Week 2

Algebraic structures:
Prime numbers, basics on vectors and 3D geometry
Crystallography

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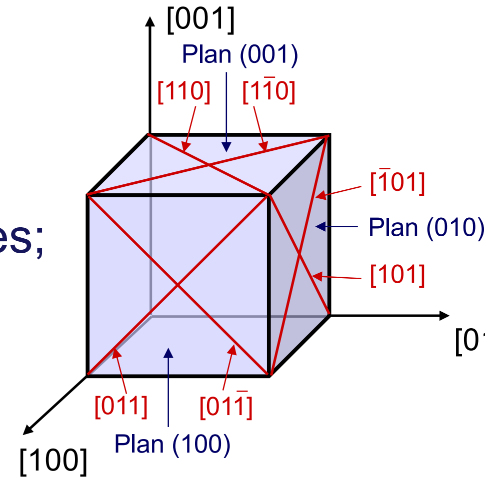
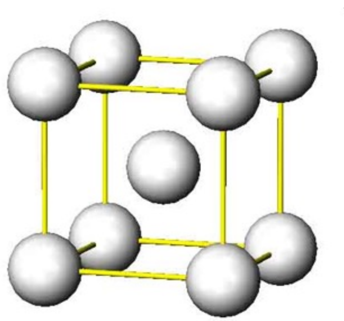
Reminder

- In Week 1, we introduced the basic notions of groups and rings, the foundation onto which number manipulations rely.



- We reviewed basic concepts in crystal symmetry:
  - We demonstrated the restrictions on rotational symmetries;
  - We built point group symmetries;
  - We discussed Space groups.

- We also reviewed important concepts regarding primitive and conventional cells, as well as the hard sphere model



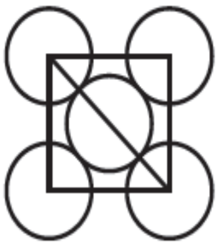
$$\vec{a}' = \frac{1}{2}(-\vec{a} + \vec{b} + \vec{c})$$

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

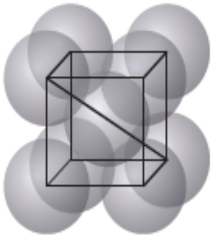
$$\vec{c}' = \frac{1}{2}(\vec{a} + \vec{b} - \vec{c})$$

Cubique simple

Cubique faces centrées



Cubique centré

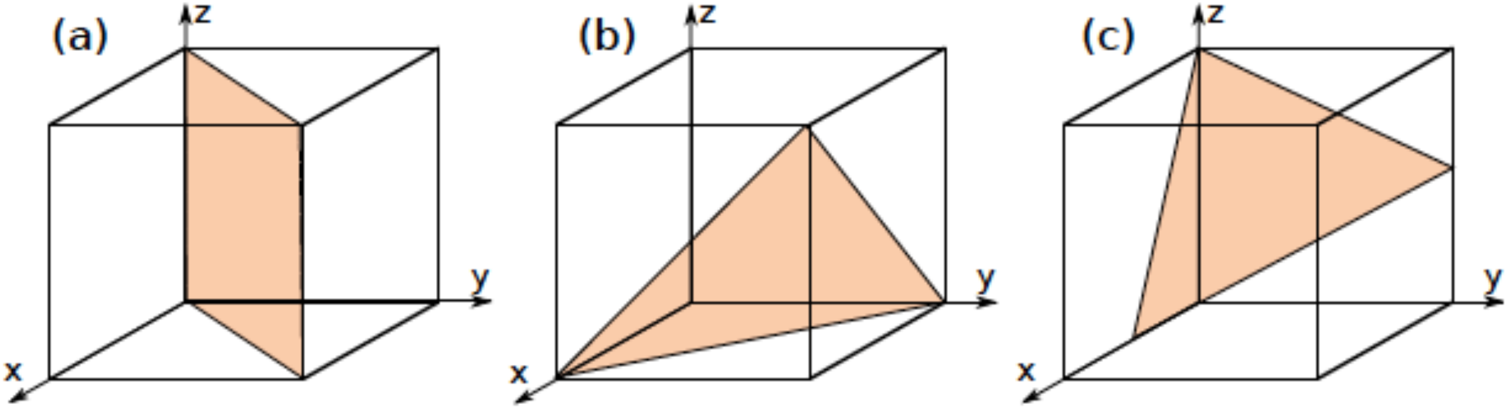


Overview

- Divisibility
- Prime numbers and Bézout relation
- Vectorial spaces and basic Euclidean geometry

Etinne Bézout 31/03/1730 – 27/09/1783

- Miller indices
- Crystal planes



Density and Free volume

From basic geomtric and vectorial consideration of the unit cell, one call calculate key properties of materials such as density and free volume.

- Density: $\rho = \frac{N_{atoms\,per\,unit\,cell} \times m_{atoms}}{V_{unit\,cell}}$

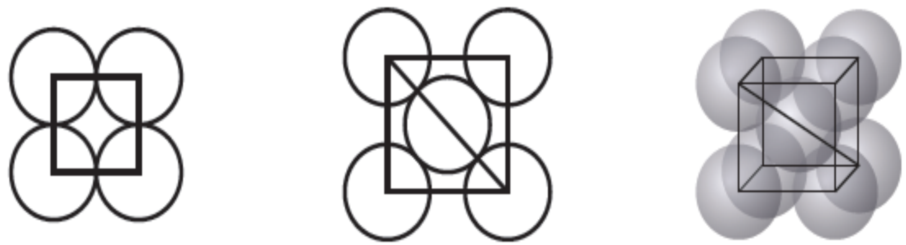
$$\rho = \frac{N_{atomes\,par\,mailles} \times m_{atome}}{V_{maille}}$$

