Week 1

Algebraic structures: Groups and Rings, Integers

Crystallography: Symmetries and Basis

F. Sorin (MX)

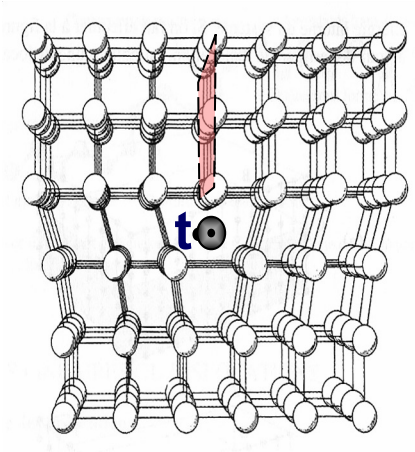
Ecole Polytechnique Fédérale de Lausanne

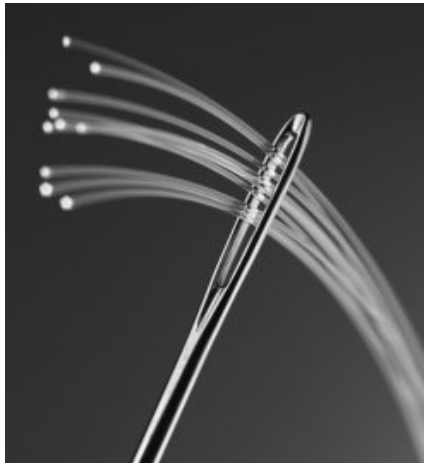
Overview

- Overview and structure of the class
- Algebraic structures: groups and Rings
- Point Group Symmetry in Crystallography
- Cells, Miller indices… (to be continued next week)

General Objectives

- To train you on applying theoretical concepts in mathematics learned at the bachelor level, to Materials Science important concepts, and engineering problems more broadly.
- Review important Materials Science concepts via the lenses of the mathematics required to treat them.





- I am not a mathematician ! But well trained in applied mathematics… and Materials Science both theoretical and experimental.
- I will teach Materials Science with an emphasis on the applied mathematics
- Prof. Carter will show you examples via computational methods to visualize mathematical concepts and use them.

General Outline

Mathematical Concepts: ***a rough schedule***

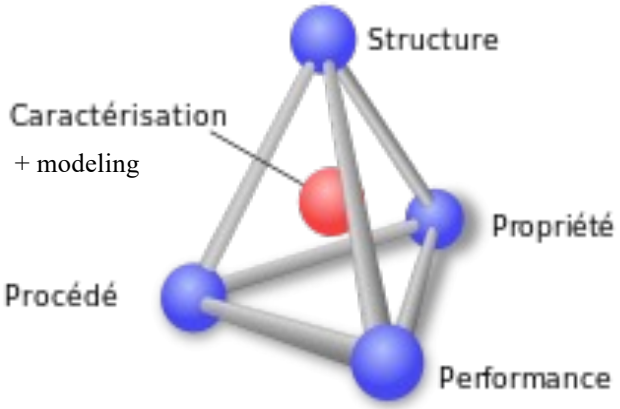
- *Weeks 1, 2 &3*: Foundations: Groups, Number theory and vectorial spaces
- *Week 3&4*: Real and Complex numbers
- *Week 4, 5 & 6*: Linear algebra;
- *Week 7 & 8*: Functions: important properties, main functions (e^x, log etc…) Integration and derivation
- Week 9: Fourier transform
- *Week 10*: Laplace transforms and ODEs
- *Week 11*: ODEs and PDEs
- *Week 12, 13 & 14*: Number theory (Cobinatorial), Probability and Statistics

- This structure is aligned with the class on Solid State Materials of Prof. Marzari
- These notions should be familiar to you and we sometimes will use one or more in classes and exercises before having reached the class dedicated to them.

General Outline

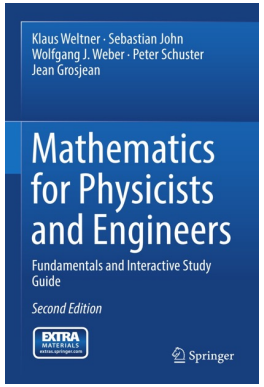
Important Materials Science Concepts:

- Structure of Materials: Crystallography
- Thermodynamics and Kinetics
- Phase diagrams and phase transformation
- Diffusion
- Mechanical properties
- Rheology and fluid dynamics
- Visco-elastic materials
- Optical properties and wave propagation
- Quantum Mechanics applied to solid states physics
- Statistical physics



Structure of the Class

- Typically, each concept will be spread over 1-2 weeks, with:
  - 2-3 hrs reminding basic concepts: 1-3 hrs applying the concepts to a Materials Science problem
  - 1-2hrs of Exercises
  - Classes will be Mondays and a bit (20 mn) Tuesday, followed by exercises.



- References:
  - Mathematics for Physicists and Engineers

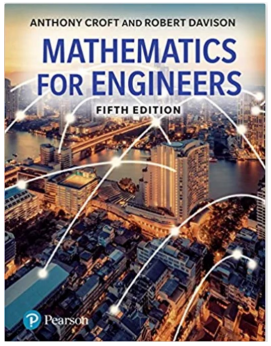
K. Weltner et. al. – Springer (2nd edition)

Availble online at the EPFL library: https://link.springer.com/book/10.1007/978-3-642-54124-7

A source of notes and exercises

  - Mathematics for Engineers

A. Croft and R. Davison – Pearson (5th edition)



  - "Algèbre Linéaire" et "Analyse", Gordon - Ellipse
  - My notes from Professor Taieb at Lycée Louis-le-Grand (1997)
    - You can't understand those… ☺

Structure of the Class

- **1 PhD assistant**:
  - Stella Laperrousaz
  - Plus Dr. Pierre-Luc Piveteau when help needed
- **The class will be held live**:
  - Mondays in MXF1, 15h15 – 17h00: Classes and Exercises
  - Tuesdays in MXF1, 09h15-11h00: Classes and Exercises
- **Examples with Computational tutorials by Prof. Carter:**
  - 5-6 such sessions will be organized so you can visualize computationally concepts learned in class.
  - The first session tomorrow !
- **Some exceptions (travels etc..):**
  - Next week: no class on Monday !
  - Will be announced in class and always check instructions also given on Moodle

Structure of the Class

- **Exam**:
  - Written exam during the exam session in January/February 2025.

- It is essential to do the exercises (**learn by doing**):
  - More exercises than what can be done in 1 hour !
  - More exercises for more opportunities to learn: ask us for exercises of previous weeks at the exercise sessions if needed.
  - Some are purely mathematical, but most mix math and materials science.

- Tutorials taught by Prof. Carter from MIT:
  - Complement the classes to revisit the concepts from a numerical perspective;
  - Present other Materials Science concepts and associated math tools;

Week 1 – Algebraic Structures

- Algebraic structures form the foundations of the mathematical objects on which are built what we use as scientists and engineers: real and complex numbers, functions, integrals, probability and statistics, linear algebra etc…

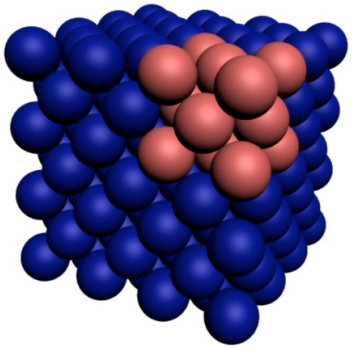
- In the first 2-3weeks we will review these structures and introduce first examples of applications that relate to Materials Science problems.

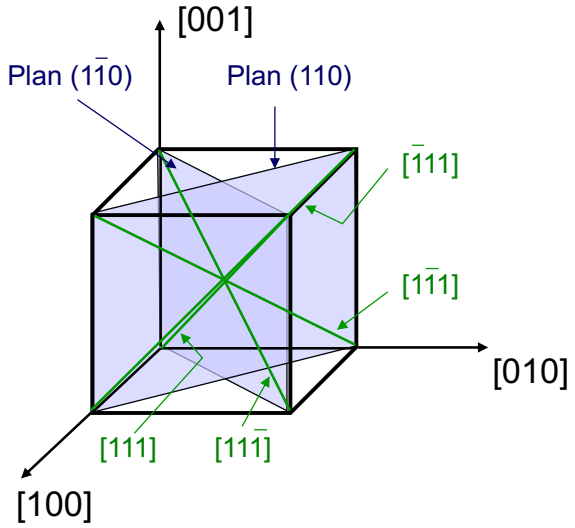
- It will establish the basis for all the classes, and we will get back to them particularly at the end of the semester when we review combinatorial with integers, probability and statistics.

- This first two classes are quite abstract and theoretical, this is just an intro, a deeper view of mathematical objects for your scientific culture. It is also an important foundation of the structure of Materials.

Relative Integers in Materials Science

- **Number theory** is the study of integers and integer-valued functions.
- It appears in the first introduction class of materials structure !





- *Notations:*
  - $\mathbb{N}$ is the ensemble of positive integers and $\mathbb{Z}$ the one for relative integers (positive and negative).
  - $\mathbb{Q}$, $\mathbb{R}$ and $\mathbb{C}$ are the ensemble of rational, real and complex numbers, respectively.
  - Number theory is quite important in Crystallography !

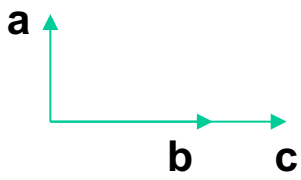
Algebraic structures – Groups and Rings

- **A *Group*** is a set G which is closed under an operation $*$, and satisfies the following properties:

- Closure: for any $x, y \in G$, $x * y \in G$
- Identity – There is an element e in G, such that for every $x \in G$, $e * x = x * e = x$
- Inverse – For every x in G there is an element $y \in G$ such that $x * y = y * x = e$
- Associativity – The following identity holds for every $x, y, z \in G$: $x * (y * z) = (x * y) * z$

A group is abelian if $*$ is commutative: for all $x, y \in G$, $x * y = y * x$

Examples: $(\mathbb{Z}, +)$ is an abelian group
$(\mathbb{Z}, x)$ is not a group.
$(\mathbb{R}^3, x)$ is not a group since the cross product x is not associative:



Other important notions: cardinal and order: number of elements in the group
Sub-groups

- **A *Ring*** is a set R which is closed under two operations + and × and satisfies the following properties:

- (R,+) is an abelian group.
- Associativity of × – For every a, b, c ∈ R, a × (b × c) = (a × b) × c
- Distributive Properties – For every a, b, c ∈ R the following identities hold: a × (b + c) = (a × b) + (a × c) and (b + c) × a = b × a + c × a
- R has an identity for x: there exists e ∈ R such that for all a ∈ R, a x e = e x a = a.

