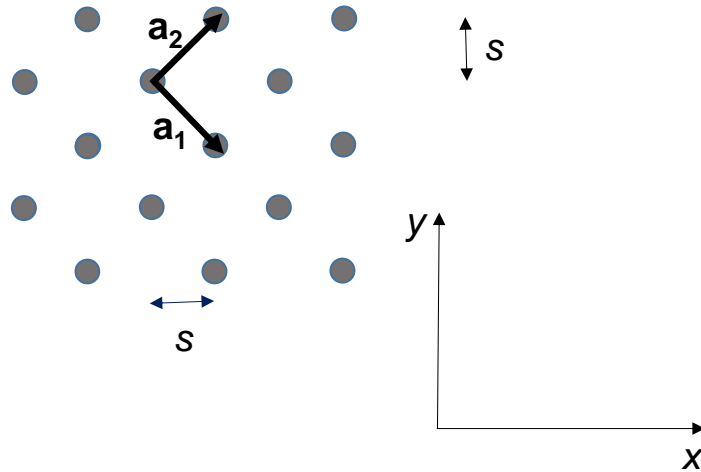


## Solution manual TFY4220 Solid state physics. May 2017.

### Problem 1

a)



A primitive unit cell is a unit cell that contains only one Bravais lattice point, often chosen to be at the corners, such as shown in the figure. The basis vectors of the primitive cell can then be chosen to be

$$\mathbf{a}_1 = s(\mathbf{i} - \mathbf{j})$$

$$\mathbf{a}_2 = s(\mathbf{i} + \mathbf{j})$$

b) If  $\mathbf{a}_i$  ( $i = 1, 2$ ) are the basis vectors of the direct lattice, vectors  $\mathbf{b}_j$  ( $j = 1, 2$ ) satisfying the relation

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

are the basis vectors of the reciprocal lattice. From the direct basis vectors given in a) the reciprocal basis vectors are obtained as

$$\mathbf{b}_1 = \frac{\pi}{s}(\mathbf{i} - \mathbf{j})$$

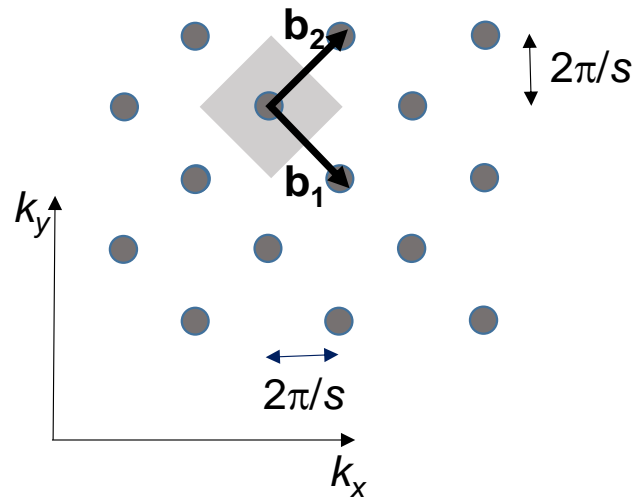
$$\mathbf{b}_2 = \frac{\pi}{s}(\mathbf{i} + \mathbf{j})$$

The Laue condition for diffraction is that the difference between the reflected wave vector  $\mathbf{k}_r$  and the incident wavevector  $\mathbf{k}_i$  equals a reciprocal lattice vector  $\mathbf{G}$ ,

$$\mathbf{k}_r - \mathbf{k}_i = \mathbf{G}.$$

It can be shown that the Laue condition is equivalent to Bragg's law.

c)

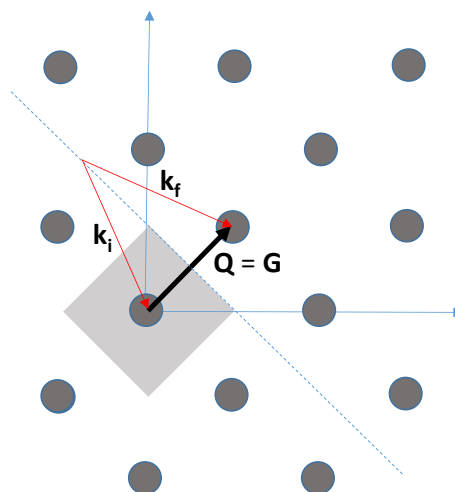


The reciprocal lattice and the first Brillouin zone (shaded square) are illustrated in the figure.

