\_\_\_ (measure this))
  - (b) water at room temperature (4.0 inch x 3.5 inch plate partially submerged; measured dimension: Height:\_\_\_\_\_\_x width\_\_\_\_\_\_x separation\_\_\_\_\_
  - (c) ethanol
- 4. Fill in the table below, for water at the different temperatures measured in lab, using the dimensions measured above. Determine the corresponding values of the relative dielectric constant,  $\varepsilon_r$ . Plot  $(\varepsilon_r 1)/(\varepsilon_r + 2)$  vs 1/T (Kelvin) for both sets of data below, and compare to figure 8.13 (p. 388, Omar).

Class data:

Area = \_\_\_\_\_; separation = \_\_\_\_\_

Temp (C)	Freq	C (pF)	E <sub>r</sub>

Comparison from CRC handbook

Temp (C)	<i>E</i> <sub>r</sub>
0	87.74
20	80.14
40	73.15
60	66.8
80	61
100	55.65

5. Measure ice as a function of frequency & compare to Omar figure 8.10. Discuss.

Dimension: Height:\_\_\_\_ x width\_\_\_\_x separation\_\_\_

Freq	C (pF)	ε <sub>r</sub>	Freq	C (pF)	ε <sub>r</sub>

6. Practical applications: inspect the temperature/humidity meter. Look for the devices used to measure each. Measure the stand-alone capacitor that resembles that in the meter as a function of exposure.

### Part II - Reflectance Spectroscopy of Thin Films

- 1. Measure the reflectance spectra to determine n, k and thickness of:
  - ~ micron thick ~Al(0.3)Ga(0.7)As on GaAs substrate
  - ~ 1 micron thick ~ Al(0.6)Ga(0.4)As on GaAs substrate
  - SiO2 on Si substrate
  - Si3N4/Si substrate

Compare the index of refraction of the two different AlGaAs samples. What does this indicate about how you would "build" a waveguide?

# 6.5 Laboratory 5: Magnetic Properties

**Objective:** The objectives of this lab are to measure the response of a material to an applied magnetic field and understand the atomic origins of macroscopic magnetic behavior.

**Outcomes:** Upon completion of the laboratory, the student will be able to:

- 1. Use a magnetometer to measure magnetic response with applied field.
- 2. Given the saturation magnetization, solve for the number of Bohr magnetons.
- 3. For a known material, explain the microscopic origins of magnetism.
- 4. Distinguish qualitatively between "hard" and "soft" ferromagnetic materials.

**Experimental Details** The purpose of this experiment is to investigate the response of different materials to an applied magnetic field, H. Plotting the measured response, B, vs. the applied field, H, indicates the type of magnetization possible, i.e. whether the material is diamagnetic, paramagnetic or ferromagnetic.

References Solymar and Walsh Chapter 11, Omar Chapter 9

**1. Magnetization of metal wires** Qualitatively observe the hysteresis behavior of the following metals. Indicate whether they are ferromagnetic or not, and why. (Hint: Look at which electronic shells are filled/unfilled in each case.)

Metal wires:

	Hysteresis? Y/N		3d		4s
Cu					
Fe					
Со					
Ni					
W					
Steel					
Stainless Steel					

Quantify the observations on the metal wires (Fe, Co, Ni, and W 1 mm diameter and Cu 0.5 mm diameter – the cross sectional area must be entered in the B-probe dimensions). Record hysteresis curves in the "intrinsic" mode (without background subtraction). Also record "initial" curves for the first three metals. Fill in the following table.

	<i>B<sub>sat</sub></i> observed	$B_{sat}$ literature	# Bohr magnetons, $n_B *$
Fe		2.158 T	
Co		1.87 T	
Ni		0.616 T	

**Question 1(a-c):** Solve for the number of Bohr magnetons per atom in Fe, Ni and Co. (Use experimental  $B_{sat}$  if the sample saturates; otherwise use literature value.)

Note:  $\mu_0 = 4\pi \times 10^{-7}T - m/A$   $B_S = \mu_0 M_S; M_s \text{in A/m or Oe}$   $M_S = nM_A; n = \# \text{ atoms/volume}$  $M_A = n_B \mu_B; \mu_B = \frac{e\hbar}{2me} = 9.27 \times 10^{-24}A - m^2 = \text{Bohr magneton}$ 

**Question 2: Hard magnet** The sintered CuNiFe pellets provide an example of a "hard" magnet. Record (plot) a hysteresis curve and compare to the "soft" ferromagnetic materials. Comment on the observed behavior.

# 2. Faraday Rotation

#### Set-up:

- Red laser pointer (operated under 3.5V!!! and 40 mA!!!)
- Glass rod (inside the solenoid coil): Diam = 5mm, length = 10 cm, SF-59.
- Solenoid coil: L = 150 mm, turns/layer = 140, layers = 10, DC Resist = 2.6 Ohm
- B = 11.1 mT/A x I, where I is in Amperes. Maximum current is 3 Amps!
- Detector: Photodiode in series with 3 resistors.

Measure the intensity of the laser vs. rotation of the polarizer with zero magnetic field. (Measure and record the intensity every two degrees or so.) Apply a magnetic field and re-measure the intensity vs. rotation. Plot on the same graph to compare. Find the difference in angle (average) between the on/off magnetic field states. Calculate the Verdet constant, *V*, where  $\theta(radians) = VB\ell$ , *B* = magnetic field strength (millitesla), and  $\ell$  = length glass rod = 10 cm.

**3. Demonstration** Heating a magnetized iron wire is one way to observe a second order phase transition involving the spin degree of freedom (upon cooling, one observes the onset of spontaneous magnetization). What is this transition called? Estimate the value of the transition temperature for this system and compare to literature values.

# 7 361 Laboratories

# 7.1 Laboratory 1: Symmetry in Two Dimensions

# Objectives

We will be working with 2-dimensional lattices. You will see the how the symmetry of the lattice and not its shape determines to which of the four axial systems it belongs. Parts A and B examine unit cells, translational symmetry, and Miller Planes. Parts C and D add rotational symmetry, mirror, and glide planes. In Part E, we will examine 2-D Si and Ga surface structures grown on a Si (100) substrate.

### Laboratory Procedure

**Part A1: Lattices and Unit Cells (see worksheet p.4)** A unit cell must be able to reproduce the lattice when translated along the axes directions. A primitive unit cell is the simplest case where there is only one lattice point per unit cell. Non-Primitive unit cells contain more than one lattice point per unit cell. All lattice points must have identical surroundings. NOTE: this lattice belongs to the Oblique axial system.

