

Materials Science and Engineering PhD Qualifying Exam

**WRITTEN EXAM: Tuesday, May 19th, 2026
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
- 1) Write clearly and legibly as the exam may be scanned to faculty for grading.
- 2) **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)
CLOSED BOOK, NO NOTES

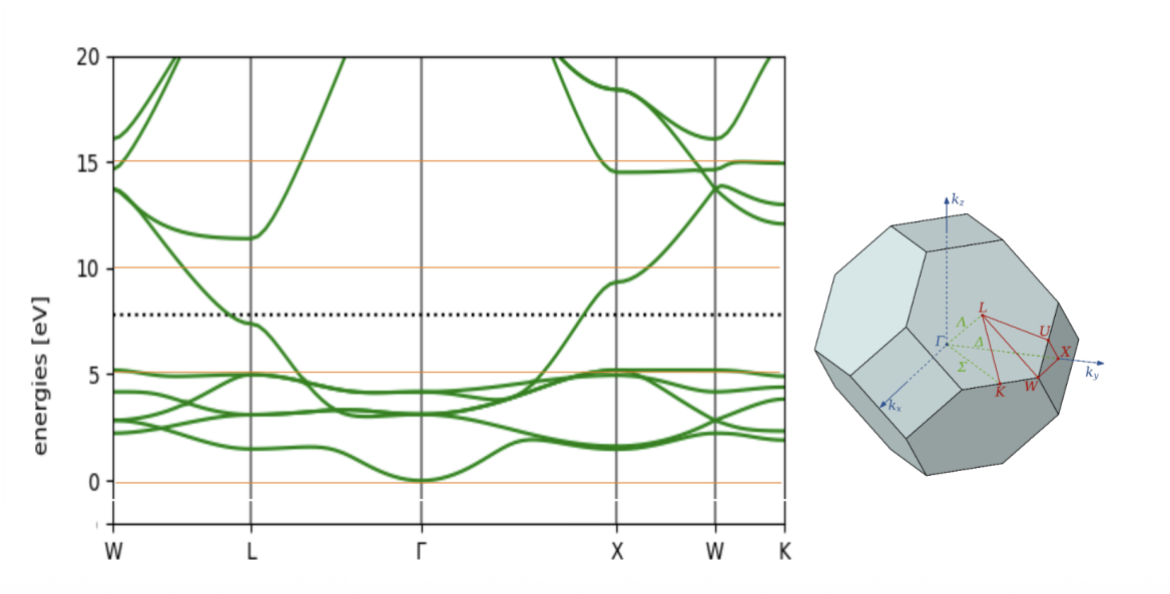
Section II: Problems 3 and/or 4: Thermodynamics and Statistical Mechanics (MS 505, Pal)
CLOSED BOOK, ONE ONE-SIDED FORMULA SHEET & GRAPH PAPER

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

1. Electronic band structure

The figure shows the calculated band structure for a crystal, the Brillouin zone is also shown. The dashed line is the Fermi energy. Using the band structure diagram and Brillouin zone, determine the following and justify each conclusion using features in the diagram. You may annotate the provided band structure diagram and Brillouin zone. For sketches and calculations, show all work and justify conclusions using features visible in the diagrams

- Identify the crystal structure.
- Determine if it is a metal or semiconductor/Insulator
 - **Metal:** Describe the overall shape of the Fermi surface. How does it intersect the Brillouin zone boundaries at the L and X points? Determine the number of valence electrons, and type (s, p, d bands, infer from band shapes).
 - **SC/I:** Determine the bandgap. Is it a direct or indirect SC/I Determine the number of valence electrons, and type (s, p, d bands, infer from band shapes). Mark a direct optical transition on the band diagram (vertical in k-space) and calculate the wavelength of light required ($E = hc/\lambda - hc \sim 1240 \text{ eV} \cdot \text{nm}$).
- Identify one band gap at a zone boundary. Explain the gap-opening in terms of the Fourier component of the periodic potential $|U_G|$. Specify the reciprocal lattice vector $\mathbf{G}$ responsible for this gap.
- In the empty lattice limit (no periodic potential, i.e., no gaps), sketch $E(k)$ for the lowest band along ΓX in the band structure diagram and state the functional form. Use the band structure to estimate the energy at $k=X$ in the empty lattice limit.



2. Phonons and heat capacity

Shown are the crystal structures and phonon dispersion curves for CsCl and Cu. Use the following information: $1.0 \text{ THz} = 4.136 \text{ meV}$; 300 K corresponds to $k_B T = 25.85 \text{ meV}$; at Einstein and Debye temperature, 92% and 94% respectively of the classical Dulong-Petit value of heat capacity is reached.

You may annotate the provided crystal structure diagrams and dispersion curves. For sketches and calculations, show all work and justify conclusions using features visible in the diagrams.

Identify the crystal structure and basis (if needed) for CsCl and Cu.

- For each material, specify the Bravais lattice type, the conventional unit cell, and the basis (number and type of atoms per unit cell).

Match each phonon dispersion curve (labeled A and B) to CsCl or Cu.

