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 ☐ ■

The reciprocal lattice is the Fourier transform of the direct lattice, a crystal is the convolution of the lattice and the motif, does the Fourier transform includes a term of the unit cell structure factor, which includes the atomic form factor of the elements of the motif and their arrangement within the unit cell.

4. One can obtain the structure of a crystal by a Fourier transform of its diffraction pattern ☐ ■

Since we can only measure the intensity, which is the square of a complex number, we lose the phase information (=the phase problem, so a simple Fourier transform is not possible. Techniques exist to retrieve the phase under certain conditions, but they are not part of these course.

Exercise 2:

You perform an X-ray diffraction experiment (at a wavelength $\lambda = 1.4$ 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 ?

The lattice parameters are the length and angles that define a given crystal structure. Since you know it is a cubic structure,

From Bragg's law:

$$2d_{(hkl)} \sin\theta = \lambda$$

Since it is the cubic systel, we know that $d_{(hkl)} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{a}{\sqrt{4}} = \frac{a}{2}$, and $\sin\left(\frac{\pi}{6}\right) = \frac{1}{2}$, this gives:

$$2 \times \frac{a}{2} \times \frac{1}{2} = \lambda$$

Or equivalently:

$$a = 2\lambda = 2.8\text{Å}$$

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

The peak intensity depends on the electron density and the {200} planes are denser in FCC than in BCC lattice. So we would expect a peak of higher intensity for the FCC lattice.

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

From Bragg's law:

$$2d_{(hkl)} \sin\theta = 2\lambda$$

$$d_{(hkl)} \sin\theta = \lambda$$

$$\theta = \arcsin\frac{\lambda}{d_{(hkl)}}$$

From question 2a. (i), we know that $d_{(hkl)} = \frac{a}{2} = \lambda$, leading to

$$\theta = \arcsin 1 = \frac{\pi}{2}$$

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 ?

Using Bragg's law as before, we have:

$$2d_{(hkl)}\sin\theta = \lambda$$

For the left hand side, we can write:

$$2d_{(hkl)}\sin\frac{\pi}{3} = 2\,d_{(hkl)}\left(\frac{\sqrt{3}}{2}\right)$$

For the right hand side, from the preivous question we know that:

$$\lambda = \frac{a}{2}$$

So:

$$d_{(hkl)} = \frac{a}{2\sqrt{3}} = \frac{a}{\sqrt{12}}$$

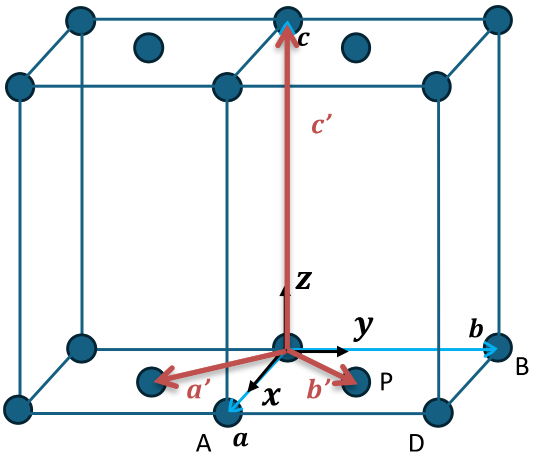
Meaning that: $h^2 + k^2 + l^2 = 12$, which is only possible if $h = k = l = \pm 2$. The family of planes if therefore {222}.

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

This can only be a BCC lattice as the {222} planes are not crystal planes of the FCC lattice, as we showed in the exercise 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 Orthorombic structure?
No, they are not. Indeed, the points "*P*" located in the middle of the faces cannot be expressed by a vector like:

$$\boldsymbol{OP} = n\boldsymbol{a} + p\boldsymbol{b} + q\boldsymbol{c}$$

With $(n, p\ q) \in \mathbb{Z}^3$. Its coordinates will include half-integers.

3b. We define the following vectors:

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

(i) Represent these vectors in the schematic above.

Look at the schematic above for the correction.

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

$$\|\boldsymbol{a}'\| = \|\boldsymbol{b}'\| = \sqrt{\frac{a^2}{4} + \frac{b^2}{4}} = \frac{1}{2}\sqrt{a^2 + b^2}$$

$$\|\boldsymbol{c}'\| = c$$

$\boldsymbol{c}'$ is orthogonal to $\boldsymbol{a}'$and $\boldsymbol{b}'$, so $\widehat{\boldsymbol{a}',\boldsymbol{c}'} = \widehat{\boldsymbol{b}',\boldsymbol{c}'} = 90°$.

