

Materials Science C



November 15-23, 2025

Instructions:

- You will have **50 minutes** to complete your exam. At the end of this time period, you must stop working. Partial credit will be awarded, so attempt as many questions as you can, and show your work!
- **Reference Materials:** Please follow national Science Olympiad rules for reference materials. Do not consult the internet, artificial intelligence, or any outside sources.
- **Calculator:** You may use a Class III graphing calculator (see Science Olympiad rules for calculator classes)
- This test is graded out of **120 points**. The highest score wins.
- Have fun!

School/Team Name: _____

Team Number: _____

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1 Multiple-Choice Questions (26 points)

1. (1 point) The theoretical maximum packing efficiency of the hexagonal close-packed structure is:
 - A. 67.0%
 - B. 74.0%**
 - C. 52.4%
 - D. 80.0%
2. (1 point) Which pair of elements would exhibit the greatest degree of covalent character according to Pauling's scale of electronegativity?
 - A. Na-Cl
 - B. Si-O
 - C. Mg-F
 - D. Al-N**
3. (1 point) The Born exponent n is the Born-Mayer potential is most closely related to:
 - A. The compressibility of the crystal**
 - B. The ionic radii ratio
 - C. The polarizability of the anion
 - D. The bond dissociation energy at zero separation
4. (1 point) A polycrystalline metal contains a tilt boundary formed by an array of edge dislocations. The grain boundary energy per unit area depends on the misorientation angle θ . If the grain boundary energy is 200 mJ/m^2 at $\theta = 5^\circ$, which of the following best described the expected energy at $\theta = 10^\circ$?
 - A. Exactly 400 mJ/m^2
 - B. Less than 400 mJ/m^2**
 - C. Greater than 400 mJ/m^2
 - D. Exactly 200 mJ/m^2
5. (1 point) Which imperfection introduces tensile stress fields in the surrounding lattice?
 - A. Interstitial atom
 - B. Vacancy**
 - C. Edge dislocation extra half-plane
 - D. Screw dislocation
6. (1 point) The burgers vector \mathbf{b} of a perfect dislocation in a BCC metal is:
 - A. $a\langle 100 \rangle$
 - B. $\frac{a}{2}\langle 111 \rangle$**
 - C. $a\langle 110 \rangle$
 - D. $\frac{a}{2}\langle 110 \rangle$
7. (1 point) Diamond has $k \sim 2000 \text{ W m}^{-1} \text{ K}^{-1}$, $\rho = 3500 \text{ kg/m}^3$, $c_p = 500 \text{ J kg}^{-1} \text{ K}^{-1}$. Its thermal diffusivity is roughly:
 - A. $10^{-8} \text{ m}^2/\text{s}$
 - B. $10^{-5} \text{ m}^2/\text{s}$
 - C. $10^{-4} \text{ m}^2/\text{s}$

- D. $10^{-3} \text{ m}^2/\text{s}$
8. (1 point) Zirconium tungstate (ZrW_2O_8) exhibits isotropic negative thermal expansion over a broad temperature range. This counter-intuitive behavior is primarily due to:
- A. **Rigid-unit transverse vibrations of WO_4 and ZrO_6 polyhedra**
 - B. Electronic delocalization upon heating
 - C. Cation-anion size-mismatch strain relief
 - D. Magnetostrictive domain reorientation
9. (1 point) In diamond, the presence of the ^{13}C isotope (1.1 % natural abundance) introduces phonon scattering that limits its thermal conductivity. The scattering rate due to isotopic disorder scales with the mass variance ($\Delta M/M$)². This type of phonon scattering is known as:
- A. **Mass-defect (isotope) scattering**
 - B. Phonon-electron scattering
 - C. Phonon-phonon Umklapp scattering
 - D. Grain-boundary (surface) scattering
10. (1 point) Creep is time-dependent deformation under constant stress. Primary creep exhibits:
- A. Increasing strain rate
 - B. **Decreasing strain rate**
 - C. Constant strain rate
 - D. Rapid failure
11. (1 point) Flexural strength (modulus of rupture) is determined from a three-point bend test by:
- A. **Maximum tensile stress at fracture**
 - B. Maximum compressive stress at fracture
 - C. Maximum shear stress at mid-span
 - D. Average stress across section
12. (1 point) In tungsten carbide (WC), the thermal expansion coefficient is $\alpha = 5 \times 10^{-6} \text{ K}^{-1}$, whereas for cobalt binder $\alpha = 13 \times 10^{-6} \text{ K}^{-1}$. Under rapid heating, this mismatch causes:
- A. Compressive stress in WC
 - B. **Tensile stress in WC**
 - C. No stress
 - D. Shear failure only
13. (1 point) The Guinier approximation in small-angle X-ray scattering is valid for $qR_g < 1$, where $q = 4\pi \sin \theta/\lambda$ and R_g is the radius of gyration. It predicts $\ln I(q) \propto -q^2 R_g^2/3$. This allows direct extraction of
- A. crystal size
 - B. particle shape
 - C. **radius of gyration**
 - D. lattice parameter
14. (1 point) A powder XRD pattern of rock-salt NaCl is collected with Cu Ka radiation. Which Miller indices respond to the 5th diffraction line?
- A. (220)

B. (222)

- C. (210)
- D. (211)

15. (1 point) A compound with $r_{cat}/r_{an} \approx 0.800$ is most likely to adopt which coordination geometry?

- A. Linear
- B. Tetrahedral
- C. Octahedral
- D. Cubic**

16. (1 point) Kikuchi lines in TEM diffraction arise primarily from

- A. elastic Bragg scattering
- B. inelastic diffraction of thermal diffuse scattering**
- C. fluorescent X-rays
- D. electron-electron scattering

17. (1 point) The "phase problem" in crystallography refers to the inability to measure directly the

- A. structure-factor amplitudes
- B. structure-factor phases**
- C. unit-cell dimensions
- D. Bragg angles

18. (1 point) In semiconductor doped Si, vacancy concentration under n-type doping:

- A. Increases
- B. Decreases**
- C. Unchanged
- D. Oscillates

19. (1 point) The Kirkendall effect demonstrates:

- A. Vacancy flow markers**
- B. Dislocation motion
- C. Grain boundary migration
- D. Precipitate growth

20. (1 point) A key advantage of powder diffraction over single-crystal methods is that

- A. it requires no single crystal**
- B. it gives directional intensities
- C. it solves phases directly
- D. it has no peak overlap

21. (1 point) Given that the pressure is constant, how many degrees of freedom does the α phase of Cu-Zn alloy have?