The lowest order Bragg reflections arise when the incoming  $k$ -vector  $\mathbf{k}_i$  originates on a plane being an extension of the Brillouin zone and terminates at the origin, see sketch. To get this insight, notice that the Laue condition states  $\mathbf{Q} = \mathbf{G}$ . Having  $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$  gives  $\mathbf{k}_f = \mathbf{Q} + \mathbf{k}_i$ , or  $k^2 = (\mathbf{k} + \mathbf{G})^2$ . Thus,

$$2\mathbf{k} \cdot \mathbf{G} = G^2,$$

which is often used as the diffraction condition. As a consequence, all incoming  $k$ -vectors  $\mathbf{k}_i$  that fulfill  $\mathbf{Q} = \mathbf{G}$  must originate on a plane which halves  $\mathbf{G}$  and terminate at the origin. This plane must be either a continuation of the Brillouin zone boundary (as in the sketch), or the zone boundary itself in the case of long wavelengths.



One important consequence of this consideration follows when studying electrons in periodic potentials: Bragg diffraction of the electron waves at the zone boundaries gives rise to electronic bandgaps.

- d) The wave representing an electron moving in a periodic potential field  $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$ , with  $\mathbf{R}$  being a lattice vector, has the form of a Bloch function:

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}),$$

where the function  $u_k(\mathbf{r})$  has the same translational symmetry as the lattice:

$$u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R}).$$

Bloch functions describe plane waves modulated by the periodic potential field. Bloch's theorem states that the energy states for an electron in a crystal can be written as Bloch waves. The exponential part of the Bloch wave is a plane wave which is closely associated with the external size and shape of the crystal through the choice of boundary conditions, while the periodic function imposes local corrections to the electronic wavefunction by the nuclei.

The Born-von Karman (periodic) boundary conditions are usually used with Bloch's theorem. If nanocrystals are studied, the formalism must incorporate more realistic boundary conditions.

## Problem 2

- a) The electron wavelength is

$$\lambda = \frac{h}{p},$$

with  $p$  implicitly given by

$$\frac{p^2}{2m} = eV,$$

$V$  being the accelerating voltage of the electrons. Thus

$$\lambda = \frac{h}{(2meV)^{1/2}}$$

which evaluates to  $0.39 \text{ \AA}$ .

The Bragg condition for diffraction reads

$$n\lambda = 2d \sin \theta.$$

For the first order diffraction minimum,

$$\sin \theta = \frac{\lambda}{2d},$$

as  $n = 1$  and  $d = 1 \text{ \AA}$ . Hence  $\theta = 11.2^\circ$ .

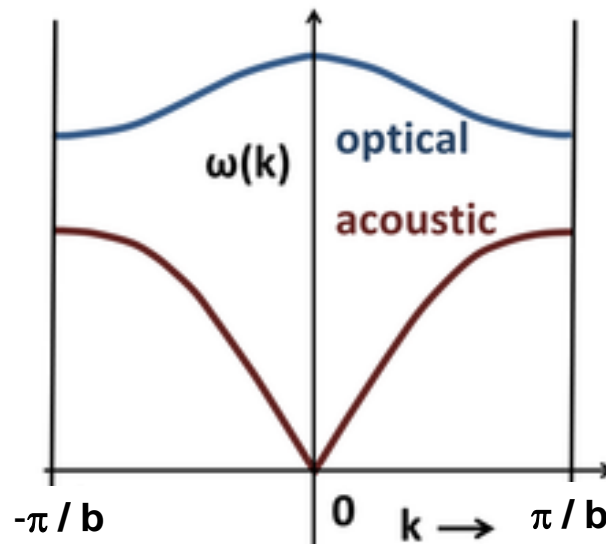
- b) In bright field TEM, the incoming transmitted beam contributes to the image formation. When a crystallite is oriented in such a way that intensity is diffracted out of the main light path, the bright image of the sample will have a darker region corresponding to the location of the crystallite.

In dark field TEM, the transmitted beam is blocked out, and the image formation is thus based on scattered radiation only. If a certain Bragg reflection is chosen, e.g.  $200$ , regions in the sample that have  $\{200\}$  lattice planes fulfilling the diffraction condition will appear bright on an otherwise dark background.

By diffraction contrast is simply meant that the contrast between different regions of the sample are caused by different diffraction properties (rather than e.g. absorption differences as is often used with ordinary light).

