Week 08

Diffraction & Crystallography

Exercise 1

	True	False
1. 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.	■	□
2. Laue diffraction uses polychromatic radiation to investigate powder samples A polychromatic radiation to investigate single crystals	□	■
3. Powder diffraction patterns display hexagonal symmetry for crystals with hexagonal crystal structure Powder diffraction patters display always cylindrical symmetry.	□	■
4. 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.	■	□

Answer these questions by true or false:

Exercise 2:

Select the correct answer(s) (more than one answer can be correct)

1. X-ray powder diffraction is…

a. A scattering technique

b. Involves elastic processes

c. Involves inelastic and elastic processes

No change in the energy of the scattered beam is taken into account, thus only elastic scattering

d. Can only be performed at a synchrotron

No, can be done also at lab-sources

2. What is a structure factor in crystallography

a. The atomic basis of a crystal

b. The vector sum of the atomic scattering factors from each atom that makes up the basis, when the crystal satisfies Bragg's law. The angles between the vectors are determined by the phases of the incident radiation that they experience

3. What is an atomic form factor

a. It is the Fourier transform of electron density distribution

b. Describes the scattering amplitude of an atom as a function of scattering angle and X-ray energy

c. Has its minimum in the forward direction

Maximum value in forward direction and decreases with increasing scattering angle

4. The Ewald sphere…

a. Is a geometrical construct facilitating the determination of whether a crystal will produce one or more diffraction spot signals

b. Has a radius equal the scattering vector q

Has a radius equal to the wavevector of radiation being used for the diffraction experiment

c. Always has the direct beam, equal to (000) Bragg peak, on its surface

5. Textured samples…

a. Have a preferred orientation of certain crystallographic directions

b. Show only defined peaks in the 2D scattering pattern

Depending on measurement direction (where the Ewald sphere cut the reciprocal space) there can be peaks, arcs or rings

c. Fibre-textured materials are used to make textiles

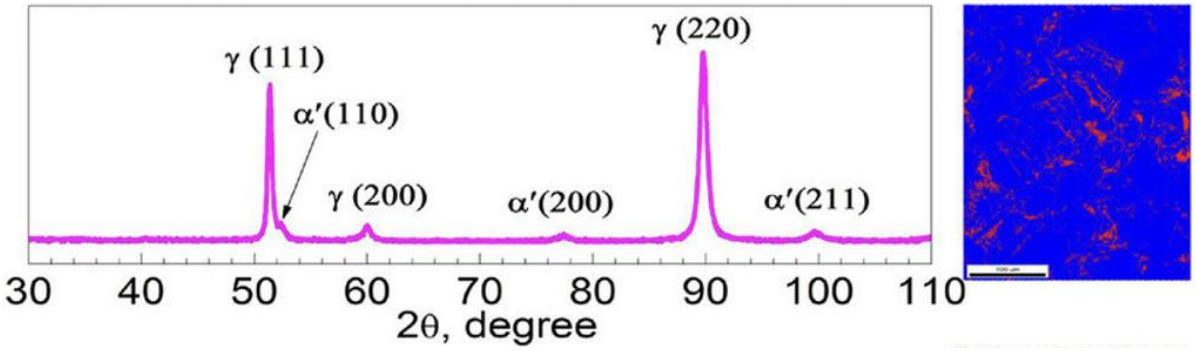
Can be correct because for semi-crystalline yarns, they would probably show fibre-texture, but fibre-texture is very common in many materials.

d. Show defined peaks in the 1D scattering curve (Intensity vs. scattering angle/scattering vector)

