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Lecture course on solid state physics for Nano, 2019

Lecture 1
Introduction in crystallography

Objectives of the course

To provide the basic knowledge necessary for the **description**, **understanding** and **investigation** of crystalline materials.

To understand the most important concepts of crystallography such as crystal lattice, unit cell, symmetry, atomic positions

To give a general idea on how the **symmetry** of a material is responsible for the **unique physical properties of crystals**

To provide with the basis knowledge of the key **X-ray and neutron diffraction techniques** used to investigate the atomic structure of crystals will also be gained.

PHYSICS

Material science

CRYSTALLOGRAPHY

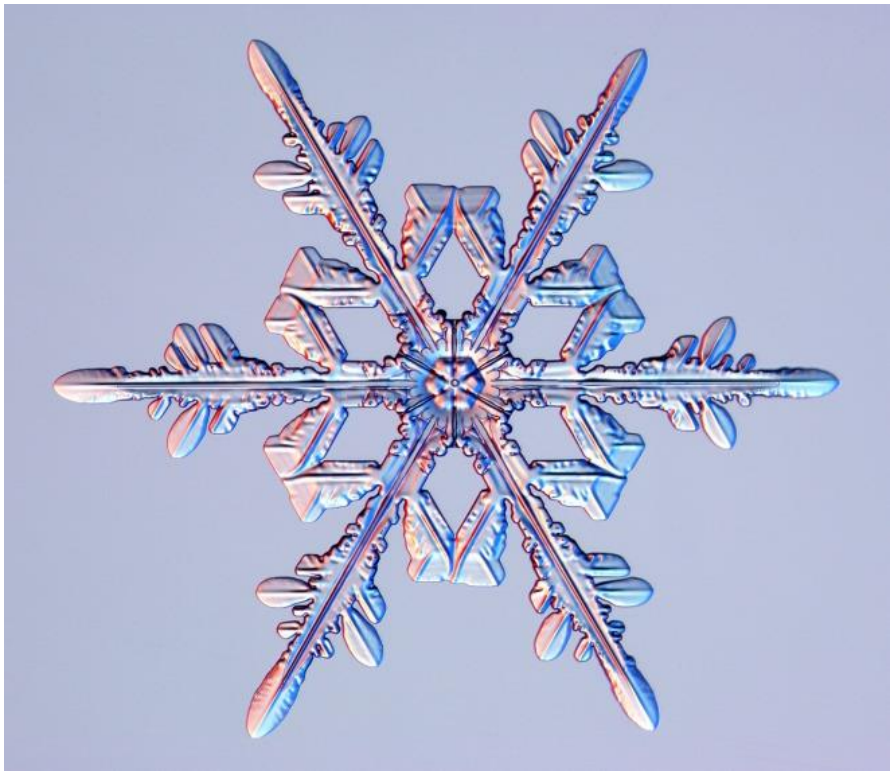
CHEMISTRY

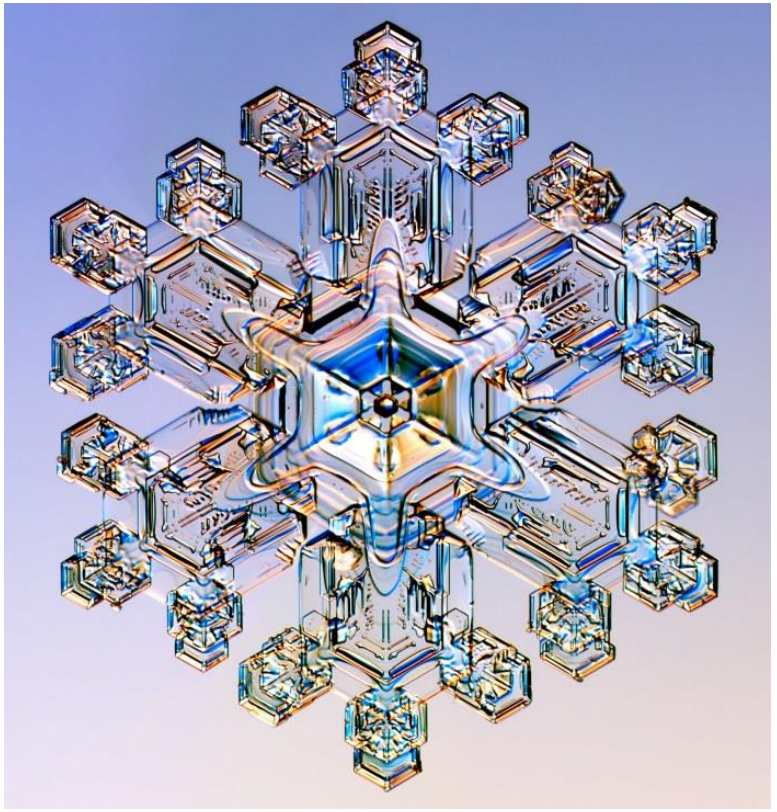
Biology

MATHS

What is a crystal?

Originally from Greek: CRYSTAL – NATURAL ICE





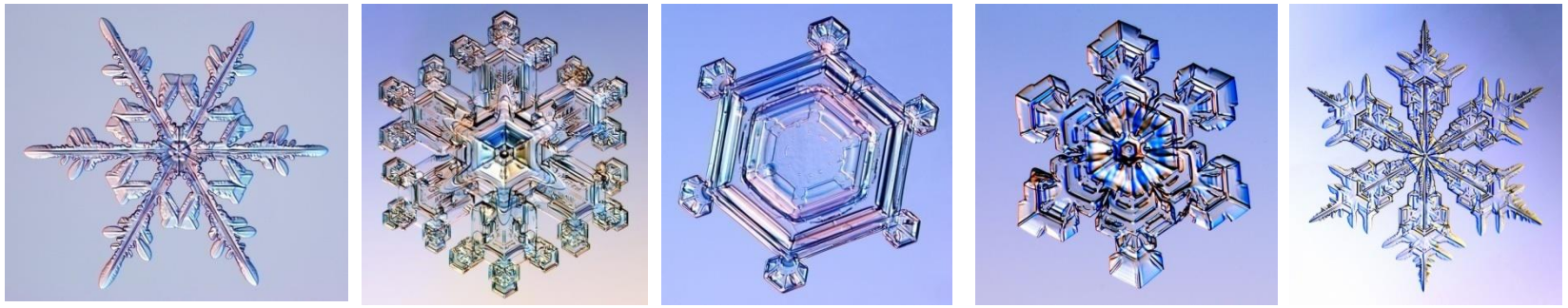
Visit www.snowcrystals.com for your own pleasure

Common feature of snow flakes

Snowflakes are found in many different morphologies. There are however two common features for all of them

1. Chemical composition: H_2O

2. Symmetry of the shapes. Independent on the particular morphology the snowflake always appear as 6 folded. There are no 4-fold, 5-fold, 7-fold, etc snowflakes found in nature.

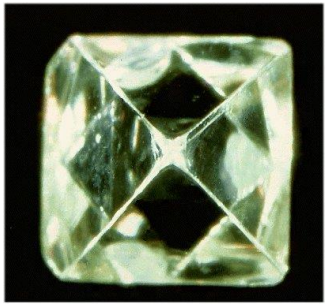


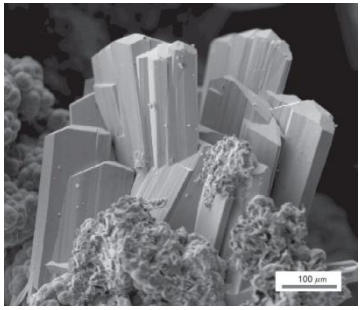
Conclusion: There is a specific feature of ***internal arrangement*** of the flakes responsible for 6-fold symmetry

Common features of minerals

Formation of natural facets

The external shape of a single mineral is a well developed polyhedron. The facets of the polyhedral are natural and flat on the atomic level.

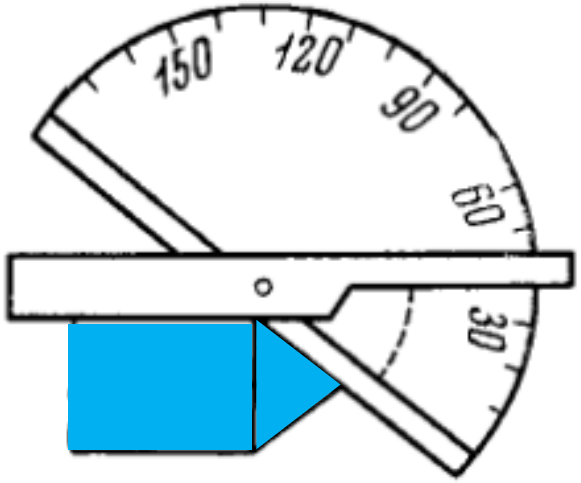


First stage of crystallography

Investigating of crystal morphologies, i.e. external shapes of natural minerals. However it was more difficult to find the common features of external shapes of minerals.