-Packing fraction:

$$c = \frac{N_{atomes\,par\,mailles} \times V_{atome}}{V_{maille}}$$

-Direction and planes of high density

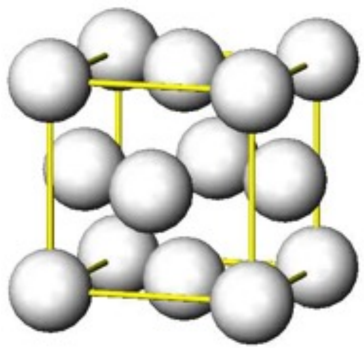
Cubique simple Cubique faces centrées Cubique centré



Structure of Metals

- Most metals crystalize in the BCC or FCC structure:

Face-centered Cubic (FCC)



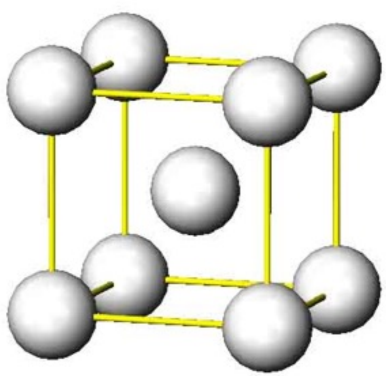
Al – Cu – Ni – Ag – Au – Fe …

Free volume : **26%**

Iron exhibits polymorphism, ie has different equilibrium structures at different temperatures:

Fe:	bcc	for $T > 1403^{\circ}C$
		and $T < 910^{\circ}C$
	fcc	for $910^{\circ}C < T < 1403^{\circ}C$

Body-centered Cubic (BCC)

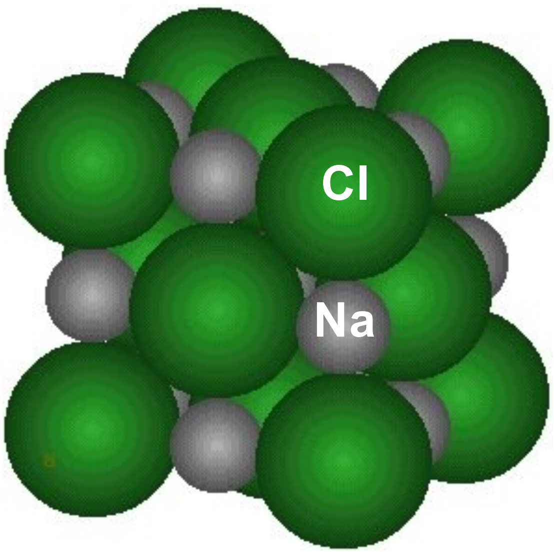


Cr – Fe – Mo – V – W – Ta …

Free volume : **32%**

Structure of Ceramics

- Ceramics possess ionic or covalent (or polar) bonds that are very strong.
- The structure can be compact like metals but more complex, as it depends on the ionic radius of the different atoms, and their valence.
- As a result, the crystallographic arrangements can be quite complex and they have a higher ability to be quenched into an amorphous structure.
- Some simple cases where the structure mostly depends on the ratio of the atomic radius:

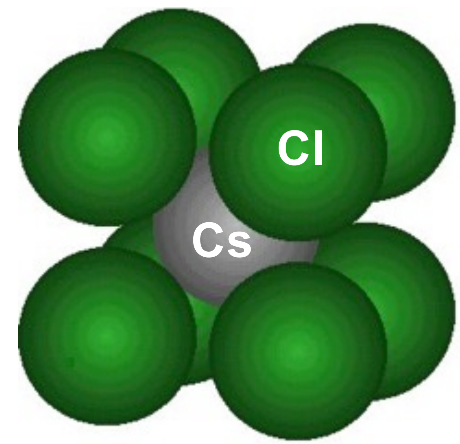


NaCl

$R_{Na+} = 1.02$ Å

$R_{Cl-} = 1.81$ Å

6	**Coordination**	**8**
0.56	**Rapport R_c/R_a**	**0.92**



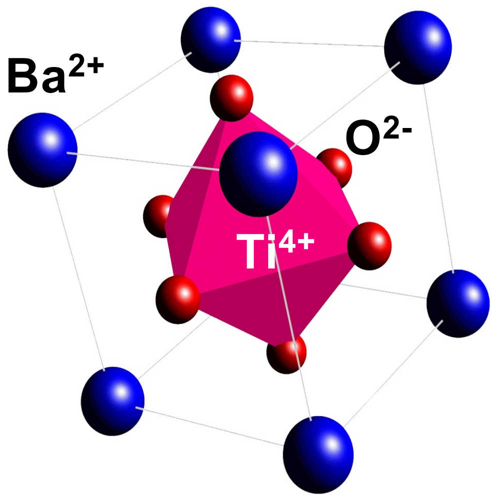
CsCl

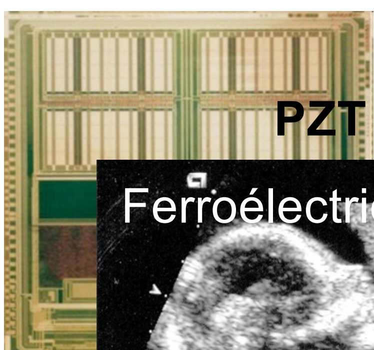
$R_{Cs+} = 1.67$ Å

$R_{Cl-} = 1.81$ Å

Structure of Ceramics

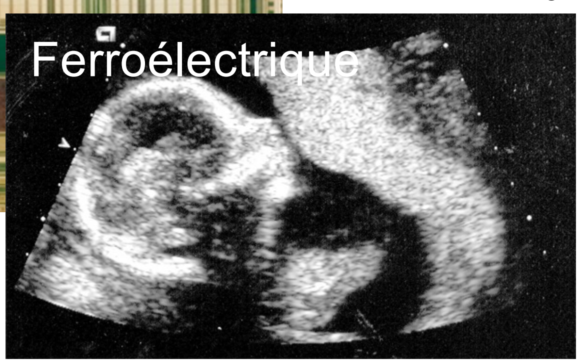
- A few "high tech" ceramics with more complex structures:

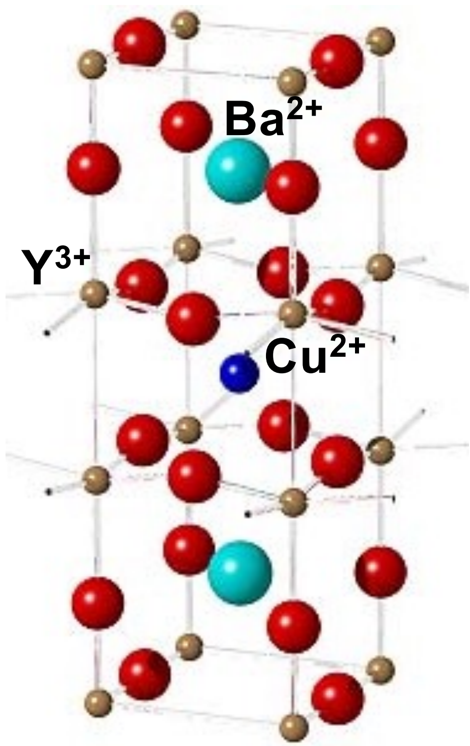


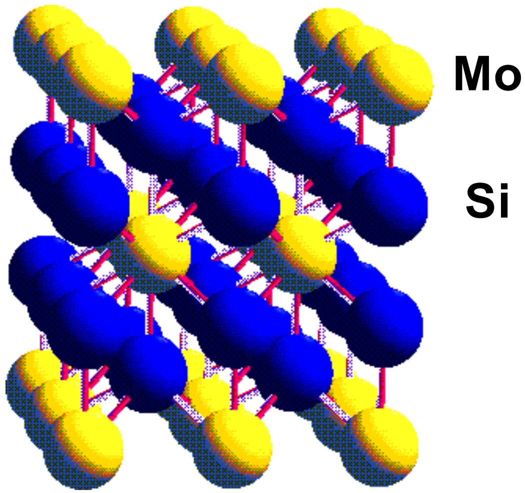


$BaTiO_3$

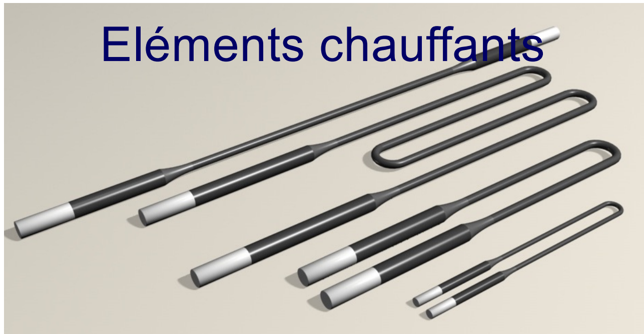
PZT $(Pb(Zr,Ti)O_3$







$MoSi_2$



Structure of Ceramics

Argile (kaolin)

$(Si_2O_5)Al_2(OH)_4$

Concrete

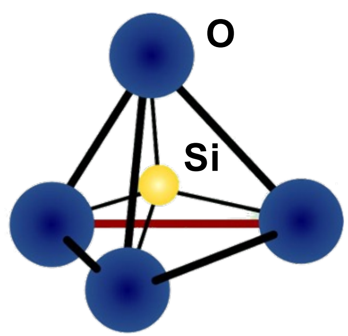
gravier + quartz + ciment

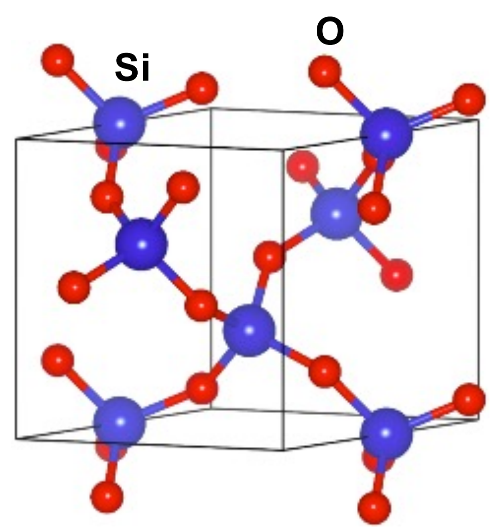
Ciment is a mix of:

$(CaO)_2SiO_2$ - $(CaO)_3SiO_2$
$(CaO)_3Al_2O_3$ - $(CaO)_4Al_2O_3Fe_2O_3$

Quartz

Tétraèdre $(SiO_4)^{4-}$

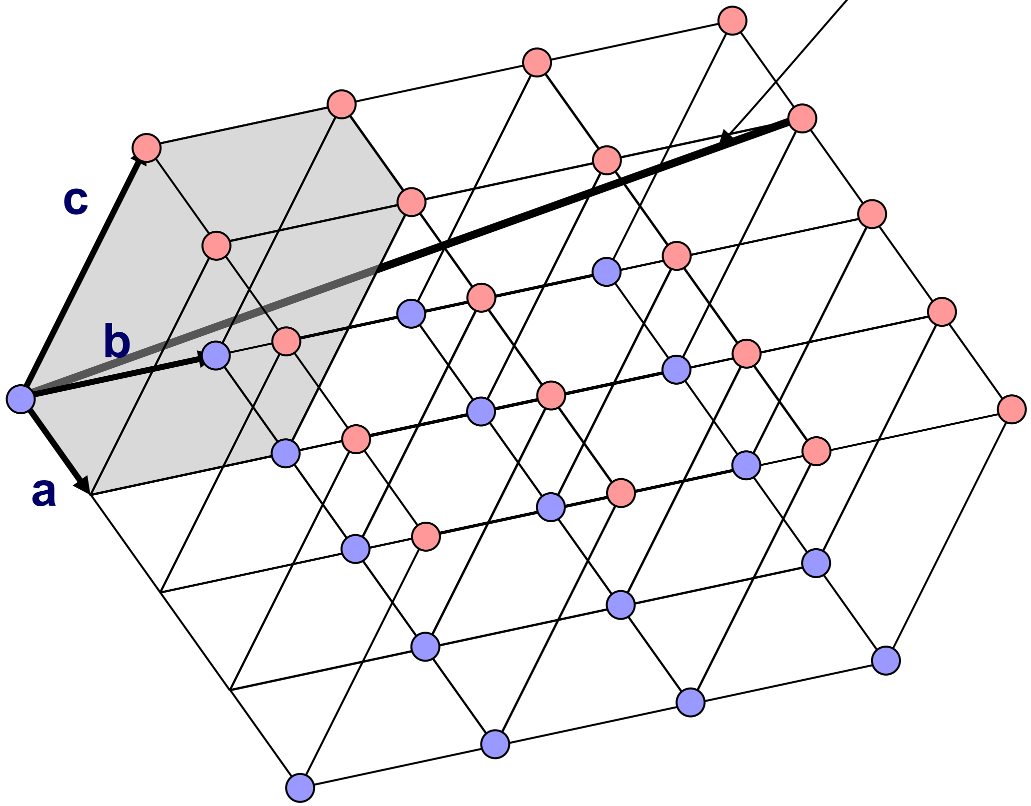




Crystal directions

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



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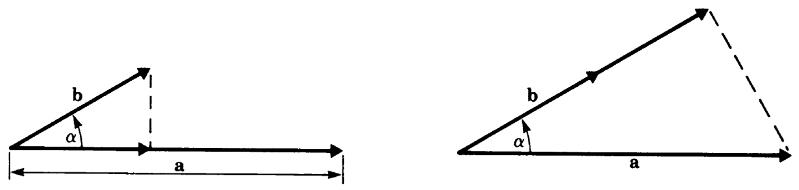
Basics of Euclidean Geometry

- 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: an algebraic operation that provides the $\mathbb{R}$-vector space with an inner product. In cartesian coordinates, for two vectors in the **orthonormal basis** $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$, we have:

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

  - The dot product brings forward the notions of length, angle and orthogonality. A geometric definition for two vectors that form an angle α is:
  - 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 $\boldsymbol{a}.\boldsymbol{b} = 0$.

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



Basics of Euclidean Geometry

Cross product

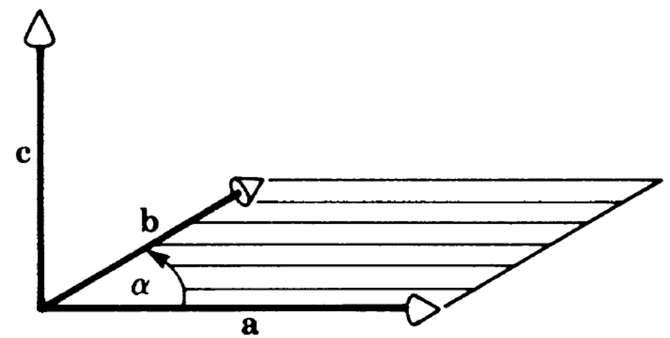
- The cross product of two vectors forming an angle α is a vector perpendicular to these vectors, with the magnitude:

$$\|\boldsymbol{a}\times\boldsymbol{b}\| = ab\sin\alpha$$

- In an orthonormal basis (***i,j,k***), the Cross product of two vectors ***a*** and ***b*** is:

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

- Examples: Torques and the Lorentz force.



- $\boldsymbol{a}\times\boldsymbol{b} = -\boldsymbol{b}\times\boldsymbol{a}$
- $\boldsymbol{i}\times\boldsymbol{j} = \boldsymbol{k}$
- Two parallel vectors have a zero cross product.
- See exercices in chapter 1&2 of the book.

- 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: :

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

Basics of Euclidean Geometry

- **Line**:
  - 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: $D = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \text{ with } \begin{matrix} a_1 x + b_1 y + c_1 z - d_1 = 0 \\ a_2 x + b_2 y + c_2 z - d_2 = 0 \end{matrix} \right\}$

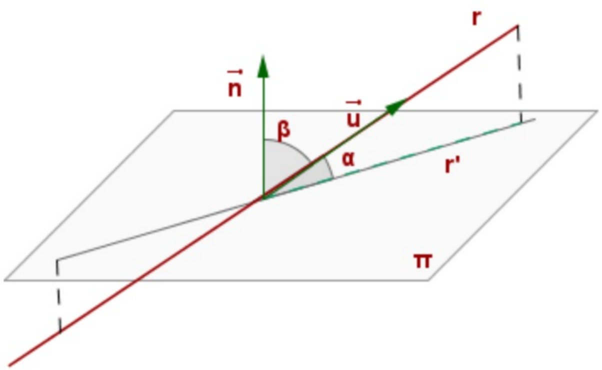
- **Plane**:
  - A plane is defined by 3 points $A = \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix}$, $B = \begin{pmatrix} x_B \\ y_B \\ z_B \end{pmatrix}$ and $C = \begin{pmatrix} x_C \\ y_C \\ z_C \end{pmatrix}$ or a point A and a normal $\boldsymbol{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix}$
  - 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 $(a, b, c, d) \in \mathbb{R}^4$, $P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, ax + by + cz - d = 0 \right\}$
  - Note that $\gcd(a, b, c, d) = 1$, or they can be re-scaled, i.e. (a, b, c, d) are co-prime.
  - Note that a line is the intersection of two planes !