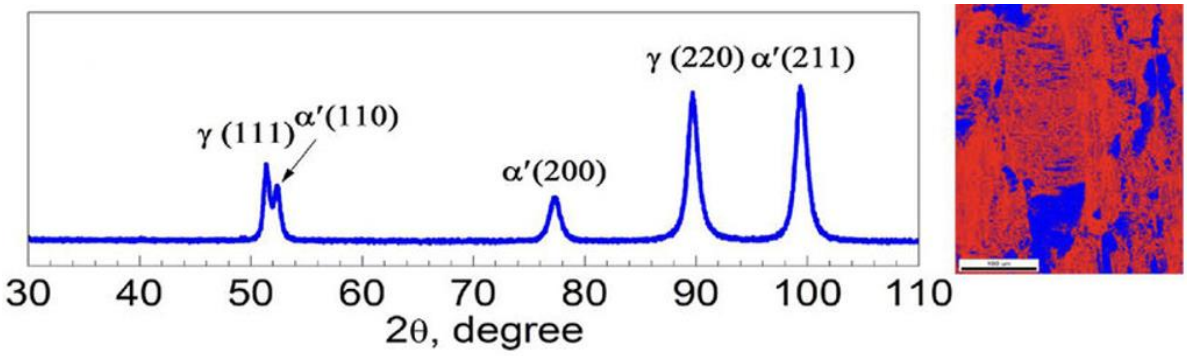
Exercise 3: Crystal phase identification

Steel can contain different amounts of Ferrite (α-phase) and Austenite (γ-phase).

Sample A:



Sample B:



What is the crystallographic structure of Ferrite and Austenite? And which one is the blue phase?

Sample A contains more of the blue phase and is according to the diffraction pattern dominated by the gamma phase, thus Austenite corresponds to blue. This gamma phase shows the (111), (200) and (220) peaks, which is consistent with FCC, while the red phase corresponds to alpha' which shows the (110), (200), (211) peaks, which is consistent with BCC. So Austenite is FCC and Ferrite is BCC.

Exercise 4: Powder diffraction

A copper crystal powder (face-centered cubic, a = 3.596 Å) is measured with 16 keV radiation.

a) Determine the scattering angle of the fourth reflection of copper (face-centered cubic, a = 3.596 Å) in a powder diffraction pattern.

The wavelength of 16-keV radiation is determined through the practical expression λ [Å] = 12.3984/E [keV], which for 16-keV photons results in λ = 0.7749 Å.

The first allowed reflections for fcc crystals are (111), (002), (220), and then (311). The (311) interplanar separation is a/√11 = 1.0842 Å. The corresponding Bragg angle is $\arcsin\left(\frac{\lambda}{2d_{311}}\right)$ = 20.938° . The scattering angle is therefore 41.876°.

b) Where does the peak appear in a powder diffraction plot with Intensity vs. scattering vector q

q = 4*pi*sin(θ)/λ, with θ = 20.938° and λ = 0.7749 Å, q = 5.795 $Å^{-1}$

c) What is the scattering angle and scattering vector q if measured with 10 keV instead?

Either solve as above with λ [Å] = 12.3984/E [keV], which for 10-keV photons results in λ = 1.23984 Å.

The corresponding Bragg angle is $\arcsin\left(\frac{\lambda}{2d_{311}}\right)$= 34.874°. The scattering angle is therefore 69.748°. q-vector (4 * pi * sin(34.874°)/1.23984 = 5.795 $Å^{-1}$

OR notice that the scattering vector q is independent of the used wave length,

thus q = 5.795 $Å^{-1}$ and the corresponding scattering angle 2θ according to q = 4*pi*sin(θ)/λ is 2*38.874° = 69.748°.

d) What is the scattering vector q if measured with thermal neutrons?

The scattering vector q is independent of type of radiation and wave length, thus q = 5.795 $Å^{-1}$

e) Assume that the powder is crystallographically perfect and unstrained nanoparticles and the diffraction pattern I vs. 2θ is corrected for instrument broadening. The (311) peak measured at 16 keV has a width of 0.25°. What is the dimension of the nanoparticles?

The wavelength of the x-rays is 12.3984/16 = 0.7749 Å, and the scattering angle 2θ according to a) is 41.876°

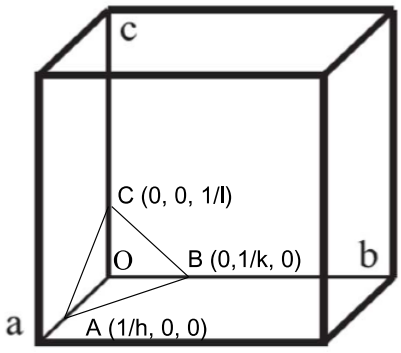
The Bragg-peak width in radians is 0.25 x π/180 = 0.004363 radians.