Then for $\widehat{\boldsymbol{a}',\boldsymbol{b}'}$:

$$\widehat{\boldsymbol{a}',\boldsymbol{b}'} = 2\tan^{-1}\left(\frac{b/2}{a/2}\right) = 2\tan^{-1}\left(\frac{b}{a}\right)$$

We could also use the dot product, with for $\widehat{\boldsymbol{a}',\boldsymbol{b}'} = \theta$:

$$\boldsymbol{a}'.\boldsymbol{b}' = \|\boldsymbol{a}'\|\|\boldsymbol{b}'\|\cos\theta$$

From the left hand side, we have:

$$\boldsymbol{a}'.\boldsymbol{b}' = \begin{pmatrix} a/2 \\ -b/2 \\ 0 \end{pmatrix} . \begin{pmatrix} a/2 \\ b/2 \\ 0 \end{pmatrix} = \frac{1}{4}(a-b)(a+b)$$

From the right hand side, we have:

$$\|\boldsymbol{a}'\|\|\boldsymbol{b}'\|\cos\theta = \frac{1}{4}(a^2 + b^2)$$

So finally:

$$\theta = \arccos\left(\frac{(a-b)(a+b)}{a^2 + b^2}\right)$$

You could also have used the dot product to show that the angles $\widehat{\boldsymbol{a}',\boldsymbol{c}'} = \widehat{\boldsymbol{b}',\boldsymbol{c}'} = 90°$.

(iii) Show that these vectors form a Bravais lattice basis for the base-centered Orthorombic 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).

To form a Bravais lattice basis, where vectors are called primitive vectors, every lattice point must have coordinates in this basis that are relative integers.

We can verify that for atoms in the conventional cell (points O, A, B, D, P on the schematics, they have relative integers as coordinates in the $\mathcal{B}_{(O,\boldsymbol{a}',\boldsymbol{b}',\boldsymbol{c}')}$ basis:

- Origin has coordiantes (0,0,0)
- The point at $\boldsymbol{OA} = \boldsymbol{a}$ is at coordinates (1,1,0). In other words: $\boldsymbol{a} = \boldsymbol{a}' + \boldsymbol{b}'$
- The point at $\boldsymbol{OB} = \boldsymbol{b}$ is at coordinates (-1,1,0). In other words: $\boldsymbol{b} = -\boldsymbol{a}' + \boldsymbol{b}'$

- The point at $\boldsymbol{OD} = \boldsymbol{a} + \boldsymbol{b}$ is at coordinates (0,2,0). In other words: $\boldsymbol{a} + \boldsymbol{b} = 2\boldsymbol{b}'$
- The point P in the middle of the base is at coordinates (0,1,0), $\boldsymbol{OP} = \boldsymbol{b}'$
- All the points in the plane above are shifted by a vector c', hence adds a +1 to the z coordinates.

Hence, all the points in the conventional cells have relative integer coordinates in the $\mathcal{B}_{(O,\boldsymbol{a}',\boldsymbol{b}',\boldsymbol{c}')}$. By translation symmetry, it is true for all the other conventional cells (you could just shift the origin and do the same demo in a neighboring cell).
So what is true in the conventional cell is also true in the entire crystal, which establishes that $\mathcal{B}_{(O,\boldsymbol{a}',\boldsymbol{b}',\boldsymbol{c}')}$ is indeed a Bravais lattice basis.

You can also use the methods developped in previous exercies, where we divided the lattice points into different types. The fact that we consider points shifted by relative integers along the axis just expresses mathematically the translation symmetry argument made above:

- First the points along the $\boldsymbol{x}$ axis can be expressed as $\boldsymbol{OA} = na\boldsymbol{x} = n(\boldsymbol{a}' + \boldsymbol{b}')$, with $n \in \mathbb{Z}$.
- Similarly for the points along $\boldsymbol{y}$ and $\boldsymbol{z}$ axes, we have respectively:

$$\boldsymbol{OB} = pb\boldsymbol{y} = p(\boldsymbol{b}' - \boldsymbol{a}')$$
$$\boldsymbol{OC} = qc\boldsymbol{z} = q\boldsymbol{c}'$$

  With $p, q \in \mathbb{Z}$.
- Then for the points at the middle of the faces we have:

$$\boldsymbol{OM} = \left(n + \frac{1}{2}\right)a\boldsymbol{x} + \left(p + \frac{1}{2}\right)b\boldsymbol{y} + qc\boldsymbol{c}$$
$$\boldsymbol{OM} = \left(n + \frac{1}{2}\right)(\boldsymbol{a}' + \boldsymbol{b}') + \left(p + \frac{1}{2}\right)(\boldsymbol{b}' - \boldsymbol{a}') + q\boldsymbol{c}'$$
$$= \boldsymbol{a}'(n - p) + \boldsymbol{b}'(n + p + 1) + q\boldsymbol{c}'$$

  As $(n, p, q) \in \mathbb{Z}^3$ then $(n - p)$, $(n + p + 1)$ and q are also integers and the vectors $\boldsymbol{a}', \boldsymbol{b}'$ and $\boldsymbol{c}'$ form a Bravais lattice basis for the base-centered Orthorombic structure.

