MSE-238
Structure of Materials

Week 4 – crystallography III

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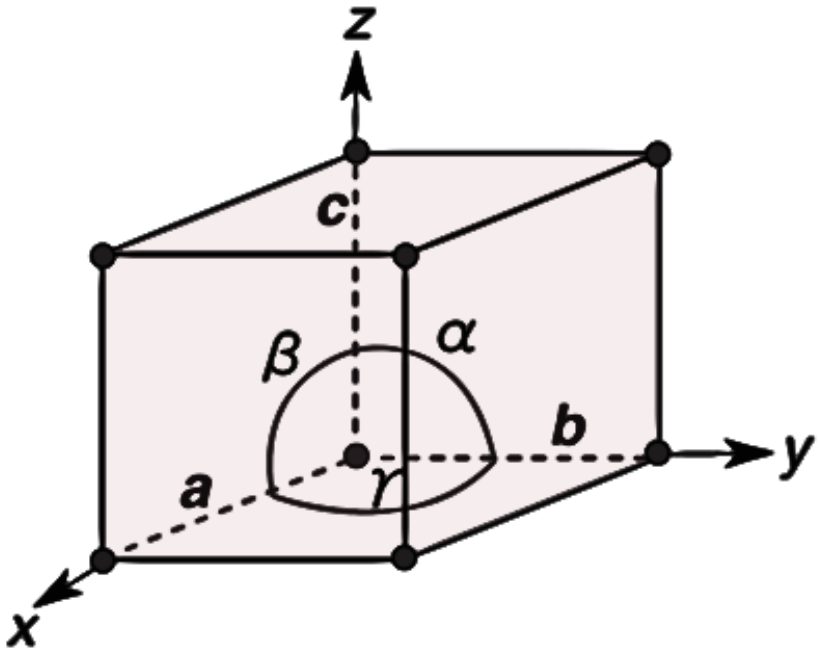
Overview

- mathematical description of the crystalline lattice
- Miller indices
- Crystal directions and family of directions
- Reminder on Basics of Euclidian Geometry
- Crystal planes and Miller indices
- Zone axis
- Hexagonal system: the Miller-Bravais indices

  - →Hammond Chapter 5

Geometry of the unit cell

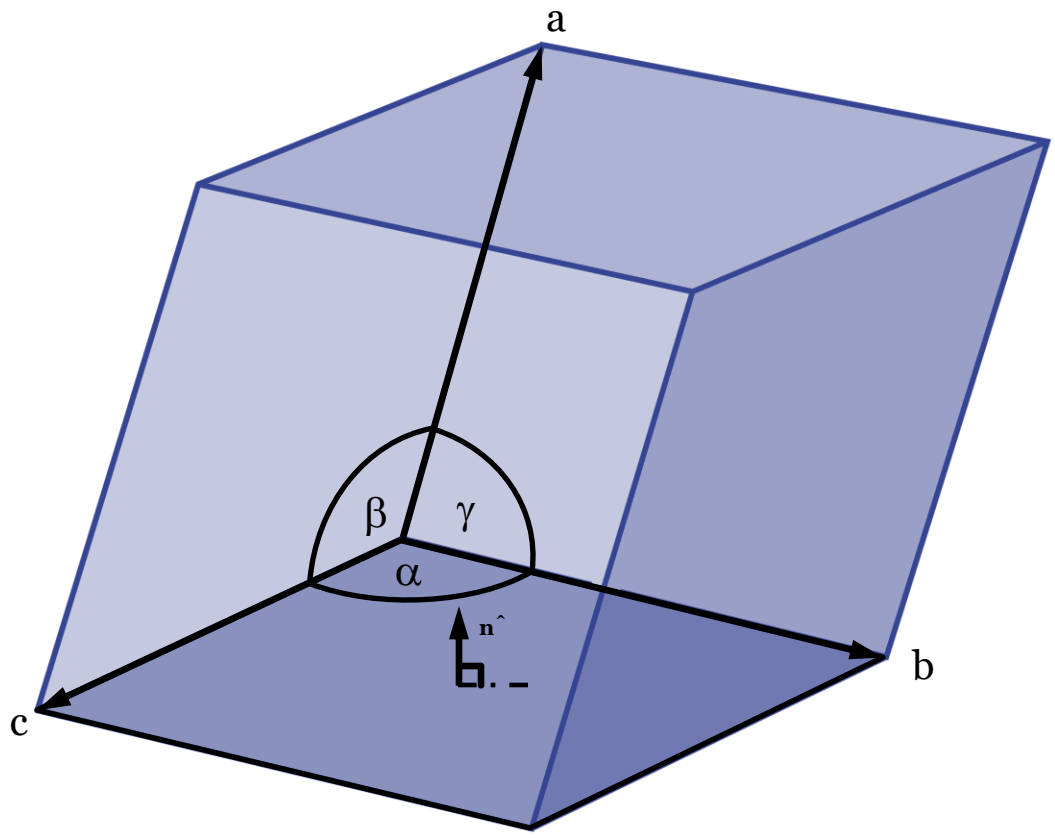


right-handed set of crystallographic axes, x,y,z which point along the edges of the unit cell.
The origin of our coordinate system coincides with one of the lattice points

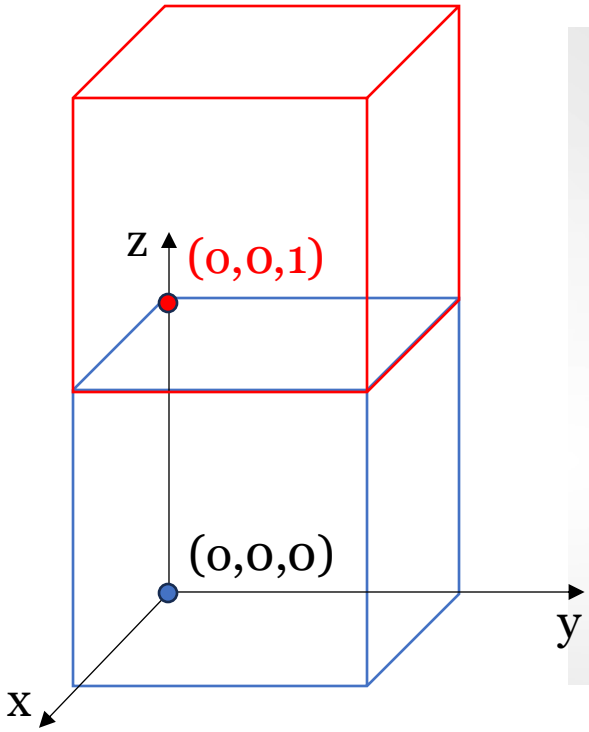
The length of the unit cell along the x,y and z direction are defined as a,b, and c. The angles between the crystallographic axis are defind by
α = the angle between b and c
β = the angle between a and c
γ = the angle between a and b

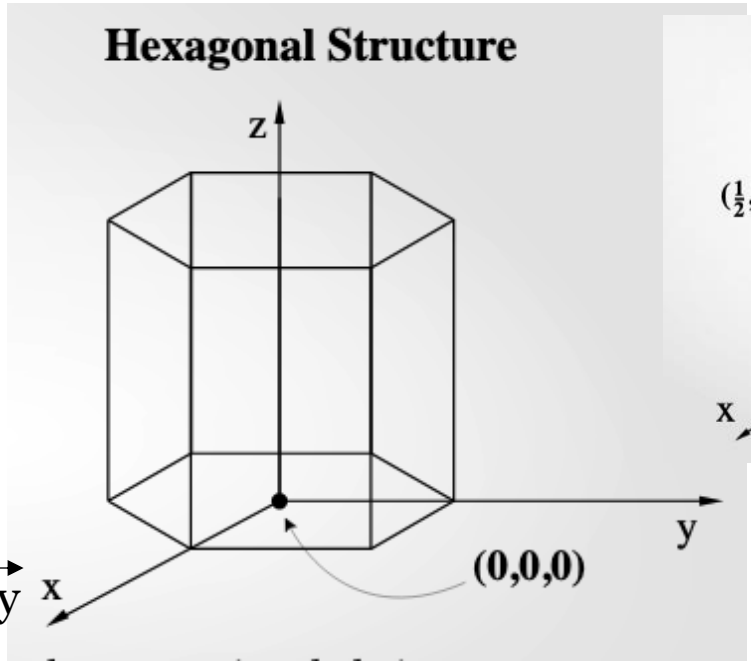
a, b, c, α, β, γ are collectively known as the **lattice parameters** (often also called 'unit cell parameters', or just 'cell parameters').

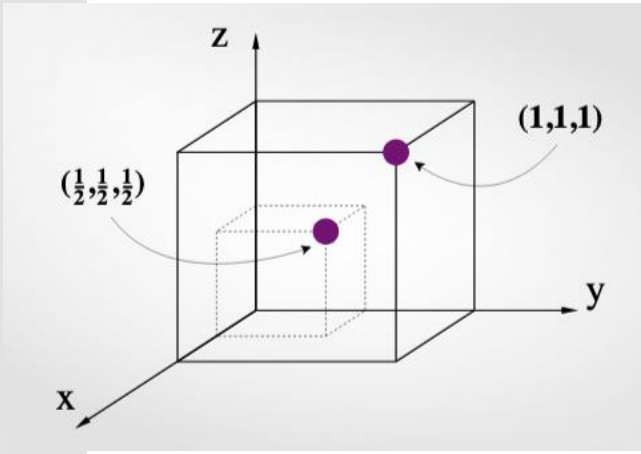
→ Miller indices are a coordinate system!
→ it depends on the unit cell structure, and with that on the crystal system


a
β
γ
α
n^
c
b

Origin and scale







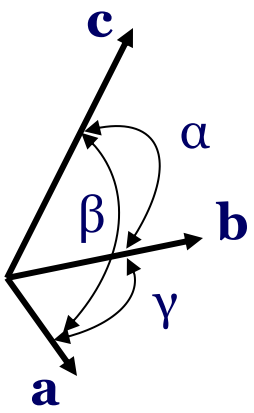
- Origin (0,0,0) can be defined anywhere in the crystal (on any lattice point)
  In most cases the back left corner of the crystal is the conventional choice
  exception: hexagonal structure
- Scale: is the size of the unit cell, if 0 is the origin of the unit cell, 1 will be the origin for the next unit cell
- the x,y, z axes may NOT be perpendicular to each other, that depends on the crystal system! for hexagonal $\gamma = 120°$

