

Note: I've finished correcting mistakes from some of the later exams but not the earlier ones. If you see a mistake, plz msg me on AIM:huangnankun or [huangnankun@berkeley.edu](mailto:huangnankun@berkeley.edu), I'll update this document as I get more info and work on it more. Good luck on your revision.

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Exam**  
**October 30, 1992**

**Problem 1:**

(a) Describe the  $\beta$ -ZnS structure and show how it is related to the FCC structure.

**Ans1**

The B-ZnS structure has one compound, presumably Zn filling out the positions of atoms on an FCC structure. A second compound, presumably S fills out the half of the 8 tetrahedral voids in the FCC structure. These voids are displaced from each of the FCC position by  $\frac{1}{4}[1,1,1]$ .

**Ans2**

(b) The  $\beta$ -ZnS structure is adopted by many covalently bonded compounds, like GaAs. Why would this structure be favored? [Ga has valence 3, As has valence 5.]

**Ans1**

Each atom in the B-ZnS structure has 4 neighbors in tetrahedral coordination. Many atoms with a covalent of 4 can naturally arrange themselves in the B-ZnS structure and form 4 bonds with 4 neighboring atoms. For a compound GaAs, a valence 3 element (Ga) and a valence 5 element, As are joined together. The average valence of these 2 joined together is 4 and the average atomic number is equal to that of the group IV element, Ge. Since Ge is diamond cubic, its not surprising that GaAs is in B-ZnS, which is the binary equivalent of the DC structure.

(c) The  $\beta$ -ZnS structure is also adopted by some ionic compounds, like AgI. What characteristic of these compounds would favor  $\beta$ -ZnS over other ionic structures?

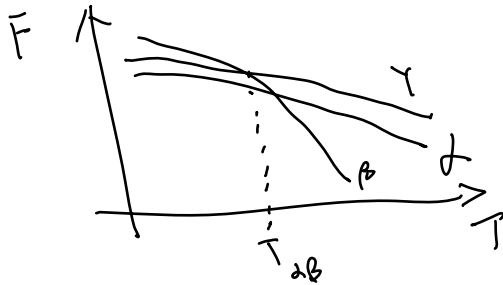
Let R be the ratio of radius of the cation to the anion. The B-ZnS structure is preferred on a structure where  $0.225 < R < 0.414$ . At this ratio, its more favorable for the cations to sit in the tetrahedral voids of the anions. B-ZnS is also more favorable when the bonding is not strongly ionic in which case the a-ZnS will give s lower energy.

**Problem 3:**

(a) A one-component material has three possible structures,  $\alpha$ ,  $\beta$  and  $\gamma$ . At high T the system is  $\alpha$ . If it is cooled slowly it transforms to  $\beta$  at  $T_{\alpha\beta}$ , and remains  $\beta$  for all lower temperatures. If it is cooled quickly it transforms to  $\gamma$  at  $T_{\alpha\gamma} < T_{\alpha\beta}$ . Sketch plausible forms of the G vs. T curves for the three phases that might lead to this behavior.

Such a phase transition can either be a first order phase transition or a second order one.

First order transition



(b) Explain why it is plausible to suppress the transformation  $\alpha \rightarrow \beta$  of part (a) by cooling rapidly to low temperature, but is ordinarily impossible to suppress the reverse transformation,  $\beta \rightarrow \alpha$ , by heating rapidly to high temperature.

For transition  $a \rightarrow b$ , temperature has to be decreased and  $b$  grows out of  $a$  through the process of nucleation. For a nucleation reaction, we can refer to the C curve below. The initiation time for nucleation decreases rapidly when the material is cooled below the transformation temperature. And increases exponentially as it's cooled further into the nucleation limited region. Thus the transformation can be suppressed entirely by cooling the material very rapidly directly into the nucleation limited region and the phase transformation can be suppressed.

For transformation  $b \rightarrow a$ , temperature has to be increased, when temperature is increased, both nucleation and growth becomes easier and thus the initiation time decreases monotonically as temperature increases. Thus it's impossible to suppress this transformation. Heating it rapidly will simply cause the transformation to happen quicker.

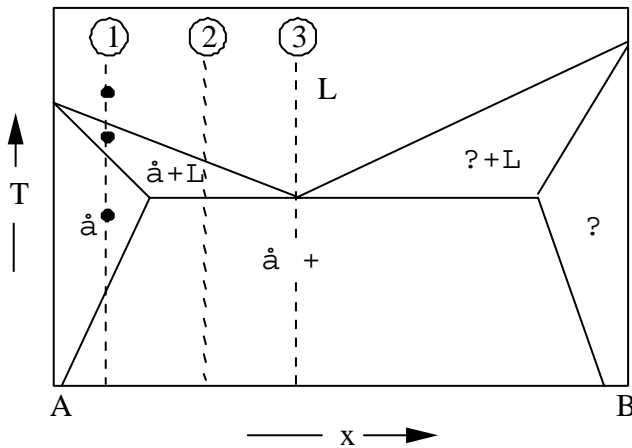
**Problem 4:**

A binary system of atoms A and B has the simple eutectic phase diagram drawn below.



(a) Give the phases present, their compositions and their mole fractions at each of the three points indicated by dots in the phase diagram. (Assume an overall

composition  $x = 0.1$  and give plausible estimates for any other compositions you need.)



First dot

Phase: L

Composition: 10%B and 90%A

Mole fraction: 100% L

Second dot

Phase: a+L

Composition: a 5%B 95%A

L 30%B 70%A

Fraction: 40% L and 60%a

Third dot

Phase: a

Composition: 10%B 90%A

Fraction: 100%a

- (b) Draw the expected microstructure of the solid that forms when a sample of composition 3 is cooled from the liquid phase. Explain why this microstructure should form.

Drawing of eutectic composition



This microstructure is the eutectic microstructure. It's formed because the system remains a liquid until the eutectic temperature is reached. At this temperature the system freezes completely, just as if it had a single component. The eutectic reaction at this point produces the above microstructure with thin plates of one phase alternating with thin

plates of the other or aligned rods of one phase setting in the continuous matrix of the other.

This microstructure forms due to kinetic reasons. Consider a stacking of parallel plates of a and b and let the stack grow into the liquid phase along the stacking of the plates. In order for the A rich plates of the a phase to grow, A atoms must diffuse from the front of the b plates. If the a and b plates are immediately adjacent to one another the distance A atoms must travel is small. So the eutectic microstructure grows with relative ease.

- (c) A sample of composition (1) is solidified by cooling from the liquid into the  $\alpha$  field. Its microstructure contains A-rich dendrites. Explain why these might form.

When the liquid is first cooled into the a+L field, it solidifies over a range of temperature to become a equilibrium phase in a first. It remains homogeneous until its temperature drops into the 2 phase a+b field. At this point small amounts of b crystals start to precipitate out of a. the first crystals that crystallize out of this phase are very "A" rich and this can be seen from the composition given by the tie line.

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Examination**  
**October 26, 1994**

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**Problem 1:**

**(a) Give a brief, 1-2 sentence description of each of the four basic types of chemical bonding.**

- 1) Covalent bonding – all available valence states on the bonding atoms are used by shared electrons; the bonds are saturated.
- 2) Metallic bonding – another type of shared electron bond; the bonds are unsaturated.
- 3) Ionic bonding – one or more electrons are transferred from one atom to another so that the neutral atoms are converted into ions with alternated positive and negative charges
- 4) Dipole bonding – dominant source of bonding between atoms of the noble gases and neutral molecules. It involves no charge transfer; has its source in the distribution of charge in the neutral atom or molecule.

**(b) How might you increase the electrical conductivity of a covalently bonded material (e.g., Si) without changing its basic crystal structure?**

To increase the electrical conductivity of a covalently bonded material like Si, we can add a solute with an excess of electrons. For example, we can add phosphorus to Si. Phosphorus has 5 valence electrons that are sufficient to fill the local covalent bonds with one electron left over. This electron can only go into an excited state, and orbits about the P ion core somewhat. It requires a relatively small energy increment to free this electron from the P core, in which case it can transport current by moving through the lattice. Thus, the conductivity of Si can rise dramatically if a small amount of P is added.

**(c) How might you increase the electrical conductivity of an ionically bonded material (e.g., NaCl) without changing its basic crystal structure?**

To increase the electrical conductivity of an ionically bonded material such as NaCl, we can introduce a paired vacancy in the ionic solid by substituting  $Mg^{++}$  for  $Na^+$  in NaCl to maintain local charge neutrality. This way the electrons can move more easily from bond to bond by exchange with the hole/vacancy, thus increasing electrical conductivity since the energy required for the exchange would be smaller.

**Problem 2:**

The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. The change in entropy in an infinitesimal change of state is

$$dS = \frac{1}{T} \left[ dE + PdV - \sum_k \mu_k dN_k \right]$$

where  $T$  is the temperature,  $E$  is the internal energy,  $P$  is the pressure,  $V$  is the volume,  $\mu_k$  is the chemical potential of the  $k^{\text{th}}$  component and  $N_k$  is the mole number of the  $k^{\text{th}}$  component.

