Week 07

Crystallography
Diffraction

Exercise 1 : Answer these questions by true or false

	True	False
1. For a similar structure, an isoelectronic ionic crystal will exhibit more systematic absence in its diffraction peaks compared to a non-isoelectronic crystal.	☐	☐
2. A systematic absence is a diffraction peak with zero intensity, where one would expect to see a peak based on the prediction from Bragg's law, as a result of the internal symmetry of the basis of the crystal.	☐	☐
3. The reciprocal lattice is the Fourier transform of a crystal	☐	☐
4. One can obtain the structure of a crystal by a Fourier transform of its diffraction pattern	☐	☐

Exercise 2:

You perform an X-ray diffraction experiment at a wavelength $\lambda = 1.4\,\text{Å}$ on a piece of iron, and you want to determine if it is in the cubic BCC or FCC lattice.

2a. You measure a first order peak at an angle of incidence $\frac{\pi}{6}$. The peak is indexed to the family of planes {200}.

(i) What is the lattice parameter ?

(ii) Would you expect a peak of higher intensity for the FCC or the BCC lattice for this plane ?

(iii) At what angle would you expect to see a second order peak ?

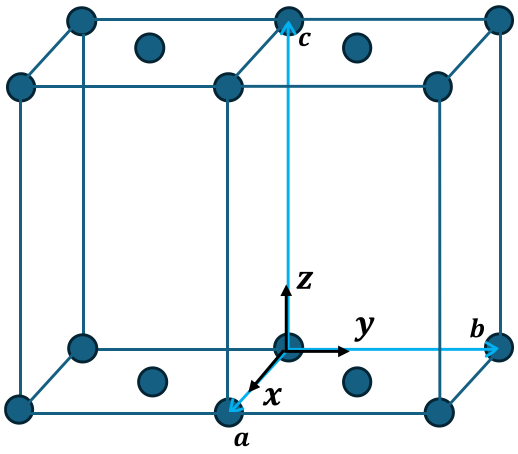
2b. You measure another first order peak at an angle of incidence $\frac{\pi}{3}$.

(i) To which family of plane would it correspond to ?

(ii) Can you conclude that the structure of Iron is BCC ?
(Hint: you can use the result of exercise 5e of week 4).

Exercise 3: Based-centered Orthorhombic

Under certain condition of temperature and mechanical stress, Titanium can transform from a BCC crystal structure into a based-centered Orthorhombic structure. Two conventional cells are shown in the schematic where we represented the origin, the orthonormal basis $\mathcal{B}_{(O,\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})}$, and the orthogonal basis $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$, with:
$\boldsymbol{a} = a\boldsymbol{x}$, $\boldsymbol{b} = b\boldsymbol{y}, \boldsymbol{c} = c\boldsymbol{z}$, with (a, b, c) are strictly positive real numbers, and $a \neq b \neq c$.



3a. Are the vectors $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$ primitive vectors for the based-centered Orthorhombic structure?

3b. We define the following vectors:

$$\boldsymbol{a}' = \frac{a}{2}\boldsymbol{x} - \frac{b}{2}\boldsymbol{y}; \quad \boldsymbol{b}' = \frac{a}{2}\boldsymbol{x} + \frac{b}{2}\boldsymbol{y}; \quad \boldsymbol{c}' = c\boldsymbol{z}$$

(i) Represent these vectors in the schematic above.

(ii) What is the length of each vectors and the angle between them ? Express them as a function of a, b and c.

(iii) Show that these vectors form a Bravais lattice basis for the base-centered Orthorhombic structure (in other words, they are primitive vectors).
(Hint: show it for the lattice point represented in one conventional cell, and use a translation symmetry argument to conclude).

3c. What is the volume of the primitive cell defined by the vectors $\boldsymbol{a}', \boldsymbol{b}', \boldsymbol{c}'$? Solve this in two ways:

(i) By calculating using the volume formula $V = \boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})$.

(ii) By comparing the volumes of the conventional and primitive cells, taking into account the number of motifs in both.

3d. Show that:

(i) The vectors of the reciprocal basis of the $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$ basis are given by:
$\boldsymbol{a_R} = \frac{2\pi}{a^2}\boldsymbol{a}$; $\boldsymbol{b_R} = \frac{2\pi}{b^2}\boldsymbol{b}$; $\boldsymbol{c_R} = \frac{2\pi}{c^2}\boldsymbol{c}$

(ii) The vectors of the reciprocal basis of the $\mathcal{B}_{(O,\boldsymbol{a'},\boldsymbol{b'},\boldsymbol{c'})}$ basis are given by:
$\boldsymbol{a'_R} = 2\pi\left(\frac{\boldsymbol{a}}{a^2} - \frac{\boldsymbol{b}}{b^2}\right)$; $\boldsymbol{b'_R} = 2\pi\left(\frac{\boldsymbol{a}}{a^2} + \frac{\boldsymbol{b}}{b^2}\right)$; $\boldsymbol{c'}_{\boldsymbol{R}} = \frac{2\pi}{c^2}\boldsymbol{c}$

3e.

