Solution week 10

Exercise 1 – The aluminium crystal

1. First of all, we calculate the number of aluminium atoms per cell. We work with the fcc conventional unit cell because it is easier to visualize than the primitive unit cell. There are 6 atoms on the square surfaces (1 atom on the center of each square surface) and 8 on the corners of the cube, so the number of atoms per cell is

$$n_{atoms/cell} = 6/2 + 8/8 = 4. \tag{1}$$

   Here we divided 6 by 2, because each atom on the square surface is shared between two neighboring cells; and we divided 8 by 8, because each atom in the corner is shared between 8 cells. By doing so we obtain how many atoms we have per cell.

   Now we compute the weight of an aluminium atom:

$$m_{Al} = 27 \cdot 1.66 \times 10^{-24}\text{g} = 4.48 \times 10^{-23}\ \text{g}. \tag{2}$$

   The density of aluminium is then

$$\rho = \frac{n_{atoms/cell} \cdot m_{Al}}{V_{cell}} = \frac{n_{atoms/cell} \cdot m_{Al}}{a^3} = \frac{4 \cdot 4.48 \times 10^{-23}}{(4.05 \times 10^{-8}\text{cm})^3} = 2.7\,\text{gr/cm}^3. \tag{3}$$

2. By looking at the unit cell, we can easily realize that the two nearest-neighbour atoms are one in the corner and one in the center of the adjacent square surface of the cube. Hence, the distance between the nearest-neighbour atoms is:

$$d_{NN} = \frac{a\sqrt{2}}{2} = \frac{a}{\sqrt{2}} = 2.86\,\mathring{A}. \tag{4}$$

   So we can write a in terms of d_{NN}:

$$a = \sqrt{2}\, d_{NN}. \tag{5}$$

3. The close–packing condition is satisfied if the radius of the spheres is half the nearest-neighbour distance:

$$r = \frac{d_{NN}}{2} = 1.43\,\mathring{A}. \tag{6}$$

4. The packing factor is computed as

$$f = \frac{V_{spheres}}{V_{cell}} = \frac{4 \cdot \frac{4}{3}\pi r^3}{a^3} = \frac{4 \cdot \frac{4}{3}\pi \frac{d_{NN}^3}{2^3}}{2^{\frac{3}{2}} d_{NN}^3} = \frac{\frac{2}{3}\pi}{2^{\frac{3}{2}}} = \frac{\pi}{3\sqrt{2}} = 0.74 \tag{7}$$

5. By knowing the density of free electrons in aluminium, we can compute the number of free electrons per atom:

$$\frac{\rho_{free}}{\rho_{atoms}} = \frac{\rho_{free}}{\frac{N_{atoms/cell}}{V_{cell}}} = 2.1 \times 10^{-1}\mathring{A}^{-3}\frac{(4.05\mathring{A})^3}{4} \approx 3.5. \tag{8}$$

   The number of free electrons is an indicator of the degree of oxidation of an atom, which in turn is often described with the oxidation state. The value obtained here is +3.5 and it is close to the nominal oxidation state of aluminium, which is 3+.

Exercise 2

1. We consider a free electron gas in a one-dimensional lattice of total size L and with lattice parameter a. Since each electron is free (*i.e.* it does not feel any potential), the one-particle Schrödinger equation is simply:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x). \tag{9}$$

The solution of this equation is a plane wave of the form $\psi(x) = Ce^{ik_0x}$, where C is a constant. By imposing the normalization condition $\int_{-L/2}^{L/2} |\psi(x)|^2 dx = 1$, we find that $C = \pm 1/\sqrt{L}$ (we have chosen a real normalization constant). The electron, in fact, must be found within the crystal, which we have set to be in the range $(-L/2; L/2)$ (any other choice is equivalent). Choosing a real and positive phase we have:

$$\psi(x) = \frac{1}{\sqrt{L}}e^{ik_0x}. \tag{10}$$

Now if we apply PBC we must have $\psi(x + L) = \psi(x)$ and thus $e^{ik_0L} = 1$ and thus $k_0L = 2\pi m$ with $m \in \mathbb{Z}$. So the k_0's are discrete and the spacing between them is $\frac{2\pi}{L}$.

