Answer Books A, B and C.

Any calculator, except one with pre-programmable memory, may be used in this examination.

LEVEL 2
Examination contributing to the Degrees of
Bachelor of Science (BSc) and Master in Science (MSci)

PHY2002
Physics of the Solid State

Wednesday, 7th August 2019 2:30 PM - 5:30 PM

Examiners: Professor P Browning
Dr P van der Burgt
and the Internal Examiners

Answer ALL TEN questions in Section A for 4 marks each.
Answer ONE question in Section B for 30 marks.
Answer ONE question in Section C for 30 marks.

Use a separate answer book for each Section.
You have THREE hours to complete this paper.

THE QUEEN'S UNIVERSITY OF BELFAST
SCHOOL OF MATHEMATICS AND PHYSICS

PHYSICAL CONSTANTS

Speed of light in a vacuum	$c = 3.00 \times 10^8 \text{ ms}^{-1}$
Permeability of a vacuum	$\mu_0 = 4\pi \times 10^{-7} \text{ Hm}^{-1}$
	$\approx 1.26 \times 10^{-6} \text{ Hm}^{-1}$
Permittivity of a vacuum	$\varepsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$
Elementary charge	$e = 1.60 \times 10^{-19} \text{ C}$
Electron charge	$= -1.60 \times 10^{-19} \text{ C}$
Planck Constant	$h = 6.63 \times 10^{-34} \text{ Js}$
Reduced Planck Constant	$\hbar = 1.05 \times 10^{-34} \text{ Js}$
Rydberg Constant for hydrogen	$R_\infty = 1.097 \times 10^7 \text{ m}^{-1}$
Unified atomic mass unit	$1u = 1.66 \times 10^{-27} \text{ kg}$
	$1u = 931 \text{ MeV}$
1 electron volt (eV)	$= 1.60 \times 10^{-19} \text{ J}$
Mass of electron	$m_e = 9.11 \times 10^{-31} \text{ kg}$
Mass of proton	$m_p = 1.67 \times 10^{-27} \text{ kg}$
Mass of neutron	$m_n = 1.67 \times 10^{-27} \text{ kg}$
Molar gas constant	$R = 8.31 \text{ JK}^{-1}\text{mol}^{-1}$
Boltzmann constant	$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$
Avogadro constant	$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$
Gravitational constant	$G = 6.67 \times 10^{-11} \text{ Nm}^2\text{kg}^{-2}$
Acceleration of free fall on the Earth's surface	$g = 9.81 \text{ ms}^{-2}$

SECTION A
Use a Section A answer book
Answer all TEN questions from this section

1   Space group number 221 is *Pm3̄m*. State which type of crystal system "P" represents in this space group, and describe the symmetry operation represented by "m".   **[4]**

2   Demonstrate that a five-fold symmetry is not consistent with the conventional definition of a crystalline lattice.   **[4]**

3   Draw the real space and reciprocal space unit cells for an orthorhombic crystal ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$) with the following lattice parameters a = 8 Å, b = 4 Å and c = 12 Å.   **[4]**

4   With reference to the manner in which the free energy changes across a phase transition, define the terms "first order" and "second order"; in addition, sketch the form of the order parameter as a function of temperature in both first and second order transitions.   **[4]**

5   Consider the following Landau-Ginzburg-Devonshire expression for the free energy (G) in a ferroelectric, as a function of the order parameter (polarisation, P), temperature (T) and applied electric field (E):

$$G = \frac{a}{2}(T - T_C)P^2 + \frac{b}{4}P^4 - E.P$$

Using this expression show that the dielectric susceptibility tends to infinity as $T \to T_C$.   **[4]**

6   A material composed of two atomic types ("A" and "B") may exist as a solid solution at high temperature but undergo exsolution or ordering on cooling. Outline what is meant by the terms exsolution and ordering and comment on how behaviour on cooling is dictated by different A-B, B-B and A-A bond energies.   **[4]**

7   Phonon $\omega - k$ dispersion relations are strictly periodic. Referring to a 1D monatomic chain, or otherwise, explain how the atomic displacements associated with a phonon at $k = 0$ are identical to those at $k = \frac{2\pi}{a}$ where a is the lattice repeat distance.   **[4]**

SECTION A

8   Discuss the key differences between optic and acoustic phonons.   **[4]**

9   Sketch the typical electrical resistivity versus temperature ($\rho(T)$) trends that are expected in the vicinity of room temperature for metals and intrinsic semiconductors, noting down the functional form of each. Identify the dominant physical processes that are responsible for these two characteristic trends.   **[4]**

10   Sketch a labelled flat energy-band diagram for a p-type doped semiconductor at $T = 0\ \mathrm{K}$ and indicate the position of the Fermi Energy. Schematically plot how the Fermi level μ is expected to change as temperature is increased and identify the limiting value. Comment on how this behaviour changes if the concentration of dopant ions is increased.   **[4]**

SECTION B
Use a Section B answer book
Answer ONE of the TWO questions in this section

11 **(a)** **(i)** Explain what a stereogram is and the advantages of using it in crystallography. **[3]**

(ii) The cubic crystal structure is the most common structure used in crystallography for examples. However, this structure contains the highest number of point groups (and space groups). Explain why this is and state the most important symmetry element that describes a cubic structure. **[3]**

(iii) Draw a stereogram for a primitive cubic system, viewed along [001]. By adding triads along the body diagonals, what new symmetry element is automatically generated and in what directions. **[4]**

(b) Under ambient conditions, $BaTiO_3$ exists in a perovskite structure with a space group P4mm (tetragonal), with lattice parameters a = 4.004 Å and c = 4.201 Å, and the following motif:

Ba: 0.5, 0.5, 0

Ti: 0, 0, 0.5

O: 0, 0, 0; 0.5, 0, 0.5; 0, 0.5, 0.5

(i) Draw an accurate structure plan of 2 x 2 unit cells, viewed along [001]. **[3]**

(ii) With reference to the structure plan, describe the $BaTiO_3$ structure in terms of linked coordination polyhedral. **[4]**

(iii) Draw an accurate reciprocal lattice section a* - c* and determine the magnitudes of a*, c* and γ*. **[3]**

(iv) A single crystal of $BaTiO_3$ is placed in a diffractometer, such that a Cu-Kα source (λ = 1.54 Å) is incident along the a axis. Using the Ewald sphere and the reciprocal lattice, show that the plane (001) undergoes diffraction under these conditions, and calculate its angle of diffraction. **[6]**

(v) X-rays from a Mo-Kα (λ = 0.71 Å) source are diffracted from a $BaTiO_3$ single crystal. Assuming that n=1, calculate the interplanar distance for (101) and angle that gives rise to this reflection. **[4]**

SECTION B

12 **(a)** **(i)** Briefly explain what is meant by "Gibbs free energy" and "order parameter" in the context of phase transitions. **[4]**

(ii) Landau theory expresses the free energy (G) in terms of the order parameter (Q). A typical Landau expression is as follows:

$$G = \frac{a}{2}(T - T_c)Q^2 + \frac{b}{4}Q^4 + \frac{c}{6}Q^6$$

Show how, under equilibrium conditions, this expression allows for the prediction of first order, second order and tricritical phase transition behaviour. **[6]**

(iii) Consider the following dataset, in which the order parameter for a phase transition (with $T_c = 400K$) has been tracked as a function of temperature. Assuming $Q \propto (T_c - T)^n$, plot an appropriate graph from which the exponent n may be determined and hence state the nature of the phase transition. **[8]**

Temperature (K)	Order Parameter
390	0.40
380	0.47
370	0.52
360	0.56
350	0.60
300	0.71
250	0.78
200	0.84
150	0.89
100	0.93

[QUESTION 12 CONTINUED OVERLEAF]

[QUESTION 12 CONTINUED]

(b) Magnetite shows two kinds of order-disorder phase transition: one in which there is a radical change in electrical conductivity and another in which ferrimagnetism emerges. Discuss both of these phase transitions and explain in each how the change in functional properties emerge. **[12]**

SECTION C
Use a Section C answer book
Answer ONE of the TWO questions in this section

13 **(a)** Explain what is meant by the term "heat capacity" and state how the heat capacity can be used to experimentally determine the enthalpy, entropy and free energy in a solid. **[5]**

(b) Einstein attempted to rationalise the variation in heat capacity as a function of temperature in a solid by first finding an expression for the internal energy. He stated that the internal energy (U) was given as follows:

$$U = 3N\langle n \rangle \hbar \omega$$

(i) Explain the physical origin of each of the main components in this equation: $3N$, $\langle n \rangle$, and $\hbar\omega$, and how the product of these components generates the internal energy. **[5]**

(ii) Assuming a Boltzmann distribution of state occupancy, show that $\langle n \rangle$ can be given by the following expression, where T is the absolute temperature:

$$\langle n \rangle = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$$

[6]

(iii) Hence, or otherwise, show that the Einstein heat capacity expression is:

$$C_v = 3Nk \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1\right)^2}$$

where $\Theta_E = \frac{\hbar\omega}{k}$. **[8]**

(c) **(i)** By considering phonon lattice vibrations under "periodic boundary conditions" show that the density of wavevectors in reciprocal-space is uniform. **[3]**

(ii) Hence show that the density of states as a function of the wavenumber is parabolic. **[3]**

SECTION C

14 **(a)** **(i)** For a three-dimensional free-electron gas, sketch both the electron energy $E(k)$ as a function of wavevector k and the corresponding density of states $D(E)$ as a function of E. **[3]**

(ii) Considering now the effect of the periodic ionic potential, sketch the electron energy $E(k)$ dispersion diagram in the extended zone scheme over the wavevector range $-3\pi/a \leq k \leq 3\pi/a$, where a is the lattice constant. On the basis that $E(k \pm 2\pi/a) = E(k)$, use illustrations to show how the reduced band scheme is constructed. Indicate an interval of k-space that contains all physically distinct wavevector solutions. **[5]**

(iii) Explain how energy band structure and occupancy can broadly account for the conductivity behaviour of metals, semiconductors and insulators. For each case, illustrate your answer with annotated $E(k)$ diagrams. Comment on the effect of applied electric fields and temperature where relevant. **[9]**

(iv) By examining the case of a fully-populated electron band compared to when the band is nearly-full, give an argument (supported by equations) as to how a current associated with a nearly-full band of electrons can be instead characterised in terms of positively-charged 'holes'. **[5]**

(b) **(i)** What is the purpose of introducing the electron 'effective mass' m^* in discussions of electron energy band structure? Assuming a parabolic energy band with $E(k) = \hbar^2 k^2/(2m^*)$, derive a general relationship between m^* and the curvature of the dispersion function $E(k)$. **[3]**

(ii) A notional energy band has the functional form:
$$E(k) = C[1 - \cos(ka)]$$
where the constants $C = 0.75$ eV and $a = 3x10^{-10}$ m.

Use your general expression for m^* from part (b)(i) to numerically calculate the effective mass for electrons with $k = 0$ and $k = \frac{\pi}{a}$, giving your answers in units of the free electron mass m_0. **[5]**

END OF EXAMINATION