- A. 0
- B. 1
- C. 2**
- D. 3

22. (1 point) The Avrami equation describes which of the following phenomena?
- A. The rate of atomic diffusion in a crystal lattice during steady-state diffusion
 - B. The kinetics of phase transformation involving nucleation and growth**
 - C. The dependence of recrystallization temperature on strain rate
 - D. The time-dependent dislocation density in cold-worked metals
23. (1 point) Why does adding oxides like CaO, Y₂O₃ or MgO to zirconia (ZrO₂) increase its stability and strength?
- A. Because Ca²⁺ ions replace some Zr⁴⁺ ions, introducing oxygen vacancies and stabilizing the cubic and tetragonal phases, which minimize crack formation and improve toughness**
 - B. Because CaO increases the grain boundary area, which impedes dislocation motion and strengthens the ceramic
 - C. Because CaO reduces the thermal conductivity of ZrO₂ allowing it to retain heat and resist fracture
 - D. Because CaO reacts with ZrO₂ to form an intermediate compound such as CaZr₄O₉, which has higher melting point and hardness
24. (1 point) A supersaturated NaCH₃COO solution remains metastable until a seed crystal is added, at which point rapid precipitation occurs. Which of the following best explains why adding a seed crystal triggers instantaneous crystallization?
- A. The seed crystal increases the volumetric free energy change ΔG_v , lowering ΔG^*
 - B. The seed crystal eliminates the surface area term in ΔG^* , making $\Delta G^* = 0$ and allowing spontaneous crystallization
 - C. The seed crystal decreases the latent heat of crystallization, making the process exothermic and instantaneous
 - D. The seed crystal reduces the effective interfacial energy γ thereby lowering ΔG^***
25. (1 point) According to Pauling's rules, which conformation of tetrahedra is most stable in ionic crystals?
- A. Edge-sharing tetrahedra
 - B. Face-sharing tetrahedra
 - C. Corner-sharing tetrahedra**
 - D. Isolated tetrahedra with no sharing
26. (1 point) Which of the following statements about the Fermi velocity (v_F) in metals is correct?
- A. It is the average drift velocity of electrons when a current flows through the metal
 - B. It is the velocity of electrons at the Fermi energy at absolute zero temperature**
 - C. It is the speed of sound in the metallic lattice
 - D. It represents the velocity at which all electrons move randomly inside the metal

2 Nucleation of ZnO Nanoparticles (20 points)

27. (15 points) A chemist is synthesizing ZnO nanoparticles by homogeneous nucleation in solution at $T = 298$ K. For one recipe, the effective interfacial energy is $\gamma_1 = 0.50 \text{ J} \cdot \text{m}^{-2}$ without any capping agents. The effective γ drops to $\gamma_2 = 0.20 \text{ J} \cdot \text{m}^{-2}$. The driving free energy density from supersaturation is $\Delta G_v = -1.0 \times 10^9 \text{ J} \cdot \text{m}^{-3}$ which is consistent for both cases.

- (a) For spherical nuclei, write the change in free energy ΔG as the function of nucleus radius r where $\Delta G_v < 0$ is the volume free energy per unit volume driving the phase change and γ is the interfacial energy between the nucleus and surrounding solvent.

Solution: $\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$

- (b) Derive expressions for the critical radius r^* and the nucleation barrier ΔG^* .

Solution: $\Delta G' = 4\pi r^2 \Delta G_v + 8\pi r \gamma$

$4\pi r^{*2} \Delta G_v + 8\pi r^* \gamma = 0$ +1pt

$r^* = -\frac{2\gamma}{\Delta G_v}$ +1pt

$\Delta G^* = \frac{16\pi}{3} \frac{\gamma^3}{(\Delta G_v)^2}$ +1pt

- (c) Calculate r^* and ΔG^* for γ_1 and γ_2 . Show numeric values in nm for radius and in joules for energy.

Solution:

For $\gamma_1 = 0.50 \text{ J m}^{-2}$,

$$r_1^* = -\frac{2(0.50)}{-1.0 \times 10^9} = 1.00 \times 10^{-9} \text{ m} = 1.00 \text{ nm.}$$

+0.75pt

For $\gamma_2 = 0.20 \text{ J m}^{-2}$,

$$r_2^* = -\frac{2(0.20)}{-1.0 \times 10^9} = 4.0 \times 10^{-10} \text{ m} = 0.40 \text{ nm.}$$

+0.75pt

For $\gamma_1 = 0.50 \text{ J m}^{-2}$,

$$\Delta G_1^* = \frac{16\pi}{3} \frac{(0.50)^3}{1.0 \times 10^{18}} = \frac{16\pi}{3} \frac{0.125}{1.0 \times 10^{18}}.$$

$$\Delta G_1^* \approx 2.09 \times 10^{-18} \text{ J.}$$

+0.75pt

For $\gamma_2 = 0.20 \text{ J m}^{-2}$,

$$\Delta G_2^* = \frac{16\pi}{3} \frac{(0.20)^3}{1.0 \times 10^{18}} = \frac{16\pi}{3} \frac{0.008}{1.0 \times 10^{18}}.$$

$$\Delta G_2^* \approx 1.34 \times 10^{-19} \text{ J.}$$

+0.75pt

$$r_1^* = 1.00 \text{ nm}, \quad \Delta G_1^* \approx 2.09 \times 10^{-18} \text{ J,}$$

$$r_2^* = 0.40 \text{ nm}, \quad \Delta G_2^* \approx 1.34 \times 10^{-19} \text{ J.}$$

- (d) Let the nucleation rates per unit volume are J_1 and J_2 for γ_1 and γ_2 , respectively. The prefactor J_0 is identical in both cases. Compute the ratio $\frac{J_2}{J_1}$.

