

# National Exams May 2010

## 98-Met-A4, Structure of Materials

3 Hours Duration

### NOTES:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.
2. Candidates may use one of two calculators, the Casio or Sharp approved models. This is a Closed Book exam. All equations, constants and diagrams are given in the appendix.
3. **Any five** questions constitute a complete paper. **Only the first five questions** as they appear in your answer book will be marked.
4. All questions are of equal value.

### Question I: Electron Structure and Bonding

1. Four quantum numbers can be used to uniquely specify the state of each electron in an atom. List each of these four parameters and briefly explain what they describe. (8 marks)
2. For the general case of an arbitrary atom, how many electron states are available in: i) the second shell, and ii) the third shell? (i.e. how many electrons states are possible when the principal quantum number  $n$  has values of  $n = 2$  and  $n = 3$ )? (2 marks)
3. The electron configuration of atomic Li ( $Z=3$ ) can be expressed as  $1s^2 2s^1$ . Give the electron configurations for atomic Mg ( $Z=12$ ) and Ti ( $Z=22$ ). (4 marks)
4. Briefly explain the differences in the electron band gap structure of intrinsic and extrinsic semiconductors. (6 marks)

### Question II: Crystal Structures

1. The density of vanadium ( $Z=23$ ) is  $5.8 \text{ g/cm}^3$ . Determine whether vanadium has the face centered cubic or the body centered cubic structure. The unit cell edge length is  $0.303 \text{ nm}$  and the molar mass is  $50.94 \text{ g/mol}$ . (6 marks)
2. At room temperature, cobalt has the HCP crystal structure ( $c/a = 1.623$ ) and an atomic radius of  $r = 0.1253 \text{ nm}$ . Calculate the theoretical density of Co. The molar mass of Co is  $58.93 \text{ g/mol}$ . (10 marks)
3. Illustrate a stacking fault in the FCC and HCP crystal structures using the stacking sequence notation, e.g. for a region of perfect FCC crystal: ABCABCABC. (4 marks)

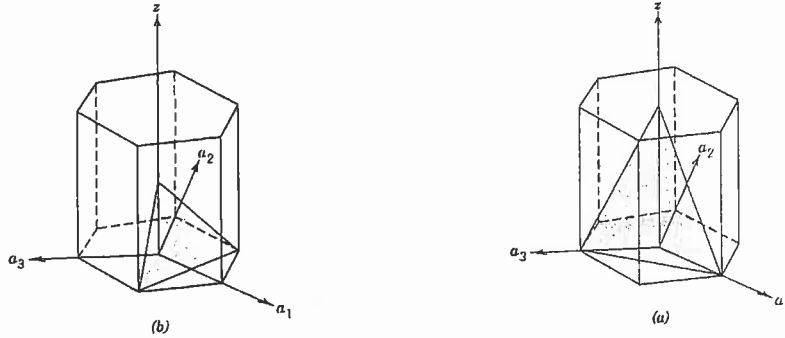
### Question III: X-ray Diffraction

Li-ion batteries having  $\text{LiCoO}_2$  cathodes are widely used to power laptops and cell-phones. Considerable research has been conducted in the last decade to find next generation Li-ion cathode materials. One promising candidate is  $\text{LiMnPO}_4$ , which has a primitive orthorhombic crystal structure with lattice parameters  $a = 0.611 \text{ nm}$ ,  $b = 1.04 \text{ nm}$ , and  $c = 0.475 \text{ nm}$ . The interplanar spacing  $d$  for an orthorhombic crystal structure can be expressed as:

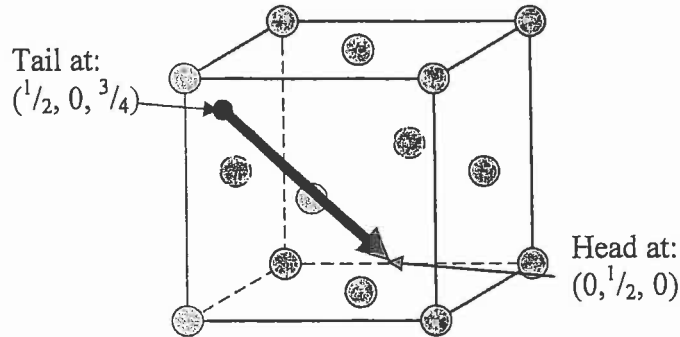
$\frac{1}{d^2} = \frac{1}{a^2}h^2 + \frac{1}{b^2}k^2 + \frac{1}{c^2}l^2$ . Sketch a schematic diagram of the expected powder diffraction pattern for  $\text{LiMnPO}_4$  giving numerical values for the  $2\theta$  diffraction angle of the first four diffraction peaks (i.e. those planes corresponding to the four smallest  $2\theta$  values) if the  $\text{LiMnPO}_4$  was characterized using  $\text{Co K}_\alpha$  radiation ( $\lambda = 0.179 \text{ nm}$ ). Note that primitive crystal structures will yield diffraction peaks for each unique interplanar spacing. (20 marks)

**Question IV: Planes and Directions**

1. Determine the indices for the planes shown below using both the Miller (3 index) and Miller-Bravais (4 index) notation for each plane. **(4 marks)**



2. Give the indices for the direction shown. **(2 marks)**



3. Draw the following planes or directions, clearly indicating the position of the origin you have chosen and the positions of the atoms in the unit cell.