- (a) Let two solids have fixed volumes and chemical contents, and let their temperatures be different. Show that if they interact only with one another energy (heat) flows from the solid with higher  $T$  to the solid with lower  $T$ .

Since energy is conserved the energy gained by subsystem 1 must be lost by subsystem 2. Hence

$$dE_2 = -dE_1$$

**The total entropy change in the process is**

$$\begin{aligned} dS &= dS_1 + dS_2 = dE_1/T_1 + dE_2/T_2 \\ &= dE_1[1/T_1 - T_2] \end{aligned}$$

Since the entropy of an isolated system must increase,  $dS > 0$ . Hence  $dE_1[1/T_1 - T_2] > 0$ . This is true if  $T_2 > T_1$ , which means that energy (heat) must flow from the solid with higher  $T$  to the solid with lower  $T$  (subsystem 1 is gaining energy).

- (b) Let a solid have a fixed chemical content and be in thermal and mechanical contact with a reservoir that fixes its temperature and pressure. Show that the equilibrium of the system is governed by its Gibbs free energy,

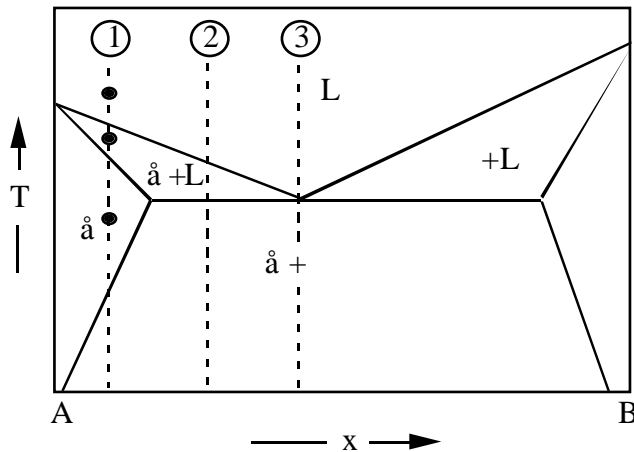
$$G = E - TS + PV$$

which must decrease in any spontaneous change.

See Problem Set 6, #1a.

**Problem 3:**

A binary system of atoms A and B has the simple eutectic phase diagram drawn below.



- (a) Give the phases present, their compositions and their mole fractions at each of the three points indicated by dots in the phase diagram. (Assume an overall composition  $x = 0.1$  and give plausible estimates for any other compositions you need.)

The system is a liquid in the L phase at the first dot (top). Since only one phase is present, its composition is the overall composition,  $x=0.1$ , of the system. The mole fractions do not apply in this case. At the second dot (middle), the system is solidifying in the a+L phase. The compositions are approximately 0.08 a and 0.13 L. The mole fractions are  $f_L = (0.1 - 0.08) / (0.13 - 0.08) = 0.4$  and  $f_a = 1 - 0.4 = 0.6$ . At dot 3 (bottom), the system is a homogeneous solid in the a phase. The composition is  $x=0.1$  in the a phase. The mole fractions do not apply in this case.

- (b) Draw the expected microstructure of the solid that forms when a sample of composition 3 is cooled from the liquid phase. Explain why this microstructure should form.

Microstructure: See p.243 in reader.

This microstructure should form due to kinetic reasons. Consider a stacking of parallel plates of a and B, and let the stack grow into the liquid phase along the long axis of the plates (see figure 9.28 on page 244 in reader)

In order for the A-rich plates of a phase to grow, A atoms must diffuse from the front of the B plates. If the a and B plates are immediately adjacent to one another the distance the A atoms must travel is very small, and lies entirely in the liquid phase, where the atom mobility is high. The B atoms counterflow through the liquid from the front of the growing a plates to the B plates. Hence the eutectic microstructure grows with relative ease.

- (c) Suppose that a sample of composition 1 is held for a long time at the temperature indicated by the dot in the  $\alpha$ -field, and is then cooled to room temperature. What microstructure is likely if the sample is cooled very rapidly? What microstructure if it is cooled slowly? Why?

The sample remains a homogeneous solid in the  $\alpha$  phase until its temperature drops into the two-phase,  $\alpha + B$  field. At that point a small amount of B-rich B-phase precipitates out of the  $\alpha$ . If the sample is cooled slowly enough to remain close to equilibrium then the microstructure be an equiaxed grain structure of the  $\alpha$  solid solution with large precipitates of B in grain interiors and on boundaries. If the sample is cooled very rapidly then the sample would not have the time necessary for the formation of sizable grains of B phase and thus would have only small and tiny amount of B precipitates in grain interiors and on boundaries (see microstructure in Fig. 9.26b on p.242 in reader).

**Problem 4:**

- (a) Why doesn't Ni burn when you touch a lighted match to it in air?
- (b) When Cu and Ni are joined together in sea water, the Ni corrodes rapidly. Why?
- (c) When Cu and Ni are together in sea water, but separated by a thin layer of  $Al_2O_3$ , the rate of corrosion of the Ni is dramatically lower than in case (b). Why?
- (d) In the situation described in (b), Cu does not corrode. But in the situation described in (c), it does, albeit slowly. Why?

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Examination**  
**November 1, 1995**

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**Problem 1:**

- (a) Almost all of the elements that crystallize in the hexagonal close-packed structure are metallic conductors. Why?

Elements that crystallize in the hexagonal close-packed structure are metallic conductors due to their nature of bonding: each atom has twelve neighbors, which makes saturated bonds impossible. In addition, materials that crystallize in the HCP structure are anisotropic, which makes them metallic conductors.

- (b) There are at least a couple of elements that crystallize in the hexagonal close-packed structure and are electrical insulators. How can this be?

- (c) The largest sphere that can be placed in a tetragonal void in a face-centered close-packed crystal of rigid, spherical atoms has radius

$$r_{tet} = 0.225 R$$

where  $R$  is the radius of the spheres that make up the FCC lattice. What is the radius of the largest sphere that can be placed in a tetrahedral void in an HCP lattice of rigid spheres?

The radius of the largest sphere that can be placed in a tetrahedral void in an HCP lattice of rigid spheres is the same as the radius of the largest sphere that can be placed in a tetragonal void in a FCC crystal:  $r_{tet} = 0.225 R$ .

**Problem 2:**

- (a) Carbon diffuses through BCC iron much more rapidly than nickel does. Why?  
 (b) At low to moderate temperature, nickel diffuses through polycrystalline iron more rapidly than through single crystal iron. Why?

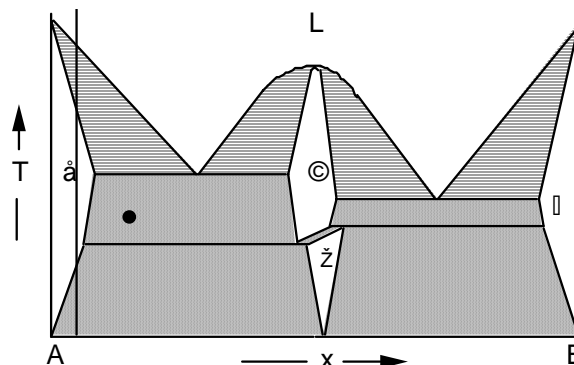
At low to moderate temperature, nickel diffuses through polycrystalline iron more rapidly than through single crystal iron because of the presence of grain boundaries in polycrystalline iron. If the material is polycrystalline, solutes can diffuse along the continuous network of grain boundaries as well as through the bulk of the crystal. Because the diffusion paths have increased, nickel can diffuse faster through polycrystalline iron,

- (c) If an iron-nickel alloy is quenched from high temperature, the diffusivity of nickel has an anomalously high value for a short time after the quench, but eventually decreases to its expected value. Why?

If an iron-nickel alloy is quenched from high temperature the high-temperature vacancy concentration is preserved for some time; the excess vacancies must diffuse to boundaries, dislocations or other sinks before they can be eliminated. Thus, the diffusivity of nickel is anomalously high immediately after a quench.

**Problem 3:**

A binary system of atoms A and B has the complex phase diagram drawn below.





- (a) A possible state of the system is indicated by the dot on the left-hand side of the diagram. Give the phases present, estimate the compositions of the phases, and estimate their fractions when the system is at equilibrium in the state shown by the dot.

The dot indicates the presence of the two-phase: a+Y phase. The compositions are approximately 0.11 a and 0.47 Y. The phase fractions are  $f_Y = (0.2 - 0.11) / (0.47 - 0.11) = 0.25$ , and  $f_a = 1 - f_Y = 1 - 0.25 = 0.75$ .

- (b) Let a liquid with the composition indicated by the vertical line on the left of the phase diagram be cooled slowly enough to preserve equilibrium. Describe the evolution of the system as it is cooled.

As the system is cooled slowly, beginning from the temperature at the top of the vertical line, the system remains liquid in the L-phase until it reaches the temperature at which the line drops into the two-phase, a+L field. It then solidifies over a range of temperature as it is cooled through the two-phase field to become a homogeneous solid in the a-phase. It remains homogeneous until its temperature drops into the two-phase, a+d phase. At that point a small amount of d precipitates out of the a. The volume and content of d phase increase as the temperature is decreased further.