Solution:

The nucleation rate per unit volume follows the classical form $J = J_0 e^{-\frac{\Delta G^*}{k_B T}}$

$$\frac{\Delta G_1^*}{k_B T} = \frac{2.094395102 \times 10^{-18}}{4.11413 \times 10^{-21}} \approx 509.2 +1pt$$

$$\frac{\Delta G_2^*}{k_B T} = \frac{1.340412863 \times 10^{-19}}{4.11413 \times 10^{-21}} \approx 32.57 +1pt$$

$$\frac{J_2}{J_1} = e^{-\frac{\Delta G_2^* - \Delta G_1^*}{k_B T}} = e^{\frac{\Delta G_1^* - \Delta G_2^*}{k_B T}}$$

Therefore,

$$\frac{J_2}{J_1} = e^{476.63}$$

+1pt

- (e) Give physical and chemical mechanisms how capping agents or solvents lower γ .

Solution:

Change in solvent polarity or solvation shell: Solvents or additives that better solvate Zn^{2+} / ZnO precursors reduce the mismatch of chemical potentials at the interface and can reduce surface tension. Additionally, specific binding of ligands can passivate dangling bonds and lower surface energy.

+1pt for replacing high-energy solid-solvent

+1pt for solvents better solvate ZnO precursors

+1pt for reduce the mismatch of chemical potentials and reduce surface tension

+1pt for replacing high-energy solid-solvent

3 An "Electrifying" Problem (15 points)

Your team is building a battery-powered "smart doorknob." When a (very small) touch current can flow through a metal-silicon contact, the lock wakes up; otherwise it sleeps to save power. You can choose the contact metal. The silicon handle is a single crystal wafer bonded inside the knob. Unless stated otherwise, assume the crystal to be silicon with a band gap of $E_g \approx 1.12\text{eV}$ and electron affinity $\chi \approx 4.05\text{eV}$, room temperature 300K. You are offered three sputtered metals and given their work functions ϕ_M : aluminum ($\phi_M = 4.1\text{eV}$), titanium ($\phi_M \approx 4.3\text{eV}$), nickel ($\phi_M \approx 5.1\text{eV}$). The silicon can be doped either n-type (N_D) or p-type (N_A) at levels you request.

28. (6 points) For lightly doped n-Si ($N_D \sim 10^{16}\text{cm}^{-3}$), decide for each metal (Al, Ti, Ni) whether the metal-Si contact will behave more like a one-way gate (rectifying) or a free highway (nearly ohmic) at small forward biases. Justify using band-edge alignment ideas: think about where the metal Fermi level would sit relative to the semiconductor bands at the surface, and what that does to the electron flow from Si into the metal. Repeat the same reasoning for lightly doped p-Si with the same metals; explain any "role reversal" you predict.

Solution: For n-Si, the electron barrier is approximately $\Phi_{Bn} = \phi_M - \chi$ (ignoring pinning). Larger $\phi_M \rightarrow$ larger barrier for electrons leaving Si \rightarrow more rectifying. For p-Si, the hole barrier $\Phi_{Bp} \approx E_g - \Phi_{Bn}$. Thus,

n-Si (lightly doped):

- Al $\Phi_{Bn} \approx 0.05\text{eV} \rightarrow$ very small barrier \rightarrow nearly ohmic
- Ti $\Phi_{Bn} \approx 0.25\text{eV} \rightarrow$ weakly rectifying to near-ohmic at small forward bias
- Ni $\Phi_{Bn} \approx 1.05\text{V} \rightarrow$ strongly rectifying

p-Si (lightly doped):

- Al $\Phi_{Bn} \approx 1.07\text{eV} \rightarrow$ rectifying for holes
- Ti $\Phi_{Bn} \approx 0.87\text{eV} \rightarrow$ rectifying
- Ni $\Phi_{Bn} \approx 0.07 \rightarrow$ nearly ohmic for holes

So low ϕ_M metals favor ohmic contact to n-Si, high ϕ_M metals favor ohmic contact to p-Si (this is the role reversal)

+1pt for each correct qualitative prediction, half credit if the numerical Φ_{Bn} is wrong.

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29. (4 points) On a hot summer day, the doorknob on the sun-facing porch starts waking the lock more often than in spring, with the exact same touch. Assume the metal and doping are such that the room-temperature contact was a one-way gate on n-Si. As the temperature rises, does the height of the energy barrier at the interface intrinsically increase, decrease, or stay constant? What does the change that explains the increased current?

Solution: Barrier height is set by band alignment and is thus constant with moderate T . What changes is the thermionic emission over the barrier and the carrier populations. Both rise strongly with T so current increases.

+2pt Correctly identifies that the barrier height is intrinsically constant with moderate temperature changes

+2pt Correctly identifies the change that causes increased current as thermionic emission *over* the barrier, OR increased carrier concentration in the conduction band, OR a combination of both (leading to higher flux/current)

30. (5 points) Your team now wants the doorknob sensor to work reliably in the cold outdoors. You use a Ti contact on n-type silicon with donor concentration $N_D = 5.0 \times 10^{17} \text{ cm}^{-3}$. Assume the effective density of states in the conduction band $N_C = 2.8 \times 10^{19} \text{ cm}^{-3}$. Take the temperature to be 250K. Determine the position of the Fermi level relative to the conduction band edge in bulk n-Si ($E_C - E_F$) at 250K. From this, calculate the built-in potential V_{bi} inside the silicon at equilibrium. Based on your numbers, explain in words whether you expect this Ti/n-Si contact to behave more like a "tunnel-ready bridge" (low-resistance/ohmic) or a "blocking barrier" (rectifying). Be explicit about why the values you computed lead you to this conclusion.