THE BIRTH OF CRYSTALLOGRAPHY : The law of constancy of the interfacial angles

Nicolaus Steno (1638-1686)

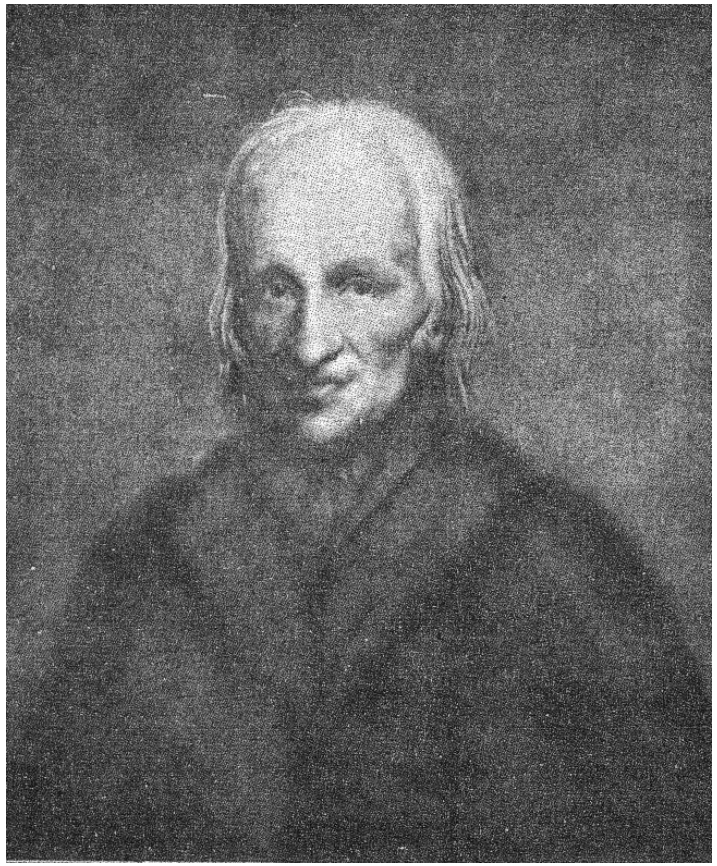


Romé de L'Isle (1736 -1790)

...The angles between the crystal faces of a *given species* are constant, whatever the lateral extension of the faces and the origin of the crystal. The set of interfacial angles is the characteristic of that species...

THE BIRTH OF CRYSTALLOGRAPHY : The law of rational indices

2. Haüy (1743-1822)



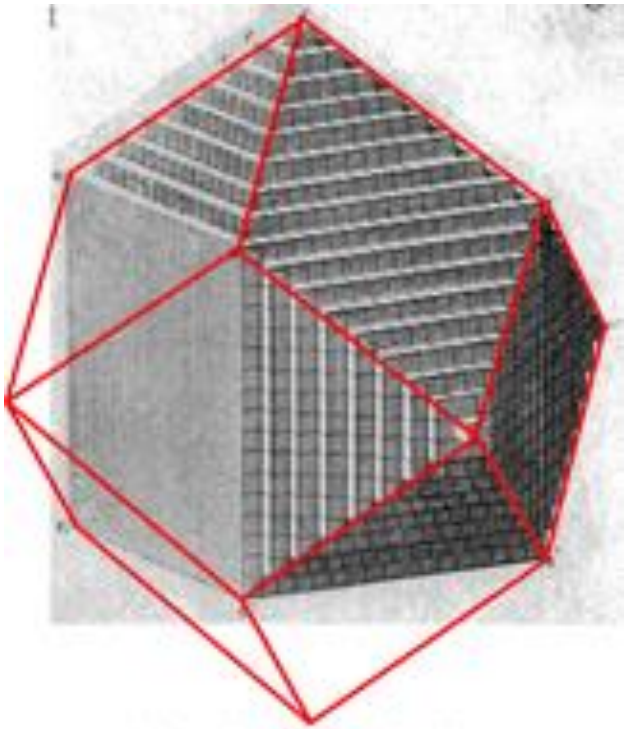
First mathematical approach to the description of the crystal faces in crystals

...For the given crystal species it is always possible to choose three vectors, a, b and c so that all the natural faces of this crystal cut the lengths proportional to the three integer numbers ...

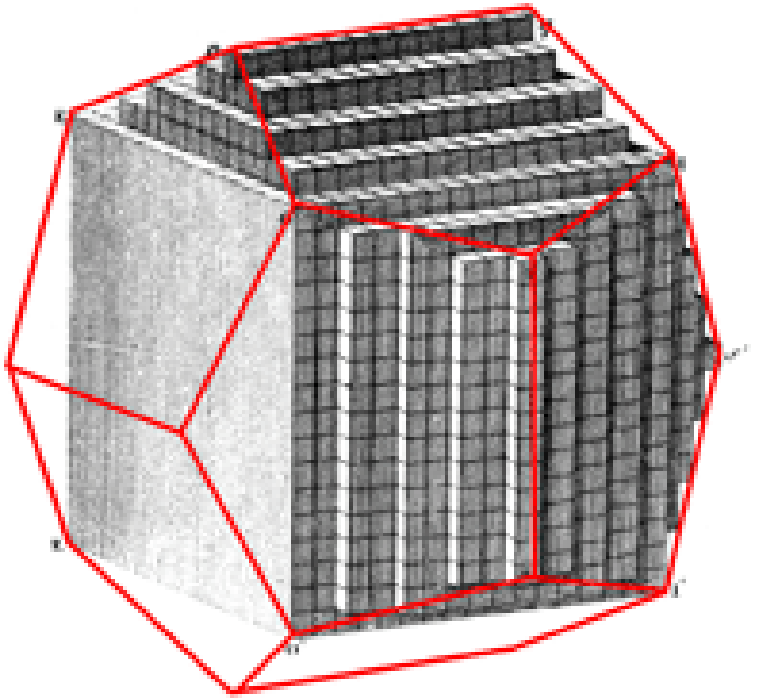
The exact meaning of these three integer numbers will be explained later

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

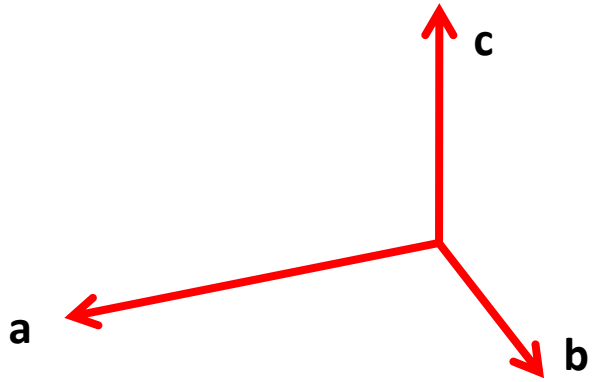
Models from Haüy's *Traité de Minéralogie* (1801)

In the works of *Nicolaus Steno (1638-1686)* , *Romé de L'Isle (1736 - 1790)* the first systematic studies of crystal shapes were performed. Result – the law of constancy of interfacial angles. This is an important empirical observation, however it does not give any insight into the internal structure.

Haüy (1743-1822) was the first who formulated the link between fascinating polyhedral shape and internal structure of crystal. His hypothesis was to explain the crystal shape by the periodic structure of a crystal.

