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Lecture course on crystallography, 2015

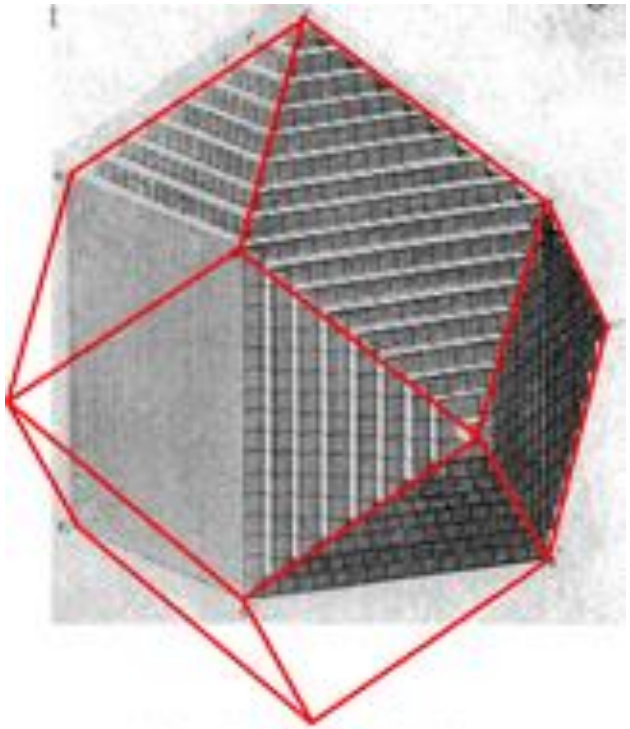
Lecture 2: Periodicity of crystal structures

The differences between crystalline (crystals) and amorphous (glasses) solids

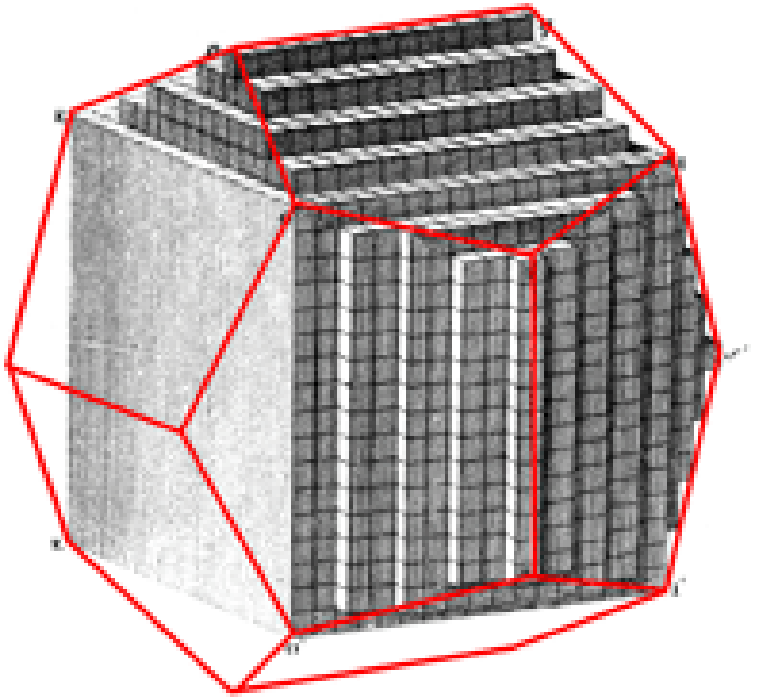
	Crystalline solids (Crystals)	Amorphous solids (Glasses)
Shape	**Polyhedral shape with naturally formed faces**	**No naturally formed faces**
Properties	**Anisotropic**	**Isotropic**
Atomic structure	**Periodic (long range ordered)**	**No periodicity. Short-order only**
X-ray Diffraction	**Well separated diffraction picture with DISTINCT spots**	**No clearly separated features**

The graphical illustration of the law of rational indices

Original idea: the crystal is formed by pilling up the ***elementary blocks*** (for example cubes or parallelopipeds). The formation of natural faces are shown below



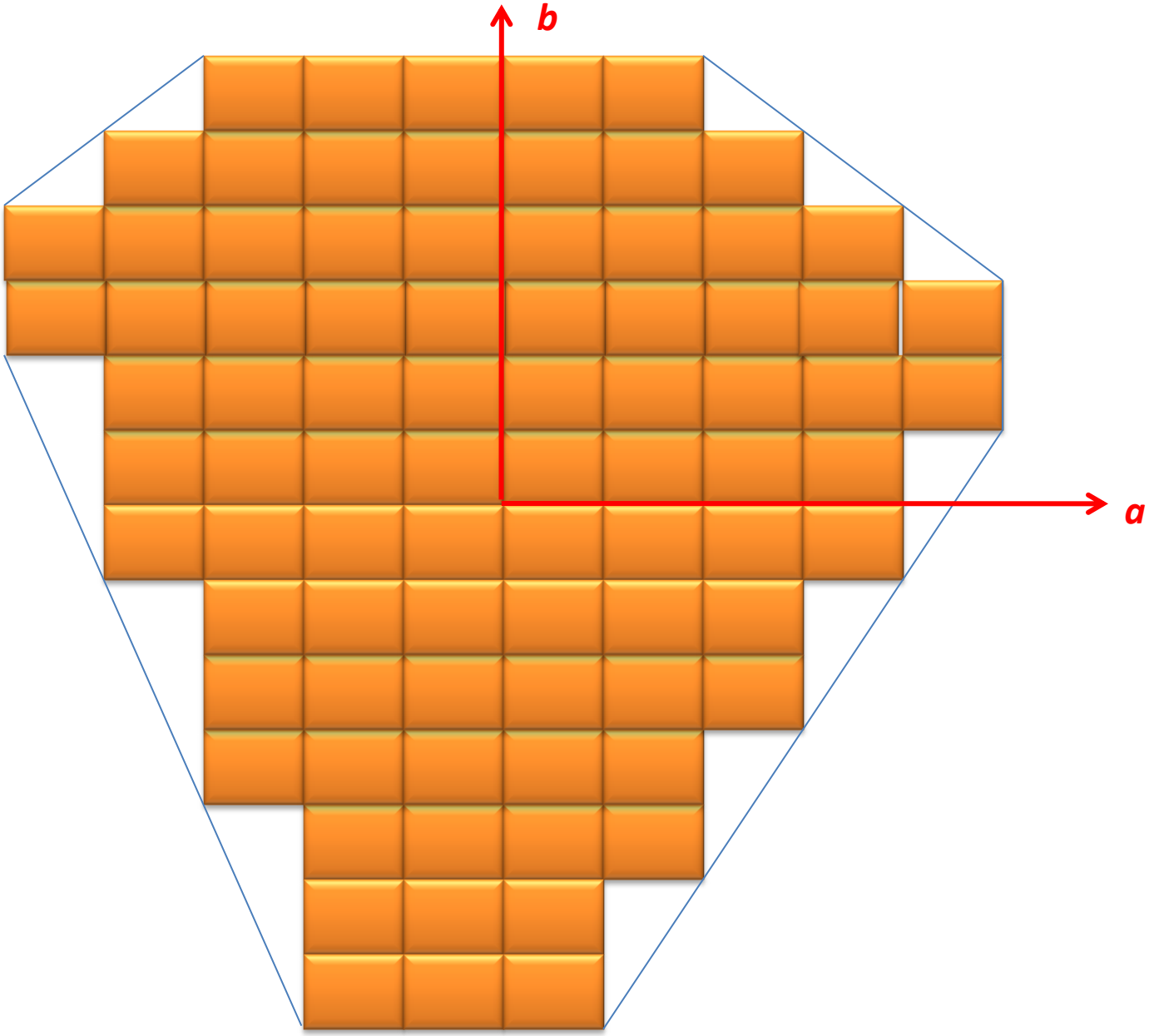
Rhomb-dodecahedron



Pentagon-dodecahedron

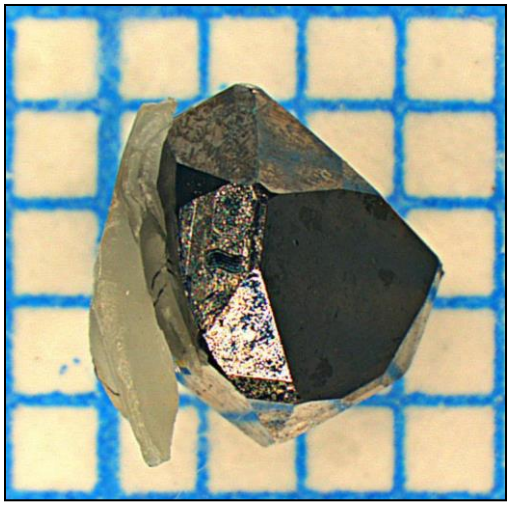
Models from Haüy's *Traité de Minéralogie* (1801)

The graphical illustration of the law of rational indices

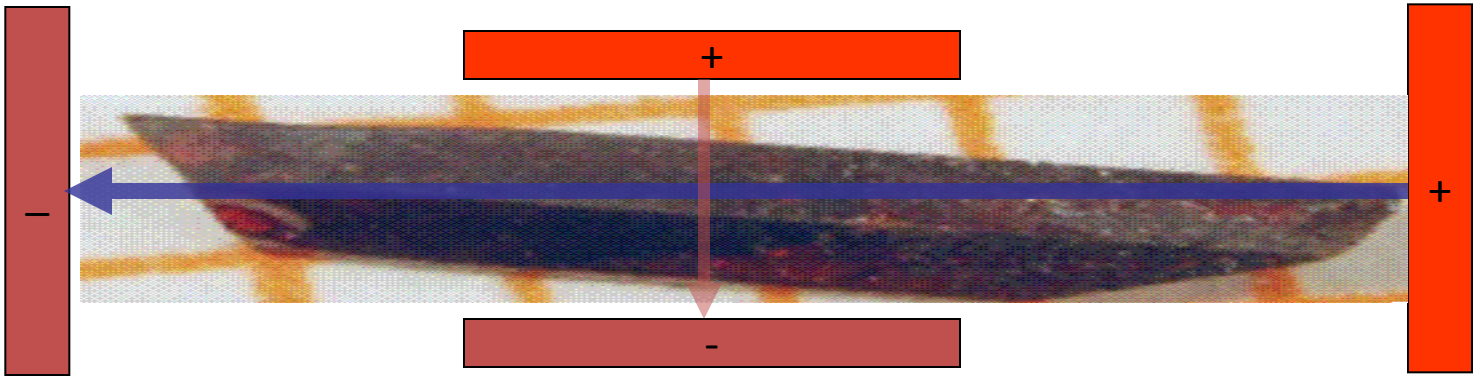


Anisotropy of physical properties

1. Growth velocity (formation of facets)



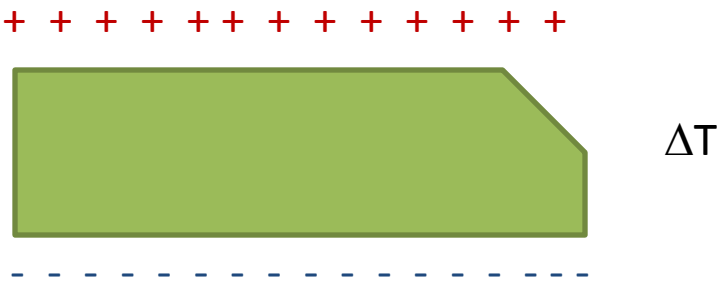
2. Electrical conductivity



Physical properties of crystals: pyroelectric effect in tourmaline

Pyroelectricity is the separation of the electric charges in a crystal by the change of temperature

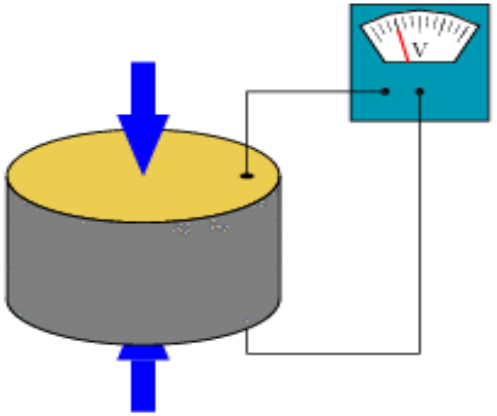
Tourmaline crystal



Important: pyroelectric effect is anisotropic, electrical charges develop only in certain directions, i.e. on the certain faces of a crystal.