Basics of Euclidean Geometry

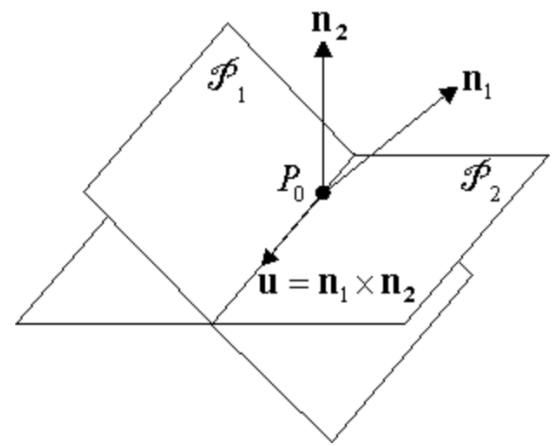
- **Angles**

  - 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

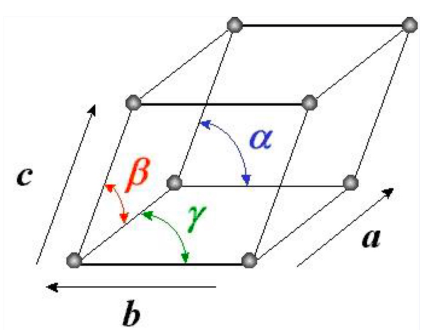


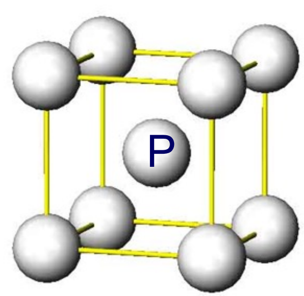
- Angle between two planes:
Angle between their normals:



- **Volume**

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

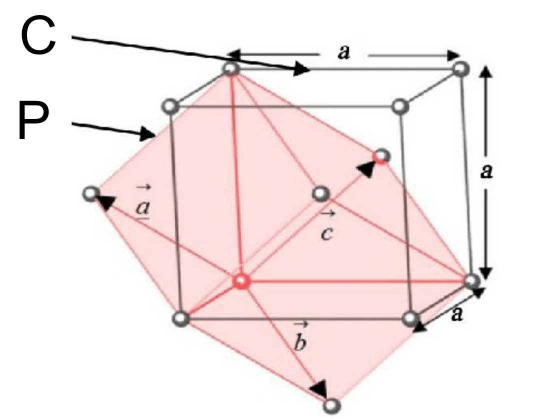




$$\vec{a}' = \frac{1}{2}(-\vec{a} + \vec{b} + \vec{c})$$

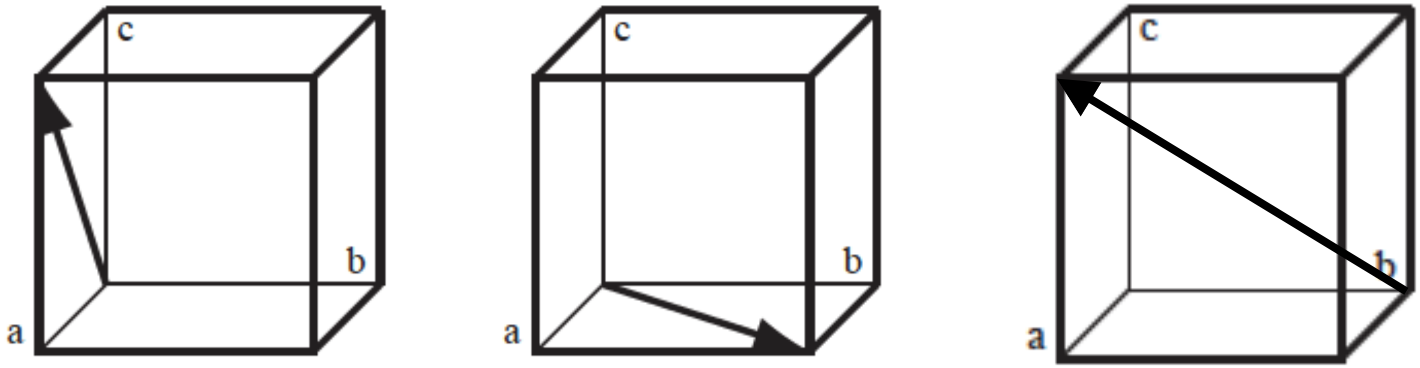
$$\vec{b}' = \frac{1}{2}(\vec{a} - \vec{b} + \vec{c})$$

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



Crystal directions

- Exemples:



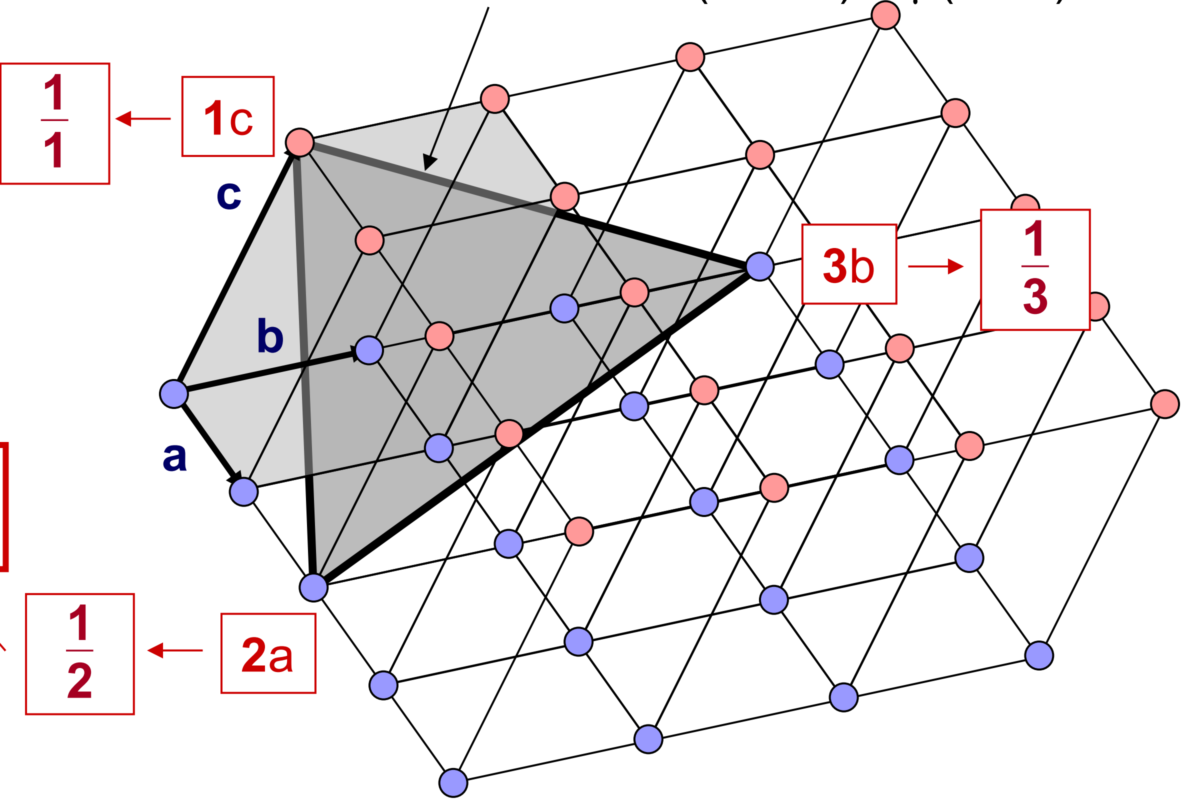
- Negative indices are represented with a barre above the number.
- If the origin is translated, the lines obtained remain parallel.
- If the axis are rotated by 90°, so is the direction. However, the atomic arrangement and physical properties along the direction remains the same from symmetry !

Crystal planes

- Crystal planes are planes that pass through at least 2 lattice points.
- They can be defined by the intercept of the plan with the basis axis:

Crystal plane:

$$\mathbf{r} = 2\mathbf{a}+\lambda(3\mathbf{b}-2\mathbf{a}) + \mu(\mathbf{c}-2\mathbf{a})$$



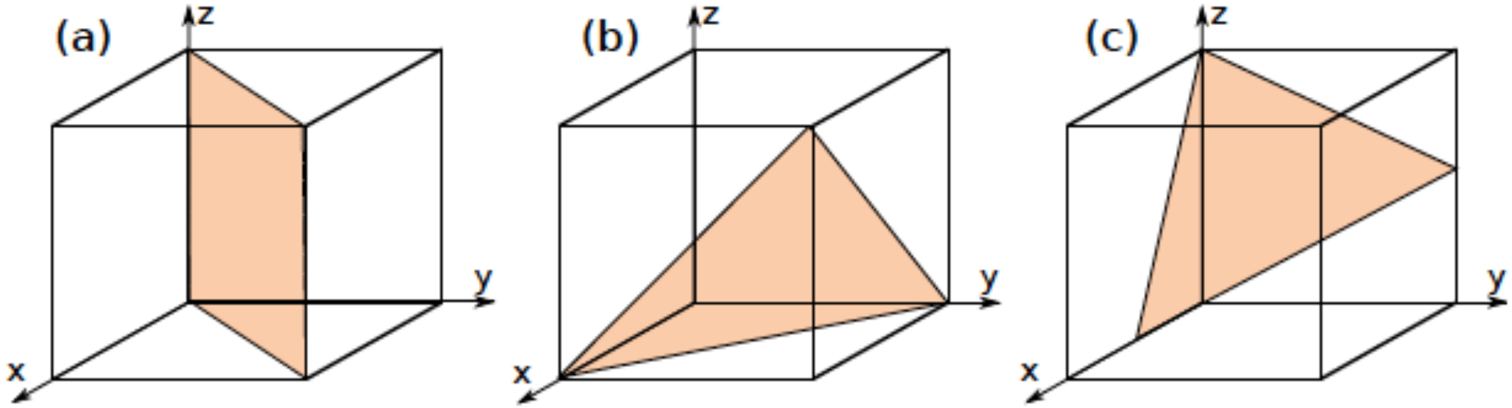
$$\left(\frac{1}{2}\ \ \frac{1}{3}\ \ \frac{1}{1}\right)\times 6\ = (3\ 2\ 6)$$

Crystal planes: Miller indices

- If the plane passes through the origin, one can translate the plane, or translate the origin, by one cell parameter along a basis vector.
- Find the coefficients (α, β, γ) such that the plan intercepts the axes (x,y,z) at $(\alpha a, \beta a, \gamma a)$ (a being the conventional lattice parameter, or the cube edge);
- If the plan is parallel to an axis, the intersection is considered to happen at infinity… (so the inverse will be zero).
- Take the inverse of these coefficients and multiply them by their lowest common multiplier (lcm)

if one of (α, β, γ) is smaller than 1, take the lcm of the coefficients greater than 1.