Solution: Electron barrier height $\Phi_{Bn} = \phi_M - \chi = 0.25 \text{ eV}$. Fermi level position $E_C - E_F = kT \ln \left(\frac{N_C}{N_D} \right) = 0.087 \text{ eV}$. Built in potential $V_{bi} = \Phi_{Bn} - (E_C - E_F) = 0.163 \text{ V}$. The barrier for electrons at the metal/semiconductor junction is only about 0.25eV and the fermi level in the doped Si lies very close to the conduction band edge. The resulting built-in potential inside Si is small, meaning that the depletion layer is narrow. A narrow depletion region at such high doping makes tunneling through the barrier very likely. Therefore, in practice, this Ti/n-Si contact should behave almost like an ohmic (low resistance), not a strongly rectifying barrier.

+1pt Correct calculation of $E_C - E_F$ (position of the Fermi level in bulk Si)

+1pt Correct electron barrier height Φ_{Bn}

+1pt Correct built-in potential

+1pt: Correctly identifies the contact as "tunnel-ready bridge" (low-resistance/ohmic)

+1pt: Correctly explains why the values lead to this conclusion, specifically by citing high doping which leads to a narrow depletion width, making tunneling the dominant current mechanism.

4 Quantum Dots (20 points)

31. (5 points) Quantum dots (QDs) are semiconductor nanostructures that confine charge carriers in all three spatial dimensions, creating discrete, atom-like energy levels.

- (a) Consider a cubic quantum dot with side length L . Electrons behave like free particles confined in a 3D infinite square well. When an electron-hole pair forms inside the quantum dot, they bind into an exciton; the energy of an exciton can be approximated as

$$E_{exciton} = E_e + E_h - \Delta$$

where E_e is the electron's confinement energy, E_h is the hole's confinement energy, and Δ is the binding energy due to Coulomb attraction. Suppose the effective mass of the electron is $m^* = 0.067m_e$, and $L = 5nm$. If a hole has effective mass $m_h^* = 0.5m_e$, compute its ground-state confinement energy using the same formula as for electrons. Express in multiples of the E_0 , where we take as given the 3D infinite-well result $E_{n_x,n_y,n_z} = E_0(n_x^2 + n_y^2 + n_z^2)$.

Solution: A hole in a semiconductor acts as a quasi-particle with effective mass m_h^* . In the same box, $E_{n_x,n_y,n_z}^{(h)} = \frac{\hbar^2}{8m_h^*L^2}(n_x^2 + n_y^2 + n_z^2) = \left(\frac{m^*}{m_h^*}\right)E_0(n_x^2 + n_y^2 + n_z^2)$. We have $\frac{m^*}{m_h^*} = \frac{0.067}{0.5} = 0.134$; ground state uses $n_x^2 + n_y^2 + n_z^2 = 3$, hence $E_{gs}^{(h)} = 0.402E_0$.

+1pt: Identifies the energy dependence on mass (explicitly stating or correctly using the fact that the confinement energy is inversely proportional to the effective mass leading to the ratio $E_h = E_e \left(\frac{m_e^*}{m_h^*}\right)$)

+1pt: Explicitly or implicitly identifying the ground state quantum numbers giving confinement factor $n_x^2 + n_y^2 + n_z^2 = 3$

+1pt: Correctly recognizing that electron's ground state is $E_e = 3E_0$

+1pt: Correct final answer

- (b) If $\Delta = 40meV$, find the exciton ground state energy in eV.

Solution: In our minimal exciton model, we use $E_e = 3E_0$, $E_h = 0.402E_0$, $\Delta = 0.040eV$. Computing E_0 is just plugging into the formula $E_0 = \frac{\hbar^2}{8m^*L^2} \approx 3.596 \times 10^{-20}J \approx 0.2245eV$. So $E_{exciton}$ numerically evaluates to $0.724eV$.

+1pt: Correct final answer (half credit if the set-up was correct but used incorrect E_h)

32. (2 points) Consider two identical quantum dots placed close enough that electrons can tunnel between them. In a (simplified) tight-binding model,¹ the Hamiltonian matrix for the electron states can be written as

$$H = \begin{bmatrix} E_0 & -t \\ -t & E_0 \end{bmatrix}$$

where $t > 0$ is the tunneling amplitude. Calculate the energy splitting between the bonding and anti-bonding states in terms of E_0 and t .

¹The tight-binding model is an approach to the calculation of electronic band structure using an approximate set of wavefunctions based upon superposition of isolated atomic wavefunctions; this is closely related to the LCAO method in chemistry.

Solution: The characteristic polynomial is $\det(H - \lambda I) = (E_0 - \lambda)^2 - t^2 = 0 \implies \lambda_{\pm} = E_0 \pm t$. Hybridization splits the single-dot level into bonding (lower, - sign) and anti bonding (higher, + sign) states; the splitting is $\Delta E = \lambda_+ - \lambda_- = 2t$.

+1pt: Correctly setting up the characteristic equation (or using some equivalent method) to find the two energy eigenvalues.

+1pt: Correctly calculating the energy splitting as the difference between the two eigenvalues.

33. (3 points) Suppose we can represent exciton creation in a basis of two quantum dots A and B . The basis states are: $|1, 0\rangle, |0, 1\rangle, |1, 1\rangle$ corresponding to one exciton in dot A , one in dot B , and one in each. The Hamiltonian in this basis is

$$H = \begin{bmatrix} E_x & -J & 0 \\ -J & E_x & 0 \\ 0 & 0 & 2E_x + U \end{bmatrix}$$

where E_x is the single exciton energy, J is the inter-dot coupling, and U is an interaction penalty for having two excitons simultaneously. If $E_x = 1.5\text{eV}$, $J = 50\text{meV}$, and $U = 200\text{meV}$, compute the full set of energies for this system.

Solution: Diagonalizing the one-exciton sector (the upper-left 2×2 block) gives $\lambda_{\pm} = E_x \pm J$, using the same algebra and sign convention as the last question. The $|1, 1\rangle$ state is decoupled (zeros in its row/column) so its energy is $E_{2x} = 2E_x + U$. Plugging values gives $E_{bond} = E_x - J = 1.45\text{eV}$, $E_{antibond} = E_x + J = 1.55\text{eV}$, $E_{2x} = 2E_x + U = 3.20\text{eV}$.