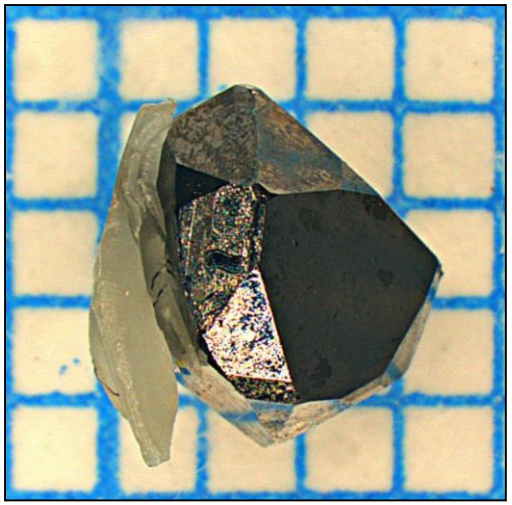
Crystal shape

Internal directions

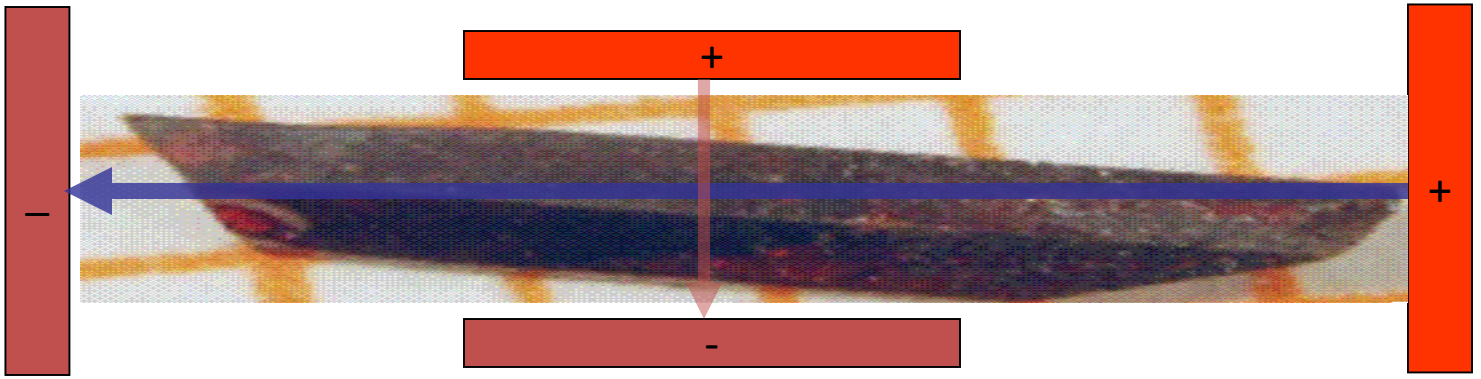


Anisotropy of physical properties

1. Growth velocity (formation of facets)



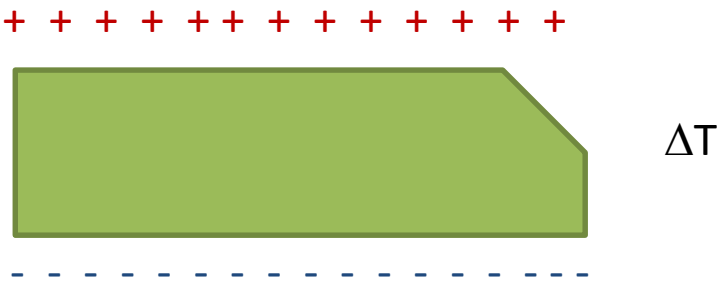
2. Electrical conductivity



Physical properties of crystals: pyroelectric effect in tourmaline

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

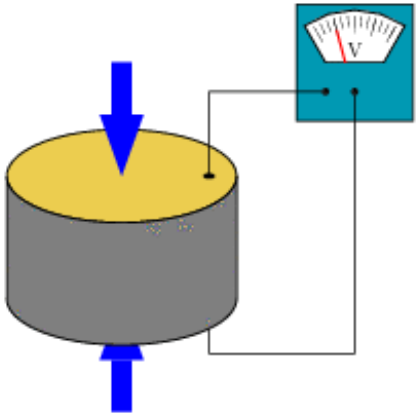
Tourmaline crystal



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

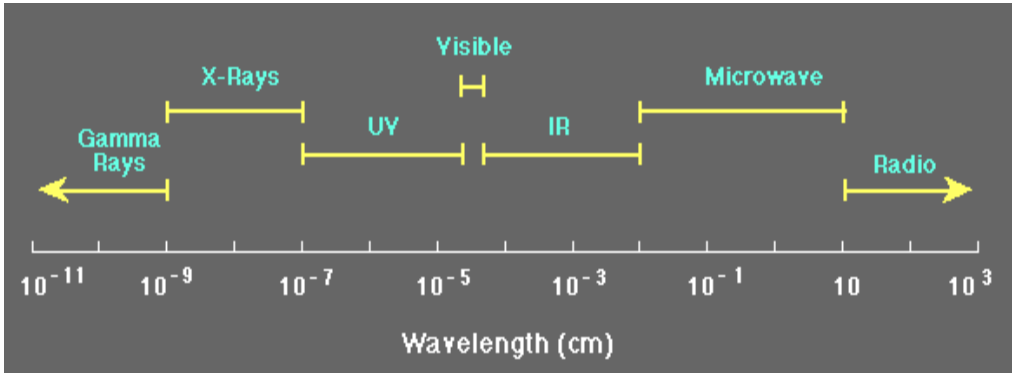
Crystallography -> birth of solid state physics

1912 **Max von Laue**

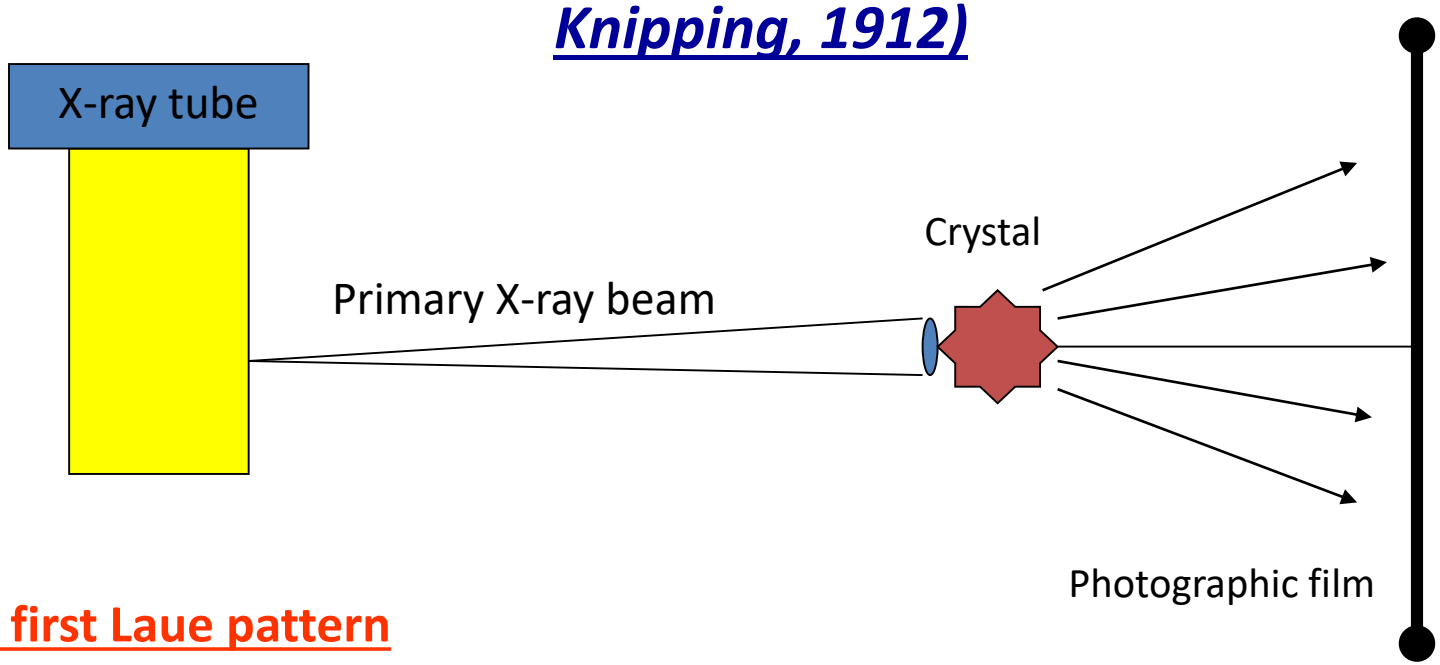
1914

Nobel prize in physics

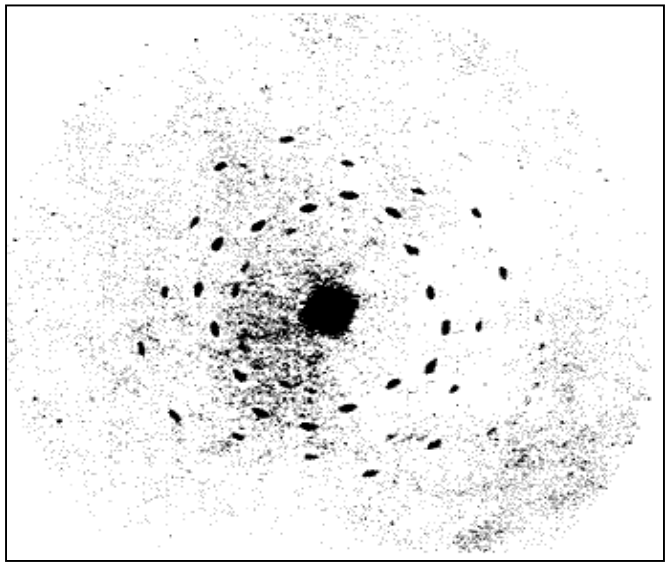
"for his discovery of the diffraction of X-rays by crystals"



