Exercise 1.

Consider a tetragonal Bravais lattice whose lattice parameters are $a, a, c = \frac{3}{2}a$ (see Fig. 1a), with $a = 0.45$ nm.

1. Determine the reciprocal lattice vectors b_1, b_2 and b_3 of the given lattice.
2. Determine the first 10 peaks that are seen if the crystal structure is investigated by means of X ray scattering, within the Debye-Scherrer technique. Determine the wavelength λ of the radiation if the first peak is seen at an angle $\varphi = 2\theta = 10.24°$.
3. Say which of the above 10 peaks would be missing if the crystal hosts a two-atom basis with equivalent atoms at $d_1=(0,0,0)$ and $d_2=(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a)$ (see Fig. 1b; here, only the basis is shown).
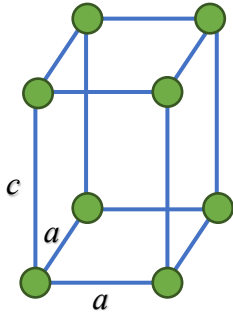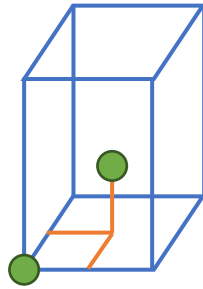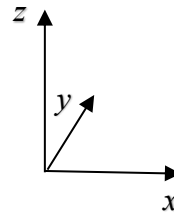

Fig. 1a   Fig. 1b

Exercise 2.

Consider a one dimensional crystal lattice with lattice parameter $a = 0.54$ nm, hosting a two-atom basis, at $d_1 = 0$ and $d_2 = \frac{1}{2}a$. Within the tight-binding approximation, the two inequivalent atoms contribute to the formation of the electron bands with s and p_x orbitals, respectively (see Fig. 2). The atomic wave functions are taken to be real, and energy levels of the atomic orbitals are $\varepsilon_s = 1.48$ eV, $\varepsilon_p = 1.32$ eV. Consider only nearest-neighbor transfer integrals with magnitude $|\gamma_{sp}| = |\gamma_{ps}| = 0.24$ eV. Neglect all other transfer integrals, all overlap integrals, and assume for simplicity that there is no shift of the atomic energy levels.
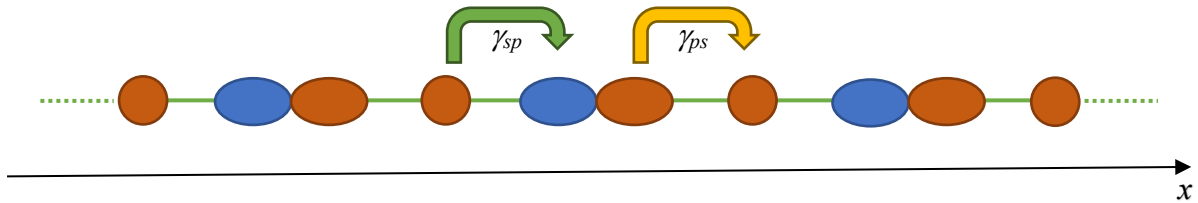

Fig. 2

1. Taking as positive the sign of the wave function of s orbitals, and the signs of the two lobes of the p_x orbitals as shown in Fig. 2 (the blue color indicates the negative sign), and assuming attractive crystal potential, $\Delta U<0$, assign the correct sign to γ_{sp} and γ_{ps}, where sp and ps stand for the hopping integral from s to p and from p to s, respectively, in the positive direction of the x axis (see Fig. 2).
2. Determine the dispersion law of the valence and conduction bands of the system, ε_k^v and ε_k^c, k being the one-dimensional wave vector.
3. Draw the band dispersion in the first Brillouin zone of the lattice, locate the maxima and minima of the valence and of the conduction bands. Assuming that each orbital provides one electron to the lattice, calculate the Fermi energy E_F and the band gap energy E_g.

Solution to exercise 1.

1. The reciprocal lattice vectors are
$$\boldsymbol{b}_1 = \frac{2\pi}{a}(1,0,0), \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}(0,1,0), \qquad \boldsymbol{b}_3 = \frac{2\pi}{c}(0,0,1) = \frac{4\pi}{3a}(0,0,1).$$

2. The condition for constructive interference within the Debye-Scherrer technique is
$$K = |\boldsymbol{K}| = \frac{4\pi}{\lambda}\sin\frac{\varphi}{2},$$

where $\boldsymbol{K} = h\,\boldsymbol{b}_1 + k\,\boldsymbol{b}_2 + l\,\boldsymbol{b}_3 = \frac{2\pi}{a}\left(h, k, \frac{2}{3}l\right) = \frac{2\pi}{3a}(3h, 3k, 2l)$ is a reciprocal lattice vector whose magnitude is

$$K = \frac{2\pi}{3a}\sqrt{9(h^2+k^2)+4l^2} = \frac{2\pi}{3a}\sqrt{N},$$

with $N=9(h^2+k^2)+4l^2$ an integer number.

