

Answer EVERY question from section A and TWO questions from section B.

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question.

Mass of the electron	m_e	=	9.11×10^{-31} kg
Charge on the electron	e	=	-1.602×10^{-19} C
Permittivity of free space	ϵ_0	=	8.854×10^{-12} F m ⁻¹
Boltzmann's constant	k_B	=	1.38×10^{-23} J K ⁻¹
Planck's constant/ 2π	\hbar	=	1.05×10^{-34} J s
Speed of light	c	=	3×10^8 m s ⁻¹

SECTION A

[Part marks]

1. Explain the terms *lattice*, *basis* and *unit cell*. [3]

Write down with justification the number of lattice points in the conventional cubic unit cell for the simple cubic, body centred cubic and face centred cubic lattices. [4]

2. The interaction potential energy $U(r)$ between two atoms at separation r may be written as

$$U(r) = U_0 \left[3 \left(\frac{r_0}{r} \right)^8 - 4 \left(\frac{r_0}{r} \right)^6 \right]$$

which is a variant of the standard Lennard-Jones potential, and U_0 and r_0 are constants.

For a molecule composed of three atoms in an equilateral triangular configuration, interacting via $U(r)$, calculate the minimum bond length and the cohesive energy in equilibrium. [3]

Make a sketch of $U(r)$ being careful to label the axes in terms of U_0 and r_0 . [3]

3. Sketch the dispersion relation of phonons (lattice waves) propagating in a one-dimensional crystal formed from alternating particles of different masses, connected by identical springs. Using their usual names, label the various branches of the dispersion relation. [3]

Describe all the possible motions of the atoms in the allowed (longitudinal) waves in the long wavelength limit. [4]

4. For a cubic system, what is the relationship between the lattice plane spacing d , the lattice constant a , and the Miller indices (h, k, l) ? [2]

Write down Bragg's law for the constructive interference of X-rays of wavelength λ scattered through an angle 2θ by lattice planes of spacing d in a crystal. [2]

Calculate the expected scattering angles 2θ of the three lowest order diffraction peaks from a simple cubic lattice of spacing $a = 4.00 \text{ \AA}$ if $\lambda = 1.50 \text{ \AA}$. [3]

5. With reference to the electronic band structure, explain what is meant by the terms *direct band gap* and *indirect band gap* semiconductors. Illustrate your answer with appropriately annotated sketches of the band structure in each case. [4]

For a semiconductor with an indirect band gap, make a sketch of the energy dependence of the photon absorption coefficient. Relate any energy scales to those shown in the sketch of the band structure, and indicate regions of transparency and opacity. [3]

6. In the free electron theory of metals the Fermi energy \mathcal{E}_F is given by

$$\mathcal{E}_F = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3}$$

where n is the number of electrons per unit volume. Lithium is a monovalent metal which crystallises in the body centred cubic structure with lattice constant $a = 3.49 \text{ \AA}$.

Calculate the Fermi energy of lithium in units of eV. [3]

Calculate the Fermi temperature of lithium, and how this helps us understand why the specific heats of metals are typically much smaller than the classical value. [3]

SECTION B

7. This is a question about semiconductors.

(a) Explain what is meant by the terms *intrinsic* and *extrinsic* semiconductors. With the aid of energy versus wavevector diagrams, distinguish between the cases of *n*- and *p*-type extrinsic semiconductors, indicating the states that give rise to extrinsic behaviour in both cases. Take care to define any terms you use. [6]

(b) The density of electron states $g(\mathcal{E})$ in the conduction band of a semiconductor with an energy gap \mathcal{E}_G is given by

$$g(\mathcal{E}) = \frac{V}{2\pi^2\hbar^3} (2m_e^*)^{3/2} (\mathcal{E} - \mathcal{E}_G)^{1/2}$$

where m_e^* is the effective mass of the electron, V is the volume and the zero of energy is equal to the top of the valence band. Show that the number of electrons per unit volume in the conduction band is given by

$$n = N_C e^{(\mu - \mathcal{E}_G)/k_B T}$$

where N_C is a temperature dependent constant which you should determine, and μ is the chemical potential. (Note: $\int_0^\infty x^{1/2} e^{-x} dx = \sqrt{\pi}/2$.) [8]

(c) Derive the corresponding expression for the number of holes p per unit volume in the valence band and hence show that for an intrinsic semiconductor

$$n = p = AT^{3/2} e^{-\mathcal{E}_G/2k_B T}$$

where A is a constant. [8]

(d) Germanium ($\mathcal{E}_G=0.66$ eV) has an intrinsic carrier concentration at 300 K of $2 \times 10^{19} \text{ m}^{-3}$. Imagine that a sample of germanium has been purified until it contains only 10^{16} impurities m^{-3} . Show that the temperature T_i above which germanium exhibits intrinsic behaviour can be written as

$$11.8 \approx \frac{3826}{T_i} - \frac{3}{2} \log_e T_i$$

Hence estimate T_i using trial and error or otherwise. [8]

8. This is a question about the phonon contributions to the specific heat and thermal conductivity of a monoatomic insulating solid.