- (c) Suppose that you are given the assignment of growing a single crystal of  $\gamma$  phase that is to be used at room temperature (which, we shall assume, is the temperature at the bottom of the phase diagram). While it may not be possible to do this, it may be possible. Describe the process you would try and explain why it might work.

I would try to cool the system rapidly after the crystal has been in the Y phase for a long time. This way there would not be enough time for sizable grains of other phases to form, and the single crystal of Y phase may be achieved at room temperature.

**Problem 4:**

Liquid silica ( $\text{SiO}_2$ ) can solidify into crystalline quartz or into a glass.

- (a) Sketch the expected form of the kinetic diagram (initiation time vs. temperature below melting point) that governs the solidification of liquid silica.

An upward sloping graph (y-axis=initiation time, x-axis=temperature).

- (b) Why is it always necessary to cool slightly below the melting point to initiate solidification?

The melting point of a solid is defined as the temperature at which the liquid and solid phases are in equilibrium. If the transformation from liquid to solid is kinetically difficult, as structural transformations generally are, the liquid phase may be retained at the melting point. The thermodynamic driving force for the liquid to solid transformation can be increased if the temperature is decreased

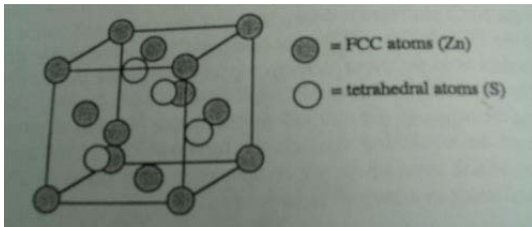
further below the melting point due to the increase in the free energy difference between the two phases.

- (c) To promote glass formation it is common to add ionic species such as  $\text{Na}^+$  to the silica melt. Why do these ionic species promote glass formation? How do they change the kinetic diagram for the transformation?

The addition of ionic solutes to the silica melt can promote glass formation because these solutes form non-directional ionic bonds with adjacent tetrahedral which disturb the local configuration of the tetrahedral and makes it more difficult for them to achieve a crystalline pattern. The graph will shift down.

**(Solution submitted by Erik Tsou)**

Engineering 45  
The Structure and Properties of Materials  
Midterm Examination  
April 3, 1997



words or pictures.  
*tetrahedral void.*

- (b) The  $\beta$ -ZnS structure is a common structure for compound semiconductors, such as GaAs. Why might you expect this?

*In  $\beta$ -ZnS structure, each atom has 4 neighbors of another atom. They form a covalently bonded tetrahedron. It turns out that electrons can only move freely through a covalent solid if they are excited to high energy states that correspond to unoccupied states of the free atom. If the required excitation energy is small, the material will conduct small currents at sufficiently high temperature, and is called a semiconductor.*

- (c) The  $\beta$ -ZnS structure is also adopted by ionic compounds, including some of the silver halides. Why might you expect this? Suggest a simple criterion that explains why some ionic compounds might prefer the  $\beta$ -ZnS structure to the CsCl or NaCl. *The number of anion that surround and coordinate a cation is usually determined by the radius ratio. Many ionic compounds will adapt to  $\beta$ -ZnS structure because the ratio of catio to anion is around  $.225 \leq r^* < 0.414$ .*

$$dS = \frac{1}{T} \left[ dE + PdV - \sum_k \mu_k dN_k \right] \quad 2.1$$

where  $T$  is the temperature,  $E$  is the internal energy,  $P$  is the pressure,  $V$  is the volume,  $\mu_k$  is the chemical potential of the  $k$ th component and  $N_k$  is the mole number of the  $k$ th component.

(a) Let two solids have fixed volumes and chemical contents, and let their temperatures be different. Show that if they interact only with one another energy (heat) flows from the solid with higher  $T$  to the solid with lower  $T$ .

*Since energy is conserved, the energy gained by subsystem 1 must be lost by subsystem 2. hence*

$$dE_2 = -dE_1$$

*total entropy change in the process is*

$$dS = dS_1 + dS_2 = dE_1/T_1 + dE_2/T_2 = dE_1 [1/T_1 - 1/T_2]$$

*where  $T_1$  and  $T_2$  are the temperatures of the two subsystems. The above equation shows that the system can only be in equilibrium if  $T_1 = T_2$ . If this is not the case then  $dS$  is positive for a transfer of energy from the high-temperature subsystem to the low-temperature one.*

(b) Let a solid have a fixed volume and chemical content and be in thermal contact with a reservoir that fixes its temperature. Show that the equilibrium of the system is

$$F = E - TS \quad 2.2$$

which must decrease in any spontaneous change.

(page 152) derivation.

(c) A one-component solid has the phase  $\alpha$  at low temperature and the phase  $\beta$  at high temperature. Show that (at least at low  $T$ )  $E_\alpha < E_\beta$ , while (at least at higher  $T$ ),  $S_\alpha < S_\beta$ .

As  $T \rightarrow 0$ ,  $dS \rightarrow 0$  because compound becomes perfectly ordered. So the conformation energy of the beta phase is higher than that of the alpha phase. At high temperature,  $dS$  is higher in the structure preferred in higher temperature. So  $S_\beta > S_\alpha$  since the beta structure is preferred in higher temperature than the alpha structure.

### Problem 3:

material below by the vector  $\mathbf{b}$ .

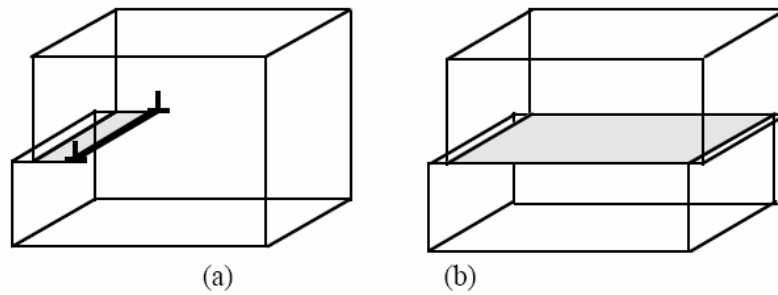
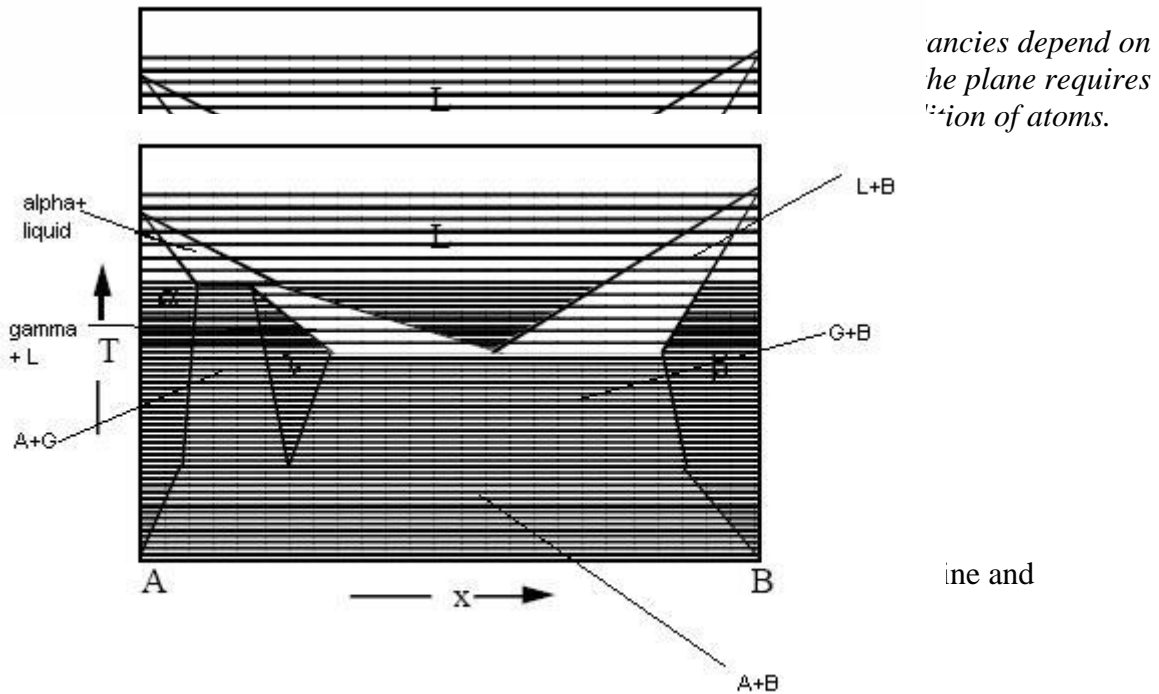


Fig. 4.4: Illustration of the plastic deformation of a crystal by the glide of an edge dislocation.