- A)  $(1\bar{1}0)$  in the body centered cubic (BCC) unit cell. **(2 marks)**
- B)  $(021)$  in the face centered cubic (FCC) unit cell. **(2 marks)**
- C)  $[125]$  in the BCC unit cell. **(2 marks)**
- D)  $[11\bar{2}1]$  in the hexagonal close-packed (HCP) unit cell. **(2 marks)**

4. The NaCl (Rock Salt) crystal structure is face centered cubic with 2 ions per lattice point ( $4 \text{ Na}^+$  and  $4 \text{ Cl}^-$  per unit cell). Draw the cation and anion positions on both the (100) and the (110) planes of the NaCl structure. **(6 marks)**

### Question V: Interstitial Sites in FCC and BCC

Carbon forms interstitial solid solutions in Fe (using a hard sphere model for C in iron, we can assume a carbon radius of 0.071 nm). In the BCC structure, the tetrahedral sites are located on the face of the unit cell at locations of the type  $\frac{1}{4} \frac{1}{2} 0$ . In the FCC structure, the octahedral sites are located at the unit cell centre and at the unit cell edges (e.g.  $\frac{1}{2} 0 0$ ). The lattice parameter is 0.3571 nm for FCC iron and 0.2866 nm for BCC iron.

1. Show by calculation whether you would expect a greater distortion of the crystal by an interstitial carbon atom in FCC or BCC iron. **(12 marks)**
2. What would be the atomic percentage of carbon in each type of iron if all the interstitial sites were filled? **(8 marks)**

### Question VI: Mechanical Deformation

1. Consider the hypothetical case of ceramic bars that were subjected to both tensile and three-point bending tests. In both cases, failure occurred by brittle fracture. However, the average failure stress in bending (modulus of rupture) was 150 MPa, while the average failure stress in tension was only 80 MPa. Briefly explain how the average failure stress could be higher in bending than in tension. **(6 marks)**
2. Briefly explain why the slip direction is  $\langle 1 \bar{1} 0 \rangle$  for dislocations in the FCC crystal structure and  $\langle 1 \bar{1} 1 \rangle$  for dislocations in the BCC crystal structure. **(6 marks)**
3. What are the two possible slip directions on the BCC (110) slip plane? What is the angle between these directions? **(4 marks)**
4. Briefly explain why it is typically more difficult to deform (A) covalently bonded crystals and (B) ionically bonded crystals by dislocation motion than metallic crystals. **(4 marks)**

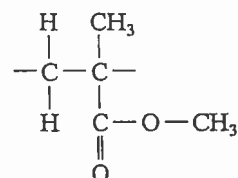
## Question VII: Polymers

For a linear polymer molecule, the extended chain length ( $L_{ext}$ ) depends on the bond length between chain atoms ( $l$ ), the total number of bonds along the chain of the molecule ( $m$ ), and the angle between adjacent backbone chain atoms ( $109.5^\circ$ ), as follows:

$$L_{ext} = ml \sin\left(\frac{109.5^\circ}{2}\right)$$

By contrast, the root-mean-square length,  $\bar{L}$ , is given by:  $\bar{L} = l\sqrt{m}$ .

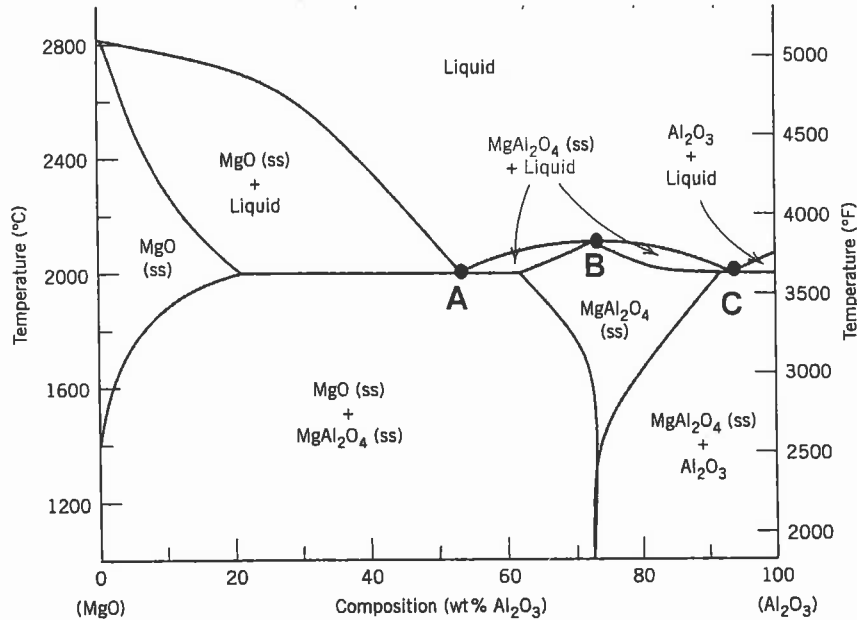
1. A linear polymethyl methacrylate (mer unit shown below) polymer has an average molecular weight,  $\bar{M}$ , of 500,000 g/mole; compute average values of  $L_{ext}$  and  $\bar{L}$  for this material. The C-C single bond length is 0.154 nm and the C=C double bond length is 0.134 nm. The molar masses of carbon, hydrogen and oxygen are:  $A_C = 12.01$  g/mole,  $A_H = 1.008$  g/mole, and  $A_O = 16.00$  g/mole. (8 marks)



