Materials Science and Engineering
PhD Qualifying Exam

WRITTEN EXAM: **Tuesday, May 16, 2017**
                             9:00AM-1:00PM, 15 Saint Mary's Street, Room 105

ORAL EXAM: **Thursday, May 18, 2017**
                             730 Commonwealth Avenue, Room 301C

General Instructions:

- Calculators are allowed.
- Only the books indicated will be allowed.

1) Please write your EXAM NUMBER on every sheet! Write clearly and legibly as the exam may be scanned to faculty for grading.

2) Complete the Required Sections as below:

Section I: Answer 1 Question
- Introduction to Solid State Physics (PY 543 Chandran) – OPEN BOOK, NO LECTURE NOTES ALLOWED.
- Electrical, Optical, Magnetic Properties of Matls (MS 577 Sharifzadeh) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided).

Section II: Answer 3 out of 4 questions
- **Problems 1 and/or 2:** Thermodynamics and Statistical Mechanics (MS 505, Pal) – OPEN NOTES (1 page, double sided)
- **Problems 3 and/or 4:** Kinetic Processes in Materials (MS 503, Basu) -- – CLOSED BOOK, NO NOTES. Equations and tables (if necessary) will be given in the question.

Section III: Answer 1 Question
- **Problem 1**: Polymers and Soft Materials (MS 504, Tsui) -- OPEN BOOK (Paul C. Hiemenz& Timothy P. Lodge, "Polymer Chemistry". NOTES ALLOWED, but no handwriting.)
- **Problem 2:** Physics of Semiconductor Materials (MS 574, Bellotti) – CLOSED BOOK, CLOSED NOTES.
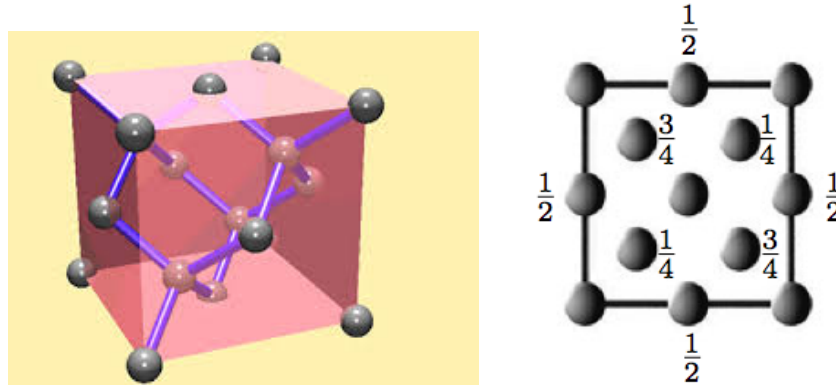
Figure 1: Lattice structure of compound X

The figure shows a picture of the lattice structure for Compound X. On the left, you see one conventional cubic unit cell. On the right, you see a planar view looking down on the $\hat{z}$ axis with the positions of the atoms in the $\hat{z}$ direction indicated. The atoms in the four corners are at $z = 0$ and $z = 1$.

The atoms are all the same and have 4 valence orbitals (which make the 4 bonds that you see emanating from each atom).

1. **(10 pts)** Write down the Bravais lattice type, a set of primitive lattice vectors for this Bravais lattice, and a basis for the corresponding *primitive* unit cell.

2. **(5 pts)** What is the Bravais lattice type of the reciprocal lattice?

3. **(8 pts)** If there is no band overlap, what valences should the atoms have if the material is to be a metal? An insulator? Please explain your logic.

4. **(15 pts)** Calculate the structure factor $S(h, k, l)$ of this compound in terms of the Miller indices (h, k, l). You will notice that some peaks are extinguished. Of the the first 4 extinguished peaks, state which ones are extinguished for any compound with the same Bravais lattice type. Do not count peaks that are related by permuting h, k, and l as distinct i.e. you should count $(1, 0, 0)$, $(0, 1, 0)$ and $(0, 0, 1)$ as one entry.

5. **(5 pts)** How will the structure factor be modified if we take the atoms at $z = 3/4$ and $z = 1/4$ in the conventional unit cell to be heavier than the atoms in compound X?

6. **(7 pts)** Sketch the family of lattice planes corresponding to the first non-zero, non-extinguished peak in the structure factor.