(c) Describe the mechanism by which an edge dislocation acts as a source or sink



(b) A competitor of your company is selling a material that is  $\gamma$ -phase, with the grain interiors decorated with  $\alpha$ -phase precipitates, for use at room temperature (the lowest temperature in the diagram). Given that it is very difficult to cast a sample of homogeneous  $\gamma$ -phase (because of chemical segregation during solidification), how do you think they do it? [Hint: do this in three steps - get a homogeneous  $\gamma$ -phase template in a composition that permits decoration by  $\alpha$ -phase precipitates, decorate with  $\alpha$ -phase in the interiors of grains, preserve this structure at room temperature. Since you know the

material is being made, it is likely that the most plausible kinetics work

*First...cool it to gamma phase...and homogenize it. Cool it down some more to the A+G field...then quench it. ☺ (pick a composition such that when you cool it down you would reach the G phase & G+A phase)*

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Exam**  
**March 18, 1998**

**Problem 1:**

(a) Describe how the  $\text{Cu}_3\text{Au}$ ,  $\text{NaCl}$  and  $\beta\text{-ZnS}$  structures are derived from FCC.

*NaCl: FCC structure with filled octahedral voids. One set of atoms sits on the sites of the FCC lattice. The other fills the octahedral voids. Since there is one octahedral void per atom in a close-packed structure, the stoichiometric composition is NaCl*

*$\text{Cu}_3\text{Au}$ : This structure is a particular ordering of atoms on the FCC lattice. The Cu atoms occupy the face centers of the FCC unit cell while the Au atoms sit on the corners. Since there are 3 face-centered atoms per unit cell and 1 corner atom, the structure has atom sties in the correct proportion to give the stoichiometric formula  $\text{A}_3\text{B}$ .*

*$\beta\text{-ZnS}$ : This structure is a tetrahedrally coordinated FCC interstitial structure. One component (say Zn) occupies the sites of the FCC lattice while the other (say S) fills  $\frac{1}{2}$  of the tetrahedral voids in the same pattern used in a diamond so that all atoms have precisely 4 equidistant neighbors in tetrahedral coordination.*

(b) Only one of these structures is commonly found in compound semiconductors. Which? Why?

*In  $\beta\text{-ZnS}$  structure, each atom has 4 neighbors of another atom. They form a covalently bonded tetrahedron. It turns out that electrons can only move freely through a covalent solid if they are excited to high energy states that correspond to unoccupied states of the free atom. If the required excitation energy is small, the material will conduct small currents at sufficiently high temperature, and is called a semiconductor.*

*The other structure, the compound cannot form saturated covalent bonds. They are more ionic in nature, therefore not a very ideal semiconductor.*

**Problem 2:**

An interface between two phases is an open system with work function

$$\Omega^S = \sigma A \quad 2.1$$

where A is the area of the interface and  $\sigma$  is its interfacial tension. Given this equation explain the following observations.

(a) A drop of water in free fall takes a spherical shape.

*The preferred shape is nearly spherical, since a spherical shape minimizes the surface area for a given volume. It is also the shape that minimizes its total interfacial energy.*

*We want to find the least sigma. (p170)*

(b) A particle of table salt takes a cubic shape.

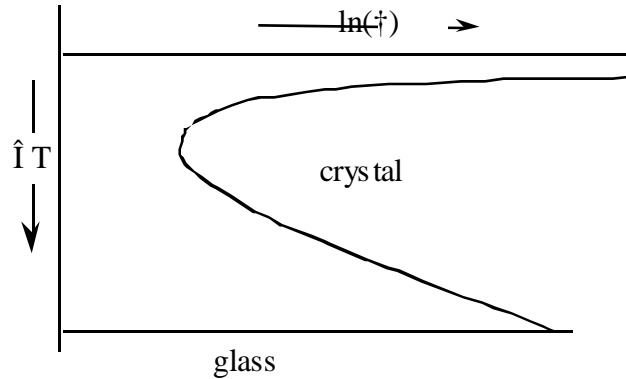
*When the crystal is ionic or strongly covalent there are crystal planes whose tensions are, relatively, very low. To minimize the total interfacial energy, ionic and covalent solids tend to assume polygonal shapes with large, flat facets parallel to the low-energy planes.*

(c) It is a good idea to clean superficial oxides and adsorbed films off of a surface before trying to wet it or bond to it.

*The superficial oxides and films exist on the surface because it lowers the sigma. If we want to wet the surface or bond to it, we should clean the surface of these oxides so that the surface will be easier to bond to since the surfaces "want" something there to lower the sigma.*

**Problem 3:**

The solidification of  $\text{SiO}_2$  is governed by kinetic relations that are roughly reproduced in the figure below, where  $\tau$  is the time necessary to initiate solidification and  $\Delta T$  is the undercooling below the melting point.



(a) Briefly explain why the kinetics of crystallization of  $\text{SiO}_2$  are governed by a c-curve like that shown in the figure.

*As we first cool the system, it becomes easier and easier to overcome the nucleation barrier. However, as we cool down even more and started getting into the growth region, it gets harder and harder because not only do the system need energy to overcome the nucleation barrier but the energy to assemble the atom in the right places. This is why we get the C shaped curve.*

(b) Why is the liquid-glass transformation governed by a horizontal line (at the “glass transition temperature”,  $T_g$ ) as shown in the figure?

*At a low enough temperature, there is not enough energy to order the compound, therefore the homogeneous ordering reaction will initiate spontaneously...forming glass.*

(c) “Glass-forming” species such as Na are added to  $\text{SiO}_2$  to promote glass formation. What is their most important effect on the kinetic relations shown in the figure?

*The addition of Na atoms increases the disorder in the system. It makes it harder to order...thus the spontaneous reaction will occur at a higher temperature. It takes more energy now to form an ordered crystal. So when Na add is added, higher temp is required to provide the energy. This means that the temperature at which the homogeneous ordering reaction will occur is higher.*

**Problem 4:**

The diffusivity of a substitutional component in a crystal with a random distribution of vacancies is given by a relation that can be written in the form

$$D = x_v D_v \quad 4.1$$

where  $x_v$  is the mole fraction of vacancies and  $D_v$  is the diffusivity of a vacancy.

(a) Explain why this relation holds.

*This relation holds because the diffusivity of a crystal is dependent on how much vacancy is present in the crystal.  $D_v$  is a given diffusivity for a vacancy, and the total diffusivity is determine by how much of these vacancy are present...therefore this relation hold because we want to find out the total diffusivity base on how much vacancies are present.*

(b) If the material is cooled quickly from high temperature,  $D$  has an anomalously high value for some time after the quench. Why?

*The equilibrium vacancy concentration is an exponential function of the temperature. If a material is brought into equilibrium at high temperature and then cooled quickly, the high temperature vacancy concentration is preserved for some time; the excess vacancies must diffuse to boundaries, dislocations or other sinks before they can be eliminated.*

(c) If the material is deformed severely enough to force some dislocation climb, D is anomalously high during the deformation. Why?

*Plastic Deformation introduces vacancies to the system thus increase the diffusivity. (page 305)*

**Completed by Brandon Chen =)**  
**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Examination**  
**April 2, 1999**

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**Problem 1:**

(a) Almost all of the elements that crystallize in the hexagonal close-packed structure are metallic conductors. Why would you expect this?

Ans: Refer to pg 65 of the book for HCP  $\alpha$ -ZnS. The HCP  $\alpha$ -ZnS structure tends to appear in compounds that are more ionic in their bonding; therefore they are metallic conductors. The  $\gamma$ -ZnS structure yields a slightly lower energy when the species are ions.

(b) There are at least a couple of elements that crystallize in the hexagonal close-packed structure and are electrical insulators. How can this be?

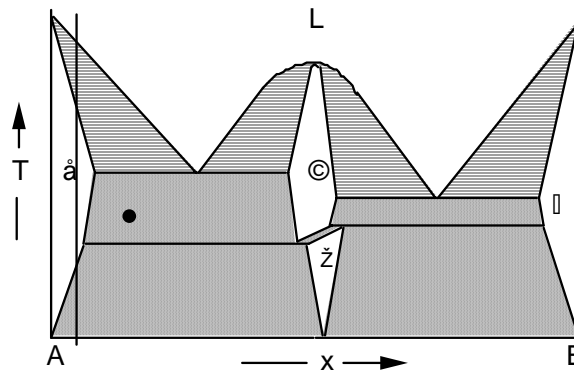
Ans: These elements have large band gaps.

(c) How is the  $\alpha$ -ZnS structure related to the HCP?

Ans: In the  $\alpha$ -ZnS structure, there are atoms on the HCP sites and  $\frac{1}{2}$  of the tetrahedral voids.

**Problem 2:**

A binary system of atoms A and B has the complex phase diagram drawn below. Only the single-phase fields are labelled; the shaded areas are two-phase fields.





- (a) A possible state of the system is indicated by the dot on the left-hand side of the diagram. Give the phases present, estimate the compositions of the phases, and estimate their fractions when the system is at equilibrium in the state shown by the dot.

Phases: alpha + g

Compositions estimate: 80% a, 20% B

Fractions:  $f_B = x - x_a / x_B - x_a = 20 - 10 / 95 - 10 = 10 / 85 = 2 / 17$  mole ratio of B/A

- (b) Let a liquid with the composition indicated by the vertical line on the left of the phase diagram be cooled slowly enough to preserve equilibrium. Describe the evolution of the system as it is cooled.

**Ans: L → alpha + L → alpha only → alpha + B streaks**

- (c) Suppose that you are given the assignment of growing a single crystal of  $\gamma$  phase that is to be used at room temperature (which, we shall assume, is near the bottom of the phase diagram). While it may not be possible to do this, it may be possible. Describe the process you would try and explain why it might work.