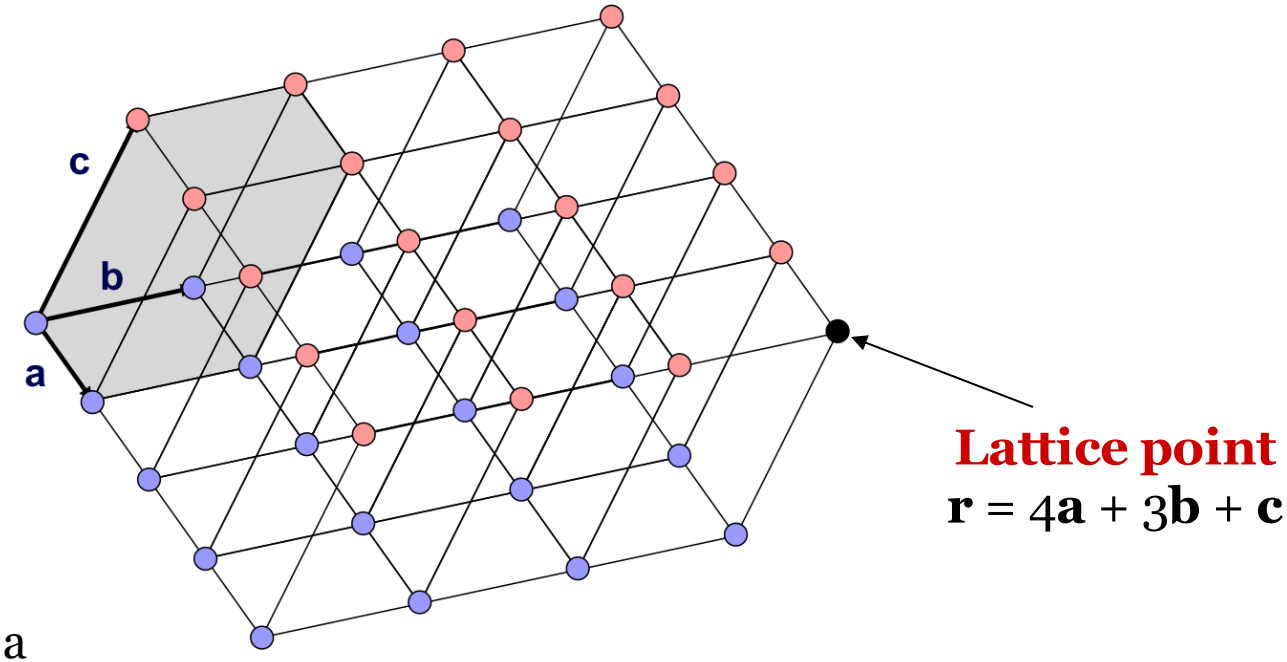
Crystalline material

- in 3D: Bravais Lattice

The Bravais lattice is expressed mathematically as an infinite set of points with translational symmetry along three axis that form a vector basis. Choosing an origin O, one can write

$$\mathcal{B} = \{P, \boldsymbol{OP} = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}, (n_1, n_2\ n_3) \in \mathbb{Z}^3\}$$

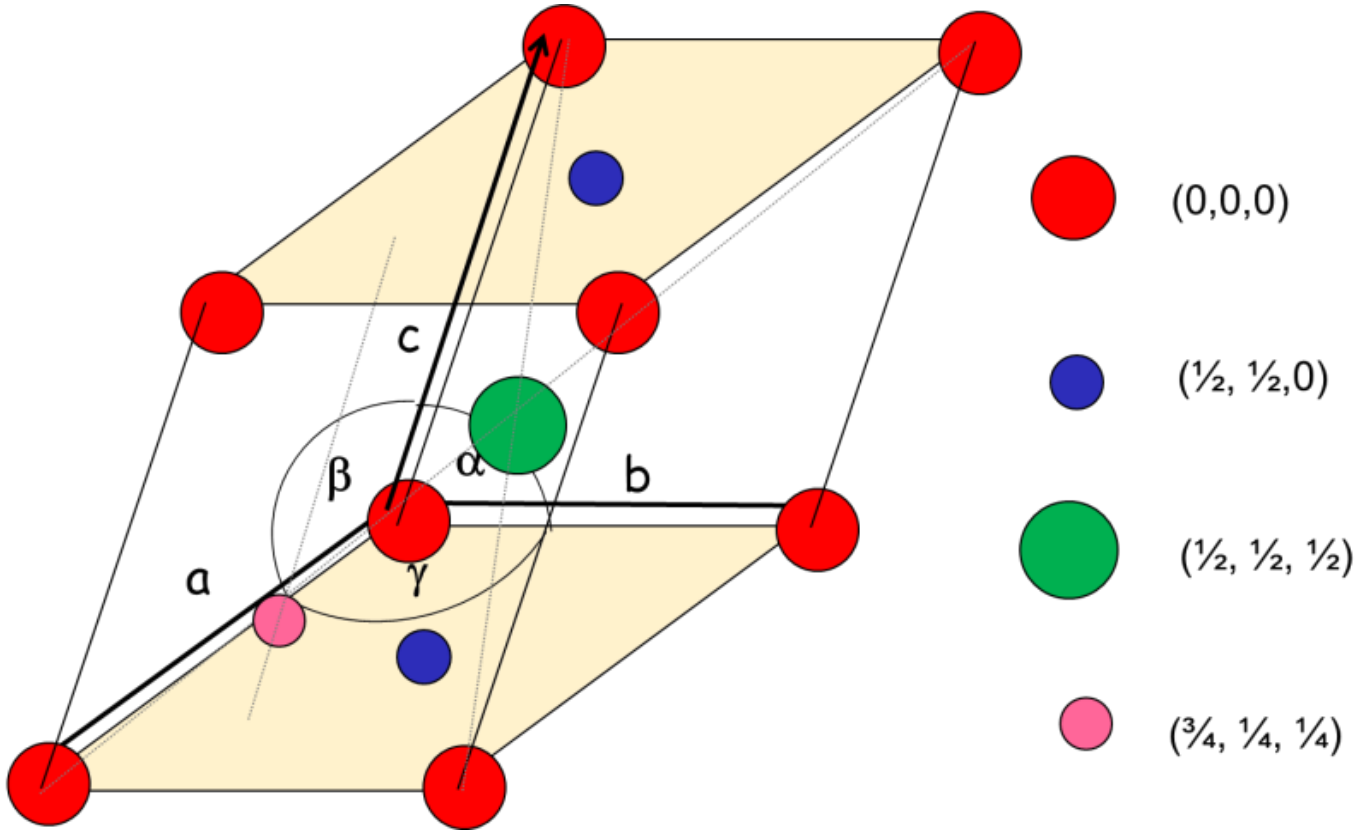




set of 3 vectors form the basis: every lattice point is a linear combination with relative integers as coefficients

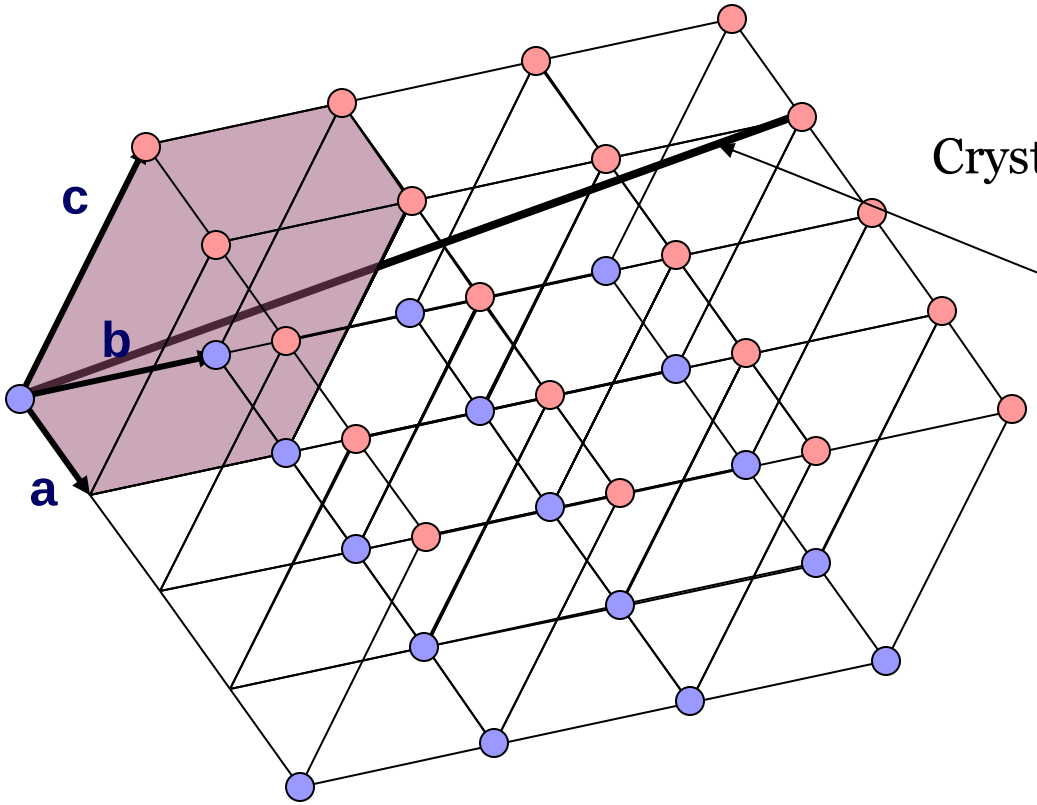
Lattice points

- Lattice points and positions of atoms are given by the coordinates in the coordinate system.
- Example:



Crystal directions

- Crystal directions are lines that pass through at least two lattice points.
- The direction can be defined by an origin (all lattice point can be an origin) and the coordinate of the other point in the lattice basis.
- The coordinates, which are relative integers, represent the Miller indices.

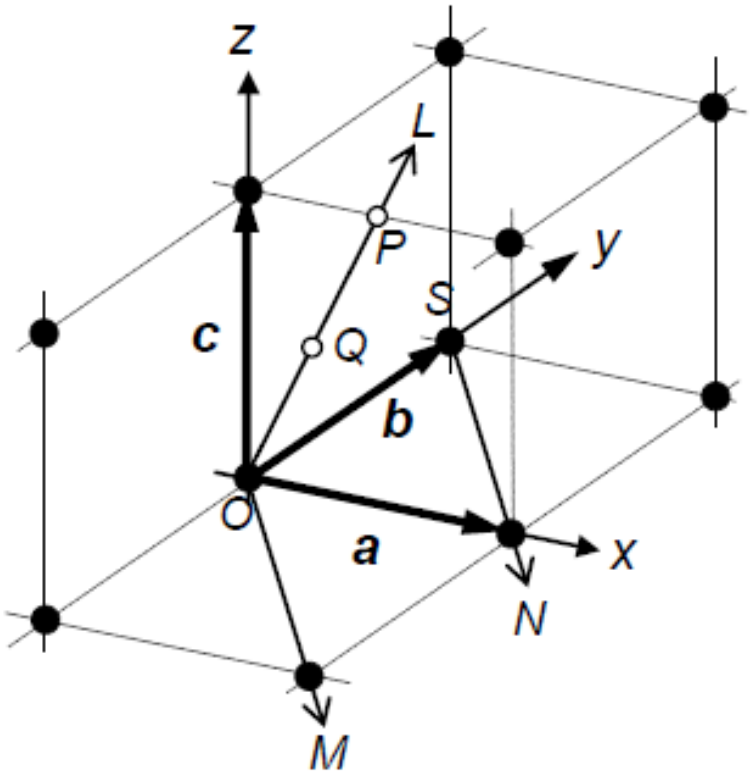


Crystal Direction : $\mathbf{r} = \lambda(1\mathbf{a} + 3\mathbf{b} + 1\mathbf{c})$

[1 3 1]

if they are not integers, multiply by common denominator to get the Miller index

Crystal directions



direction OP and OQ

Coordinates point P: ½, 0,1
vector **OP** = ½ **a** + **c** or [1/2 0 1]