Graphene forms a two-dimensional honeycomb lattice with a two-atom basis

a) The direct lattice vectors of graphene can be described as
$$a1 = a(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}), \quad a2 = a(\frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y})$$
where a defines the distance between nearest neighbor carbon atoms. Calculate the reciprocal lattice vectors and show that the reciprocal lattice is a hexagonal lattice.

b) What are the positions of the basis atoms in this crystal?

c) Now consider a simple 2D hexagonal lattice with one basis atom. Calculate the tight binding energy expression for the valence bandstructure.

d) Considering the tight-binding approximation, what features of the bandstructure can be modified to improve conductivity? How would you modify the material properties to improve conductivity?

1. The objective of this question is to quantify the difference between the isothermal elastic stretching of a material and the isentropic stretching.

   Consider a material of length l and surface area A to which a force is being applied as shown in Figure 1. This force causes only *elastic deformation*. Poison effects can be neglected.

   Note: The Young's modulus E of a material can be defined as $(1/L)(\partial L/\partial \sigma)$

   The stress σ is the force per unit area (A)

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   a. Derive a relation between the isentropic Young's modulus and the isothermal Young's modulus in terms of the known properties of the material (Note: "known properties" are coefficient of linear thermal expansion, heat capacities, temperature, and molar volume).

   b. Assuming that the product of E_T and E_S can be approximated as $<E^2>$, estimate the *relative* difference between the isentropic Young's modulus and the isothermal Young's modulus for a typical metal (e.g. Al, Fe, Cu etc.) at 300 K. (Note: show clearly what estimates you use for the properties; assume specific heat at constant stress is same as at constant pressure; assume coefficient of linear thermal expansion at constant stress for most metals is on the order of 10^{-5} K^{-1}, and you may assume that E is on the order of 100 GPa). Answer should be as % difference between isentropic and isothermal modulus.

2. **a.** Calculate the equilibrium partial pressures of Cd and Pb over a Cd-Pb binary solution containing 20 mole% Cd and 80 mole% Pb at 773 K. The activity coefficients of Cd and Pb in the liquid alloy solution at 773 K are 1.2 and 0.9 respectively. The saturated vapor pressures over pure Cd and Pb at 773 K are 0.0176 atm and 2.16 x 10^{-8} atm, respectively.

   b. Is this a regular solution? Justify your answer.

   c. Relative volatility of A with respect to B at a given temperature is defined as:

   $\alpha_{A-B} = \dfrac{\gamma_A P_A^0}{\gamma_B P_B^0}$, where the gamma terms are activity coefficients of A and B in the liquid solution and the P^0 terms are respective saturated vapor pressures over the respective pure liquid phases. It describes the relative ease with which A can be separated from B (in the liquid solution) by distillation. Assuming the liquid and the gas phase contains only A and B derive a relationship for the concentration of A (mole fraction of A) in the gas phase, $X_{A(g)}$, as a function of the concentration of A (mole fraction of A) in the liquid solution, $X_{A(l)}$,

and the relative volatility of A with respect to B (α_{A-B}). Using the data from part (a) determine α_{Cd-Pb} at 773 K and calculate the expected concentration (mole fraction) of Cd in the gas phase ($X_{Cd(g)}$) when the Cd content in the Cd-Pb liquid phase is 1 mole % ($X_{Cd(l)} = 0.01$). Comment on the prospect of separating these two components by distillation.

May 2017 MSE Qualifier Questions: MS 503

Closed book, NO additional notes

Some physical constants and kinetic formulas that may or may not be relevant:

Gas constant, $R = 8.314$ J/mole-K

Avagadro's constant, $N_{Av} = 6.023 \times 10^{23}$ mole^{-1}

Plank's constant, $h = 6.626 \times 10^{-34}$ J-s

Boltzman's constant, $k = 1.381 \times 10^{-23}$ J/K

Charge of an electron, $e = -1.602 \times 10^{-19}$ Coulombs

$$D(\text{vacancy mechanism}) = \gamma a^2 \nu_D p_v \exp\left(-\frac{\Delta G_m^v}{RT}\right),$$

$$D(\text{interstitial mechanism}) = \gamma a^2 \nu_D \exp\left(-\frac{\Delta G_m^i}{RT}\right),$$