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



The first Laue pattern



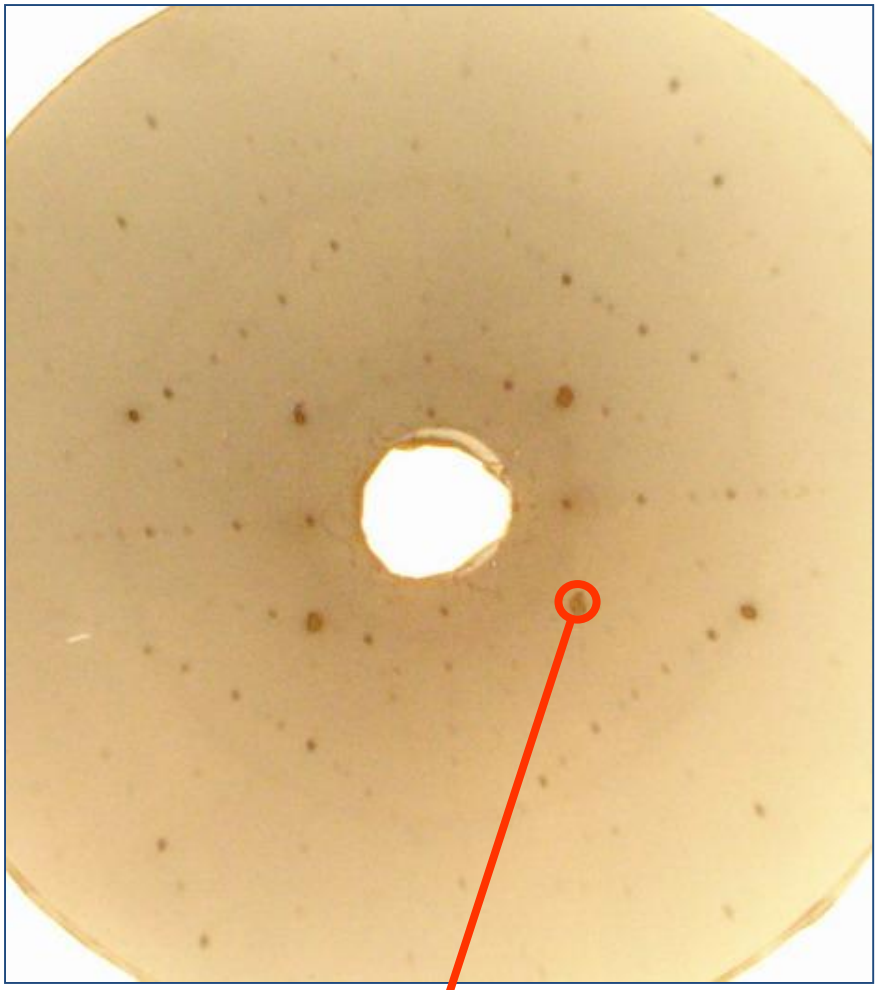
Conclusions

1. X-rays are electromagnetic waves

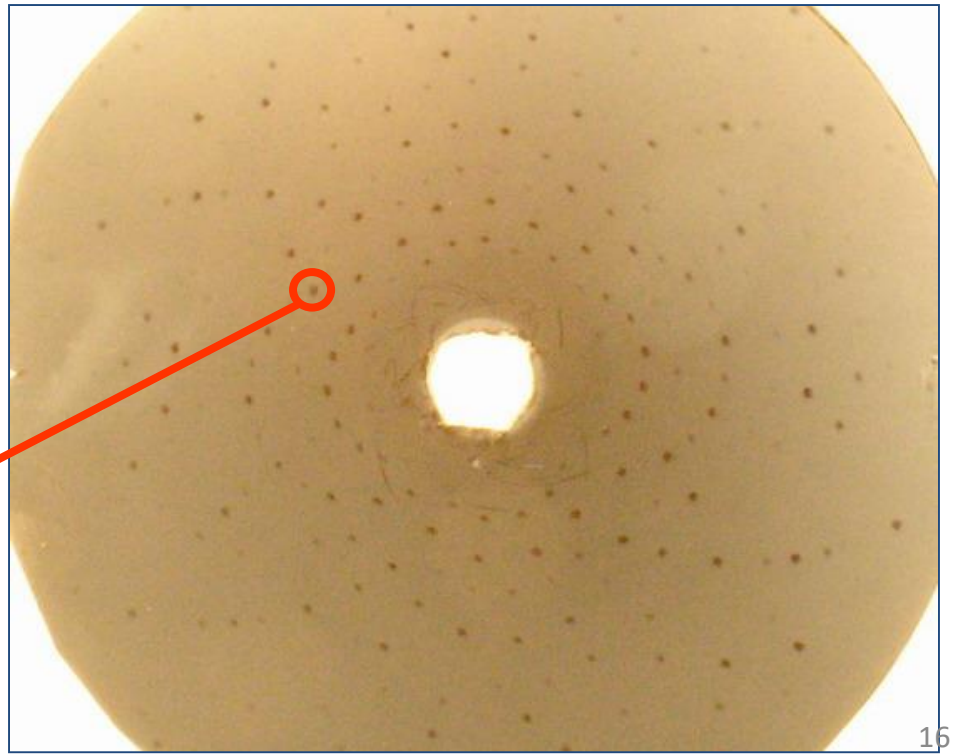
2. Crystal structures are periodic

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

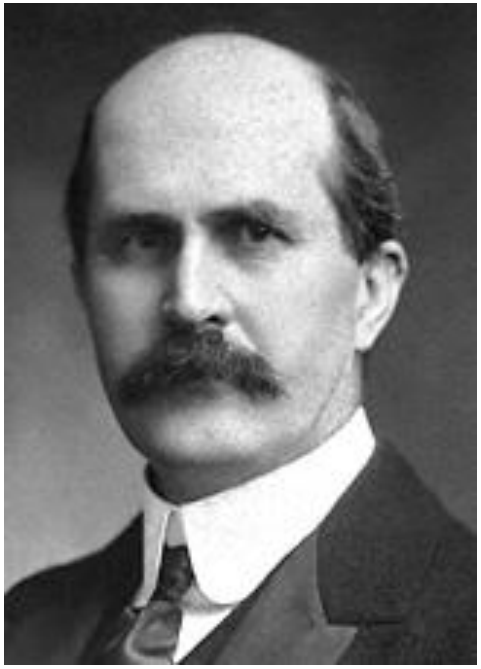
The discovery of X-ray diffraction by Max von Laue (1912) is the final and ultimate proof of the periodic structure of crystals. Moreover it was shown that the period of a crystal structure has the order of *Å* = 10^{-10} *m*

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

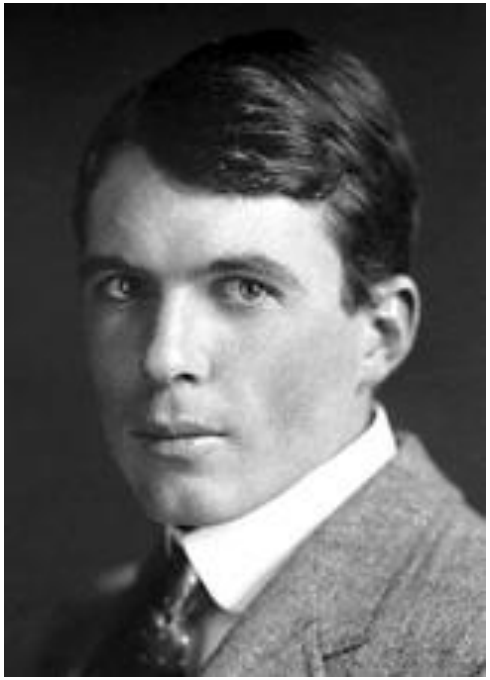
Nowadays X-ray diffraction is the main tool for the solving, determination and characterization of crystal structures

The first REAL crystal structure

1915
Nobel prize in physics
"for their services in the analysis of crystal structures by means of X-rays "

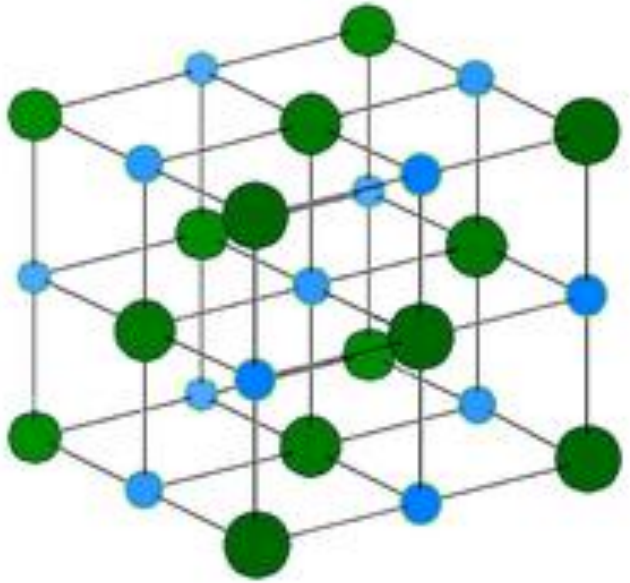


Sir William Henry Bragg



William Lawrence Bragg

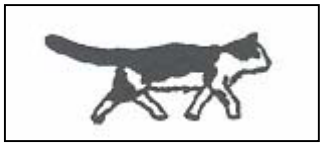
Atomic structure of NaCl, KCl, LiF was established



Take home message: what is a crystal

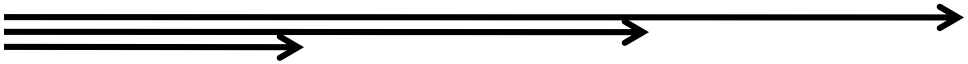
	Crystalline solid	Amorphous solid
Shape	**Polyhedral shape with naturally formed faces**	**No naturally formed faces**
Properties	**Anisotropic**	**Isotropic**
Atomic structure	**Periodic (long range ordered)**	**No periodicity. Short-order only**
X-ray Diffraction	**Well separated diffraction picture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