R is commutative if x is commutative.

Example: $(\mathbb{Z}, +, .)$ is a commutative Ring.

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

- Important notions we will use:
  - Order:

It is very intuitive, but the groups $\mathbb{N}$ and $\mathbb{Z}$ are fully ordered. Any finite sub-group admits a maximum and a minimum element (easy to show via proof by contradiction (also called the method of reductio ad absurdum)).

  - Recurrence relation:
    - An equation that expresses each element of a sequence as a function of the preceding ones.

  - Proof by induction (”Principe de récurence”)

For $n_0 \in \mathbb{N}$, for a proposition P(n) ($n \in \mathbb{N}$) to be true for all $n \geq n_0$, it is necessary and sufficient that:

- $P(n_0)$ is true
- For all $n \geq n_0$, if P(n) is true, then P(n+1) is also true.

  - Strong induction

It is equivalent to show that: if it is true for n_0, and for all integers < n, then P(n) is also true.

These are important notions are very useful to demonstrate many formulae used in modeling various concepts in Materials Science:

- Toughness and the progression of a crack: in exercises
- Optical reflection of a thin layer
- etc..

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

- With Groups and Rings structures, one can already create the theoretical basis for number theory.

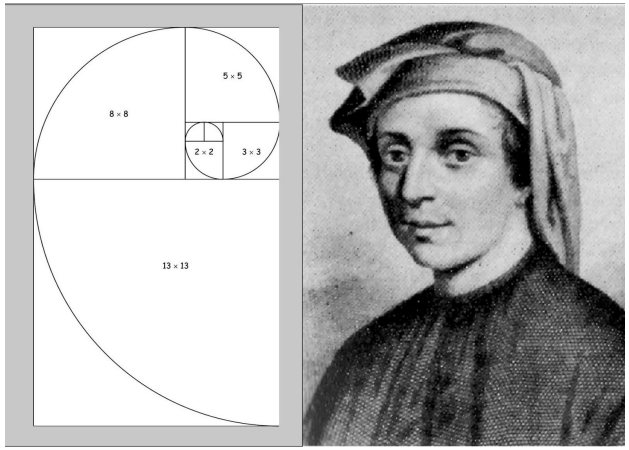
- Despite the seemingly simple nature of adding and multiplying integers (positive or negative), the complexity of problems is endless, the beauty of demonstrations and number structures are unimaginable, and the applications to materials Science problems already significant as we will see.

Examples:

- *Fermat last theorem*: for $(x, y, z, n) \in \mathbb{N}^*$ and $n \geq 3$, there is no solution to the relation: $x^n + y^n = z^n$

Envisioned by Fermat in 1637 or so, demonstrated by Andrew Wiles in 1994.

- *The Fibonacci sequence*: $F_n = F_{n-1} + F_{n-2}$

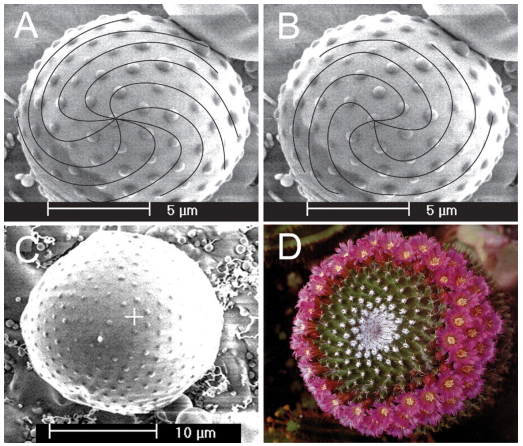


$$F_n = \frac{\varphi^n - \psi^n}{\sqrt{5}}$$

Golden ratio:

$$\varphi = \frac{1+\sqrt{5}}{2}$$

$$\psi = -\frac{1}{\varphi} = \frac{1-\sqrt{5}}{2}$$



Li et. al., Science 309, 909 (2005)

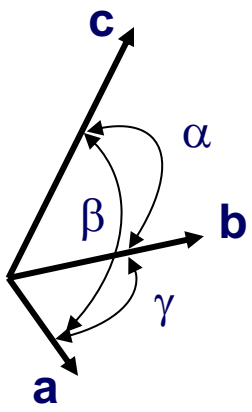
- Present in some patterns in nature, it also appears in some stress related phenomena in materials, but also in quantum computing, in resistor networks, in photonics, hydrogen bonds… interesting review: https://arxiv.org/ftp/arxiv/papers/1801/1801.01369.pdf

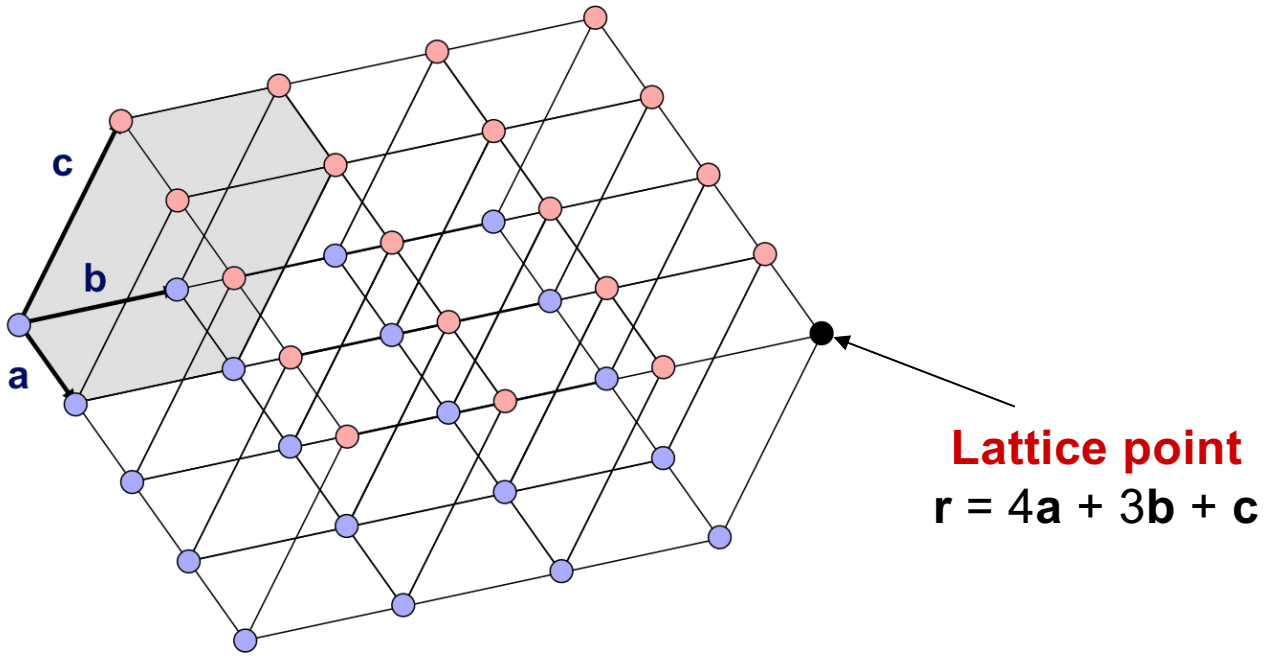
$\mathbb{N}$ and $\mathbb{Z}$: Fibonacci at EPFL

Crystalline state

Materials in a crystalline state are organized into ordered arrangements of atoms. The chemical composition of the material forms a **motif**, that is placed at prescribed positions on a lattice called the **Bravais Lattice**.

A set of 3 vectors for the basis for such a Bravais lattice, where every point is a linear combination with **relative integers** as coefficients.





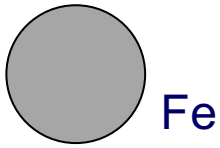
On each point of the lattice, the crystal appears identical: there is a translational symmetry along the vectors **a**, **b** and **c.**

Crystalline state

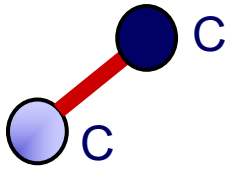
One can distinguish **7 crystal systems**, that reflect the symmetry of the crystal. **14 Bravais lattice** (see next slide).

Crystal = 1 Motif + 1 Bravais lattice

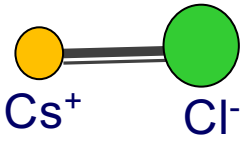
Motif: represents the nature of the materials, its chemical composition, that is repeated in space to form the crystal.



