Materials Science and Engineering
PhD Qualifying Exam

WRITTEN EXAM: **Tuesday, January 16th, 2024**
9:00AM-1:00PM, 15 Saint Mary's Street, Room 105

- **NO ELECTRONIC DEVICES** (smartphone, iPad, smartwatch) permitted
- Calculators and a ruler are allowed.
- CLOSED BOOK. Only the notes indicated below will be allowed.

INSTRUCTIONS:

1) Write your **EXAM NUMBER** on every sheet of paper

2) Write clearly and legibly as the exam may be scanned to faculty for grading.

3) **Answer 5 out of 6 questions** completely in the three required sections below:

Section I:
- **Problems 1 and/or 2:** Electrical, Optical and Magnetic Properties of Materials (MS 577, Swan)
    - CLOSED BOOK, 1-ONE-SIDED FORMULA SHEET

Section II: **Problems 3 and/or 4:** Thermodynamics and Statistical Mechanics (MS 505, Pal)
- CLOSED BOOK, 1-ONE-SIDED FORMULA SHEET

Section III: **Problems 5 and/or 6**: Kinetic Processes in Materials (MS 503, Basu)
- CLOSED BOOK, NO NOTES

*AM refreshments and grab n go lunch boxes served

ORAL EXAM: **Thursday, January 18th, 2024**
12:00PM-5:00PM, 15 St. Mary's Street, Room 105

Tentative Oral Exam Schedule		
Time Slot	**Student**	**Committee**
12PM-1PM		
1PM-2PM		
2PM-3PM		
3PM-4PM		
4PM-5PM	Committee Meeting	

Section 1, MS 577

No books or formula sheets allowed.

1. The bandstructure and first Brillouin zone of Na (Sodium) is shown in the figures below where G stands for the Γ point (k=0), and the Brillouin zone boundary points is given by the conventional reciprocal vectors $H\colon \frac{2\pi}{a}\{100\}, P\colon \frac{\pi}{a}\{111\}, N\colon \frac{\pi}{a}\{110\}$. (The indicated vectors b1-b3 are the *primitive reciprocal vectors*). Na has a body centered cubic (BCC) structure, and conventional unit cell size a= 0.423 nm. **Motivate all answers.**

a) Mark the Fermi-level in the bandstructure diagram.

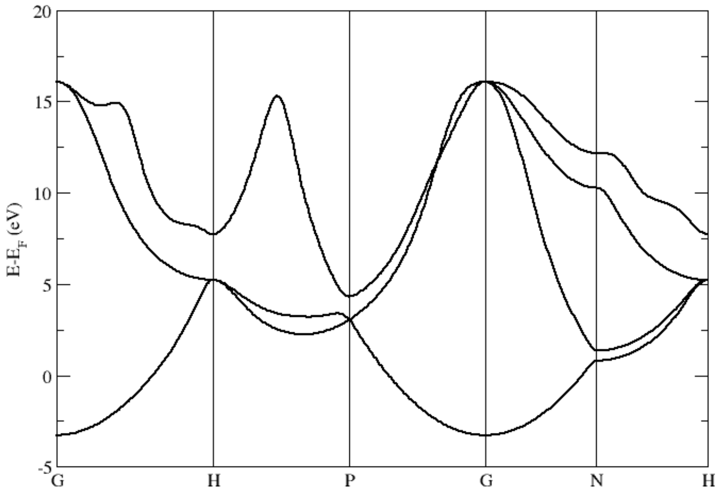
b) What fraction of the 1st Brillouin zone states is filled with electrons?

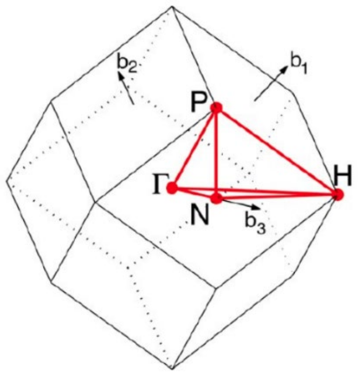
c) Is the Fermi surface for Na gap-free? Is it free-electron like? (i.e., spherical?)

d) Is the reciprocal vector $\frac{2\pi}{a}\{100\}$ involved in opening a gap at the H point?

e) Is the reciprocal vector $\frac{2\pi}{a}\{110\}$ involved in opening a gap at the N point?

f) Does Na have both acoustic and optical phonons?