### Problem 3

a)



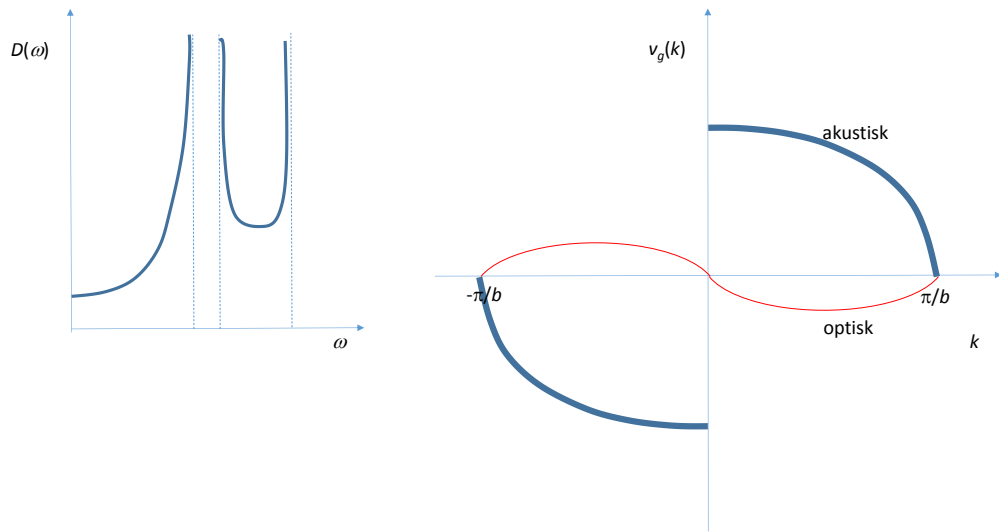
Only  $k$ -values within the 1<sup>st</sup> Brillouin zone are of interest, because all other  $k$ -values can be mapped into the 1<sup>st</sup> BZ. This is a result of the fact that the atomic displacements are only defined at the lattice points, which implies that the shortest physically meaningful wavelength is given by twice the repetition distance. Thus,  $k_{max} = \pm 2\pi/2b = \pm\pi/b$ .

- b) To derive the dispersion relation, a chain of infinite length is assumed. If instead a finite chain of  $N$  repetitions is assumed, the derivation proceeds the same way, giving the same dispersion relation, however, with additional constraints on  $k$ . Thus, if assuming periodic boundary conditions, one must have

$$\exp(ikx) = \exp(ik(x+L))$$

where  $L = Nb$ . Consequently,  $\exp(ikL) = 1$  or  $k = \frac{2\pi}{bN} m$ , with  $m$  an integer. As a result, the continuous branches shown in the sketch above will be broken into  $N$  points equally spaced in  $k$ .

c)



d) Clearly,  $M_1 = M_2$  reduces the periodicity from  $b$  to  $a = b/2$ . Consequently, the size of the 1<sup>st</sup> Brillouin zone is doubled. One obtains

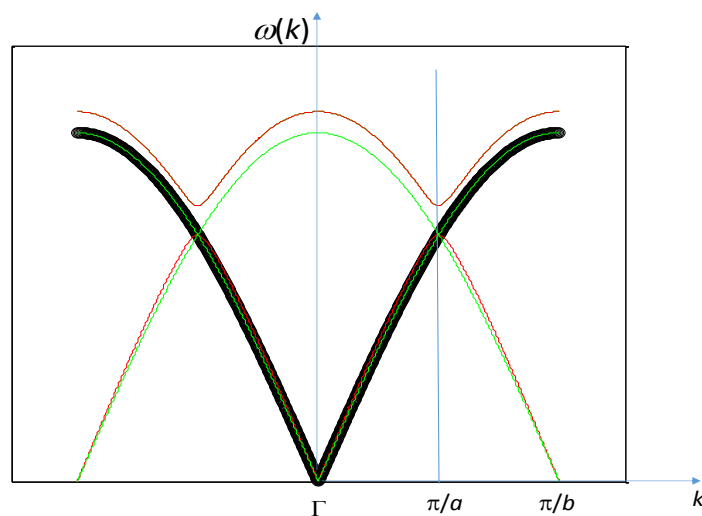
$$\omega = \frac{1}{2} \omega_0 \sqrt{2 \pm 2 \cos(kb/2)} = \begin{cases} \omega_0 \cos(kb/4) = \omega_0 \cos(ka/2) \\ \omega_0 \sin(kb/4) = \omega_0 \sin(ka/2) \end{cases}$$

where  $\omega_0^2 = 4\gamma/M$ .

Plot these seemingly conflicting results together:

- One atomic model (thick black line)
- Two-atomic model,  $M_1 / M_2 = 0.8$  (thin red line)
- Two-atomic model,  $M_1 / M_2 = 1$  (thin green line)

One sees that the standard one-atomic model is indeed accounted for by the two-atomic model, with the higher energy branches corresponding to other Brillouin zones. The optical mode disappears in the one-atomic model, but in the derivation above, the cell is still centered.



- e) Dulong-Petit. The classical partition theorem states that each degree of freedom appearing squared in the energy function contributes on average  $0.5 k_B T$  per molecule, or equivalently,  $0.5 RT$  per mole ( $R$  is the universal gas constant). For a 1D harmonic oscillator (kinetic and potential energy terms), this gives  $1 k_B T$ ; for a 3D oscillator,  $3 k_B T$ . The heat capacity,  $C = dU/dT$  is thus  $3 k_B$  per molecule or  $3 R$  per mole. This constant value for the heat capacity works well at high temperatures, but fails to model the experimental observations for low  $T$ .