Metallic Bond



Covalent Bond



Ionic Bond

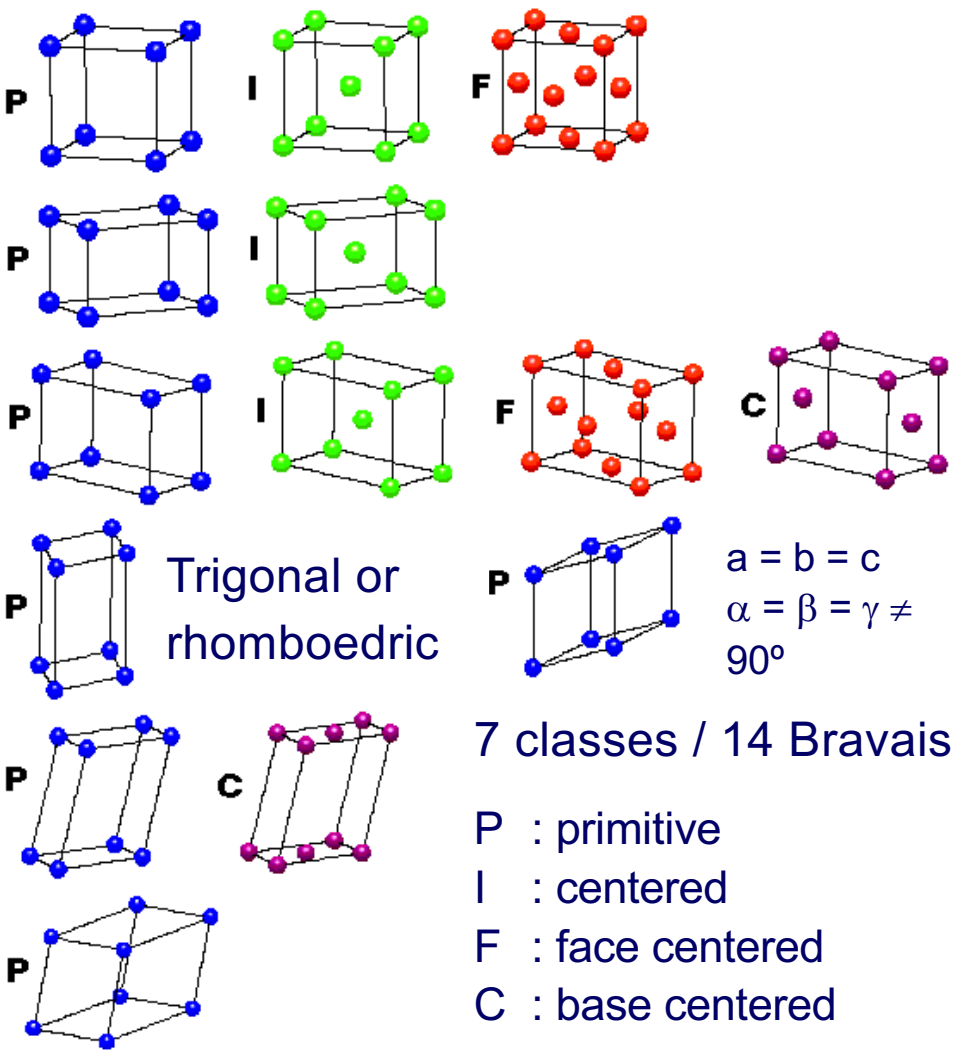
Bravais lattice: mathematical construction of an infinite set of points with translational symmetry along three axis that form a vector basis.

$$B\left(O,\vec{a},\vec{b},\vec{c}\right)=\left\{M/\overrightarrow{OM}=l\vec{a}+m\vec{b}+n\vec{c},(l,m,n)\in\mathbb{Z}^3\right\}$$

Crystalline state

One can distinguish **7 crystal systems**, that reflect the symmetry of the crystal. **14 Bravais lattice:**

Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^o$
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^o$
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^o;\ \gamma = 120^o$
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^o \neq \beta$
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$



7 classes / 14 Bravais

P : primitive
I : centered
F : face centered
C : base centered

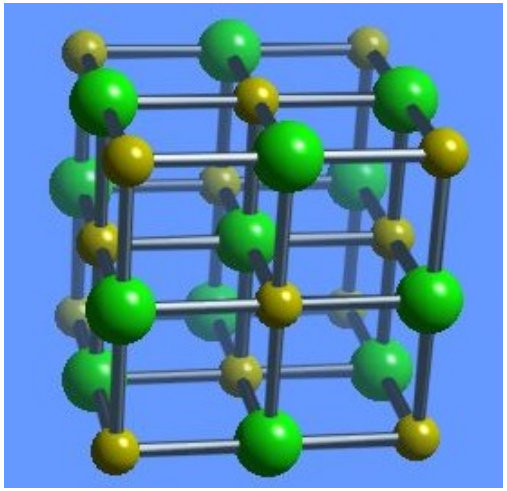
http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lecture1/Bravais.gif

The cubic system

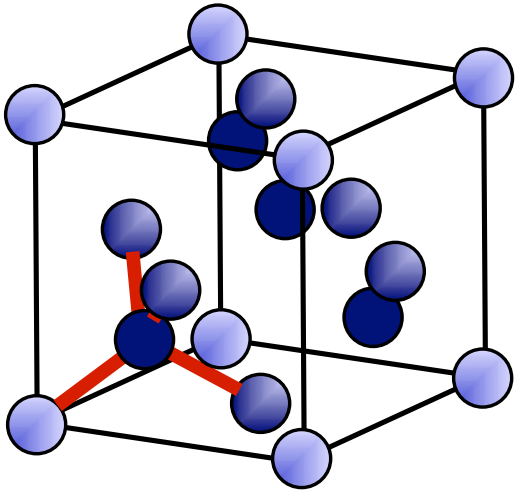
Examples:

Lattice:

Aluminium



NaCl

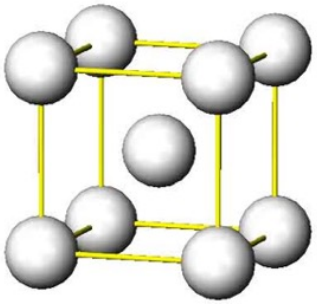


Diamond

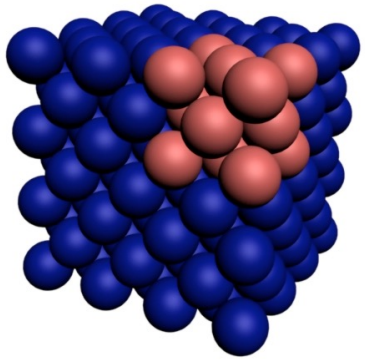
Motifs:

Crystalline state: examples

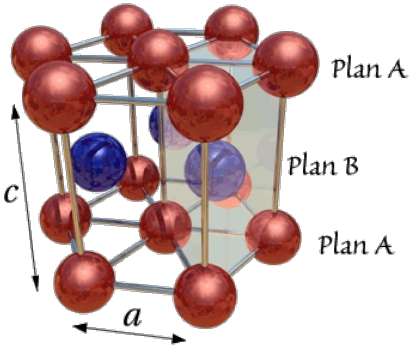
- Because of the nature of their bonds, metals tend to form highly compact structures such as body-centered and face-centered cubic or hexagonal compact:



Cr – Fe – Mo – V – W…

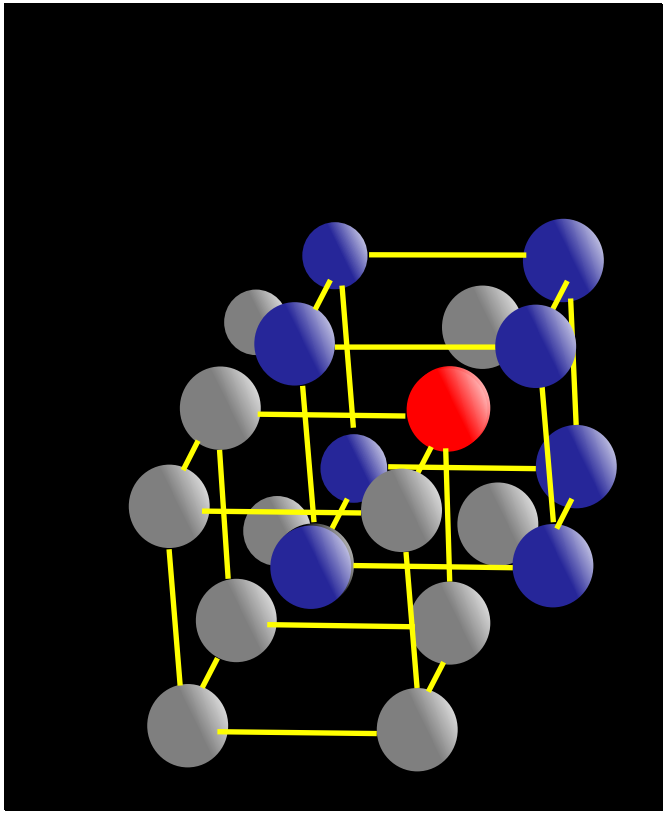


Al – Cu – Ni – Ag – Au …



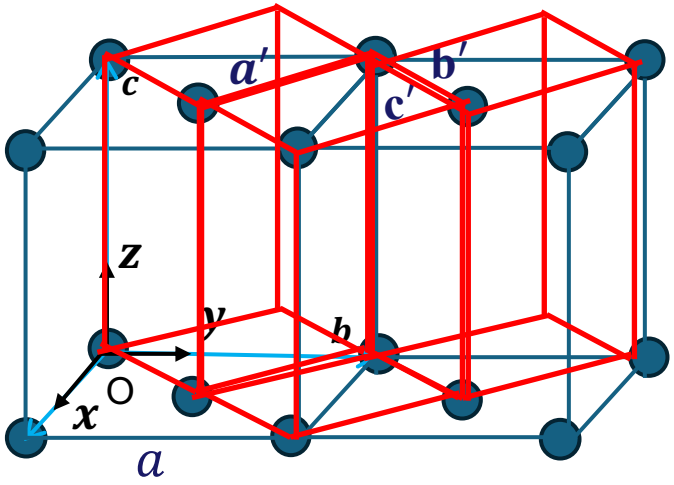
Zn – Mg – Ti – Zr …

- The configuration is the same on every lattice point:



Crystals and Symmetries

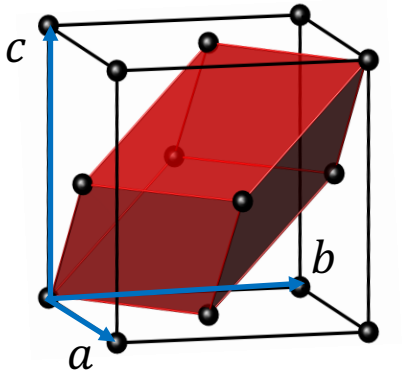
- Crystals can be first apprehended by their symmetry, which govern their classification in the different crystal classes and Bravais lattices.
  - Example: why not a base-centered cubic structure ?



  - It is a Primitive tetragonal !