Using the Scherrer equation, we can determine the particle size τ:

τ = 1 x 0.7749/(0.004363 x cos(20.938°)) = 190 Å.

EXTRA EXERCISES TO PART I: CRYSTALLOGRAPHY

Exercise 5 : Family of crystal planes



We consider a family of plans {*hkl*} in a primitive cubic lattice structure of edge *a*, with the basis (O, **a**, **b**, **c**) as shown in the schematic. One of these planes is the one intercepting the points A, B and C on the schematic. To simplify the visualization, we consider without loss of generality that *h*, *k* and *l* are strictly positive integers (as in the schematic) that are co-prime. (greatest common divisor is 1)

5a. The plan defined by the points A, B and C is a lattice plane, with equation in the ortonormal basis:

$$\mathcal{P}_1^{(hkl)} = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, hx + ky + lz = a \right\}$$

(i) Is the plane parallel to $\mathcal{P}_1^{(hkl)}$ and passing through the lattice point defined as the origin O, a lattice plane ?

The origin O is a lattice point. $\mathcal{P}_1^{(hkl)}$ is a lattice plane, if we translate this plane along its normal until it intersects a lattice point again, e.g. the origin O, the environment of this point O will be identical to that of any lattice point $M \in \mathcal{P}_1^{(hkl)}$. As a consequence, the plane parallel to $\mathcal{P}_1^{(hkl)}$ and passing through the lattice point defined as the origin O must intersects additional lattice points, and is indeed a lattice plane.

(ii) Show that its equation is given by: $\mathcal{P}_0^{(hkl)} = \{(x, y, z) \in \mathbb{R}^3, hx + ky + lz = 0\}$

The plane is perpendicular to the direction [hkl]. Since the origin O belongs to the plane, we must find the set of points M$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ such that $\boldsymbol{OM.n_{(hkl)} = 0}$, $\boldsymbol{n_{(hkl)}} = \begin{pmatrix} ha \\ ka \\ la \end{pmatrix}$ being normal to the plan *(hkl)* in the cubic structure. Since $\boldsymbol{OM} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$, we can write:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} . \begin{pmatrix} ha \\ ka \\ la \end{pmatrix} = a(hx + ky + lz) = 0$$

So the equation in the orthonormal basis is: $hx + ky + lz = 0$

5b. In class, we calculated the distance between the origin (the plane $\mathcal{P}_0^{(hkl)}$) and $\mathcal{P}_1^{(hkl)}$, see week 4, slide 26. However, we didn't explicitly verify that there is no plane in the {*hkl*} family that is in between these two planes, i.e. that intercepts the axis **a**, **b** and **c** closer to the origin O at points A'($a/H,0,0$), B'($0,a/K,0$) and C' $0,0,a/L$) with (H,K,L) integers and $H \geq h, K \geq$

$k, L \geq l$. In other words, we translate $\mathcal{P}_0^{(hkl)}$ along its normal $[hkl]$, and see if we intercept a crystal plane of the $\{hkl\}$ family before $\mathcal{P}_1^{(hkl)}$:

(i) Show that one equation of this plan containing A', B' and C', is given by:

$$\mathcal{P}^{(HKL)} = \left\{(x, y, z) \in \mathbb{R}^3, hx + ky + lz = \frac{ah}{H}\right\}$$

Like above, we calculate the equation from the dot product $\boldsymbol{A'M.n_{(hkl)} = 0}$, $\boldsymbol{n_{(hkl)}} = \begin{pmatrix} h \\ k \\ l \end{pmatrix}$

$$\begin{pmatrix} x - a/H \\ y \\ z \end{pmatrix}.\begin{pmatrix} h \\ k \\ l \end{pmatrix} = hx - \frac{ah}{H} + ky + lz = 0 \text{ or } hx + ky + lz = \frac{ah}{H}$$

