



**QUEEN'S
UNIVERSITY
BELFAST**

PHY2002

Exam Time Table

Code PHY2002

Use lined, single-sided A4 paper
with a black or blue pen.

Write your student number
at the top of every page.

Any non-graphical calculator, except those 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 - EXAM
Physics of the Solid State
Monday, 18th May 2020, 9.30 AM - 13.30

Examiners: Prof S Matthews, Dr P van der Burgt
and the Internal Examiners
Dr J Greenwood (j.greenwood@qub.ac.uk)

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.
You have FOUR hours to complete and upload this paper.

Contact the module coordinator if you have a query at
m.gregg@qub.ac.uk and copy to mpts@qub.ac.uk

By submitting the work, you are declaring that:

1. The submission is your own original work and no part of it has been submitted for any other assignments;
2. You understand that collusion and plagiarism in an exam are major academic offences, for which a range of penalties may be imposed, as outlined in the Procedures for Dealing with Academic Offences.

THE QUEEN'S UNIVERSITY OF BELFAST
DEPARTMENT OF PHYSICS AND ASTRONOMY

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	$\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$
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

Answer ALL ten questions from this section (four marks each)

- 1 Using a conventional cubic crystal, with designated general axes and lattice vectors, sketch the following planes and directions (be as clear as possible):
- (i) $(\bar{1}10)$
 - (ii) (313)
 - (iii) $[210]$
 - (iv) $[101]$
- [4]**
- 2 Explain the difference between a primitive and a non-primitive unit cell, and clearly prove that a triangle is not suitable as a unit cell in a crystal lattice.
- [4]**
- 3 Demonstrate that the packing efficiency for a body-centred cubic (BCC) structure is 68%.
- [4]**
- 4 Explain what is meant by the terms *internal energy* and *entropy*. In addition, state explicitly how internal energy and entropy can be determined through knowledge of the variation in heat capacity as a function of temperature.
- [4]**
- 5 Discuss an example which illustrates the equivalence of order parameters with the same magnitude, but opposite sign. Hence justify why the Landau-Ginzburg free energy expression usually only contains the sum of even exponents in the order parameter.
- [4]**
- 6 State the energy and momentum conditions which must be met for phonon-phonon coalescence scattering events to occur. Hence, explain the phenomenon of Umklapp scattering among phonons.
- [4]**
- 7 The “Harmonic Approximation” is often used to allow straightforward treatment of the interatomic potential energy function, when bond lengths are close to their zero Kelvin equilibrium value. However, to rationalize properties such as thermal expansion, anharmonic terms must be included. Explain why this is the case.
- [4]**

- 8 Magnetite undergoes an order-disorder phase transition (called the Verwey transition) at approximately 120K. Discuss the nature of this phase transition and how it leads to a dramatic change in electrical conductivity.

[4]

- 9 Describe how the electron energy-wavevector ($E-k$) dispersion of the free electron gas is affected by the introduction of the crystal lattice potential, illustrating your answer with sketches of the $E-k$ dispersion plots. How does this modified dispersion then allow for the prediction of insulating behaviour and of semiconducting behaviour?

[4]

- 10 The number of free carriers per unit volume, $n(T)$, in a pure semiconductor is given by

$$n(T) = C e^{-\left(\frac{\Delta E}{2k_b T}\right)}$$

where C is a constant, k_b is the Boltzmann constant, and T is temperature.

What is the meaning of the parameter ΔE in the above formula? Use the plot in Figure A10.1 to estimate the value of ΔE , giving your answer in units of eV. [Note that the y-axis has a base-10 logarithmic scale.]