$\|\boldsymbol{a}'\| = \|\boldsymbol{b}'\| = a\frac{\sqrt{2}}{2}$,
$\|\boldsymbol{c}'\| = a$
$\widehat{(\boldsymbol{a},\boldsymbol{b})} = \widehat{(\boldsymbol{a},\boldsymbol{c})} = \widehat{(\boldsymbol{b},\boldsymbol{c})} = \frac{\pi}{2}$

- However, one can show that the FCC is also another lattice, a rhombohedric structure !
  - And yet FCC is classified with its own Bravais Lattice…



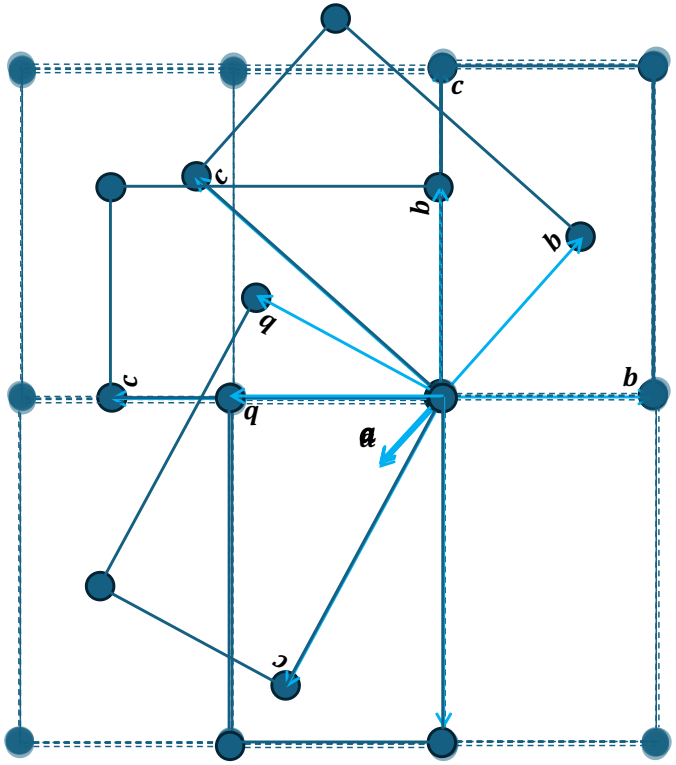
  - For the FCC, the Bravais lattice vectors are given by:

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

The primitive cell $\|\boldsymbol{a}'\| = \|\boldsymbol{b}'\| = \|\boldsymbol{c}'\| = a\frac{\sqrt{2}}{2}$,
$\widehat{(\boldsymbol{a},\boldsymbol{b})} = \widehat{(\boldsymbol{a},\boldsymbol{c})} = \widehat{(\boldsymbol{b},\boldsymbol{c})} = \frac{\pi}{3}$

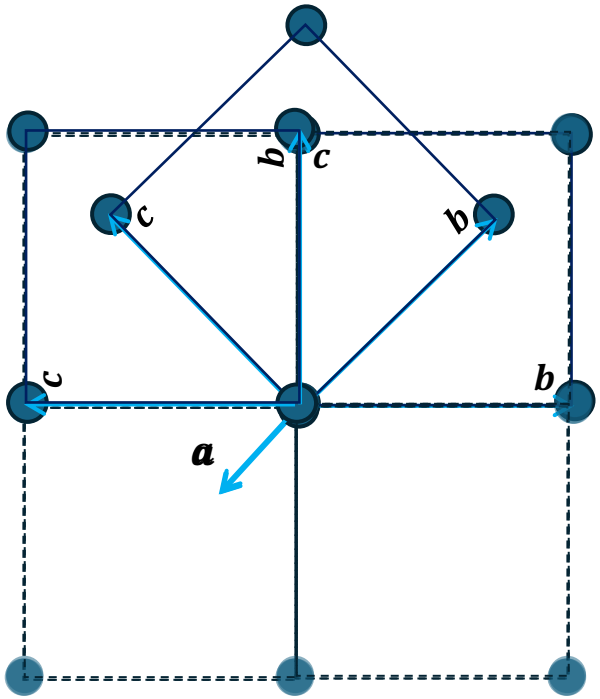
Crystals and Symmetries

- The classification is not about lattice parameter values, it classifies by level of symmetry.
  - A rhombohedric with a certain value of lattice parameters acquire novel symmetries that makes it have a specific Bravais lattice in the cubic structure system.
  - Other example: tetragonal vs cubic



Tetragonal structure: $c > a$

2-fold rotational symmetry



Cubic structure: $c = a$

4-fold rotational symmetry

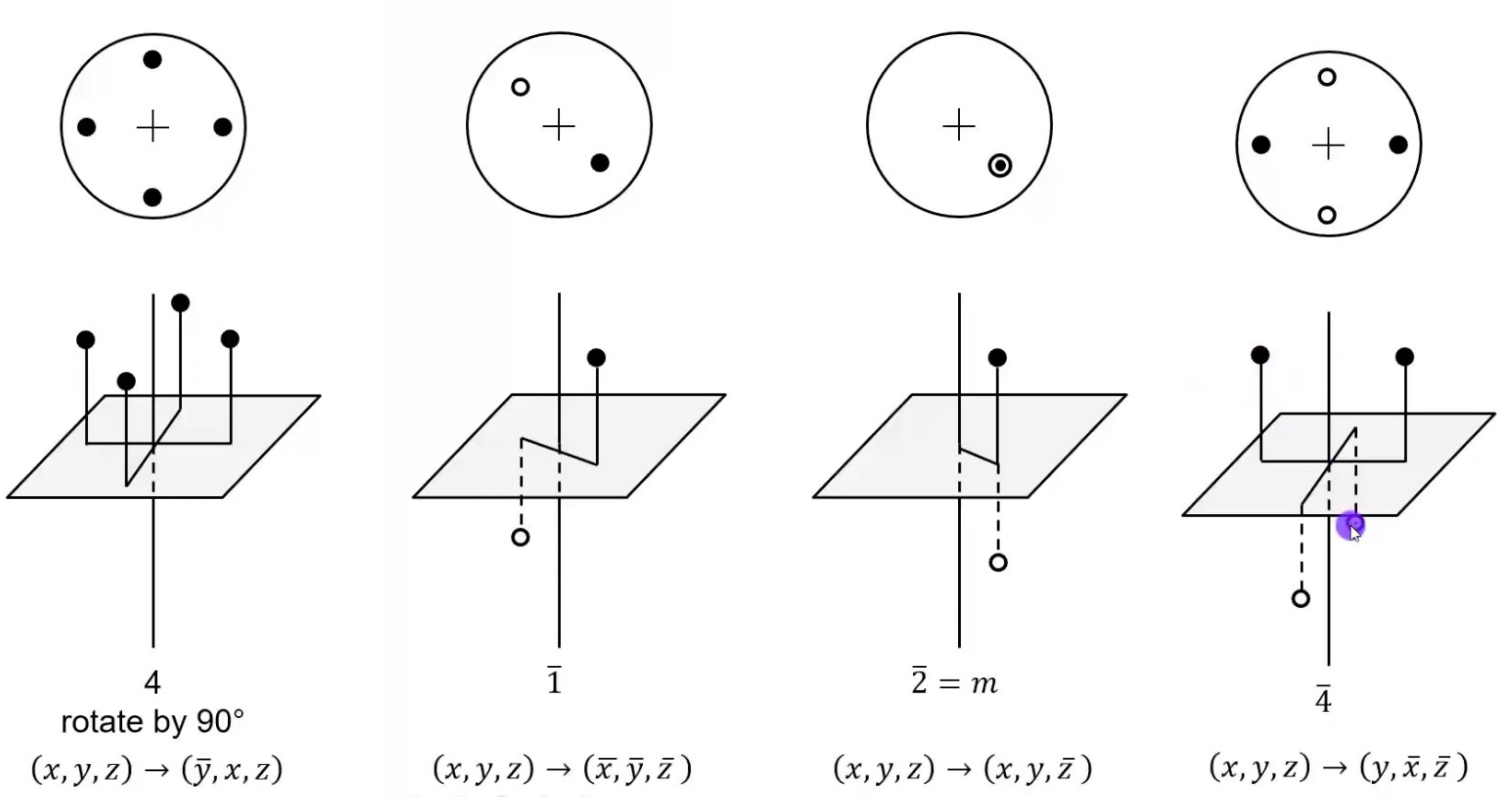
Symmetry Operations: Point symmetries

- **A symmetry operation** is an action that leaves an object unchanged.
- **Point symmetries** are operations that leaves at least one point of an object unchanged. The element unchanged (point, line, plane…) is called a **symmetry element**.
- There are different kinds of **Point symmetry operations** that can be reduced to the following:

  - **Identity (1)**
    - *Symmetry element*: entire object
  - **Inversion ($\bar{1}$)**
    - *Action*: inversion through a point
    - *Symmetry element*: a point
  - **Rotation (N)**
    - *Action*: N-fold rotation around an axis (360/N)
    - *Symmetry element*: a line
  - **Mirror plane or reflection (m)**
    - *Action*: Reflection through a plane
    - *Symmetry element:* a plane
  - **Roto-inversion ($\bar{N}$)**
    - *Action:* Rotation +Inversion
    - Symmetry element: a point

Symmetry Operations

- Exemples of symmetry operations in 3D:



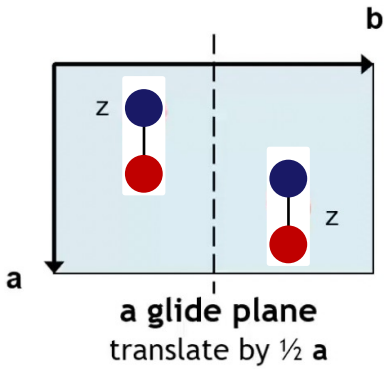
- In 2D:
  - A rotation is always around an axis perpandicular to the 2D plane, so an inversion is a rotation by 180°.
  - There is hence no roto-inversion, as they are just another rotation.

Symmetry Operations

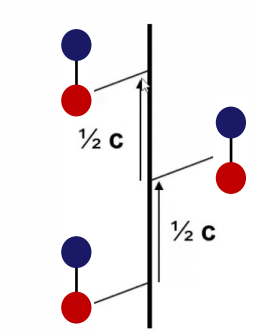
- The Bravais lattice is an infinite object with translational symmetry: this brings new symmetry operations that can leave no point unchanged !