- Justify your identification using the number and character of phonon branches visible in each plot.
- Identify branches (A-acoustic/O-optical). Explain why the number of modes is different in A and B.

Material A:

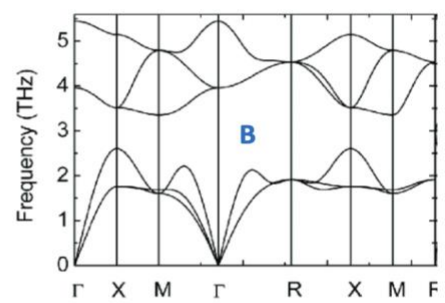
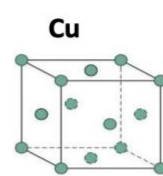
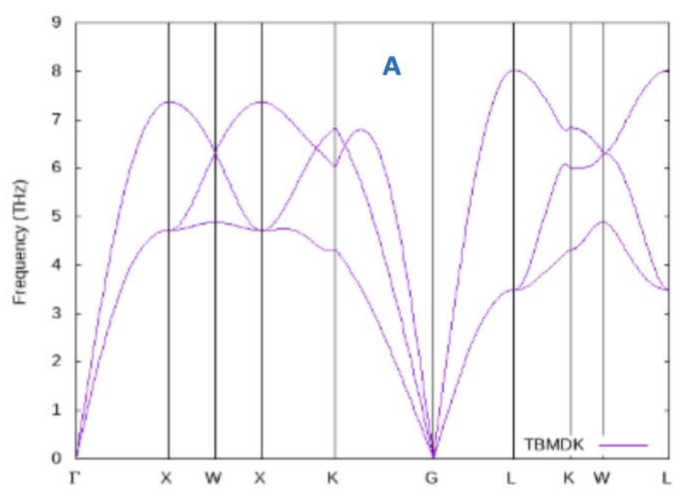
- What model, Debye or Einstein, should be used to calculate heat capacity? Determine the Debye/Einstein temperature from the dispersion curve. Give answer in degrees Kelvin.
- What is the classical Dulong-Petit result for material A (in terms of # of k_B /atom)?

Material B:

- What model, Debye or Einstein, should be used to calculate heat capacity? Determine the Debye/Einstein temperature from the dispersion curve. Give answer in degrees Kelvin.
- What is the classical Dulong-Petit result for material B (in terms of # of k_B /atom)?

At very low temperature ($T \rightarrow 0$):

- Does the heat capacity of Cu and CsCl differ qualitatively? What are the contributions to C_v in each case?



MS 505: Thermodynamics and Statistical Mechanics of Materials – PhD Qualifying
Exam – Spring 2026

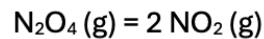
Problem 1

A binary substitutional solid solution A–B forms on a single lattice. At sufficiently low temperatures, a miscibility gap exists in this system. The molar Gibbs free energy of mixing is described by a regular solution model with the interaction parameter $\alpha = 20 \text{ kJ/mol}$.

- Compute the critical temperature – the temperature below which the system phase separates into two solid solutions. Schematically draw the miscibility gap that forms in this system.
- Find the temperature at which the composition of one of the co-existing phases in the miscibility gap is $X_B = 0.75$; What is the composition of the other coexisting phase?
- Consider the state of a system of composition $X_B = 0.4$ at a temperature of 1000 K. Does this state correspond to a stable, metastable or unstable state? (50 points)

Problem 2

Consider the gas phase reaction,



- Initially the system has 1 mole of $\text{N}_2\text{O}_4 (\text{g})$. At a fixed temperature, assuming a total pressure of P (atm), compute the degree of dissociation (β) at equilibrium. The degree of dissociation β may be defined as the number of moles of $\text{N}_2\text{O}_4 (\text{g})$ that have reacted. Your answer should be in terms of the equilibrium constant K_{eq} and the total pressure P .
- Based on the expression you derived in Part a, mathematically examine the limits of β at very high and very low pressure. Explain your results in terms of the LeChatelier principle.
- The standard enthalpy change for the reaction $\Delta H^0 = 57.2 \text{ kJ/mol}$ and can be assumed to be constant through the temperature range of interest. Further, it is known that at 298 K, the equilibrium constant is 0.144. Using the van't Hoff equation compute the equilibrium constant at 400 K. Assuming a total pressure of 10 atm, compute the degree of dissociation at 298 K and at 400 K. Explain your results using the LeChatelier principle. (50 points)

May 2026 MSE Qualifier Questions: MS 503

Closed book, NO additional notes

Some physical constants, equations and tables that may or may not be relevant:

Gas constant, $R = 8.314 \text{ J/mole-K}$
Avagadro's constant, $N_{Av} = 6.023 \times 10^{23} \text{ mole}^{-1}$
Plank's constant, $h = 6.626 \times 10^{-34} \text{ J-s}$
Boltzman's constant, $k = 1.381 \times 10^{-23} \text{ J/K}$
Charge of an electron, $e = -1.602 \times 10^{-19} \text{ Coulombs}$
 $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