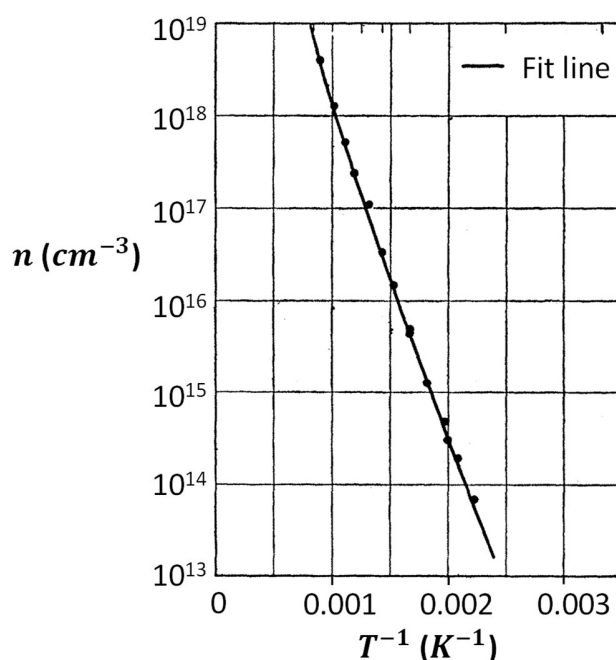


Fig A10.1 Semi-log plot of carrier density as a function of reciprocal temperature. Adapted from: Morin & Maita *Phys. Rev.* 96, 28 (1954).

[4]

SECTION B

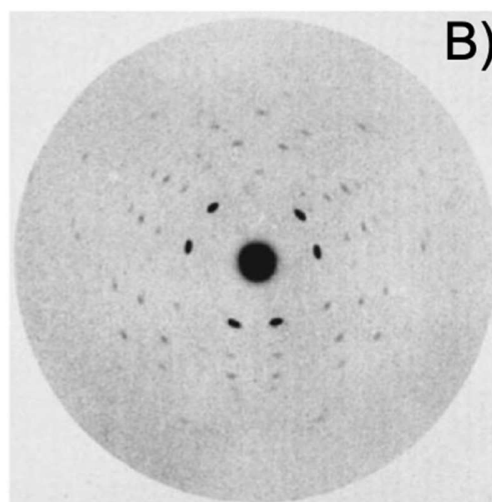
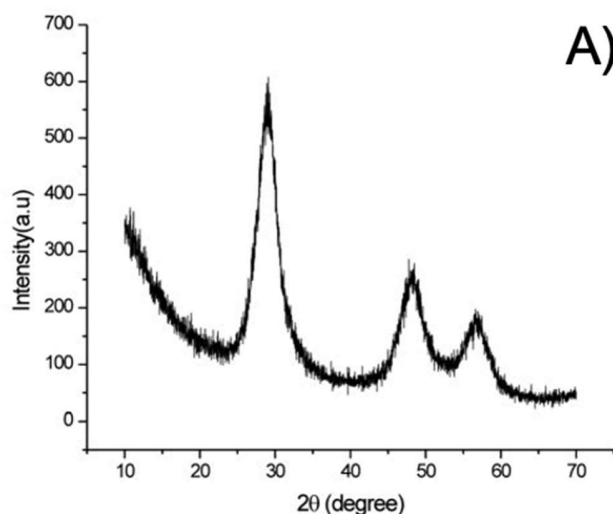
Answer 1 of the 2 questions in this section

- 11 (a) Nickel Arsenide (NiAs) has a primitive hexagonal lattice ($P6_3/mmc$) with the following motif:
- As: $(0,0,0)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$
 Ni: $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$
- (i) Draw a 2x2 structure plan viewed down the $[001]$ axis. What is the shape of the coordination polyhedron which surrounds each nickel atom and how can the NiAs structure be described in terms of these polyhedra? [4]
- (ii) The lattice parameters for NiAs are: $a = 3.61\text{\AA}$ and $c = 5.038\text{\AA}$. Sketch the primary lattice vector sets of the real and the reciprocal lattices and determine values for: a^* , b^* , c^* and γ^* . Use the reciprocal lattice to determine the angle at which the (120) and (020) planes intersect. [4]
- (iii) Explain what the Ewald sphere is and how it can be used to determine the crystal orientations in an observed diffraction pattern. [4]
- (iv) Explain why the entire reciprocal lattice is not imaged when a diffraction experiment is carried out on a single crystal. [3]
- (b) A polymorph of ZnS has a $F\bar{4}3m$ space group, and lattice parameters $a = 3.85\text{\AA}$. Figure "A" below shows the diffractogram for nanoparticles of ZnS obtained using a Cu - $K\alpha$ source (of wavelength $\lambda = 1.54\text{\AA}$) and Figure "B" shows a transmission Laue photograph for ZnS, with the beam normal to (111) .