Ans: Have 50% a, 50% B and heat to liquid. Cool to moderate temp so g can begin forming, then quickly quench it. If you quench it, you can suspend the material in a meta-stable g phase.

**Problem 3:**

The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. The change in entropy in an infinitesimal change of state is

$$dS = \frac{1}{T} \left[ dE + PdV - \sum_k \mu_k dN_k \right]$$

where T is the temperature, E is the internal energy, P is the pressure, V is the volume,  $\mu_k$  is the chemical potential of the  $k^{\text{th}}$  component and  $N_k$  is the mole number of the  $k^{\text{th}}$  component.

- (a) Let two solids have fixed volumes and chemical contents, and let their temperatures be different. Show that if they interact only with one another energy (heat) flows from the solid with higher T to the solid with lower T.

Ans:

**T1 > T2**

**Assume -dE1 = dE2**

$$ds = 1/T [dE]$$

$$\text{Sum}(ds) = 1/T1(-dE1) + 1/T2[dE2]$$

$$= T_2 (-dE_1)/(T_1 T_2) + T_1 (dE_1)/(T_1 T_2) = dE_1(T_1 - T_2)/(T_1 T_2)$$

Since  $T_1 > T_2$ , the sum of the entropies is POSITIVE. Therefore the heat travels from higher T to lower T and  $-dE_1 = dE_2$ .

- (b) Let a solid have a fixed volume and chemical content and be in thermal contact with a reservoir that fixes its temperature and pressure. Show that the equilibrium of the solids is governed by its Helmholtz free energy,

$$\mathbf{F = E - TS}$$

which must decrease in any spontaneous change.

Ans: Refer to pg. 152

$$ds_2 = dE_2/T = -dE_1/T$$

$$dS = dS_1 + dS_2 = dS_1 - dE_1/T = -1/T [dE_1 - TdS_1] = -1/T * d[[E_1 - TS_1]]$$

The thing inside the [[[ ]]] is  $F = E_1 - TS_1$

In this case,  $S_1$  is like the slope of the function, so if there is a spontaneous change (where  $S_1 > 0$ ), then  $dF < 0$ .

- (c) A one-component solid has the phase  $\beta$  at low temperature and the phase  $\alpha$  at high temperature. Show that (at least at low T)  $E^\beta < E^\alpha$ , while (at least at higher T),  $S^\beta < S^\alpha$ .

Ans: Recall that  $G = E - TS$  and we want G to be the lowest in order for a phase to be represented.

At low temp, the B curve is lower than the alpha curve. Since  $T \rightarrow 0$  at low temp, we assume  $G = E(B)$  and  $E(\alpha)$ .

At high temp, we see the alpha phase. This means the alpha phase has a higher entropy S or a steeper slope. Therefore  $S^\beta < S^\alpha$ .

## Engineering 45

### The Structure and Properties of Materials Midterm Exam March 13, 2000

#### Problem 1:

(a) Describe the  $\beta$ -ZnS structure and show how it is related to the FCC structure.

Ans: Refer to pg. 64. One kind of atom fills the sites of an FCC lattice while the other fills  $\frac{1}{2}$  of the tetrahedral voids.

(b) The  $\beta$ -ZnS structure is adopted by many covalently bonded compounds, like GaAs. Why would this structure be favored? [Ga has valence 3, As has valence 5.]

Ans: It favors a binary structure with total valence = 8, such that each atom has saturated orbitals. The average valence of each atom = 4.

(c) The  $\beta$ -ZnS structure is also adopted by some ionic compounds, like AgI, while substitutionally ordered FCC structures, like  $\text{Cu}_3\text{Au}$  are not. Why is  $\beta$ -ZnS a suitable ionic structure while ordered FCC is not?

Ans: Pg. 62.  $\beta$ -ZnS is a tetrahedral structure, so the same charged ions will be furthest apart from each other. This is not the case for a  $\text{Cu}_3\text{Au}$  structure.

#### Problem 2:

(a) Draw an edge dislocation in a simple cubic crystal.

Ans: You can see one on pg. 84.

(b) Show how the glide of that dislocation produces plastic deformation.

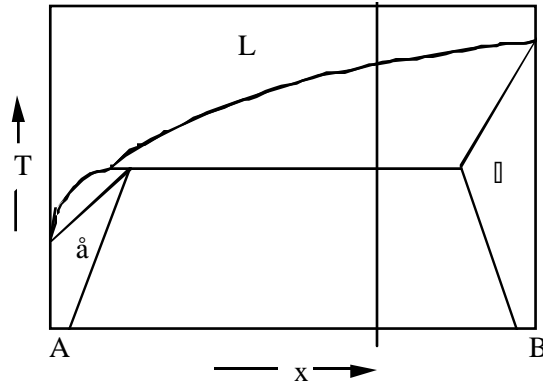
Ans: See diagram on pg. 86

(c) Explain why it is difficult for an edge dislocation to climb unless the temperature is high.

Ans: In order for climb to occur, we must create vacancies or eliminate vacancies. This only occurs at high temperature because the atoms are moving more rapidly and have more energy to do this.

#### Problem 3:

A binary system of atoms A and B has the complex phase diagram drawn below.



(a) Label the two-phase fields in the diagram.

Ans: Underneath the halfway line is  $\alpha + B$ . The other is  $B + L$ .

(b) Let a liquid with the composition indicated by the vertical line on the phase diagram be cooled from the liquid slowly enough to preserve equilibrium. Describe the evolution of the system as it is cooled.

Ans:  $L \rightarrow B + L \rightarrow \alpha + B$  streaks.

(c) Suppose that you are given the assignment of purifying a B-rich solution until it is almost pure B. How would you proceed?

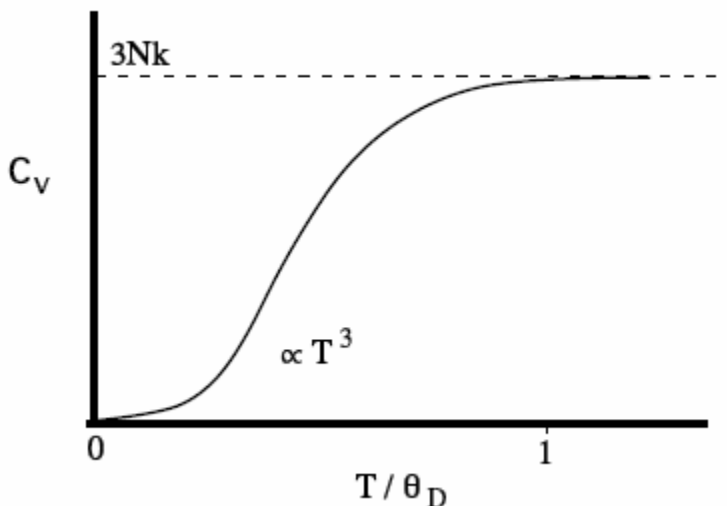
Ans: Heat it up to the  $B + L$  phase then take away the liquid to get only B.

**Problem 4:**

(a) Silica glass is a good thermal insulator, while Ag is not (have you ever drunk chilled wine from a silver goblet?). Why?

Ans: Silica glass contains many dislocations and defects that prevent phonons from colliding with each other and transferring heat energy. There is a small mean free path. Ag crystal is an open structure where phonons can travel through. There is a larger mean free path resulting in more thermal conductivity.

(b) BCC sodium has a higher Debye temperature than HCP sodium. Which of the two phases is likely to be preferred at high temperature? Why?



The specific heat varies with temperature as shown above. Since

$$S = \int_0^T \frac{C_V}{T} dT$$

It follows that the entropy of the phase with a lower Debye temperature is higher and thus it'll be the preferred phase at high temperature since  $F = E - TS$  and crystals always seem to minimize energy. So HCP is the structure preferred at high temperature.

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Exam**  
**March 21, 2001**

**Problem 1:**

(a) Describe the diamond cubic structure and explain why it is a natural structure for group IV semiconductors and insulators (e.g., C, Si, Ge).

The DC or diamond cubic structure can be visualized as an FCC structure with half of its tetrahedral vacancies filled. In such a structure, each atom has 4 equidistant neighbors. Due to this reason, this structure lends itself naturally to group 4 elements which must bond covalently with 4 neighboring elements to fulfill its valence shell.

(b) If a small concentration of P substitutes for Si in the diamond cubic lattice the conductivity increases significantly. Why?

P has a valence of 5 while Si has a valence of 4. When P is put into the lattice, it has an extra electron and this electron is donated to the lattice, thus calling P a donor when it substitutes for Si and this electron is free to move throughout the crystal lattice to conduct electricity.

(c) If diamond transforms to graphite its conductivity increases significantly (in fact, it becomes a metallic conductor). Why?

Diamond has a valence of 4 and in a sheet of graphite, each atom has only 3 neighbors, thus the bonds in graphite become unsaturated (much like bonds in metals) and the free electrons can move within the sheet. However, these electrons cannot move out of the plane of the sheet as graphite planes are held together by van der Waals force. Thus, graphite is an isotropic conductor.

**Problem 2:**

(a) What is meant by the phrase "cross-linking" in a polymer?

