

**Solutions, Exam TFY4220 Solid State Physics. June 2019**

1.1 Condensed matter physics largely considers physical processes over what range of energies?

Answer: A ( $\mu\text{eV}$  to eV)

1.2 What is the approximate distance between atoms in a copper crystal?

Answer: C (0.3 nm)

1.3 The number of different 3D Bravais lattices is

Answer: B (14)

1.4 In its cubic unit cell,  $\text{BaTiO}_3$  (barium titanate) has barium atoms positioned at the 8 cell corners, a titanium atom in the middle, and oxygen atoms centred at each of the 6 faces. What is the number of atoms in the crystal basis?

Answer: C (5)

1.5 Which structure has the highest packing fraction?

Answer: B (Hexagonal close packed)

1.6 At small wave vector  $k$ , the group velocity and phase velocity coincide for which one of the following categories of phonon modes?

Answer: A (Acoustic)

1.7 If a crystal with two atoms per primitive basis is forced into an oscillation mode in the forbidden frequency region, it can be shown that the corresponding wave vector  $k$  gets complex. What consequence does the complex  $k$  have?

Answer: D (The wave gets exponentially damped and dies out over a short distance.)

1.8 Which statement is true regarding the electrical conductivity of materials?

Answer: C (The electrical conductivity of a metal decreases with increasing temperature)

1.9 For metals the conduction band and valence band are

Answer: C (Overlapping)

1.10 The electron and hole concentrations in an intrinsic semiconductor are  $n_i$  and  $p_i$ , respectively. When doped to a p-type material, these change to  $n$  and  $p$ , respectively. Then:

Answer: D ( $np = n_i p_i$ )

1.11 The Fermi level represents an energy level with probability of occupation equal to:

Answer: C (50%)

1.12 What is the Fermi speed  $u_F$  for gold (Au)? Remember that  $u_F$  is the speed of a conduction electron whose energy is equal to the Fermi energy  $E_F$ . For Au,  $E_F = 5.55$  eV.

Answer: B ( $1.4 \times 10^6$  m/s)

1.13 The total heat capacity of a material is the sum  $C = C_{\text{el}} + C_{\text{ph}}$  of its electron and phonon contributions. Which of the following graphs describes a metal at low  $T$ ?

Answer: B (Fig. B)

1.14 Free electrons with wavefunction  $\psi \sim e^{i\mathbf{k}\cdot\mathbf{r}}$  are characterized by a quantum number  $\mathbf{k} = (k_x, k_y, k_z)$  and have energy  $E(\mathbf{k}) = \hbar^2 |\mathbf{k}|^2 / 2m$ .

Which of the following correctly describes the ground state of  $N$  electrons in a volume  $V$  with Fermi energy  $E_F = (\hbar^2 / 2m)(3\pi^2 N / V)^{2/3}$ ?

Answer: B (all states with  $(k_x^2 + k_y^2 + k_z^2)^{1/2} < (3\pi^2 N / V)^{1/3}$  are filled)

1.15 A diatomic gas is held at room temperature. Which of the following excitation modes is NOT significantly occupied?

Answer: E (electronic)

## 2.1 About X-rays

- What energy (in units of eV) and corresponding wavelength (in units of nm) must X-ray photons have if they are to be used in diffraction experiments with the purpose of characterizing crystal structure?
- When X-rays scatter from a material, how do they interact with the atoms?

*Answer:*

In order to use X-rays to characterize a crystal structure with diffraction, the wavelength of the radiation must be comparable to the characteristic interatomic distances in the crystal lattice. The spacing in crystal lattices is typically in the order of a few Ångström, therefore the X-rays should have a wavelength of about of 0.1 nm. In eV this corresponds to  $E = h\nu = hc/\lambda \sim 10 \text{ keV}$ .