[QUESTION 11 CONTINUED OVERLEAF]

[QUESTION 11 CONTINUED]

- (i) Explain the difference between a transmission Laue photograph and a Bragg-Brentano (single crystal) scan. **[4]**
- (ii) State the different kinds of symmetry elements present in this space group, with their direction, and identify at least one symmetry element present in the Laue photograph. **[4]**
- (iii) From Figure "A)", calculate the interplanar spacing for the three main peaks. Comment on how the peak position would change if a shorter wavelength, such as Mo - $K\alpha$ ($\lambda = 0.7 \text{ \AA}$) is used instead? **[3]**
- (iv) A Cu- $K\alpha$ source ($\lambda = 1.54 \text{ \AA}$) is directed along $[100]$ on a ZnS single crystal. Using the reciprocal lattice, calculate the interplanar spacing for the (220) planes and calculate the angle at which the (020) plane will be observed. **[4]**



SECTION B

- 12 (a) Consider a transformation in which a mechanical mixture of two elements (one composed of A atoms only and the other composed of B atoms only) changes to a solid solution, characterised by completely random bonding amongst A and B atoms.

- (i) If the energy associated with the formation of an A-A bond, B-B bond and A-B bond is given by ω_{AA} , ω_{BB} and ω_{AB} , show that the change in bond energy associated with the creation of the solid solution is as follows:

$$\Delta H_{\text{mix}} = \frac{Nz}{2} x_A x_B (2\omega_{AB} - \omega_{AA} - \omega_{BB})$$

where N is the total number of atoms, z is the bonding coordination number and x_A and x_B are the number fractions of A and B atoms respectively.

[5]

- (ii) Given that the entropy change per mole on creating the solid solution can be expressed as:

$$\Delta S_{\text{mix}} = -R(x_A \ln x_A + x_B \ln x_B)$$

demonstrate that solid solutions represent the lowest free energy at high temperatures, but that, on cooling either exsolution or ordering may occur. Be sure to discuss the relative bond energies associated with either exsolution or ordering and, where appropriate, augment discussion of the Free Energy of Mixing as a function of composition using sketch plots.

[9]

[QUESTION 12 CONTINUED OVERLEAF]

[QUESTION 12 CONTINUED]

- (b)** A general Landau-Ginzburg free energy (G) expression may be given as a function of the primary order parameter (Q), applied field (H) and temperature (T) as:

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

where a is a positive constant, b and c are constants and T_C is a critical temperature.

- (i)** Describe what is meant by the term *order parameter*.

[2]

- (ii)** Explain the origin of the $(T - T_C)$ term in this energy expression.

[4]

- (iii)** When no field is applied (i.e. $H = 0$), show that, under equilibrium conditions, the Landau-Ginzburg expression predicts the existence of first order, second order and tricritical phase transitions.

[6]

- (iv)** When a system undergoes a phase transition, in the presence of a finite field (i.e. $H \neq 0$), transformation plasticity is observed. Show how transformation plasticity, in a second order phase transition, can be predicted using the Landau-Ginzburg expression given above.

[4]

SECTION C

Answer 1 of the 2 questions in this section

- 13 (a) (i) With reference to the interatomic potential energy, as a function of bond length, explain what is meant by the “Harmonic Approximation” and thereby justify the notion that crystalline solids may be modelled by balls held together with springs.

[4]

(ii) Using the Harmonic Approximation and assuming effective spring constants of bonds to be given as μ , consider the net force on an atom of mass m , which is part of a one-dimensional chain of **identical** atoms, when thermal energy has induced atomic movement. Hence develop and solve an equation of motion for this atom and show that the angular frequency (ω), associated with its motion, can be given as a function of wavenumber (k) by the following expression:

$$\omega^2 = \frac{4\mu}{m} \left(\sin \frac{ka}{2} \right)^2$$

where a is the equilibrium interatomic separation at zero Kelvin.