1 Dimensional crystal (1D periodic structures)



Unit cell

Crystal lattice



Lattice vectors

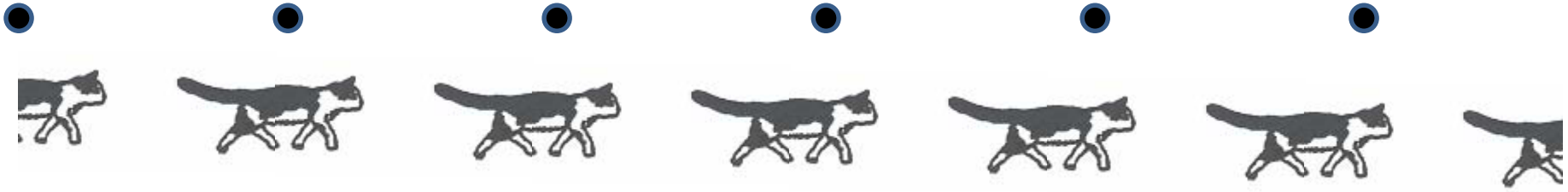
To obtain the whole crystal structure one has to translate the UNIT CELL to each LATTICE POINT

Different choices of unit cell

Unit cell

+

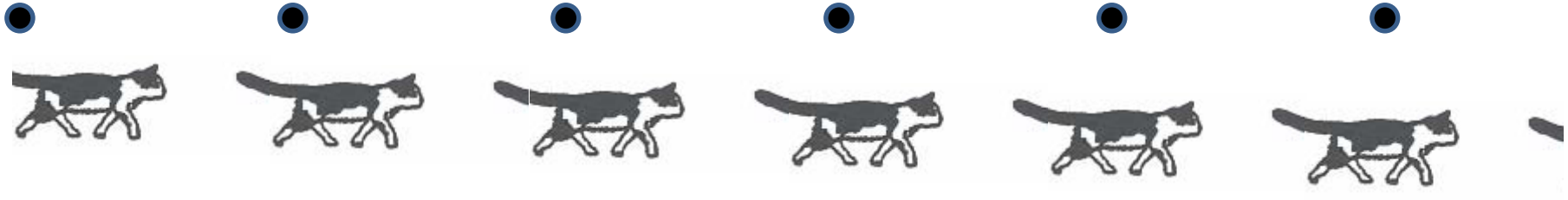
Crystal lattice



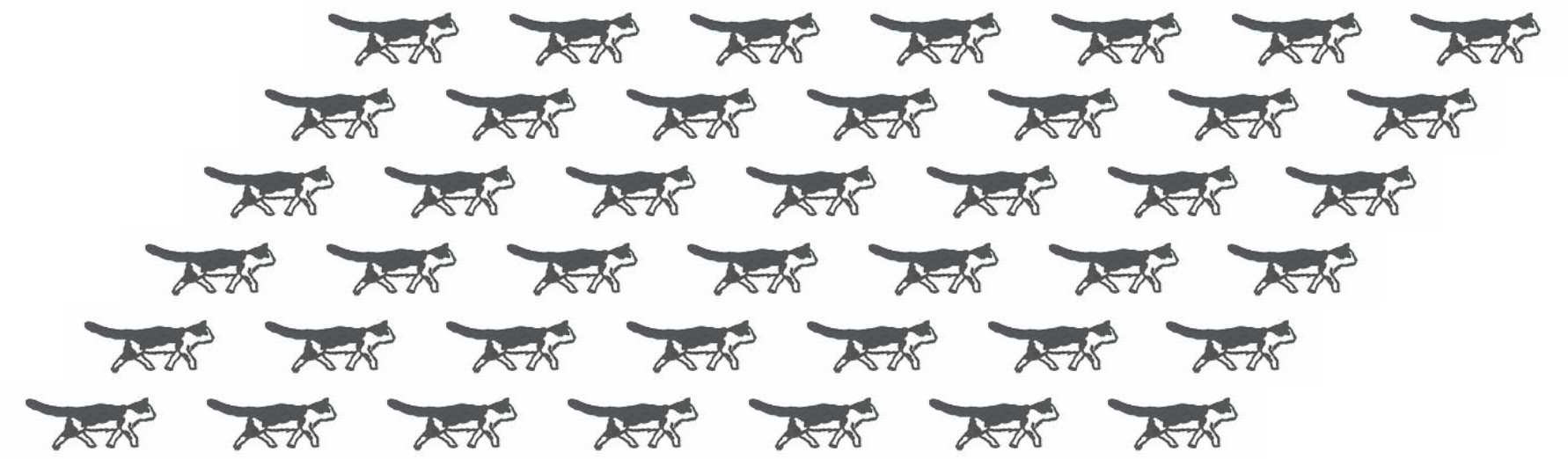
Unit cell

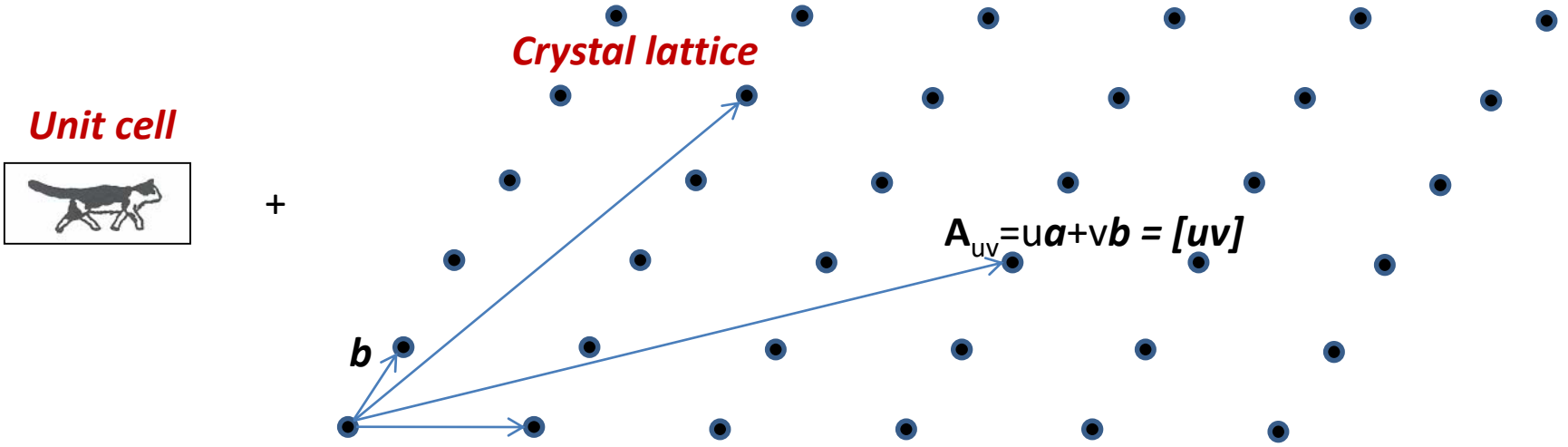
+

Crystal lattice



2 Dimensional crystal (2D periodic structures)





IMPORTANT MESSAGES!!!

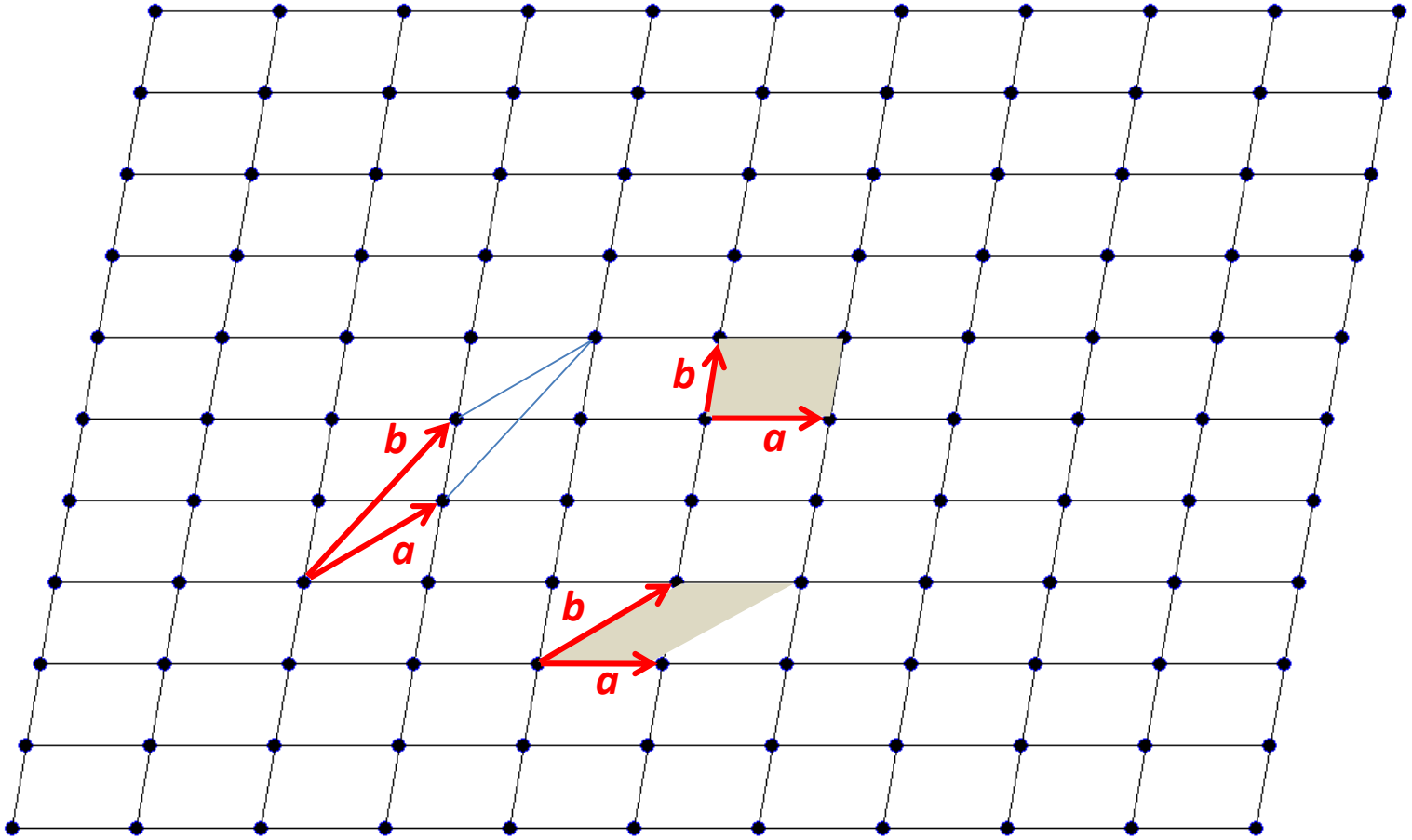
- **Crystal lattice is the mathematical object, describing the periodicity of crystal structure.**