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 $V = \boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})$.

$$\boldsymbol{b}' \times \boldsymbol{c}' = \begin{pmatrix} a/2 \\ b/2 \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix} = \begin{pmatrix} bc/2 \\ -ca/2 \\ 0 \end{pmatrix}$$

$$\boldsymbol{a}'.(\boldsymbol{b}' \times \boldsymbol{c}') = \begin{pmatrix} a/2 \\ -b/2 \\ 0 \end{pmatrix} . \begin{pmatrix} bc/2 \\ -ca/2 \\ 0 \end{pmatrix} = \frac{abc}{4} + \frac{abc}{4} = \frac{abc}{2}$$

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

We know that we have 2 motifs per conventional cell:

- 8 corners counting each as 1/8;
- 2 atoms on faces each counting for ½.

The volume of the primitive cell must be the volume of the conventional cell divided by the number of motif in the conventional cell.

So the volume of the primitice cell should be:

$$V_{Primitive} = \frac{V_{Conventional}}{2} = \frac{abc}{2}$$

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:

$\boldsymbol{a_R} = \frac{2\pi}{a^2}\boldsymbol{a}$; $\boldsymbol{b_R} = \frac{2\pi}{b^2}\boldsymbol{b}$; $\boldsymbol{c_R} = \frac{2\pi}{c^2}\boldsymbol{c}$

By definition:

$$\boldsymbol{a_R} = \frac{2\pi}{V}\boldsymbol{b} \times \boldsymbol{c} = \frac{2\pi}{abc}\begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix} = \frac{2\pi}{abc}\begin{pmatrix} bc \\ 0 \\ 0 \end{pmatrix} = 2\pi \begin{pmatrix} 1/a \\ 0 \\ 0 \end{pmatrix} = \frac{2\pi}{a^2}\boldsymbol{a}$$

Similarly:

$$\boldsymbol{b_R} = \frac{2\pi}{V}\boldsymbol{c} \times \boldsymbol{a} = \frac{2\pi}{abc}\begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix} \times \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} = 2\pi \begin{pmatrix} 0 \\ 1/b \\ 0 \end{pmatrix} = \frac{2\pi}{b^2}\boldsymbol{b}$$

$$\boldsymbol{c_R} = \frac{2\pi}{V}\boldsymbol{a} \times \boldsymbol{b} = \frac{2\pi}{abc}\begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} = 2\pi \begin{pmatrix} 0 \\ 0 \\ 1/c \end{pmatrix} = \frac{2\pi}{c^2}\boldsymbol{c}$$

(ii) The vectors of the reciprocal basis of the $\mathcal{B}_{(O,\boldsymbol{a'},\boldsymbol{b'},\boldsymbol{c'})}$ basis are given by:

$\boldsymbol{a}'_{\boldsymbol{R}} = 2\pi\left(\frac{\boldsymbol{a}}{a^2} - \frac{\boldsymbol{b}}{b^2}\right)$; $\boldsymbol{b}'_{\boldsymbol{R}} = 2\pi\left(\frac{\boldsymbol{a}}{a^2} + \frac{\boldsymbol{b}}{b^2}\right)$; $\boldsymbol{c'}_{\boldsymbol{R}} = \frac{2\pi}{c^2}\boldsymbol{c}$

$$\boldsymbol{a'}_{\boldsymbol{R}} = \frac{2\pi}{V}\boldsymbol{b}' \times \boldsymbol{c}' = \frac{4\pi}{abc}\begin{pmatrix} a/2 \\ b/2 \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix} = \frac{4\pi}{abc}\begin{pmatrix} bc/2 \\ -ac/2 \\ 0 \end{pmatrix} = 2\pi \begin{pmatrix} 1/a \\ -1/b \\ 0 \end{pmatrix} = 2\pi\left(\frac{\boldsymbol{a}}{a^2} - \frac{\boldsymbol{b}}{b^2}\right)$$

$$\boldsymbol{b'}_{\boldsymbol{R}} = \frac{2\pi}{V}\boldsymbol{c}' \times \boldsymbol{a}' = \frac{4\pi}{abc}\begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix} \times \begin{pmatrix} a/2 \\ -b/2 \\ 0 \end{pmatrix} = 2\pi \begin{pmatrix} 1/a \\ 1/b \\ 0 \end{pmatrix} = 2\pi\left(\frac{\boldsymbol{a}}{a^2} + \frac{\boldsymbol{b}}{b^2}\right)$$