Coordinates point Q: ¼ ,0, ½
vector **OQ** = ¼ **a** + ½ **c** or [1/4 0 ½]

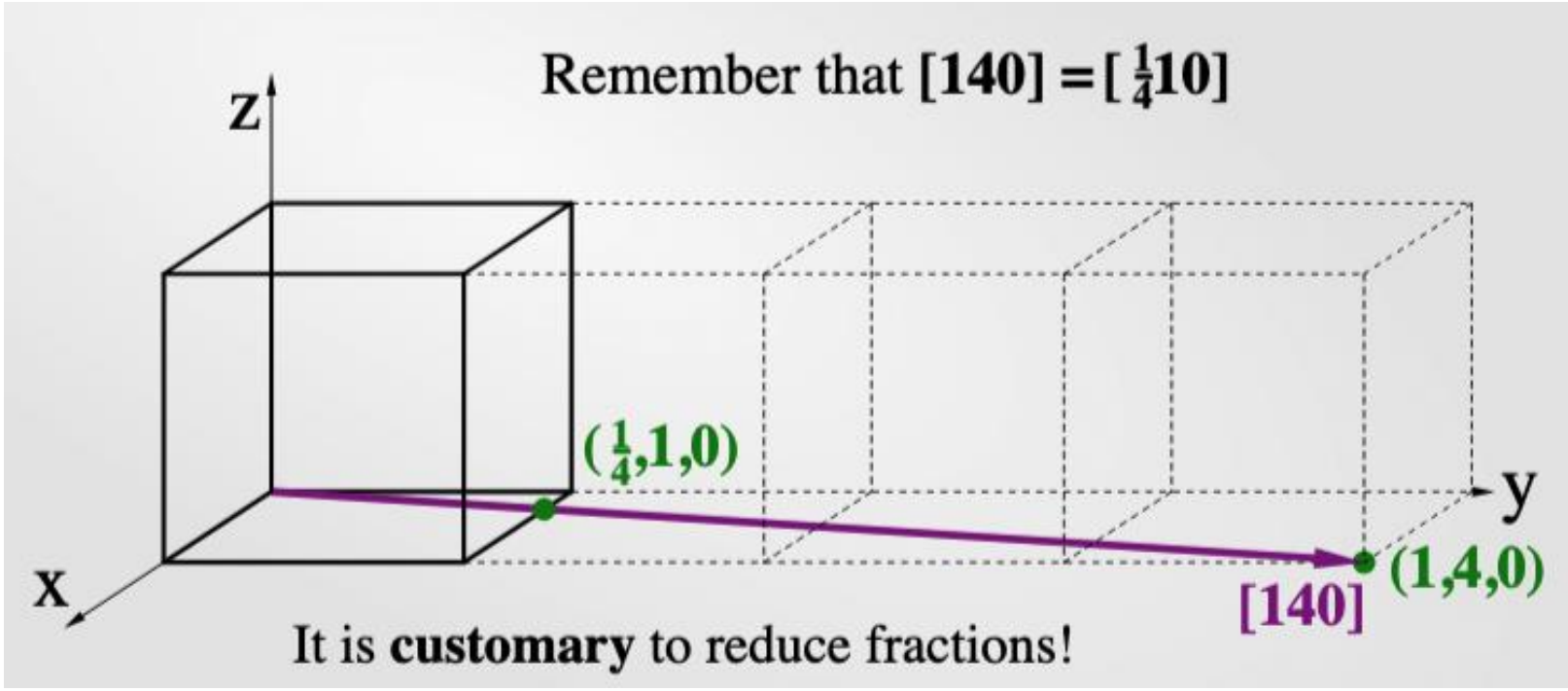
Both vectors define the direction OP = OQ = OL
Directions are expressed with whole numbers:
[102] direction

direction SN
consider OM which is parallel to SN
Coordinates M: 1,-1,0
vector **OM** = **a**-**b**
direction SN and OM [$1\bar{1}0$] : when the number is negative a bar is added above the number

direction of basics lattice vectors **a**, **b**, **c**
[100], [010] and [001]

Crystal directions

to indicate directions, one reduces fractions



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Crystal directions

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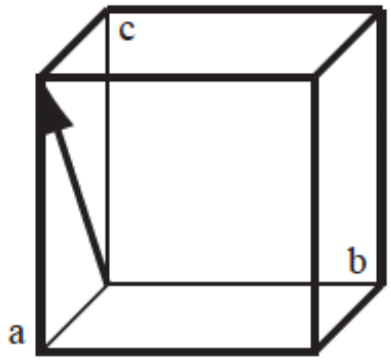
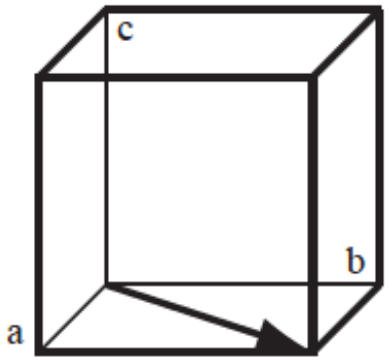
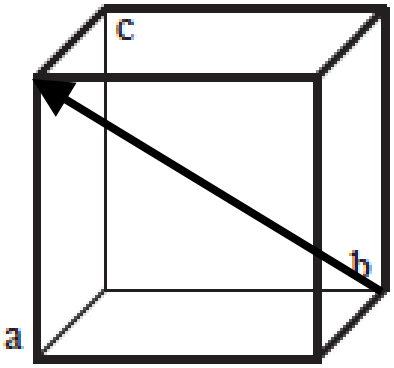


[101]

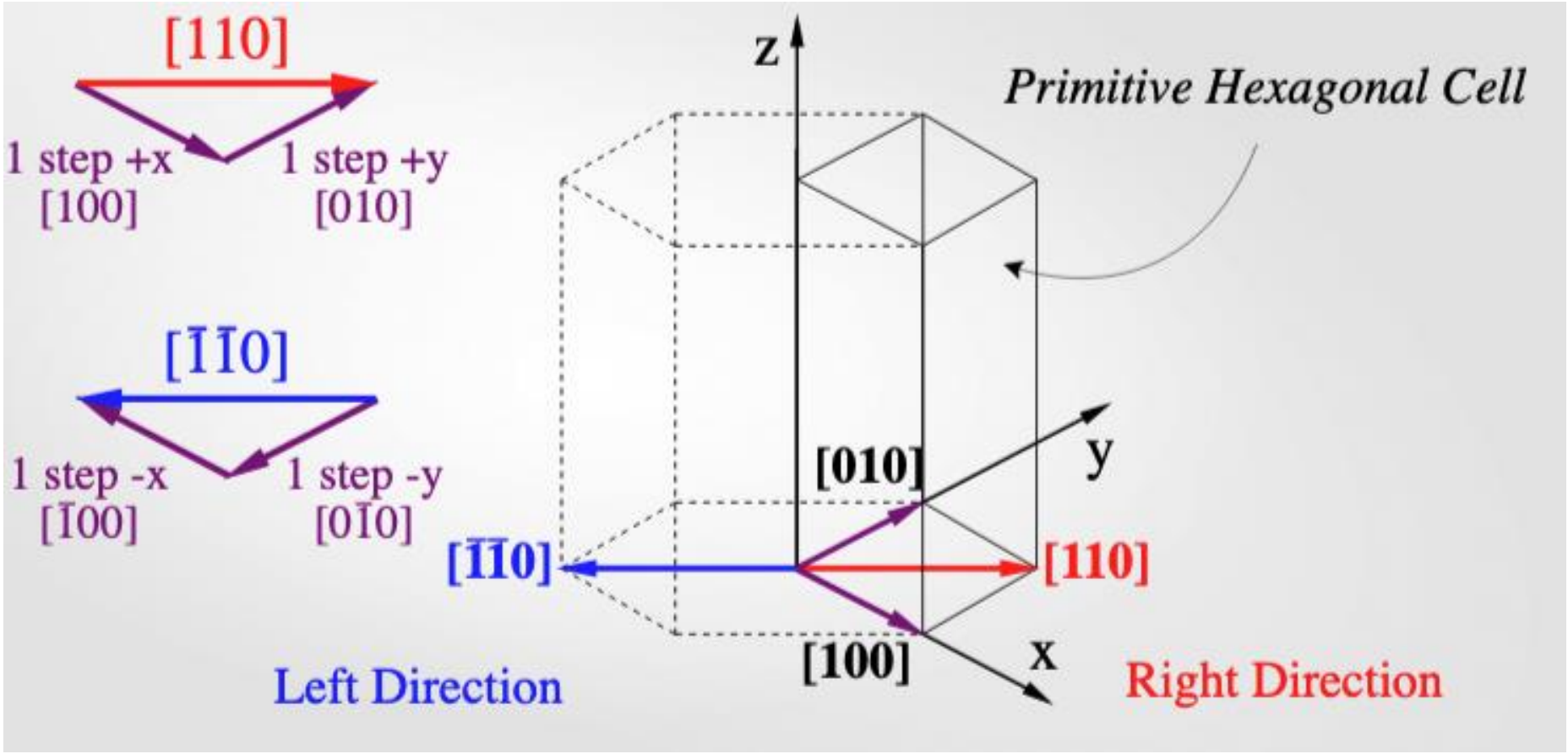


[110]



$[1\bar{1}1]$

Directions in hexagonal crystal



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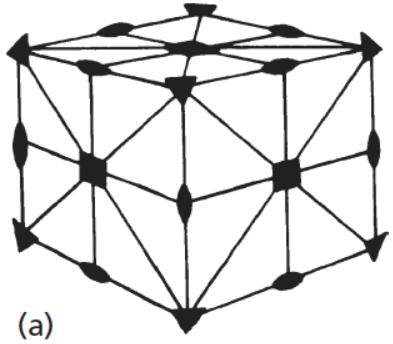
A family of directions

Depending on the **symmetry** of the crystal system different directions are equivalent


(a)