Fick's Laws and solutions:

$$J = -D \frac{\partial c}{\partial x}, \quad \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right)$$

$$\text{Thin film solution: } c(x,t) = \frac{S}{\sqrt{4\pi Dt}} \exp(-x^2/4Dt)$$

$$\text{Error function solution: } c(x,t) = A + \text{Berf}(x/2\sqrt{Dt})$$

$$\text{Degassing (series) solution: } c(x,t) = \frac{4c^0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin\left(\frac{(2j+1)\pi x}{l}\right) \exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right)$$
$$\bar{c}(t) = \frac{8c^0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right), \quad \frac{\bar{c}}{c_0} = \exp\left(-\frac{t}{\tau}\right), \quad \tau = \frac{l^2}{\pi^2 D}$$

Other general diffusivity relationships:

$$x \sim \sqrt{Dt}, \quad D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad \frac{Q}{R} = \frac{q}{k}$$

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

$$D(\text{vacancy mechanism}) = \gamma a^2 \nu_D p_v \exp\left(-\frac{\Delta G_m^v}{RT}\right), \quad p_v = \exp\left(-\frac{\Delta G_v}{RT}\right), \quad \nu_D = \frac{kT}{h}, \quad \gamma = \frac{Z}{6}$$

Point defects in non-stoichiometric oxides:

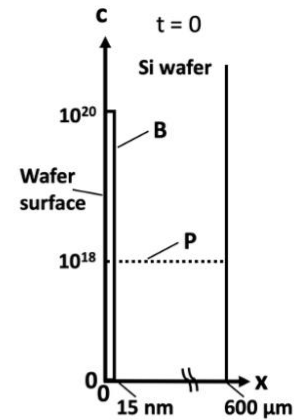
$$\text{For MO: } [V_M''] [V_O^{\bullet\bullet}] = \exp\left(-\frac{\Delta g_S}{kT}\right); \quad [V_M''] [M_i^{\bullet\bullet}] = \exp\left(-\frac{\Delta g_F}{kT}\right)$$

$$\text{For the reaction: } aA + bB \leftrightarrow cC + dD, \quad \exp(-\Delta G^0/RT) = (a_C)^c (a_D)^d / (a_A)^a (a_B)^b$$

$$\text{For point defects, } a = X, \text{ for gas phase } O_2, a = p_{O_2}$$

Problem 1. Si (with 4 valence electrons) doped with phosphorous (P, which has 5 valence electrons) is considered *n*-doped, while Si doped with boron (B, which has 3 valence electrons) is considered *p*-doped.

A 600 μm thick Si wafer is uniformly *n*-doped with P at a concentration of 10^{18} atoms/ cm^3 . The surface of this wafer is implanted with B (*p*-type dopant) such that the B concentration in a 15 nm layer at the surface is uniform at 10^{20} atoms/ cm^3 , and zero in the rest of the wafer, as shown in the figure. The wafer is then annealed for 1 hour at 1000°C , causing B to diffuse into the Si wafer.



a) Which solution (thin film, error function, series solution, etc.) would you choose to best describe the B diffusion profile in the Si wafer? Explain your answer.

b) The diffusivity of B in Si is $5 \times 10^{-16} \text{ cm}^2/\text{s}$ at 900°C , and $10^{-12} \text{ cm}^2/\text{s}$ at 1100°C . Assuming an Arrhenius temperature dependence of diffusivity, what is the diffusivity of B in Si at 1000°C ?

c) The *p-n* junction corresponds to the location in the Si wafer where the concentrations of *n* and *p* dopants are equal. What is the depth of the *p-n* junction from the surface (in nm) after the 1 hour anneal at 1000°C ?

d) Where would the *p-n* junction be located if the wafer is annealed for a very long (infinite) time at 1000°C ?

Problem 2. NiO is a *p*-type oxide when non-stoichiometric.

a) What are the two possible major point defects that can occur in non-stoichiometric NiO (for this part do not consider if the defects are likely or unlikely, only possible)? Write the defect reactions for both defects. Assume for this part of the question, the magnitude of the effective charge of the dominant point defect is 2 (i.e., +2 or -2 depending on your answer).

b) Which one of the two is more likely? Justify. Would you express non-stoichiometric NiO as Ni_{1-x}O , Ni_{1+x}O , NiO_{1-x} or NiO_{1+x} ?

c) Based on Part b), do you expect the ratio $\frac{[V_{\text{Ni}}'']}{[V_{\text{O}}']}$ to be $\gg 1$ or $\ll 1$? Explain.

d) Now assume that it is not known if the effective charge of the vacancies is +/- ('+' for oxygen vacancies, and '-' for nickel vacancies) 1 or 2. Your laboratory is equipped to measure the diffusivity of Ni (D_{Ni}) in non-stoichiometric NiO as a function of T and p_{O_2} . What experiment would you carry out to determine if the effective charge of the vacancies is (+/-) 1 or 2? Explain clearly what you would measure as a function of what variable. Write the appropriate defect reactions and clearly state the predictions for both cases? Use appropriate equation and figures to explain your answer.

