WRITTEN EXAMINATION OF 24/06/2024 (Profs. M. Grilli and A. Polimeni)
Exercise 1
Consider two compound lattices with cubic symmetry and chemical formula XY and WZ, where XY and WZ form a two-atoms base.
When measuring the X-ray diffraction pattern of the sample using the powder method by a radiation with λ=0.154056 nm, seven diffraction peaks are obtained with the scattering angle 2θ as shown below.
XY) 2θ (°): 23.3281, 33.2272, 40.9960, 47.7004, 53.7535, 59.3687, 69.7562
WZ) 2θ (°): 30.8254, 35.7432, 51.4434, 61.1826, 64.2191, 75.7251, 83.9551.
1) Identify the cubic lattice type and label each diffraction peak using the Miller indexing. Compute the average lattice parameter a.
2) Indicate which of the above peaks would disappear if the atoms were the same and one atom were positioned in the origin (0,0,0) and the other atom were positioned at a (1/4,1/4,1/4).
3) Evaluate the Debye wavevector associated only to the acoustic modes for the two crystals.

Exercise 2
Given a simple cubic monoatomic lattice with two valence orbitals d_{xz} and p_y and using the tight-binding approximation considering the first-neighbors interaction, only:
i) write the analytic expression of the electron bands in terms of the overlap (hopping) integrals $\gamma_{pp}^{x,y,z}, \gamma_{dd}^{x,y,z}, \gamma_{pd}^{x,y,z}$ of the various orbitals along the x, y and z directions, specifying and neglecting those that are zero by symmetry. Also establish the sign and which are larger or smaller in absolute value. The terms $(E_d - \beta_d) > (E_p - \beta_p)$ are also known and $(E_d - \beta_d) - (E_p - \beta_p) \gg \gamma$ for any γ.
ii) Assume $(E_d - \beta_d) - (E_p - \beta_p) = 5$ eV, and the values $|\gamma_1|$=0.5 eV for the large overlap integrals and $|\gamma_2|$=0.1 eV for the small ones. Knowing that there are two valence electrons per atom, find the k points in the Brillouin zone where the energy for the optical absorption is minimal and its numerical value.
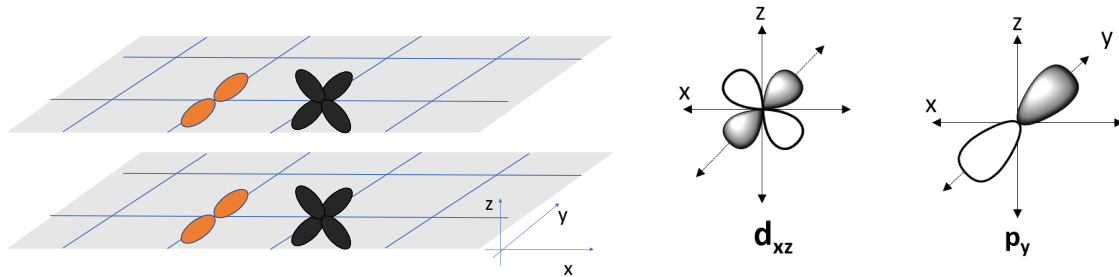
For the sake of clarity, the p and d orbitals are drawn separately, but in every atomic site of the 3D cubic lattice both orbitals are present.

SOLUTIONS

Exercise 1
1) XY is a simple cubic lattice

n	2θ (°)	d (nm)	$(d_1/d_i)^2$	(hkl)	$(h_{1n}^2 + k_n^2 + l_n^2)/(h_1^2 + k_1^2 + l_1^2)$	a (nm)
1	23.32814	0.381	1	100	1	0.381
2	33.22723	0.26941	2	110	2	0.381
3	40.99595	0.21997	3	111	3	0.381
4	47.70036	0.1905	4	200	4	0.381
5	53.75354	0.17039	5	210	5	0.381
6	59.36868	0.15554	6	211	6	0.381
7	69.75619	0.1347	8	220	8	0.381