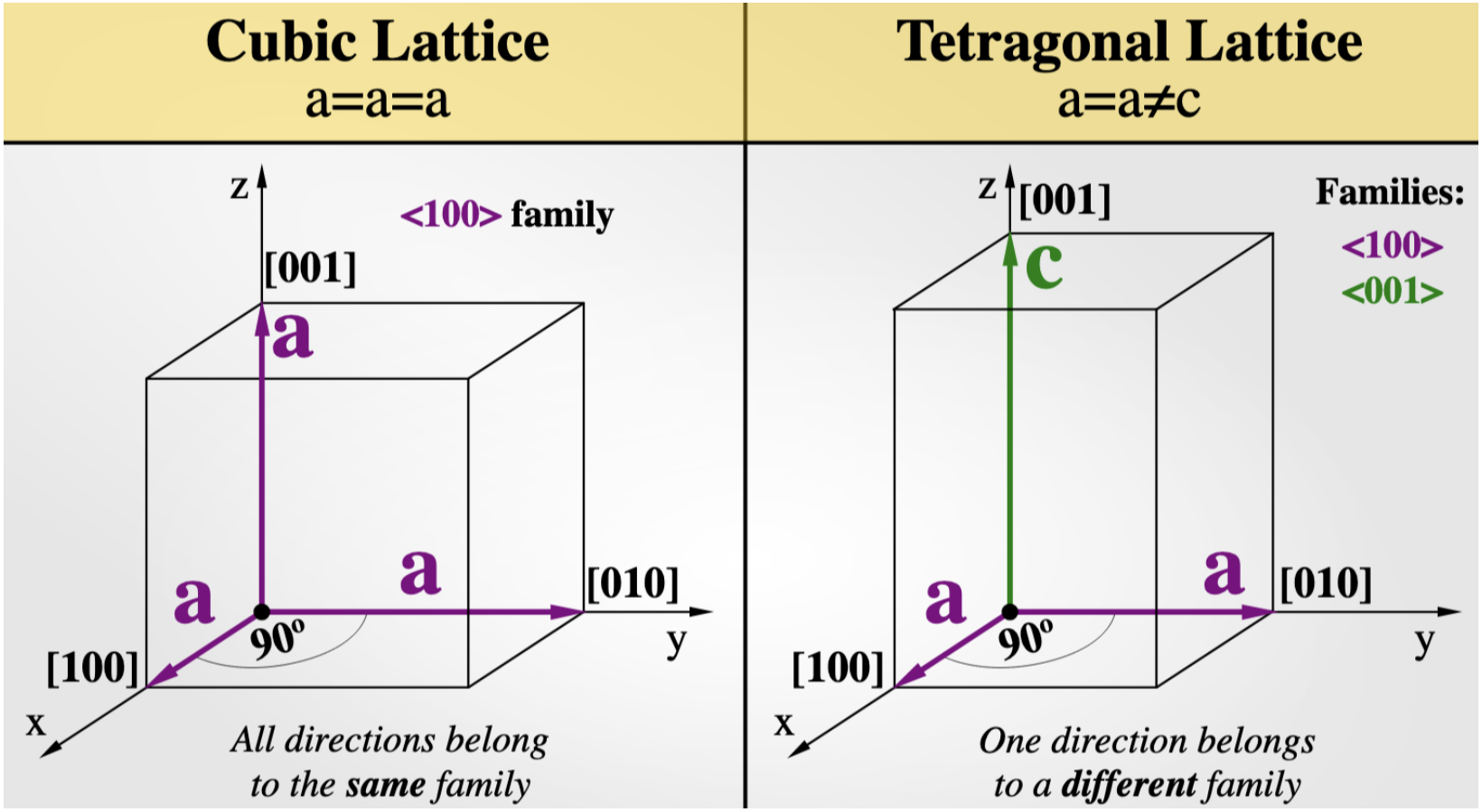
For cubic crystals, the directions [1 0 0], [$\bar{1}$ 0 0], [0 1 0], [0 $\bar{1}$ 0], [0 0 1], [0 0 $\bar{1}$] are all equivalent by symmetry.

There is a special notation for directions of the same form: <100>, which in this case means the family made of the three basis axis **a**,**b**,**c**
the number of equivalent directions is called the **multiplicity** of the direction

the **direction** depends on the choice of origin and orientation of the axis, but the properties along a **family of directions** will be the same, by the symmetry of the crystal

what is the multiplicity of : <111> in the cubic system?

Family of directions: depending on crystal system



Reminder: Basics of Euclidian Geometry

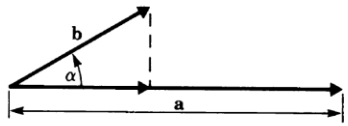
- If we define an origin (0,0,0), all vectors are generated by the linear combination of (1,0,0), (0,1,0) and (0,0,1), that in engineering are often referred to as $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$.
- A vector $\boldsymbol{a}$ is then a linear combination: $\exists (a_x, a_y, a_z) \in \mathbb{R}^3$: $\boldsymbol{a} = a_x \boldsymbol{i} + a_y \boldsymbol{j} + a_z \boldsymbol{k}$
- The following notation will be used: $\boldsymbol{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$
- Reminders:
  - The magnitude (or norm) of a vector: $\|\boldsymbol{a}\| = \sqrt{{a_x}^2 + {a_y}^2 + {a_z}^2}$
  - The **scalar (or dot) product**: In cartesian coordinates, for two vectors in the **orthonormal basis** $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$, we have:

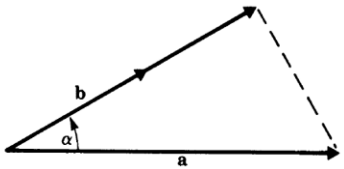
$$\boldsymbol{a} \cdot \boldsymbol{b} = a_x b_x + a_y b_y + a_z b_z$$

  - The dot product brings forward the notions of length and angle and orthogonality. A geometric definition for two vectors that form an angle α is:

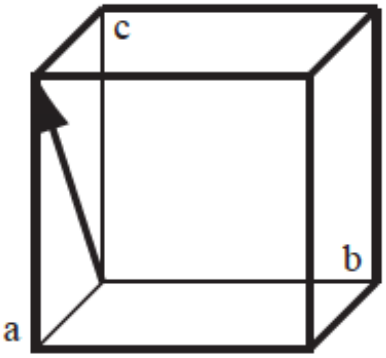
$$\boldsymbol{a} \cdot \boldsymbol{b} = ab \cos \alpha$$

  - With $a = \|\boldsymbol{a}\|$ and $b = \|\boldsymbol{b}\|$. It is the projection of $\boldsymbol{a}$ on $\boldsymbol{b}$, or of $\boldsymbol{b}$ on $\boldsymbol{a}$.
  - If $\boldsymbol{a}$ and $\boldsymbol{b}$ are orthogonal, then $\boldsymbol{a}.\boldsymbol{b} = 0$.

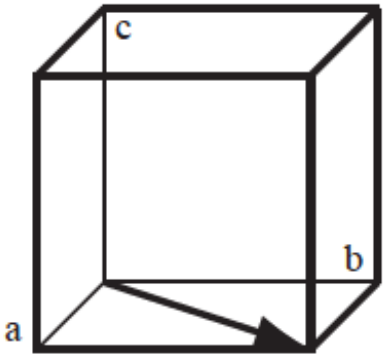




cubic lattice: angle between directions



[101]



[110]

angle between direction [110] and [101]

$\boldsymbol{a} \cdot \boldsymbol{b} = a_x b_x + a_y b_y + a_z b_z$ $\qquad$ $\boldsymbol{a} \cdot \boldsymbol{b} = ab\cos\alpha$

$(1,1,0) \cdot (1,0,1) = 1 \cdot 1 + 1 \cdot 0 + 0 \cdot 1 = 1$

magnitudes $\qquad a = \sqrt{1^2 + 1^2 + 0^2} = \sqrt{2}$

$b = \sqrt{1^2 + 0^2 + 1^2} = \sqrt{2}$

$1 = 2\cos\alpha \quad \rightarrow \alpha = 60°$

Reminder: Basics of Euclidian Geometry

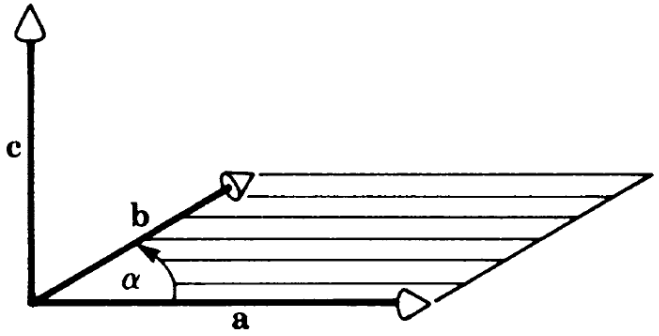
Cross product

- The cross product of two vectors forming an angle α is a vector perpendicular to these vectors, with the magnitude:
- $\|\boldsymbol{a} \times \boldsymbol{b}\| = ab\sin\alpha$

- In an orthonormal basis ($\boldsymbol{i},\boldsymbol{j},\boldsymbol{k}$), the Cross product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is:

$$\boldsymbol{a} \times \boldsymbol{b} = (a_y b_z - a_z b_y)\boldsymbol{i} + (a_z b_x - a_x b_z)\boldsymbol{j} + (a_x b_y - a_y b_x)\boldsymbol{k}$$

- $\boldsymbol{a} \times \boldsymbol{b} = -\boldsymbol{b} \times \boldsymbol{a}$
- Two vectors parallel have a zero cross product.



- Calculation methods:
  - Determinant:

$$\boldsymbol{a} \times \boldsymbol{b} = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ a_x & a_y & a_z \\ b_x & b_y & b_z \end{vmatrix}$$

  - Practical way: :

$$\begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} \times \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} \times \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} \boldsymbol{i} - \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} \times \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} \boldsymbol{j} + \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} \times \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} \boldsymbol{k}$$

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Reminder: Line in 3D

- A line is defined by 2 points $A = \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix}$ and B $= \begin{pmatrix} x_B \\ y_B \\ z_B \end{pmatrix}$ or a point A and a direction $\boldsymbol{AB} = \begin{pmatrix} x_B - x_A \\ y_B - y_A \\ z_B - z_A \end{pmatrix}$:
- This can be expressed in two ways:
  - Parametric equation: $D = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \; \exists \lambda \in \mathbb{R} \; \boldsymbol{AM} = \lambda \boldsymbol{AB} \right\}$
  - which we can write:

$$\begin{cases} x = x_a + \lambda(x_B - x_A) \\ y = y_a + \lambda(y_B - y_A) \\ z = z_a + \lambda(z_B - z_A) \end{cases}$$

  - A set of linear equations: $D = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \; with \; \begin{matrix} a_1 x + b_1 y + c_1 z - d_1 = 0 \\ a_2 x + b_2 y + c_2 z - d_2 = 0 \end{matrix} \right\}$

→ line as intersect of two planes

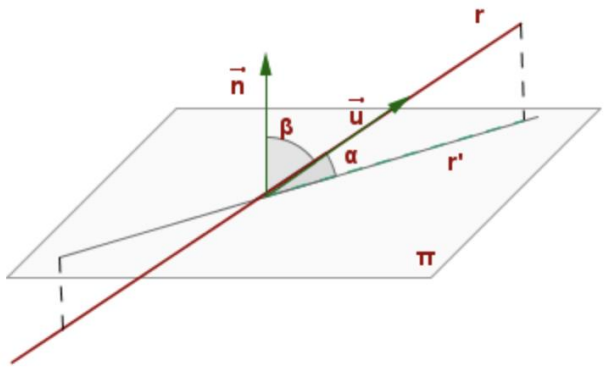
Reminder: plane in 3D

- A plane is defined by 3 points $A = \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix}$, B $= \begin{pmatrix} x_B \\ y_B \\ z_B \end{pmatrix}$ and C $= \begin{pmatrix} x_C \\ y_C \\ z_C \end{pmatrix}$ or a point A and a normal $\boldsymbol{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$
- This can be expressed in a simple way as: $P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \boldsymbol{AM}.\boldsymbol{n} = 0 \right\}$
- One can extract the linear equation: for $(a, b, c, d) \in \mathbb{R}^4, P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, ax + by + cz - d = 0 \right\}$

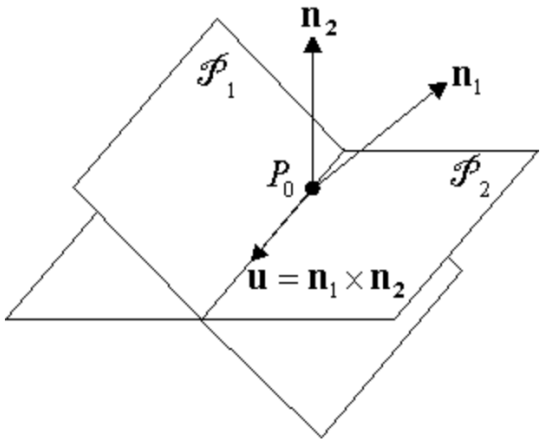
Reminder: Basics of Eucledian Geometry

- **Angles**
  - The angle between two vectors can be calcluated from the dot or the scalar products.