- 1. You are to locate and outline two different primitive unit cells. Use as your lattice point the
- 2. angle corner of the triangle. Note that any point would be equally valid as a lattice point but I chose that so everyone would use the same point.
- 3. Now locate and outline a non-primitive unit cell.
- 4. Label your unit cells 1,2, and 3. For all unit cells, locate a corner where the angle  $\geq 90^{\circ}(\gamma)$  and mark it as the origin. Using a right-handed convention, (i) label the axes **a**,**b** and (ii) measure **a**,**b**, and  $\gamma$ . In the worksheet margin, calculate the unit cell area:

Area = 
$$(ab)sin\gamma$$

You will note that non-primitive cells have an area that is an integer multiple of the area for a primitive cell.

### Part A2: Miller Indices

- 1. Draw a line parallel to MN and another to OP inside each of your cells; the lines must touch somewhere on the cell axes. Label them MN' and OP'. For convenience, you may want to make these lines intersect a cell axis at: 1, 1/3, 1/10, 3/4 ... etc of the unit length.
- 2. Using the table at the bottom of the worksheet, calculate the Miller Indices for each line (six total).

**Part B: More Lattices** Select a printed fabric. Note: all fabrics belong to the Oblique axial system. Choose a feature in the pattern that "stands out to your eye" as a lattice point. Locate a primitive unit cell. Examine it for translational symmetry. Trace the primitive unit cell on 2 the tracing paper provided. Measure and label a, b,  $\gamma$ , and record the pattern number.

### Part C: Symmetry, Plane Group, Plane Lattice, and Axial System (worksheets p.5, 6)

- See the example. Look for symmetry in the pattern #1 and draw the appropriate symbol at all the locations. (e.g. 3-fold ▲, mirror plane , glide plane —-)
- 2. In the blank area to the right of hte pattern, make a sketch of the primitive unit cell.
- 3. Draw the appropriate symbols for all the symmetry you found at the locations where you found them on your sketch. It should match up with a plane group in Hammond p.67. 4) On the work sheet state the: 1) plane group 2) axial system (Symmetry Notes) and 3) plane lattice (Hammond p.62). At home do the same for patterns #2 and #3. These are more difficult.

# Part D: Motif (asymmetric) For two Escher drawings:

- 1. On tracing paper, repeat what you did in Part C.
- 2. Trace the motif of the pattern.

**Part E: Surface Reconstruction (worksheet p.7)** The lattice vectors for a surface structure will be different from those of the substrate. This change is known as a surface reconstruction. If we define the lattice vectors of the substrate as **a** and **b**; the lattice vectors for a given surface structure can then expressed in terms relative to the substrate. The unit length of the surface vectors will be

$$\mathbf{a}_{surface} = N \mathbf{a}_{substrate}$$
  $\mathbf{b}_{surface} = M \mathbf{b}_{substrate}$ 

e.g. If  $\mathbf{a}_{surface} = 3\mathbf{a}_{substrate}$  and  $\mathbf{b}_{surface} = 5\mathbf{b}_{substrate}$ , then N=3, M=5. The surface is then called a 3x5(NxM). Now consider the two surface structures on the Si (001) substrate Here, Ga-addimers have been adsorbed on a surface consisting of Si-dimers on top of a Si (001) bulk. Sketch the primitive lattice of: 1) Si bulk 2) Si-dimer 3) Ga ad-dimer layers with the NxM for each structure. Ignore the symmetry of the pattern. I am only interested in the primitive unit cells.

### Deliverables

Please do everything asked for. Make everything neat and orderly so as to get full credit. Erase all unnecessary lines, marks etc.

### Symmetry Notes

I. Periodic structures or patterns in two dimensions belong to one of four axial systems. These are named according to the shape of the unit cell: oblique (parallelogram), rectangular, square, hexagonal (triangular).

There are, however, a total of five two-dimensional plane lattices (Hammond p.62) in which all lattice points have equivalent surroundings; these are analogous to the 14 Bravais lattices in three dimensions. The two-dimensional plane lattices (or nets) are sketched below. Four are primitive and one is non-primitive (rectangular centered/diamond).



Figure 7.1: 2-D plane lattices

II. The preceding applies to arrays of featureless points, or, if you prefer, circles, which have "perfect" symmetry. A real pattern is made up of motifs (asymmetric objects, e.g."7"), which have certain spatial relations. Each lattice point has one or more motifs associated with it. Any pattern can be classified by the symmetry of the collection of motifs at each (or any) lattice point. There are only 17 different patterns in two dimensions; every periodic wallpaper, decorator fabric, etc. conforms to one of these. Such classification is beyond the scope of this course, but a few instructions or conventions are useful. (The summary of the 17 patterns plane groups Hammond p.67).

	Cell 1		Cell 2			Cell 3						
	(M	IN)′	(O	P)′	(M	[N)′	(O	P)′	(M	IN)′	(O	P)′
	а	b	а	b	а	b	a	b	a	b	а	b
Intercept												
Reciprocal												
Miller Indice												

Table 7.1: Part A2



Figure 7.2: Part A1 example



Figure 7.3: Part C Example



**Figure 7.4:** Part C # 1-3





Figure 7.5: Part E

# 7.2 Laboratory 2: Symmetry in Three Dimensions

Reading: Cullity and Stock sec 2.5, 2.6, 2.7, 2.9, 2.10, 2.11, Hammond Sec 12.1, 12.2, 12.3

# Part A1: Crystal Shapes and Point Group Symmetry

Inspection of a crystal can provide significant information about its symmetry. One can observe the presence (or absence) of mirror planes, rotation axes, rotoinversion axes and inversion centers. These identify the crystal system and the orientation of the conventional unit cell. One can do even better: the presence of more than the minimum crystal symmetry (C&S table 2.3) specifies the point group symmetry within the crystal system. There are 32 of these: stereographic projections are from the International Tables of Crystallography vol. 1.

You have 5 crystal models; each is from a different crystal axial system (trigonal is combined with hexagonal and orthorhombic will be studied in Part 2). Inspect each for symmetry: mirror planes, rotation axes, roto-inversion axes, and inversion center. Make a stereographic projection of the collection symmetry you found using the symbols below. Next to this, make a perspective sketch of the model indicating which face is at the projection point (center) of your stereographic projection.



Consult the point group symmetry table only after you have thoroughly examined your models to help find any symmetry elements you may have missed. On your worksheet you should have: 1) the identifying number 2) the stereographic projection along with a simple sketch of the model 3) state the axial system 4) state whether the crystal <u>has</u> or <u>does not</u> have a inversion center. **NOTE: Please do not draw on the models and be careful with them; they are very fragile.** 

### Part A2: Wulff net (orthorhombic)

Use a right-handed coordinate system and make 1) a simple sketch the model, 2) label the axes **a**, **b**, **c** 3) record the axes ratio **a**:**b**:**c**, and include the model number.

Now select two faces (only one can be a {100} type) and label these faces "A" and "B" on your sketch. Approximate the angle of the plane-normal between the faces relative to the axes and plot these as **poles** on the provided stereographic (m) (2) (3) (4) (6) (6) 2 projection. Use the **c** axis as the projection point (center).

