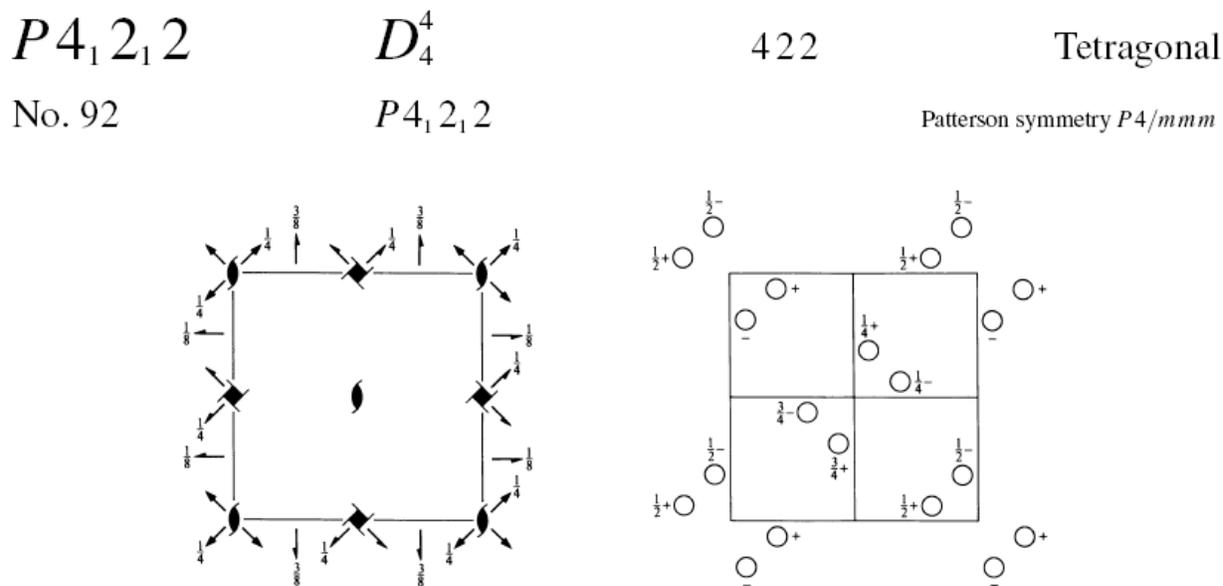


Condensed Matter Physics Option Question Sheet 2

1. Notation in the International Tables

Fig. 1 below shows part of a page of the International Tables.



Origin on $2[110]$ at $2, 1(1, 2)$

Figure 1: Part of the IT page for space group 92.

- (a) Explain the meanings of the top two lines of information.
- (b) List the coordinates of the general equivalent positions in this space group
- (c) Suppose an atom is placed directly on a 2-fold axis of symmetry. Write out its equivalent positions.
- (d) Derive the systematic absences due to
 - The 4_1 axis in the z direction
 - The 2_1 axis in the x direction.

2. Vibration modes of a simple molecule

Figure 2 below is a schematic representation of the water molecule in the ground state.

- (a) Determine the point group of the molecule in 3D and ascertain that the operators of this group commute with each other, i.e., $g \circ f = f \circ g \forall f, g$. Groups of this kind are called *Abelian*.
- (b) By trial and error (or any other method of your choice) construct displacement modes with the following special symmetry properties:

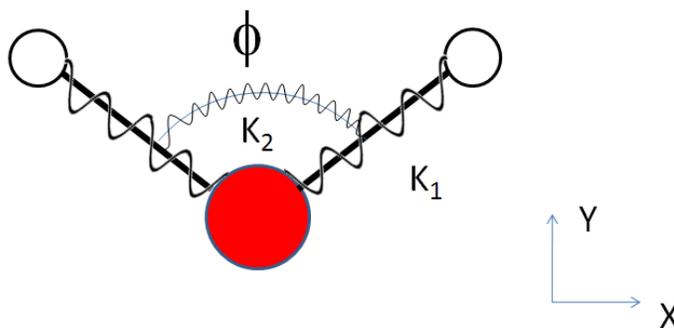


Figure 2: A schematic representation of the water molecule. K_2 is a torsion spring, which reacts to the change in the angle Φ .