- **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**

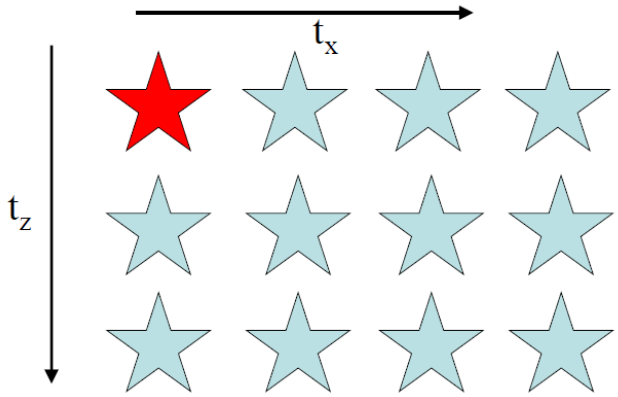
Different choices of basis vectors and lattice parameters



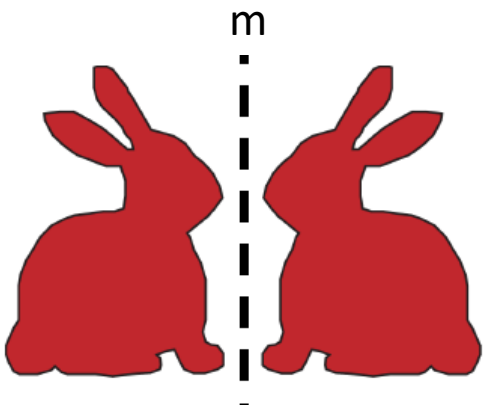
There is a freedom of choice of the lattice basis vectors and therefore lattice parameters

Symmetry elements

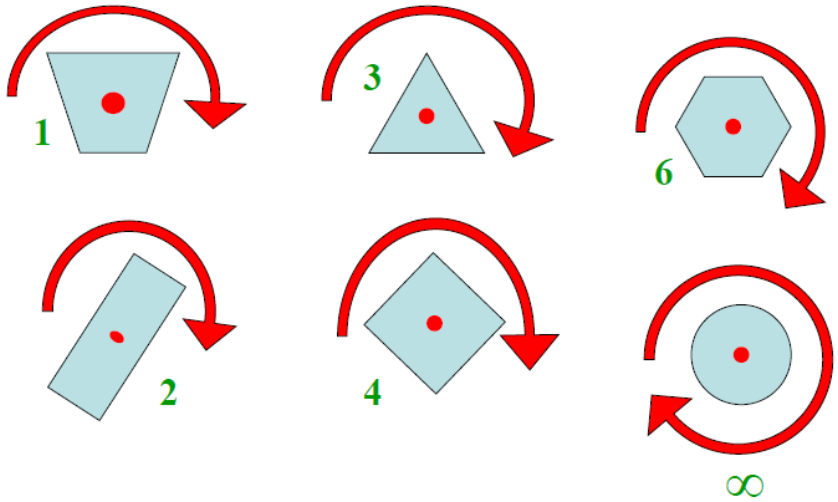
Translation



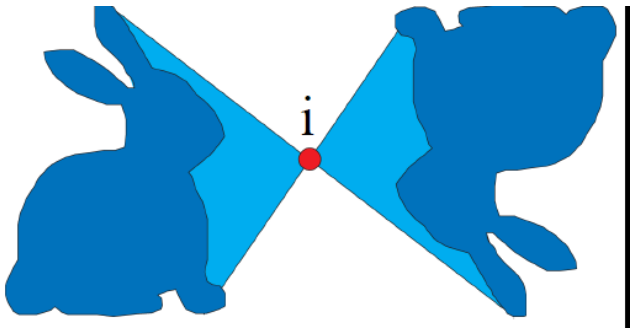
Mirror



Rotation



Inversion



Combination of symmetry elements

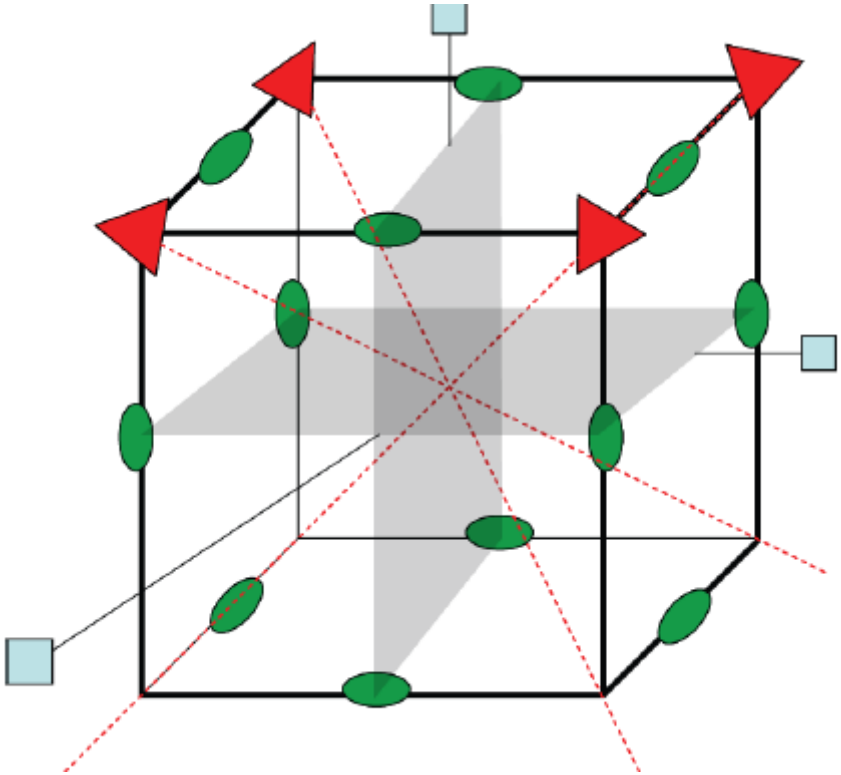
Combination of symmetry elements

Cubic symmetry

3 x 4-fold axes

4 x 3-fold axes

6 x 2-fold axes



2D Bravais lattices

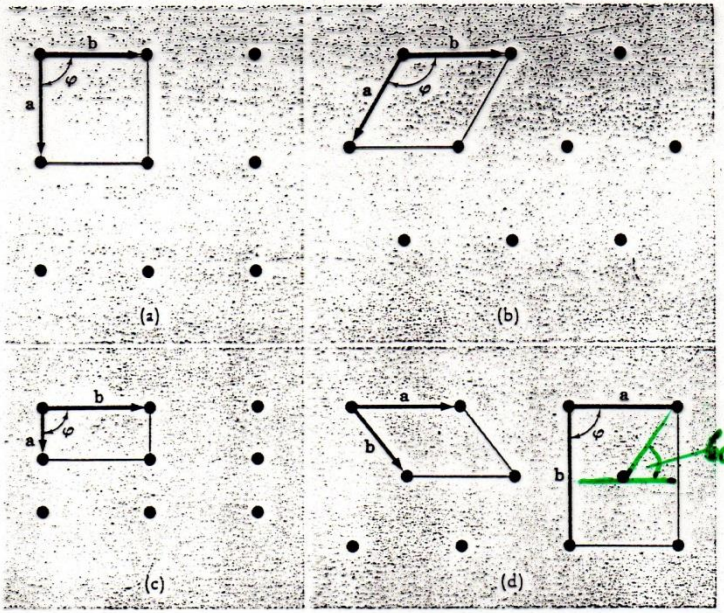
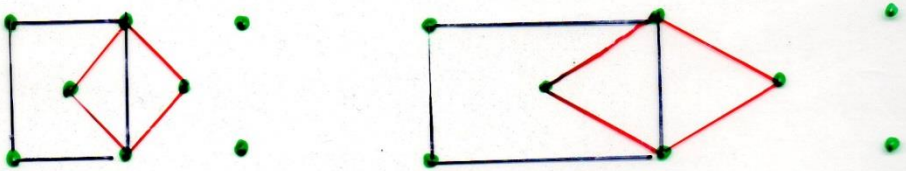