GRADUATE STUDENTS: (after class) From the three direction cosines for both poles and the axis ratio **a**:**b**:**c** , calculate and normalize the ratio of integers h : k : l (C&S p. 82.) These are the Miller Indices of the crystal faces.

# Part B: Crystal Models-Cubic

You are provided with open and space filling models of FCC and an open diamond cubic model.

1. Inspect the FCC structure; this can be formed by stacking close packed planes (ABCABC...) which become {111} in the cubic representation. There are octahedral voids (CN=6) at 1/2, 1/2, 1/2 + fct and tetrahedral voids (CN=4) at 1/4, 1/4, 1/4, etc. (one in each corner).

a. After class, calculate the radius of the void(r) in terms of the lattice parameter(a) and radius of the atom(R). Do this for both the octahedral and tetrahedral voids.

b. GRADUATE STUDENTS (after class): Consider the primitive unit cell of the FCC structure. (Hammond section 5.8.) Write Miller indices for planes in the primitive cell (HKL) in terms of (hkl) in the FCC cell. You can consult Azaroff p. 53-54. The figure 3-19 is incorrect. Switch  $a_{01}$  and  $a_{02}$  (**a b** in the primitive cell) so the axis system is right handed.

2. Examine the Diamond Cubic structure. Tetrahedral coordination of each atom should be evident. Note the "diamond glide" planes. <110> 2 per face.

- a. Give the coordinates of each atom in primitive unit cell.
- b. Are all atoms equivalent? Briefly explain your answer with a simple sketch. \_
- c. Is the three-fold axis along <111> a 3 or 3? Briefly explain. \_
- d. Is the four-fold axis along < 100> a 4 or 4? Briefly explain.

e. Identify "diamond glide" planes (2 per face). Note both the plane orientation {hkl} and glide direction <uvw>. Briefly explain.

# Part C: Crystal Models - Hexagonal

For the open HCP model, primitive hexagonal, locate the 2 atoms per unit cell. Observe the 6 roto-inversion axis that is present in this structure with 3 inversion centers at z=0, z=1/2. Identify the 4 tetrahedral voids per cell. The two "internal" ones are easy to see and the others are on vertical edges.

- 1. Locate the octahedral interstices (voids) and give the coordinates; 2 per unit cell.
- 2. All the octahedral sites could be occupied in a compound. Alumina, Al2O3, presents an interesting variation. The O-2 form an HCP structure however; the Al+3's occupy only 2/3 of the available octahedral sites. Note the pattern of occupation varies from layer to layer.
  - (a) How many layers are required for the structure to repeat? Hint: Start counting at the midpoint of the bottom most HCP structure.
- 3. The crystal system is actually rhombohedral (trigonal), but the model and structure are most easily visualized in a hexagonal setting. To determine the proper symmetry, show the following:
  - (a) A 6 fold is not present along c.
  - (b) A 3 fold is present along c. \_
  - (c) A 6 is not present along c (this is trickier; consider both O and Al atoms).

# 7.3 Laboratory 3: Laue Diffraction Patterns

Reading: Cullity sec. 16-1, 16-2, 2-13, Hammond sec 12.1, 12.2, 12.3

# Lab Summary

You will use the Laue Back Scattering technique to determine the crystallographic orientation of a single crystal. Then you will re-orientate the crystal to a different plane.

# Introduction

The Laue method records the x-ray diffraction pattern on a CCD camera, image plate or photographic film. The Back Reflection Laue technique is for high x-ray absorbing samples at diffraction angles  $(2\theta)$  between  $120^{\circ}$  and  $180^{\circ}$ . The Front Reflection Laue method is used for  $0^{\circ} < 2\theta < 60^{\circ}$  but is suitable only with low absorbing samples like polymers.



Figure 7.6: Back Reflection and Front Reflection Laue

While Laue methods are used for several purposes, one of the most important is to determine the orientation of single crystals. Well-grown crystals have habits (shapes or facets) that indicate the symmetry possessed by the lattice on which the crystal was "constructed". But if a crystal is poorly formed or was made in such a way that facet development is prevented, xrays can be used to determine the presence and orientation of planes within a crystal using Bragg Diffraction. Bragg Diffraction or Bragg Scattering only occurs when:

i) the Bragg condition is satisfied,  $n\lambda = 2d_{hkl}sin\theta$ 

ii)  $r_{hkl}^*$  the normal to a plane(hkl), bisects the incident and diffracted x-rays. This is shown in the figure above.

Crystals have many planes of atoms with different values of  $d_{hkl}$ . To ensure that the Bragg condition will be satisfied for many of these, a large range of  $\lambda$ 's are supplied by the white or Bremsstrahlung radiation of the x-ray tube. Generally Mo or W anode x-ray tubes are used for Laue because of the greater white component to their spectrum at lower operating voltages but any target material (e.g. Cu, Cr, etc.) is suitable.

The incident x-rays are collimated into a beam, pass through a hole in the film holder and strike the sample. X-rays backscatter onto the film where the pattern is recorded. The sample is mounted on a goniostat, a device that permits the rotation of the sample about its horizontal and vertical axes (see figure page 3). The position of a diffraction spot enables us to determine the direction of  $r*_{hkl}$ , if we remember that  $r*_{hkl}$  bisects So the incident beam direction and S the scattered beam direction.

# **Experimental Procedure**

With both goniostat axes set to 0.0°, record a back reflection Laue pattern of the MgO crystal. Your instructor will give you recommended voltage, current, and exposure times. Note the symmetry apparent in the diffraction pattern. Given that MgO has the sodium chloride crystal structure, which pole (plane normal) is nearly parallel to the x-ray beam?

With the assistance of your instructor, locate six zones and label them as 1,2,3 etc. Measure the position of each zone using the Greninger Chart. The Greninger Chart is a device that saves tedious trigonometric calculations, allowing you to read directly the latitude ( $\gamma^{\circ}$ ) and longitude ( $\delta^{\circ}$ ) of individual poles. We will further simplify the work by measuring  $\tilde{a}^{\circ}$  for an entire zone of poles simply by rotating $\varepsilon^{\circ}$  (the Greninger Chart) and aligning  $\gamma^{\circ}$ . Make a table of  $\varepsilon^{\circ}$ , its direction(CW/CCW), and  $\gamma^{\circ}$ . For accuracy, read all angles to the nearest 1/2°.

To Plot: Orientate the Wulff Net with NS axis **horizontal** to make tracing easier. You need to rotate the Wulff Net the same direction as the Greninger Chart to plot the zones. However, the Wulff Net will be remaining stationary and you will be rotating the tracing paper. Therefore, you need to rotate the tracing paper in the **opposite** direction that you rotated the Greninger Chart. Plot zones as great circles.