The dominant scattering mechanism of X-rays at  $\sim 10 \text{ keV}$  is Rayleigh scattering, as known also from scattering of other kinds of electromagnetic radiation. The incoming electromagnetic wave induces oscillations of the electron cloud, and the resulting fluctuating dipole moment gives rise to photons being emitted with the same energy (frequency) as the incoming radiation. This scattering mechanism is elastic, meaning that the energy of the scattered photons is the same as for the incoming photons.

## 2.2 Beta-carotene

Beta-carotene, a molecule abundant in carrots, has a UV-vis absorption spectrum as shown above.

- Explain shortly how a spectrum like this is obtained!
- Explain why this spectrum is consistent with beta-carotene being a semiconductor!
- What is the energy (in units of eV) of the bandgap?

*Answer:*

A UV-vis spectrum is a measurement of the absorption of the sample. The following principal parts are needed: a radiation source giving out a continuum of frequencies, a monochromator to choose only one wavelength/frequency at the time, a sample, and a detector. As indicated by the name, "UV-vis", one uses radiation in the UV and visible ranges. In order to get reliable results, a reference measurement, usually arranged in a parallel optical branch, is recorded to correct for variations in the intensity of the incoming light.

As seen in the spectrum, there is no absorption of radiation by beta-carotene for low photon energies (corresponding to long wavelengths). This transparency is because the photon energy is too low to give electronic transitions. We see that for wavelengths shorter than approximately 510 nm, the absorption increases, as the photon energy becomes large enough to excite electrons across the energy gap  $E_g$  between the valence and conduction bands. In short, the energy of the incoming radiation must be higher than the bandgap for absorption to occur.

Here we take  $\lambda_g = 510 \text{ nm}$  as a threshold value, giving  $E = hc/\lambda_g \sim 2.4 \text{ eV}$ . This value of the bandgap is below 3 eV, the value often used to distinguish between semiconductors and insulators.

### 3a) Graphite phonon dispersion I

- How many atoms are there per primitive cell? Explain briefly, based on the dispersion relation.

*Answer:*

The dispersion relation shows three optical and three acoustical branches for the phonon vibrations of the material. The lower three branches are acoustic modes (neighbouring atoms oscillate with similar phase) and the upper three are optical modes (neighbouring atoms oscillate out of phase).

We know that in 3D there are 3 acoustic branches and  $3s - 3$  optical branches, where  $s$  is the number of atoms in the primitive cell. These conditions are both fulfilled for  $s = 2$ . Thus, there are 2 atoms per primitive cell.

### 3b) Graphite phonon dispersion II

ZA and ZO in Fig. a) denote out-of-plane acoustic and optical branches, respectively.

- Based on your knowledge of graphite as a layered material, comment on the frequency  $\omega$  of the ZO branch compared the other optical modes!

*Answer:*

We know that graphite is a layered material consisting of graphene layers, being 2D sheets of carbons with a honeycomb structure. Within each layer, there are strong covalent bonds between carbon atoms ( $sp^2$  hybridized), whilst there are only weak van der Waals forces between the layers. This statement is equivalent to saying that the structure is stiffer with regards to in-plane deformations, and softer with regards to out-of-plane, including shear, deformations.

Correspondingly, we see in the dispersion relation that TO and LO have higher energies and thus higher frequencies than the ZO branch. Because the intermolecular forces between the layers are weaker than those within the layers, it is expected that the phonons involving inter-layer relative movements will be of lower frequency (and thus lower energy). Within each layer the bonds keeping the carbons in place are strong, meaning that any perturbation from an equilibrium position will be forcefully counteracted, resulting in high-energy, high-frequency oscillations. Between the adjacent layers, the weak van der Waals forces keep the layers in place, so displacements will be more gently counteracted, resulting in lower frequency oscillations (slower movements).

### 3c) Graphite phonon dispersion III

- Estimate the sound velocity for the LA modes.

