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

Answer Books A, B and C

LEVEL 2

EXAMINATION CONTRIBUTING TO THE DEGREES OF BACHELOR OF SCIENCE (BSc) AND MASTER IN SCIENCE (MSci)

PHY2002
Physics of the Solid State

Duration: 3 Hours

Monday, 13th August 2018 9:30 AM - 12:30 PM

Examiners: Prof. P. Browning
Dr. P. van der Burgt
and the Internal Examiners

**Answer ALL TEN questions in Section A.
Answer ONE question in Section B.
Answer ONE question in Section C.**

**Use a separate answer book for each Section.
Follow the instructions on the front of the answer book. Enter
your Anonymous Code number and Seat number, but NOT your name.**

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 10 questions from this section**

1   State the Weiss Zone Law, used in crystallography, and demonstrate that it holds

   irrespective of the crystal system within which it is applied.   **[4]**

2   Calcite ($CaCO_3$) is trigonal (a=b≠c; $\alpha=\beta=90°$, $\gamma=120°$) with lattice parameters a=4.99Å

   and c=17.06Å. By considering an appropriate section of the reciprocal lattice,

   determine the inter-planar spacing between successive (410) planes.   **[4]**

3   One of the 230 space groups is given as: $P4_2nm$. State the different kinds of symmetry

   elements that occur in this space group and describe their specific operation.   **[4]**

4   Explain what is meant by the term "heat capacity" and state how the variation in heat

   capacity as a function of temperature can be used to explicitly determine the enthalpy

   and entropy of a system.   **[4]**

5   The Gibb's Free Energy (G) for a system undergoing a phase transition at T_C is

   illustrated below (figure A5.1). Explain how the order of a phase transition (first order,

   second order or tricritical) can be determined from this kind of information. Hence

   determine the order of the phase transition at T_C.   **[4]**
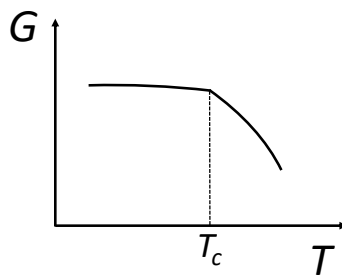
Figure A5.1: Free energy as a function of temperature for a system undergoing a phase transition

6   Briefly discuss how an increase in the total bond energy associated with changing a

   mechanical mixture of two elements into a solid solution, results in complex exsolution

   behaviour on cooling.   **[4]**

continued …

7 Briefly discuss the key differences between the Einstein and Debye treatments of heat capacity as a function of temperature. **[4]**

8 The diagram below (figure A8.1) shows the form of the thermal conductivity (κ) as a function of temperature for an insulating material. Explain the temperature dependence in terms of the heat capacity and phonon behaviour.
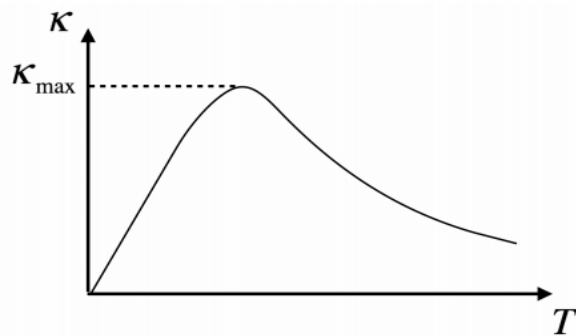
Figure A8.1: Schematic sketch of the variation in the thermal conductivity of an insulator with temperature.

[4]

9 One of the main successes of the classical Drude theory of electrical conduction in metals is the prediction of Ohm's Law. Give two examples where Drude's theory does **not** agree with experiment and explain what is predicted classically. **[4]**

10 Using electron energy-momentum band diagram sketches, explain the difference between a *direct* and *indirect* band gap semiconductor. Why would an indirect band-gap semiconductor be unsuitable for use in a light emitting diode? **[4]**

SECTION B

Use a section B answer book

Answer 1 of the 2 questions in this section

11 Lead titanate ($PbTiO_3$) is a perovskite oxide, belonging to the tetragonal crystal system ($a=b\neq c$; $\alpha=\beta=\gamma=90^o$). Its lattice type is primitive and its motif has Pb, Ti and O atoms with the following fractional coordinates in the unit cell:

Pb: 0 0 0.1

Ti: ½ ½ 0.6

O: ½ ½ 0; ½ 0 ½; 0 ½ ½

(a) **(i)** Draw an accurate 2x2 unit cell structure plan of $PbTiO_3$ viewed down [001].