Now measure the interplaner angles between zones simply by placing two poles (intersecting zones) on the same great circle and measuring the angle between them. Index all intersecting zones with this technique referring to the table of inter-axial angles for cubic crystals provided in lab. Note: If you cannot match a pole, label it with a "?". Bad guesses will be graded as incorrect. When you finish, you should find at least one pole to be a {111} or {110}. Reorientate the sample to one of these reflections by adjusting the goniostat arcs. Record the diffraction pattern and note the symmetry.

# **Report:**

Provide the experimental conditions: x-ray tube anode material, voltage, current, exposure times, beam size, and sample to film distance. Attach both photographs, table of zones with  $\gamma$ ,  $\varepsilon$ , CW/CCW, and goniostat setting for the second photo. Lastly, *index* your stereographic projection using a standard projection (Cullity fig 2-40.)

# 7.4 Laboratory 4: X-Ray Diffractometer Part I

# Lab Summary

Labs IV and V examine the principle of operation of the X-ray Diffractometer system. The instrument you will be using is a Rigaku Dmax. Note that both labs will be combined into one report. This week you will investigate the details of: 1) the X-ray spectrum emitted from the X-ray tube, 2) absorption of X-rays by materials.

# **Experimental Procedure**

The instrument is equipped with a Cu anode X-ray tube. The source is a line, 10mm high x 0.4mm wide at a 6° "takeoff angle". The apparent source size therefore is 0.04mm or  $0.01^{\circ}$  at a sample distance of 185mm, the "radius of the diffractometer." With your instructors assistance and X-rays off

: 1) Inspect the X-ray generator and X-ray shutter operation to be certain how they work together with the indicator lights.

2) Note the X-ray collimating system with the incident beam slit "Divergence Slit" (DS), and the scattered beam slits, "Receiving Slit" (RS) and "Scatter Slit" (SS). These are used to define the incident and scattered beam directions  $S_0$  and S. 3) Note the Specular Reflection geometry of the diffractometer with the sample axis  $\theta$  and detector axis  $2\theta$  as they change simultaneously. The X-ray detector is a scintillation type and uses an electronic device called a Pulse Height Analyzer (PHA). We will need to re-adjust the PHA for this weekfs lab. Record the initial PHA settings: Baseline (BL) and Window (W) voltages. Adjust the BL to 0.5V and the W to 5.0V.

# Part A: X-ray Tube Emission Spectrum

Energize the X-ray tube to -20kV and 2mA. X-rays will irradiate a LiF (100) single crystal that acts like a diffraction grating scattering X-rays. LiF has the FCC NaCl crystal structure. Scan  $2\theta$  from 15° to 50°, Appendix L4A1. Ignoring the absorption effects of: 1) the X-ray tube Be window, 2) the detector Be window, 3) air, and 4) the Al absorber foil, you have recorded the emission spectrum of the Cu anode X-ray tube.

Note that the most intense peak in the spectrum is from the Cu  $K_{\alpha 1}$  emission line,  $\lambda = 1.54056$ Å. You will now determine a more precise  $2\theta$  position for the line by scanning with a smaller step size, L4A2. Now having an accurate value for the Cu  $K_{\alpha 1}$  position, calculate the exact value for  $LiFd_{200}$ . For your report, using Bragg's Law and  $d_{200}$  of LiF, calculate  $\lambda$  for all the notable lines and features present in the spectrum i.e. the Bremsstrahlung radiation, short wavelength limit (SWL), and **all** emission lines. Identify the element(s) responsible for each noted emission line, see Cullity app 7. (Hint: What impurity metal is present inside the X-ray tube?) Also include in your report, the comparison between your measured  $\lambda_{SWL}$  wavelength and the calculated value using the X-ray tube operating voltage (kV).

# Part B: Scattering from LiF (400)

Calculate the  $2\theta$  position for the LiF (004)  $CuK_{\alpha 1}$  line. Scan  $2\theta$  from 99° to 101° (L4B) to determine the exact angles for  $CuK_{\alpha 1}$  and  $K_{\alpha 2}$  wavelengths. Compare measured and calculated positions.

# Part C: Absorption of X-rays by Al

Move the detector to the Cu  $K_{\alpha 1}$  line. Use the Ratemeter to count the X-ray intensity for ten one-second measurements, average these values ( $I_0$ ), and record. CLOSE THE SHUTTER, insert two sheets of Al foil in front of the detector, open the shutter and average 10 more one-second measurements. Repeat, adding two foils at a time until I = 0.1  $I_0$ . For your report plot ln I vs. t (foil thickness in cm). If the detector response is linear, this will be a straight line. From the slope of this line you can calculate the absorption coefficient  $\mu$ . Calculate the Al foil thickness given the density = 2.70  $g/cm^3$  and the weight of 100  $cm^2$  of foil = 0.439g. Compare your value of  $f\hat{E}$  to that found in the *International Tables for X-ray Crystallography* (*SEL*).

# Part D: Absorption of X-rays by Ni

Insert the Ni filter. Scan  $2\theta$  from  $39^{\circ}$  to  $46^{\circ}$  to include the Cu  $K_{\beta}$  and Cu  $K_{\alpha}$  emission lines (L4D). Note the differences in the spectrum, especially the relative intensities of the  $K_{\beta}$  and  $K_{\alpha}$  lines by comparing to L4A1. Re-plot the region between the  $K_{\beta}$  and  $K_{\alpha}$  peaks to experimentally locate the K absorption edge of Ni. For your report, calculate the thickness of the Ni filter using the data from the Cu  $K_{\beta}$  absorption. You will need to look up the  $\frac{\mu}{\rho}$  and  $\rho$  values for Ni. Calculate the wavelength of the Ni K absorption edge and compare this to the value in the International Tables. Close the shutter, turn off the X-rays, and return the PHA to the original settings.

# APPENDIX

File Name	Start ( $2\theta^{\circ}$ )	Stop $(2\theta^{\circ})$	Step Size ( $2\theta^{\circ}$ )	Dwell (s)	Axis
L4A1	15	50	0.05	1	$2\theta/\theta$
L4A2	44.5	45.5	0.02	1	$2\theta/\theta$
L4B	99	101	0.02	1	$2\theta/\theta$
L4D	39	46	0.05	1	$2\theta/\theta$

# 7.5 Laboratory 5: X-Ray Diffractometer Part 2

Reading, Cullity and Stock: sec 6-7, 6-9, 6-11, and p.201-202

### Lab Summary

This week you will study the details of the X-ray detector system. You will: 1) perform measurements to determine the energy resolution of the NaI scintillation detector 2) select filters and make adjustments to the PHA to produce a monochromatic X-ray beam from the polychromatic X-ray source suitable for Powder X-ray Diffraction (PXRD) experiments.