$$\boldsymbol{c'}_{\boldsymbol{R}} = \frac{2\pi}{V}\boldsymbol{a}' \times \boldsymbol{b}' = \frac{4\pi}{abc}\begin{pmatrix} a/2 \\ -b/2 \\ 0 \end{pmatrix} \times \begin{pmatrix} a/2 \\ b/2 \\ 0 \end{pmatrix} = 2\pi \begin{pmatrix} 0 \\ 0 \\ 1/c \end{pmatrix} = \frac{2\pi}{c^2}\boldsymbol{c}$$

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 $(11\bar{1})$.

The Miller indices are defined in the conventional basis $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$, so the normal to the plane $(11\bar{1})$ is:

$$N^* = 1 \times \boldsymbol{a_R} + 1 \times \boldsymbol{b_R} + (-1)\boldsymbol{c_R}$$

And from the previous section, we know that:

$$\boldsymbol{a_R} = \frac{2\pi}{a^2}\boldsymbol{a} = \frac{2\pi}{a}\boldsymbol{x}; \qquad \boldsymbol{b_R} = \frac{2\pi}{b^2}\boldsymbol{b} = \frac{2\pi}{b}\boldsymbol{y}; \qquad \boldsymbol{c_R} = \frac{2\pi}{c^2}\boldsymbol{c} = \frac{2\pi}{c}\boldsymbol{z}$$

So:

$$\boldsymbol{N}^*_{(hkl)} = \frac{2\pi}{a}\boldsymbol{x} + \frac{2\pi}{b}\boldsymbol{y} - \frac{2\pi}{c}\boldsymbol{z}$$

In the $\mathcal{B}_{(O,\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})}$ basis.

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

By definition:

$$d_{hkl} = \frac{\boldsymbol{OA}.\boldsymbol{N}^*_{(hkl)}}{\left\|\boldsymbol{N}^*_{(hkl)}\right\|}$$

Where the point A is $\begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix}$ in the $\mathcal{B}_{(O,\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})}$, so:

$$\boldsymbol{OA}.\boldsymbol{N}^*_{(hkl)} = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} . \begin{pmatrix} 2\pi/a \\ 2\pi/b \\ -2\pi/c \end{pmatrix} = 2\pi$$

$$\left\|\boldsymbol{N}^*_{(hkl)}\right\| = 2\pi\sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}}$$

And:

$$d_{hkl} = \frac{\boldsymbol{OA}.\boldsymbol{N}^*_{(hkl)}}{\left\|\boldsymbol{N}^*_{(hkl)}\right\|} = \frac{1}{\sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}}}$$

One can also directly use the distance in the Orthorombic crystal structrure given by:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

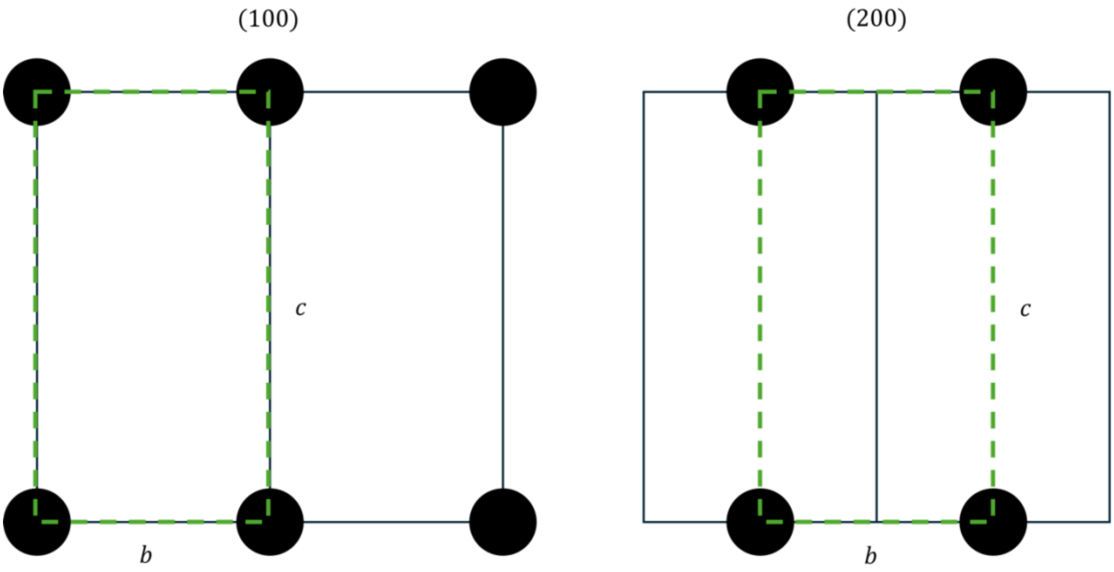
And apply it for the case $h = 1, k = 1, l = -1$.