By substituting Eq. (10) in Eq. (9), we find that the energy corresponding to the wave function $\psi(x)$ is $E = \frac{\hbar^2 k_0^2}{2m}$, with the k_0's above.

2. The hypotheses of Bloch theorem are satisfied since the potential is zero and zero is a periodic function of a. Thus the eigenvalues found in the previous point must satisfy Bloch theorem.

3. From the previous point we know $k_0 = \frac{2\pi m}{L} = \frac{2\pi m}{Na}$, with $m \in \mathbb{Z}$. So we can divide $m = n' + nN$ where $n' = \{-N/2, \dots, N/2 - 1\}$. Thus $k_0 = \frac{2\pi m}{Na} = \frac{2\pi\, n'}{Na} + n\frac{2\pi}{a} = k + G_n$, since $n\frac{2\pi}{a}$ its a G reciprocal vector of our lattice and $\frac{2\pi n'}{Na}$ is a k vector inside the first Brillouin zone. Thus:

$$\psi(x) = \frac{1}{\sqrt{L}}e^{ik_0x} = \frac{1}{\sqrt{L}}e^{i(k+G_n)x} = e^{ikx}\left(\frac{e^{iG_nx}}{\sqrt{L}}\right) \tag{11}$$

We can observe that $\frac{e^{iG_nx}}{\sqrt{L}} = u_n(x)$ of Bloch theorem since it satisfies: $u_n(x) = u_n(x + a)$ and that k is inside the first Brillouin zone. We have then concluded our proof. We note that for this simple problem the $u_n(x)$ have just one Fourier component equal to one, as opposed to the general case treated in Homework 9. We also observe that eigenfunctions for this problem can thus be rewritten as Bloch theorem dictates:

$$\psi_{n,k}(x) = \frac{1}{\sqrt{L}}e^{i(k+G_n)x}, \tag{12}$$

with corresponding energy:

$$E_{n,k} = \frac{\hbar^2(k + G_n)^2}{2m}, \tag{13}$$

with k inside the first Brillouin zone. A good trick to plot the energy bands is to draw different parabolas with a vertex shifted by a G vector Fig. 1 left, and then look at the resulting plot inside the first Brillouin zone, those are the bands of a material with empty lattice with a cell of size a (right plot in Fig. 1).

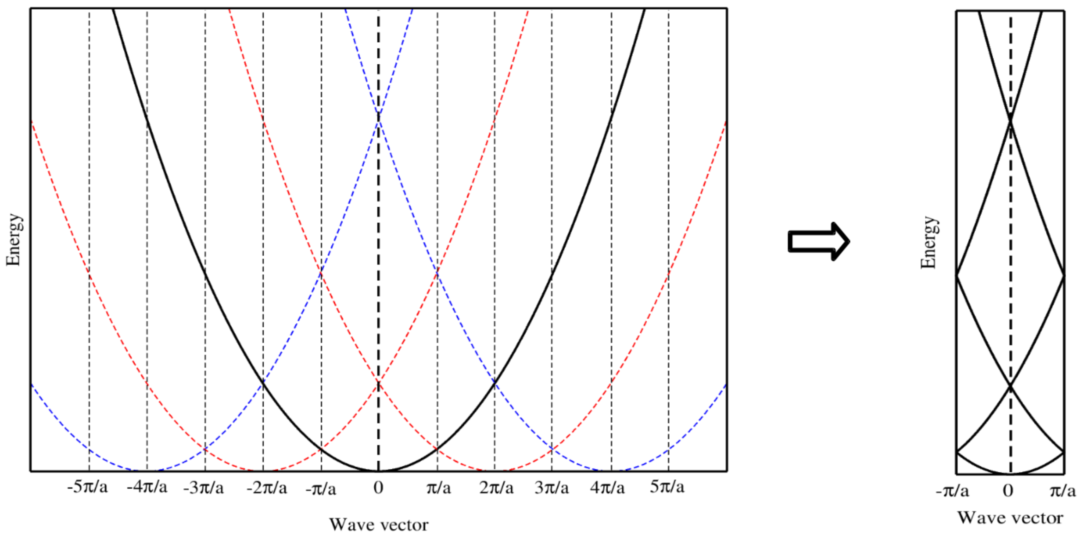

Figure 1: Left: trick to plot the folded energy dispersion (aka bands) of an empty lattice with cell size a. Right: the bands of an empty lattice with cell size a.

