Materials Science and Engineering
PhD Qualifying Exam

WRITTEN EXAM: **Monday, May 22, 2023**
9:00AM-1:00PM, 110 Cummington Mall, Room 245

- **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 **NAME and ANSWER SECTION** on every sheet of paper

2) Write answers on **ONE SIDE only,** clearly and legibly exams will be scanned for grading.

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

Section I:

- **Problems 1 and/or 2:** Electrical, Optical and Magnetic Properties of Materials (MS 577, Sharifzadeh)
  - 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: Answer Question

- **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, May 25, 2023**
9:00AM-4:00PM, 15 St. Mary's Street, Room 105

Individual Oral Exam Time slots will be assigned after grading

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Section I: Electrical, Optical, Magnetic Properties of Materials

Closed Book: One, 1-sided sheet of notes allowed.

1. Ge crystallizes in the diamond structure with the bandstructure shown in Figure 1.

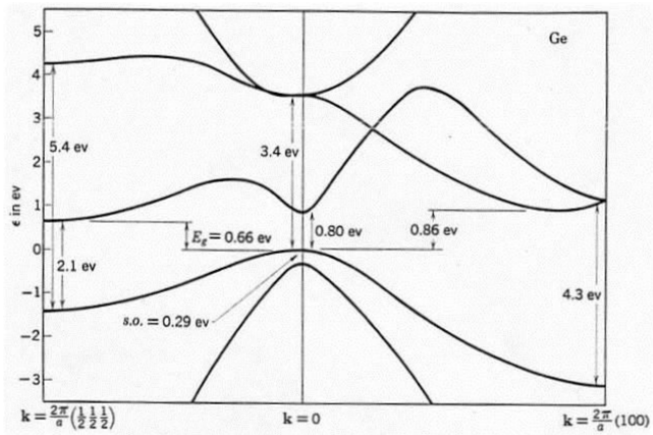

Figure 1: The band structure of Ge with the top of the valence band set to zero energy. Ref: Karol Jan Kuchar Dissertation, Wroclaw (2014)

a) At what k-points are the valence band maximum and conduction band minimum?
b) What is the band gap? Is it direct or indirect?
c) Are electrons or holes heavier?

2. For the 1D crystal with lattice vector a, shown below,

a) Write the equations of motion for u_s. Assume the atoms have mass M.
b) Find the solution for a), assuming they are harmonic plane waves [i.e. *us* is of form $e^{i(ska-wt)}$; s=integer]. In other words, find the ω vs. *k* relationship.
c) How many branches are there? Classify them as optical or acoustic branches.

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Section II: Kinetic Processes in Materials

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, $N_{Av} = 6.023X10^{23}$ mole^{-1}
Plank's constant, h = $6.626X10^{-34}$ J-s
Boltzman's constant, k = $1.381X10^{-23}$ J/K
Charge of an electron, e = $-1.602X10^{-19}$ Coulombs

$$c(x,t) = \frac{S}{\sqrt{4\pi Dt}}\exp(-x^2/4Dt), \quad c(x,t) = A + B\,erf(x/2\sqrt{Dt}),$$

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

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

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

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

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

For MO: $[V_M''][V_O^{\bullet\bullet}] = exp\left(-\frac{\Delta g_S}{kT}\right)$; $[V_M''][M_i^{\bullet\bullet}] = exp\left(-\frac{\Delta g_F}{kT}\right)$

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

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

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

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

$$G = H - TS$$

$$\frac{\varepsilon}{2} = \frac{L_S}{ZN_{Av}}$$

For FCC: $\sqrt{2}a = 4r$

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Section II: Kinetic Processes in Materials

Problem 1.

a) Sintering of TiO_2 powders is rate controlled by the bulk diffusion of oxygen ions in TiO_2. TiO_2 is non-stoichiometric and can be written as TiO_{2-x}. Oxygen ions diffuse in TiO_2 by the vacancy mechanism. Write the reaction leading to non-stoichiometry in TiO_2 and **derive** the dependence of the oxygen partial pressure inside the sintering furnace on the sintering kinetics of TiO_2. If it takes 1 hour to sinter at a pO_2 of 0.3 atm, how long will it take at a pO_2 of 0.1 atm?

b) Two identical shaped samples made of TiO_2 powders are sintered side by side in the sintering furnace. Everything is the same, except the powder size. Sample A has a powder size of 5 µm, while sample B has a powder size of 2 µm. If sample A needs 1 hour to sinter to 98% theoretical density, how long will it take the sample B to reach the same density? **Show all calculations.** The sintering rate can be expressed as: $rate\ \alpha\ \frac{\nabla\mu\ A}{L\ \nabla V}$.

Problem 2.

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 = $\sqrt{3}\ a^3$, volume = $\frac{a^3}{6\sqrt{2}}$.

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Section III: Thermodynamics & Statistical Mechanics of Materials

Closed book: 1-page, double side notes allowed

1. a. Derive a relationship starting from first law that describes the rate of change of temperature of an adiabatic dry parcel of air as it moves up or down in the atmosphere; assume that air behaves as an ideal gas. Given g (acceleration due to gravity) is 9.8 m/s^2 and C_p for dry air is 1,005 J/kg-K what is temperature change of the parcel of air when it moves up 3 km? Discuss the implications of the rate of change of temperature with height if the parcel of air is saturated with water vapor. **(75 points)**

   b. Suppose 30 degree C air parcel at the ground level has a dew point temperature of 14 degree C and it is rising up through the atmosphere. Estimate the altitude at which the clouds begin to form if the dew point drops by 2 degree C/km? **(25 points)**

2. A calorimeter (adiabatic container) containing 3.2 kg of liquid lead at 400 C is used to determine the heat of mixing of two metals, A and B. By previous experiments it was determined that the heat capacity of the liquid lead bath at 400 ^{0}C is 130 J/kg-C. With the bath originally at 400 C, the following two experiments were performed.

- A mechanical mixture of 1 g of A and 1 g of B (both at 25 C) is dropped into the calorimeter. When the two have dissolved, the temperature of the bath is found to have increased by 0.2 C.
- 2 g of a 50/50 (wt. percent) A-B alloy at 25 C is dropped similarly. The temperature decreases by 0.4 C.

a. What is the heat of mixing of the 50/50 (wt percent) A-B alloy (per gram of alloy)? **(70 points)**

b. To what temperature does it apply? **(10 points)**

c. How will you change the experiment if you want to measure the heat of mixing of a 75/25 (wt. percent) A-B alloy at 50 C? **(20 points)**