Further studies of physical properties of crystals. Pierre Curie (1859-1906)

Discovery of piezoelectricity in QUARTZ

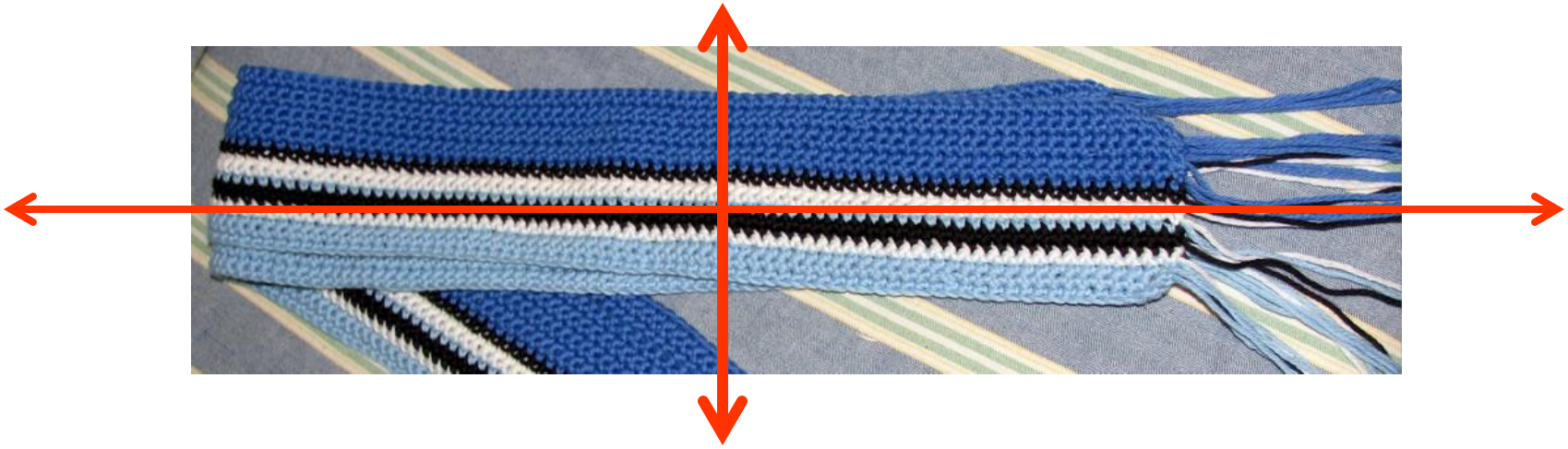


Piezoelectricity is a physical phenomena occurring in some crystals, related to the generation of electric charges by external pressure.

General for crystals – ANISOTROPY of PHYSICAL properties

"Life" example of anisotropic physical properties

Cutting a scarf is a typical example of the *directional* dependence



The reason for that is the special STRUCTURE made by the stitching

BONDS

Hypothesis of Pierre Curie – anisotropy of crystals is due to the periodic structure

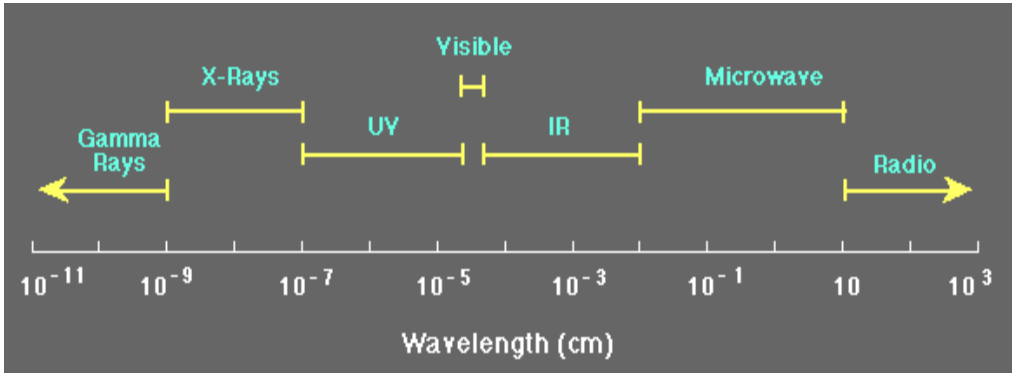
X-ray Crystallography -> birth of solid state physics

1912 **Max von Laue**

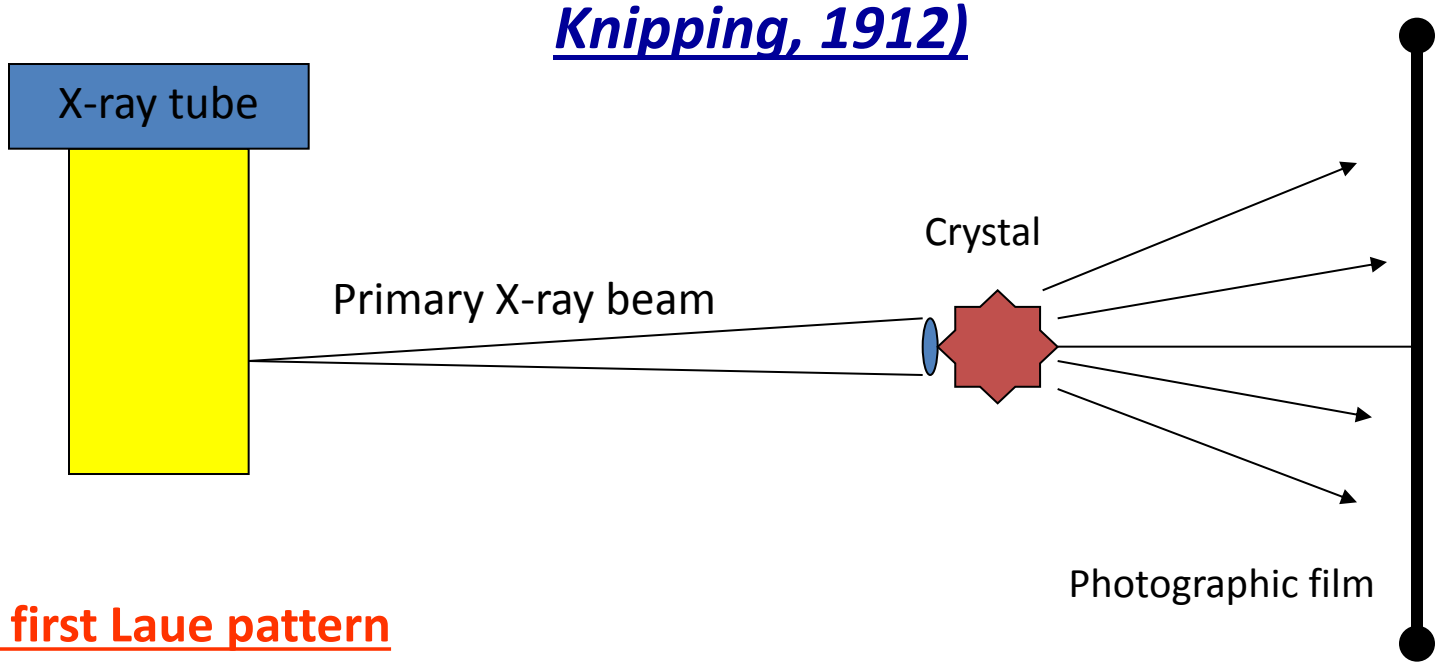
1914

Nobel prize in physics

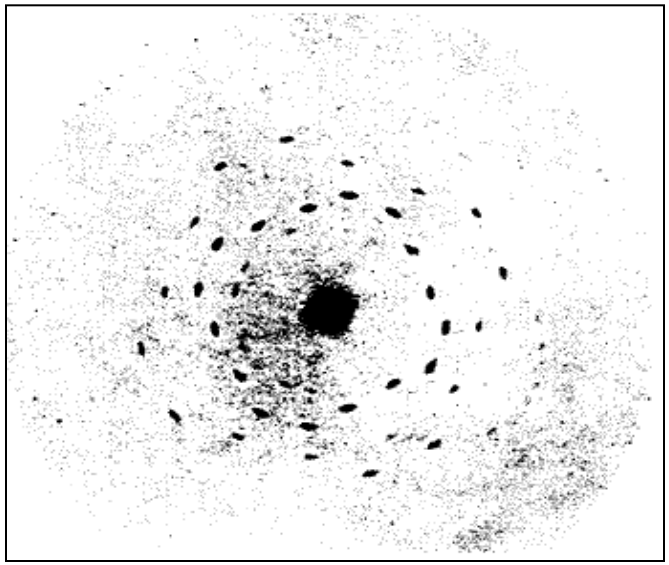
"for his discovery of the diffraction of X-rays by crystals"



Discovery of X-ray diffraction (Max von Laue, Friedrich, Knipping, 1912)