Answer:

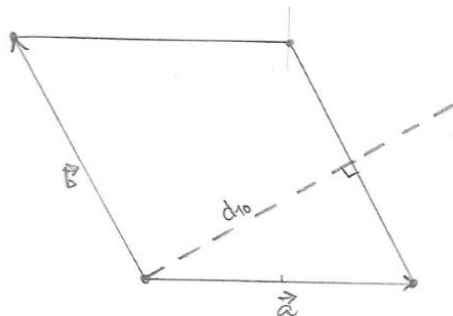
The sound velocity of the LA modes can be found as the group velocity  $v_g = d\omega/dk$  at small values of  $k$  in the dispersion relation (where the acoustic mode has a linear slope). We see that the LA mode is approximately linear when going from  $\Gamma$  to M. We can thus approximate  $d\omega/dk \approx \Delta\omega/\Delta k$ , and need to find numbers for both  $\Delta\omega$  and  $\Delta k$ .

Fig. a) suggests  $\Delta E = 1500 \text{ cm}^{-1}$ . By the given unit conversion, this corresponds to  $\Delta E = 1500 \cdot 0.000123986 \text{ eV} = 0.186 \text{ eV}$ . Through  $E = hf$ , the corresponding frequency change is  $\Delta\omega = 2\pi\Delta E / h = 2.83 \cdot 10^{14} \text{ Hz} = 283.0 \text{ THz}$ .

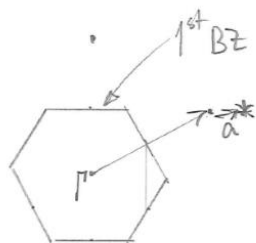
As seen in Fig. b), the M point is on the Brillouin zone boundary, with a distance from the  $\Gamma$  point equal to half the length of the primitive reciprocal lattice vector. Noting that the unit cell is hexagonal, one finds that the length of the reciprocal vector  $\mathbf{b}^*$  is given by  $b^* = 4\pi / (a\sqrt{3})$ , as shown in the sketch. The change of momentum is thus  $\Delta k = b^* / 2 = 2\pi / (a\sqrt{3}) = 1.48 \cdot 10^{10} \text{ m}^{-1}$ .

Finally, the estimated speed of sound for the longitudinal wave is

$$v_g = \Delta\omega/\Delta k = 19126 \text{ m/s} \approx \underline{19 \text{ km/s}}$$



$$|\vec{a}^*| = \frac{2\pi}{d_{10}}, \quad d_{10} = \frac{\sqrt{3}}{2} a$$



$$\frac{1}{2} a^* = \frac{1}{2} \frac{2\pi}{d_{10}} = \frac{\pi}{\sqrt{3} a}$$

**4a) Cu<sub>2</sub>O, lattice**

Explain shortly the terms Bravais lattice and basis.

With the atomic coordinates as given, is the lattice *b.c.c.*, *f.c.c.* or *primitive*?

*Answer:*

By definition, a Bravais lattice is a mathematical construction being an infinite lattice in which the surroundings of every lattice point are identical. Equivalently, lattice vectors  $\mathbf{R}_{mno} = m\mathbf{a} + n\mathbf{b} + o\mathbf{c}$  ( $m, n, o$  are integers;  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  primitive vectors) can be found that connect every point in the (3D) Bravais lattice. All Bravais lattices can be chosen as primitive, with each unit cell having only one lattice point. Still, some Bravais lattices (including *b.c.c.* and *f.c.c.*) are conventionally displayed with *centered* lattices, having more than one lattice point per unit cell, in order to better visualize the symmetry of the lattice. There are 5 distinct Bravais lattices in 2D, and 14 in 3D.

Any crystal lattice can be described as a convolution between a Bravais lattice and a basis. The basis describes the object (for a crystal, the object will be a collection of atoms) that is repeated at every lattice point. For example, with a two-atom basis, there will be two atoms associated with every Bravais lattice point.

