

Answer any THREE QUESTIONS

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	=	9.11×10^{-31} kg
Planck's constant h	=	$2\pi \times 1.05 \times 10^{-34}$ Js
elementary charge e	=	1.60×10^{-19} C
one electron volt	=	1.60×10^{-19} J
Boltzmann's constant k_B	=	1.38×10^{-23} JK ⁻¹
permittivity of vacuum ϵ_0	=	8.85×10^{-12} Fm ⁻¹
Avogadro's number	=	6.02×10^{23}

[Part marks]

1. (a) What is meant by the cohesive energy of a solid? Discuss the nature of the interactions that contribute to the cohesive energy of solids. [7]
- (b) What are the two structures of ionic crystals of the type X⁺Y⁻ which have coordination numbers of six and eight respectively? [1]
- (c) If the radius of the lithium ion is 0.078 nm and the radius of the fluoride ion is 0.133 nm, show that the structure of lithium fluoride must have a coordination number of six. [5]
- (d) The short-range repulsive potential as a function of distance r between a lithium ion and a fluoride ion may be modelled as $V(r) = A \exp(-r/\rho)$ where A and ρ are constants.
Write down an expression for the cohesive energy of lithium fluoride as a function of the nearest-neighbour distance, assuming that $V(r)$ acts only between nearest-neighbour ions. [1]
- (e) Hence, by using the equilibrium condition for the stability of the structure, or otherwise, show that the cohesive energy per ion pair at the equilibrium nearest-neighbour distance, r_0 , is given by
$$|U| = \frac{Me^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0}\right)$$
where M is the Madelung constant for the structure. [4]
- (f) The cohesive energy and the nearest-neighbour distance for lithium fluoride are 10.7 eV per ion pair and 0.1996 nm respectively. The Madelung constant for the structure taken by lithium fluoride is 1.748. Determine the constants A and ρ in the expression for the short-range interaction. [2]

2. (a) What is meant by the term *density of states* for phonons and electrons in solids? [1]

(b) What is the phonon dispersion relation in the Debye approximation? Explain the meaning of the Debye frequency. [2]

(c) The phonon density of states in the Debye approximation is given by $G(\omega) = 9N\omega^2/\omega_D^3$ where N is the number of atoms in the solid and ω_D is the Debye frequency. Given also that the heat capacity for a simple harmonic oscillator at temperature T is

$$C_V(\omega) = \frac{\hbar^2\omega^2}{k_B T^2} \exp\left(\frac{\hbar\omega}{k_B T}\right) \left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^{-2}$$

show that within the Debye approximation, the heat capacity is proportional to T^3 at low temperatures and determine the constant of proportionality. [5]

You may use the following result

$$\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^2}{15}$$

(d) Discuss the effect of temperature on the distribution of electron energies for a free electron gas. [2]

(e) According to the classical equipartition theorem, what contribution to the heat capacity of a solid would you expect from (i) the lattice vibrations and (ii) the free electron gas? [2]

(f) Explain why these two contributions to the heat capacity are much less than the classical values at low temperatures. [2]

(g) Why does the heat capacity for lattice vibrations reach the equipartition limit in most solids as the temperature is raised, whereas the heat capacity for electrons never does? [4]

(h) The heat capacity of N free electrons in a solid is given by

$$C_V = \frac{Nk_B^2\pi^2T}{2E_F}$$

where E_F is the Fermi energy. If the Fermi energy of monovalent potassium is 2.12 eV and the Debye frequency is 11.91×10^{12} Hz, determine the temperature at which the electronic and phonon contributions to the heat capacity are equal. [2]

(i) Experiments show that the heat capacity of potassium (in units of mJ per mole per K) can be described by the relation $C_V/T = 2.08 + 2.57T^2$. Compare this with the values you have calculated and discuss any discrepancies. [2]

3. (a) Describe the way charge carriers in a solid respond to an external electric field. Derive the drift velocity and current density in terms of the carrier mass m , charge q , density n and relaxation time (or half the period between scattering events) τ . [6]

- (b) A Hall field \mathcal{E}_H along the z -axis appears as a result of current flow along the y -axis in a material in the presence of a magnetic field B along the x -axis. It is given by

$$\mathcal{E}_H = R_H B j$$

where j is the current density. Express the Hall coefficient R_H in terms of the carrier properties. [4]

- (c) Sketch the form of the dispersion relation $E(k)$ for electrons able to move along a chain of atoms separated by distance a , according to the nearly-free electron model. [1]

- (d) The effective mass of an electron as a function of wavevector k is

$$m^* = \left(\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \right)^{-1} .$$

Consider two situations for the electronic structure of the chain, with the Fermi level just above the bottom and just below the top of a band, respectively. Use your sketch of the nearly-free electron dispersion relation to show that the effective masses for the electrons at the Fermi level have opposite signs in the two situations. [2]

- (e) Show that the mean drift velocity of electrons over a range of wavevector $-\pi/a \leq k \leq \pi/a$ is zero. [2]

- (f) The Hall coefficient for copper is negative while that of cadmium is positive. How can we interpret these facts in the light of the above model? [5]

4. (a) Define what is meant by the terms *lattice*, *basis*, *conventional unit cell* and *primitive unit cell*. [4]
- (b) Specify the lattice, basis and coordination number of the diamond structure. [3]
- (c) Carbon and tin are members of Group 4 of the Periodic Table, and hence have four electrons in their outer shell. They can both take the diamond structure in the solid state. Tin in the diamond structure is called grey tin; it is an opaque material with poor mechanical properties.
Interpret the optical properties of diamond and grey tin in terms of the band theory of electrons in solids. [2]
- (d) The more familiar form of tin is a slightly distorted bcc structure called white tin, with metallic properties. It is stable at room temperatures, while grey tin is stable at lower temperatures.
- i. Explain why the band theory of solids suggests that elements in Group 4 are poor electrical conductors. [4]
- ii. How can one explain, on the other hand, the fact that white tin is a good conductor of electricity? [2]
- iii. It is said that the tin buttons holding together the uniforms of Napoleon's soldiers in Russia in 1812 disintegrated as they transformed from white to grey tin.
Outline the calculations Napoleon should have made, starting from a pair potential for tin atoms, to estimate the transition temperature between these two structures. [5]

5. The mean energy of an electron in a metal according to the free electron model is

$$\bar{E} = \frac{3}{5}E_F$$

where the Fermi energy E_F is given by

$$E_F = \frac{\hbar^2(3\pi^2n)^{2/3}}{2m}$$

and n and m are the density and mass of free electrons, respectively.

- (a) Using the result $dE = -pdV$, where E is the total energy of electrons in volume V , derive an expression for the pressure p of the free electron gas. [4]
- (b) Hence show, using the appropriate thermodynamic definition, that the chemical potential (the Gibbs free energy per electron) at $T=0$ is equal to E_F . [2]
- (c) Calculate the chemical potential for the free electrons in pure silver, assuming one valence electron is made available per primitive cell, the volume of which is $1.7 \times 10^{-29} \text{ m}^3$. [2]
- (d) By adding divalent magnesium as an impurity at a concentration of one atom per million atoms of silver, by how much is the chemical potential altered? [4]
- (e) Silicon is an intrinsic tetravalent semiconductor with a band gap of about 1.1 eV. Discuss and explain the change in chemical potential of the electrons brought about by adding pentavalent or trivalent impurities at a concentration of one atom per million atoms of silicon. Contrast this behaviour with the case of the silver-magnesium alloy just considered. [8]