The first Laue pattern



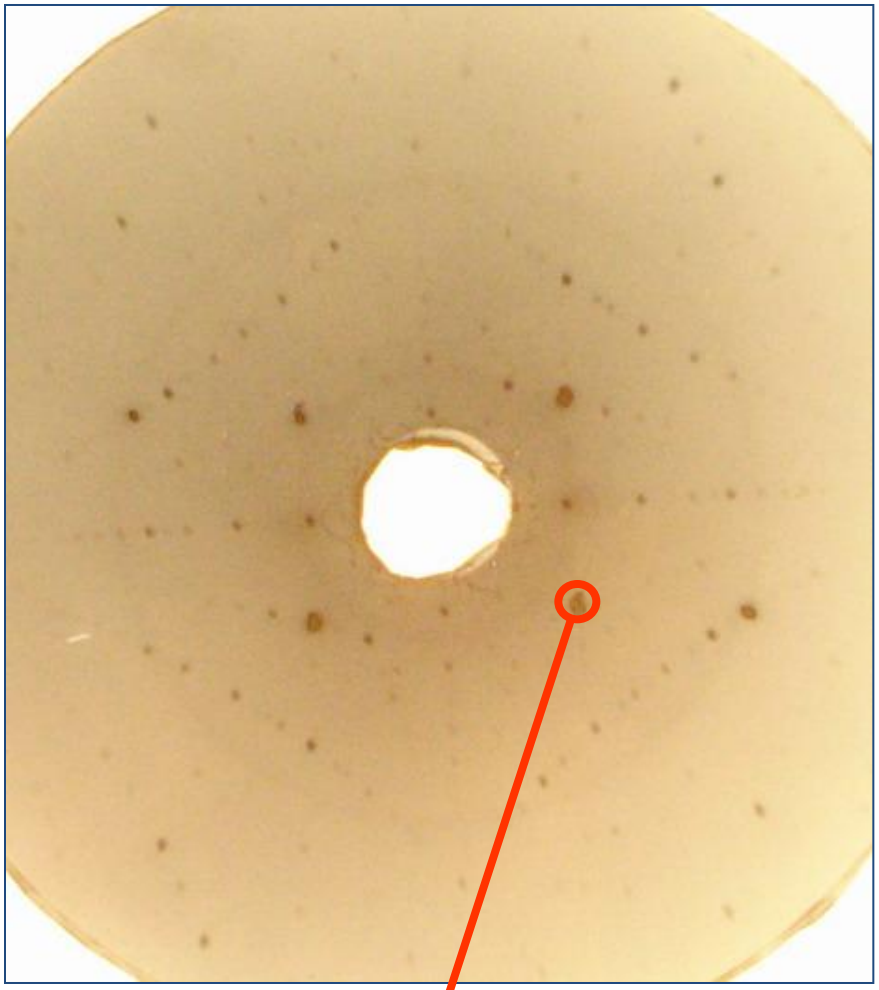
Conclusions

1. X-rays are electromagnetic waves

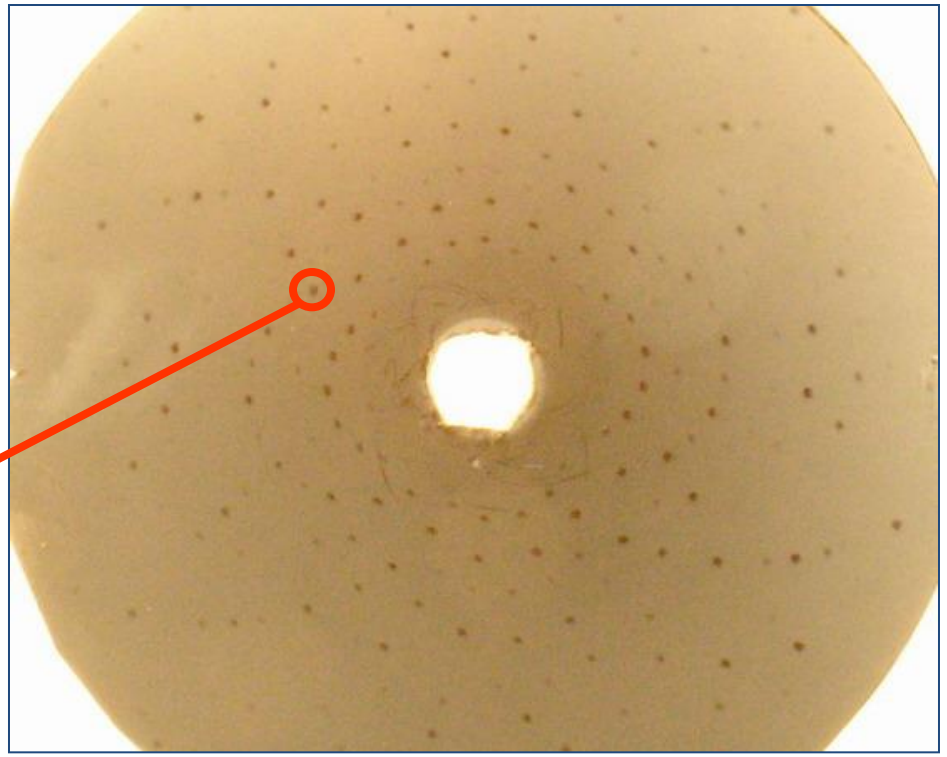
2. Crystal structures are periodic

3. The period of crystal lattice has the order of the wavelength of X-rays

Laue diffraction patterns



α-Quartz crystals (SiO_2)



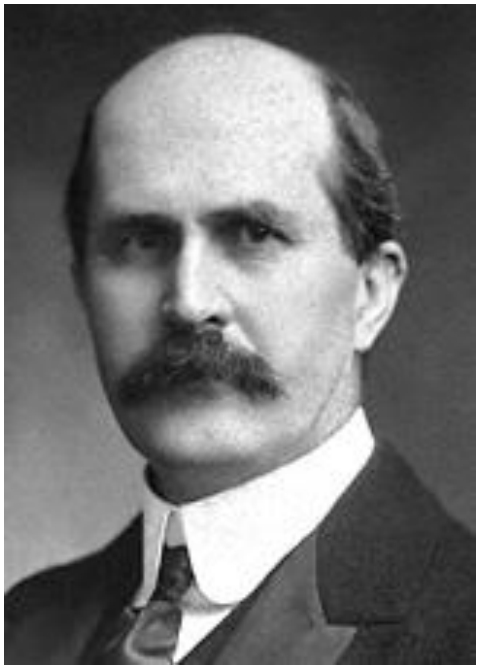
Bragg peaks

The first REAL crystal structure

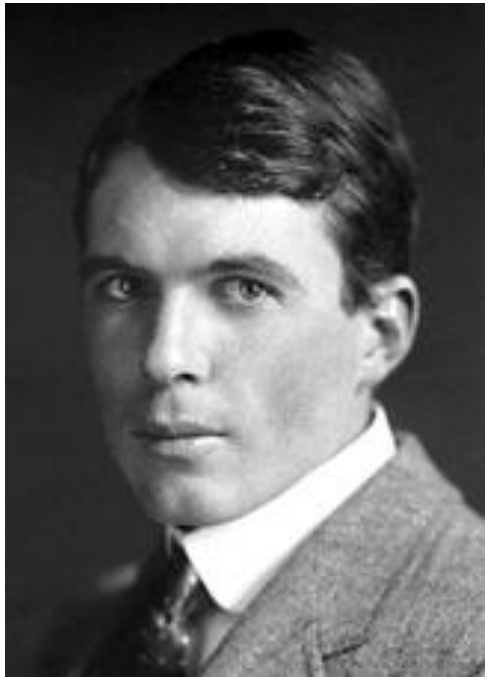
1915

Nobel prize in physics

"for their services in the analysis of crystal structures be means of X-rays "

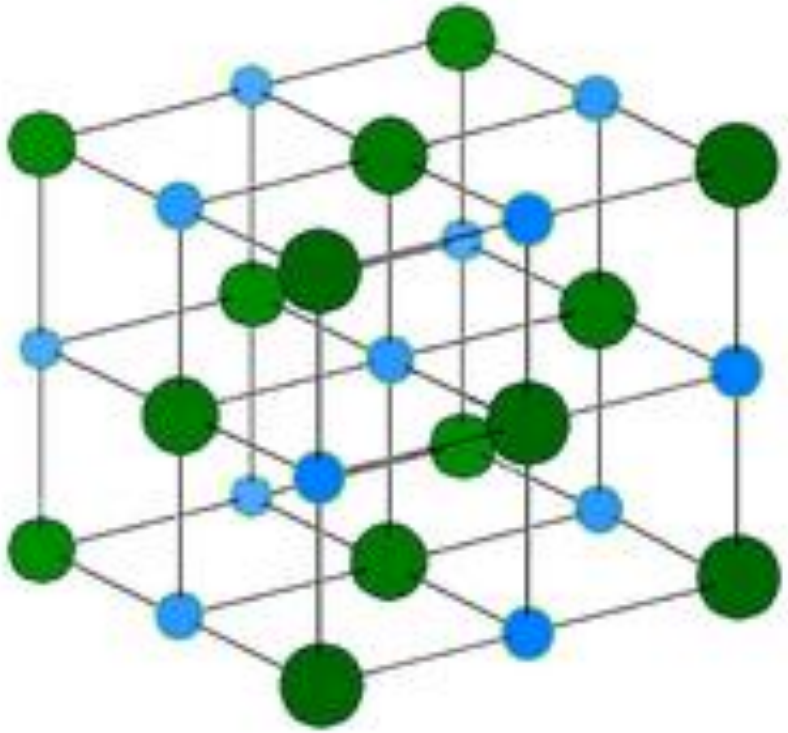


Sir William Henry Bragg



William Lawrence Bragg

Atomic structure of NaCl, KCl, LiF was established



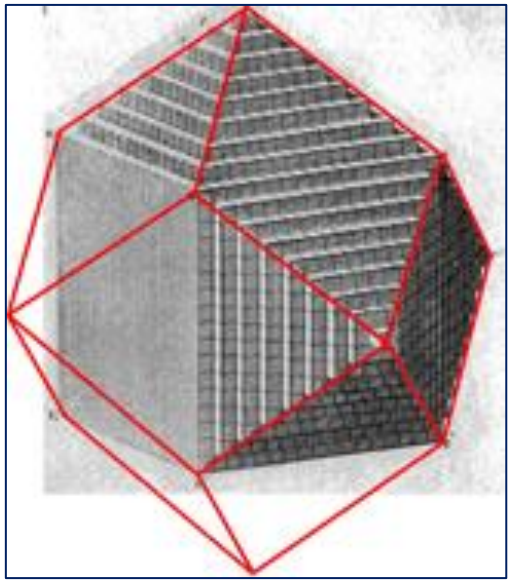
The discovery of X-ray diffraction by Max von Laue (1912) is the final and ultimate proof of the periodic structure of crystals. Moreover it was shown that the period of a crystal structure has the order of *Å* = 10^{-10} *m*

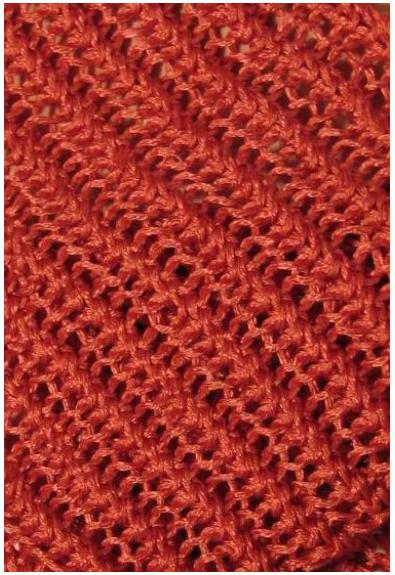
The works of W.H. Bragg and W.L.Bragg allowed to establish the first crystal structures, i.e. the real arrangement of atoms in a crystal

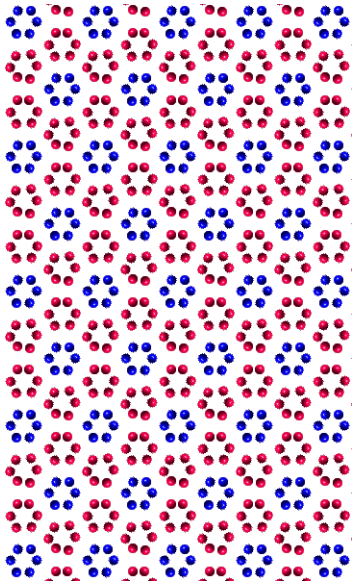
Nowadays X-ray diffraction is the main tool for the solving, determination and characterization of crystal structures

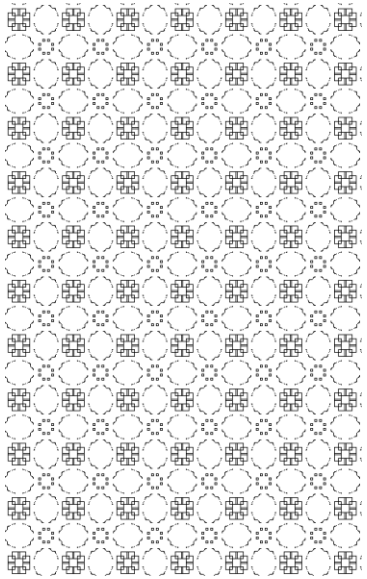
The concept of long-range order

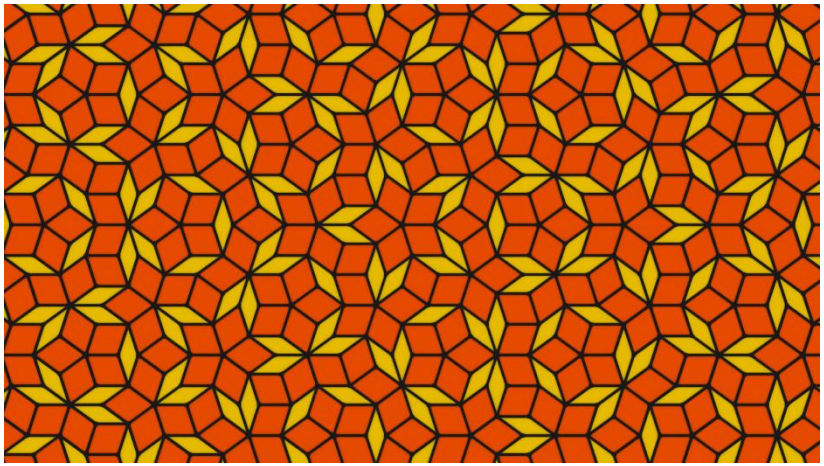
Long-range order is the geometrical law of expansion maintained over long (in comparison to interatomic) distances!