+1pt: Correctly identifying the energy of the decoupled state.

+1pt: Correctly plugging in values and computing the energy of the two-exciton state.

+1pt: Correctly identifying and calculating the two coupled energies (bond and anti-bond).

34. (3 points) Quantum dots exhibit size-tunable optical properties because electron and hole confinement shifts the effective band gap. This is exploited in QD-LED displays and biomedical tagging. An example of a substance that can be manufactured as a nanoparticle and exhibit quantum confinement is cadmium selenide (CdSe). CdSe has bulk band gap $E_g = 1.74\text{eV}$, $m_e^* = 0.13m_e$, $m_h^* = 0.45m_e$. Take $L = 4.0\text{nm}$, $\Delta = 0.050\text{eV}$. Compute ground-state emission energy and wavelength; if visible light spans 400-700nm, identify which transitions fall in the visible range.

Solution: The electron confinement for the ground-state is given by $E_e = 3E_{0,h} \approx 3(0.1807) \approx 0.542\text{eV}$. Hole confinement is $E_h = 3E_{0,e} \approx 3(0.05233) \approx 0.157\text{eV}$.

The emission energy $E_{\gamma} = E_g + E_e + E_h - \Delta \approx 2.39\text{eV}$ The wavelength $\lambda = hc/E_{\gamma} \approx 519\text{nm}$ which is in the visible range.

For higher-energy transitions in a cubic well energy scales with $S = n_x^2 + n_y^2 + n_z^2$. Photon energy for a transition (S_e, S_h) is $E_{\gamma} = E_g + S_e E_{0,e} + S_h E_{0,h} - \Delta$, from which one can verify that the following transitions fall within the visible range: (111,111), (211,111), (111,211), (211,211), (111,221), (111,311).

+0.5pt: Computes ground state energies for electron confinement and hole confinement.

+0.5pt: Uses the correct formula for emission energy (give credit even if incorrect)

ground state energies)

+0.5pt: Uses correct wavelength

+0.25pt for every transition found within visible range. -0.25pt for every transition stated that is not in visible range. The minimum score for this question is 0pts.

35. (5 points) Now consider three quantum dots placed in a line, each with the same size $L = 4.0\text{nm}$. In a tight-binding approximation, their emission states hybridize; the Hamiltonian is

$$H = \begin{bmatrix} E_0 & -J & 0 \\ -J & E_0 & -J \\ 0 & -J & E_0 \end{bmatrix}$$

- (a) (3 points) Using your ground state energy from the last question E_0 , and $J = 40\text{meV}$, compute the three hybridized energies.
- (b) (2 points) Explain qualitatively how such a coupling could broaden the emission spectrum in real QD arrays.

Solution: a) The eigenvalues are

$$E_0 - \sqrt{2}J, \quad E_0, \quad E_0 + \sqrt{2}J$$

With $E_0 = 2.389\text{eV}$ and $J = 0.040\text{eV}$, that gives us **2.332eV**, **2.389eV**, ad **2.446eV**.

+1pt: Correctly identifying the three eigenvalues

+1pt: Correctly converting J to eV and using the value of E_0 to get a numerical answer (half credit if the set-up is correct but the E_0 value is wrong)

+1pt: Correctly computing the three final numerical energies, must have all three correct.

b) Coupling splits a single emission line into multiple closely spaced hybridized states. In real arrays, variations in J , dot sizes, and phonon/disorder effects smear these into a broadened band rather than a sharp line.

+1pt: Correctly identifies that coupling (tunneling) between dots causes a single, sharp energy level (E_0) of an isolated dot to split into multiple closely-spaced hybridized energy levels.

+1pt: Correctly explaining that in a real array, variations in dot size, inter-dot spacing, or the surrounding environment/defects (disorder/phonons) mean that the splitting magnitude is not uniform resulting in a continuum or broadened band of emission energies rather than a sharp line.

36. (5 points) Address the following.

- (a) (2 points) For cubic confinement, argue why ground-state exciton is optically allowed for all polarizations.
- (b) (3 points) For excited states, explain why anisotropy leads to polarization-dependent absorption/emission.

Solution: a) The ground-state envelope in a cubic box is totally symmetric (s-like, (1,1,1)); combined with the interband dipole from Bloch functions, transitions are allowed for any polarization—no preferred direction in a cubic, isotropic potential. Thus, ground-state exciton emission is optically allowed for all polarizations.

+1pt: Correctly identifies that the ground state envelope wavefunction (or the total exciton state) is totally symmetric (e.g. s-like, non-degenerate, (1, 1, 1)).

+1pt: Correctly explains that because the state is totally symmetric and the confinement potential is isotropic (cubic), there is no preferred direction/axis for the dipole transition moment, meaning the transition is allowed for all polarizations.

b) Excited states have p-like (or higher) envelopes with directional nodes; any anisotropy (shape, strain, crystal-field splitting of heavy-/light-hole bands, surface/ligand effects) breaks isotropy, aligning oscillator strength along certain axes. As a result, we have a polarization-dependent absorption/emission for excited states.

+1pt: Correctly identifies that excited states have directional character (e.g. p-like, d-like, states with nodes)

+1pt: Correctly identifies that anisotropy is necessary to break the rotational symmetry of the system

+1pt: Correctly links the broken symmetry to the optical consequence: the oscillator strength (dipole moment) becomes aligned along anisotropic axes, leading to polarization-dependent absorption/emission (i.e. selection rules that depend on the direction of light's electric field).

5 Creep (15 points)

In addition to predicting the mechanical responses of linear viscoelastic materials like amorphous polymers, springs and dashpots can be used to create models of creep and recovery in crystalline materials. (Reminder: A spring creates a force proportional to displacement, and a dashpot dampens a system by creating a force proportional to velocity, in the opposite direction of velocity. These are ubiquitous in modeling mechanical behaviors in engineering.)

37. (4 points) Although springs and dashpots are used to predict the behavior of amorphous polymers and crystalline materials in response to mechanical loading, they are predicting two very different ways of dissipating mechanical energy. Explain the difference, precisely but concisely, in terms of elasticity, plasticity, and atomic/molecular mechanisms.