Note that also other arguments can be used to arrive at the expression  $C = 3R$ . For example, it is the high-temperature limit for the heat capacity in the Einstein model.

Integral expression:

$$U(T) = 3 \int_0^{\infty} \hbar \omega D(\omega) \frac{1}{e^{\hbar \omega / k_B T} - 1} d\omega$$

Here, the Bose-Einstein statistics has been inserted.  $D(\omega)$  is the density of states.

We mention that the main assumptions in the Debye model, being a theory for low temperatures, are that all optical phonons can be discarded and the acoustic phonons modeled as linear,  $\omega(k) = v_g k$ , where  $v_g$  is the group velocity. With these assumptions, a cutoff “Debye frequency”  $\omega_D$  (and a corresponding Debye temperature  $T_D$ ) can be defined to simplify the integral above. Carrying out the integral and subsequently differentiating with respect to  $T$  to get the heat capacity, gives  $C \sim T^3$ , which compares favorably with experiments.

#### Problem 4

- a) Free electrons have the dispersion relation  $E = \frac{\hbar^2 k^2}{2m}$ .

Periodic boundary conditions give  $\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{aN} (n_x, n_y, n_z)$ ,  $aN = L$ .

By filling all states from  $n = 0$  to  $N/2$ , where the factor 2 is caused by the spin of the electrons, one gets

$$\frac{N}{2} = \frac{4}{3} \pi n_{max}^3, \text{ or}$$

$$n_{max} = \left( \frac{3N}{8\pi} \right)^{1/3}.$$

Thus:

$$E(N) = \frac{\hbar^2 k_{max}^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{2\pi}{L} \right)^2 n_{max}^2 = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}.$$

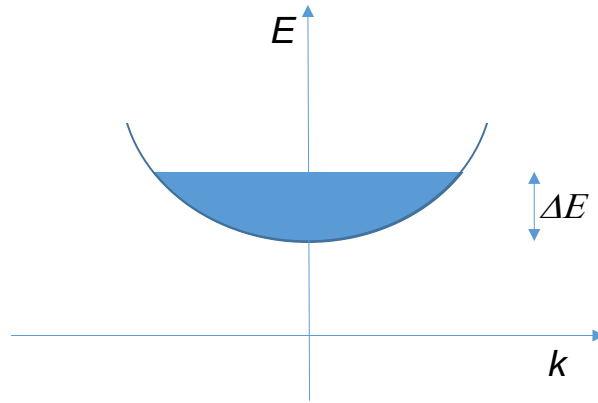
- b) By definition, the density of states is given by  $D(E) = dN/dE$ :

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_0},$$

where we have

- 1) replaced  $m$  by  $m^*$  to allow for the facts that the conduction electrons in metals are just *almost* free. The notion of an effective mass is a convenient means to parameterize the curvature of the conduction band.
- 2) replaced  $E$  by  $E - E_0$  which allows to freely define the zero-level of the energy (the bottom of the valence band).





The number of conduction electrons is

$$N = \int_{E_0}^{E_0 + \Delta E} D(E) dE = \frac{V}{3\pi^2} \left( \frac{2m^*}{\hbar^2} \Delta E \right)^{3/2}$$

which gives

$$m^* = \frac{\hbar^2}{2\Delta E} \left( \frac{3\pi^2 N}{V} \right)^{2/3}$$

- c) Sodium (or any other alkaline earth metal) is better described by the free-electron model than most other metals, arguably for three reasons:
- Being in the first column of the periodic table, each Na atom has an electron it easily lets go.
  - The remaining electrons form a closed shell, thus minimally perturbing the conduction electrons.
  - With only one electron per atom in the conduction band, the density of “free” electrons is not too high, reducing the need of correction for interactions between the conduction electrons.

From b), we have

$$m^* = \frac{\hbar^2}{2\Delta E} \left( \frac{3\pi^2 N}{V} \right)^{2/3} = \frac{\hbar^2}{2\Delta E a^3} (6\pi^2)^{2/3}$$

where we have exploited that the electron density was given,  $n = N / a^3$ .

With numbers:

$$\Delta E = 3.0 \text{ eV} = 3 \cdot 1.602 \cdot 10^{-19} \text{ J}$$

$$a = 4.25 \cdot 10^{-10} \text{ m}$$

$$\underline{\underline{\text{We get } m^* = 9.73 \cdot 10^{-31} \text{ kg} = 1.07 m_e.}}$$

Note that  $k_B T \sim 0.025 \text{ eV}$  at room temperature. In other words, corrections for temperature effects are not necessary.