Cross-linking refers to the formation of bonds across polymer chains. One characteristic example is the vulcanization of rubber where sulfur joins up chains of rubber together by forming bonds with the carbon.

(b) Good elastomers, like vulcanized rubber, are cross-linked. Why?

Vulcanization cross-links the polymer chains with sulfur bonds; since sulfur has valence 6, it can bond to two carbon atoms and sulfur builds cross-links like those shown below. The cross-links bind neighboring chains and prevent them from sliding with respect

to each other. When vulcanized rubber is stretched, the chains stretch by straightening the kinks at the remaining carbon double-bonds. When the rubber is released, the cross-links ensure that the chains return to their original positions. The strain is elastic, and rubber is a good elastomer.

(c) Thermoplastic polymers are not cross-linked (or very lightly cross-linked). Why?

Thermoplastic polymers are usually made of linear chains of polymer weakly linked to each other so that it'll be easy to deform them plastically once they are heated to a certain temperature and the weak links are overcome by thermal agitation. The presence of extensive cross linking prevents plastic deformation and cause the polymer to be rigid. Polymer with extensive cross linking are usually thermosetting.

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Exam**  
**March 18, 2002**

**Problem 1:**

(a) Draw the face-centered cubic structure (fcc), and identify the positions of the octahedral and tetrahedral voids within it.

*Straightforward*

(b) Describe how the NaCl structure is related to fcc. The NaCl structure is a common structure for binary compounds with ionic bonding, but not covalent bonding. Why?

*The NaCl structure of an AB compound has one element (A) on the fcc sites and the other (B) in the octahedral voids. The structure is a natural for ionic bonding since the nearest neighbors of the A atoms are all B, and the nearest neighbors of the B atoms are all A. It is not favorable for covalent compounds since each atom has six neighbors, making it difficult to saturate covalent bonds by sharing electrons.*

(c) Describe how the  $\beta$ -ZnS structure is related to fcc. The  $\beta$ -ZnS is a common structure for binary compounds that are covalently bonded. Why?

*The  $\beta$ -ZnS structure of an AB compound has one element (A) on the fcc sites and the other (B) in one-half of the tetrahedral void sites (need to indicate which ones by drawing, listing site indices or noting that the ABC stacking of fcc becomes AaBbCc where a, b, c indicate the tetrahedral void sites above each atom in the stacking of close-packed planes). It is a common structure for covalent compounds since each atom has exactly 4 nearest neighbors and, if A and B have an average of 4 valence electrons (valences 4-4, 3-5 or 2-6), one can saturate bonds by sharing electrons among four equivalent covalent bonds to each of the four neighbors.*

**Problem 2:**

Draw an edge dislocation in a simple cubic crystal. Indicate its “Burgers vector” and its “glide plane”.

*The drawing is straightforward. The Burgers vector is one atomic spacing perpendicular to the dislocation line. The glide plane is the plane that contains both the dislocation line and the Burgers vector.*

(b) Show how the glide of an edge dislocation causes plastic deformation.

*Draw or simply state that passing the dislocation all the way through the crystal causes the top half of the crystal to slip over the bottom half by the Burgers vector. This changes the shape of the crystal and is, hence, plastic deformation.*

(c) Now let the dislocation have the form of a circular loop in its glide plane. Show how the expansion of the loop leads to plastic deformation.

*The dislocation loop is the border of an area within which the crystal has slipped by the Burgers vector,  $\mathbf{b}$ . As the loop expands, more and more of the glide plane is slipped. When the loop expands to cover the whole plane, the effect is the same plastic deformation as if an edge dislocation had passed over it; the crystal above the plane has slipped by  $\mathbf{b}$  with respect to the crystal below it.*



**Problem 3:**

The elements A and B have a simple eutectic phase diagram.

(a) Draw a possible form for the phase diagram and label the phase fields. Which phases are solid solutions?

*The drawing is straightforward. The terminal solid phases below the eutectic are solid solutions.*

(b) For any given point in the phase diagram (T,x) you can obtain three pieces of information: the phases present, the compositions of all phases present and the fractions of all phases present. How?

*The phases present from the phase field in which the point (T,x) lies, the compositions from the intersections of an isothermal line with the boundaries of the two-phase field (the composition is just the overall composition if the point is in a one-phase field), and the phase fractions from the lever rule (they should show it graphically on the phase diagram or give the equation).*

*[I have occasionally gotten a question about what you do when the point lies on a line, particularly the three-phase equilibrium line that passes through the eutectic point. This is not an issue since the line corresponds to a perfectly defined temperature, and temperature cannot be controlled exactly in nature].*

(c) Given the phase diagram that you drew, what is the maximum solubility of B in A at one-half the eutectic temperature? Assuming your diagram is drawn correctly, what is the maximum solubility of B in A in the limit  $T \rightarrow 0$ ?

*The maximum solubility is just the composition at the edge of the A-rich solid solution ( ) phase field at 0.5 of the eutectic temperature. The maximum solubility in the limit  $T \rightarrow 0$  is zero by the Third Law.*

**Problem 4:**

(a) The principal contribution to the specific heat of a metal comes from the lattice vibrations. The valence electrons are, ordinarily, much less important. Why are the valence electrons unimportant?

*The valence electrons do not contribute much to the specific heat because, given the Pauli exclusion principle, only that small fraction of the valence electrons that have energies very close ( $<kT$ ) to the Fermi level can be excited into empty states. Only these electrons contribute to the specific heat. Their contribution is small because their fraction is small.*

(b) The entropy of a solid solution of A and B is always higher than the entropy of an ordered compound of the same elements. Why?

*A solid solution has configurational entropy as well as vibrational entropy. An ordered compound has no vibrational entropy.*

(c) While valence electrons do not contribute much to the specific heat of a metal, they are the primary source of its thermal conductivity. Why?

*The thermal conductivity is the transport of heat, which depends on both the number of particles available to transport heat and how fast they move:*

$$k = \frac{1}{3} C_v v \langle l \rangle$$

*where  $k$  is the thermal conductivity due to electrons,  $C_v$  is the electronic specific heat,  $v$  is the electron velocity and  $\langle l \rangle$  is the mean free path. While  $C_v$  is not high, the velocity of an electron is very high, comparable to light speed, while the velocity of a phonon is comparable to sound speed.*

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Exam**  
**March 17, 2004**

**Problem 1:**

(a) The following materials are good electrical insulators: diamond (DC structure), MgO (NaCl structure), and polyethylene (amorphous structure). In each case, explain why you would expect this.

Diamond is a good electrical insulator because there's saturated covalent bonds. The diamond modification of carbon consists of four valence electrons that are covalently bonded and there are no valence electrons left. Because of this saturation, there is no movement of electrons and so there's no electric flow and hence diamond is an electric insulator.

MgO, like NaCl, is ionic, and when there are two atoms of different ionization potentials, Mg<sup>+</sup> and O<sup>-</sup> ions will try to minimize their energies by surrounding themselves with the opposite ion charge. Since the valence electrons are localized and tightly bond to individual ions, there is restricted movement for electrons to move create electric flow and thus ionically bonded solids. Also, MgO, isn't as heavy as ZnO and thus the ionic character is not decreased due to increased weight and so MgO follows the general rule that ionically bonded solids are electric insulators.

Polyethylene is an amorphous structure and irradiated polyethylene result in stronger bonds.

We also know that...

Long molecules => tougher; stronger (chains more entangled)

And the more entangled the chains, the more difficult it to pass electric current and therefore it is an insulator.

**crosslinked polymer** - a polymer that includes interconnections between chains, either formed during polymerization (by choice of monomer) or after polymerization (by adding a specific reagent)

(b) The following materials are excellent conductors: Al, Cu and Na (if you can keep it from oxidizing). What property do they have in common that would cause you to expect this?

The charges on these 3 materials leave unfilled valence electrons and therefore the availability of valence electrons means there is more electron flow and therefore better conductivity.

(c) If I asked you whether Fe or Zn would feel colder to the touch, the values of which material property would you look up? If you could not find this property anywhere, what other property could you use instead?

From the Second Law, we know that temperature differences between two objects will cause heat to flow across decreasing temperature and the stops when there is no temperature difference. Whichever one has a better heat conduction means they will transfer the heat from my hand faster and therefore feel cooler to the touch.

## Problem 2:

The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. The change in entropy in an infinitesimal change of state is

$$dS = \frac{1}{T} \left[ dE + PdV - \sum_k \mu_k dN_k \right] \quad 2.1$$

where  $T$  is the temperature,  $E$  is the internal energy,  $P$  is the pressure,  $V$  is the volume,  $\mu_k$  is the chemical potential of the  $k^{\text{th}}$  component and  $N_k$  is the mole number of the  $k^{\text{th}}$  component.