[8]

- (b) When solutions for the equations of motion of atoms in a one-dimensional **diatomic** chain (where the two different atoms involved have masses M_A and M_B) are determined, the following relationship between angular frequency (ω) and wavenumber (k) can be established:

$$\omega^2 = \frac{\mu}{M_A M_B} \left\{ (M_A + M_B) \pm [(M_A + M_B)^2 - 4M_A M_B \sin^2(ka)]^{\frac{1}{2}} \right\}$$

- (i) By considering values for ω^2 at maximum and minimum values of $\sin^2(ka)$, sketch the form of the allowed $\omega - k$ functions.

[6]

[QUESTION 13 CONTINUED OVERLEAF]

[QUESTION 13 CONTINUED]

- (ii) Identify the acoustic and optic branches and outline why these nomenclatures are used. Also identify the extent of the Brillouin Zone and justify why $\omega - k$ information outside the Brillouin Zone is redundant.

[4]

- (c) Einstein developed an expression for the internal energy (U) of a crystal, at finite temperature, by treating atoms as quantum oscillators within a harmonic potential energy well (again using the Harmonic Approximation). It is as follows:

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

- (i) Explain the terms involved in this expression.

[3]

- (ii) Given that:

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

use Einstein's expression for the internal energy to derive an expression for the heat capacity of the crystal.

[5]

SECTION C

- 14 (a)** The electron energy levels E in a three-dimensional free electron gas of N_e electrons contained in a cubic volume of side L , and volume $V = L^3$, are given by:

$$E = \frac{\hbar^2}{2m} k^2,$$

where m is the electron mass, and k is the electron wavevector, such that

$k^2 = k_x^2 + k_y^2 + k_z^2$. When periodic boundary conditions are assumed, the permitted

discrete values of $k_x = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L} \dots$, and similarly for k_y and k_z .

- (i) By considering the geometry of k -space in three dimensions, clearly show that the total number of states having wavevector up to some value of k can be estimated as:

$$N(k) = \frac{V}{3\pi^2} k^3.$$

Remember to account for spin degeneracy in your answer. **[4]**

- (ii) Using the result from (i), clearly show that the density of energy states $D(E)$ can be written as:

$$D(E) = \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{V}{2\pi^2} E^{\frac{1}{2}}.$$

[3]

- (iii) Identify what the band occupation profile looks like at $T = 0$ K for a metal and explain the rationale for this. Hence, write down an integral expression by which the total number of occupied states N_e may be determined from $D(E)$ at $T = 0$ K. **[4]**
- (iv) Hence, evaluate the integral expression for N_e to show that the Fermi Energy, E_F , can be obtained:

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N_e}{V} \right)^{\frac{2}{3}}.$$

[3]

- (v) In a metal, no current flows in the absence of an applied electric field. Explain how this observation is rationalised in the energy band picture. Also explain, with the aid of energy band diagrams, the expectation of a current flow when an electric field is applied. **[6]**

[QUESTION 14 CONTINUED OVERLEAF]

[QUESTION 14 CONTINUED]

- (b) (i) For an intrinsic semiconductor, sketch a typical E - k band diagram in the reduced zone scheme format, including the 'conduction' and 'valence' bands. Indicate whether any bands are 'full', 'empty' or 'partially-filled' at $T = 0$ K. Indicate where the Fermi Energy is found at $T = 0$ K and give a rationale for this. **[3]**
- (ii) GaAs is a direct bandgap semiconductor with a bandgap of 1.42 eV. What is meant by the term 'direct' in this context? A GaAs sample is illuminated with an IR light source having wavelength $2\text{ }\mu\text{m}$. By carrying out a suitable calculation, explain if this light source will be effective for generating electron-hole pairs in GaAs. **[3]**
- (iii) Silicon is doped with phosphorous which has a dopant level 0.045 eV below the conduction band. At a temperature of $20\text{ }^{\circ}\text{C}$, the Fermi level μ is measured at 0.2 eV below the conduction band. Estimate the fractional occupancy of the dopant level for these conditions and comment on whether the dopant carrier population is likely to be available to contribute to conduction. **[4]**

END OF EXAMINATION