Bild 13: (a) Quadratisches Gitter $|\mathbf{a}| = |\mathbf{b}|$; $\varphi = 90°$; (b) Hexagonales Gitter $|\mathbf{a}| = |\mathbf{b}|$; $\varphi = 120°$; (c) Rechtwinkeliges Gitter $|\mathbf{a}| \neq |\mathbf{b}|$; $\varphi = 90°$; (d) Zentriertes rechtwinkeliges Gitter. Es sind die Achsen der primitiven Zelle und die der rechtwinkeligen Einheitszelle eingezeichnet. Für die rechtwinkelige Einheitszelle gilt $|\mathbf{a}| \neq |\mathbf{b}|$; $\varphi = 90°$.

Tabelle 1: Die fünf zweidimensionalen Bravais-Gitter. (Die Bezeichnung *mm* bedeutet, daß zwei Spiegellinien vorhanden sind.)

Gitter	gebräuchl. Einheitszelle	Achsen der gebräuchl. Einheitszelle	Punktgruppensymmetrie des Gitters um einen Gitterpunkt
schiefwinkelig	Parallelogramm	$a \neq b$, $\varphi \neq 90°$	2
quadratisch	Quadrat	$a = b$, $\varphi = 90°$	4 *mm*
hexagonal	60° Raute	$a = b$, $\varphi = 120°$	6 *mm*
einfach rechtwinkelig	Rechteck	$a \neq b$, $\varphi = 90°$	2 *mm*
zentriert rechtwinkelig	Rechteck	$a \neq b$, $\varphi = 90°$	2 *mm*

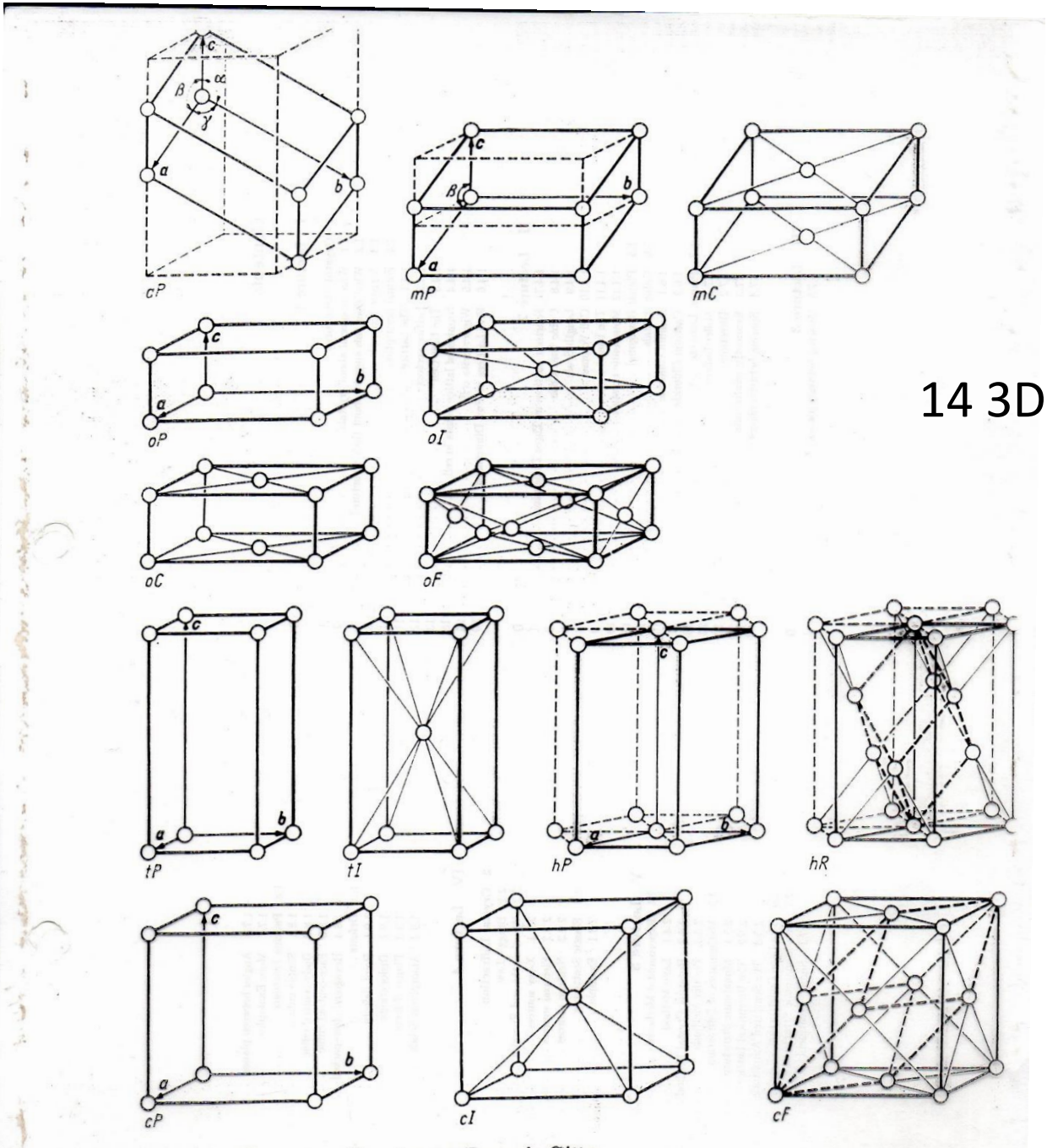


Seven 3D crystal systems

System	Lengths & Angles	Number of Lattices
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	3
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	2
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	4
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	1
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	2
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	1
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$	1

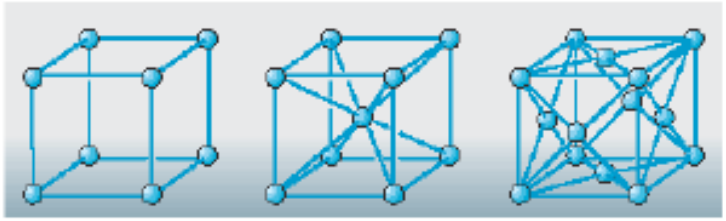
Kristallsystem	Gitterkonstanten	Charakteristische Symmetrie-Elemente	Bravais-Gitter
triklin	$a, b, c, \alpha, \beta, \gamma$ beliebig	nur 1-zählige Achsen	P
monoklin	a, b, c beliebig $\alpha = \gamma = 90°$, β beliebig	2-zählige Achsen in nur einer Richtung (parallel y)	P, C
orthorhombisch	a, b, c beliebig $\alpha = \beta = \gamma = 90°$	2-zählige Achsen in drei senkrecht aufeinander stehenden Richtungen (parallel x, y und z)	P, I, C, F
tragonal	$a = b, c$ beliebig $\alpha = \beta = \gamma = 90°$	4-zählige Achsen in einer Richtung (parallel z)	P, I
trigonal	wie hexagonal	3-zählige Achsen in einer Richtung (parallel z)	P, R
hexagonal	$a = b, c$ beliebig $\alpha = \beta = 90°$, $\gamma = 120°$	6-zählige Achsen in einer Richtung (parallel z)	
kubisch	$a = b = c$ $\alpha = \beta = \gamma = 90°$	symmetrieäquivalente -zählige Achsen in Richtung der Diagonalen eines Würfels	P, I, F

