

## NATURAL SCIENCES TRIPOS Part IA

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Friday 6 June 1997 1.30 to 4.30

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### MATERIALS AND MINERAL SCIENCES

Answer **five** questions; **two** from each of Sections **A** and **B** and **one** from Section **C**.

Begin each answer at the top of a sheet.

Write on **one** side of the paper only.

Graph paper and the Data Book are provided.

Candidates using electronic calculators are advised to indicate clearly the sequence of steps in their working. Appropriate credit can then be given for the intermediate stages even if the final stage is incorrect.

The answer to **each question** must be tied up **separately** with its own cover-sheet.

Write the relevant **question number** in the square labelled 'Section'. Also on each cover-sheet, list the numbers of **all** questions attempted.

### SECTION A

1 Metallic platinum has the cubic close-packed structure with  $a = 3.924 \text{ \AA}$ . Explain what is meant by a *lattice* and state the lattice type of Pt. Determine the metallic radius of Pt. Draw a plan on (001) of a  $2 \times 2$  block of unit-cells of the Pt structure and mark in the rotation tetrads parallel to [001] and the mirror planes parallel to [001]. Indicate on your plan the tetrahedral interstices in the Pt structure and state their coordinates.

The mineral *cooperite*, of composition PtS, has tetragonal symmetry with  $a = 3.47 \text{ \AA}$ ,  $c = 6.10 \text{ \AA}$ . The coordinates of the atoms in this unit-cell have been determined as Pt:  $0 \frac{1}{2} 0$ ;  $\frac{1}{2} 0 \frac{1}{2}$  and S:  $0 0 \frac{1}{4}$ ;  $0 0 \frac{3}{4}$ . Draw a plan on (001) of a  $2 \times 2$  block of unit-cells of the cooperite structure and mark in the rotation axes parallel to [001] and the mirror planes parallel to [001]. Describe the coordination of Pt about S and of S about Pt and evaluate the Pt–S distance.

Show how the structure of cooperite can be regarded as a distorted ccp arrangement of Pt atoms with S in selected tetrahedral interstices. Given that the covalent radius of sulphur in 4-fold coordination is  $1.02 \text{ \AA}$ , that the covalent radius of Pt in 4-fold coordination is  $1.29 \text{ \AA}$ , and that in ionic compounds the radius of  $S^{2-}$  is  $1.82 \text{ \AA}$  and of  $Pt^{2+}$  is  $0.60 \text{ \AA}$ , comment on the Pt–S bonding in cooperite.

(TURN OVER)

2 Explain carefully the use of indices to describe (i) *lattice planes* and *crystal faces* and (ii) *lattice vectors* and *zones*. Deduce the Weiss zone equation and give two examples of its use.

What is meant by a *Widmanstätten microstructure*? The relationship between the lamellae of the nickel-rich low-temperature  $\alpha$ -Fe solid solution and the high-temperature  $\gamma$ -Fe solid solution in an Fe-Ni meteorite may be described as  $(111) \parallel (110)$  ;  $[1\bar{1}0] \parallel [1\bar{1}1]$  . Sketch the arrangement of atoms on (i) a (111) plane of  $\alpha$ -Fe and (ii) a (110) plane of  $\gamma$ -Fe and hence account for the relationship between the two phases. Describe the appearance of the Widmanstätten microstructure which would be seen on a polished and etched surface parallel to (a) (110) and (b)  $(2\bar{1}\bar{1})$  of  $\alpha$ -Fe.

3 Give brief descriptions of the terms *screw dislocation*, *edge dislocation*, *Burgers vector* and *slip system*.

Show that the elastic strain energy per unit length of a screw dislocation can be expressed as

$$U = \frac{1}{2} G b^2$$

where  $G$  is the shear modulus and  $b$  is the magnitude of the Burgers vector.

An aluminium wire is being pulled through a die so as to reduce its diameter. The tensile stress needed to draw the wire in this way is 20 MPa. Assuming that 1% of the mechanical energy input is converted into dislocation strain energy in the drawn wire, and the rest remains in the wire as heat, estimate:

- the increase in dislocation density induced by the drawing process and
- the rise in temperature as the wire passes through the die.