- **Travel symmetry operations**:

  - **Glide plane**
    - *Action:* Reflect through a plane then translate parallel to it



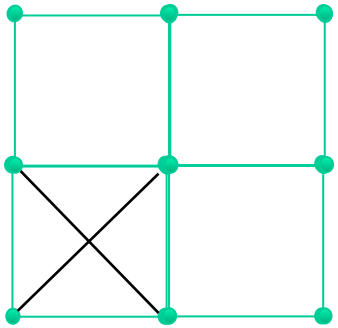
  - **Screw axis**
    - *Action*: Rotation by 360/N around an axis and translation along the axis

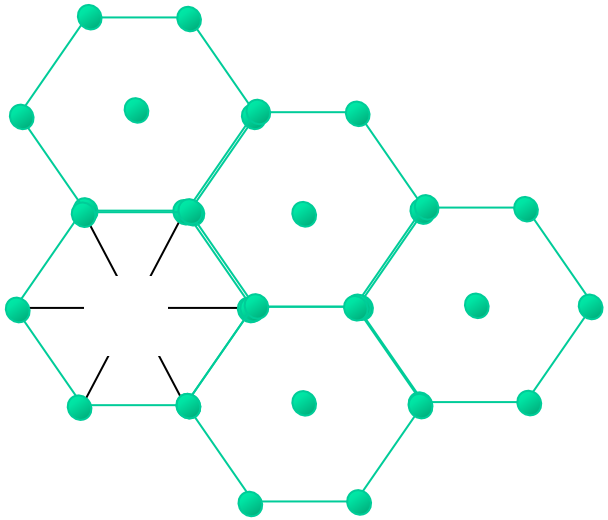


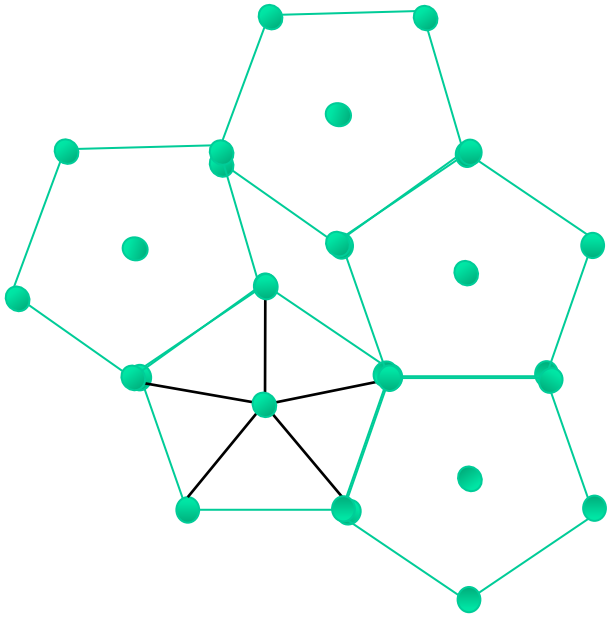
- In 2D:
  - There is only glide plane operations

Crystals and Symmetries

- There are an infinite possibilities of Bravais lattices as the lattice parameters (vector norms and angles) can be chosen arbitrarily.
- For certain values however, symmetries appear: why only certain rotations allowed ?
  - For discrete objects, rotational symmetries can only be discrete: $\frac{2\pi}{n}, n \in \mathbb{N}$
- Possible cells in 2D
  - Need to fill the space without void (translational symmetry of the Bravais Lattice);
  - This restricts the possible rotational symmetries.

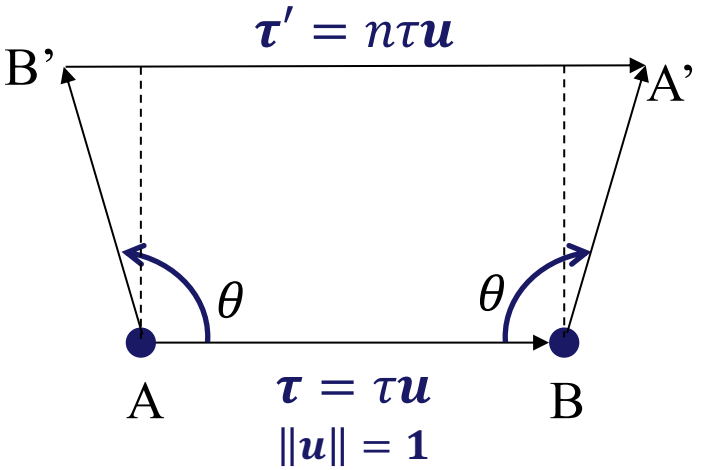






Possible Rotational Symmetries

- This fact reveals the interplay between translational symmetry and a rotational symmetry.
- For a rotational symmetry of angle θ to exist, translational symmetry indeed brings severe restrictions:



$$n\tau = \tau - 2\tau\cos(\theta), n \in \mathbb{Z}$$

Or: $n = 1 - 2\cos(\theta)$

$$\rightarrow \cos(\theta) = \frac{1-n}{2}$$

Which has real solutions only for: $n = -1, 0, 1, 2, 3$

With corresponding possible angles:

$$\frac{2\pi}{1}, \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}$$

- So, only 1-, 2-, 3-, 4- and 6-fold rotations are allowed.
  - 1-fold is the identity. Triclinic only has this symmetry (with an inversion symmetry ($\bar{1}$).
  - 6-fold only found in hexagonal structure;
  - 3-fold found in Trigonal and cubic;
  - 4-fold found in tetragonal and square;
  - 2-fold is found in all structures except Triclinic.

Building Point Groups

- Point groups: a set of point symmetries that apply to a given object, the motif or the lattice, that form a group.

- In crystallography, we will only look for point groups with the restricted rotational symmetries.

- A *Group* is a set G which is **closed under an operation** $*$ (that is, for any x, y $\in$ G, x $*$ y $\in$ G) and satisfies the following properties:

- Identity (fixed point) – There is an element e in G, such that for every x $\in$ G, e $*$ x = x $*$ e = x
- Inverse – For every x in G there is an element y $\in$ G such that x $*$ y = y $*$ x = e
- Associativity – The following identity holds for every x, y, z $\in$ G: x $*$ (y $*$ z) = (x $*$ y) $*$ z

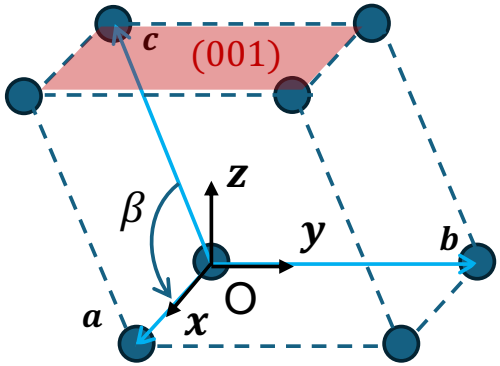
- Point Group Symmetry
  - Closure: The combination of symmetry operators is a symmetry operator in the group.
  - All symmetry operators have an inverse, some are their own inverse.
  - Identity is part of all the Point group symmetry.
  - Associativity is respected

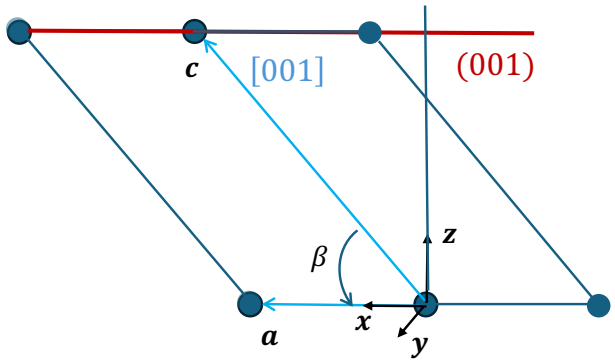
- Examples: Can we create a point group with the 2-fold or 4-fold rotation ?
  - Point Group 2
    - It contains the identity (1 - 2π rotation) and the 2-fold rotation 2.
    - The 2-fold identity is its on inverse: $2o2 = 1$

  - Point Group 4

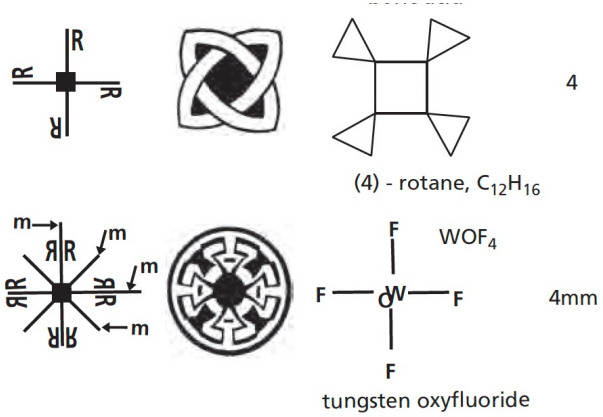
Building Point Groups

- Let's consider the Monoclinic structure and build a point symmetry group for this discrete object.
- We can visualize a group called 2/m (see exercise for solving this with





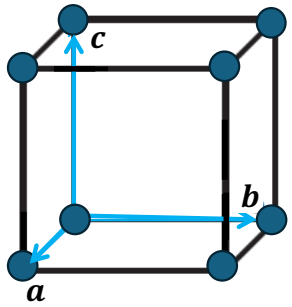
- Another example are the Group 4 in 2D



- A motif with a 4-fold symmetry doesn't have necessarily a mirror symmetry
- A motif with a 4-fold symmetry plus mirror symmetries, with some planes perpendicular.

Point Groups

- Examples: point group of the cube.



- A cube, or a motif formed by four points at the corners, have the highest symmetry, with a point group of order 48, i.e. with 48 symmetries.
- Order of a group: its cardinal, or number of elements in the group.