(ii) Since we supposed that $\mathcal{P}^{(HKL)}$ is a crystal plane, show that

$$\exists (n_1, n_2, n_3) \in \mathbb{N}^3, H \times (hn_1 + kn_2 + ln_3) = h$$

If $\mathcal{P}^{(HKL)}$ is a crystal plane, it includes lattice points. So necessarily, there exist relative integers (n_1, n_2, n_3) such that the point $\begin{pmatrix} n_1 a \\ n_2 a \\ n_3 a \end{pmatrix}$ verifies the plane equation. Hence: $hn_1 a + kn_2 a + ln_3 a = \frac{ah}{H}$ which we can rewrite: $H \times (hn_1 + kn_2 + ln_3) = h$

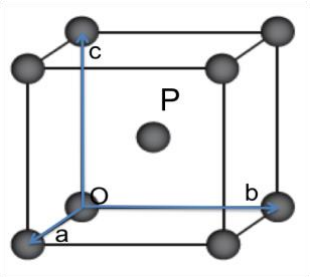
(iii) Conclude that necessarily, $H = h$ and so that $\mathcal{P}^{(HKL)} = \mathcal{P}_1^{(hkl)}$, and there is no $\{hkl\}$ plane between $\mathcal{P}_0^{(hkl)}$ and $\mathcal{P}_1^{(hkl)}$, so what we calculated in class was indeed the distance between two closest planes.

We see that H divides h, and hence since also we assumed $H \geq h$, necessarily $H=h$. We could do exactly the same reasoning for $K=k$ and $L=l$. As a result, $\mathcal{P}^{(HKL)} = \mathcal{P}_1^{(hkl)}$

So there is no crystal plane perpendicular to [hkl] between $\mathcal{P}_0^{(hkl)}$ and $\mathcal{P}_1^{(hkl)}$.

Exercise 6 : Primitive cell of the BCC structure

Consider the body centered-cubic unit cell shown to the right with the origin marked as O and the three orthogonal axis of length the cube edge a.



6a. Verify that the formula for the volume of the cell defined by the basis vectors, i.e. $V = \boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})$, gives $V = a^3$.

$$\vec{b} \times \vec{c} = a^2 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = a^2 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\vec{a}.(\vec{b} \times \vec{c}) = a^3 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = a^3 = V_{cell}^{conventional}$$

6b. In the basis (O, **a**, **b**, **c**), what are the coordinate of the point P at the center du cube ? Is this basis a Bravais lattice for the BCC cubic structure ?

The point P has for coordinates (1/2, 1/2, 1/2) in the basis (O, **a**, **b**, **c**). Thus this basis is not a Bravais lattice for the BCC cubic structure, as each lattice nodes should have 3 relative integers as coordinates.

6c. We consider the same origin O and define three new vectors **a'**, **b'** and **c'** such that :

$$\vec{a}' = \frac{1}{2}(-\vec{a} + \vec{b} + \vec{c})\,;\ \vec{b}' = \frac{1}{2}(\vec{a} - \vec{b} + \vec{c})\,;\ \vec{c}' = \frac{1}{2}(\vec{a} + \vec{b} - \vec{c})$$

(i) Express the vectors **a**, **b** and **c** as a function of **a'**, **b'** and **c'**.

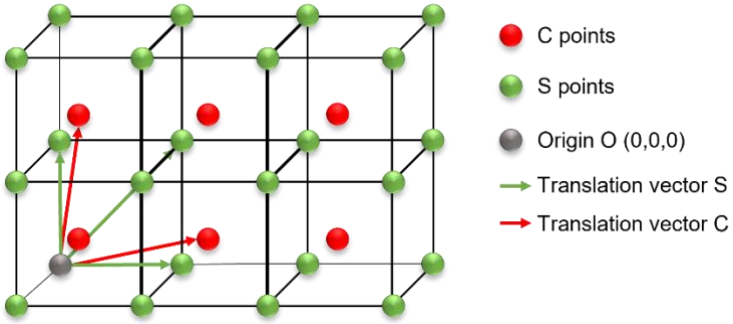
By adding the vectors two by two, it follows that:

$$\vec{a} = \overrightarrow{b'} + \overrightarrow{c'};\ \vec{b} = \overrightarrow{a'} + \overrightarrow{c'};\ \vec{c} = \overrightarrow{a'} + \overrightarrow{b'}$$

(ii) Show that for all point M of the BCC lattice, one can find relative integers n, p and q, such that:

$\overrightarrow{OM} = \frac{n}{2}\vec{a} + \frac{p}{2}\vec{b} + \frac{q}{2}\vec{c}$, with *(n,p,q)* either all even numbers, or all odd numbers.