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

All planes belong to different families because $a \neq b \neq c$. If you look at the atomic configuration, the distance between atoms and positions are not the same.

3g.

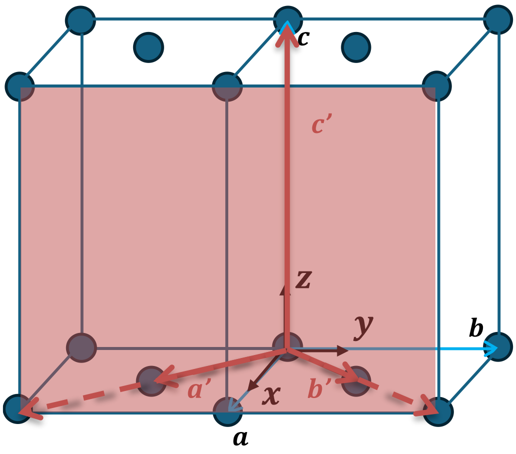
(i) Draw the atom configuration in the planes (100) and (200). Do they belong to the same family ?



These two planes belong to the same family. You can see from the schematic above that the atomic configuration in these planes is identical.

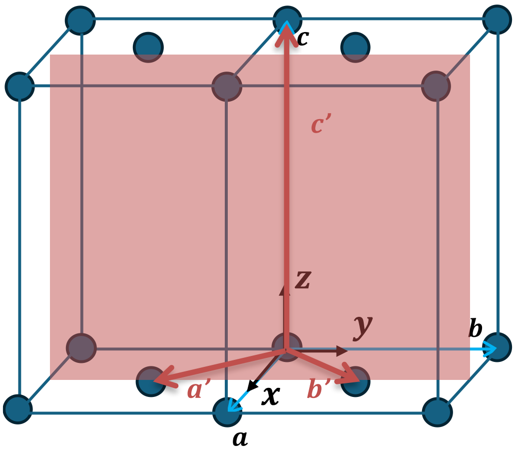
(ii) What are the Miller indices of these planes in the $\mathcal{B}_{(O,\boldsymbol{a}',\boldsymbol{b}',\boldsymbol{c}')}$ basis ?

You can find the Miller indices from the schematics below, i.e. by finding the interceptions of the plane with the axes $\boldsymbol{a}'$, $\boldsymbol{b}'$ and $\boldsymbol{c}'$. First for the plane (100), we can see



that the insersections with $\boldsymbol{a}'$, $\boldsymbol{b}'$ and $\boldsymbol{c}'$ are respectively 2, 2 and 0, so the plane is (110) $\left(2 \times \left(\frac{1}{2},\frac{1}{2},0\right)\right)$.

For the plane (200), we have:



And we see that this would correspond to the plane (110) too.

Another way to find the Miller indices of the plane (100) in the $\mathcal{B}_{(O,\boldsymbol{a'},\boldsymbol{b'},\boldsymbol{c'})}$ basis is:

- First express the normal to the plane in the $\mathcal{B}_{(O,\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})}$ basis:

$$\boldsymbol{N}_{(100)} = 1 \times \boldsymbol{a_R} + 0 \times \boldsymbol{b_R} + 0 \times \boldsymbol{c_R} = \frac{2\pi}{a}\boldsymbol{x} = \frac{2\pi}{a^2}\boldsymbol{a} \qquad 3.1$$

- Then find the new indices h', k' and l' such that:

$$\boldsymbol{N'}_{(h'k'l')} = h' \times \boldsymbol{a'_R} + k' \times \boldsymbol{b'_R} + l' \times \boldsymbol{c'_R} = \frac{2\pi}{a^2}\boldsymbol{a}$$

$$\boldsymbol{N'}_{(h'k'l')} = 2\pi h' \times \left(\frac{\boldsymbol{a}}{a^2} - \frac{\boldsymbol{b}}{b^2}\right) + 2\pi k' \times \left(\frac{\boldsymbol{a}}{a^2} + \frac{\boldsymbol{b}}{b^2}\right) - \frac{2\pi l'}{c^2}\boldsymbol{c}$$