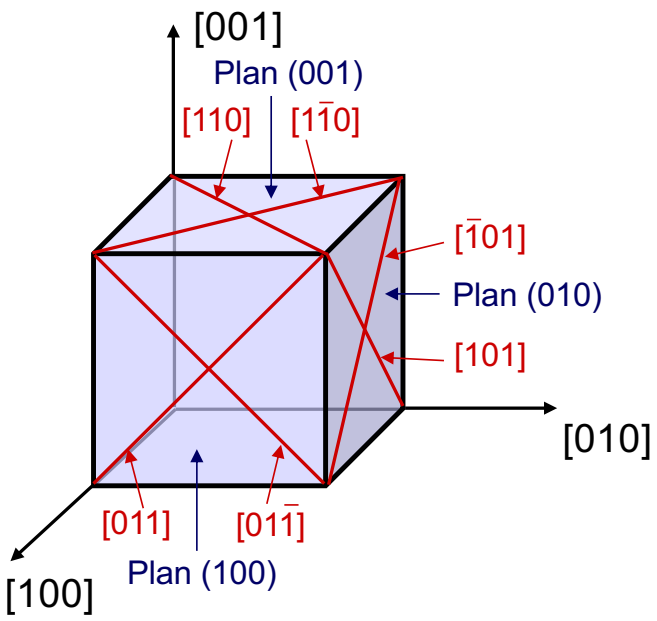
Symmetry operations

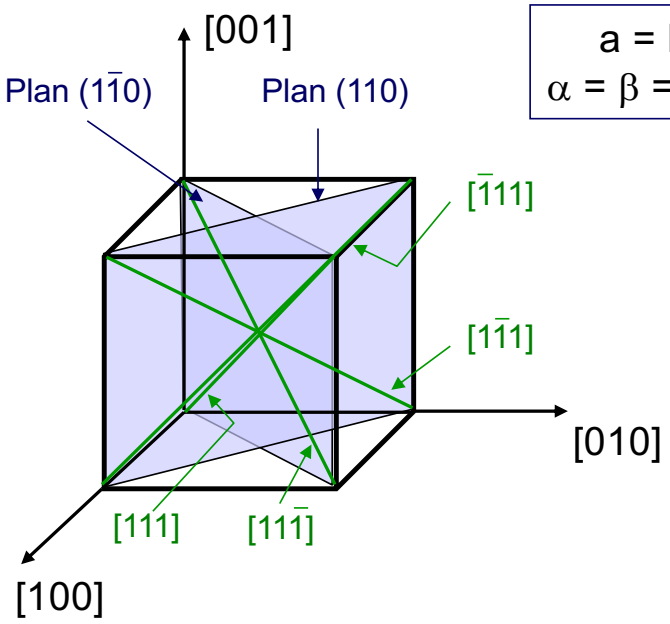
(1) 1	(2) $2\ \ 0,0,z$	(3) $2\ \ 0,y,0$	(4) $2\ \ x,0,0$
(5) $3^+\ x,x,x$	(6) $3^+\ \bar{x},x,\bar{x}$	(7) $3^+\ x,\bar{x},\bar{x}$	(8) $3^+\ \bar{x},\bar{x},x$
(9) $3^-\ x,x,x$	(10) $3^-\ x,\bar{x},\bar{x}$	(11) $3^-\ \bar{x},\bar{x},x$	(12) $3^-\ \bar{x},x,\bar{x}$
(13) $2\ \ x,x,0$	(14) $2\ \ x,\bar{x},0$	(15) $4^-\ 0,0,z$	(16) $4^+\ 0,0,z$
(17) $4^-\ x,0,0$	(18) $2\ \ 0,y,y$	(19) $2\ \ 0,y,\bar{y}$	(20) $4^+\ x,0,0$
(21) $4^+\ 0,y,0$	(22) $2\ \ x,0,x$	(23) $4^-\ 0,y,0$	(24) $2\ \ \bar{x},0,x$
(25) $\bar{1}\ \ 0,0,0$	(26) $m\ \ x,y,0$	(27) $m\ \ x,0,z$	(28) $m\ \ 0,y,z$
(29) $\bar{3}^+\ x,x,x;\ 0,0,0$	(30) $\bar{3}^+\ \bar{x},x,\bar{x};\ 0,0,0$	(31) $\bar{3}^+\ x,\bar{x},\bar{x};\ 0,0,0$	(32) $\bar{3}^+\ \bar{x},\bar{x},x;\ 0,0,0$
(33) $\bar{3}^-\ x,x,x;\ 0,0,0$	(34) $\bar{3}^-\ x,\bar{x},\bar{x};\ 0,0,0$	(35) $\bar{3}^-\ \bar{x},\bar{x},x;\ 0,0,0$	(36) $\bar{3}^-\ \bar{x},x,\bar{x};\ 0,0,0$
(37) $m\ \ x,\bar{x},z$	(38) $m\ \ x,x,z$	(39) $\bar{4}^-\ 0,0,z;\ 0,0,0$	(40) $\bar{4}^+\ 0,0,z;\ 0,0,0$
(41) $\bar{4}^-\ x,0,0;\ 0,0,0$	(42) $m\ \ x,y,\bar{y}$	(43) $m\ \ x,y,y$	(44) $\bar{4}^+\ x,0,0;\ 0,0,0$
(45) $\bar{4}^+\ 0,y,0;\ 0,0,0$	(46) $m\ \ \bar{x},y,x$	(47) $\bar{4}^-\ 0,y,0;\ 0,0,0$	(48) $m\ \ x,y,x$

- The n-fold rotations have the coordinates of the rotation axis.
- The mirror symmetry (m) have the plane of symmetry indicated.
- We see the presence of roto-inversion symmetries.

Miller Indices and Symmetries

- The point groups shows have all the symmetries around axis we described before (see next slide). Many other elements are present that ensures the closure property of the group.
  - 1 and $\bar{1}$
  - The counter clockwise 3 and 4-fold
  - The roto-inversion $\bar{3}$ and $\bar{4}$ (not $\bar{2}$ because it is equivalent to a mirror symmetry)
  - 2-fold symmetries around the edges that are the composition of two 4-fold symmetries.





a = b = c
$\alpha = \beta = \gamma = 90°$

3 directions <100>, symmetry 4
6 directions <110>, symmetry 2
3 plans {100} of symmetry

4 directions <111>, symmetry 3
6 plans {110} of symmetry

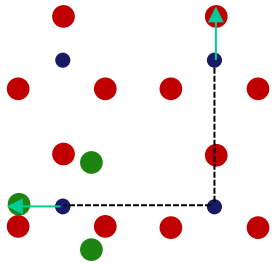
Crystals and Symmetries

- Each point group must be associated to a certain Bravais Lattice, but all kind of new symmetries can come from merging a Motif in a Lattice

Crystal System	Lattice	Required symmetry	Point groups
Cubic	Cubic	3-fold axes along body diagonals	23, $m\bar{3}$, $\bar{4}3m$, 432, $m\bar{3}m$
Tetragonal	Tetragonal	4-fold axis	4, $\bar{4}$, $4/m$, 422, $4mm$, $\bar{4}m2$, $4/mmm$
Hexagonal	Hexagonal	6-fold axis	6, $\bar{6}$, $6/m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$
Trigonal	Hexagonal or Rhombohedral	3-fold axis	3, $\bar{3}$, 32, $3m$, $\bar{3}m$
Orthorhombic	Orthorhombic	Three mutually perpendicular 2-fold axes or mirror planes	222, $2mm$, mmm
Monoclinic	Monoclinic	2-fold axis or mirror plane	2, m, $2/m$
Triclinic	Triclinic	none	1, $\bar{1}$

Point Groups

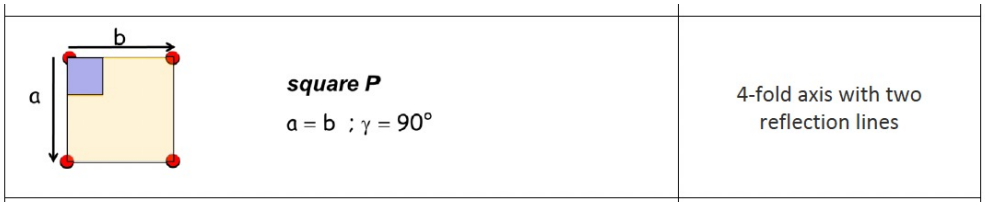
- Considering now the lattice and the motif together, new restrictions appears when looking at the symmetry of the crystal.
- Since we are limited to 1,2,3,4 and 6 fold rotations because of translational symmetry, we will not be able to construct a crystal with a motif that has a different rotational symmetry element.

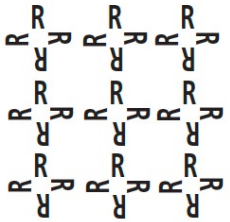


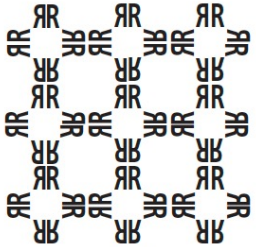
- When we want to merge the symmetry of the motif and the one of the Bravais lattice, restrictions occur and the symmetry of the crystal will result of this analysis.
  - The rotational symmetry of the motif must coincide with the one of the Lattice;
  - So each point group can be associated to a certain Bravais Lattice, but all kind of new symmetries can come from merging a Motif in a Lattice.

Symmetries in 2D: Plane Groups

- Exemple: 4 fold symmetry will only be associated to the square lattice.

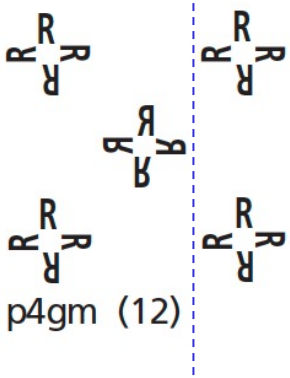



p4 (10)


p4mm (11)

- One could think that there is only 2 plane groups (like space groups but in 2D) associated with the 2 point groups noted 4 and 4mm.

- There is however a third one ! Associated to a glide plane symmetry noted g.
- Adding glide and screw symmetries create a new class of group of symmetries called space group in 3D.


p4gm (12)

Symmetries in 3D: Space Groups

- The construction of the space groups associated to the 3D 14 Bravais lattices, from the 32 3D point groups, proceed similarly, with noticeable differences:
  - 3D has 32 point groups and not 10, because of extra possible symmetry operations: inversion and roto-inversion.
  - For glide planes, the glide can happens along different directions in 3D;
  - Screw axis operations also occur: n_m is a n-fold rotation followed by a translation

- The first letter is a capital letter indicating the Bravais lattice, and many different types occur: P, I, F, and other letters depending on the base-centered plane.