Solution: Amorphous polymers (modeled with springs + dashpots for viscoelasticity):

- **Elasticity:** Spring elements represent reversible elastic stretching of polymer chains (bond stretching + bond angle distortions).
- **Viscosity (dashpot):** Dashpots are time-dependent molecular rearrangements — e.g. chain segmental motion, slippage past one another.
- **Mechanism:** Energy dissipation comes from internal friction as polymer chains overcome intermolecular forces and entanglements.
- **Nature:** This is viscoelastic deformation — reversible on short timescales, but with time-dependent relaxation.

Crystalline materials (modeled with springs + dashpots for creep and recovery):

- **Elasticity:** Springs represent the reversible, lattice-based elastic deformation (bond stretching in the crystal lattice).
- **Plasticity (dashpot):** Dashpots here do not represent viscous flow, but irreversible slip of dislocations through the lattice.
- **Mechanism:** Energy dissipation arises from the motion of dislocations, climb, or diffusion-controlled processes — not from chain friction.
- **Nature:** This is elasto-plastic deformation — with a permanent plastic strain component once dislocations move.

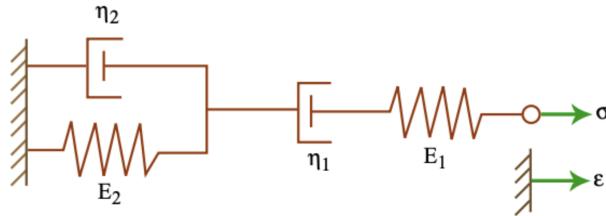
+1pt: Elasticity: states that springs represent elastic reversible deformation (bond stretching in polymers/lattice distortion in crystals). +0.5 if mentioned only vaguely without connecting to molecular/atomic level.

+1pt: Amorphous: Explains that dashpots model viscous, time-dependent chain motion (internal friction → viscoelasticity). +0.5 if just mentions "energy dissipated as heat" without linking to polymer chain rearrangement.

+1pt: Crystalline: Explains that dashpots represent plasticity via dislocation motion (irreversible slip in crystal lattice). +0.5 if only says plastic deformation without mentioning dislocations or irreversibility.

+1pt: Clearly distinguishes polymers are recoverable viscoelastic dissipation, crystals are irreversible plastic dissipation. +0.5 if the difference is implied but not explicitly compared side by side.

38. (4 points) Below is a model that accurately captures the creep and recovery response of several micro-crystalline materials. For the given model, describe qualitatively how the strain in the microcrystalline material evolves over time under a step-stress applied at $t = 0$ and removed after a long time $t = t_1 >> 0$. In particular, explain the roles of each element (E_1 , E_2 , η_1 , η_2) in the creep and recovery response.



Solution:

- At $t = 0$ applying a step stress causes an instantaneous jump in strain due to elastic springs E_1 and E_2 , corresponding to reversible bond stretching in the crystal lattice.
- η_1 in series with E_1 produces a gradual, time-dependent increase in strain under constant stress, representing dislocation glide and other microstructural creep mechanisms.
- η_2 in parallel allows continuous strain accumulation with time under stress, modeling permanent, unrecoverable deformation associated with long-term dislocation movement and plastic slip.
- When stress is removed, elastic strains recover immediately; the time dependent strain from the series spring-dashpot partly recovers, but not fully. The strain accumulated in η_2 remains as permanent offset, representing unrecoverable plastic creep.

+1pt: Explains initial instantaneous elastic strain from E_1

+0.25pt: Notes time-dependent creep due to η_1

+0.25pt: Notes time-dependent creep due to $E_2-\eta_2$ arm

+0.5pt: Mentions eventual steady-state strain

+0.5pt: Explains that upon loading, the E_1 spring recovers immediately

+1pt: Notes partial delayed recovery from $E_2-\eta_2$ branch AND η_1 contribution is permanent

+0.5pt: Identifies η_1 as permanent, irreversible strain

39. (2 points) Returning to viscoelastic materials, the two simplest common models of describing stress and strain for such materials are the Kelvin-Voigt model and the Maxwell model. The Kelvin-Voigt model consists of one dashpot in parallel with one spring, while the Maxwell model consists of one dashpot in series with one spring. Give one advantage and one limitation of each model.

Solution: Kelvin-Voigt model realistically captures creep behavior, cannot describe stress relaxation. Maxwell captures stress relaxation but not creep behavior.

+0.5pt: Kelvin-Voigt model captures creep

+0.5pt: Kelvin-Voigt model cannot describe stress relaxation OR no instantaneous strain jump at stress application

+0.5pt: Maxwell model captures stress relaxation

+0.5pt: Maxwell model cannot describe creep

40. (5 points) Consider a Kelvin-Voigt material (elastic modulus E , viscosity η), subject to a harmonic strain $\epsilon(t) = \epsilon_0 \sin(\omega t)$. Derive an expression for the average dissipated power per unit volume (rate of energy dissipated as heat). (Hint: Write $\epsilon(t) = \epsilon_0 e^{i\omega t}$ and solve for the complex (dynamic) modulus $E^*(\omega) = \frac{\sigma(t)}{\epsilon(t)}$. The imaginary part E'' of $E^*(\omega)$ is the loss modulus; the energy dissipated per unit volume in one cycle is the area of the stress-strain hysteresis loop $W_d = \oint \sigma d\epsilon = \pi E'' \epsilon_0^2$)

Solution: There are A LOT of ways I can think of to solve this problem. First, from the hint: The constitutive law from taking a spring and dashpot in parallel is $\sigma(t) = E\epsilon(t) + \eta\dot{\epsilon}(t)$. Imposing $\epsilon(t) = \epsilon_0 e^{i\omega t} \implies \dot{\epsilon} = i\omega\epsilon$ (you can obtain this without using calculus—try it yourself!). So $\sigma(t) = (E + i\omega\eta)\epsilon(t)$. Thus the complex (dynamic) modulus is $E^*(\omega) = E' + iE'' = E + i\omega\eta$ with $E''(\omega) = \omega\eta$. Plugging in $W_d = \pi\omega\eta\epsilon_0^2$. The average dissipated power per unit volume is then $\bar{P} = \frac{\omega}{2\pi} W_d = \frac{1}{2}\omega^2\eta\epsilon_0^2$.