(i) Express a vector in the orthonormal basis $\mathcal{B}_{(O,\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})}$ that is orthogonal to the plane of Miller indices $(11\bar{1})$.

(ii) What is the distance between the $(11\bar{1})$ parallel planes ?

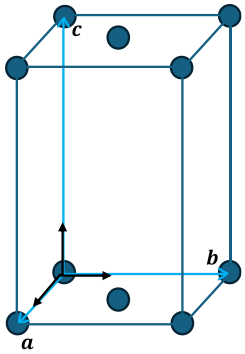
3f. Which planes belong to the same family: (100), (010), (001) ?

3g.

(i) Draw the atom configuration in the planes (100) and (200). Do they belong to the same family ?

(ii) What are the Miller indices of these planes in the $\mathcal{B}_{(O,\boldsymbol{a'},\boldsymbol{b'},\boldsymbol{c'})}$ basis ?

Exercise 4: Structure Factor of base-centered orthorhombic



We consider the same base-centered Orthorhombic structure studied in exercise 3, and shown again to the right, with one atom per motif. It can also be seen as a primitive Orthorhombic with a motif of more than one atom.

4a. Circle such motif.

4b. Deduce that, for the reflection of an incident X-ray on an arbitrary plane of Miller indices (hkl), the structure factor is given by:

$$S = f_a\left(e^{-iN^*.\boldsymbol{D_O}} + e^{-iN^*.\boldsymbol{D_P}}\right)$$

where $N^* = h\boldsymbol{a_R} + k\boldsymbol{b_R} + l\boldsymbol{c_R}$ is the reciprocal lattice vector in the reciprocal basis $\mathcal{B}_{(O,\boldsymbol{a_R},\boldsymbol{b_R},\boldsymbol{c_R})}$. $\boldsymbol{D_O}$ and $\boldsymbol{D_P}$ are vectors in the direct lattice $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$ of coordinates (0,0,0), and (1/2,1/2,0) respectively. f_a is the form factor of the atom.

4c. Show that $S = f_a(1 + e^{-i\pi(h+k)})$.

4d.

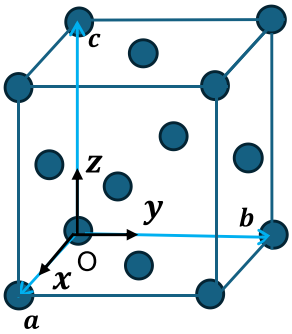
(i) Will the plan $(11\bar{1})$ studied in question 3e exhibit a systematic absence in the X-ray diffraction pattern ?

(ii) How about the planes (100) and (200) studied in question 3g ? Explain the difference of behavior for these two planes.

Exercise 5: Structure factor of NaCl

We first consider a FCC structure of a metal as shown on the schematics. Such structure has one atom per motif, translated along the Bravais lattice (or primitive) vectors of the FCC structure.

To find the structure factor however, we can view the crystal as a primitive (or simple) cubic structure with an imaginary motif of several atoms.



5a. How many atoms are in this imaginary motif ? Circle it.

5b. What are the coordinates of the atoms in the motif in the $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$ basis?

5c.

(i) For a given (hkl) plane, deduce that the structure factor for the FCC crystal structure is given by:

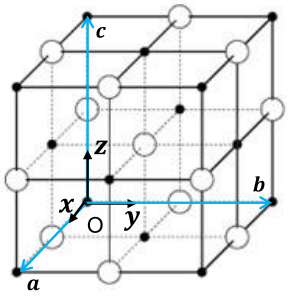
$$S(K) = f_a(1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)})$$

(ii) Conclude that:

$S(K) = 4f_a$ *if* (h, k, l) are all even, or (h, k, l) all odd

$S(K) = 0$ otherwise.

5d. We consider now the structure of sodium chloride (NaCl) shown to the right, where the black dots represent the Sodium ions. The structure is FCC with a motif of one atom of Na and one of Cl.



(i) What is the coordination number ?

(ii) Knowing that the ions radius are 1 Å for Na^+, and 1.8 Å for Cl^-, would you expect this coordination number from the radius ratio rule?

5e. The structure factor will now take into account the two atoms in the motif, plus the "imaginary" motif described above. The NaCl motif is taken such that the Na atom is at the origin O, and the Cl atom at coordinates (½,½, ½) in the $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$ basis.

(i) Show that the structure factor is given by:

$$S(K) = \left(f_{Na} + f_{Cl}e^{-i\pi(h+k+l)}\right)\left(1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)}\right)$$

(ii) Justify that we observe diffraction peaks for the planes like (111), (200) and (311).

(iii) For the crystal Potassium Chloride (KCl) with the same crystal structure, the peaks (111) and (311) disappear. Could you explain why ?