Let's have a look at the schematic below:



In the basis (O, a, b, c), one can distinguish the points S located on the vertices of the cube, and the points C at the center of the cube. The points S are equivalent to the points of a simple cubic lattice. We can therefore find three integers N, P and Q such that $\overrightarrow{OS} = N\vec{a} + P\vec{b} + Q\vec{c}$. By setting $n = 2N, p = 2P$ and $q = 2Q$ (or equivalently $\frac{n}{2} = N$, $\frac{p}{2} = P$ and $\frac{q}{2} = Q$) we have the desired relation with the three integers n, p and q all even.

For a point C at the center of a cube, from the point S(N, P, Q) we have an additional translation of (½ , ½, ½). So this points can be defined as: $\overrightarrow{OC} = (N + \frac{1}{2})\vec{a} + (P + \frac{1}{2})\vec{b} + (Q + \frac{1}{2})\vec{c}$. By setting $n = 2N + 1, p = 2P + 1$ and $q = 2Q + 1$ we have the desired relation with the three integers n, p and q all odd. We therefore have for any point M of the lattice $\overrightarrow{OM} = \frac{n}{2}\vec{a} + \frac{p}{2}\vec{b} + \frac{q}{2}\vec{c}$ with (n, p, q) all even if M is on the vertex of a cube, and (n, p, q) all odd if M is at the center of a cube.

(iii) Using i), express the **OM** vector in the (O, **a'**, **b'**, **c'**) basis.

By replacing the expressions of **a**, **b** and **c** from i), we obtain that for all point M in the lattice:

$$\overrightarrow{OM} = \frac{p+q}{2}\overrightarrow{a'} + \frac{n+q}{2}\vec{b}' + \frac{n+p}{2}\vec{c}$$

(iv) Conclude that this basis is indeed a primitive basis for the BCC structure.

Knowing that the sum of two even numbers and the sum of two odd numbers are indeed even, the coefficients in front of the vectors **a'**, **b'** and **c'** are integers. Indeed:

1. If M is on the vertex of a cube, n, p and q are even, then the sum of two of them is also even and the three coefficients of the vector $\overrightarrow{OM}$ are integers.
2. If M is at the center of a cube, n, p and q are odd and the sum of two of them is even, which leads again to integer coefficients for the vector $\overrightarrow{OM}$.

This means that $\forall M$, you can find three integers n', p' and q' which satisfy:

$$\overrightarrow{OM} = n'\overrightarrow{a'} + p'\vec{b}' + q'\vec{c}$$

The basis (O, **a'**, **b'**, **c'**) is therefore a primitive basis for the centered cubic Bravais lattice. The volume formed by these three vectors constitutes the smallest volume that can be translated along these vectors to fill all the space. It is called the primitive cell, which has a single atom per cell. It is however more convenient to consider the conventional lattice as we do, with two atoms per lattice and the orthogonal vectors a, b and c, because it reproduces the cubic symmetry of the structures. Directions and reticular planes are also easier to manipulate and visualized.

6d. Using the same formula as in 6a, and the expression found in of the primitive lattice vectors given in 6c, calculate the volume occupy by the BCC primitive cell.

From 6c we calculate the coordinate of the different vectors:

$$\overrightarrow{a'} = \frac{a}{2}\begin{pmatrix}-1\\1\\1\end{pmatrix}, \overrightarrow{b'} = \frac{a}{2}\begin{pmatrix}1\\-1\\1\end{pmatrix}, \overrightarrow{c'} = \frac{a}{2}\begin{pmatrix}1\\1\\-1\end{pmatrix}$$

Then from 6a:

$$\overrightarrow{b'} \times \overrightarrow{c'} = \frac{a^2}{4}\begin{pmatrix}1\\-1\\1\end{pmatrix} \times \begin{pmatrix}1\\1\\-1\end{pmatrix} = \frac{a^2}{4}\begin{pmatrix}0\\2\\2\end{pmatrix}$$

$$\overrightarrow{a'}.\left(\overrightarrow{b'} \times \overrightarrow{c'}\right) = \frac{a^3}{8}\begin{pmatrix}-1\\1\\1\end{pmatrix}.\begin{pmatrix}0\\2\\2\end{pmatrix} = \frac{a^3}{2} = V_{cell}^{primitive}$$

(Note that it is important to do this calculation in the orthonormal basis.)

