

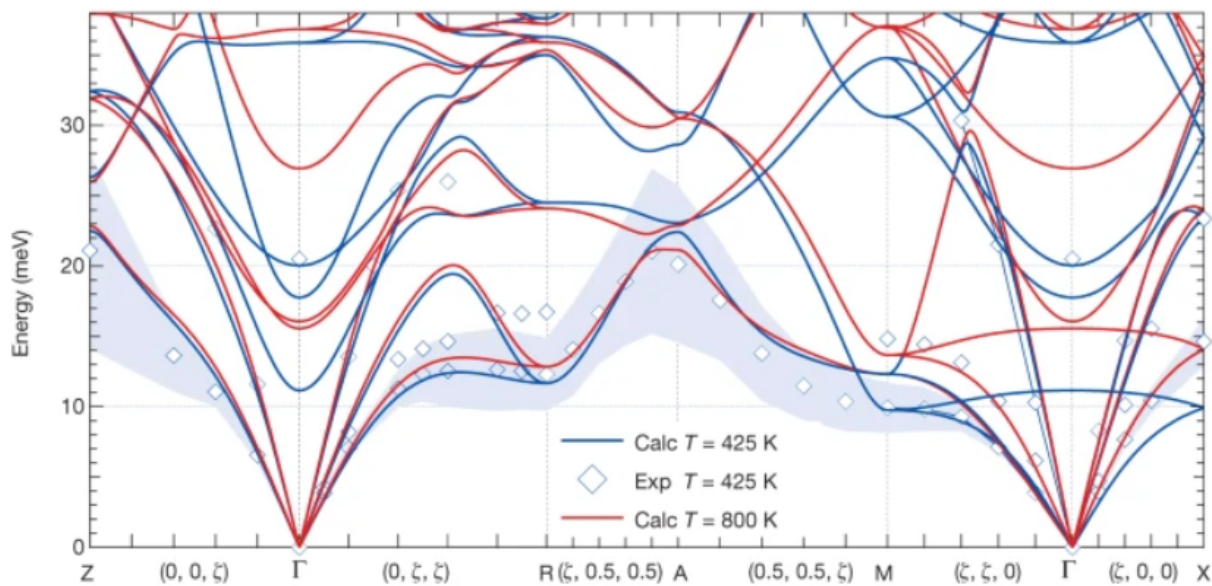
## Assignment 2 for PHY2002: Physics of the Solid State

Date of issue: 11/03/2022  
Module Code / Title: PHY2002  
Deadline for submission on Canvas: Mon 28<sup>th</sup> March 2022 (10pm)

**Note:** Only .pdf file submissions will be accepted.

### Thermal properties (50 marks)

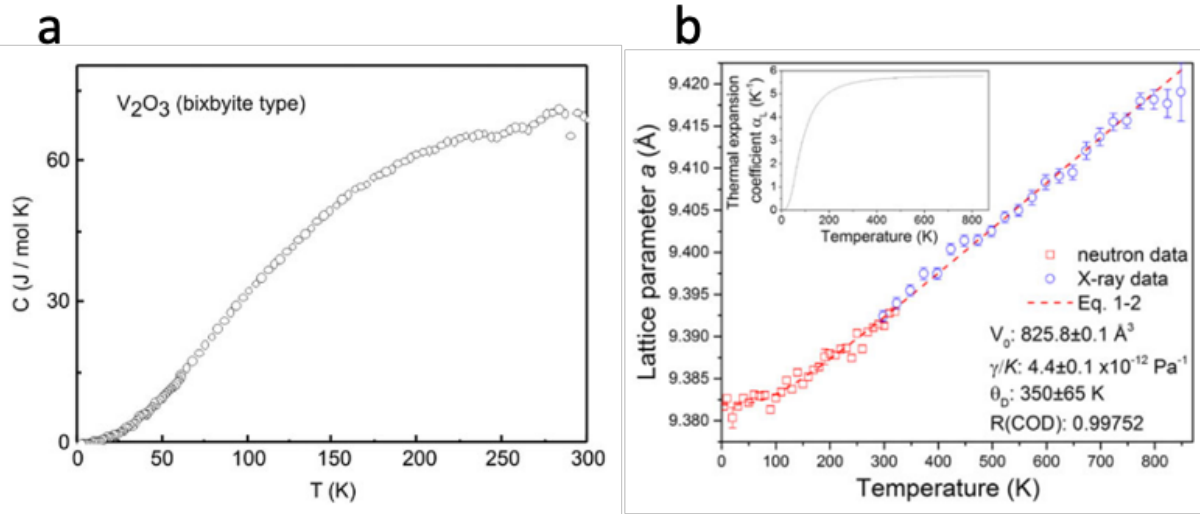
- 1.(a) In figure 1.1 below, the energies of different lattice vibration states in vanadium dioxide ( $\text{VO}_2$ ) are plotted as a function of their normalized wavevectors, along different reciprocal lattice directions (figure taken from J. D. Budai *et al.* Nature **515** 535 (2014)).



**Figure 1.1:** Phonon dispersion curves for vanadium dioxide, calculated at 425K (blue) and 800K (red), along with experimental data taken at 425K.