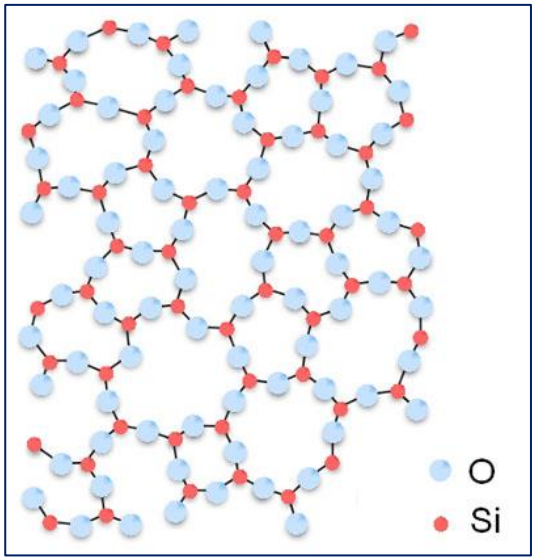


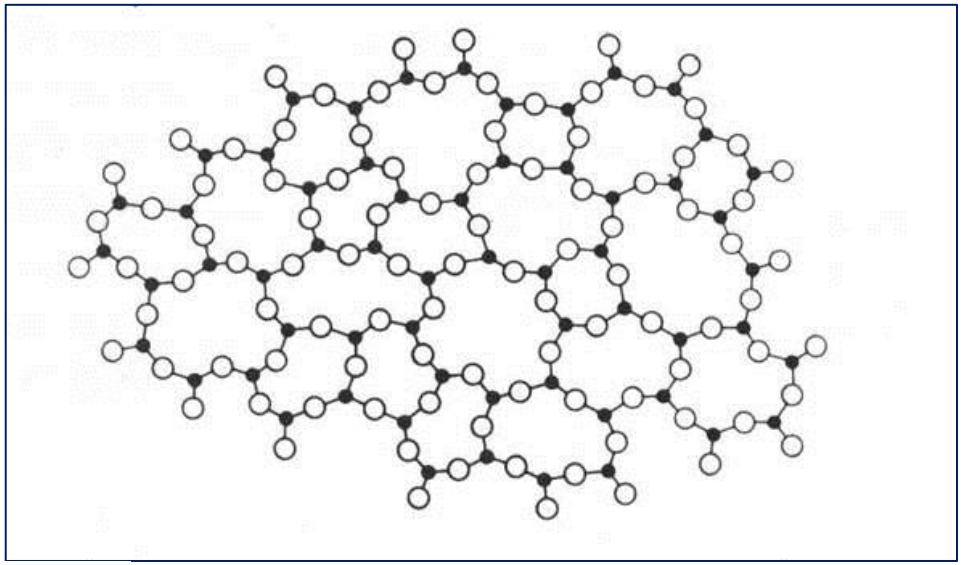


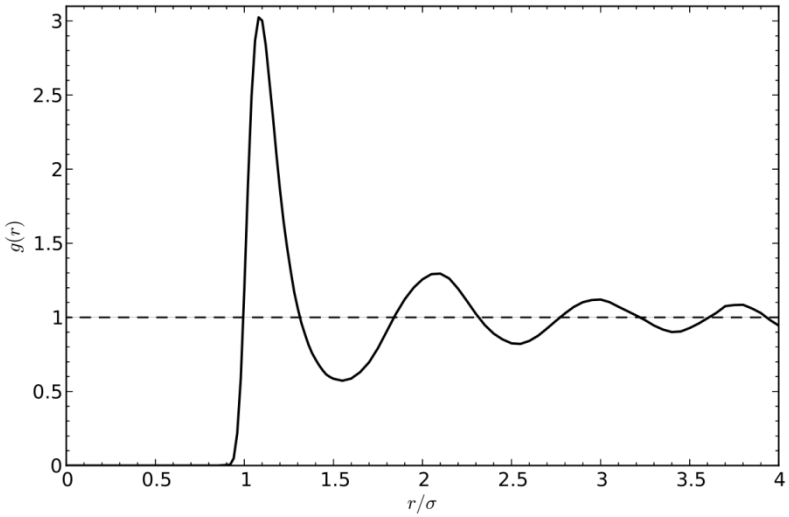


The concept of short-range order

Short-range order is the geometrical law of expansion maintained over short distances only







The structures of amorphous solids and liquids are commonly described by probability laws, based on the so-called radial distribution functions and pair-distribution functions (PDFs).

CRYSTAL: Official definition

International Union of CRYSTALLOGRAPHY

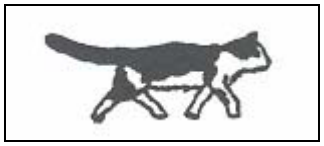
A material is a crystal if it has **essentially** sharp diffraction pattern. The word **essentially** means that most of the intensity of the diffraction is concentrated in relatively sharp **Bragg peaks**, besides the always present diffuse scattering

Further public domain materials

https://www.youtube.com/watch?v=uqQlwYv8VQI

https://www.youtube.com/watch?v=Z7hXiKiZZPs

1 Dimensional crystal (1D periodic structures)



Unit cell

Crystal lattice

Lattice vectors

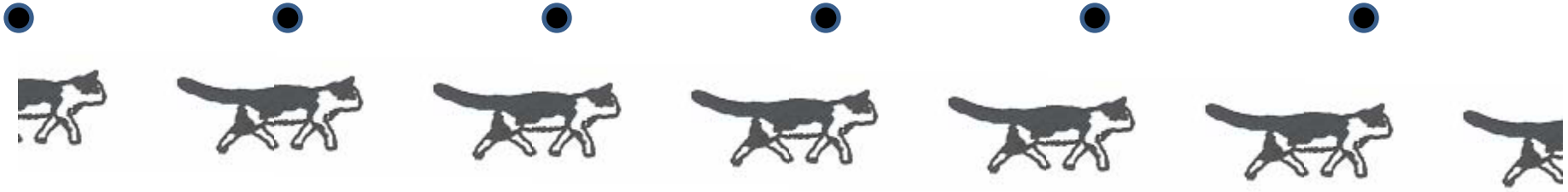
To obtain the whole crystal structure one has to translate the UNIT CELL to each LATTICE POINT