6e. How many motifs do the conventional and primitive cell contain ? Justify your answer relating to the respective volume of these two cells.

The density of the material must stay constant, which implies:

$$\rho = \frac{N_{atoms}^{primitive} \times m_{atoms}}{V_{cell}^{primitive}} = \frac{N_{atoms}^{conventional} \times m_{atoms}}{V_{cell}^{conventional}}$$

By comparing 5a and 5d, we can see that: $V_{cell}^{primitive} = 2 \times V_{cell}^{conventional}$. Thus it follows that:

$$\frac{N_{atoms}^{primitive}}{V_{cell}^{primitive}} = \frac{N_{atoms}^{conventional}}{2 \times V_{cell}^{primitive}}$$

Finally, a primitive cell must contain only one atom, so $N_{atoms}^{primitive} = 1$, and:

$$N_{atoms}^{conventional} = 2$$

Thus, the conventional BCC cell has two motifs per unit cell.

6f. Following the same approach, demonstrate that the Bravais Lattice for the face-centered cubic lattice is:

$$\vec{a}' = \frac{1}{2}(\vec{b} + \vec{c})\,;\, \vec{b}' = \frac{1}{2}(\vec{a} + \vec{c})\,;\, \vec{c}' = \frac{1}{2}(\vec{a} + \vec{b})$$

Let's proceed as with the BCC lattice. For the FCC lattice, the relationship between **a**, **b** and **c** vectors and **a'**, **b'** and **c'** can be found by adding the vector from the new basis:

1. By adding **b'** and **c'**:

$$\vec{b}' + \vec{c}' = \vec{a} + \frac{1}{2}(\vec{b} + \vec{c}) = \vec{a} + \vec{a}' \text{ so } \vec{a} = \vec{b}' + \vec{c}' - \vec{a}'$$

2. Similarly:

$$\vec{b} = \vec{a}' + \vec{c}' - \vec{b}'$$

$$\vec{c} = \vec{a}' + \vec{b}' - \vec{c}'$$

In the basis (O, **a**, **b**, **c**), we can distinguish the points S located at the vertices of a cube, and the point P at the center of the faces.

The points S are equivalent to the points of a simple cubic lattice. We can therefore find three relative integers N, P and Q such that $\overrightarrow{OS} = N\vec{a} + P\vec{b} + Q\vec{c}$. By setting $n = 2N, p = 2P$ and $q = 2Q$, we have the desired relation with the three integers n, p and q all even.

A point C at the center of a face is obtained from a point located on a vertex by a translation (1/2,1/2,0) or (1/2,0,1/2) or (0,1/2,1/2) or (1/2, 1/2, 1) or (1/2, 1, 1/2) or (1, 1/2, 1/2). In the first case, we can therefore find three relative integers N, P and Q such that : $\overrightarrow{OC} = (N + \frac{1}{2})\vec{a} + (P + \frac{1}{2})\vec{b} + Q\vec{c}$. By setting $n = 2N + 1, p = 2P + 1$ and $q = 2Q$, we have the desired relation with the odd integers n, p. In the other cases we will have in the same way n, q odd or p, q odd. Note if the third coordinate was 1 instead of 0, we would have: $\overrightarrow{OC} = \left(N + \frac{1}{2}\right)\vec{a} + \left(P + \frac{1}{2}\right)\vec{b} + (Q + 1)\vec{c}$ and the conclusions would be identical as $Q + 1$ is also an integer, and $q = 2(Q + 1)$ must be even.

We therefore have for any point M of the lattice $\overrightarrow{OM} = \frac{n}{2}\vec{a} + \frac{p}{2}\vec{b} + \frac{q}{2}\vec{c}$ with (n, p, q) all even if M is on the vertex of a cube, and (n,p,q) with two odd numbers if M is at the center of a face.