[5]

(ii) Identify the shape of the coordination polyhedron surrounding each Ti atom. Outline these polyhedra on the structure plan drawn for **(a)(i)** and hence describe lead titanate in terms of a coordination polyhedral network. **[4]**

(iii) By examining the structure plan drawn in **(a)(i)**, identify any symmetry elements present and hence suggest a possible point group for lead titanate.

[4]

(iv) Draw another structure plan viewed down the [100] direction containing 2 unit cells along the c-axis, but only one along the b-axis (the ratio of c:a in this crystal is 1.06). Assuming the valence states as Pb^{2+}, Ti^{4+} and O^{2-} plot the positions of the centres of negative and positive charge in each unit cell. Hence determine the direction of the electrical dipole in $PbTiO_3$.

[Hint: for the centre of positive charge consider a shifted unit cell with the Pb^{2+} ions at the vertices]. **[7]**

[QUESTION 11 CONTINUED OVERLEAF]

(b) Below (figure B11.1) is a representative stereogram of the symmetry present in the point group 42m (solid lines are mirror planes and the rotoinversion axis is parallel to the c-axis of the crystal)
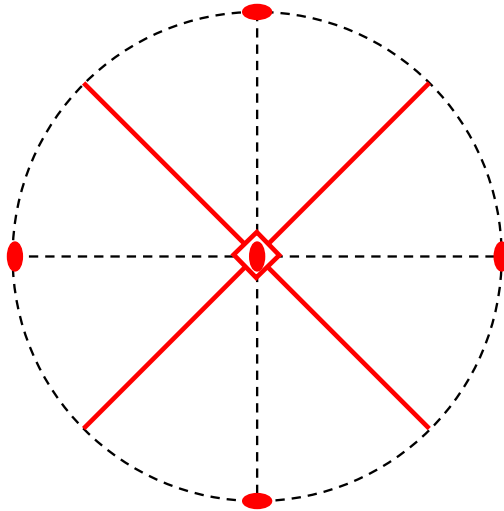
Figure B11.1: Stereogram of the symmetry elements associated with the point group 42m.

(i) On a separate sketch stereogram, plot the general pole and all other poles related to it by the symmetry indicated in figure B11.1. Hence, state whether or not this point group has a centre of symmetry and explain your reasoning. **[4]**

(ii) What can be said about the multiplicity of the [001] direction under this symmetry ? **[2]**

(iii) Point groups do not contain any glide planes or screw axes. Describe the operation of a general screw axis N_m and that of an n-glide. **[4]**

SECTION B

12 **(a)** **(i)** Explain what is meant by the terms "Free Energy" and "Order Parameter".

[4]

(ii) The values of the order parameter as a function of temperature, for a specific phase transition with T_C=560K, are given in Table B12.1 below. Given that there are no discontinuities in the derivatives of the free energy with respect to temperature, consider the data in the table and plot a suitable graph to allow the order of the phase transition to be determined. State its order and explain your reasoning.

Table B12.1: The order parameter as a function of temperature across a phase transition.

Temperature / K	Order Parameter
600	0
580	0
560	0
540	0.53
520	0.62
500	0.69
480	0.75
460	0.79
440	0.82
420	0.86
400	0.89

[9]

(b) In Landau theory, the free energy difference between states ($G(Q,T)$) may be expressed in terms of the order parameter (Q) as follows:

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

[QUESTION 12 CONTINUED OVERLEAF]

[QUESTION 12 CONTINUED]

(i) Explain why this expression contains only even powers in Q and why the prefactor $(T\text{-}T_c)$ is used. **[5]**

(ii) Demonstrate that, under equilibrium conditions, the order parameter behaviour with temperature predicted by the Landau free energy expression is consistent with the existence of first order, second order and tricritical phase transitions. **[6]**

(iii) Sketch the form of the order parameter as a function of temperature for first order, second order and tricritical phase transitions. **[3]**

(iv) The physical transition process is often referred to as "displacive" or "reconstructive". Comment on the notion that reconstructive phase transitions tend to be first order and displacive transitions second order in nature. **[3]**

SECTION C

Use a section C answer book

Answer 1 of the 2 questions in this section

13 **(a)** **(i)** By considering the form of the potential as a function of interatomic separation, justify how the harmonic approximation can be sensibly used for describing physics associated with the movements of atoms away from their equilibrium positions. How does this relate to the common representation of bonds as springs? **[6]**

(ii) Under what circumstances would this harmonic approximation break down and anharmonic effects be observed? **[3]**

(iii) Using the harmonic approximation, demonstrate that the vibrations sustained in a 1D monatomic chain must obey a relation of the form: $\omega^2 = \frac{4\mu}{m}\left[\sin\left(\frac{ka}{2}\right)\right]^2$, where ω is the angular frequency, k is the wavevector, a is the equilibrium interatomic separation, μ is the spring constant of the effective interatomic bonds and m is the mass of each atom. **[9]**