- The coefficients $h = \frac{lcm(\alpha,\beta,\gamma)}{\alpha}$, $\mathrm{k} = \frac{lcm(\alpha,\beta,\gamma)}{\beta}$, $l = \frac{lcm(\alpha,\beta,\gamma)}{\gamma}$ are the Miller indices of the plane
- These coefficients are co-prime !



$\mathbb{N}$ and $\mathbb{Z}$ - Divisibility

- Divisibility, congruent and prime numbers are essential parts of number theory.

- Euclidean division:

Given two integers $(a,b) \in \mathbb{Z}^2$, with $b \neq 0$, there exist <u>unique</u> integers q and r such that:

$a = bq + r$ and $0 \leq r < |b|$,

- Demonstration (hints):

Existence: consider $(a,b) \in \mathbb{Z} \times \mathbb{N}^*$, and the ensemble E = $\{p \in \mathbb{Z},\ a \geq bp\}$

- E is not empty and is bounded.
- E therefore has a maximum q such that $q \in E$ and $\forall p \in E, p \leq q$.
- We define the relative integer r as $r = a-bq$:
    - $r \geq 0$ since $q \in E$ and hence $a \geq bq$;
    - $r < b$ since otherwise $q+1 \in E$ which is impossible.

Unicity: let's (q,r) and (q',r') verify the relation above, we have: $b(q'-q) = r-r'$

Since $r < |b|$ and $r' < |b|$, $|r-r'| < |b|$, which implies that $|q-q'| < 1$, so $q = q'$ and also $r = r'$

- Given two integers $(a,b) \in \mathbb{Z}^2$, a divides b if there exists an integer q such that $a = bq$.

- An equivalent definition is a divides b if and only if the rest r of the Euclidean division is zero.

$\mathbb{N}$ and $\mathbb{Z}$ - gcd and lcm

- We consider $\{x_k, k \in \mathbb{N}, and\ x_k \in \mathbb{Z}^*\}$.

- The set of the dividers of the x_k admits a maximum, called the greatest common divider and defined as gcd(x_k).

It exists because the ensemble is not empty (1 divides all x_k) and it is bounded (by any of the x_k).

Reminder: every set of finite number of integers admits an upper and lower bound.

- The set of the multiples of the x_k admits a minimum, called the lowest common multiple and is defined as lcm(x_k)

It exists since the product of the x_k is a common multiple, and it is bounded since it is greater than one.

Note that if the x_k are of different signs, we usually consider the gcd and lcm of their absolute values.

- Modular arithmetic:
  - Given an integer n > 1, called a modulus, two integers a and b are said to be congruent modulo n, noted $a \equiv b[n]$ if n is a divisor of their difference.

$\mathbb{N}$ and $\mathbb{Z}$ - prime numbers

- A prime number is a number greater than one that is only divided by 1 and itself.
- p is a prime number if and only if a divides p implies that $a = 1$ or $a = p$.
- Fundamental theorem of arithmetic (unique factorization, or prime factorization theorem):
  - Every integer greater than 1 can be represented uniquely as a product of prime numbers, up to the order of the factors.
    In other words, for all integers n there exists prime numbers p_i and integers n_i $(1 \leq i \leq k)$, such that

$$n = \prod_{i=1}^{k} p_i^{n_i}$$

- Demonstration:
  - Existence: using strong induction: 2 is a prime. If it is true for all integers < n, either n is prime, or there is two integers a and b such that $n=ab$. Since $a < n$ and b < n, a and b have a representation in prime numbers, and so also does n.
  - Uniqueness: Let's n be the smallest integer to have two sets of primes p_i and q_i such that $n = p_1 \ldots p_k = q_1 \ldots q_l$. p_1 divides $q_1 \ldots q_l$, so according to the Euclid lemma, p_1 divides one of the q_i, which by re-ordering could be q_1. Since they are both primes, $p_1 = q_1$. As a result, $p_2 \ldots p_k = q_2 \ldots q_l < n$, which contradicts the hypothesis on n.
  - Euclid's lemma: If a prime p divides the product ab of two integers a and b, then p must divide at least one of those integers a or b. We will see it soon using the relation of Bezout.

- Prime numbers are the building blocks, the fundamental particles, of numbers.
- A parallel can be made between prime number and bonds in materials !

$\mathbb{N}$ and $\mathbb{Z}$ - mutually prime numbers

- Two integers *a* and *b* are mutually prime (or co-prime, relatively prime), if *gcd(a,b) = 1*. In other words, they don't have a common prime number in their factorization.

  Example: 6 and 25 are not prime numbers but are mutually prime: 6 =2x3 and 25 = 5^2

- This definition can be extended to *n* integers x_i , which are called mutually prime if $gcd(x_1,\ldots,x_n) = 1$.