For the atomic coordinates given, one observes that even though the coordinates for Cu and O describe (diagonally shifted) *f.c.c.* and *b.c.c.* lattices, there is no way to choose a centered unit cell that simultaneously describes both of the lattices. Therefore, Cu<sub>2</sub>O is *primitive* (simple cubic).

**4b) Cu<sub>2</sub>O, lattice**

The powder X-ray diffraction pattern for Cu<sub>2</sub>O is given above. The scattering angle is denoted by  $2\theta$ . The *111* diffraction peak is at  $2\theta = 36.29^\circ$ . The side length of the unit cell is  $a = 4.288 \text{ \AA}$ .

- Based on the information about the *111* reflection, derive the wavelength of the (approximately monochromatic) X-ray radiation used for the diffraction experiment.
- What information is contained in the peak widths?

*Answer:*

The easiest way to proceed is by Bragg's law, reading  $n\lambda = 2d \sin \theta$ . The lattice spacing is given by  $d_{111} = a / \sqrt{3}$ . With  $n = 1$  (first harmonic), the wavelength is thus given by

$$\lambda = 2 \frac{a}{\sqrt{3}} \sin\left(\frac{2\theta}{2}\right).$$

By inserting the given values, the wavelength  $\lambda = 1.54 \text{ \AA}$ , recognized as the  $K_\alpha$  line of Copper, is obtained.

The peak widths can be described as the convolution between the instrument resolution and the intrinsic diffraction peak width from the sample. The latter contains information mainly

about the *size* of the scattering object (narrower peak for larger crystallites, often estimated through the use of the Scherrer formula) and *strain*.

#### 4c) Cu<sub>2</sub>O, structure factor

- Derive the general expression for the unit cell structure factor, i.e., starting out with  $F(\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r}$ , show that  $F_{hkl} = \sum_j f_j \exp(2\pi i(hx_j + ky_j + lz_j))$ , where the symbols have their usual meaning.
- Explain in particular how one arrives at the scattering condition  $\mathbf{Q} = \mathbf{G}$ .
- Explain (calculations not needed) why the  $\bar{2}00$  and  $210$  diffraction peaks are not indicated in the diffractogram.

*Answer:*

(See derivation on separate pages).

It can be shown that the diffraction condition  $\mathbf{Q} = \mathbf{G}$  is equivalent to Bragg's law. A limitation of Bragg's law, in addition to the poorly motivated assumption of specular reflection from atomic planes, is that it does not give information about the intensity of the various diffraction peaks.

The scattered intensity is proportional to the amplitude squared of the unit cell structure factor. When calculating the structure factor, some Bragg peaks might be zero for certain combinations of  $h, k, l$ . These «extinct» or «missing» peaks do not appear in the diffraction pattern, and are physically caused by destructive interference between the scattering from different atoms in the crystal. In the present case, the  $210$  is an example of a Bragg peak which is nearly extinct (it can be discerned near  $2\theta = 53^\circ$ ). The  $\bar{2}00$  Bragg peak is physically equivalent to  $200$  and will thus appear at the same position in the powder diffractogram – such equivalent Bragg peaks are conventionally not listed.

$$F(\vec{Q}) = \int \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$$

// Kinematical scattering, Fraunhofer regime.

If we rewrite  $\rho(\vec{r})$  as  $\sum_{\text{all atoms}} f_j \delta(\vec{r} - \vec{r}_j)$ , one gets

$$\begin{aligned} F(\vec{Q}) &= \sum_{\text{all atoms}} \int f_j \delta(\vec{r} - \vec{r}_j) e^{i\vec{Q} \cdot \vec{r}} d\vec{r} \\ &= \sum_{\text{all atoms}} f_j e^{i\vec{Q} \cdot \vec{r}_j}, \quad f_j \text{ is the atomic form factor} \end{aligned}$$