What factors would you expect to limit the maximum reduction in sectional area which could in practice be achieved in a single drawing pass of this type?

[For Al,  $G = 28$  GPa and  $C_v = 3 \times 10^6$  J K<sup>-1</sup> m<sup>-3</sup>.]

4 What is meant when a material is described as *brittle*? Why are ceramic materials generally much more brittle than metals?

Using a simple model for the stress field, show that, in order for an internal crack of length  $2a$  to propagate under an applied stress  $\sigma$ , the toughness of the material,  $G_c$ , must be no greater than a critical value given by

$$G_c = \frac{a\sigma^2}{2E}$$

where  $E$  is Young's modulus. Why is this likely to be an underestimate?

The cylindrical boiler of a steam locomotive, which operates with an internal pressure of 2.0 MPa, has a diameter of 2.0 m and a wall thickness of 6 mm. The steel of which the boiler is made may contain internal flaws of up to 1 mm in size. Using the above relationship, estimate the minimum toughness which the steel must have in order to ensure that there is no danger of the boiler exploding (failing by fast fracture).

Comment on your answer in the context of relevant property values in the Data Book.

[For steel, Young's modulus,  $E = 200 \text{ GPa}$ . The maximum (hoop) stress in an internally pressurised cylinder is given by  $\sigma = \frac{Pr}{t}$ , where  $P$  is the pressure,  $r$  is the cylinder radius and  $t$  is the wall thickness.]

## SECTION B

5 Explain how the reciprocal lattice is derived from the lattice in real space. How are the reciprocal lattice parameters  $a^*$ ,  $b^*$ ,  $c^*$  related to the direct lattice parameters  $a$ ,  $b$ ,  $c$  in (i) the tetragonal system, (ii) the hexagonal system? Relate the reciprocal interaxial angles  $\alpha^*$ ,  $\beta^*$ ,  $\gamma^*$  to the interaxial angles in real space  $\alpha$ ,  $\beta$ ,  $\gamma$  in these two systems.

A crystal of the mineral *beyerite*, which is known to be tetragonal with  $a = 4 \text{ \AA}$  and  $c = 22 \text{ \AA}$ , is mounted on an X-ray diffractometer with [001] vertical. A horizontal beam of CuK $\alpha$  radiation is incident on the crystal, which is rotated about [001] until the 330 reflexion is obtained. The Bragg angle  $\theta$  is observed to be  $60.25^\circ$ . Calculate the lattice parameter  $a$ . It is found that the 1,1,12 reflexion also occurs exactly at this setting of the crystal. Sketch the  $x^*y^*$  section of the reciprocal lattice and the section of the reciprocal lattice containing  $z^*$  and [330]. On each section mark the trace of the Ewald sphere for this setting. Thence calculate the lattice parameter  $c$ . What lattice types are possible for *beyerite*?

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6 For a transformation from one phase to another of the same composition, show that the radius  $r^*$  of a critical nucleus of the new phase is given by

$$r^* = \frac{2\sigma}{G_V},$$

where  $G_V$  is the free energy driving force for the transformation (per unit volume), and  $\sigma$  is the interfacial energy (per unit area) between the old and new phases. What is the significance of the critical nucleus for growth of the new phase?

Show also that  $G_V$  is given by

$$G_V = S_V (T_e - T),$$

where  $S_V$  is the entropy difference (per unit volume) between the two phases, and  $T_e$  is the temperature at which the two phases are in equilibrium.

A glass has a population  $2.4 \times 10^{13} \text{ m}^{-3}$  of quenched-in nuclei, evenly distributed over the range of radius from 2 nm to 5 nm. On annealing it undergoes crystallization to a single phase of the same composition as the glass. At what temperature should the annealing be carried out to obtain an average grain diameter of 50  $\mu\text{m}$  in the final, fully crystallized material?

[  $\sigma_{\text{glass/crystal}} = 0.18 \text{ J m}^{-2}$ ; for the liquid/crystal transformation  $S_V = 890 \text{ kJ K}^{-1} \text{ m}^{-3}$ ,  $T_e = 1770 \text{ K}$ .]