- Modes that leave the symmetry of the point group of the molecule invariant (3 modes).
- Modes that are invariant under the the mirror plane *containing* the molecule and antisymmetric (i.e., change sign) by two other operations (3 modes).
- Modes that are invariant under the the mirror plane *perpendicular* to the molecule and antisymmetric by two other operations (2 modes).
- Modes that are antisymmetric by both mirror planes (1 mode).

Show that all the displacements in the molecule can be written as linear combination of these nine modes. *Hint* Construct separate modes for the hydrogens and for the oxygen atom. Choose *hydrogen* displacements that are either *parallel* or *perpendicular* to the H-O bonds or along the z axis. Choose *oxygen* displacements along x , y or z axes.

- (c) How many normal vibrational modes will you expect? Determine the energy of all the modes involving displacements out of the plane of the molecule, and state why the normal-mode problem is effectively 2D.
- (d) Only modes that transform "in the same way" (see rules at (a) above) can be mixed together to form normal modes. Determine the possible mixing combinations of the in-plane modes into normal modes, and state which will have non-zero frequencies. Can you recognise the normal modes named "Bend", "Symmetric stretch" and "Asymmetric stretch"? Are these modes IR-active or Raman-active?

3. Measurements of phonons by triple-axis neutron scattering

The phonon dispersion relations of a primitive tetragonal crystal ($a = 3.87 \text{ \AA}$, $c = 9.49 \text{ \AA}$) are measured via inelastic scattering of monochromatic neutrons ($E_i = 25 \text{ meV}$) using a triple-axis spectrometer. The crystal is aligned with the c -axis vertical, normal to the horizontal scattering plane of the instrument, and can be rotated around the c -axis. One of the optical phonon modes has energy $E = 12 \text{ meV}$ at the zone-boundary point $X(1/2, 0, 0)$.

- (a) Draw a diagram of the ab reciprocal space of the crystal and indicate all symmetry-equivalent points to X in the 1st Brillouin zone (1st Wigner-Seitz unit cell) and also the X points in the next set of Wigner-Seitz unit cells further out.

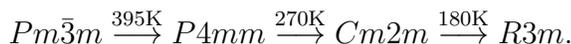
- (b) Consider processes whereby neutrons scatter inelastically by exciting a phonon (energy loss scattering); show that such processes cannot occur to excite the above optical phonon mode at $(1/2,0,0)$. Show, however, that the above phonon mode can be observed by inelastic neutron scattering at an X point in a further out Wigner-Seitz cell. Find the total scattering angle γ and the rotation angle of the crystal around the c-axis required to observe this excitation, assuming that the neutron beam is initially along the a-axis. [Hint: consider the conservation of energy and momentum, use the inelastic scattering convention for momentum transfer $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ (vectors)].
- (c) Could the phonon mode at $(1/2,0,0)$ be observed in energy gain scattering, i.e. neutrons scattering by absorbing energy from a phonon? What should the temperature of the crystal be for such scattering processes to have sizeable intensity?

4. Thermal conductivity - 1D models

- (a) A phonon wavepacket consisting of a narrow distribution of wavevectors centred on k_p is created on a one-dimensional monatomic chain. Explain why no heat energy is transported by the wavepacket when $k_p = 0$ and $k_p = \pm(\pi/a)$. Give an expression for the value of k_p which maximizes the rate of energy flow by such a phonon wavepacket. Why is it that in the absence of impurity scattering the thermal conductivity tends to infinity as T tends towards absolute zero? Explain why the result would be different if all phonons scattering process (not only *umklapp* processes) led to equilibrium.
- (b) Consider next, still in 1D, a process in which two phonons combine to give a third (or one phonon decays into two others). Let all phonons be acoustic, assume that the two transverse branches lie below the longitudinal branch, and assume that $d^2\omega/dk^2 \leq 0$ for all three branches.
- (b.1) Draw a diagram of the processes, showing “phonons-in” and ‘phonons-out’.
- (b.2) Using the conservation laws for energy and crystal momentum, show that there can be no process in which all three phonons belong to the same branch,
- (b.3) Show that the only possible processes are those in which the single phonon is in a branch *higher* than at least one of the members of the pair, i.e.,
 Transverse + transverse \leftrightarrow longitudinal
 Transverse + longitudinal \leftrightarrow longitudinal