- Glides bring several new types of symmetries and notations:
  - a,b,c: glide translation along half the lattice vector of this face;
  - N,d: glide translation along half and a quarter respectively, along the face diagonal
  - e: two glides with the same glide plane and translation along two half-lattice vectors.

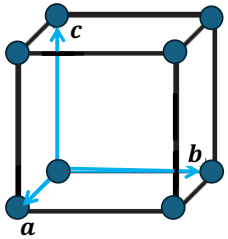
- There are 230 space groups that can be built from the 32 point group in 3D.

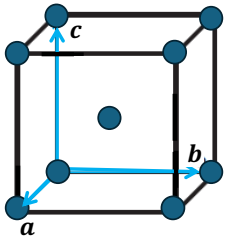
- A list of all the space groups can be found here: https://en.wikipedia.org/wiki/List_of_space_groups

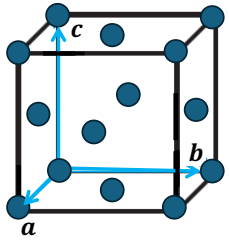
- A more concise one: https://en.wikipedia.org/wiki/Space_group

- You can find them all here: https://onlinelibrary.wiley.com/iucr/itc/Ac/contents/

Symmetries in 3D: Space Groups

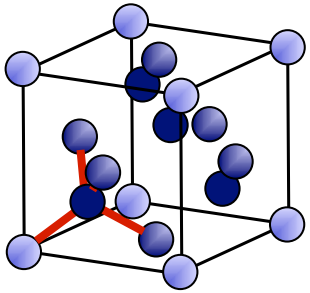






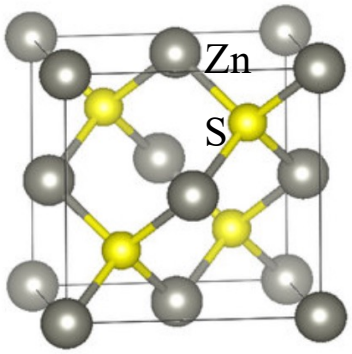
- For the cubic Bravais Lattice, the BCC and FCC structures add atoms that do not change the symmetry operations !
- Space groups are then $P4/m\bar{3}2/m$, $\mathrm{I}4/m\bar{3}2/m$ and $\mathrm{F}4/m\bar{3}2/m$ respectively.
  - Example: let's look at $\mathrm{F}4/m\bar{3}2/m$ (#225)

- What happens when we change the motif ? Diamond structure:



  - The extra atom in this case changes the possible symmetries
  - Space group: $\mathrm{Fd}\bar{3}m$ (#227): apparition of a glide symmetry.
  - Also highly symmetric, order of the group 48 !

- As the motif looses symmetry, the symmetry of the resulting crystal tends to be lower.
  - Space group $\mathrm{F}\bar{4}3m$ (#216): less symmetries ! Order of the group 24

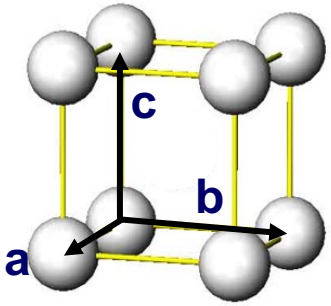


The cubic system

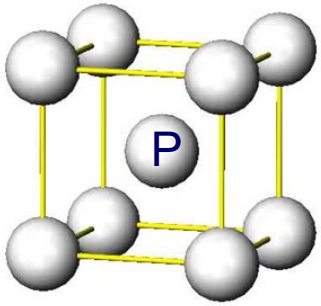
- Symmetry is an important way to approach the crystalline state. However, it is equally important and very useful to describe crystals in a more geometric way.
- This approach leads to deeper understanding of crystal orientations, X-ray diffractions and reciprocal spaces.
- To represent crystals, we use different types of unit cells. The conventional unit cell is the most commonly used as it exhibits the symmetry of the crystal. They can however contain several motifs.
- Primitive unit cells are cells with one motif.

- In this approach, number theory and Euclidean geometry find profound usefulness.

- (**a**,**b**,**c**) is not a basis for the BCC, as P has the coordinates (½, ½, ½).



Primitive cubic
basis: (**a**,**b**,**c**)



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

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

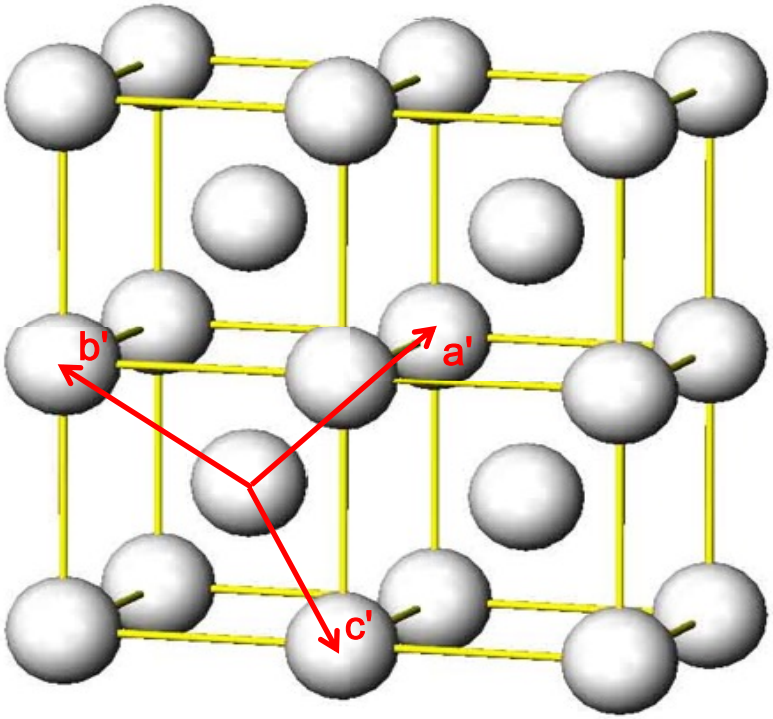
$$\vec{c}' = \frac{1}{2}(\vec{a} + \vec{b} - \vec{c})$$

Body-centered cubic
basis: (**a'**,**b'**,**c'**)

The cubic system

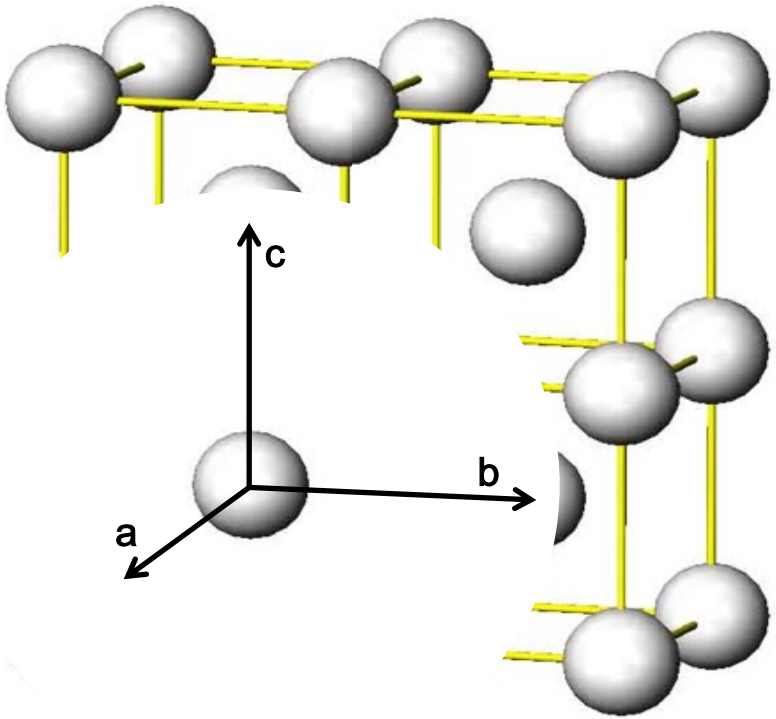
Primitive cell

- Find the motif;
- Translate it along the BCC lattice;



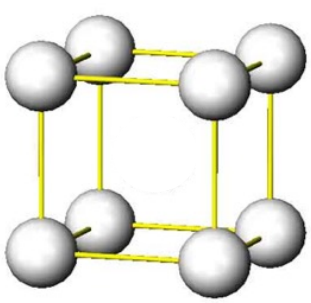
Conventionnal cell

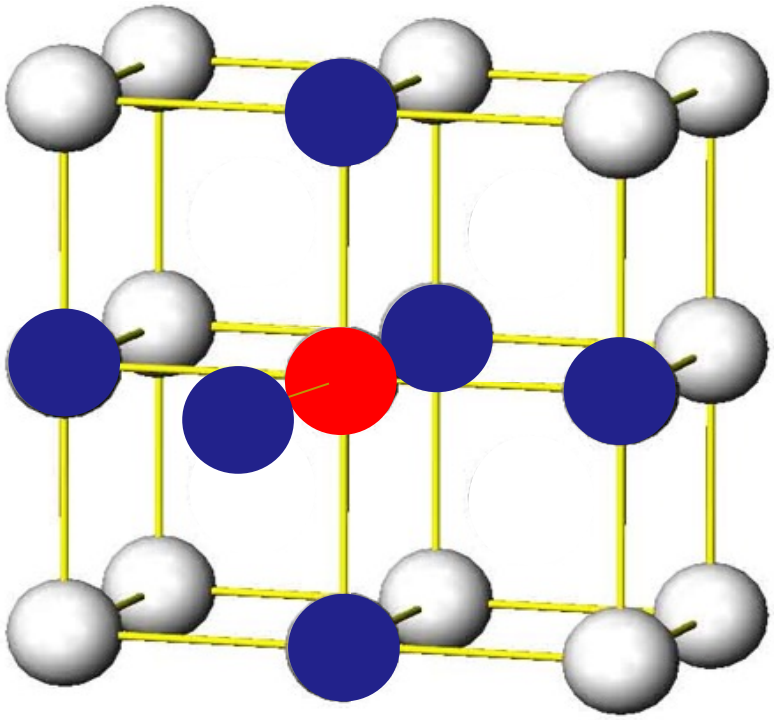
- Find the motif;
- Place it within the Conventional cell;
- Translate the cell along the orthonormal basis **a**, **b** and **c** of the cubic system;