- Angle between a line and a plane:
Complementary of the angle between the line direction and the normal of the plan

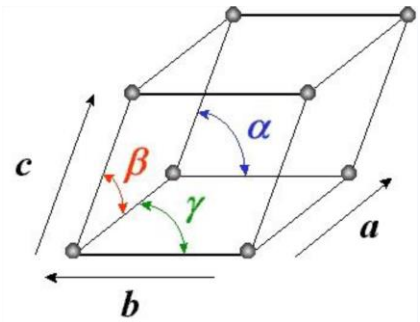


- Angle between two planes:
Angle between their normals:



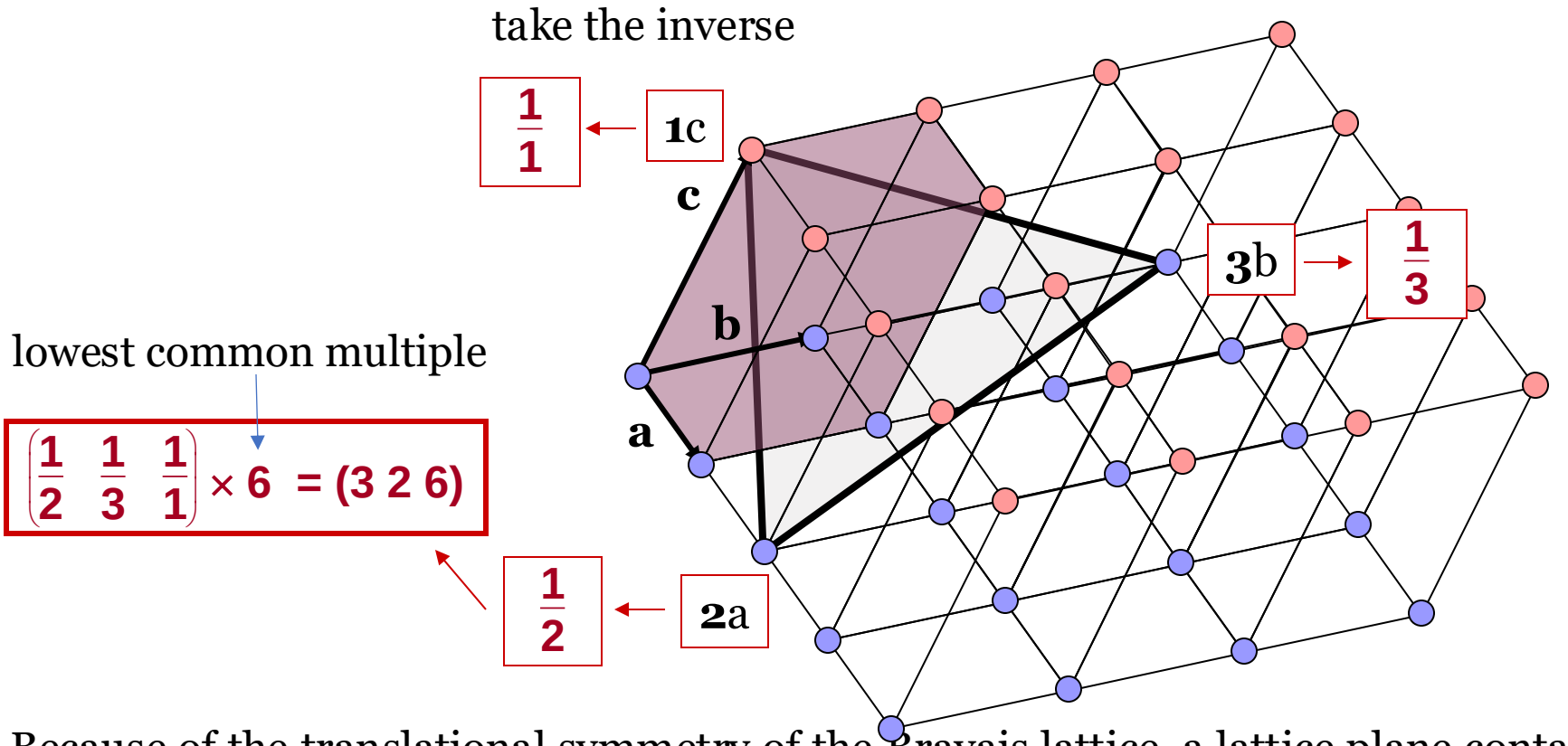
- **Volume**

$$V = (\vec{a}, \vec{b}, \vec{c}) = \vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})$$



Crystal planes

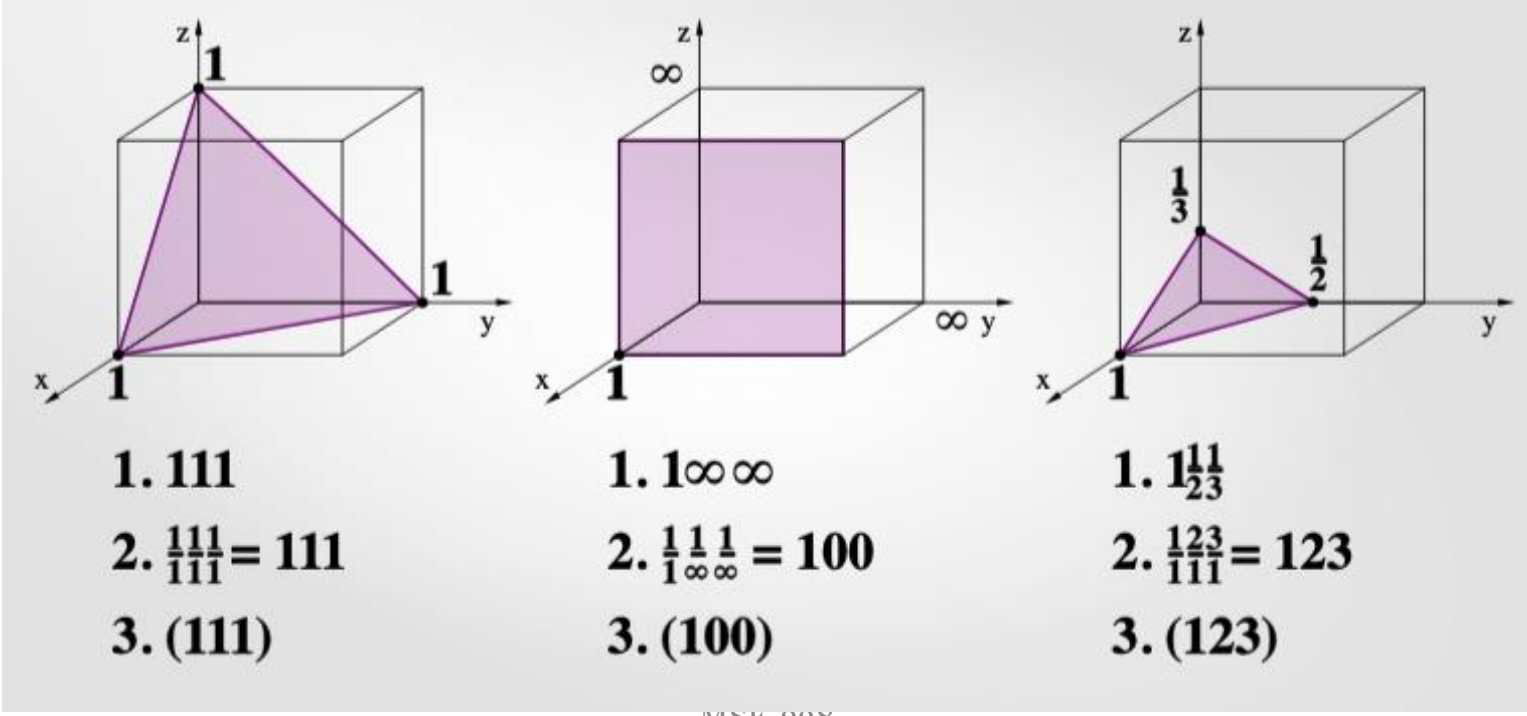
- Crystal or lattice planes are planes that pass through at least 3 lattice points.
- They can be defined by the intercept of the plane with the basis axis:



- Because of the translational symmetry of the Bravais lattice, a lattice plane contains an infinite number of lattice points

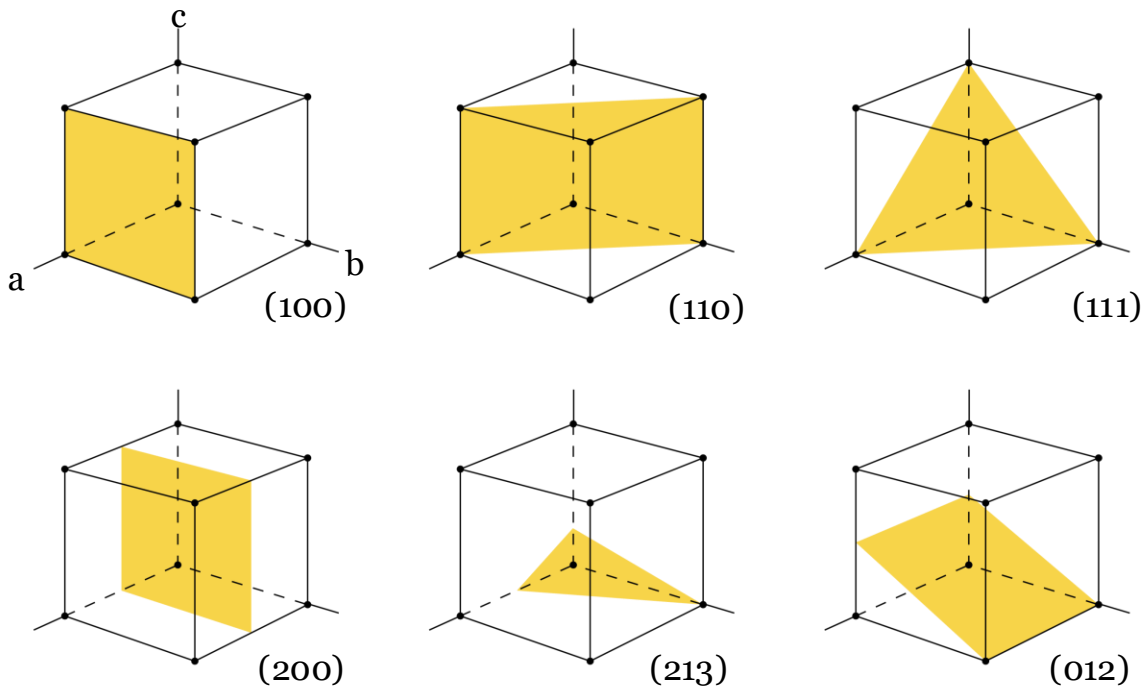
How to find Miller indices for planes

1. Find the point where the plane intersects each axis. If the plane never intersects an axis because it is parallel to that axis, the intersection point is ∞. If the plane goes to the origin, you have to look at a plane parallel to it (or change the origin)
2. Take the inverse of each intersection point,
3. Put those 3 values in the proper (hkl) format. Miller indices are integers with no common factors