5. Phase transitions and macroscopic properties

Barium titanate (BaTiO_3) becomes ferroelectric below $T_C = 395\text{ K}$, and undergoes the following sequence of structural phase transitions on cooling:



The different phases are related by small distortions of the lattice. The table below gives the directions of the unit cell axes for the three ferroelectric phases in terms of

the Cartesian axes of the cubic $Pm\bar{3}m$ phase.

$P4mm$	[100]	[010]	[001]
$Cm2m$	[110]	$[\bar{1}10]$	[001]
$R3m$	[101]	[110]	[011]

- (a) Explain what is meant by *ferroelectricity*. State the symmetry requirement for a crystal to be ferroelectric.
- (b) For each of the three ferroelectric phases,
- i) explain the meaning of the space group symbol and draw a diagram showing the point group symmetries;
 - ii) deduce the direction of the ferroelectric polarization relative to the cubic axes, explaining your reasoning;
 - iii) determine how many distinct ferroelectric domains can exist [Hint: consider all the possible directions of the polarisation with respect to the original cubic axes].
- (c) Explain how you might detect the structural change from $Pm\bar{3}m$ to $P4mm$ using x-ray powder diffraction data. When a single crystal of $BaTiO_3$ is cooled through T_C no net ferroelectric polarization is observed. Explain why not, and suggest an experiment that could measure the ferroelectric polarization.

6. Landau theory of phase transitions

A ferroelectric crystal is one in which certain ions are displaced parallel to each other from sites of high symmetry to form an electrically polar material with spontaneous polarisation denoted P . On raising the temperature, the crystal undergoes a phase transition at T_0 to a structure in which the ionic displacements become zero i.e. $P = 0$. The spontaneous polarisation for such a transition is the *order parameter* for this transition. According to the Landau theory of phase transitions, the excess free energy with respect to free energy F_0 in the high-temperature phase can be expanded in terms of a power series in P , thus:

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots$$

- (a) Suggest why there are no odd powers in this expansion.
- (b) Assume that the coefficient a is temperature-dependent approximating to

$$a = a'(T - T_0)$$

and that $b > 0$ and is temperature-independent. Let all terms higher than P^4 be taken to be zero. Now, by minimising with respect to the *order parameter*, show that there are the following solutions to the free energy equation:

$$P = 0$$

$$P = \pm \left(\frac{a'}{b}\right)^{\frac{1}{2}} (T_0 - T)^{\frac{1}{2}}$$

- (c) Explain the physical meaning of these solutions. Sketch the graph of P against temperature and $F - F_0$ against P^2 for different temperature regimes and state whether the phase transition is of 1st or 2nd order.
- (d) Derive formulae for the temperature behaviour of the dielectric susceptibility below and above T_0 .
- (e) Now sketch the equivalent graphs assuming $b < 0$ (this time you will need to include the term in P^6), and again state the order of the phase transition.
- (f) Derive a formula for the temperature variation of P when $b = 0$ and discuss the meaning of this result.
- (g) In practice, the spontaneous polarisation P is accompanied by a corresponding change in lattice strain ϵ , so that the free energy expansion can be modified to

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{2}\lambda\epsilon P^2 + \frac{1}{2}C_{el}\epsilon^2 \dots\dots$$

λ represents the amount of coupling between polarisation and strain, and C_{el} is an elastic constant. Show that the free energy expression can be recast as

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}\left(b - \frac{\lambda^2}{2C_{el}}\right)P^4 + \dots\dots$$

and discuss how strain-coupling can change the phase transition order.

Note: In general similar results can be applied to many other types of phase transition, where the order parameter can be assigned instead to many other quantities, such as strain, magnetisation, structural distortions, etc. depending on the precise nature of the phase transition. The Landau theory, despite its apparent simplicity, works remarkably well over many classes of phase transitions.