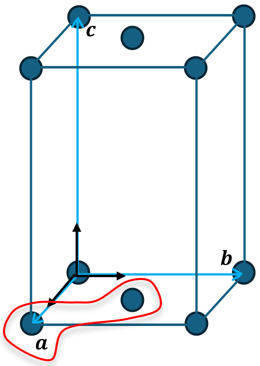
$$\boldsymbol{N'}_{(h'k'l')} = \frac{2\pi}{a^2}(h' + k')\boldsymbol{a} + \frac{2\pi}{b^2}(h' - k')\boldsymbol{b} - \frac{2\pi l'}{c^2}\boldsymbol{c} \qquad 3.2$$

In order to have equations 3.1 and 3.2 equal we must have: $l' = 0$, $h' - k' = 0$ or $h' = k'$ and $h' + k' = 1$. This would lead to the plane $(\frac{1}{2}, \frac{1}{2}, 0)$, which in reality is (110) as h', k' and l' must be integers.

You can proceed similarly for the plane (200) and you would find once again that the Miller indices in the $\mathcal{B}_{(O,\boldsymbol{a'},\boldsymbol{b'},\boldsymbol{c'})}$ basis are also (110).

Exercise 4: Structure Factor

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 be seen as a primitive Orthorhombic with a motif of more than one atom.



4a. Circle such motif.

See the schematic for the correction.

4b. Deduce that, for the reflexion 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.

By definition, the structure factor is given by:

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K})e^{-i\boldsymbol{K}.\boldsymbol{r}_j}$$

We are thus making a sum on all the atoms in the motif. In our case we have two atoms of same nature, and thus with the same form factor f_a, and with coordinates $\boldsymbol{r}_0 = \boldsymbol{D_0} = \begin{pmatrix}0\\0\\0\end{pmatrix}$ and $\boldsymbol{r}_1 = \boldsymbol{D_P} = \begin{pmatrix}1/2\\1/2\\0\end{pmatrix}$ in the $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$ basis.

In addition, when we have a diffraction peak, $\boldsymbol{K}$ belongs to the reciprocal lattice and can thus be written as:

$$\boldsymbol{K} = h\boldsymbol{a_R} + k\boldsymbol{b_R} + l\boldsymbol{c_R} = \boldsymbol{N}^*$$

As a consequence, Eq. 2.1 becomes:

$$S(\boldsymbol{K}) = f_a e^{-i\boldsymbol{N}^*.\boldsymbol{D}_0} + f_a e^{-i\boldsymbol{N}^*.\boldsymbol{D}_P} = f_a\left(e^{-i\boldsymbol{N}^*.\boldsymbol{D}_0} + e^{-i\boldsymbol{N}^*.\boldsymbol{D}_P}\right)$$

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

Let's compute the two dot products :

$$\boldsymbol{N}^*.\boldsymbol{D}_0 = 0$$

$$\boldsymbol{N}^*.\boldsymbol{D}_P = (h\boldsymbol{a_R} + k\boldsymbol{b_R} + l\boldsymbol{c_R}).\left(\frac{1}{2}\boldsymbol{a} + \frac{1}{2}\boldsymbol{b}\right) = \frac{h}{2}\boldsymbol{a}_R\boldsymbol{a} + \frac{k}{2}\boldsymbol{b}_R\boldsymbol{b} = \pi(h+k)$$

Indeed, remember that by construction $\boldsymbol{a_R a} = \boldsymbol{b_R b} = \boldsymbol{2\pi}$ and $\boldsymbol{a_R b} = \boldsymbol{b_R a} = \boldsymbol{c_R a} = \boldsymbol{c_R b} =$ 0.

Finally, this gives:

$$S(\boldsymbol{K}) = f_a\left(e^{-i\times 0} + e^{-i\times\pi(h+k)}\right) = f_a\left(1 + e^{-i\pi(h+k)}\right)$$

Another way to solve this question is presented below. Be careful to express all vectors in the orthonormal basis $\mathcal{B}_{(O,\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})}$ if you want to employ this method.

From exercise 3, we demonstrated that in the orthonormal basis $\boldsymbol{N}^* = h\boldsymbol{a_R} + k\boldsymbol{b_R} + l\boldsymbol{c_R}$ with $\boldsymbol{a_R} = \frac{2\pi}{a^2}\boldsymbol{a} = \frac{2\pi}{a}\boldsymbol{x}$, $\boldsymbol{b_R} = \frac{2\pi}{b^2}\boldsymbol{b} = \frac{2\pi}{b}\boldsymbol{y}$ and $\boldsymbol{c_R} = \frac{2\pi}{c^2}\boldsymbol{c} = \frac{2\pi}{c}\boldsymbol{z}$, so we have:

$$\boldsymbol{N}^*.\boldsymbol{D}_0 = \begin{pmatrix} 2\pi h/a \\ 2\pi k/b \\ 2\pi l/c \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = 0$$

$$\boldsymbol{N}^*.\boldsymbol{D}_P = \begin{pmatrix} 2\pi h/a \\ 2\pi k/b \\ 2\pi l/c \end{pmatrix}\begin{pmatrix} a/2 \\ b/2 \\ 0 \end{pmatrix} = \pi(h+k)$$

Similarly we find that:

$$S(\boldsymbol{K}) = f_a\left(e^{-i\times 0} + e^{-i\times\pi(h+k)}\right) = f_a\left(1 + e^{-i\pi(h+k)}\right)$$

4d.