Different choices of unit cell

Unit cell

+

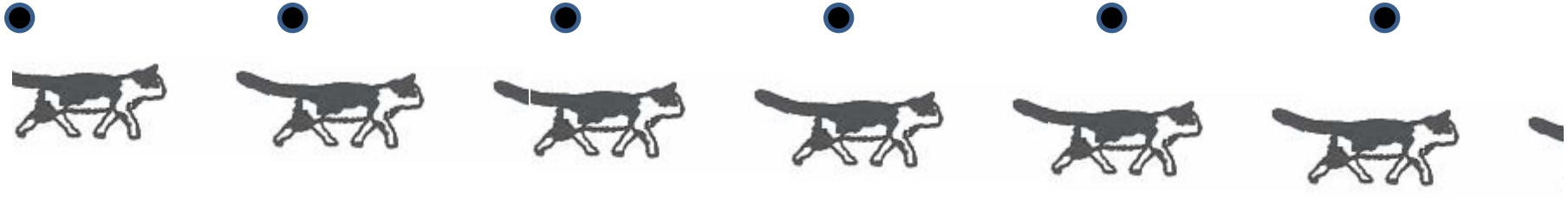
Crystal lattice



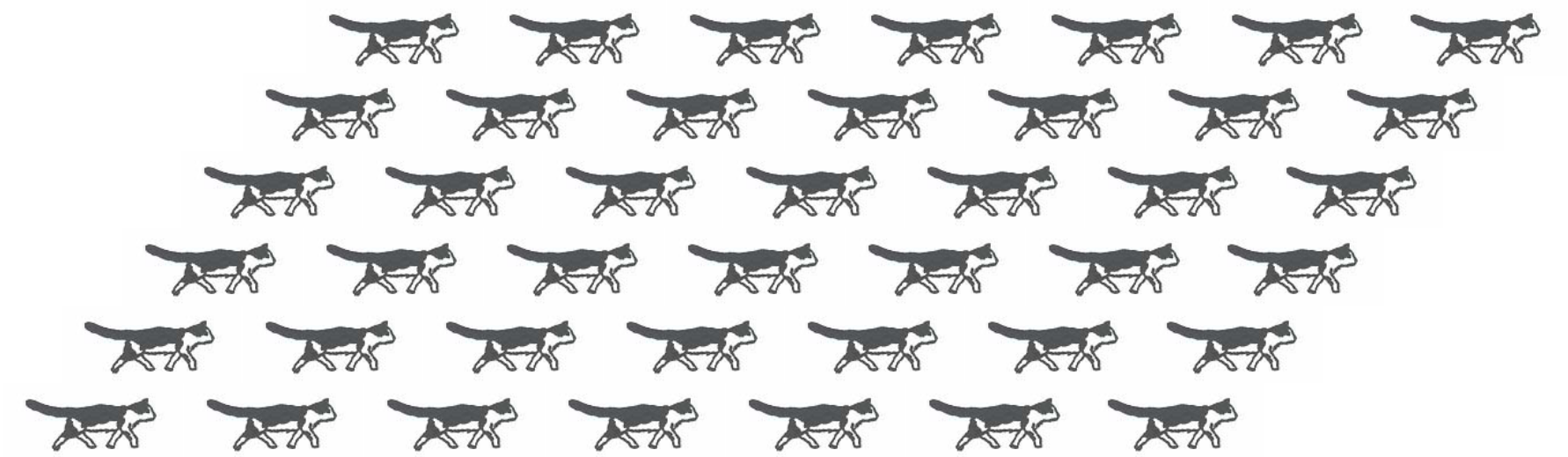
Unit cell

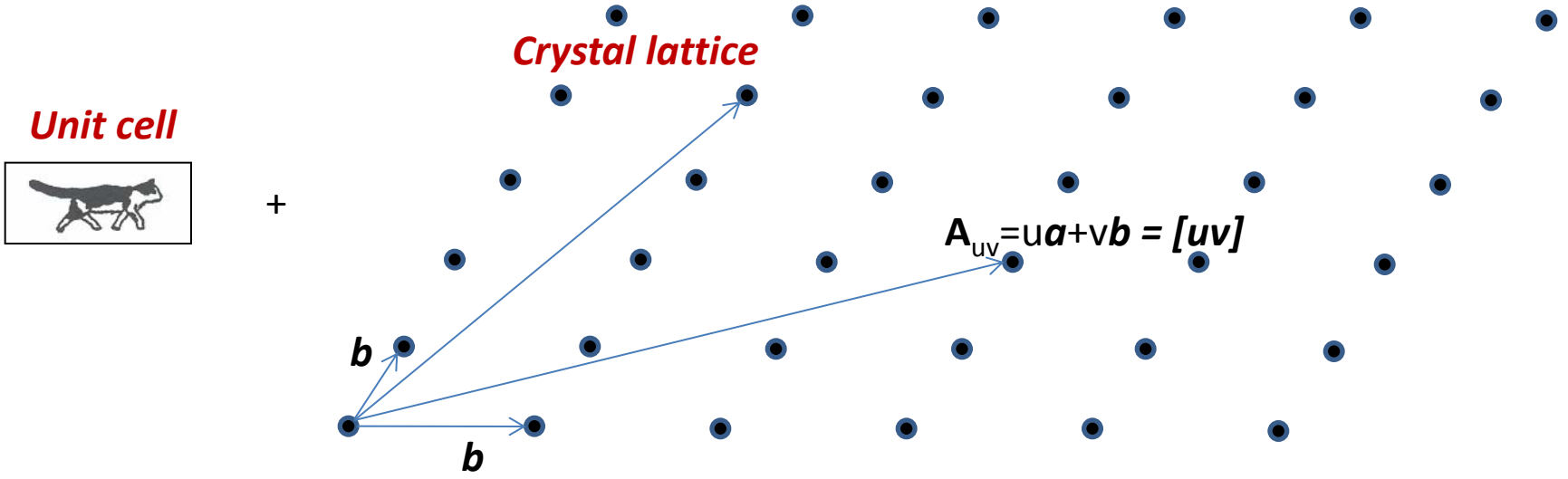
+

Crystal lattice



2 Dimensional crystal (2D periodic structures)





IMPORTANT MESSAGES!!!

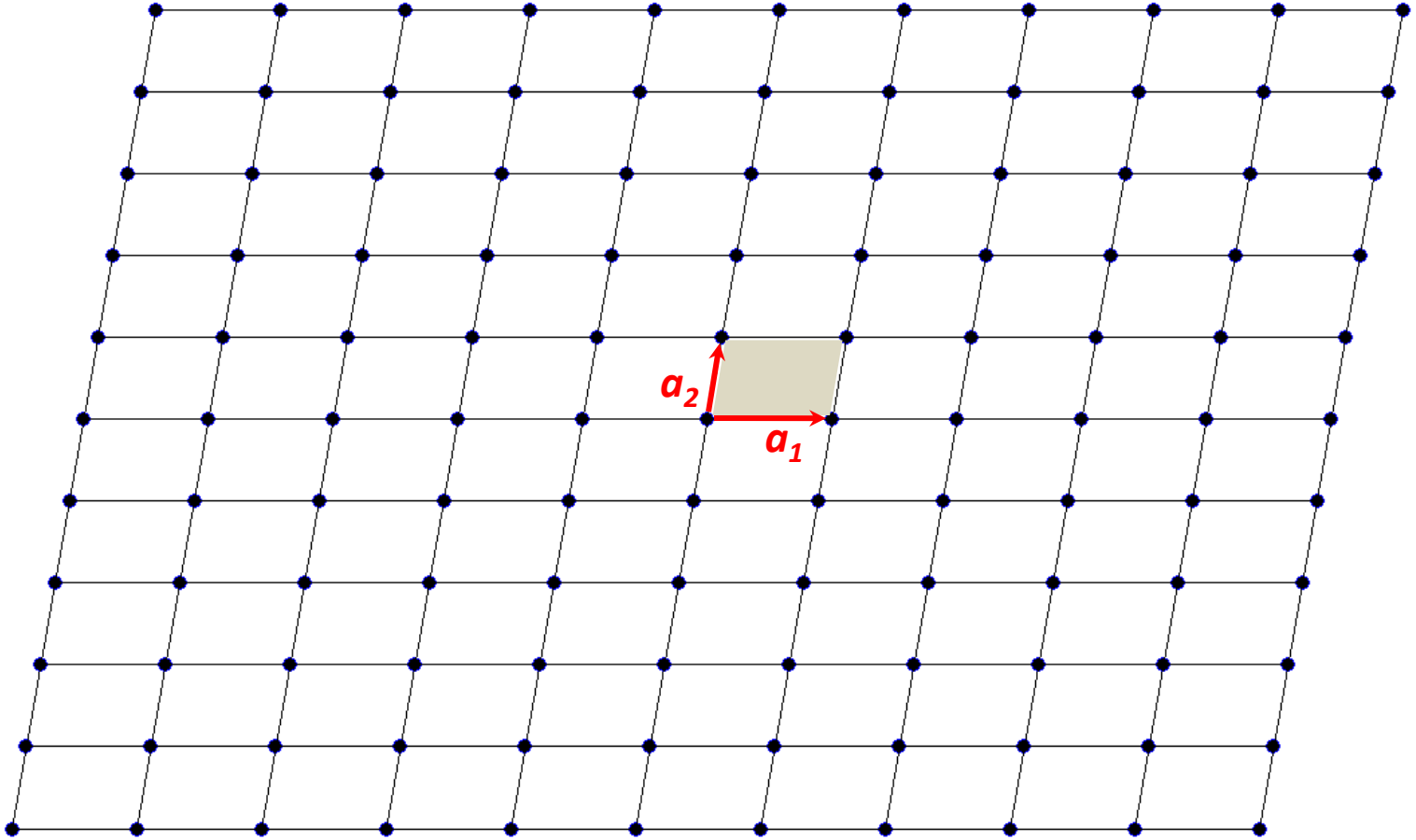
- **Crystal lattice is the mathematical object, describing the periodicity of crystal structure.**

- **Do not confuse crystal lattice with crystal structure**

- **Crystal structure is UNIT CELL * CRYSTAL LATTICE**

- **In order to get the whole crystal structure one has to translate the unit cell to the all lattice points**

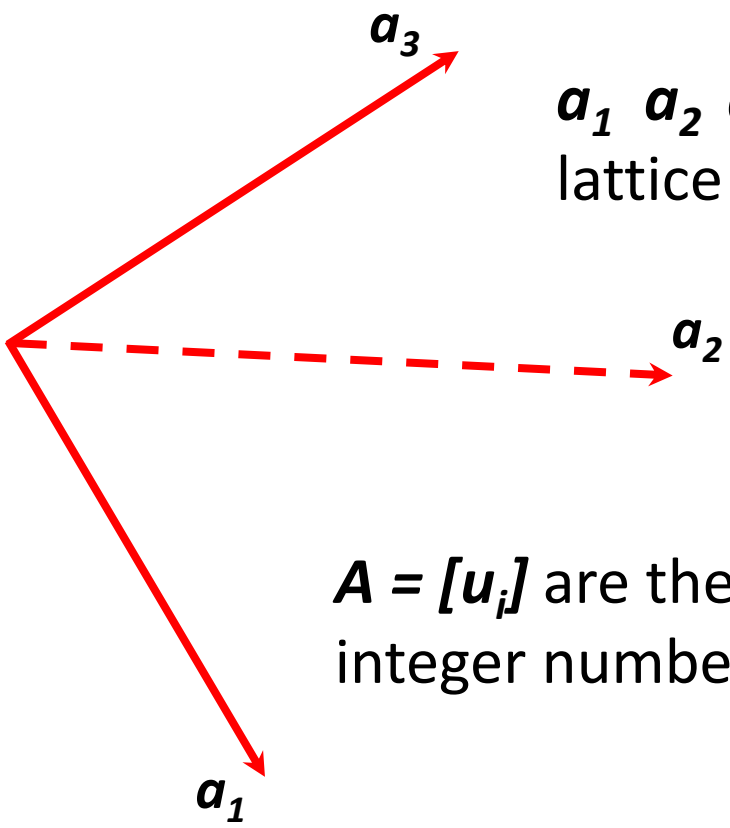
BASIS VECTORS and CRYSTAL LATTICE PARAMETERS



Lattice parameters for two dimensional case: $a=|\boldsymbol{a_1}|$, $b=|\boldsymbol{a_2}|$, $\alpha=\angle(\boldsymbol{a},\boldsymbol{b})$

For the given example: a=1.5, b=1, α=80 deg

BASIS VECTORS and CRYSTAL LATTICE PARAMETERS in 3D

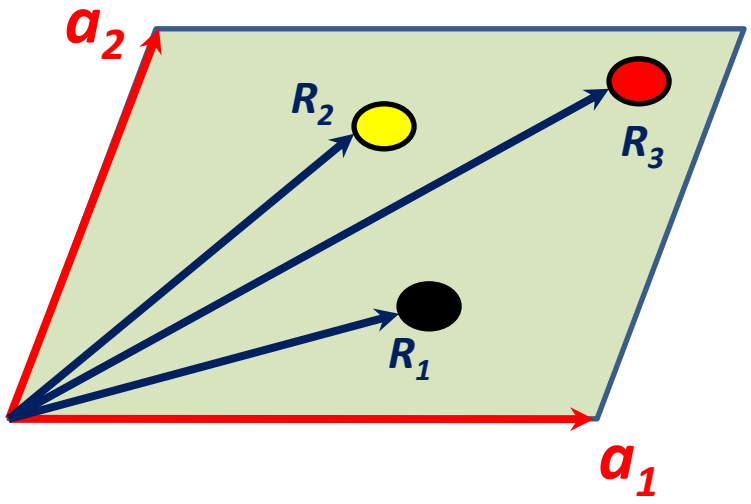


a_1 a_2 a_3 are the BASIS VECTORS of a crystal lattice

$A = [u_i]$ are the set of LATTICE POINTS (u_1, u_2, u_3 are integer numbers)