4. The electrons' mean velocity is defined as:

$$v_{n,k} = \frac{1}{\hbar}\frac{\partial E_{n,k}}{\partial k}\,. \tag{14}$$

We are interested in the lowest electronic band, which corresponds to $n = 0$. Since $E_{0,k} = \frac{\hbar^2 k^2}{2m}$, we obtain:

$$v_{0,k} = \frac{\hbar k}{m}. \tag{15}$$

The center of the IBZ is at $k = 0$, while the zone boundaries are located at $k = \pm\frac{\pi}{a}$ (see right panel in Figure 1). The mean velocity at the zone center $v_{0,0}$ is thus zero, while at the zone boundaries the mean velocity is $v_{0,\pm\pi/a} = \pm\frac{\hbar\pi}{ma}$.

Exercise 3

1. Let's consider the electronic configurations of Al and Cu, which are $1s^2 2s^2 2p^6 3s^2 3p^1$ and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ (note: Cu is an exception to the *aufbau* rules), respectively. The valence bands are formed from the hybridization of the external orbitals of the atoms. Therefore, in the case of Al we expect the valence bands to be created mainly from the $3s$ and $3p$ states, while in Cu we expect the valence bands to be created mainly from the $3d$ and $4s$ states.

   We know that electrons of the s- and p- character give rise to more dispersive bands due to the larger overlap between orbitals of neighboring atoms, which makes these electrons very delocalized. In contrast, electrons of d-character are more localized, and the overlap between orbitals of neighboring atoms is smaller. The higher localization of d-electrons gives rise to bands that are much less dispersive (more 'flat').

   In the left panel of Figure 2(a) of the homework we observe a group of rather flat bands between $-1\,\text{eV}$ and $-5\,\text{eV}$. The flatness of these bands suggests that they are of d-character. As we said above, we expect to have electrons of d character in the valence bands of Cu. Therefore, we can conclude that the left panel of Fig. 2a corresponds to the electronic band structure of Cu. In the right panel, all valence bands are characterized by a strong dispersion, which is typical for electrons of s- and p- type. This band structure thus corresponds to Al. Also note how the lowest bands in the right panel of Fig. 2(a) remind us of the parabolic dispersion that is characteristic of free electrons. This means that Al has a free-electron-like electronic band structure.

   For what concerns the DOS plots, we can easily assign them to the corresponding electronic band structures. In the right panel of Figure 2(b) there are very sharp peaks between $-1\,\text{eV}$ and $-5\,\text{eV}$, which correspond to flat d-bands. Thus, this DOS plot corresponds to the electronic band structure of Cu. Conversely, the left panel of Figure 2(b) shows a free-electron-like DOS (it resembles a $\sqrt{E}$ trend), which means that it corresponds to the electronic band structure of Al.

2. Si and Ge are indirect band gap semiconductors, while GaAs is a direct band gap semiconductor. In Si, the top of the valence band is at the Γ point, and the bottom of the conduction band is close to the X point (in the direction from Γ to X). In Ge, the top of the valence band is again at the Γ point, and the bottom of the conduction band is exactly at the L point. In GaAs, both the top of the valence band and the bottom of the conduction band are at the Γ point.