The sum can be rewritten as a sum over all the crystal lattice points and over the basis:

$$\begin{aligned} F(\vec{Q}) &= \sum_{\substack{n \\ \text{lattice} \\ \text{points}}} \sum_{\substack{j \\ \text{basis}}} f_j e^{i\vec{Q} \cdot (\vec{R}_n + \vec{r}_j)} \\ &= \underbrace{\sum_n e^{i\vec{Q} \cdot \vec{R}_n}}_{\substack{n \text{ is large} \\ \text{number.}}} \underbrace{\sum_j f_j e^{i\vec{Q} \cdot \vec{r}_j}}_{\substack{\text{unit cell} \\ \text{structure} \\ \text{factor.}}} \end{aligned}$$

The lattice sum will be of order unity unless the scattering vector  $\vec{Q} = \vec{G}_{hkl}$  a reciprocal lattice vector. By definition,  $e^{i\vec{G}_{hkl} \cdot \vec{R}_n} = 1$ , and in this case the lattice sum becomes enormous,  $n \neq$  lattice points.



$$\vec{G}_{hkl} \equiv h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$\vec{r}_j$  can be written as  $\vec{r}_j = x_j\vec{a} + y_j\vec{b} + z_j\vec{c}$ ,  
where  $x_j, y_j, z_j$  are fractional coordinates.

Thus, knowing that  $\vec{Q} = \vec{G}_{hkl}$  for diffraction,  
the unit cell structure factor can be written

$$F_{hkl} = \sum_j f_j e^{i(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \cdot (x_j\vec{a} + y_j\vec{b} + z_j\vec{c})}$$

$$= \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

where the orthogonality relations  
between the real and reciprocal  
space coordinates have been used.  $\square$ .

#### Task 4d)

The relevant part of the electronic band structure of  $\text{Cu}_2\text{O}$  near the Fermi level (at  $E = 0$ ) is given in the figure. As usual,  $\Gamma$  denotes the center of the 1st Brillouin zone. (The double lines are caused by different assumptions for the bandstructure calculations and should be ignored).

Based on the band structure, explain whether there is a bandgap, direct or indirect, and whether  $\text{Cu}_2\text{O}$  is a metal, semimetal, insulator or semiconductor.

*Answer:*

There is a region with no energy bands above the Fermi level, which implies that  $\text{Cu}_2\text{O}$  has a bandgap. The energy gap is about 0.5 eV, typical of semiconductors. Because the highest point of the valence band and the lowest point of the conduction band appear at the same value for  $k$ ,  $\text{Cu}_2\text{O}$  is a direct bandgap semiconducting material.

**Task 4e)**

Explain briefly the consequences of an *indirect* bandgap for the absorption of light, and its relevance to solar cells.

Finally, explain how the band structure of a semimetal differs from a semiconductor and how this difference is revealed in the electronic density of states.

*Answer:*

An indirect bandgap means that the maximum of the valence band and the minimum of the conduction band are at different values of wavevector  $k$ . In this case, one can define two values of the bandgap energy:  $E_g^{\text{optical}}$  and  $E_g'$ . The first of these is the difference in energy between the maximum of the valence band to the point of the conduction band directly above, while  $E_g'$  is the difference between the maximum and minimum that occur at different  $k$ . While photons carry high energy and low momentum, the opposite holds for phonons. To excite across  $E_g'$ , contributions («assistance») from phonons are needed to preserve energy and crystal momentum.

The main consequence of the indirect bandgap for solar cells is that the absorption process becomes less likely, and the solar cell less efficient. To increase the likelihood of the photons to be absorbed, the thickness of the solar cell is thus increased (giving higher economic cost). Silicon is an indirect bandgap semiconductor, and massive efforts, e.g. nano-structuring, are invested in reducing the drawbacks of the indirect bandgap.

Semimetals also have an indirect bandgap, but these materials distinguish themselves by having a negative bandgap – i.e., the minimum of the conduction band occurs at a *lower* energy than the maximum of the valence band. Consequently, there is no energy gap in the density of states, but usually the density of states near the Fermi level will be low and the semimetal is thus less conducting than metals.