#### Part A: Energy resolution of the NaI detector

When a single X-ray photon enters a scintillation detector, it produces a voltage pulse whose amplitude (in volts) is linearly proportional to the X-ray energy. However, there is a limit (resolution) where a small change in  $\lambda$  produces no change in voltage.

**Procedure** Adjust the PHA, slits, and the X-ray tube power to that used last week. Scan the LiF (200) crystal (L5) to locate the Cu  $K_{\alpha 1}$  emission line and move the detector to the position.

- 1. Open the shutter so X-rays from the  $CuK_{\alpha 1}$  emission line enter the detector. (Note:  $\Delta\lambda/\lambda$  is ~ 0.1%)
- 2. Adjust the PHA: Baseline = 0.4V, Window = 0.2V. Lock the Window setting, as it must remain constant throughout the entire measurement!
- 3. Use the Ratemeter function and average ten one-second readings and record: i) Intensity (counts), ii)  $V_{detectoroutput} = V_{Baseline} + 1/2V_{Window}$
- 4. Increase the  $V_{BL}$  by 0.5V and repeat step 3.
- 5. Keep repeating until the upper limit of  $V_{BL}$  is reached.
- 6. Collect additional data around the maxima by stepping  $V_{BL}$  at 0.2V intervals. A plot of I vs. Vdetector is the differential voltage curve for the detector. Measuring the Full Width Half Maximum (FWHM) of the curve yields the resolution:

$$Resolution\% = 100 \times \frac{FWHM}{V_{det}(maxima)}$$

More useful plots are of I vs.  $\lambda(A)$  and especially I vs. E (keV) as

$$\Delta V/V = \Delta \lambda/\lambda = \Delta E/E$$

To plot I vs. E:

$$E(ke) = (V_{BL} + 0.1V) \times \frac{8.05keV}{V_{det}(maxima)}$$

To plot I vs.  $\lambda$ :

$$\lambda(\mathring{A}) = \frac{12.4}{E(keV)}$$

You have now calibarated the PHA for Energy (keV), Wavelength ( $\mathring{A}$ ) and Voltage (V).

#### Part B: Adjusting the PHA for a 90% Window

The PHA can be adjusted to prevent the scattering from unwanted wavelengths from being recorded in an X-ray pattern. That is desirable in kinematic scattering experiments like PXRD. Also, to keep the intensity high, you will set a "90% window" as it allows 90% of the intensity to pass to the counter and rejects 10%.

**Procedure** Open the shutter to allow Cu  $K_{\alpha 1}$  radiation to enter the detector

- 1. Set  $V_{BL} = 0.5$ V and  $V_W = 5.0$ V.
- 2. Start the Ratemeter and record I0 (average ten one-second readings.) Note this is the integrated intensity (100%) of the differential curve: I vs. *V*<sub>det</sub>
- 3. Increase  $V_{BL}$  and reduce I0 by 5%, record  $V_{BL}$  4) Without changing  $V_{BL}$ , decrease  $V_W$  to reduce I by another 5%, record  $V_W$ .

You have now set the PHA to pass 90% of the intensity. Consequently, x-rays whose energy is lower than  $V_{BL}$  or higher than  $(V_{BL} + V_W)$  will be rejected and not be counted.

For your report on each plot I vs. E, I vs.  $\lambda$ , and I vs. V, indicate the positions of:

1)  $\operatorname{Cu} K_{\alpha 1}$  2)  $\operatorname{Cu} K_{\beta}$  3)  $V_{BL}$  4)  $V_{BL} + V_W$ .

For your report answer the following questions: With the PHA set to pass 90% of the Cu  $K_{\alpha 1}$ :

1) What range of wavelengths are: i) passed and ii) eliminated by the 90% window?

- 2) What energies are: i) passed and ii) eliminated?
- 3) Is Cu K $\beta$  eliminated by the 90% window?

# Part C: Powder X-ray Diffraction (PXRD)

With instructor's assistance, replace the LiF single crystal with a polycrystalline LiF sample. Scan the sample with the same conditions as L5, (L5C1). Note the difference. With your instructor's assistance, remove Al absorber, increase the tube power, and change slits to increase the diffracted intensity. Scan  $2\theta$  from  $35^{\circ}$  to  $70^{\circ}$  (L5C2). For your report, 1) discuss why the intensity is lower (L5C1) 2) identify all the diffraction peaks present in L5C2

### Part D: Determining the best condition for PXRD

For a PXRD experiment, you want to have monochromatic radiation in order to simplify interpretation of the diffraction pattern. You also would like high peak intensities and a low background. We will investigate various combinations of PHA settings and the Ni filter to determine the optimum conditions for recording a diffraction pattern. The best condition will result with a high-diffracted intensity ( $I_p$ ) for only one wavelength  $\lambda$  and a low background level ( $I_b$ ). Note: Do not use the Jade peak finder.

- 1. Set the PHA, BL = 0.5V, W= 5.0V, and scan the  $K_{\beta}$  and  $K_{\alpha}$  peaks for LiF (200) (L5D1).
- 2. Close the shutter, insert the Ni filter and scan the same region (L5D2).
- 3. Set the PHA for a 90% window determined in Part B. Scan again (L5D3).
- 4. Close the shutter, remove the Ni filter and scan again. (L5D4).

In your report, calculate  $(I_p - I_b)$  and  $(I_p - I_b)/I_b$  for the  $K_{\alpha}$  peak for each of the four conditions. Also calculate  $\sigma = \sqrt{N}/N$  for  $N = (I_p - I_b)$  and the ratio  $(I_p)K_{\alpha}/(I_p)K_{\beta}$  in each case. This data should be presented in a table. The best condition is a large value of  $(I_p - I_b)/I_b$  for  $K_{\alpha}$ , subject to a small  $\sigma$  for  $(I_p - I_b)$  and a relatively small  $K_{\beta}$  peak. In other words, we want a large peak-to-background ratio and a high intensity for only one peak. (We cannot eliminate the  $K_{\alpha 2}$  radiation.) Your report should identify the best condition for obtaining the powder diffraction pattern.

File Name	Start $(2\theta^{\circ})$	Stop ( $2\theta^{\circ}$ )	Step Size $(2\theta^{\circ})$	Dwell (s)
L5	44.5	45.5	0.02	1
L5C1	44.5	45.5	0.02	1
L5C2	35	70	0.1	0.5
L5D1	39	46	0.1	1
L5D2	39	46	0.1	1
L5D3	39	46	0.1	1
L5D4	39	46	0.1	1

### APPENDIX

# 7.6 Laboratory 6: Quantitative Analysis of a Mixture

Reading: Cullity and Stock. sec 6-1,2,3, 9-1,2,3,7, 10-1,2,3 Supplement for Lab VI at the end of this handout.

# Lab Summary

You are supplied with a mixture of two unknown powdered materials. One has a cubic structure and the other is non-cubic. We will collect a powder diffraction pattern for the mixture and use Search/Match software to identify the unknowns. After class, you will get information online or from the SEL library and calculate the volume fraction for each phase in the mixture.