$$D(\text{vacancy mechanism}) = \gamma a^2 \upsilon_D p_v \exp(-\Delta G_m/RT)$$

For chemical reaction: $aA + bB = cC + dD$;

$$D_{gb} = D_{gb}^0 \exp\left(-\frac{\Delta G_m^{gb}}{RT}\right), D_l = D_l^0 \exp\left(-\frac{\Delta G_m^l}{RT}\right)$$

$$\Delta G = V\Delta G_V + A\sigma$$

$$I = (n_0 D_{interface}/\lambda^2) \exp(-\Delta G^*/kT)$$

Problem 3.
a) The oxide MO is non-stoichiometric, with the M/O ratio less than 1. If the majority defects in MO is doubly charged, write **two** possible defect incorporation reactions. Which of these two is **probable**? Explain your reasons. Is the oxide *n*- or *p*-type?

b) During sintering of MO, both cation and anion species need to diffuse; so the **slowest** diffusing species would determine the rate-controlling step. In MO, do you expect anion or cation diffusion to be rate controlling? Explain your reasoning along with any assumptions you have made.

c) In order to reduce sintering time, you need to increase the kinetics of the rate-controlling step. Would you add small quantities of XO_2 or Y_2O to reduce sintering time? Write appropriate defect incorporation reactions to explain.

d) Would you increase or decrease the oxygen partial pressure in the sintering furnace to reduce the sintering time? Why?

Problem 4. The newly discovered element, Bostonium is an FCC metal. There is some debate about the shape of the Bostonium nuclei during **homogeneous** nucleation on solidification. Researchers from Harvard claim that the nuclei are cubic in shape, bounded by 6 {100} surfaces. Researchers from MIT claim that they are tetrahedral in shape, bounded by 4 {111} surfaces. Both groups have submitted $500M proposals to study solidification of Bostonium to back up their respective claims.

a) You claim that having taken MS 503, you can use the 'broken bond model' to resolve this problem without spending any money. Which nuclei shape will be preferred and why?

b) What would be the shape of the nuclei if the surface (interfacial) energy is isotropic (independent of orientation)? Explain.

DATA: For a tetrahedron of side 'a', total surface area $= \sqrt{3}\, a^2$, volume $= \dfrac{\sqrt{2}}{3}\, a^3$.

May 2017 MSE Problem for ME 504 / MS 504 Polymer Physics and Soft Matters

- Open book
- Lecture handouts are allowed provided they do not contain any hand-writings.

1. Consider a polymer with $N = 10$.

   (a) (2 points) What are the criteria in terms of the χ value for a solvent to be (i) good and (ii) poor, respectively?

   (b) (2 points) What is the criterion in terms of the χ value for a solution of the polymer to be miscible?

   (c) (10 points) Can this polymer be immiscible in its good solvent?

   (d) (10 points) Can this polymer be miscible in its poor solvent?

   (e) (16 points) Provide <u>physical</u> explanations for your answers to (c) and (d) **separately**. <u>If you are only comparing χ values against criteria, you will receive zero for this part</u>.

You have an a harmonic oscillator with $\alpha = (mk/\hbar^2)^{1/4}$, where k is the oscillator spring constant and $\omega = (k/m)^{1/2}$ the corresponding frequency. The eigenfunctions solution of the Schroedinger equation are given by:

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi}\, 2^n\, n!} \right)^{1/2} e^{-\frac{\alpha^2 x^2}{2}} H_n(\alpha x)$$

and the corresponding generating function of the Hermite polynomia is:

$$H_n(\xi) = (-1)^n\, e^{\xi^2}\, \frac{d^n\, e^{-\xi^2}}{d\xi^n}$$

− Based on the information you have, you are asked to construct a three-dimensional harmonic oscillator for which the first excite state is doubly degenerate. What parameter do you use/change to construct the 3D Hamiltonian? Write the complete expressions of the eigenvalues and the first three eigenfunctions of the three-dimensional oscillator and explicitly determine the degeneracies.

− Subsequently you are asked to measure the energy of your system. After an infinite number of tests you obtain that the measured value is 50% of the time the ground state, 40% the first excited state, and 10% the second excited state. Write an explicit expression for the state function.

− What is the corresponding expectation value of the energy?