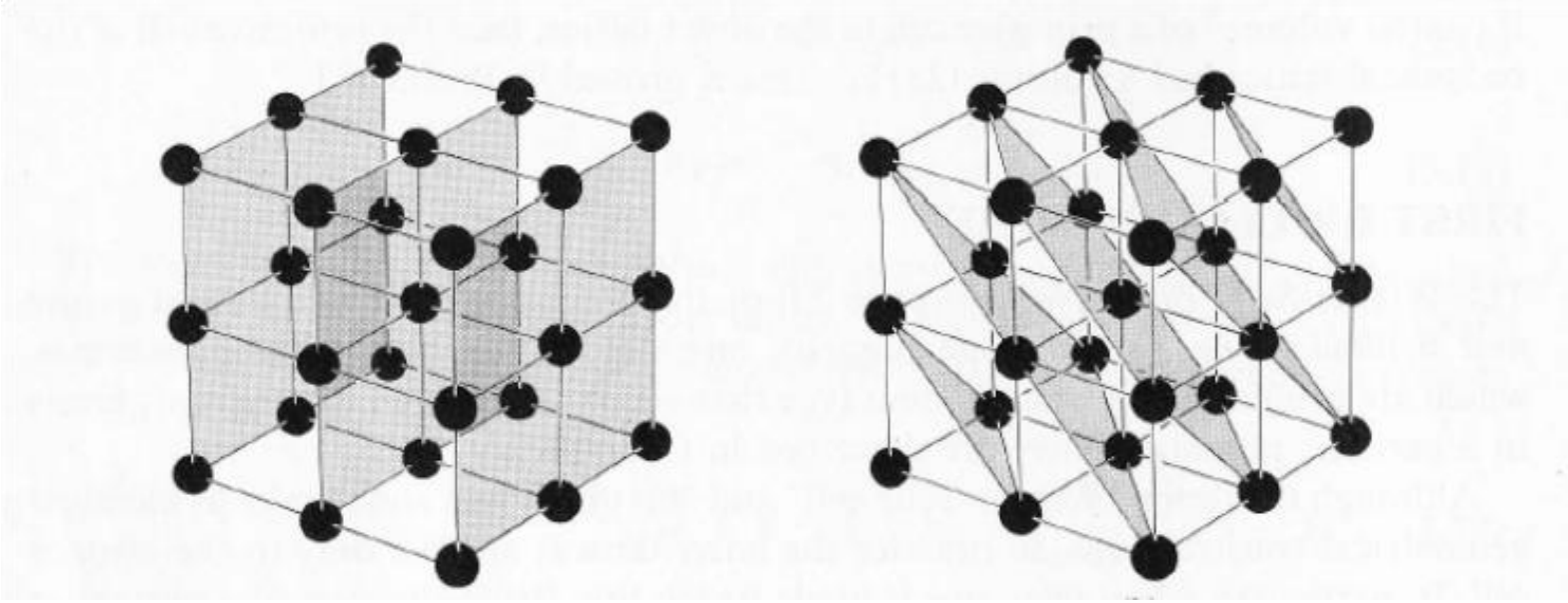


Crystal planes and Miller indices

- Find the intercepts of the crystal plane on the crystal axes in units of their respective lattice constants a, b, and c
- Take the reciprocals of these numbers and then reduce these to the smallest three integers that have the same ratio. The result (hkl) are the Miller indices of that plane

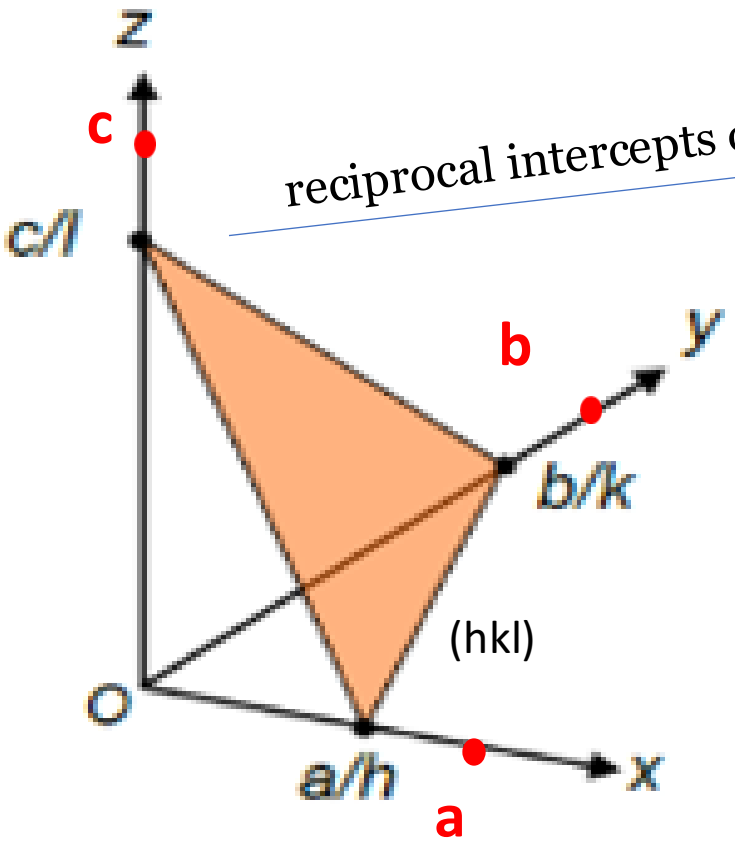


Lattice/crystal planes



We consider not just one plane but the crystal/lattice planes is a set of parallel equally spaced lattice planes which together contain all the points of the Bravais lattice. Such families play an important role in X-ray diffraction as we will see later. In the example above all planes on the left hand side picture belong to one family, all planes on the right hand side to another family

Miller indices of lattice planes



reciprocal intercepts of the plane

coordinates as a fraction of the unit vector along the axis x,y,z

$$\rightarrow \frac{h}{a}x+\frac{k}{b}y+\frac{l}{c}z=1$$

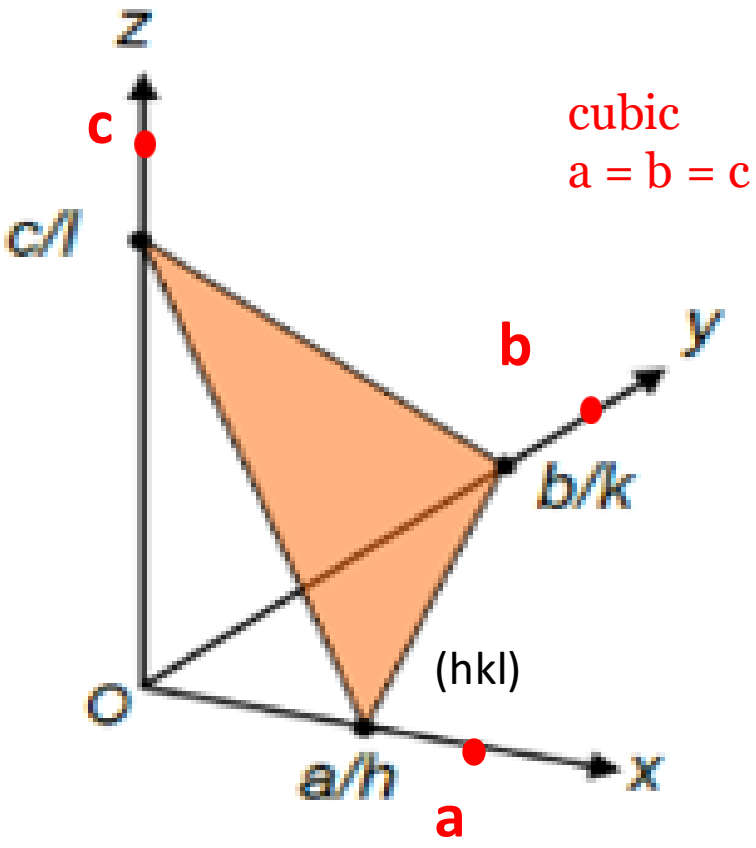
lattice plane is characterized by its Miller indices (hkl)

any other plane parallel to it can be written as

$$\frac{h}{a}x+\frac{k}{b}y+\frac{l}{c}z=C$$

where C is a constant

Miller indices of lattice planes in cubic system



For a **cubic lattice** where a=b=c (orthonormal basis), this simplifies to

$hx+ky+lz=Ca$

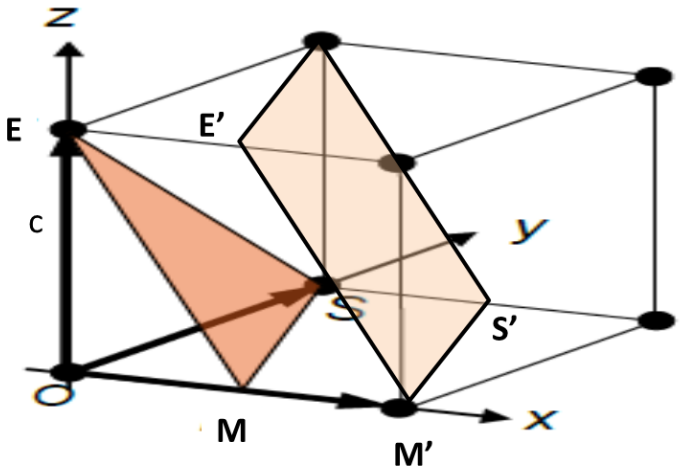
one can also express this as in the orthonormal basis $\mathcal{B}(O, \boldsymbol{x}, \boldsymbol{y}, \boldsymbol{z})$**,** the equation of an (hkl) plane that intercepts the axis at points $A\left(\frac{a}{h}, 0,0\right); B\left(0, \frac{a}{k}, 0\right); C\left(0,0, \frac{a}{l}\right)$ where a is the edge of the cube, is given by:

$$\mathcal{P}^{(hkl)} = \{(x, y, z) \in \mathbb{R}^3 / h\,x + ky + lz = a\}$$

and any other plane parallel to it as

$$\mathcal{P}_n^{(hkl)} = \{(x, y, z) \in \mathbb{R}^3 / hx + ky + lz = na\}$$

Miller indices of planes



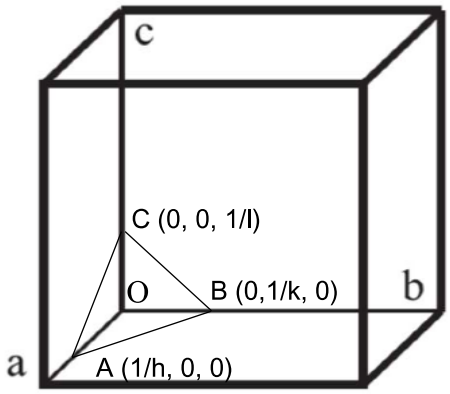
The intersects of plane EMS: ½, 1, 1,
Inverse of the intercepts: 2,1,1,

so the Miller index is (211)