(a) From the Second Law, show the condition of thermal equilibrium: the temperature of a system is constant at equilibrium; [This problem is solved in Chapt. 7 in the notes.] Consider two neighboring volumes within the material, and let them exchange an infinitesimal amount of energy without changing the volume or chemical content of either. This exchange describes a *thermal interaction*. Since energy is conserved the energy gained by subsystem 1 must be lost by subsystem 2. Hence

$$dE_2 = -dE_1$$

The total entropy change in the process is

$$\begin{aligned} dS &= dS_1 + dS_2 = \frac{dE_1}{T_1} + \frac{dE_2}{T_2} \\ &= dE_1 \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \end{aligned}$$

$$dE_2 = -dE_1$$

the total entropy change in the process is

$$\begin{aligned} dS &= dS_1 + dS_2 = dE_1/T_1 - dE_2/T_2 \\ &= dE_1[1/T_1 - 1/T_2] \end{aligned}$$

where  $T_1$  and  $T_2$  are the temperatures of the two subsystems. Equation 1.2 shows that the system can only be in equilibrium if  $T_1 = T_2$ . If this is not the case then  $dS$  is positive for a transfer of energy from the high-temperature subsystem to the low-temperature one.

Hence the two subvolumes are not in equilibrium with one another unless their temperatures are the same.

The same reasoning applies to any choice of subvolumes within the system. It also applies when the system is not isolated, since a system cannot be in equilibrium if it is out of equilibrium with respect to internal changes that do not affect its environment. We are therefore led to the *condition of thermal equilibrium*, which holds in general: *a system in equilibrium has a uniform temperature.*

$T = \text{const.}$

(b) Let a solid have a fixed volume and chemical content and be in thermal contact with a reservoir that fixes its temperature. Show that the equilibrium of the system is governed by its Helmholtz free energy,

$$F = E - TS \quad 2.2$$

which must decrease in any spontaneous change.  
Pg 151-152. directly copy

(c) A one-component solid has the phase  $\alpha$  at low temperature and the phase  $\beta$  at high temperature. Show that (at least at low T)  $E^\alpha < E^\beta$ , while (at least at higher T),  $S^\alpha < S^\beta$ .

Repeated question from previous midterm

(d) Let a two-component solid have several possible phases. Suppose you know which of those phases has the least free energy for a given set of values, T, P and x. That information is not sufficient to determine the equilibrium state of the system at T, P, x. Why not?

Given that there are several possible phases, we don't necessarily know whether the phase curves will cross each other or not. We only know the values for the least free energy. This information is not sufficient to tell us whether there is a congruent point. If so, the equilibrium state varies depending on whether the curves intersect.

**Problem 3:**

The elements A and B have a simple eutectic phase diagram.

(a) Draw a possible form for the phase diagram and label the phase fields. Which phases are solid solutions?

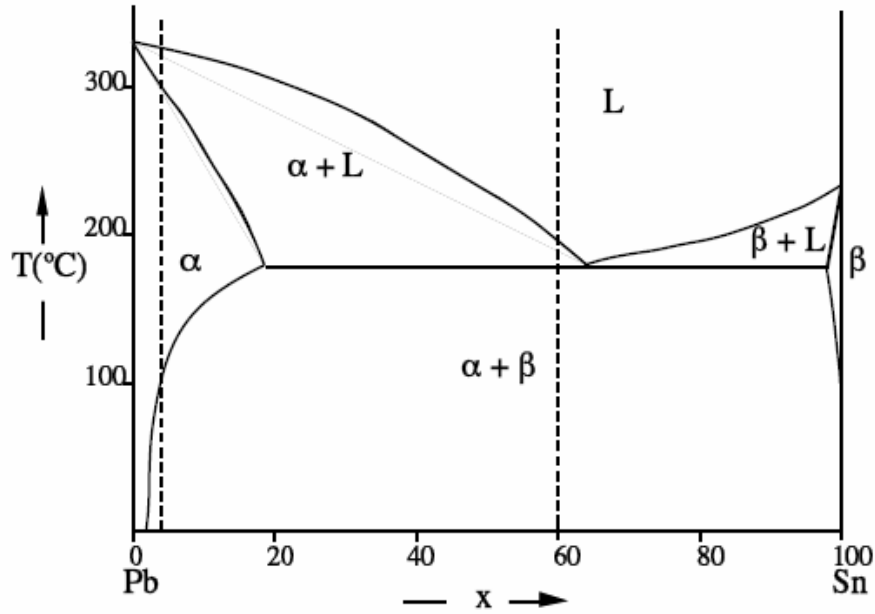


Fig. 7.2: Pb-Sn phase diagram with 60Sn-40Pb and 95Pb-5Sn indicated.

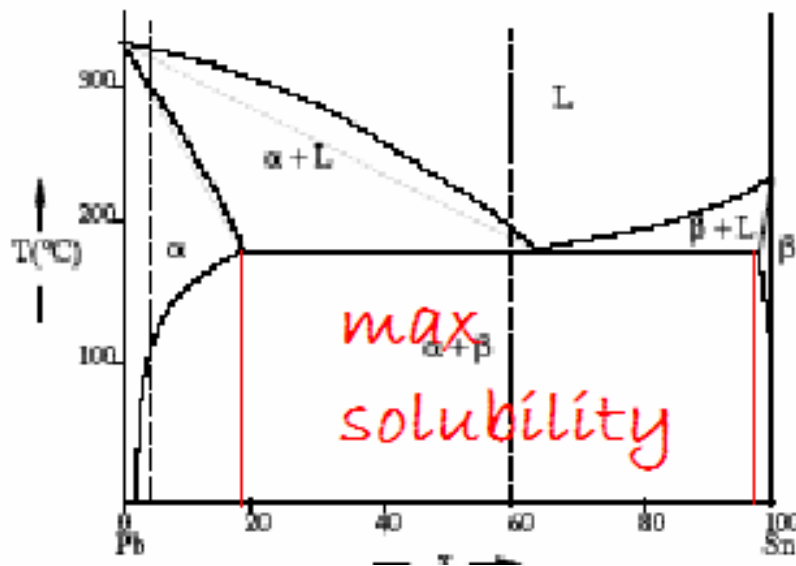
(b) For any given point in the phase diagram  $(T,x)$  you can obtain three pieces of information: the phases present, the compositions of all phases present and the fractions of all phases present. How?

The binary phase diagram is a map of the equilibrium phases that appear in the system as a function of its temperature and composition. It contains three pieces of information for each temperature and composition. First, the phases present at equilibrium at  $(T,x)$  are given by the phase field in which the point  $(T,x)$  appears. In the example given in Fig. 6.1 the equilibrium state is a two-phase mixture of  $\alpha$  and  $\beta$  solid solutions. Second, the phase diagram gives the compositions of the phases present. If the system has only a single phase then its composition is, of course, the overall composition,  $x$ . If the system contains two phases, however, their compositions differ. The two compositions can be found by drawing an isothermal line through the point  $(T,x)$ , as shown in the figure. The compositions of the two phases are given by the intersections of the isothermal line with the boundaries of the single-phase fields on either side of it, as shown in the figure. Third, the fractions of the phase present can be found from the "lever rule". In the example below, the fraction of  $\alpha$ ,  $f_\alpha$ , at  $(T,x)$  is

$$f^\alpha = \frac{x_\beta - x}{x_\beta - x_\alpha}$$

$$f^\beta = 1 - f^\alpha = \frac{x - x_\alpha}{x_\beta - x_\alpha}$$

(c) Given the phase diagram that you drew, what is the maximum solubility of A in B at one-half the eutectic temperature? (Indicate it on your phase diagram – you don't need numbers.) Assuming your diagram is drawn correctly, what is the maximum solub.



(d) You are given a solid that has the overall composition,  $x = .3$  (i.e., the solution is 30 atom percent B). You are asked to extract a pure component (either A or B) from it, where “pure” means 0.9944 pure. Given your phase diagram, which component could you extract in pure form and, qualitatively, how would you do it?

want 99.44% of B

make everything liquid and begin to cool until you get richest in B and pull out all the B and melt again(which shifts the line to the right towards B)

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Exam**  
**March 19, 2003**

**Problem 1:**

(a) Describe the B-ZnS structure and show how it is related to the FCC structure.

B-ZnS structure: Zn occupies the sites of the FCC lattice while the other fills  $\frac{1}{2}$  of the tetrahedral voids from the FCC structure in the same pattern used in diamond so the atoms have 4 equidistant neighbors in tetrahedral shape.

(b) The B-ZnS structure is adopted by many covalently bonded compounds, like GaAs. Why would this structure be favored? [Ga has valence 3, As has valence 5.]

B-ZnS has 4 neighbors and so it is a good structure of covalent bonds. Structures like GaAs have on average 4 valence electrons, perfect to fill the tetrahedral shape with four neighbors so that they are all covalently bonded

(c) The B-ZnS structure is also adopted by some ionic compounds, such as AgI. What features of the B-ZnS structure makes it suitable for ionic materials?

Since all the neighbors of an FCC atom in B-ZnS are tetrahedral atoms, this has a good structure for the alternating pattern of cations and anions necessary for compounds like AgI. Also, there is a stacking pattern such as AaBbCc such that the pattern alternates so we can have cations or anions in the voids and the other in FCC positions.

(d) Consider a series of binary compounds (AB) that bond ionically, let  $R_A$  be the radius of the A ion and  $R_B$  the radius of the B ion. As the ratio  $R_A/R_B$  decreases from 1.0, the structure tends to change from CsCl to NaCl to B-ZnS. Why?