- Theorem of Bézout:
  For *n* non zero integers x_i, $gcd(x_1, \ldots, x_n) = d$. Then, $\exists\ (d_1, \ldots, d_n) \in \mathbb{Z}^n$ such that

$$\sum_{i=1}^{n} d_i x_i = d$$

- Proof:
  Let's consider the ensemble $S = \{\sum_{i=1}^{n} u_i x_i, : (u_1, \ldots, u_n) \in \mathbb{Z}^n \ and \sum_{i=1}^{n} u_i x_i \ > 0\}$
  S is not empty ($x_1 or -x_1 \in$ S) and it is then bounded and has a minimum $\mathrm{d} = \sum_{i=1}^{n} d_i x_i$.
  d divides all x_k : if $x_k = dq_k + r_k$, and $0 < r_k < d$, then $r_k = (1 - d_k q_k) x_k + \sum_{k \neq i} d_i x_i \ \in S$ which contradicts that d is the minimum of S, so necessarily $r_k = 0$ and *d* divides x_k.
  d is the gcd: if $\exists\ c, \forall k, c / x_k$, then c/d, and hence necessarily $c \leq d$.
  So *d* is the greatest divider of all x_k, or *d* = $gcd(x_1,\ldots,x_n)$ and the $(d_1, \ldots, d_n)$ verify the proposition.

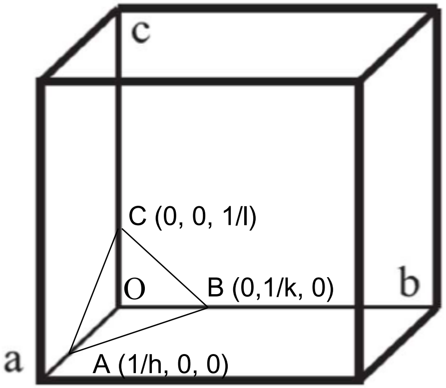
- No need to know the proofs of theorems, but rather how to apply them to practical problems.

$\mathbb{N}$ and $\mathbb{Z}$ - mutually prime numbers

- Important corollary to Bézout's theorem:
  If n non zero integers x_i are mutually prime, or co-prime, ie if $gcd(x_1, \dots, x_n) = 1$,
  then $\exists\ (d_1, \dots, d_n) \in \mathbb{Z}^n$ such that:

$$\sum_{i=1}^{n} d_i x_i = 1$$

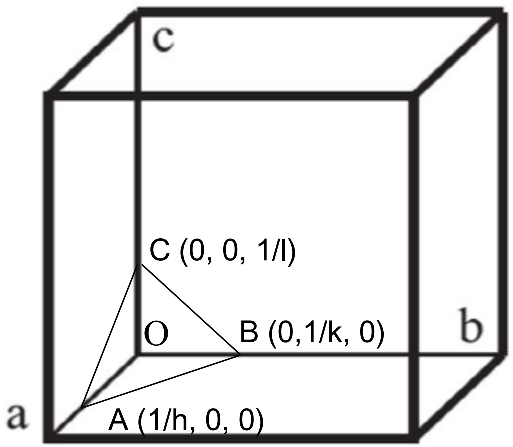
- Important results from Bézout formulation:
  - If for n integers x_i, there is $(d_1, \dots, d_n) \in \mathbb{Z}^n$ such that $\sum_{i=1}^{n} d_i x_i = 1$, then the x_i are mutually prime.
    Straightforward since if $\delta = \gcd(x_i)_{\ 1 \le i \le n}$ then $\delta | \sum_{i=1}^{n} d_i x_i$ and so $\delta = 1$.
  - Corollary: $\forall\ (a, b, c)(\mathbb{Z}^*)^3, \{c|b\ \&\ \gcd(a, b) = 1\ \} \Longrightarrow \gcd(a, c) = 1.$
  - Gauss Theorem: $\forall\ (a, b, c) \in (\mathbb{Z}^*)^3, \{a|bc\ \&\ \gcd(a, b) = 1\ \} \Longrightarrow a|c$



- For any three co-prime numbers (*h,k,l*), the plan shown here cutting the axis at points A, B and C is a crystal plan.

  This can be shown using Bézout relation !

Crystal (or lattice) planes



- This plan can be defined in two ways:
  - $P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \boldsymbol{AM}.\boldsymbol{n} = 0 \right\}$ where ***n*** is the normal to the plane;
  - $P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \boldsymbol{AM} = \lambda \boldsymbol{AB} + \mu \boldsymbol{AC}, (\lambda, \mu) \in \mathbb{R}^2 \right\}$
- The normal to the plane is given by $\boldsymbol{N}_{(\boldsymbol{hkl})} = \boldsymbol{AB} \times \boldsymbol{AC}$
- **In the cubic system, the direction [hkl] and the planes (hkl) are perpendicular !**
- In an orthonormal basis, the equation of the plane is obtained as follow:

$$\mathcal{P}_1^{(hkl)} = \{(x, y, z) \in \mathbb{R}^3 / hx + ky + lz = a\}$$

- Does it really intercept lattice points ?
- Using Bézout on the co-prime h,k and l numbers defined previously, we hence know that:

$$\exists (n_1, n_2, n_3) \in \mathbb{Z}^3, hn_1 + kn_2 + ln_3 = 1$$

- We can deduct that the point $P(n_1 a, n_2 a, n_3 a) \in \mathcal{P}_1^{(hkl)}$.

SUMMARY

- We introduced the basic notions of divisibility, prime and co-prime numbers, and discussed several important concepts like the Bézout relation, or the Euclid lemma, that can be useful in understanding discrete configurations such as Bravais lattices.

- We also reviewed basic calculation in 3D geometry involving vectors, directions and planes.

- We use all these notions to review a foundational aspect of Materials Science that is crystallography and the structure of materials. Notions discussed:
  - Bravais lattices;
  - Crystal directions and planes, Miller indices
  - The cubic structure
  - The hard sphere model

- <u>Next week</u>
  - We will show a few examples of using number theory to approach crystal planes, reciprocal spaces and X-ray diffraction.
  - We will review some properties of real and complex numbers;
  - We will give some examples as to how to manipulate them, and of their use in Materials Science and engineering.