The set of lattice parameters for the 3D lattice

UNIT CELL and ATOMIC POSITIONS

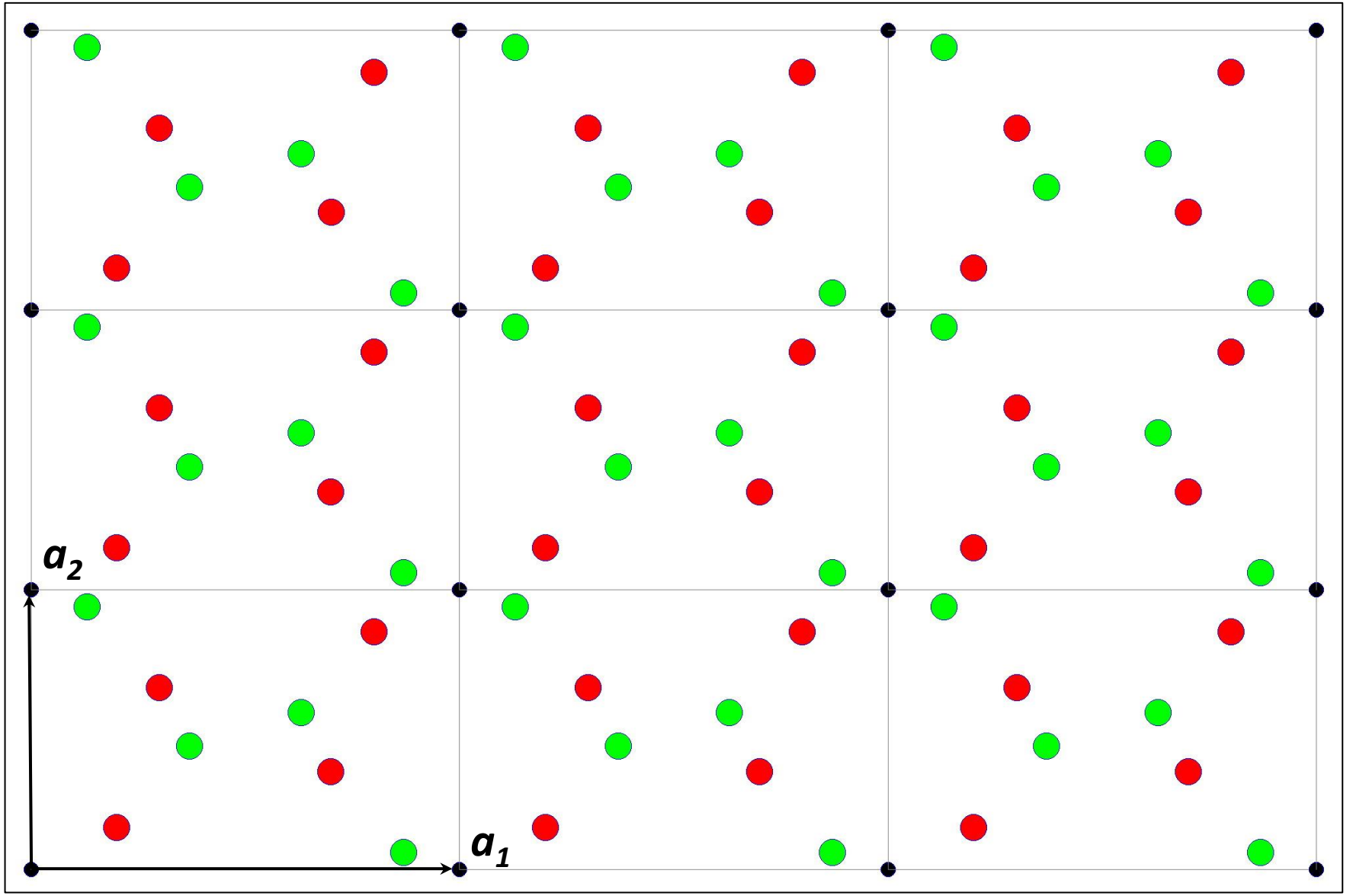


Consider a crystal lattice. We chose the pair (triple) of basis vectors: a_1,a_2 and a_3. The crystallographic unit cell is defined by putting atoms, molecules, etc to the sites, ***R_1 , R_2 ,..., R_n inside the parallelogram based on the vectors a_1, a_2 and a_3.*** The site of each and every atom in the unit cell is given by the *fraction atomic positions, x_1, x_2 and x_3.*

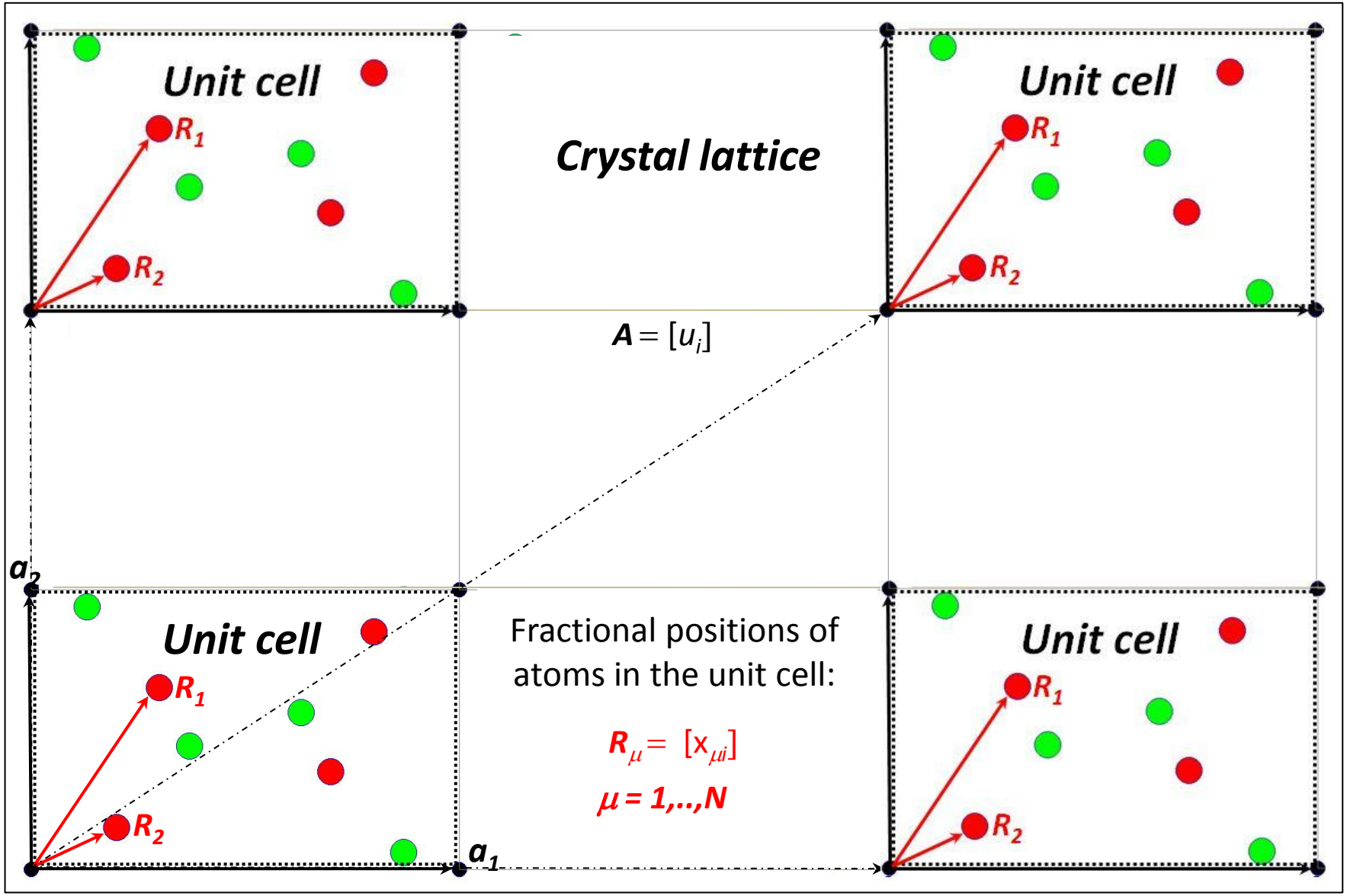
$$R = x_1a_1 + x_2a_2 + x_3a_3$$
$$\text{with } 0 \le x_i < 1$$

The lattice translations are applied to each atomic positions, i.e. if there is an atom with the coordinate [x_i] then there is also an atom with the coordinates [x_i+u_i]. Translation [u_i] is regarded as symmetry operation