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

$$S(\boldsymbol{K}) = f_a\left(1 + e^{-i\pi(h+k)}\right) = f_a\left(1 + e^{-i2\pi}\right) = 2f_a \neq 0$$

Therefore we don't expect a sysematic absence in the X-ray diffraction pattern for the plane $(11\bar{1})$.

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

For (100):

$$S(\boldsymbol{K}) = f_a\left(1 + e^{-i\pi}\right) = 0$$

For (200):

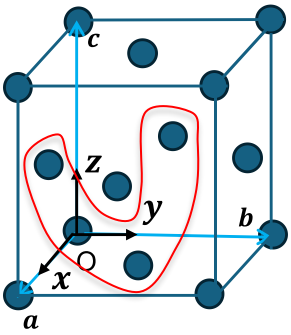
$$S(\boldsymbol{K}) = f_a\left(1 + e^{-i2\pi}\right) = 2f_a$$

So we expect an extinction for (100) but not for (200).

The planes (100) and (200) are the same, as was shown in 3gi) and for Miller indices in the primitive unit cell of the planes (100) and (200) planes are identical (see exercise 3g (ii)), which means that only one peaks exists. This can be shown either with the structure factors as shown above, or also by looking at Bragg law as we have done in the lecture (see lecture notes slides 53)

Exercise 5: Structure factor of NaCl

We 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.

There are 4 atomes in the motif (see schematic). This is actually expected because if we view the crystal as a primitive cubic structure, we should have one motif per unit cell (definition of the primitive cell). If we now count the number of atoms per unti cell, we have: $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ atoms. As a consequence: 1 motif = 4 atoms.

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

The coordinates in the $\mathcal{B}_{(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})}$ are: $\boldsymbol{r_0} = (0,0,0), \boldsymbol{r_1} = \left(\frac{1}{2},\frac{1}{2},0\right), \boldsymbol{r_2} = \left(\frac{1}{2},0,\frac{1}{2}\right), \boldsymbol{r_3} = \left(0,\frac{1}{2},\frac{1}{2}\right)$.

5c.

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

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

By definition, the structure factor is:

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{-i\boldsymbol{K}.\boldsymbol{r}_j}$$

As explained in question 5a., with the approach considered we have 4 atoms of same nature in the motif and at positions $\boldsymbol{r_0}, \boldsymbol{r_1}, \boldsymbol{r_2}$ and $\boldsymbol{r_3}$. In addition, we know that when a diffraction peak is observed, $\boldsymbol{K}$ must belong to the reciprocal lattice and can thus be written $\boldsymbol{K} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$. As a consequence, Eq. 3.1 becomes:

$$S(\boldsymbol{K}) = f_a\left(e^{-i\boldsymbol{K}.\boldsymbol{r}_0} + e^{-i\boldsymbol{K}.\boldsymbol{r}_1} + e^{-i\boldsymbol{K}.\boldsymbol{r}_2} + e^{-i\boldsymbol{K}.\boldsymbol{r}_3}\right)$$

Using the same reasoning as question 4c.:

$$\boldsymbol{K}.\boldsymbol{r_0} = 0$$

$$\boldsymbol{K}.\boldsymbol{r_1} = (h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*).\left(\frac{\boldsymbol{a}}{2} + \frac{\boldsymbol{b}}{2}\right) = \frac{h}{2}\boldsymbol{a}^*\boldsymbol{a} + \frac{k}{2}\boldsymbol{b}^*\boldsymbol{b} = \pi(h+k)$$

$$\boldsymbol{K}.\boldsymbol{r_2} = (h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*).\left(\frac{\boldsymbol{a}}{2} + \frac{\boldsymbol{c}}{2}\right) = \pi(h+l)$$

$$\boldsymbol{K}.\boldsymbol{r_3} = (h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*).\left(\frac{\boldsymbol{b}}{2} + \frac{\boldsymbol{c}}{2}\right) = \pi(k+l)$$

Finally, we obtain:

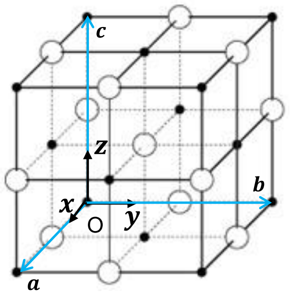
$$S(\boldsymbol{K}) = f_a\left(1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)}\right)$$

(ii) Conclude that:

$$S(K) = 4f_a \text{ if (h, k, l) are all even, or (h, k, l) all odd}$$
$$S(K) = 0 \text{ otherwise.}$$

We have 4 different possibilities to evaluate:

- (hkl) all even: $h+k$, $h+l$ and $k+l$ all even and all the exponential exponents are a multiple of 2π. Thus $S(\boldsymbol{K}) = 4f_a$
- (hkl) all odd: : $h+k$, $h+l$ and $k+l$ all even and all the exponential exponents are a multiple of 2π. Thus $S(\boldsymbol{K}) = 4f_a$
- If only one odd indice and two even: : let's assume h is odd and k and l are even. This would lead to $h+k$ and $h+l$ being odd numbers and:
  $$S(\boldsymbol{K}) = f_a(1 - 1 - 1 + 1) = 0$$
  You would obtain the same result assuming that k or l are odd while all other indices are even.
- If two indices are odd and one even: let's assume h and k are odd and l is even. As a consequence two of the indice sums are odds, namely $h+l$ and $k+l$ and as before we obtain:
  $$S(\boldsymbol{K}) = f_a(1 + 1 - 1 - 1) = 0$$



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 ?

The coordination number is 6.

(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?

The radius ratio $\rho = \frac{r_+}{r_-} = \frac{r_{Na^+}}{r_{Cl^-}} = \frac{1}{1.8} = 0.56$. We indeed expect a coordination number of 6 for $0.4142 < \rho < 0.7320$.

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:

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

The structure factor is:

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K})e^{-i\boldsymbol{K}.\boldsymbol{r}_j}$$

If one considers the FCC structure, the motif is now made of 2 atoms, Na and Cl. However, to find the structure factor we will use the same procedure as before and view this FCC structure as a primitve cubic structure with an imaginary motif of 8 atoms (4 Cl and 4 Na). Let's do the analysis of the two atom types separately.

First for Na, we have the same structure factor as found in question 3c (i) as the atoms have the same coordinates:

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

For the Cl atoms, their coordinates are equivalent to the coordinates of the Na atoms + a translation of $\boldsymbol{t} = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$. This gives:

$$\begin{aligned} S_{Cl}(\boldsymbol{K}) &= f_{Cl}\left(e^{-i\boldsymbol{K}.(\boldsymbol{r}_0+\boldsymbol{t})} + e^{-i\boldsymbol{K}.(\boldsymbol{r}_1+\boldsymbol{t})} + e^{-i\boldsymbol{K}.(\boldsymbol{r}_2+\boldsymbol{t})} + e^{-i\boldsymbol{K}.(\boldsymbol{r}_3+\boldsymbol{t})}\right) \\ &= f_{Cl}e^{-i\boldsymbol{K}.\boldsymbol{t}}\left(e^{-i\boldsymbol{K}.\boldsymbol{r}_0} + e^{-i\boldsymbol{K}.\boldsymbol{r}_1} + e^{-i\boldsymbol{K}.\boldsymbol{r}_2} + e^{-i\boldsymbol{K}.\boldsymbol{r}_3}\right) \end{aligned}$$

With:

$$\boldsymbol{K}.\boldsymbol{t} = (h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*).\left(\frac{\boldsymbol{a}}{2} + \frac{\boldsymbol{b}}{2} + \frac{\boldsymbol{c}}{2}\right) = \pi(h + k + l)$$

So finally:

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

And:

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

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

- Plane (111):

$$S(\boldsymbol{K}) = 4(f_{Na} - f_{Cl}) \neq 0$$

- Plane (200):

$$S(\boldsymbol{K}) = 4(f_{Na} + f_{Cl}) \neq 0$$

- Plane (311):

$$S(\boldsymbol{K}) = 4(f_{Na} - f_{Cl}) \neq 0$$

Therefore as $S(\boldsymbol{K}) \neq 0$ for all these planes, we expect to observe a diffraction peak.

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

Potassium and Chloride have very similar electronic structures and through the formation of an ionic bond between them, the two atoms end up with the same number of electrons. As the form factor f depends on the electronic density of the atoms, for KCl we will have $f_K \approx f_{Cl}$ and thus for the planes (111) and (311):

$$S(\boldsymbol{K}) = 4(f_K - f_{Cl}) = 0$$

For a similar structure, an isoelectronic ionic crystal will exhibit more systematic absence in its diffraction peaks compared to a non-isoelectronic crystal.