By replacing the expressions of **a**, **b** and **c**, we immediately obtain that for any point M of the network:

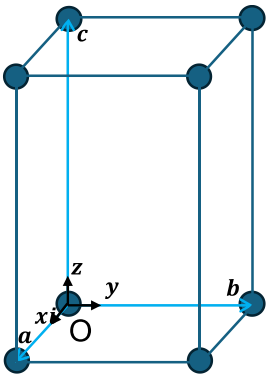
$$\overrightarrow{OM} = \frac{p + q - n}{2}\vec{a'} + \frac{n + q - p}{2}\vec{b'} + \frac{n + p - q}{2}\vec{c'}$$

Since the sum (or difference) of three even numbers or of two odd numbers and one even number is always even, the above coefficients are integers. Indeed: if M is on the vertex of a cube, n, p and q are even, their sum (or difference) is therefore also even and the three coefficients of the vector **OM** are relative integers.

If M is at the center of a face, two of the coefficients n, p and q are odd, so their sum (or difference) is even, which again gives integer coefficients for **OM**.
For all M, we have therefore found relative integers n', p' and q' which satisfy:

$$\overrightarrow{OM} = n'\overrightarrow{a'} + p'\overrightarrow{b'} + q'\overrightarrow{c'}$$

The basis (O, **a'**, **b'**, **c'**) is therefore indeed a primitive basis for the face-centered cubic Bravais lattice.



Exercise 7: Rotation and mirror symmetry

We consider the tetragonal primitive structure as shown to the right (as we have seen in exercise 2 of week 5). We represent 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:

$\boldsymbol{a} = a\boldsymbol{x}$, $\boldsymbol{b} = a\boldsymbol{y}, \boldsymbol{c} = c\boldsymbol{z}$, and $a \neq c$.

7a.

(i) What is the new vector $\boldsymbol{c}' = \mathcal{R}_{\left(\boldsymbol{b},\frac{\pi}{2}\right)}(\boldsymbol{c})$ under a rotation around the axis **b** and of angle $\frac{\pi}{2}$?

$\boldsymbol{c}$ becomes a vector along the axis $\boldsymbol{x}$ of norm $||\boldsymbol{c}|| = c$. So $\boldsymbol{c}' = c\boldsymbol{x} = \frac{c}{a}\boldsymbol{a}$.

(ii) Find a condition on a and c so that $\boldsymbol{c}'$ belongs to the Bravais Lattice.

We must have:

$$\frac{c}{a} = p \in \mathbb{N}$$

Or $c = pa$ with $p = 1, 2, 3 \ldots$

7b.

(i) What angle of rotation around the **b** axis leaves the lattice invariant ?

- If $c = a$, a rotation of $\frac{\pi}{2}$ leaves the crystal invariant.
- If $c \neq a$, a rotation of π is needed
- If $c = pa$, $p \in \mathbb{N}$ and $p > 1$, a rotation of π is also needed. Indeed, for a $\frac{\pi}{2}$ rotation, the vector $\boldsymbol{a}$ would not be on a Bravais lattice point since $R(\boldsymbol{a}) = -\frac{\boldsymbol{c}}{p}\boldsymbol{z}$ so the tip of the rotated vector would be along the **c** axis but not on a Bravais lattice point.

(ii) How about around the **c** axis?

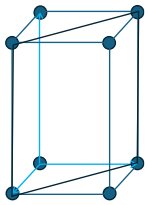
Around the **c** axis, we find the symmetry of the cube, so a rotation of $\frac{\pi}{2}$.

7c.

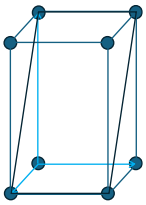
(i) Is the plane (110) a plane of symmetry for the tetragonal structure?

As discussed in class, the plane (110) is a plane of symmetry for the tetragonal structure. Every mirror symmetry of a Bravais lattice point is another Bravais lattice point.

(110)



(101)



(ii) How about the plane (101) ?

The plane (101) is not a plane of symmetry (unless $c = a$). If we represent the mirror symmetry operation in the plane defined by vectors **a** and **c**, we see that the image of the lattice point is not a lattice point.