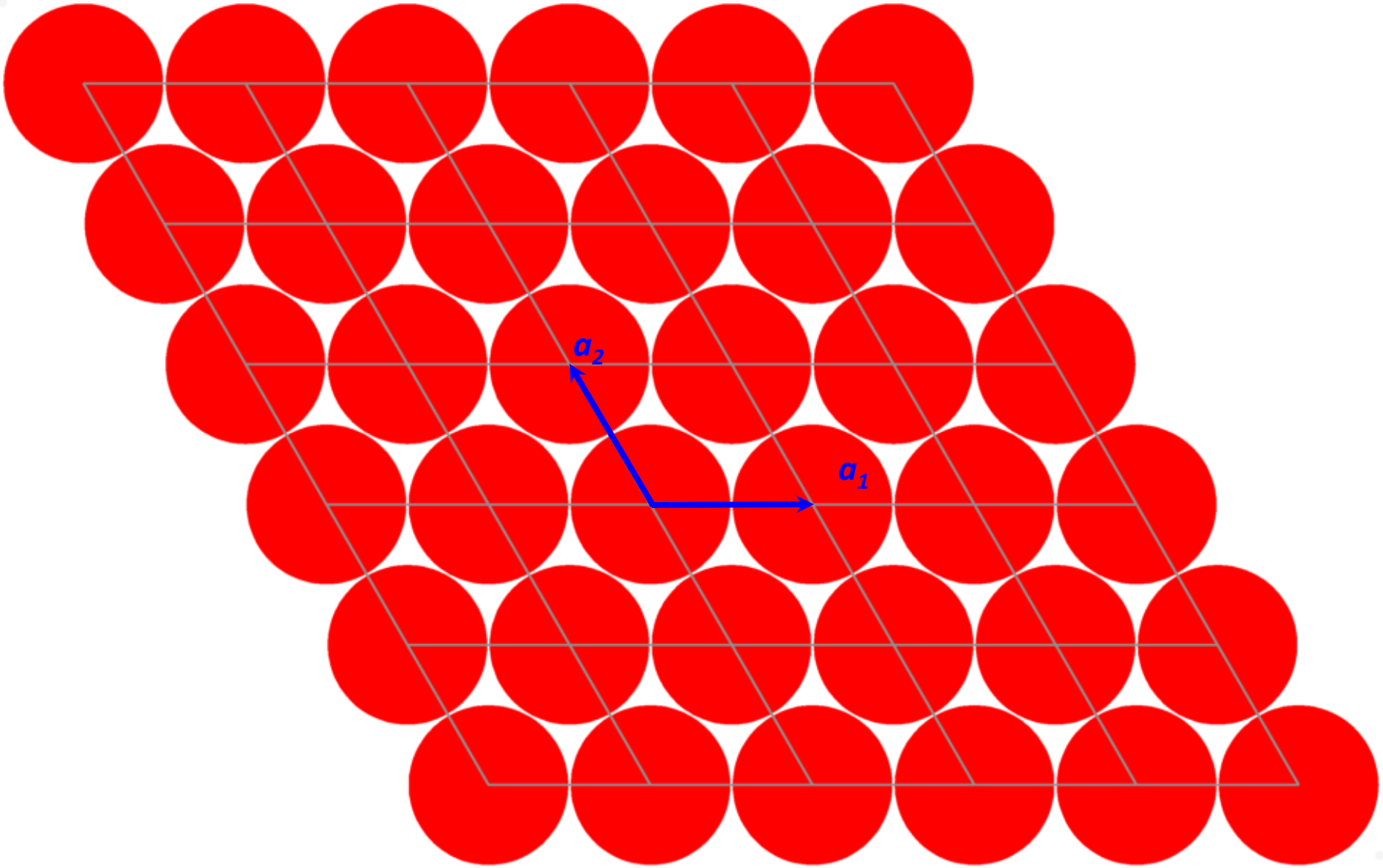
An example of 2D periodic structure



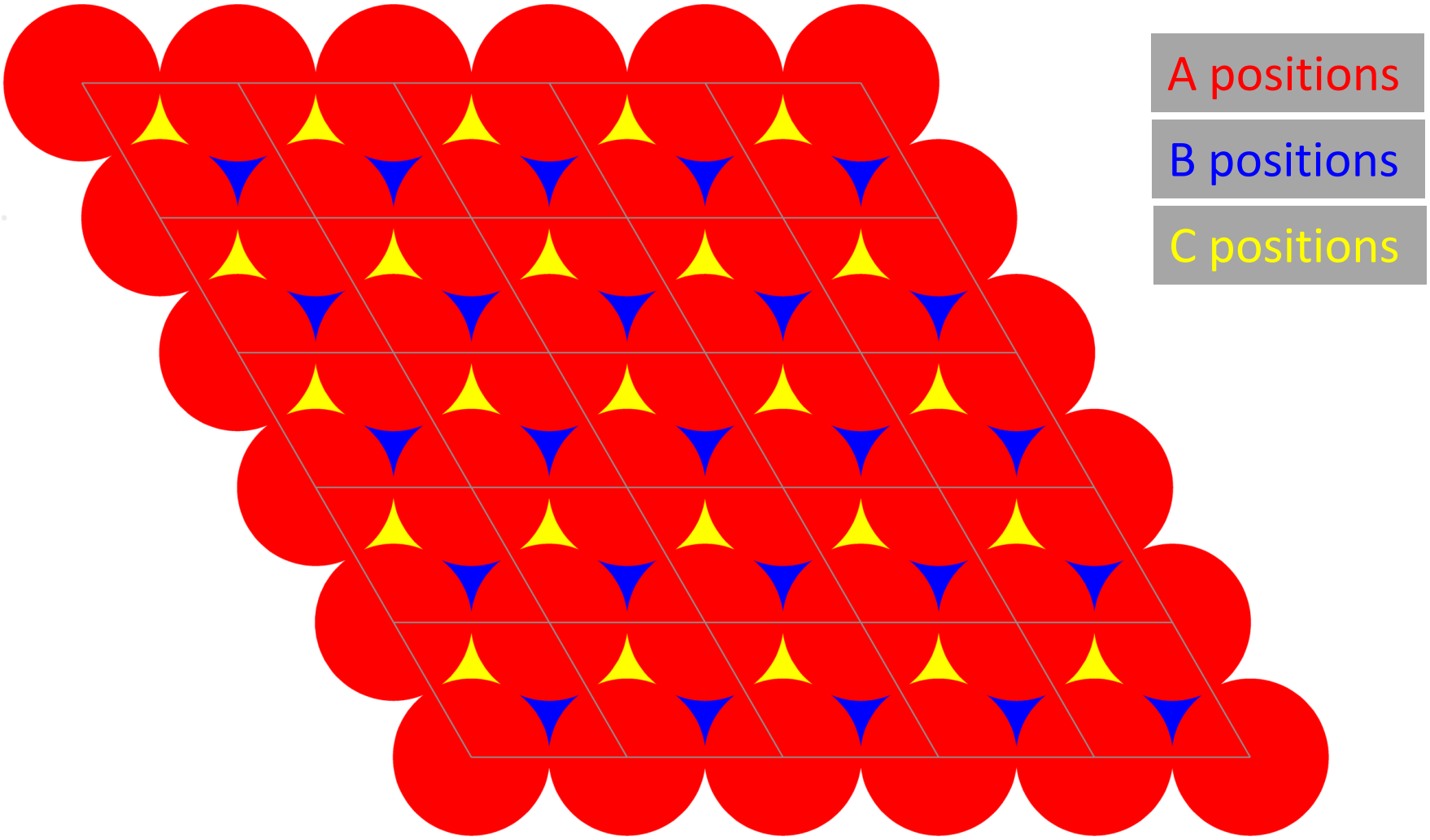
Unit cell and crystal lattice



Example: hexagonal lattice !



Hexagonal close packing (HCP)