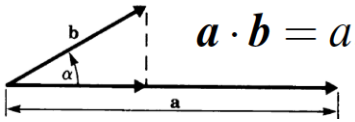
obtained by considering E'M'S'
Intersects: 1,2,2
Inverse of intersects: 1, ½,½
which expressed as whole numbers give the same Miller indices (211)

The Miller indices h,k,l must be integer values and they must be co-prime, meaning they have no common factor other than 1

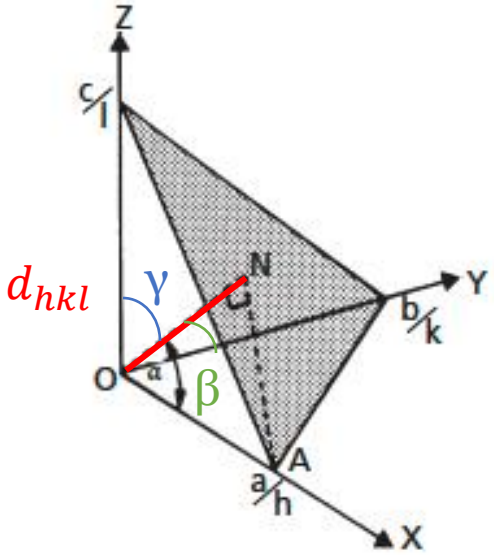
Distance between crystal planes



- The plane parallel to the plane (ABC) and passing through the origin O is a crystal plane belonging to the family of planes $\{hkl\}$.
- Assuming that the distance between two (hkl) planes is the same for all consecutive planes, this distance is given by ***ON,*** which is the projection of the vector ***OA*** on the normal to the plane
- $ON = d_{(hkl)} = \boldsymbol{OA} \cdot \boldsymbol{n_{hkl}}$



$\boldsymbol{a} \cdot \boldsymbol{b} = ab\cos\alpha$



$$\text{OA}\cos\alpha = \text{ON} \quad \text{or} \quad (a/h)\cos\alpha = d_{hkl} \quad \text{or} \quad \cos\alpha = \left(\frac{h}{a}\right) d_{hkl}.$$

$$\cos\beta = \left(\frac{k}{b}\right) d_{hkl} \quad \text{and} \quad \cos\gamma = \left(\frac{l}{c}\right) d_{hkl}.$$

For orthogonal axes $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$ (Pythagoras' theorem),

$$\left(\frac{h}{a}\right)^2 d_{hkl}^2 + \left(\frac{k}{b}\right)^2 d_{hkl}^2 + \left(\frac{l}{c}\right)^2 d_{hkl}^2 = 1.$$

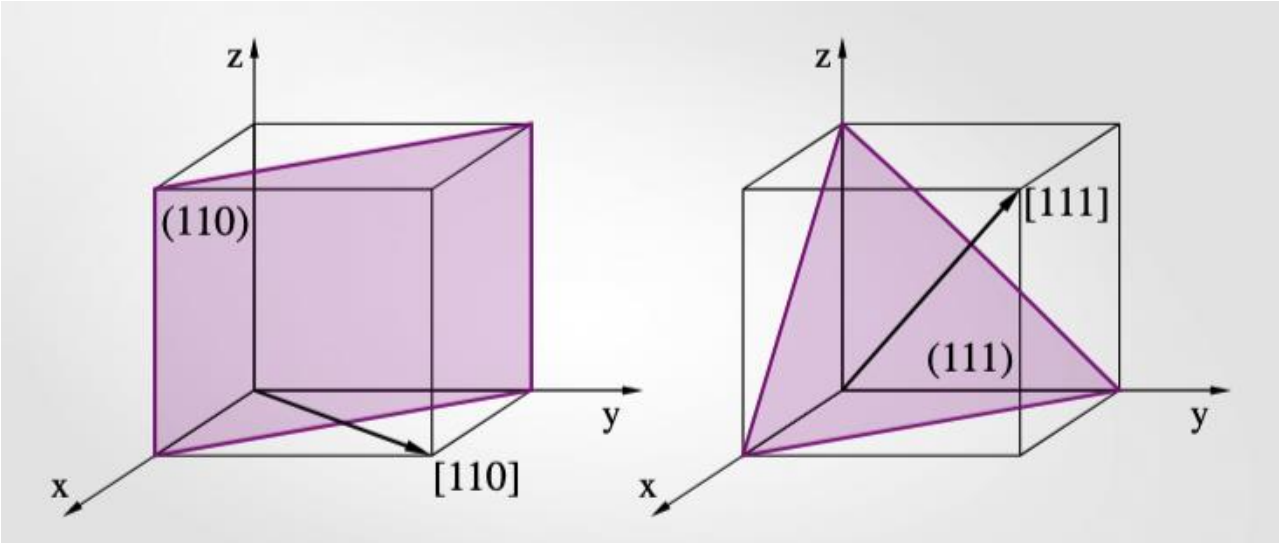
For a cubic crystal $a = b = c$, $\dfrac{1}{d_{hkl}^2} = \dfrac{h^2 + k^2 + l^2}{a^2}$. $d_{(hkl)} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

•The distance between crystal planes $d_{(hkl)}$ is very important in crystallography and X-ray diffraction.

$n\lambda = 2d_{hkl}\sin\theta$ Bragg law

Cubic system

For the **cubic system**, crystal directions [hkl] are perpendicular to the crystal planes (hkl).



$a = b = c$
$\alpha = \beta = \gamma = 90^o$

This is only true when (hkl) and [hkl] are defined in the orthonormal basis!

Miller indices of planes

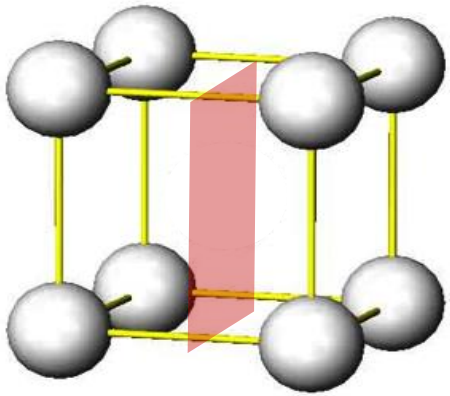
- Familiy of planes, not just the ones which are parallel but equivalent by the symmetry of the lattice

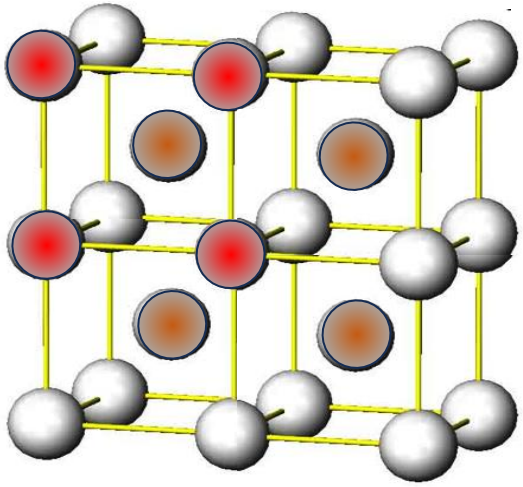
  {hkℓ}

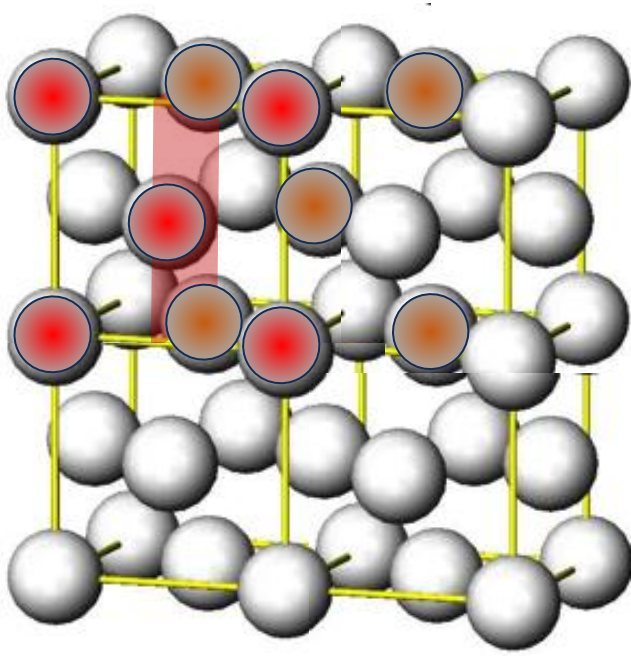
- Same as for the family of direction, the **multiplicity depends on the symmetry** of the crystal system

- cubic crystal system the (110) and (011) planes belong to the same {110} set of planes.
- tetragonal crystal system the (110) and (011) are not equivalent and belong to different sets {110} and {011}

Lattice/Crystal planes and Miller indices





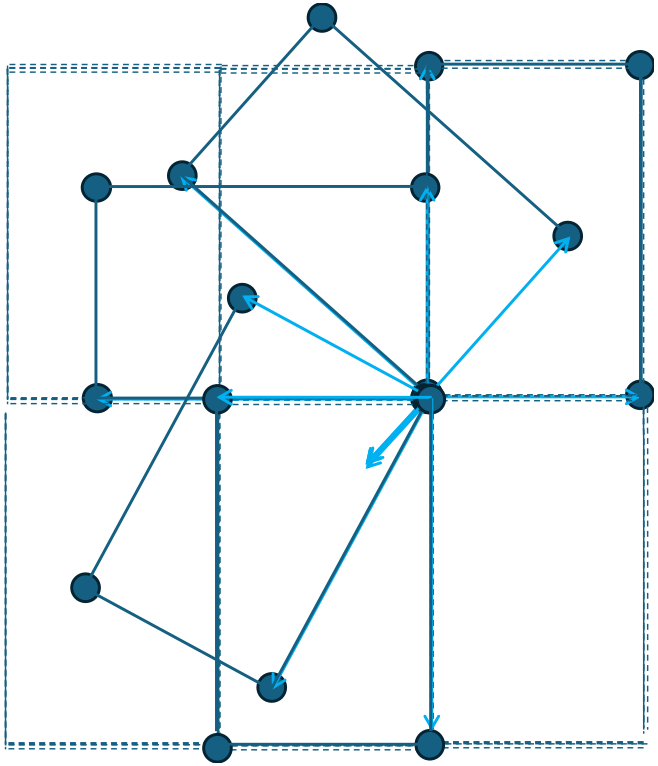


- The Miller indices provide a way to identify a plane, but this plane does not have to be a lattice or crytal plane.
- So for the (020) plane: it is not a crystal plane for the primitive cubic, but it is one for the BCC and FCC

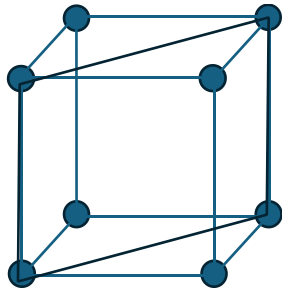
  → note that 0,2,0 are not co-prime, one can divide by 2! This rule holds for primitive unit cells
- Note that the configuration of atoms in the {100} and the {200} lattice planes, in the BCC and FCC structures, is the same ! These belong to the same family of planes.
- The position of an atom in a motif does not always coincide with a Bravais lattice point

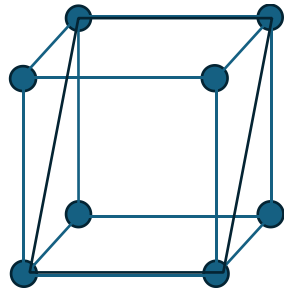
Miller indices and lattice planes

Leaving the cubic structure, as we reduce the symmetry of the crystal structure, we change the rotational symmetry we have shown before



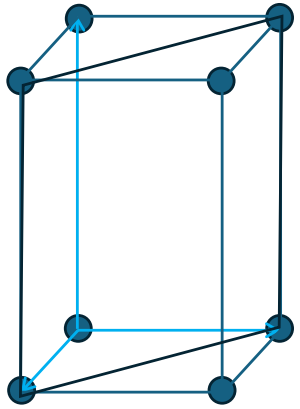
Cubic Primitive:

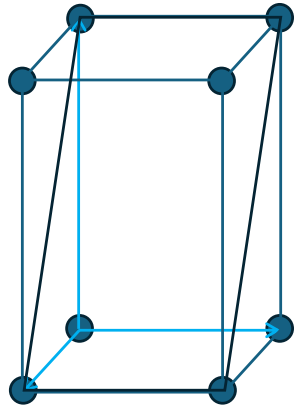




- Family of planes of symmetry {110}
- Same atom configuration and same symmetry

Tetragonal Primitive:





- Different atom configuration and different symmetry.