2. Briefly explain the factors which control polymer crystallinity. (4 marks)
3. A company blends 50 mol % ethylene ( $\text{C}_2\text{H}_4$ ) and 50 mol % vinyl chloride ( $\text{C}_2\text{H}_3\text{Cl}$ ) to form a block copolymer. Each block is 3 mers long, and the polyvinyl chloride blocks are isotactic. Draw the structure of the original polymer. Include at least two blocks of each type of mer. (4 marks)
4. If the weight average molecular weight of the block copolymer in Question VII Part 3 is 24,000 g/mole, what is the weight average degree of polymerization? The molar masses of chlorine is  $A_{\text{Cl}} = 34.45$  g/mole. (4 marks)

### Question VIII: Phase Diagrams

Answer the following questions for the MgO-Al<sub>2</sub>O<sub>3</sub> system, phase diagram shown below. Note that (ss) on the phase diagram indicates a solid solution.



1. Give the reaction type at points **A**, **B**, and **C** marked on the phase diagram. **(3 marks)**
2. Draw a schematic diagram of the microstructure for a MgO-70wt%Al<sub>2</sub>O<sub>3</sub> sample at 1200 °C, clearly labeling the phases. What is the composition of each phase? What is the weight fraction of each phase? **(6 marks)**
3. What is the atomic concentration of Al in a MgO-80wt.%Al<sub>2</sub>O<sub>3</sub> sample? The density of the solid phases are: MgO = 3.58 g/cm<sup>3</sup>, MgAl<sub>2</sub>O<sub>4</sub> = 3.64 g/cm<sup>3</sup>, and Al<sub>2</sub>O<sub>3</sub> = 3.69 g/cm<sup>3</sup>. The molar mass of Mg, Al, and O are:  $A_{Mg} = 24.30$  g/mol,  $A_{Al} = 26.98$  g/mol, and  $A_O = 16.00$  g/mol. **(8 marks)**
4. Give three factors that govern the limit of substitutional solid solubility. **(3 marks)**

## Appendix: Equations and Constants

$$N_D = N \exp\left(-\frac{Q_D}{kT}\right) \quad N = \frac{N_A \rho}{A} \quad \varepsilon = \frac{\Delta l}{l_0} \quad \sigma = \frac{F}{A_0}$$

$$E = 2G(1+\nu) \quad \tau = G\gamma \quad \sigma = E\varepsilon \quad \tau = \frac{F}{A_0} \quad \nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\varepsilon_y}{\varepsilon_z}$$

$$U_r = \frac{\sigma_y \varepsilon_y}{2} = \frac{\sigma_y^2}{2E} \quad \%EL = \left(\frac{l_f - l_0}{l_0}\right) \times 100 \quad \%RA = \left(\frac{A_0 - A_f}{A_0}\right) \times 100 \quad \sigma_T = \frac{F}{A_f}$$

$$\sigma_T = \sigma(1+\varepsilon) \quad \varepsilon_T = \ln \frac{l_f}{l_0} \quad \varepsilon_T = \ln(1+\varepsilon) \quad \sigma_T = K\varepsilon_T^n$$

$$n\lambda = 2d \sin \theta \quad d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \tau_R = \sigma \cos \phi \cos \lambda \quad \sigma_y = \frac{\tau_{CRSS}}{(\cos \phi \cos \lambda)_{\max}}$$

$$a = 2R \quad a = 2\sqrt{2}R \quad a = \frac{4R}{\sqrt{3}} \quad APF = \frac{V_s}{V_c}$$

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C \cdot N_A} \quad \rho = \frac{n \cdot A}{V_C \cdot N_A} \quad \theta = \cos^{-1} \left[ \frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{\sqrt{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)}} \right]$$

$$k = 1.38 \times 10^{-23} \text{ J/atom}\cdot\text{K} = 8.62 \times 10^{-5} \text{ eV/atom}\cdot\text{K}$$

$$R = 8.31 \text{ J/mol}\cdot\text{K}$$

$$T_K = T_C + 273$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$