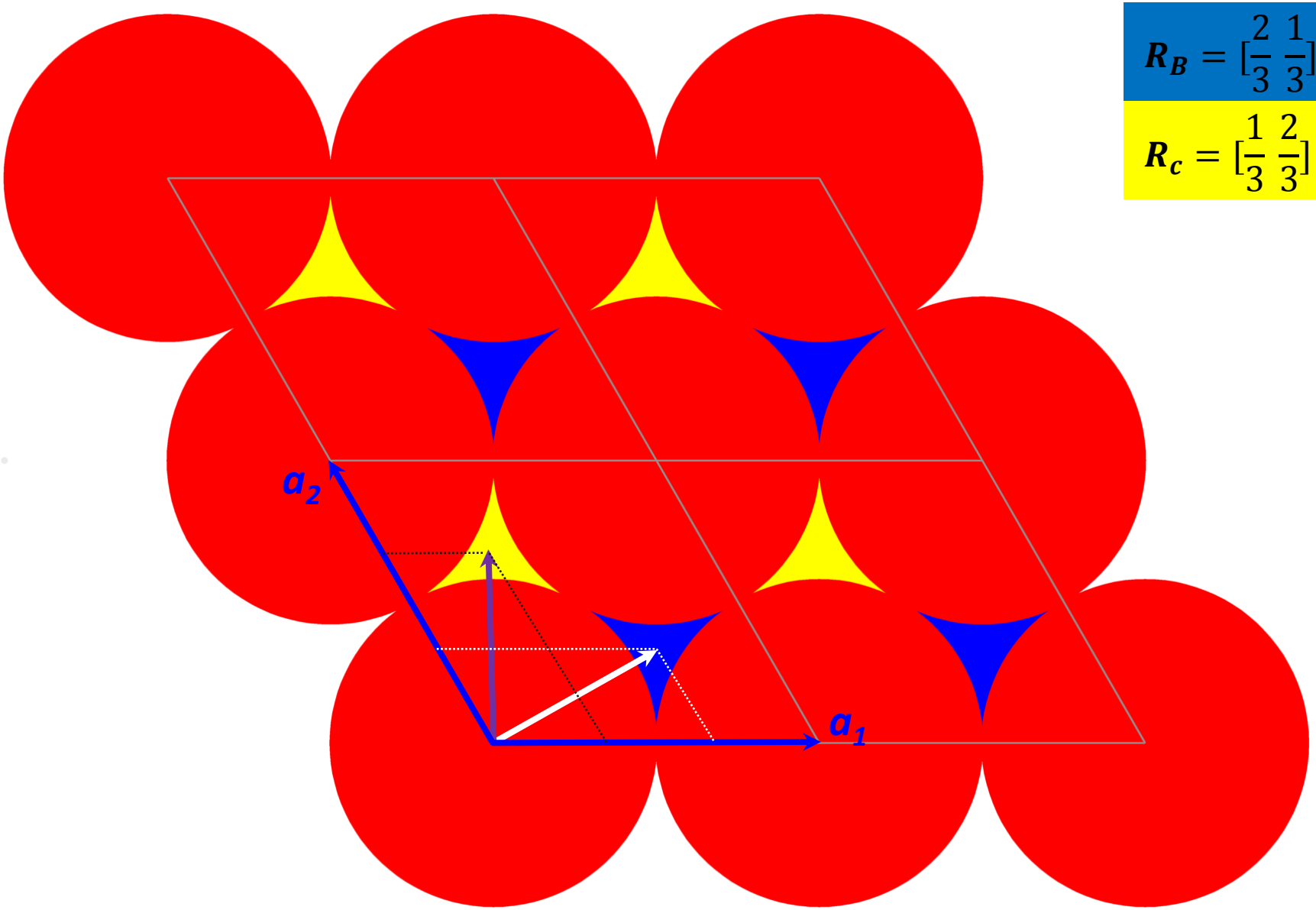


HCP positions

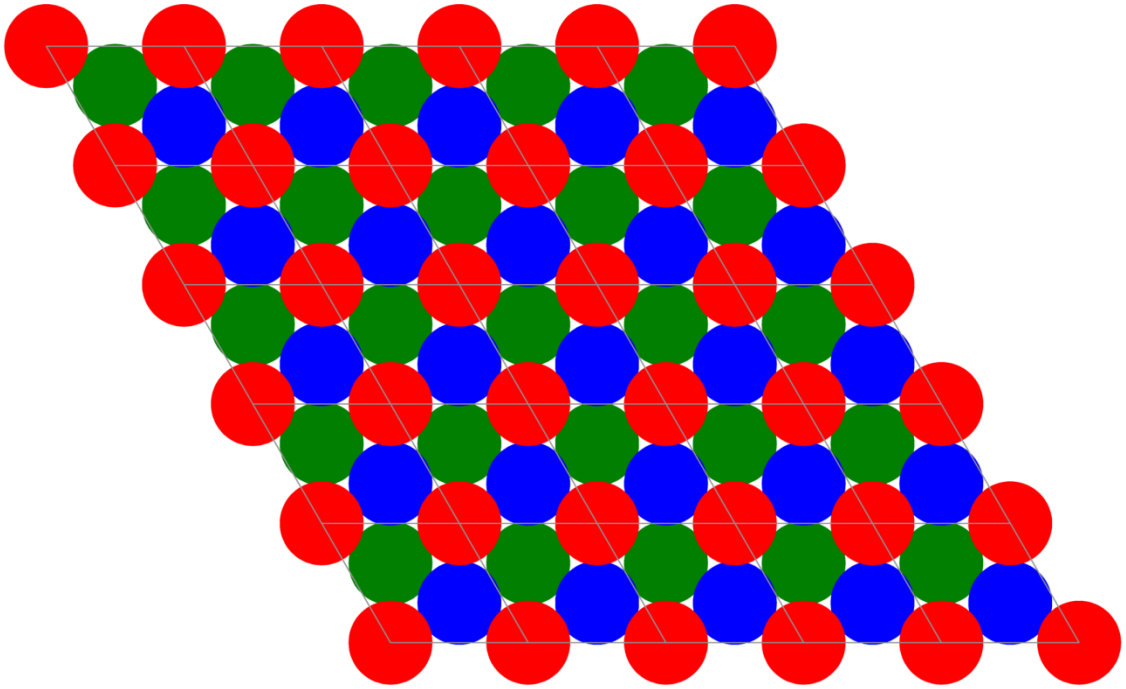
$R_A = [00]$

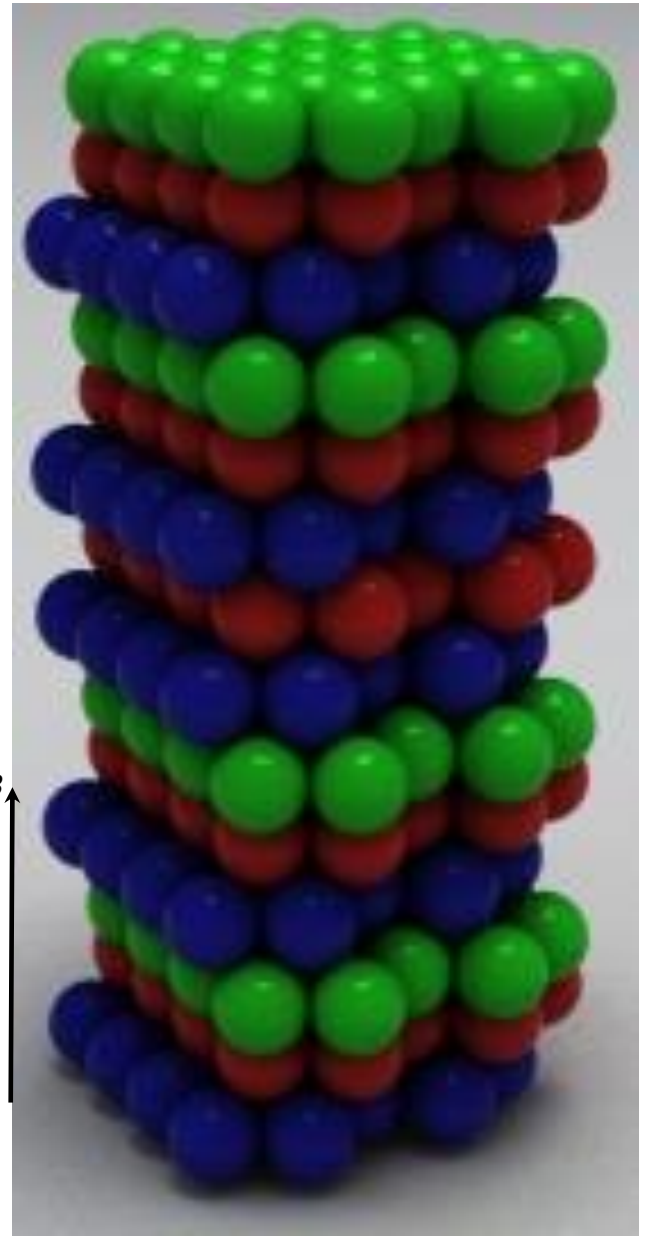
$R_B = [\frac{2}{3}\ \frac{1}{3}]$

$R_c = [\frac{1}{3}\ \frac{2}{3}]$



Three dimensional HCP structure



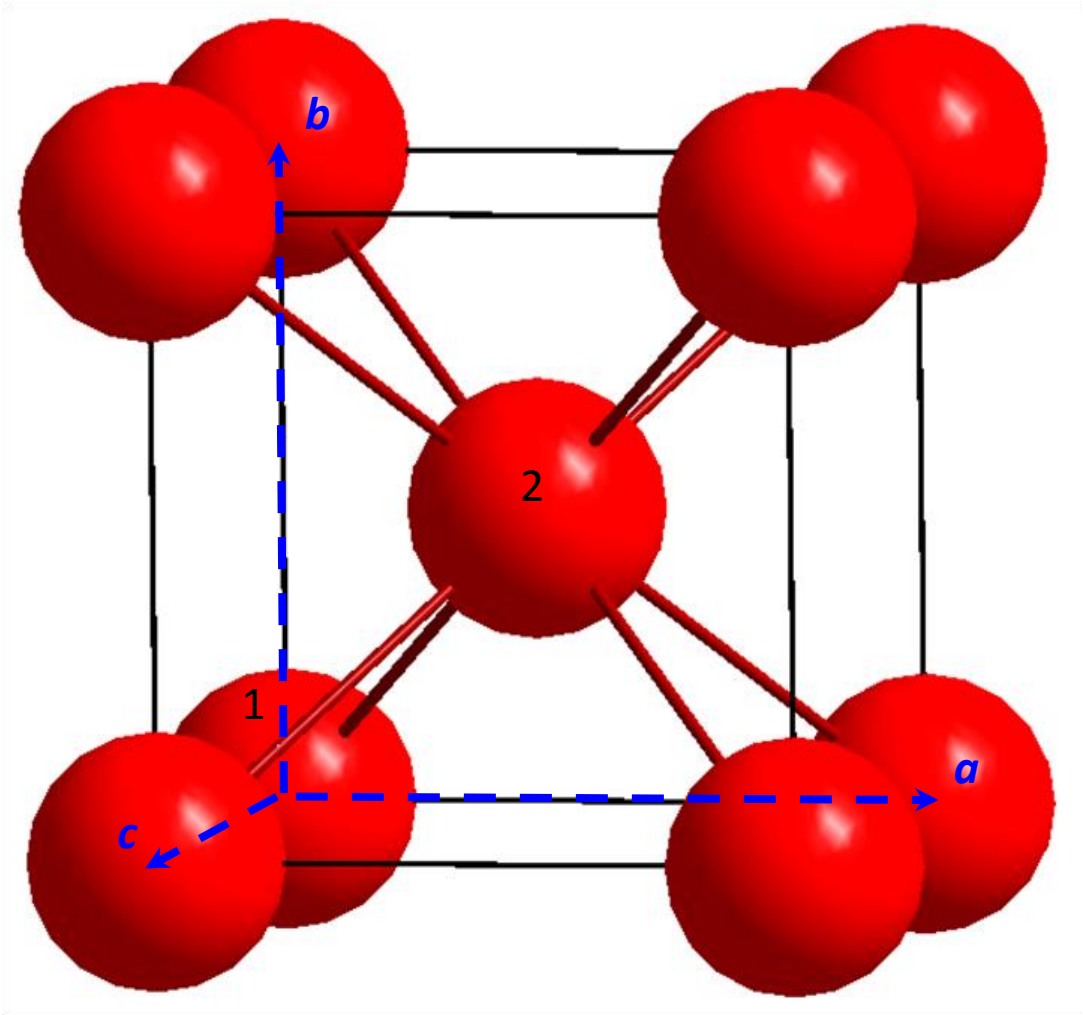


$$R_A = [000]$$

$$R_B = [\frac{2}{3}\ \frac{1}{3}\ \frac{1}{3}]$$

$$R_c = [\frac{1}{3}\ \frac{2}{3}\ \frac{2}{3}]$$

Example: Body-centred cubic (BCC) structure



$a = b = c$

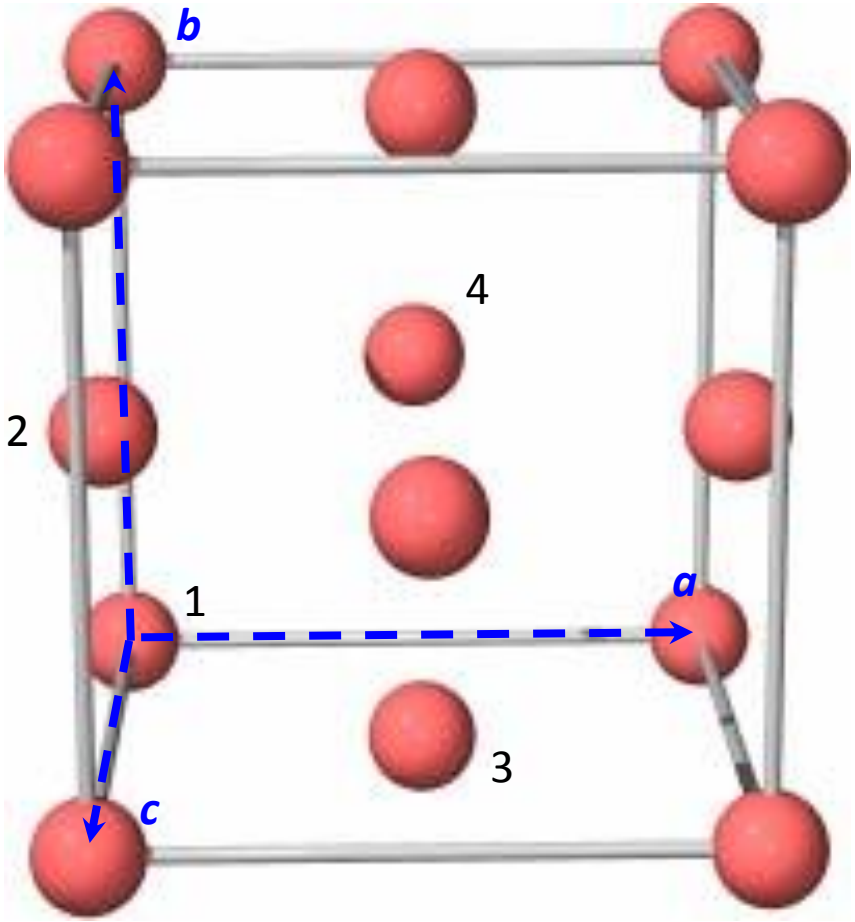
$\alpha = \beta = \gamma = 90$

$R_1 = [000]$

$R_2 = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$

Two atoms per unit cell

Example: Face-centred cubic (FCC) structure



$a = b = c$

$\alpha = \beta = \gamma = 90$

$$\boldsymbol{R_1} = [0\ 0\ 0]$$

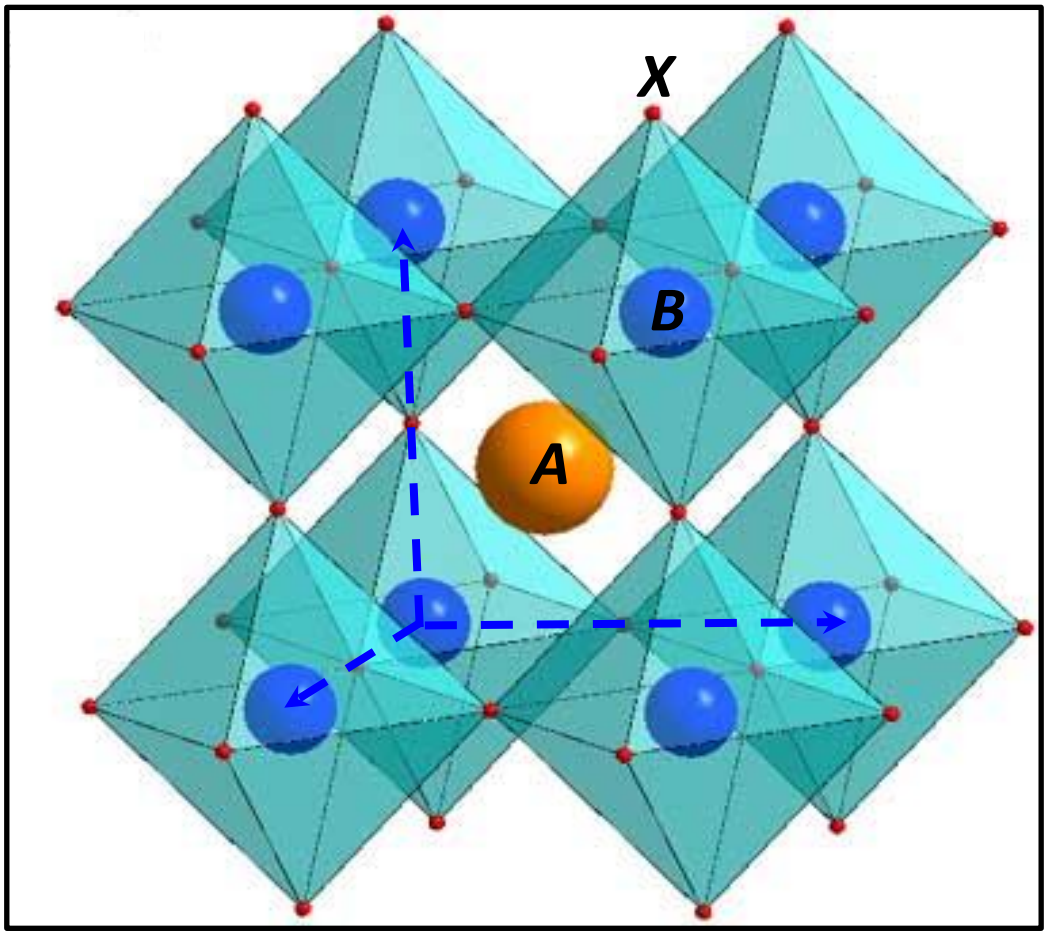
$$\boldsymbol{R_2} = [0\ \frac{1}{2}\ \frac{1}{2}]$$

$$\boldsymbol{R_3} = [\frac{1}{2}\ 0\ \frac{1}{2}]$$

$$\boldsymbol{R_4} = [\frac{1}{2}\ \frac{1}{2}\ 0]$$

4 atoms per unit cell

Example: CUBIC PEROVSKITE, ABO3



5 atoms per unit cell

$a = b = c$

$\alpha = \beta = \gamma = 90$

$$R_B = [0\ 0\ 0]$$

$$R_A = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$$

$$R_{X1} = [\frac{1}{2}\ 0\ 0]$$

$$R_{X2} = [0\ \frac{1}{2}\ 0]$$

$$R_{X3} = [00\ \frac{1}{2}]$$