Then, to list the reciprocal lattice vectors in order of increasing magnitude (i.e., in order of increasing N), we can produce the following table:

hkl	N
001	4
100 } 010 }	9
101 } 011 }	13
002	16
110	18
111	22
102 } 012 }	25
112	34
200 } 020 } 003 }	36
201 } 021 }	40

that correspond to the first ten peaks in the X ray diffraction pattern of the given crystal.

For the first peak $K = \frac{4\pi}{3a}$, hence $\lambda = 3a\,\sin\frac{\varphi}{2} = 0.12$ nm.

3. The structure factor is

$$S_K = 1 + e^{i\boldsymbol{K}\cdot\boldsymbol{d}_2} = 1 + e^{i\pi\left(h+k+\frac{2}{3}l\right)},$$

so, all the peaks in the diffraction pattern with $h + k + \frac{2}{3}l$ an odd integer will not be visible, which means that $h + k$ must be odd and l must be a multiple of 3, including 0. In the present case, the peak meeting these conditions is the second, corresponding to hkl =100 or 010.

Solution to exercise 2.

1. From the definition of transfer integrals
$$\gamma_{ij} \equiv \gamma_{ij}(\boldsymbol{r}_{nn}) = -\int d\boldsymbol{r}\,\varphi_i(\boldsymbol{r})\Delta U(\boldsymbol{r})\varphi_j(\boldsymbol{r} - \boldsymbol{r}_{nn}),$$
with $\boldsymbol{r}_{nn} = \frac{1}{2}a$ is the vector that locates the nearest neighbor site along the positive direction of the x axis, and $i=s$, $j=p$ or $i=p$, $j=s$. In our case, since $\Delta U(r)<0$, then $\gamma_{sp}<0$ and $\gamma_{ps}>0$. Henceforth, the notation $\gamma_{sp}=-\gamma$, $\gamma_{ps}=\gamma$, with $\gamma=0.24$ eV, will be adopted.

2. We have $\gamma_{ij}(\boldsymbol{r}_{nn}) = -\gamma_{ij}(-\boldsymbol{r}_{nn})$, then, the eigenvalue equation yielding the band structure of the system is
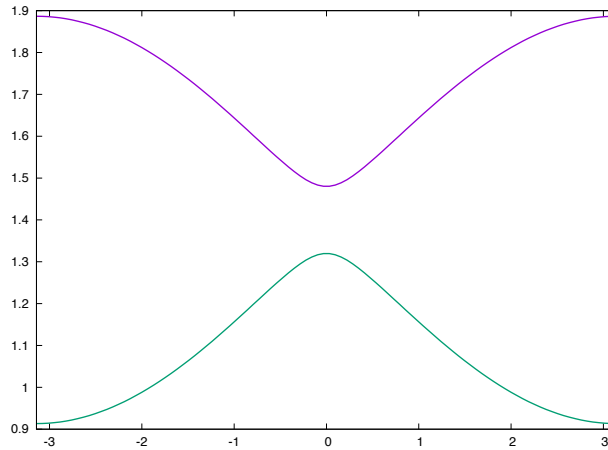$$\begin{cases}(\varepsilon_s - \varepsilon_k)b_s + 2i\gamma \sin\frac{ka}{2}\, b_p = 0, \\ (\varepsilon_p - \varepsilon_k)b_p - 2i\gamma \sin\frac{ka}{2}\, b_s = 0.\end{cases}$$
Imposing that the determinant is zero, to find nontrivial solutions of the homogeneous system, we have
$$\varepsilon_k^{\pm} = \varepsilon \pm \sqrt{\Delta^2 + 4\gamma^2\sin^2\frac{ka}{2}},$$
where $\varepsilon \equiv \frac{1}{2}(\varepsilon_s+\varepsilon_p)$ and $\Delta \equiv \frac{1}{2}(\varepsilon_s-\varepsilon_p)$. The valence band corresponds to the solution with the minus sign, $\varepsilon_k^v = \varepsilon_k^-$, the conduction band to the solution with the plus sign, $\varepsilon_k^c = \varepsilon_k^+$.

3. The band structure is given in the figure

where the conduction band is the purple line, the valence band is the green line. The minimum of the conduction band and the maximum of the valence band are located at $k = 0$, where $\varepsilon_{k=0}^c = \varepsilon_s$ and $\varepsilon_{k=0}^v = \varepsilon_p$. With each orbital contributing one electron, this is a direct gap superconductor, with $E_F = \varepsilon_p = 1.32$ eV and $E_g = \varepsilon_s - \varepsilon_p = 0.16$ eV. The top of the conduction band and the bottom of the valence band are located at the boundary of the Brillouin zone, where

$$\varepsilon_{k=\pm\pi/a}^c = \varepsilon + \sqrt{\Delta^2 + 4\gamma^2} = 1.89 \text{ eV}, \quad \varepsilon_{k=\pm\pi/a}^v = \varepsilon - \sqrt{\Delta^2 + 4\gamma^2} = 0.91 \text{ eV}.$$