where $d=\lambda/(2\sin\theta)$

WZ is a face centered cubic lattice

n	2θ (°)	d (nm)	$(d_1/d_n)^2$	(hkl)	$(h_n^2 + k_n^2 + l_n^2)/(h_1^2 + k_1^2 + l_1^2)$	a (nm)
1	30.82539	0.28983	0.99997	111	1	0.502
2	35.74315	0.251	1.3333	200	1.33333	0.502
3	51.44338	0.17748	2.6666	220	2.66667	0.502
4	61.18255	0.15136	3.66657	311	3.66667	0.502
5	64.21906	0.14491	3.9999	222	4	0.502
6	75.72505	0.1255	5.3332	400	5.33333	0.502
7	83.95507	0.11517	6.33317	331	6.33333	0.502

where $d=\lambda/(2\sin\theta)$

2) For the XY lattice, if we set the basis as $\rho_1=(0,0,0)$ and $\rho_2=a(1/4,1/4,1/4)$ and the reciprocal lattice vectors of the SC given by $G=h\,g_1+k\,g_2+l\,g_3$, where $g_1=2\pi/a(1,0,0)$, $g_2=2\pi/a(0,1,0)$, $g_3=2\pi/a(0,0,1)$, the basis structure factor is equal to $[1+e^{-i\pi/2(h+k+l)}]$. This factor is zero for (h+k+l)=2(2n+1). The disappearing peaks are those for which (h+k+l)=2, 6, … , namely the (110) and the (200) peaks.

Likewise for the WZ lattice, if we set the basis as $\rho_1=(0,0,0)$ and $\rho_2= a(1/4,1/4,1/4)$ and the reciprocal lattice vectors of the SC given by $G=h\,g_1+k\,g_2+l\,g_3$, where $g_1=2\pi/a(-1,1,1)$, $g_2=2\pi/a(1,-1,1)$, $g_3=2\pi/a(1,1,-1)$, the basis structure factor is equal to $[1+e^{-i\pi/2(h+k+l)}]$. Also in this case, this factor is zero for (h+k+l)=2(2n+1). The disappearing peaks are those for which (h+k+l)=2, 6, … , namely the (200) and the (222) planes.

3) $q_D = \sqrt[3]{6\pi^2 n}$. For XY $n=1/a^3$ and thus $q_D=10.23$ nm^{-1}. For WZ $n=4/a^3$ and thus $q_D=12.30$ nm^{-1}.

Exercise 2
i) For symmetry reasons the overlap integrals between p and d orbitals are zero. Moreover

$$\gamma_{dd}^x = \gamma_{dd}^z < 0; \quad \gamma_{dd}^y > 0; \quad \gamma_{pp}^x = \gamma_{pp}^z > 0; \quad \gamma_{pp}^y < 0$$

$$\left|\gamma_{dd}^x\right| = \left|\gamma_{dd}^z\right| \approx \left|\gamma_{pp}^y\right| > \gamma_{pp}^x = \gamma_{pp}^z \approx \gamma_{dd}^y$$

Two bands are formed each of pure p or d character

$$E_d(\vec{K}) = E_d - \beta_d + 2\left|\gamma_{dd}^{xz}\right|\left(\cos(k_x a) + \cos(k_z a)\right) - 2\gamma_{dd}^y \cos(k_y a)$$

$$E_p(\vec{K}) = E_p - \beta_p - 2\gamma_{pp}^{xz}\left(\cos(k_x a) + \cos(k_z a)\right) + 2\left|\gamma_{pp}^y\right|\cos(k_y a)$$

Since the level difference largely exceeds the oveerlap integrals

$$(E_d - \beta_d) - (E_p - \beta_p) >> \gamma$$

the two bands do not overlap in energy.

ii) If two electrons per atom are present, the lower band $E_p(k)$ is completely filled. The chemical potential then falls in the middle (at T=0) of the gap between the two bands.The minimum of the upper band occurs at $K_{min}=(\pi/a)(1,0,1)$, as well as the maximum of the lower p band $K_{max}=(\pi/a)(1,0,1)$. The gap is therefore direct ($K_{min}=K_{max}$) and is

$$E_d(\vec{K}_{min}) - E_p(\vec{K}_{max}) = \left(E_d - \beta_d - 4\left|\gamma_{dd}^{xz}\right| - 2\gamma_{dd}^y\right) - \left(E_p - \beta_p + 4\gamma_{pp}^{xz} + 2\left|\gamma_{pp}^y\right|\right) =$$

$$5 - 4\times0.5 - 2\times0.1 - 4\times0.1 - 2\times0.5 = 1.4eV$$