### **Experimental Procedure**

Prepare a powder xrd sample holder with the unknowns as instructed in lab. Slit sizes to use are 1°DS/SS and 0.3mm RS 0.1°, Ni filter. Adjust the x-ray tube power to 40kV and 20mA. Perform a  $2\theta/\theta$  scan from  $2\theta$  from  $20^{\circ}$  to  $115^{\circ}$ , 0.05 step size, and 1s count time (L6A). Note the  $CuK_{\alpha 1,2}$  peak splitting at the higher angles. Examine the data to see that for all peaks there are least three data points within the FWHM. Check that the receiving slit has an angular size that is smaller than the FWHM. Also, the peak height for the six most intense peaks should have adequate counts to better define the peak shape ( $\sigma = .03 \sim 1000$  counts.)

**Identify the diffraction lines using Jade.** With the instructor's assistance, use the diffraction analysis software to identify peaks. Check the pattern carefully that Jade did not miss any peaks or incorrectly chooses a peak from  $CuK_\beta$  or a tungsten L line. Use the peak editor tool to correct peak finder. Print the peak list, as you will need the info for the Volume % calculation you do at home.

**Search Match using Jade**. Per instructor's assistance, perform a Search/Match for your unknowns. Overlay the many results of the search on your data to solve the unknowns.

**GRADUATE STUDENTS:** Texture can be a problem in this type of analysis. The theory assumes that each phase is randomly oriented, which may not be the case. You can check this assumption by comparing the calculated and observed intensity ratios for more than one pair of peaks. Check for random orientation by comparing the ratios for a second set of using different (*hkl*'s). Do not try to correct your derived volume fraction for any texture effect you may have. Simple knowledge of how close your intensities are to those with random orientation is adequate for this laboratory.

### **Deliverables (non-formal report):**

1) Experimental conditions: tube target and power, slit sizes, sample ID number, survey-scan, other scans and peak reports.

2) A table of: The unknowns, *hkl*, *f*, F\*F(show work), multiplicity, LP factor, unit cell volume and measured integrated intensities. You will use one peak for each phase (undergraduates) or two peaks for each phase (graduates). The instructor will tell you which peaks you should use for this.

3) Calculation of volume fractions of phases from XRD. See Supplement for Lab IV

To calculate F, you will need to look up the  $x_n$ ,  $y_n$ ,  $z_n$  atom positions for the given structure:

1) Use ICCD tables to determine structure space group number, lattice constants and *z*, the number of atoms per unit cell.

2) Online databases or the R.W.G. Wyckoff (SEL library ref. section)"Crystal Structures, 2nd., ed., Wiley (1963) to obtain  $x_n, y_n, z_n$ .

# Supplement for Lab IV

The following is to clarify the ideas and procedure of Laboratory IV from Azaroff Ch 19. We start with the result of the powder diffraction theorem (Azaroff eq.19-5):

$$I_{hkl} = I_o C \frac{F_{hkl}^2 m L P}{V_c^2} V_x$$

Here C is a constant (involving  $\lambda$ , electron characteristics and diffractometer geometry),  $V_c$  is the unit cell volume and  $V_s$  is the effective diffracting volume of the sample (which depends on sample absorption coefficient  $\mu$ ). This is for <u>one</u> material. If you have a two-component mixture, with material A present with volume fraction  $v_A$ , the intensity of a reflection from that material is given by:

$$\frac{I_{hkl}^{A}}{I_{hkl}^{B}} = \frac{\left[F_{hkl}^{2}mLP/V_{c}^{2}\right]_{A}}{\left[F_{hkl}^{2}mLP/V_{c}^{2}\right]}\frac{v_{A}}{v_{B}}$$

The left hand side is from the experimental data. The first ratio on the right hand side is calculated. This gives you  $v_A/v_B$ , or  $v_A$  since  $v_B = 1 - v_A$ . Azaroff is incorrect in omitting from the denominators in eqs: 19-5, 19-7 and 19-9 of the text.

To use this you must be able to evaluate  $F_{hkl}^2$  for the two materials. An example will be worked here. Take the case of antimony (Sb). You must know its crystal structure. The JCPDS file says that the crystal system is "Rhombohedral (Hex)". That means that the <u>primitive</u> unit cell is rhombohedral, but that the pattern is indexed (*hkl*) with the larger (more convenient) hexagonal cell (a = b,  $\gamma = 120^{\circ}$ ). There are three lattice points in the hexagonal cell at 000; 2/3 1/3 1/3; 1/3 2/3 2/3 (Azaroff, pp. 49 ff; Cullity, Appendix 4). You must look up the crystal structure of Sb (it is not HCP!). A good reference is: R.W.G. Wyckoff, *Crystal Structures*, 2nd. edn., Wiley (1963). This multivolume set is in the reference section of SEL. There you find that there are two Sb per lattice point with displacements  $\pm z = 0.233$ . This information locates the 6 Sb atoms per hexagonal unit cell. In writing down structure factors, it is convenient to factor the positions of lattice points and the atom displacements from the lattice points (you have done this with FCC structures such as diamond/silicon or NaCl):

$$F_{hkl} = f \left[ 1 + e^{\frac{2\pi i}{3}(2h+k+l)} + e^{\frac{2\pi i}{3}(h+2k+l)} \right] \left[ e^{2\pi i zl} + e^{-2\pi i zl} \right]$$

Recalling that  $e^{ix} + e^{-ix} = 2cosx$  and that  $F^2 = FF^*$ , straightforward algebra yields:

$$F_{hkl}^{2} = 4f^{2} \left[ 3 + 2\cos\frac{2\pi}{3}(2h+k+l) + 2\cos\frac{2\pi}{3}(h+2k+2l) + 2\cos\frac{2\pi}{3}(h-k-l) \right] \cos^{2}2\pi z l$$

Remember that the arguments of the trigonometric functions are in <u>radians</u>. An easy check on  $F^2$  is to see that it gives  $Z^2 f^2$  when h = k = l = 0; here Z = 6 is the number of atoms per unit cell.

Multiplicity *m* is looked up or derived for each reflection, and LP factor and *f* depend on  $2\theta$  (or  $sin\theta/\theta$ ). The remaining factor to be calculated is  $V_c = a \cdot b \times c = abccos30^\circ (\neq abc$  in hexagonal systems!). Do the same calculations for the other material and solve for  $v_A$ .

# 7.7 Laboratory 7: Rotating Crystal Method (et al.)

Reading: Lecture notes: "Rotating Crystal Method" (bring to lab), Cullity pp. 111-113, sec 5-2, 5-6, Hammond App. 6 Table A6.1, "Correction Term For Powder Diffractometry" (attached), and Digital Image Plates (Lab Documents Folder).