(iv) Plot a schematic phonon dispersion relation ($\omega(k)$) derived from the equivalent treatment of a 1D chain, in which there are both cations and anions with differing masses. Describe the key differences between the "optic" and "acoustic" solutions. **[4]**

(b) Demonstrate how the consideration of phonon energies can be used to predict the following thermal variation in heat capacity (C_v), as derived by Einstein:

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

Where N is the number of atoms (oscillators), k is the Boltzmann constant, θ_E the Einstein temperature and T the absolute temperature. **[8]**

SECTION C

14 (a) (i) Consider a one-dimensional free electron gas of N electrons with electron orbitals ψ_n, and of energy ε_n, described by the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \varepsilon_n\psi_n.$$

For an electron of mass m confined to a length L by infinite potential barriers, assume a sinusoidal form for ψ_n (where n is the orbital quantum number) to show that the following expression for $\varepsilon(k)$ can be obtained:

$$\varepsilon(k) = \left(\frac{\hbar^2}{2m}\right)k_n^2,$$

and then determine an expression for ε_F, the energy of electrons at the Fermi level. **[8]**

(ii) Use the expression for $\varepsilon(k)$ to obtain a one-dimensional expression for the effective mass m_{eff} in terms of the energy-band curvature. **[3]**

(iii) For the notional $\varepsilon(k)$ plots shown below (figure C14.1), rationalise any expected difference in effective mass of electrons in bands (1) and (2) in the vicinity of $k = 0$.
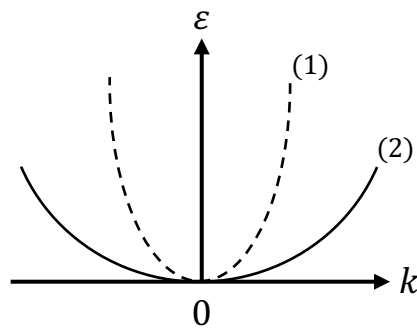

Figure C14.1: Plots of electron energy ε as a function of wavevector k.

[3]

[QUESTION 14 CONTINUED OVERLEAF]

(b) The Hall effect can be used to determine both the carrier type and concentration in semiconducting materials. A semiconducting slab of unknown doping, and carrier density n, is shown in figure C14.2(a) and is biased such that a current I flows in the direction indicated. In figure C14.2(b), a magnetic field B is also applied and an electrostatic charge distribution is seen to develop along the top/bottom faces.
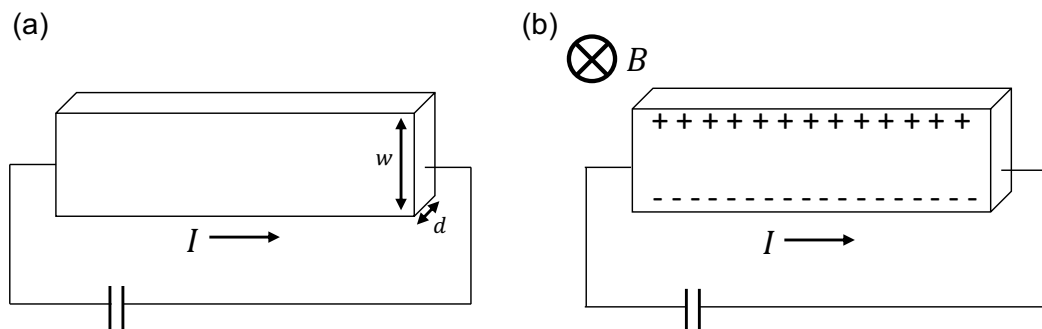
Figure C14.2: (a) Current I flowing through a schematic semiconducting slab. **(b)** An applied B-field generates a charge distribution across the top and bottom faces.

(i) Identify the direction of drift velocity v_d for electrons and holes, relative to the current flow direction shown in figure C14.2(a). **[2]**

(ii) Using figure C14.2(b), and by considering the action of the Lorentz force on the majority carriers, determine if the semiconductor is n-type or p-type. Clearly show your rationale. **[4]**

(iii) Considering the slab to have cross-sectional area $A = wd$, show that the magnetic field-induced Hall voltage V_H, when B is oriented perpendicular to the direction of current flow, is expressed:

$$V_H = \frac{IB}{nqd}, \text{ where } q \text{ is carrier charge.}$$ **[8]**

(iv) Determine the carrier density n if the measured Hall voltage $|V_H| = 200 \ mV$ for an applied magnetic field $B = 0.15 \ T$ and current $I = 20 \ mA$ flowing in a slab of thickness $d = 0.05 \ cm$.

[2]