7 State briefly the factors that influence the intensities of X-ray powder diffraction lines.

$\text{LiZnN}$  is known to have a face-centred cubic lattice and to adopt the *antifluorite* structure in which the N atoms occupy the anion sites at 000 etc. and the Li and Zn atoms the cation sites at  $\frac{1}{4} \frac{1}{4} \frac{1}{4}$  etc. Calculate the intensities of the 111 and 200 powder lines by assuming (i) that Li and Zn are statistically disordered on the cation sites, and (ii) that the Li atoms occupy the sites at  $\frac{1}{4} \frac{1}{4} \frac{1}{4}$  etc. and the Zn atoms occupy the sites at  $\frac{3}{4} \frac{3}{4} \frac{3}{4}$  etc. It is observed that  $I(200) > I(111)$ . Is  $\text{LiZnN}$  ordered or disordered?

The observed powder line with the lowest  $d$ -value when using  $\text{CuK}$  radiation corresponds to the 422 reflexion. It is a doublet with  $\theta = 70.54^\circ$  and  $70.86^\circ$ . Calculate the value of the cell parameter  $a$  and estimate its accuracy.

[Atomic scattering factors may be taken as  $f_{\text{Li}^+} = 2$ ,  $f_{\text{Zn}^{2+}} = 28$ ,  $f_{\text{N}^{3-}} = 10$ .]

8 Explain what is meant by the terms *optical indicatrix* and *optic axis*. Why is the optic axis of a trigonal crystal necessarily parallel to the triad?

Tourmaline is trigonal with  $a = 15.84 \text{ \AA}$ ,  $c = 7.10 \text{ \AA}$  and principal refractive indices  $n_e = 1.615$  and  $n_o = 1.633$ . Determine the vibration directions [UVW] and the refractive indices for light travelling normal to (301). State the optic sign of tourmaline.

### SECTION C

9 Show that the slopes of phase boundaries on a pressure-temperature (P–T) diagram are given by

$$\frac{dP}{dT} = \frac{S}{V}$$

where  $S$  and  $V$  are the entropy and volume differences between the phases. Why are such phase boundaries approximately straight?

In the earth's lower mantle  $\text{MgSiO}_3$  exists in a number of distinct phases, the thermodynamic data for three of which are given below:

	$H$ (kJ mol <sup>-1</sup> )	$S$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$V$ (cm <sup>3</sup> mol <sup>-1</sup> )
pyroxene	0	67.86	31.47
ilmenite	61.05	53.82	26.53
perovskite	128.95	65.49	24.51

The enthalpy ( $H$ ), entropy ( $S$ ) and volume ( $V$ ) have been calculated for  $P = 0$  and  $T = 800 \text{ K}$  to  $2400 \text{ K}$ ; the values are independent of  $T$  at  $P = 0$ , but only values of  $S$  and  $V$  are independent of  $P$ . Which is the stable phase at  $1000 \text{ K}$  and  $P = 0$ ?

At constant  $T$ , the pressure dependence of the Gibbs free energy  $G$  is given by

$$G(P) = G(P = 0) + PV.$$

Using this expression to plot values of  $G$  as a function of  $P$ , or otherwise, deduce the sequence and pressures of phase transitions expected at  $1000 \text{ K}$  as  $P$  is raised from  $0$  to  $30 \text{ GPa}$ .

By considering the slopes of the phase boundaries in the  $P$ - $T$  phase diagram at  $1000 \text{ K}$ , estimate the temperature above which the ilmenite phase is not stable at any pressure. (This is most readily done on an accurate drawing of the  $P$ - $T$  phase diagram over the ranges  $1000 \text{ K}$  to  $2400 \text{ K}$  and  $0 \text{ GPa}$  to  $30 \text{ GPa}$ .) At what pressure is the ilmenite phase stable to the highest temperature?

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**10** What is meant by the terms *solution treatment* and *age hardening*? Explain why the yield stress of an age-hardening metal alloy tends to go through a maximum as ageing is continued. Outline a simple method for estimating the peak yield stress from a knowledge of the changing microstructure during ageing.

For a binary alloy, showing age hardening, which exhibits a series of metastable precipitate phases, describe and explain the changes in matrix composition which occur during age hardening.