   From Figure 3 of the homework we can determine the band gap energies (they correspond to the height of the shaded area). In particular, we have $E_{\text{Ge}} \approx 0.7\,\text{eV}$, $E_{\text{Si}} \approx 1.1\,\text{eV}$, and $E_{\text{GaAs}} \approx 1.4\,\text{eV}$. The energy of a photon with wavelength λ is given by:

   $$E = h\frac{c}{\lambda}\,. \tag{16}$$

   Therefore, by knowing the band gap energies, we can easily determine the corresponding photon wavelengths:

   $$\lambda_{\text{Ge}} = \frac{hc}{E_{\text{Ge}}} = \frac{4.136 \cdot 10^{-15}\,(\text{eV}\cdot\text{s}) \cdot 2.998 \cdot 10^{8}\,(\text{m/s})}{0.7\,(\text{eV})} \approx 1771\ \text{nm}\,. \tag{17}$$

   $$\lambda_{\text{Si}} = \frac{hc}{E_{\text{Si}}} = \frac{4.136 \cdot 10^{-15}\,(\text{eV}\cdot\text{s}) \cdot 2.998 \cdot 10^{8}\,(\text{m/s})}{1.1\,(\text{eV})} \approx 1127\ \text{nm}\,. \tag{18}$$

$$\lambda_{\mathrm{GaAs}} = \frac{hc}{E_{\mathrm{Si}}} = \frac{4.136 \cdot 10^{-15}\,(\mathrm{eV}\cdot\mathrm{s}) \cdot 2.998 \cdot 10^{8}\,(\mathrm{m/s})}{1.4\,(\mathrm{eV})} \approx 885\ \mathrm{nm}\,. \tag{19}$$

From the obtained wavelengths we can compute the corresponding photon momenta using the de Broglie equation:

$$p_{ph} = \frac{h}{\lambda}, \tag{20}$$

and compare these to the momenta that correspond to electrons with wavevectors equal to the size of the Brillouin zones:

$$p_{el} = \hbar|\mathbf{k}| = \hbar\frac{2\pi}{a} = \frac{h}{a}\,. \tag{21}$$

Therefore, we obtain:

$$p_{ph}^{\mathrm{Ge}} = 3.74 \times 10^{-28}\,\mathrm{kg\ m\ s^{-1}} \qquad \ll \qquad p_{el}^{\mathrm{Ge}} = \frac{h}{a_{\mathrm{Ge}}} = 1.17 \times 10^{-24}\,\mathrm{kg\ m\ s^{-1}} \tag{22}$$

Therefore, we obtain:

$$p_{ph}^{\mathrm{Ge}} = 3.74 \times 10^{-28}\,\mathrm{kg\ m\ s^{-1}} \qquad \ll \qquad p_{el}^{\mathrm{Ge}} = \frac{h}{a_{\mathrm{Ge}}} = 1.17 \times 10^{-24}\,\mathrm{kg\ m\ s^{-1}} \tag{23}$$

$$p_{ph}^{\mathrm{Si}} = 5.88 \times 10^{-28}\,\mathrm{kg\ m\ s^{-1}} \qquad \ll \qquad p_{el}^{\mathrm{Si}} = \frac{h}{a_{\mathrm{Si}}} = 1.22 \times 10^{-24}\,\mathrm{kg\ m\ s^{-1}} \tag{24}$$

$$p_{ph}^{\mathrm{GaAs}} = 7.49 \times 10^{-28}\,\mathrm{kg\ m\ s^{-1}} \qquad \ll \qquad p_{el}^{\mathrm{GaAs}} = \frac{h}{a_{\mathrm{GaAs}}} = 1.17 \times 10^{-24}\,\mathrm{kg\ m\ s^{-1}} \tag{25}$$

In all three cases the momentum of the photon is negligible when compared to the momentum of the electron. Therefore, due to the requirement of momentum conservation, only excitations with $\Delta k \approx 0$ can take place (*i.e.* excitations where the momentum of the electron does not change). The excitation of an electron by absorption of a photon with energy equal to the energy of the band gap can thus occur only in GaAs. In this material, in fact, the electron is excited from the top of the valence band to the bottom of the conduction band at the same **k**-point (Γ). In Ge and Si, in order to excite electrons from the top of the valence band to the bottom of the conduction band, the electrons need to gain energy, but also momentum, which can be provided by “phonons” (*i.e.* lattice vibrations).