The ratio decreases from 1 as the structure goes from CsCl to NaCl to B-ZnS. CsCl follow the DC configuration where all the ions are spaced pretty far apart. Next NaCl follow FCC and fill the octahedral voids. This reduces the radius by .5. Lastly, B-ZnS fills FCC structure and the tetrahedral voids. There are more tetrahedral voids than octahedral so they are even more packed. The distance is about  $\frac{4}{10}$  of the lattice atom so the ratio is reduced to .4

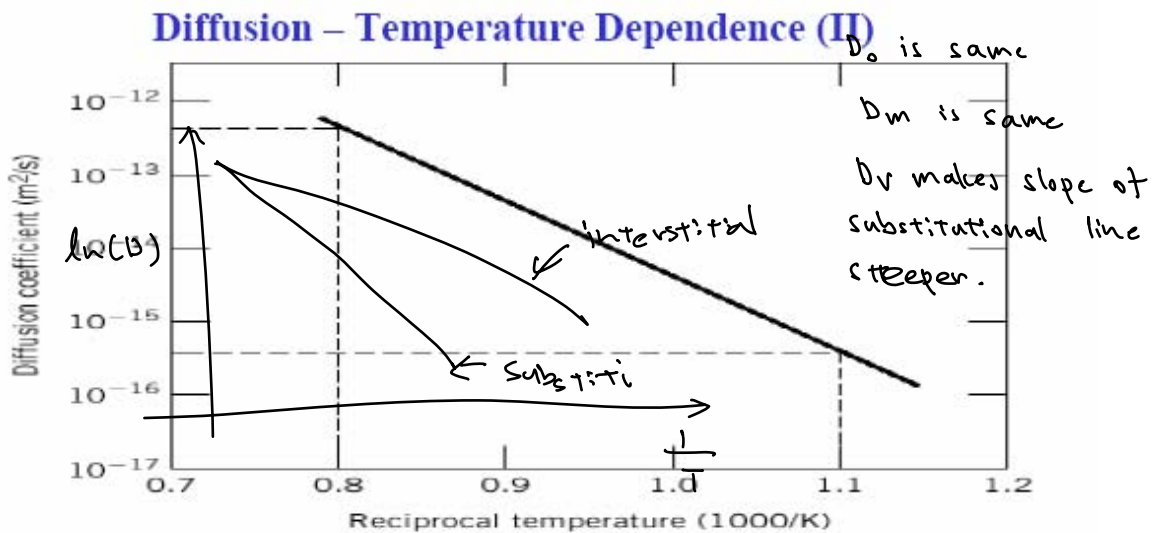


**Problem 2:**

(a) In a given crystal, interstitial species diffuse much more rapidly than substitutional species. Why?

Interstitial doesn't need vacancies. 1/6 times, there is going to be movement and requires only vibrations because it doesn't require the shifting of atoms to create vacancies. This doesn't require diffusion of vacancies. They can diffuse from one site to another to another. In substitutional species, there are vacancies to move other atoms in order to have vacancies for further movement. This is difficult and therefore interstitial species are faster.

(b) Plot, schematically  $\ln(D)$  vs.  $1/T$  for an interstitial and a substitutional species



(c) How would you determine the activation energies for diffusion from this plot? Why are the activation energies similar at low temperature?

At low temperature, interstitial requires high frequency ...at low temperature there is little vibration and so interstitial diffusion is going to go away since atoms can't move through the nonmoving atoms (that otherwise would vibrate) similarly substitutional species can't move since there is no more energy for it to move atoms. Check Gradient

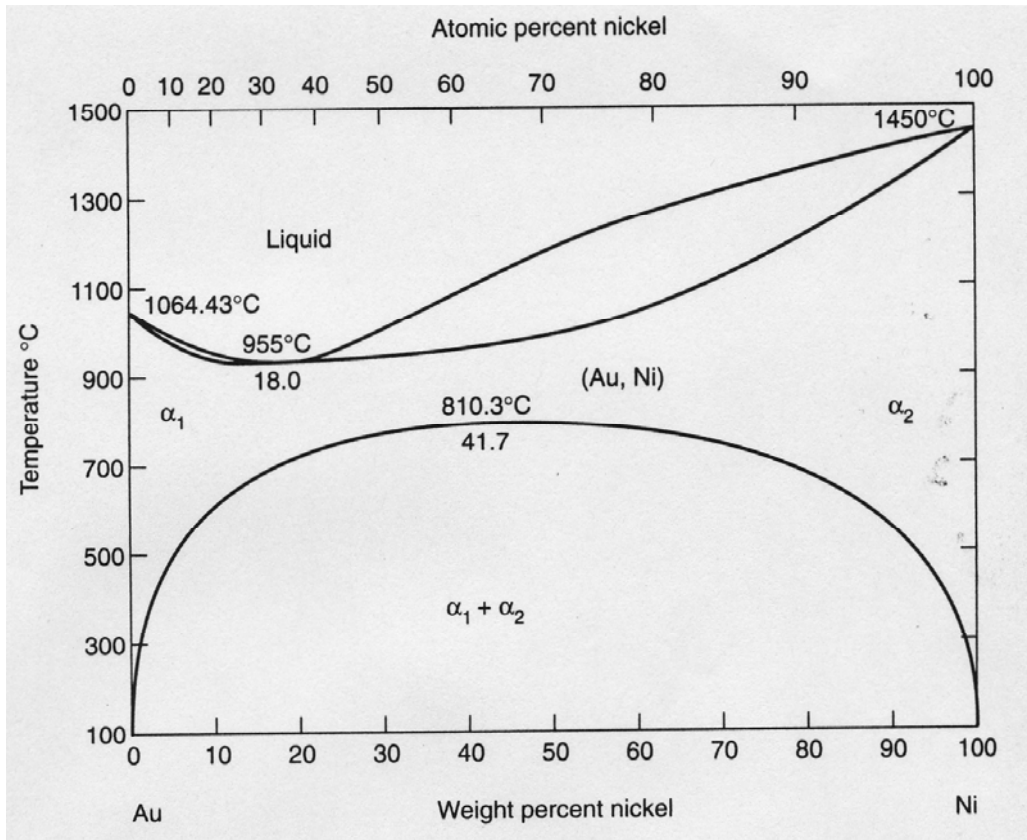
(d) If you quench a crystalline solid from high temperature, the diffusivity of a substitutional species is very high immediately after quenching, but decreases with time until it asymptotes at the value appropriate to the final temperature. Why?

At high temperature, there won't be little beta particles or precipitate in the crystal. This follows the equation number of vacancies =  $A \cdot \exp(-\Delta G/kT)$  At low temperatures, there is random walk diffusion where the vacancies go towards the grain boundaries and then are filled by particles there such that the vacancies disappear as temperature decreases. When the crystalline solid is quenches, there is no time for random diffusion. Accordingly,  $x = \sqrt{2Dt}$  shows that there needs to be time,  $t$ , in order to move a distance  $x$ . In order for the vacancies to move towards grain boundary, there needs to be some time  $t$ . However, quenching doesn't allow for enough time to pass to induce vacancies to

do the random walk diffusion.

**Problem 3:**

A binary system Au and Ni has the complex phase diagram drawn below.



(a) Find the phases present, their compositions and the phase fractions for the following cases ( $x$  = weight percent Ni in the overall system):

		PHASE	COMP	Phase FRACTION
$x = 10$	$T = 900^\circ\text{C}$	alpha	10% Au-Ni	100% of alpha
$x = 10$	$T = 300^\circ\text{C}$	$\alpha_1 + \alpha_2$	$x_{\alpha_1}$ 2% Ni, 98% Au	8.33% of $\alpha_2$
			$x_{\alpha_2}$ 98% Ni, 2% Au	
$x = 50$	$T = 900^\circ\text{C}$	alpha	50% Au-Ni	100% alpha
$x = 50$	$T = 1100^\circ\text{C}$	L+alpha	45% L	50% $\alpha_2$

(b) Au has the FCC crystal structure. Reasoning from the phase diagram, what is the crystal structure of Ni? How do you know?

From the miscibility gap, we know that below the critical temperature at 810C, the solid solution decomposes into separate alpha 1 and alpha 2 (in this case, Au and Ni). Above

this critical temperature and in the miscibility gap, the system freezes into a solid solution alpha which is the same structure, but has different compositions. Therefore if Au has the structure FCC then so does Ni.

(c) Reasoning from the phase diagram, do Ni and Au form stronger bonds to themselves (Ni-Ni and Au-Au) or to one another (Ni-Au)? How do you know? The melting point was lowest when there was Ni and Au as shown by the concave up direction of the phase before everything turned to liquid. Ni-Ni and Au-Au form stronger bonds since they have a higher melting point.

(d) Ni and Au form a solid solution at all compositions at high temperature, but not at lower temperature. Explain this behavior in terms of the interplay of energy and entropy.

3rd law of thermodynamics. Entropy decreases to 0 as  $T \rightarrow 0$  This makes sense as solids are less random than liquids so as we approach solids at lower temperature, entropy is decreased. Energy is vibrational energy. since we want to minimize free energy, as temperature decreases, then vibrational energy will also decrease. this makes sense because solids have less vibrations since atoms are more trapped in their locations.