2. Consider a 1D lattice with a 2-atom basis with mass M1 and M2, located at n*a* and (n+1)*a* for n=1 to N, along the x-axis.
    a. What is the real space unit cell and reciprocal unit cell? Identify the Brillouin zone boundary.
    b. Assume that the atoms are connected by classical springs with force constant C. Write out the equation of motion of atoms along the periodic direction.
    c. Plot a schematic of the phonon dispersion and label the acoustic and optical modes. Discuss the reason for the different energies for the long-wavelength regime (k~0).
    d. Assume the atoms can move in the direction perpendicular to the lattice. Draw a schematic illustrating the motion of atoms for a transverse optical mode near k~0 (long wavelength). Indicate the unit cell.
    e. What is the wavelength (in units of *a*) for a phonon with $k = \frac{k_{ZB}}{10}$?

Section 2: MS 505 Materials Ph.D. Qualifying Examination Thermodynamics

(Allowed: 1-page 1-sided formula sheet and a calculator)

1. It was observed that when the atom percent of Cu was greater than or equal to 12.5 in the Cu-Au alloy ($X_{Cu} \geq 0.125$), Cu_2O formed when exposed to air (79%N_2 and 21%O_2) at 800 C. Assuming that the Cu-Au alloy exhibits a regular solution behavior, express the excess free energy of mixing of the alloy as a function of composition at 800 C. Does the solution have a negative or a positive deviation from ideality? **(60 points)**

   Given: 2 Cu(s) + ½ O_2 (g) = Cu_2O (s), $\Delta G^\circ = -162{,}200 + 69.24T \quad (J)$
   The standard state of Cu is pure solid Cu, that of O_2(g) is pure oxygen gas at one atmosphere and that of Cu_2O is pure solid Cu_2O.

   b. Will the heat of mixing of this Cu-Au alloy change as a function of temperature? Will the Cu-Au alloy ($X_{Cu} = 0.125$) oxidize at 700 C? Justify your answer? **(40 points)**

2. Briefly answer the following questions Not just yes or no. Provide justification. **(100 points)**

   a. Is chemical potential of a component in the system dependent on the choice of standard state for the component? State all factors that determine the chemical potential of a component in the system?
   b. Is the equilibrium constant for a reaction dependent on the choice of standard states of the reactants and the product? For a reaction it is observed that the equilibrium constant decreases with increase in temperature. From this observation can you state if the reaction is endothermic or exothermic and whether the entropy change is positive or negative?
   c. What kind of a solution results in a miscibility gap (phase separation) when cooled? Justify your answer.
   d. How will you experimentally determine if a solution has a regular solution behavior?
   e. Show that in a dilute solution when the solute follows Henrian behavior, the solvent follows Raoultian behavior.

Section 3. January 2024 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, $N_{Av} = 6.023\text{X}10^{23}$ mole^{-1}
Plank's constant, $h = 6.626\text{X}10^{-34}$ J-s
Boltzman's constant, $k = 1.381\text{X}10^{-23}$ J/K
Charge of an electron, $e = -1.602\text{X}10^{-19}$ Coulombs

$$J_1 = -D_1 \,{}^{\partial c_1}\!/_{\partial x} = -L_{11} \,{}^{\partial \mu_1}\!/_{\partial x}, D_1 = B_1 RT\left(1 + \frac{\partial ln\gamma_1}{\partial lnX_1}\right)$$

$$c(x,t) = {}^{S}\!\Big/_{\sqrt{4\pi Dt}} \exp(-x^2/4Dt),\ c(x,t) = A + Berf(x/2\sqrt{Dt}),$$

$$c(x,t) = \frac{4c^0}{\pi}\sum_{j=0}^{\infty}\frac{1}{2j+1}\sin\left(\frac{(2j+1)\pi x}{l}\right)\exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right)$$

$$\overline{c}(t) = \frac{8c^0}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^2}\exp\left(-\left(\frac{(2j+1)}{l}\right)^2 Dt\right)$$

$$D(vacancy\ mechanism) = \gamma a^2 \gamma_D exp\left(-\frac{\Delta G_v}{RT}\right) exp\left(-\frac{\Delta G_m^v}{RT}\right)$$