- Family of planes and directions differ as the symmetry of the Bravais lattice changes.

Zone axis, intersection of planes

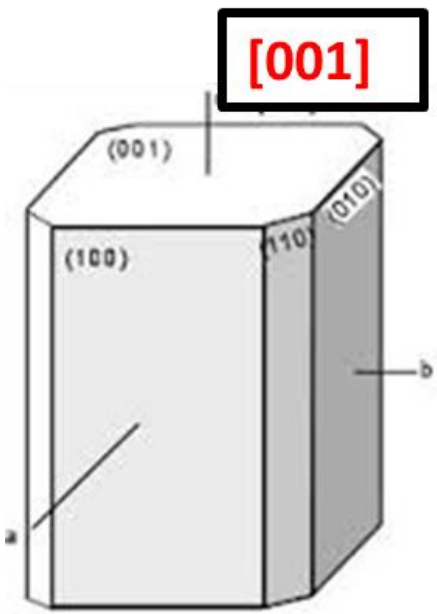
- a zone is defined as a set of faces or planes in a crystal whose intersections are all parallel
- the common direction of the intersection is called the **zone axis**, all directions in crystals are zone axes

the six faces of a pencil all lie in a zone because they all intersect along one direction – the pencil lead direction – which is the zone axis

can also be more or less faces (think of a match box)

→ each crystal axis is the zone axis for four faces, or two crystallographically equivalent pairs of faces. Each face lies in two zones
→ a crystal plane lies in two zones

Zone axis



the [001] direction is the zone axis of the {100} and {110} family of planes.

If two planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ belong to the same zone, then their **zone axis** [u v w] satisfies the **zone law equation** also called Weiss zone law

$$h_1u+k_1v+l_1w=0$$
$$h_2u+k_2v+l_2w=0$$

This means that the direction [u v w] is perpendicular to the the two plane normals → find the vector which is perpendicular to two the two normals
→ cross product of the two normals

in the **cubic system**, the normal to the plane (hkl) is the direction [hkl]

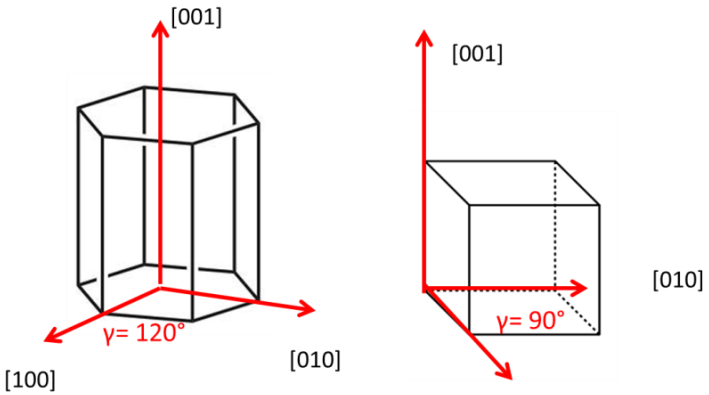
orthonormal basis (***i,j,k***)

$$\begin{pmatrix}1\\0\\0\end{pmatrix}\times\begin{pmatrix}1\\1\\0\end{pmatrix}=\mathbf{i}(0\cdot0-0\cdot1)+\mathbf{j}(1\cdot0-0\cdot1)+\mathbf{k}(1\cdot1-0\cdot1)=\begin{pmatrix}0\\0\\1\end{pmatrix}\rightarrow[001]$$

Importance of zone axis

- When a crystal is aligned along a zone axis, many crystallographic planes that belong to that zone contribute to the diffraction pattern.
- This leads to a high-symmetry diffraction pattern, where spots are arranged according to the symmetry of the zone axis.
- In transmission electron microscopy (TEM), indexing diffraction patterns relies on identifying zone axes.

Trigonal and hexagonal Bravais lattices: Miller-Bravais indices



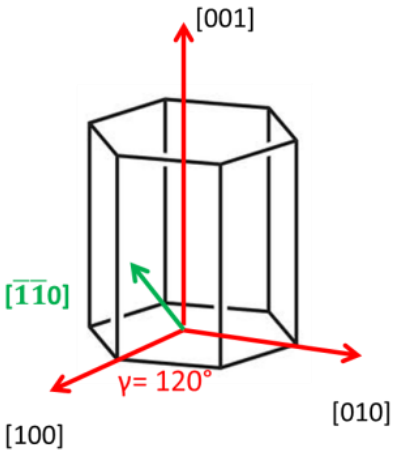
Miller indices discussed so far are valid for all Bravais lattices, however they are not very convenient for trigonal and hexagonal systemes

We have seen that, for a cubic system, we can list all the members of a family {*hkl*} by writing down all the permutations of the three numbers *h*, *k*, and *l* and their negatives.

If the symmetry of the system is lower than cubic, then the members of a family are still given by permutations, but not all permutations belong to the same family. For instance in the tetragonal system for {110} and {011}. In the rhombohedral system we have {100} = {*(100), (-100), (010), (0-10), (001), (00-1)*} as a family set of equivalent planes. In the orthorhombic system {100} = {*(100), (-100)*} contains just two type of planes.

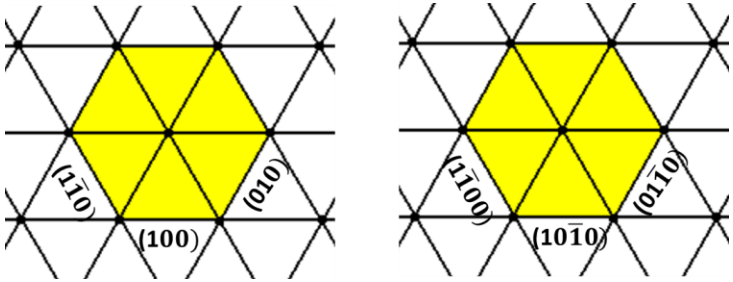
The only exception to this rule of index permutations is the *hexagonal crystal system*.

Trigonal and hexagonal Bravais lattices: Miller-Bravais indices

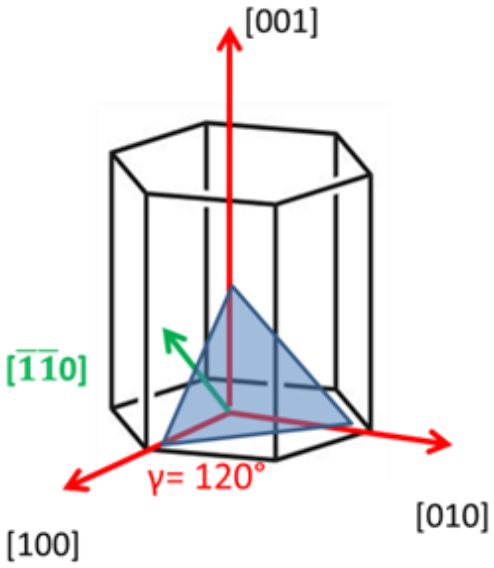


In the hexagonal system one does not obtain equivalent planes by permutation of the numbers
Here we would have in the Miller notation for instance
{100}hexagonal = (100), (010) and (-110)

To overcome this problem, often a fourth axis is used in the hexagonal system: i.e. an . The index on this axis is called "i"
The Miller-Bravais indices for a plane are now
(hkil) where i= -(h+k)



This notation has the advantage that the planes of the zone belonging to the z-axis can be obtained by permutation



Plane intersections: 1, 1, ½
Miller plane (1 1 2)

Plane intersections: 1,1, -1/2, ½
Miller-Bravais plane : (11$\bar{2}$2)

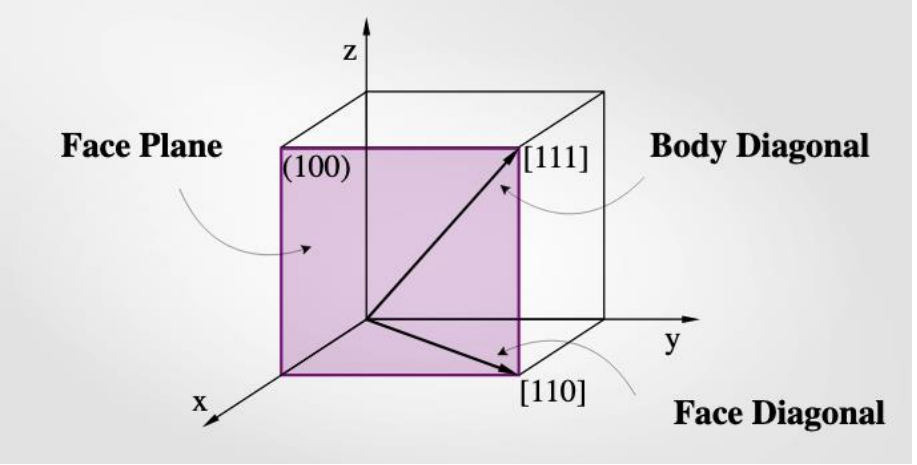
(i=-(h+k))

Summary of notations

(h, k, l) is for points. Remember to use the negative sign (-*h*) instead of bar sign ($\bar{h}$) and **don't** reduce fractions–these rules apply to directions and planes.

[hkl] is for a specific direction.
<hkl> is for a family of directions.

(hkl) is for a specific plane. Remember about reciprocal (inverse) space in planes!
{hkl} is for a family of planes.



Summary

- we defined the mathematical description of the crystalline lattice
- we introduced Miller indices for points, directions and planes
- we talked about family of directions which depend on the symmetry of the crystal system
- reminder of dot product, cross product, equations of lines and planes and how they are used in crystallography
- The cubic system in the orthonormal basis leads to easy calculation
- We defined zone axis and how to find them
- mentioned

→ next week: reciprocal space lattice and diffraction