

**Engineering 45**  
**The Structure and Properties of Materials**  
**Midterm Exam**  
**March 17, 2010**

**Problem 1: (25 points)**

(a) Describe how the Cu<sub>3</sub>Au, NaCl and β-ZnS structures are derived from FCC.

(b) Binary compounds with the Cu<sub>3</sub>Au structure are invariably metals, those with the β-ZnS structure are usually semiconductors, and those with the NaCl structure are usually insulators. Why might you expect this behavior?

**Problem 2 (25 points):**

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<sup>th</sup> component and  $N_k$  is the mole number of the k<sup>th</sup> 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. [Hint: Remember that energy is conserved. If the solids interact only with one another,  $dE_1 + dE_2 = 0$ .]

(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,

$$G = E - TS + PV \quad 2.2$$

which must decrease in any spontaneous change. [Hint: Let the solid and the reservoir together form an isolated system. Then the energy and volume are conserved in any interaction between them. Moreover, the reservoir is, by definition, so large that its temperature and pressure remain constant when it interacts with the system.]

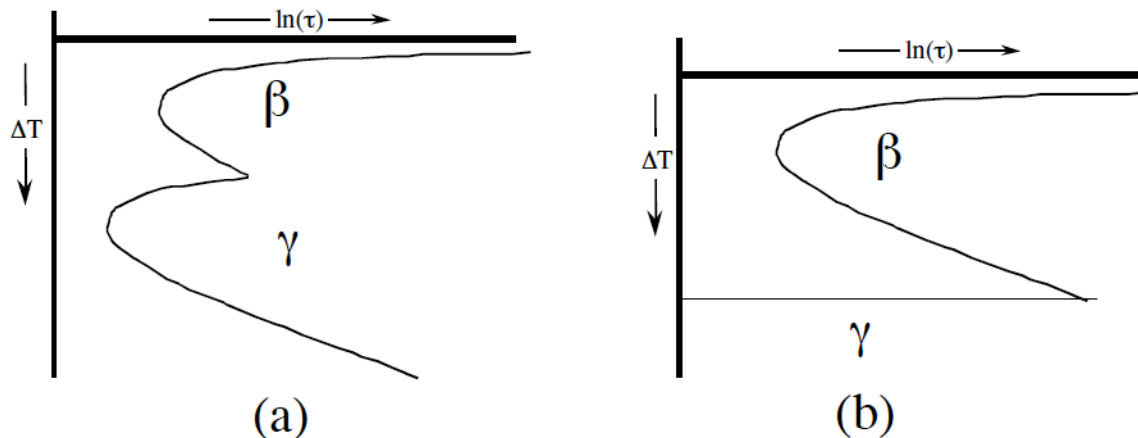
**Problem 3 (25 points):**

(a) A binary system of atoms of types A and B has a simple eutectic phase diagram. The A-rich solid solution ( $\alpha$ ) has a maximum solubility of 8 atom percent B at the eutectic temperature (500 K), but dissolves much less than 1 atom percent B at room temperature (273 K). The B-rich solid solution ( $\beta$ ) has a maximum solubility of 5 atom

percent A at the eutectic temperature, and dissolves 2 atom percent A at room temperature. Show the qualitative form of the phase diagram and label the phase fields.

(b) You are given a sample of the solution that contains 4 atom percent B. You wish to process it into a homogeneous (supersaturated)  $\alpha$  solid solution at room temperature. Starting from the liquid state, describe a thermal processing sequence that might achieve this, and explain why it might work.

**Problem 4: (25 points)**



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  $T < T_{\alpha\beta}$ , and remains  $\beta$  for all lower temperatures. If it is cooled quickly it transforms to  $\gamma$  at  $T_{\alpha\gamma} < T_{\alpha\beta}$ .

(a) Suppose that both the  $\alpha \rightarrow \beta$  and  $\alpha \rightarrow \gamma$  transformations occur by nucleation and growth. Sketch plausible forms of the free energy vs. temperature curves for the three phases that might lead to this behavior.

(b) Are the kinetics of the nucleated transformations more likely governed by fig. (a) or fig. (b)? Explain.

(c) Now consider the case in which phase  $\alpha$  is a liquid, phase  $\beta$  is a crystalline solid and phase  $\gamma$  is a glass. Are the kinetics of the transformation more likely governed by (a) or (b) in this case? Explain.

(d) While it is possible to suppress the  $\alpha \rightarrow \beta$  transformation by rapid cooling, it is not ordinarily possible to suppress the  $\beta \rightarrow \alpha$  transformation by rapid heating. Why?