- (i) By considering simple 1D classical models for the equations of motion of atoms, bonded together in the solid state, discuss how salient features in figure 1.1 can be broadly replicated. [10]
- (ii) Comment on the implied validity of the Harmonic Approximation in reproducing features of phonon dispersion relations at 425K. [5]
- (b) In figure 1.2 below, the heat capacity and “a” lattice parameter of  $\text{V}_2\text{O}_3$  are given as a function of temperature (figure panels taken from D. A. Weber *et al.* J. Mater. Res. **32** 2397 (2017)).
- (i) Explain how the variation in heat capacity with temperature can be understood using a quantum picture, in which the only allowed atomic wavefunctions are those representing solutions to the time-independent Schrodinger equation, in a parabolic interatomic potential well. [10]
- (ii) Comment on the implied validity of the Harmonic Approximation from zero to 300K. [5]
- (iii) Explain how the primary features of the variation in the lattice parameter of  $\text{V}_2\text{O}_3$ , as a function of temperature, result from a consideration of time-averaged interatomic separations (bond lengths). [10]

- (iv) State explicitly what the change from linear temperature dependence to nearly temperature-independent behaviour means for the temperature range over which the Harmonic Approximation remains valid. [5]



**Figure 1.2:** Experimentally determined heat capacity and unit cell lattice parameter for  $V_2O_3$  as a function of temperature.

- (c) By considering all of the physics explored in (a) and (b) comment on the temperatures at which the Harmonic Approximation succeeds and fails and highlight any inconsistencies. [5]

### Electrons in metals and semiconductors (50 marks)

- 2.(a) The density of states  $D(E)$ , (i.e. number of states  $dN$  per unit energy  $dE$ ) can be expressed using the chain rule for differentiation as:

$$D(E) = \frac{dN(E)}{dE} = \frac{dN}{dk} \cdot \frac{dk}{dE},$$

where  $k$  is the wavevector.

- (i) Consider a quadratic electron  $E$ - $k$  dispersion, and the geometry of  $k$ -space in 3d, to determine expressions for  $dE(k)/dk$  and  $dN(k)/dk$  respectively for a free electron gas. [6]

- (ii) Use these expressions, and suitable substitutions, to show that the density of states is given as:

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

where  $m_e$  is the electron mass and  $V$  is the volume occupied by the free electron gas. Remember to account for spin degeneracy in your answer. [4]

- (iii) Using the expression in (ii), the 'Fermi Energy' ( $E_F$ ) can be evaluated as:

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

Explain what assumptions about electron state occupation have been made to obtain the above expression. [3]

- (iv) An estimate of the average electron energy  $\langle E \rangle$  in the free electron gas can be obtained as:

$$\langle E \rangle = \frac{E_{total}}{N} = \frac{\int E \eta(E) dE}{\int \eta(E) dE}$$

where  $\eta(E)dE$  is the number of occupied electron states in an energy interval  $E$  to  $E + dE$ . Introduce a suitable expression for  $\eta(E)$  and limits of integration, to show that the average electron energy at  $T = 0$  K in the free electron gas is  $\langle E \rangle = 0.6E_F$ . Briefly comment on why  $\langle E \rangle$  is greater than  $0.5E_F$ . [5]

(v) Determine  $\langle E \rangle$  numerically at  $T = 0$  K for Zinc, which has a relative atomic mass of 65.4, a mass density of  $\rho = 7.13 \times 10^3 \text{ kgm}^{-3}$ , and is assumed to contribute two free electrons per atom for conduction. Give your answer in units of eV. [5]

(vi) Consider the definition of wave group velocity ( $v_g$ ) to verify that  $E = 0.5mv_g^2$  when a quadratic electron dispersion relationship is assumed. [3]

(vii) Hence, obtain an estimate for the average electron velocity in Zinc and compare it to the RMS velocity expected from classical theory at  $T = 300$  K (i.e. by equipartition of energy). Fundamentally, why is a larger velocity estimate obtained in the quantum picture even though the effect of temperature has been ignored? [5]

(viii) Metallic conduction can be described as due to the movement of electrons at the Fermi level which have a carrier density  $n_f$  and travel with the Fermi velocity  $v_f$ . We can estimate  $n_f$  as  $n_f = D(E_f)\Delta E$  where  $D(E_f)$  is the density of states at the Fermi Level and  $\Delta E$  is the amount of energy acquired by a Fermi electron between electron-ion collisions when driven by an electric field. By considering the resulting current density  $J$ , show that the conductivity in 1D is:

$$\sigma \sim e^2 v_f^2 \tau D(E_f)$$

where  $\tau$  is the scattering time between electron-ion collisions. [4]

(b) Usually, the appropriate function for describing electron state occupation in solids is the Fermi-Dirac distribution,  $f_F$ . However, under certain circumstances, this can be well approximated by a classical Boltzmann distribution,  $f_B$  (i.e. where the "+1" term in the denominator of  $f_F$  has been omitted). We can define the percentage error,  $\Delta f(\%)$ , in approximating  $f_F$  by  $f_B$  with the expression:

$$\Delta f(\%) = \frac{100(f_B - f_F)}{f_F}$$

(i) By substituting expressions for  $f_F$  and  $f_B$  (see lecture notes), show that  $\Delta f(\%)$  can be expressed as:

$$\Delta f(\%) = \frac{100}{e^{\left(\frac{E-\mu}{kT}\right)}},$$

where  $E$  is energy and  $\mu$  is the Fermi level. [4]

(ii) Determine  $\Delta f(\%)$  for energy levels above and below the Fermi level by an amount  $kT$ . [4]

(iii) Determine  $\Delta f(\%)$  for intrinsic silicon at the bottom of the conduction band and for an energy level  $kT$  above the bottom of the conduction band. In both cases, let  $T = 300$  K. You can assume that the bottom of the conduction band is at an energy that is 0.55 eV larger than the Fermi Level. [4]

(iv) Hence, do you think that the classical Boltzmann statistics is an acceptable approximation for either of the scenarios described in (ii) and (iii)? Can you rationalise why/why not based on the form of the  $f_F$  and  $f_B$  functions? [3]