(a) State the key assumptions used in the Debye theory of the specific heat of insulating solids. [3]

(b) Given that the phonon density of states as a function of frequency ω in three dimensions is given in Debye theory by

$$g(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{v_s^3}$$

explain why the internal energy U of a solid may be written as

$$U = A \int_0^{\omega_D} \frac{\omega^3}{\exp(\hbar\omega/k_B T) - 1} d\omega$$

where V is the sample volume, v_s is the speed of sound, A is a constant independent of temperature, and ω_D is the Debye frequency. (You do not need to evaluate explicitly A or ω_D). [7]

(c) Using the expression for U , derive an expression for the specific heat C_V . Determine the temperature dependence of C_V in the limit $T \rightarrow 0$, and hence sketch its temperature dependence up to and including its classical limiting value at high temperature. (Note that $\int_0^\infty x^4 e^x / (e^x - 1)^2 dx = 4\pi^4/15$.) [10]

(d) Explain briefly what are meant by the terms *normal* and *Umklapp* processes in the context of heat transport by phonons. [4]

(e) From kinetic theory, the thermal conductivity of a gas of phonons can be written as

$$\kappa = \frac{1}{3} \bar{v} \ell C_V$$

where \bar{v} is the average phonon speed and ℓ is the mean-free path between phonon collisions. Using this result, discuss how κ varies with temperature providing suitably annotated sketches where appropriate. You may take \bar{v} to be independent of temperature. [6]

9. This question is about the formation of electronic energy bands in crystalline solids.

Start by considering a free-electron model of a one-dimensional metal formed from a chain of N atoms separated by a distance a and of overall length L .

(a) Using periodic boundary conditions, show that the spacing of allowed wavevectors is given by $\Delta k = 2\pi/L$. Hence by identifying the coordinates in reciprocal space of the first Brillouin zone (BZ) boundary, show that including spin degeneracy there are $2N$ allowed k states in the first BZ. [4]

(b) Sketch the electronic dispersion relation for this model, identify the position of the BZ boundaries, and indicate where the Fermi level would lie for a monovalent and a divalent system. [6]

Now take into consideration the fact that the electrons interact with the periodic potential $V(x)$ from the positively charged ion cores.

(c) Discuss in detail what happens when the electron's wavevector lies on the BZ boundary. [5]

(d) Justify why the electronic wavefunction at the BZ boundary can be written as

$$\psi^\pm(x) = \frac{1}{\sqrt{2L}} (\exp(i\pi x/a) \pm \exp(-i\pi x/a))$$

Discuss what the two forms represent both in terms of the spatial distribution of electronic charge and the consequences for the band structure in the vicinity of the BZ boundary. [5]

(e) Assuming that the periodic potential is given by

$$V(x) = - \sum_n V_n \cos\left(\frac{2\pi nx}{a}\right)$$

use first-order perturbation theory to show that the effect of $V(x)$ is to produce an energy gap given by

$$\mathcal{E}_g = \frac{2}{L} \sum_n V_n \int_0^L \cos\left(\frac{2\pi nx}{a}\right) \cos\left(\frac{2\pi x}{a}\right)$$

and hence that the energy gap at the first BZ boundary is equal to V_1 . [10]

10. This question is about using X-rays to determine the structure of an unidentified element which is known to have either the body centred cubic (BCC) or face centred cubic (FCC) structure.
- (a) By adopting a conventional cubic unit cell, describe using annotated figures how the BCC and FCC structures can be decomposed into a simple cubic lattice and a basis. In each case, identify the basis atoms and write down their coordinates. [6]
- (b) Write down the general expression for the X-ray unit cell structure factor being careful to define any terms that you introduce. [3]
- (c) Obtain expressions for the unit cell structure factor of the BCC and FCC structures using the conventional unit cell and deduce the restriction on values of (hkl) for the observation of diffraction peaks. [6]
- (d) In an X-ray scattering experiment using a monochromatic beam of wavelength 1.0 \AA on a powdered sample of the unknown element, the first three Bragg peaks are observed at scattering angles $2\theta = 24.69, 28.58$ and 40.87° . Using these data assign Miller indices to these reflections and hence deduce whether the material adopts either the BCC or FCC structures and calculate its lattice constant. [10]
- (e) Now imagine a different material where the choice is between simple cubic, BCC and FCC. Explain how this affects the correct assignment of the structure and what experiment would have to be performed to reliably determine the structure. [5]