Otherwise, we can write stress for sinusoid $\sigma = E\epsilon_0 \sin \omega t + \eta\epsilon_0 \omega \cos \omega t$, average over a cycle $\langle E\dot{\epsilon} \rangle = 0$, $\langle (\dot{\epsilon})^2 \rangle = \frac{1}{2}\epsilon_0^2\omega^2$, $\bar{P} = \langle \sigma\dot{\epsilon} \rangle = \frac{1}{2}\eta\omega^2\epsilon_0^2$

Otherwise, we can multiply both sides of KV law to obtain the instantaneous power density $p = \sigma\dot{\epsilon} = E\epsilon\dot{\epsilon} + \eta\dot{\epsilon}^2$. Over a full period, $\langle \epsilon\dot{\epsilon} \rangle = 0$ since it's a perfect time derivative with zero net change, so $\bar{P} = \langle p \rangle = \eta\langle (\dot{\epsilon})^2 \rangle$; $\dot{\epsilon} = \epsilon_0 \omega \cos \omega t$ and $\langle \cos^2 \omega t \rangle = \frac{1}{2}$ so $\bar{P} = \frac{1}{2}\eta\omega^2\epsilon_0^2$

Otherwise, writing ϵ and $\dot{\epsilon}$ in their sinusoidal forms, we can rewrite stress $\sigma = \sigma_0 \sin(\omega t + \delta)$ with $\sigma_0 = \epsilon_0 \sqrt{E^2 + (\omega\eta)^2}$ and $\tan \delta = \frac{\omega\eta}{E}$; for Lissajous σ - ϵ loops the area per cycle is $W_d = \pi\sigma_0\epsilon_0 \sin \delta$ so $W_d = \pi\omega\eta\epsilon_0^2$ so $\bar{P} = \frac{\omega}{2\pi} = \frac{1}{2}\eta\omega^2\epsilon_0^2$

Otherwise, form phasors $\dot{\epsilon} \leftrightarrow i\omega\epsilon$, $\sigma = (E + i\omega\eta)\epsilon$; instantaneous power $p = \Re\{\sigma\}\Re\{\dot{\epsilon}\}$, average over time equals $\frac{1}{2}\Re\{\sigma\dot{\epsilon}^*\}$, $\sigma\dot{\epsilon}^* = (E + i\omega\eta)\epsilon(-i\omega\epsilon^*)$ so real part $\omega^2\eta|\epsilon|^2$, with $|\epsilon| = \epsilon_0$ we get $\bar{P} = \frac{1}{2}\eta\omega^2\epsilon_0^2$.

Otherwise, Parseval's theorem gives $\bar{P} = \langle \eta\dot{\epsilon}^2 \rangle$; in frequency domain $\dot{\epsilon}$ has a single line at ω with amplitude $\epsilon_0\omega$; time average of square equals half the squared amplitude so $\langle (\dot{\epsilon})^2 \rangle = \frac{1}{2}(\epsilon_0\omega)^2$ thus $\bar{P} = \frac{1}{2}\eta\omega^2\epsilon_0^2$.

AWARD FULL CREDIT IF CORRECT ANSWER IS OBTAINED WITH JUSTIFICATION. Otherwise, award the following partial credit: +2pt: Writes Kelvin-Voigt $\sigma = E\epsilon + \eta\dot{\epsilon}$ (accept v or some other rate of change of a displacement for $\dot{\epsilon}$)

+1pt: Finds $\dot{\epsilon} = i\omega\epsilon$ or $\epsilon_0\omega \cos \omega t$.

+1pt: Gets $E'' = \omega\eta$ +1pt: Solves for work instead of power (and correctly obtains $W_d = \pi(\omega\eta)\epsilon_0^2$)

+0.5pt: Gets W_d wrong, but at least $W_d \propto \omega\eta\epsilon_0^2$

6 Astro Marathon (20 points)

A team of space-people (?) has shrunk down to the nanometer scale to investigate a new futuristic material called Hongjinium, a nanomaterial designed for spacecraft heat shields. Hongjinium forms a 2D crystalline sheet. A single sheet has dimension $1\mu m \times 1\mu m$ and its thickness is $1nm$.

41. (2 points) Calculate the surface area-to-volume ratio (SA/V) of this sheet in units of nm^{-1} . Briefly explain why this high SA/V ratio is beneficial for heat dissipation in a spacecraft heat shield.

Solution: The surface area of a rectangular prism would be the sum of the area of its faces. If we take its dimensions to be $a \times b \times c$ then that's $2(ab + ac + bc)$, so $SA = 2004000nm^2$. Volume of a rectangular prism is $V = abc = 1000000nm^3$. So SA/V is $2.004nm^{-1}$. Enormous SA/V promotes rapid heat exchange and lateral heat spreading; more interface per volume so faster dissipation and lower hot-spot temperatures.

+1pt: Correct SA/V

+1pt: Gives at least one plausible reason why high SA/V ratio is beneficial in the context of heat spreading (at least one of the reasons given above)

42. (2 points) Two scientists debate how Hongjinium was made. Johnny says it was milled and etched down from a bulk crystal. Alex says it was built atom-by-atom using chemical vapor decomposition. Identify which scientist describes a top-down method and which describes a bottom-up method. Who's more likely correct, and why?

Solution: Johnny is describing top-down and Alex is describing bottom-up. Bottom-up is likelier for an ultra-thin 2D sheet because it offers atomic-layer control, fewer defects, continuous films; top-down risks damage, rough edges, and non-uniform thickness at the nm scale.