# Lab Summary

Polyethylene -( $CH_2$ )- crystallizes into an orthorhombic unit cell. One sample has been heated and drawn causing it to have a strong **c**-axis orientation along the draw direction but random in the **a-b** plane. The other is an isotropic polycrystalline sheet.

A) This week you will perform a rotating crystal experiment using the Cylindrical Camera to determine lattice parameter and Miller Indices for an orientated polyethylene sample.

B) For isotropic polyethylene, you will perform PXRD to measure, 1) the average crystallite size, 2) the percent of the crystalline and amorphous phases, and 3) the  $2\vartheta$  peak shift due to sample displacement for the Bragg/Brentano diffractometer geometry.

# Part A: Determine Lattice Parameter and Index Sample

With your instructor's assistance, mount the sample in the cylindrical camera with the sample draw direction along the axis of the camera and insert the Image Plate (IP, a film like image recording media). Mount the camera to a point focus port of a Ni filtered Cu x-ray tube (monochromatic radiation,  $\lambda$ =1.5418Å). Record a diffraction pattern for 5min at 40 kV, 11 mA. Process the IP.

Use the image analysis program "Image Quant" to process your data. You will observe two "layer lines" corresponding to l = 0 and l = 1. With the software, convert the image to an *Intensity vs. Distance* plot and with the peak finder function, locate peak positions. Print data.

After lab:

Use the data from the layer line l = 0 and  $r*_{H}^{2}$  for each of the first two diffraction lines and solve for  $\mathbf{a}^{*}$  and  $\mathbf{b}^{*}$ . You will have two equations and four unknowns. Start by guessing values for *h* and *k*. (Hint: *h* and *k* are not (10) or (01)). Understand that *h* and *k* can only be integers and start with numerically low values. Once  $\mathbf{a}^{*}$  and  $\mathbf{b}^{*}$  are known, you can now index all other diffraction lines (use a spreadsheet program) for both the l=0 and l=1. Do this for six line pairs for each the l = 0 and l = 1 layer lines (12 total). Make a table of the measured  $r*_{H}^{2}$  and compare with calculated  $r*_{H_{calc}}^{2}$  (using the  $\mathbf{a}^{*}$  and  $\mathbf{b}^{*}$  from above) to check accuracy.

# Part B: Perform a PXRD scan

Cu *K*<sub>α</sub>, 40kV, 5mA, DS/SS=2/3°, RS=0.1°(0.6mm), Ni filter, 2ϑ from 10°-50°, step= 0.05°, dwell=1s (L7B).

1) **Determine crystallite size.** Measure the FWHM (convert to radians) for each of the first eight peaks. Use the Scherrer equation to average the results to calculate the apparent average crystallite size D.

2) **Determine percent crystallinity.** Some materials are not totally crystalline or totally amorphous like glass, but a mix of both. In the diffraction pattern, a distinct amorphous halo will be seen mixed with the crystalline diffraction peaks. The percentage of each is determined by the ratio of the integrated intensities after subtracting background i.e.  $%crystallinity = I_{crystalline} / (I_{crystalline} + I_{amorphous})$ . Use the peaks in the range of 2 $\vartheta$  from 10° to 28°.

3) **Peak shift due to sample displacement.** To simulate the error produced by an off-center sample, the instructor will displace the sample holder with the spacer. Rescan  $2\vartheta$  from  $20^{\circ}-23^{\circ}$  (L7B3). Note the peak shift and calculated the thickness of the spacer using the attached handout: "Correction term for Powder Diffractometry." The radius(R) of the Rigaku Ultima diffractometer is 285mm.

# Report

**Part A** 1) Make a table of the peaks #1-6 for both layer lines l=0, l=1 with: x, y, measured  $r*_{H}^{2}$ , *hkl*,  $a^{*}$ ,  $b^{*}$ ,  $c^{*}$ , calculated  $r*_{H}^{2}$ , and Miller Indices. Include the multiple (ambiguous) indexing as appropriate.

2) Make another table with **a**, **b**, **c**,  $V_c$  (unit cell volume).

3) Based on your unit cell parameters and a density of  $1 g/cm^3$ , how many -*CH*<sub>2</sub>- units are there per unit cell?

4) Look for the systematic absences of Miller Indices to determine the Bravais lattice (Hammond Table A6.1).

**Part B** 1) Calculate percent crystallinity, include calculations for background and integrated intensities and L7B plot. 2) The crystallite size calculation with a table of peak widths (degrees, radians) for the first six peaks, and the averaged grain size. Check that the angular size of the RS  $(0.6mm=0.1^{\circ}) < FWHM$  in order to make a valid measurement. 3) For the displaced sample, include plot (L7B3) for the shifted  $2\vartheta$  peak. Referring to the attached handout, calculate (show work) the spacer thickness ( $\vartheta$ ) from the  $\Delta 2\vartheta$  peak shifts. Explain how sample absorption (the depth that x-rays penetrate the sample) can cause shifting of peaks.

#### APPENDIX

**Correction Term For Powder Diffractometry** If the sample is displaced from the center of the powder camera or diffractometer of radius R by a distance of  $\delta(\delta \text{ may be due to misalignment and/or sample absorption}), the following diagram applies:$ 



Figure 7.7: Powder diffractometry geometry

Using  $\frac{\sin(angle)}{\text{side opposite}} = constant$ ,  $\frac{\sin(\Delta 2\theta)}{\delta/\sin\theta} = \frac{\sin(180-2\theta)}{R} = \frac{\sin 2\theta}{R}$ For small errors,  $sin(\Delta 2\theta) \approx \Delta 2\theta = \frac{-\delta sin2\theta}{Rsin\theta} = \frac{-\delta 2sin\theta cos\theta}{Rsin\theta} = -\frac{2\delta cos\theta}{R}$ To determine effect on d, use  $d = \lambda/(2sin\theta)$ 

$$\Delta d = \frac{-\lambda}{2} (sin\theta)^{-2} \Delta sin\theta = \frac{-\lambda}{2sin^2\theta} cos\theta \Delta \theta = \frac{-\lambda \Delta \theta}{2tan\theta sin\theta}$$

$$\frac{\Delta d}{d_o} = \frac{-\lambda \Delta \theta / (2tan\theta sin\theta)}{\lambda / (2sin\theta)} = \frac{-\Delta \theta}{tan\theta} = \frac{\delta cos\theta}{Rtan\theta}$$
$$\frac{\Delta d}{d_o} = \frac{\delta cos^2\theta}{Rsin\theta}$$

Complete Nelson-Riley function also corrects for vertical divergence of beam, leading to additional term of  $cos^2\theta/\theta$ ; see Cullity, p. 356.