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

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

$$\frac{\partial \Delta G}{\partial P} = \Delta V; \Delta V_m = 0.15V_{molar}, \Delta V_v = 0.55V_{molar}, \Delta V_{si} = -0.3V_{molar}$$

$$pV = nRT$$

$$D_{eff} = \eta\, D_{gb} + (1-\eta)\, D_l$$

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

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

$$\frac{d[C]}{dt} = -\frac{c}{a}\frac{d[A]}{dt}$$

$$\exp(-\Delta G^0/RT) = \exp(-\Delta g^0/kT) = (a_C)^c(a_D)^d/(a_A)^a(a_B)^b$$

$$\text{Reaction rate} = K_f[A]^{\alpha}\,[B]^{\beta} - K_b[C]^{\gamma}[D]^{\delta}$$

Problem 1.

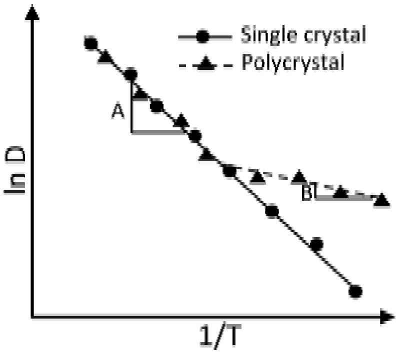
Justify, using figures and equations where necessary, why the following are **TRUE** or **FALSE**. If FALSE, give an alternate statement that is TRUE, wherever possible. (NOTE: Simply guessing TRUE or FALSE with no explanations will not earn you any points, even if the guess is correct!)

i) Matter **ALWAYS** diffuses from regions of high concentration to regions of low concentration.

ii) Atoms diffusing by a vacancies mechanism **ALWAYS** diffuse faster than atoms diffusing by an interstitial mechanism since vacancy diffusion has a smaller activation energy of migration.

iii) Cu atoms in copper diffuse by vacancy mechanism, while Si atoms in silicon diffuse by self-interstitial mechanism. As the hydrostatic pressure, P, increases, self-diffusivity of Cu should **decrease**, while self-diffusivity of Si should **increase**.

iv) The figure shows a famous experiment, with an Arrhenius plot of diffusivity of Ag in a single crystal and a polycrystalline Ag bar. Ag diffuses by a vacancy mechanism. The single crystal points lie on a single line with slope A, while the polycrystal points lie on two lines with slopes A and B. The reason for this is that at higher temperatures, grain growth caused the polycrystalline bar to become a single crystal.



Problem 2.

The oxides of iron are ***p*-type** non-stoichiometric oxides.

a) One form of iron oxide is FeO (wüstite) where the valence of Fe is +2. Write two possible defect incorporation reactions that lead to non-stoichiometry in FeO. Which option is likely and why? How would you write the formula for non-stoichiometric FeO (i.e., $Fe_{1-x}O$, $Fe_{1+x}O$, FeO_{1-x} or FeO_{1+x})?

b) Another form of iron oxide is Fe_2O_3 (hematite) where the valence of Fe is +3. Again, Write two possible defect incorporation reactions that lead to non-stoichiometry in Fe_2O_3 and identify which option is likely and why? How would you write the formula for non-stoichiometric Fe_2O_3.

c) Assume that you have the ability to measure the diffusivity of Fe (D_{Fe}) in iron oxide(s) as a function of p_{O_2} at a fixed temperature. You plot log (D_{Fe}) versus log (p_{O_2}) for both wüstite and hematite at a fixed temperature on the same graph. Explain in **detail**, how the **slope** of the two plots will be different.

DATA: Ionic radii of relevant ions are: O^{-2} = 0.126 nm; Fe^{+2} = 0.076 nm; Fe^{+3} = 0.064 nm