+0.5pt: Correctly notes Johnny is describing top-down and Alex is describing bottom-up

+0.5pt: Concludes bottom-up is likelier

+0.75pt: Offers a plausible advantage

+0.25pt: Gives a disadvantage of top-down

43. (5 points) The space-people bring out their instruments, and observe the following:

- X-ray diffraction: Sharp peaks observed
- Transmission electron microscopy: Reveals thin sheet-like patterns
- Energy dispersive spectroscopy: Confirms presence of embedded metal atoms

What does each technique reveal about Hongjinium? Together, how do these results confirm its 2D crystalline structure with metal atoms?

Solution: XRD sharp peaks reveals crystalline long-range order and lattice spacing (Bragg peaks). TEM (sheet-like contrast/possible lattice fringes) shows morphology and thickness, can resolve atomic planes to confirm 2D layering/defects. EDS metal signal gives elemental composition and maps embedded metal atoms within/onto the lattice. So, XRD confirms it's crystalline, TEM confirms its 2D, EDS proves metal

incorporation; altogether, we have a 2D crystalline sheet containing embedded metal atoms.

+1pt: XRD reveals crystalline structure

+1pt: TEM shows morphology/shows 2D layering

+1pt: EDS metal gives elemental composition and maps embedded metal atoms with/onto lattice

+2pts: Concludes 2D crystalline sheet containing embedded atoms

44. (3 points) They observe 90% absorption of visible light at 500nm wavelength. Give 3 reasons for why strong absorption of visible light might occur in such a nanomaterial?

Solution:

- Localized surface plasmon resonances (LSPR); embedded metal atoms or clusters can act as plasmonic centers, and when their resonance frequency overlaps with visible light, collective oscillations of conduction electrons enhance absorption
- Metal atoms act as dopants or substitutional defects, introducing new electronic states within the bandgap enabling optical transitions lying in visible spectrum
- Charge transfer between metal atoms and host 2D lattice (ligand-to-metal or metal-to-ligand)
- Metal embedding can locally alter orbital hybridization so it modifies band structure reducing the bandgap or creating flat bands that strongly couple to visible light
- 2D materials have strong excitonic effects due to reduced dielectric screening, metal atoms can localize or stabilize excitons enhancing visible-light absorption
- Metal atoms can act as scattering centers concentrating the local electromagnetic field and boosting light-matter interaction strength
- Metal embedding might induce polarons or modifies phonon modes, resonant coupling with visible light enhances absorption

+1pt For each plausible answer, maximum 3 points; -0.75pt for each implausible answer if more than 3 are given. Minimum score awarded is 0.

+0.75pt: If no plausible + detailed answer is given, but at least notes that quantum confinement modifies electronic bands

45. (2 points) Hongjinium has a thermal conductivity of $2000 \text{ W/m} \cdot \text{K}$, while typical stainless steel only has $15 \text{ W/m} \cdot \text{K}$. Explain how this extraordinary thermal conductivity would protect a spacecraft during re-entry.

Solution: Fourier's law predicts that very high thermal conductivity spreads incoming heat laterally, reducing temperature gradients and peak surface temperatures, lowering thermal stresses, and moving heat to radiative or sacrificial layers more quickly.

+2pts: Explains high thermal conductivity spreads heat quickly through material, mentioning that it prevents localized hot spots and/or mentioning reduced peak surface temperature

+1pt: Incomplete explanation, but states that "heat is conducted away" without connecting to reduced local heating.

46. (3 points) At low temperatures and in very clean crystals, heat can travel as a wave rather than by ordinary diffusion. This phenomenon—second sound—arises when quantized lattice vibrations (phonons) behave collectively like a fluid. In the lab, the spacepeople can cool Hongjinium and excite it with a pulsed laser to watch how heat moves in the 2D sheet. For a 2D crystalline sheet like Hongjinium, list

two material or environmental conditions that would favor observing second sound. Briefly justify each in terms of phonon behavior.

Solution:

- **Low temperature, well below dominant scattering thresholds:** Ensures momentum-conserving (normal) phonon collisions dominate over momentum-destroying processes. Quantum mechanically, the phonon population is restricted to long-wavelength modes with reduced phase space for resistive events.
- **High crystalline purity/few defects and roughness:** Defects, grain boundaries, and edge roughness introduce elastic momentum-relaxing scattering that breaks collective phonon flow. Quantum view: added scattering centers disrupt coherent phonon populations needed for hydrodynamic transport.
- **Large phonon mean free path relative to feature size:** Micron-scale regions with smooth boundaries allow many normal collisions before momentum is lost to boundaries. In quantum terms, the phonon gas can equilibrate internally (shared drift) faster than it loses momentum.
- **Suppressed Umklapp processes:** Choosing temperatures where reciprocal-lattice momentum transfer is rare (narrow phonon occupation) prevents decay of the collective drift. This maintains the hydrodynamic regime required for a propagating temperature wave.

+3pts: Student identifies two correct conditions from above and justifies them in terms of phonon dynamics. -1pt for each impausible condition if more than 2 are given. Minimum score awarded is 0.

+2pts: Student gives two correct conditions but justification is weak, vague, or missing, OR student lists only one condition with strong justification

+1pt: Student provides one correct condition with only a vague or incomplete justification

+0pt: Incorrect or irrelevant answers, or one condition stated with no justification.

47. (3 points) Hongjinium contains embedded metal atoms in its lattice. Predict whether these inclusions are more likely to promote or suppress second sound, and explain your reasoning using quantum mechanical ideas about phonon scattering.

Solution: Mostly suppress: Embedded metal atoms introduce mass and force-constant disorder, producing additional phonon scattering channels that randomize momentum and shorten coherence. Quantum mechanically, they alter the phonon spectrum and increase phase-breaking events, tipping the balance away from momentum-conserving collisions toward resistive ones.

Possible narrow exception: If the metals self-organize periodically and hybridize with host vibrations, they could open well-defined phonon branches with reduced resistive phase space in a limited range—potentially aiding hydrodynamic flow only in that narrow, engineered band. In a random embedding, suppression is the expected outcome.

+1.75pt: Predicts suppression of second sound.

+1.25pt: Explanation correctly ties to phonon scattering

+0.5pt: Gives partially correct or vague explanation

No points awarded for problem if opposite effect predicted.