# 7.8 Laboratory 8: Single Crystal Epitaxial Thin Film

Reading: C.R.Wie, Introduction sec1,2,3, sec2.1, 3.1, 3.2

# Lab Summary

The sample to be studied is a PTO ( $PbTiO_3$ ) (001) single crystal thin film grown epitaxially by MOCVD on a STO ( $SrTiO_3$ ) (001) single crystal substrate. Several things will be examined: 1) Measure the thickness of the PTO film. 2) Determine the quality (how single crystal it is) of the PTO single crystal film. 3) Generate a simulated data set to compare with raw data to better refine measured parameters.4) Determine the angular resolution limit of the x-ray diffraction system using the "perfect crystal" STO substrate as a standard.

Note you will be using an instrument that has been optimized for thin film diffraction studies. That is: 1) the radiation source is  $CuK_{\alpha 1}$  having  $CuK_{\alpha 2}$  removed by using a monochromator and slit, 2) the incident beam divergence is ~0.02°.

### Introduction

Both materials have the perovskite crystal structures, with the STO substrate forming a cubic perovskite and the PTO forming a tetragonal perovskite structure at RT (room temperature.) The current interest in PTO thin films arises from its ferroelectric properties; under an applied electric field, the  $O^{2-}$  anion sublattice can shift in position with respect to the  $Pb^{2+}$  and  $Ti^{4+}$  cation sub-lattices, resulting a net dipole moment along the **c** axis. This shift is depicted in Figure 7.8 below, which shows an a axis projection of the PTO perovskite at its two different stable polarization states. Investigating this ferroelectric behavior in thin films requires very high crystalline perfection. Since the cubic a-axis lattice constant (a=3.905 Å at RT) of bulk STO matches closely with the a-axis lattice constant of bulk PTO (a=3.905 Å at RT), the PTO film grows in the c-axis direction (for film thicknesses less than a critical thickness of 600 Å). The bulk PTO at RT is tetragonal with a c/a ratio of 1.063 (c = 4.151 Å.)



FIG. 1. The *a* axis projection of the PbTiO<sub>3</sub> tetragonal "up" and "down" perovskite unit cells. For the bulk unit cell at 20 °C a=3.905 Å and c=4.156 Å. For the up unit cell with the origin chosen to coincide with the Pb<sup>2+</sup> ion, the fractional *c*-axis displacement of the three O<sup>2-</sup> ions from the face-centered positions is -0.112 and the Ti<sup>4+</sup> ion from the body-centered position is -0.040(Ref. 1). In comparison, SrTiO<sub>3</sub> is a cubic perovskite with *a* =3.905 Å at 20 °C (Ref. 1). The solid and dashed horizontal lines mark the lattice positions of the (001) and (002) diffraction planes,



### **Experimental Procedure**

- 1. Perform the "Half Beam Alignment" sample alignment procedure with the aid of lab instructor, to align the sample with the x-ray beam.
- 2. Calculate  $2\theta$  for Bragg peaks of both the substrate and film (001) reflections, given that the xray source is Cu  $K_{\alpha 1}$  $\lambda = 1.54056 \text{ Å}$  and move  $2\theta/\theta$  the STO (001) peak. Located and maximize the scattering intensity by making small positional corrections to  $2\theta$ ,  $\theta$  and  $\chi$  to better align the substrate scattering vector to the scatter plane. Perform a " $\omega$  or Rocking Scan" of the STO (001) peak and record the peak width. Rocking scans measure the distribution of plane-normals of the domains within the sample. The smaller the angle, the more "single crystal" it is. Because the STO is a "perfect" crystal, the value will be the minimum angular divergence of the instrument.
- 3. Perform a  $2\theta/\theta$  scan along a path in reciprocal space that passes through the (001) peaks for both the PTO film and STO substrate peaks. Thus you will be able to determine the c lattice constants for both the film and substrate from their respective  $2\theta$  peak positions. Compare these to the bulk values. Depending on the amount of perpendicular

strain on the film due to any lattice mismatch, the peak separation can vary from the amount predicted by the bulk lattice constants of PTO. With the data plotted on a log scale, you will also note the kinematic thickness fringe peaks about the film peak maxima. From the  $2\theta/\theta$  scan it is possible to calculate the film thicknesses from the width of the diffraction peaks by understanding the one dimensional interference function,

 $I(s) = K \frac{\sin^2(M\pi s \cdot c)}{\sin^2(\pi s \cdot c)}$  where the scattering vector magnitude is  $s = 2sin\theta/\lambda$  and M= number of unit cells. Note that the film thickness is t = Mc. This interference function, which is based on simple kinematical diffraction theory, can describe the  $2\theta/\theta$  scan scattered intensity from a thin epitaxial film such as the PTO. This measured intensity I(s) will consist of the primary diffraction peaks from the film and the substrate. It will also show the thickness fringes from the film. From the numerator of the interference function it can be seen that the fringe periodicity (angular spacing) is directly related to the thickness of the film by:  $\Delta s = \frac{1}{tcos\theta}$ .

4. Move  $2\theta/\theta$  to the PTO (001) and locate the peak position. Optimize  $2\theta$ ,  $\theta$  and  $\chi$  again. Perform a rocking scan of the PTO (001) peak and record the peak width. This angular width quantifies the film quality. You can then determine if the film is epitaxial as depicted in Fig. 1. For example, if the film were polycrystalline with no preferred growth direction an  $\omega$ -scan of the PTO peak position would be rather flat and featureless. If on the other hand the  $\omega$ -scan shows a sharp peak then there is a preferred growth direction.

**Simulation of kinematical diffraction** Once c (PTO (001)) and the film thickness t are known, use a spreadsheet program and plot the diffraction pattern from the PTO (001) film using the one dimensional interference function described above plotting log I vs.  $q(A^{-1})$ . Over-lay the simulation output on your  $2\theta/\theta$  data (convert  $2\theta$  to q(A-1)) and re-scale the intensity if necessary. Refine the values of t (M(t)) and **c** so the simulation will best match your data.

### Deliverables

For your report:

- 1. Include the instrument parameter information: slits, target, scan parameters etc,
- 2. Rocking scans plots for STO and PTO with width measured and discuss the significance of each plot.
- 3. A log plot of the  $2\vartheta/\vartheta$  scan over the film and substrate peaks show thickness fringes and calculation of the film thickness.
- 4. A simulation plot with t and c refined for the best match to your raw data (overlaid.) Report the refined values you found for c(PTO (001) and t. (see example below).



Figure 7.9: Simulation plot example

**Simulation example**: A  $2\theta/\theta$  scan at l = 1.540 Å of t ~103 Å thick PTO (001) film grown by MOCVD on a (001) STO substrate. Note the thickness fringes about the broad PTO (001) peak. The solid line is a fit to the experimental data using the interference function corrected for absorption from the film and substrate. (From C. Thompson, C. Foster, J.A. Eastman, and G. B. Stephenson, Appl. Phys. Lett. 71, 3516 (1997).)