Coordination

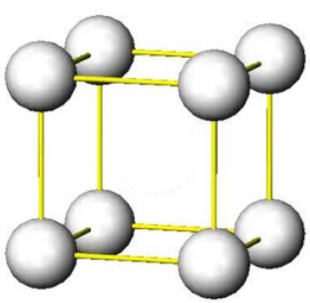
- One can represent atoms as rigid spheres to give some insights about the atomic arrangement and resulting properties.
- A first important notion is the coordination number: number of closest neighbors, ie when spheres are in contact.
- For primitive cubic:





Coordination

- Coordination number:



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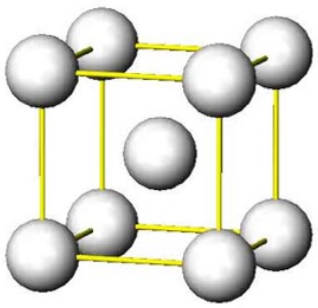

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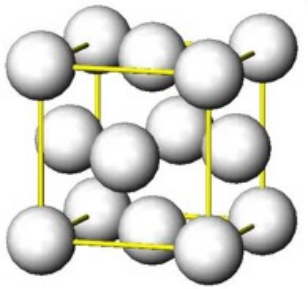
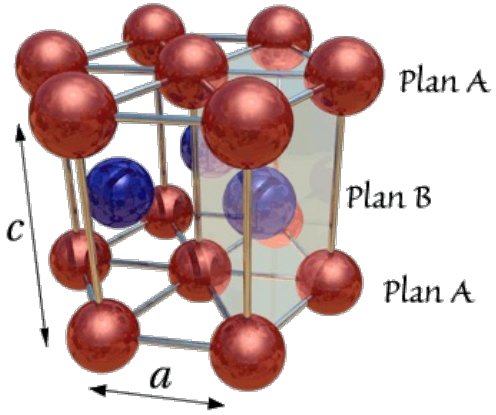


12

- Close-packed planes



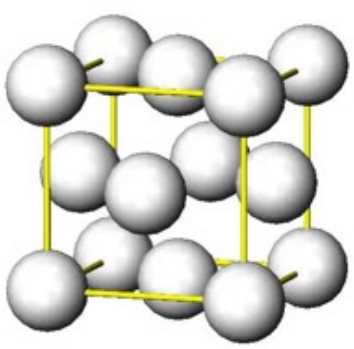
Hexagonal close-packed :

-Coordination: 12

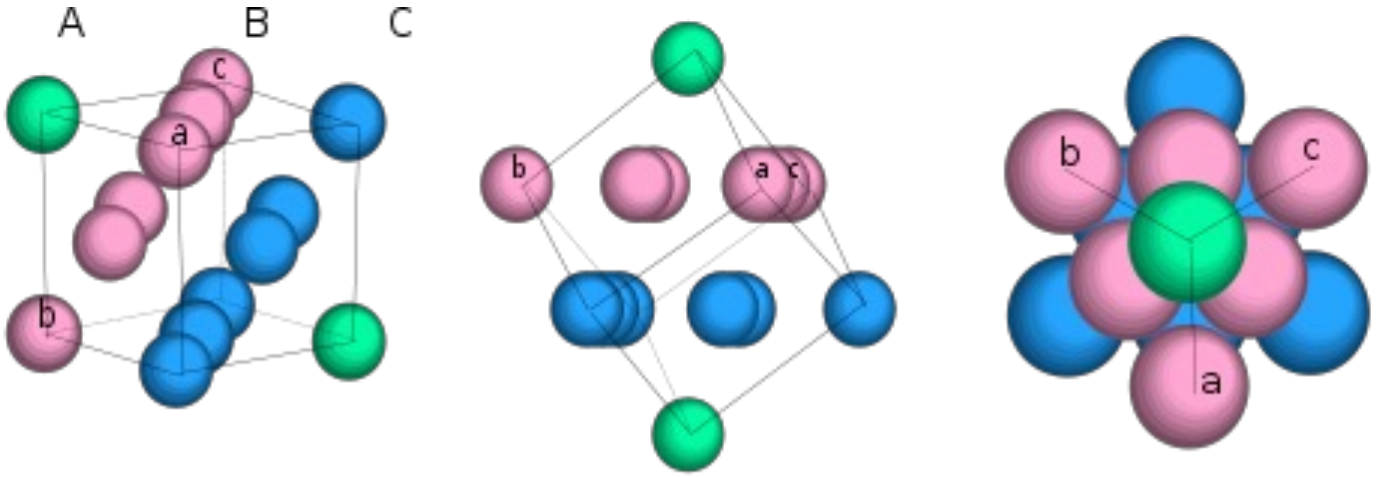
-Close-packed plans are the (1000)

Coordination

- Face-centered Cubic:



- Coordination: 12
- Close-packed plans (111)

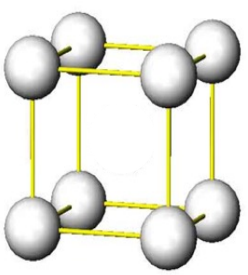


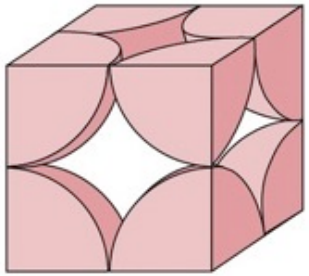
Empilement compact Cubique Faces Centrées
(cubic close- pack CCP, ABC)

Number of atoms per unit cell

- Primitive cubic:

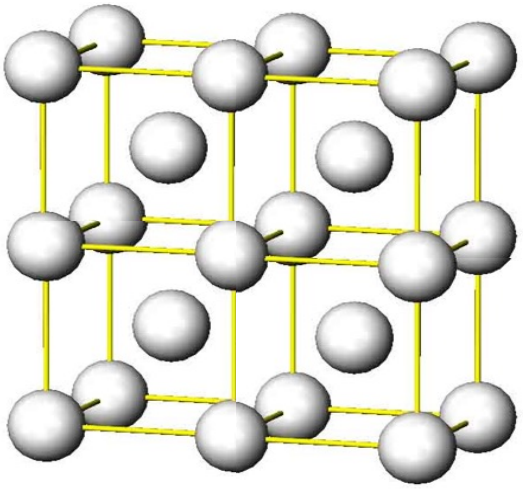
  - Motifs at the corners of the cube count for 1/8
  - The primitive cell has as expected 1 motif.





- Body-centered conventional cell:

  - Motifs at the corners of the cube count for 1/8
  - The motif inside the cell count for 1.
  - Hence the BCC conventional unit cell has 2 motifs.



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.

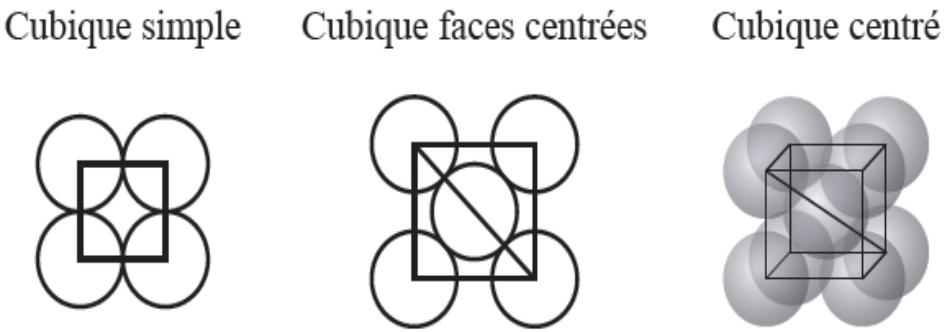
- Density: $\rho = \frac{N_{atoms\ per\ unit\ cell} \times m_{atoms}}{V_{unit\ cell}}$

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

-Packing fraction:

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

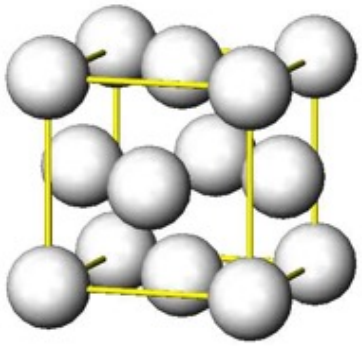
-Direction and planes of high density



Structure of Metals

- Most metals crystalize in the BCC or FCC structure:

Face-centered Cubic (FCC)

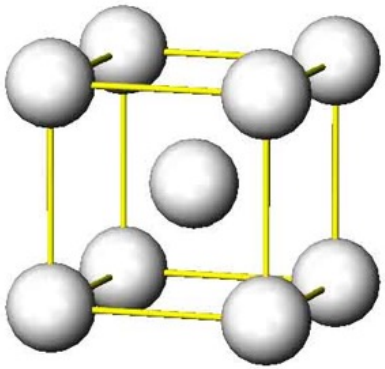


Al – Cu – Ni – Ag – Au – Fe …

Free volume : **26%**

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

Body-centered Cubic (BCC)



Cr – Fe – Mo – V – W – Ta …

Fe:	bcc	for T > 1403ºC and T < 910ºC
	fcc	for 910ºC < T < 1403ºC

Free volume : **32%**

SUMMARY

- We introduced the basic notions of groups and rings, the foundation onto which number manipulations relies.
- We reviewed some basic concepts of symmetry in crystals;
- We defined and gave examples of point group symmetries.
- We introduced other notions of crystallography that will be useful for the rest of the class.
- Next week
  - We will remind the concepts of divisibility and prime numbers in the context of crystallography
  - We continue reviewing the foundation by discussing fields and vector spaces;
  - We will then derive important results regarding the cubic structure of materials using prime numbers and basic geometry calculations.