7 crystal systems

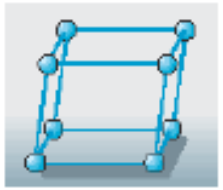


14 3D Bravais

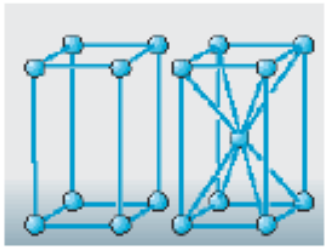
14 Bravais lattices



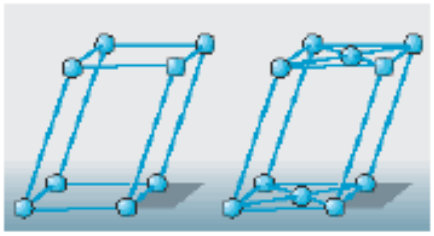
cubic



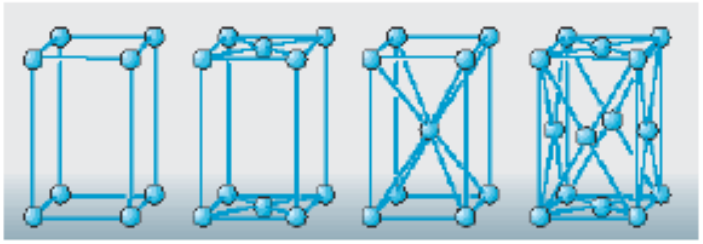
rhombohedral



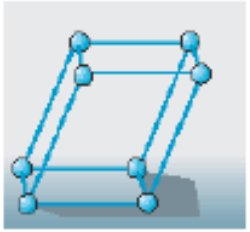
tetragonal



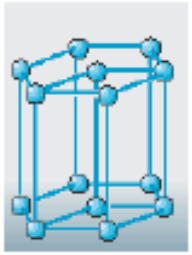
monoclinic



orthorhombic



triclinic



hexagonal

Composed lattices

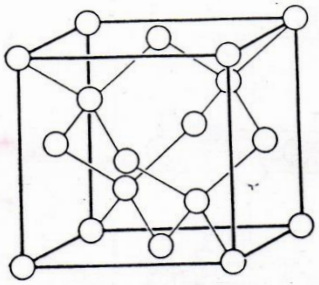


Bild 2.31. Kristallstruktur von Diamant

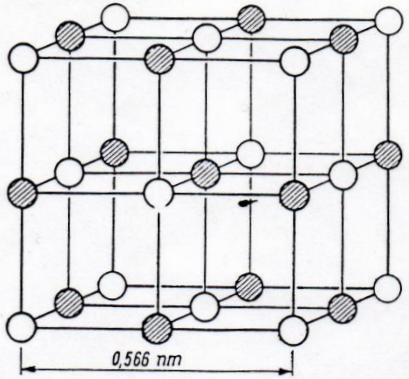


Bild 1.2. NaCl-*Struktur, schematisch*

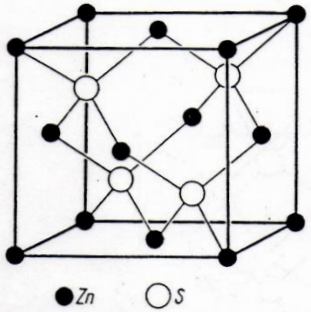
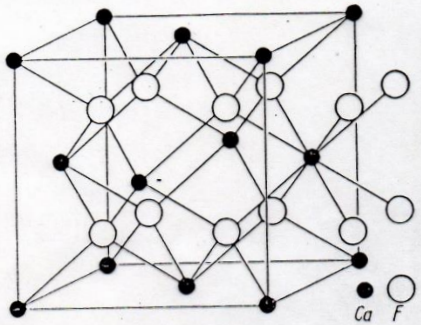
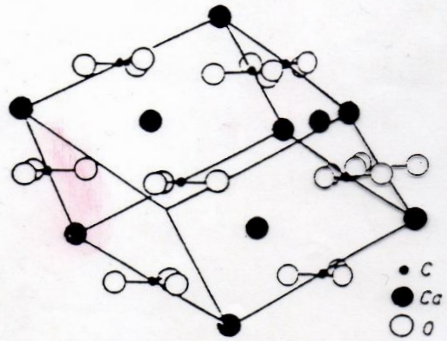
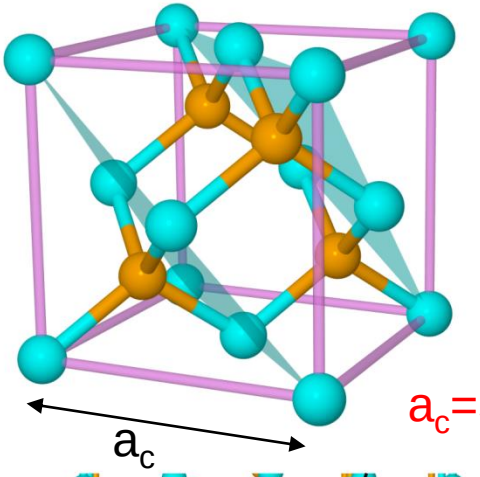


Bild 2.32. Kristallstruktur von Sphalerit (Zinkblende)



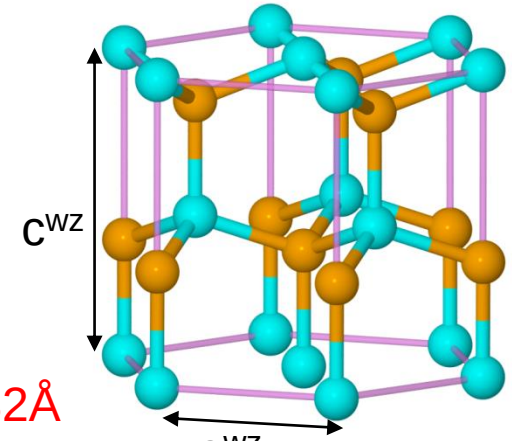


zinc-blende (ZB)



a_c=5.6532Å

wurtzite (WZ)



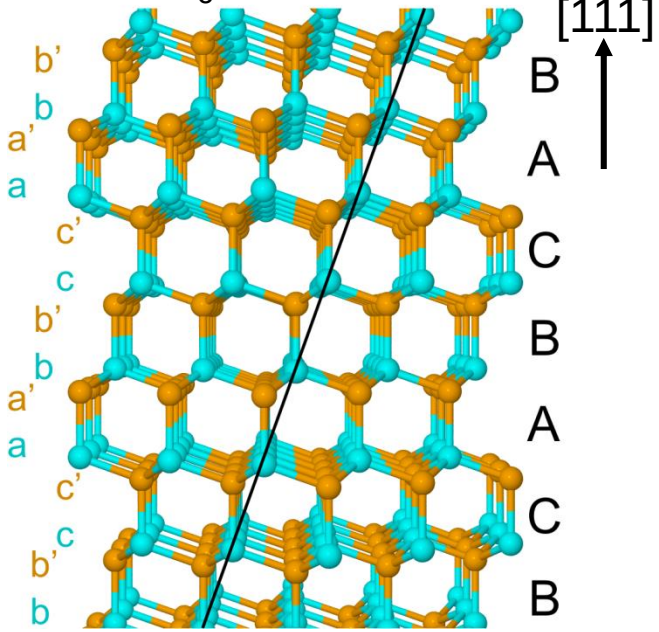
ZB and WZ have slightly different lattice parameters! (and Band-gap)

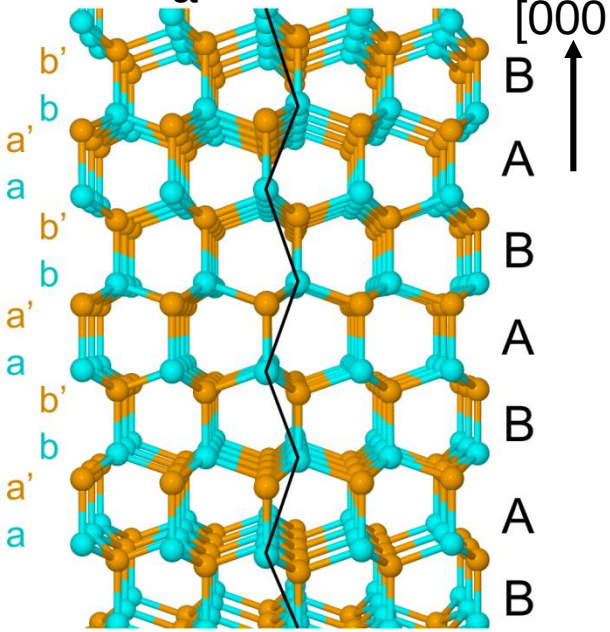
$c^{wz} > 2/\sqrt{3}\ a_c$

$a^{wz} < 1/\sqrt{2}\ a_c$

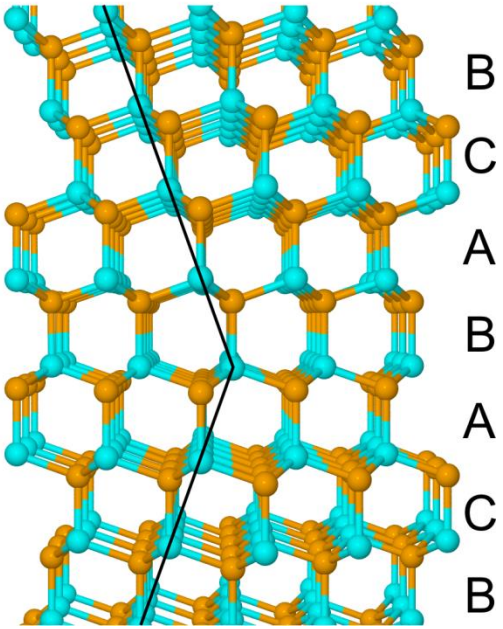
a^{wz}=3.987Å

c^{wz}=6.573Å





twinned ZB



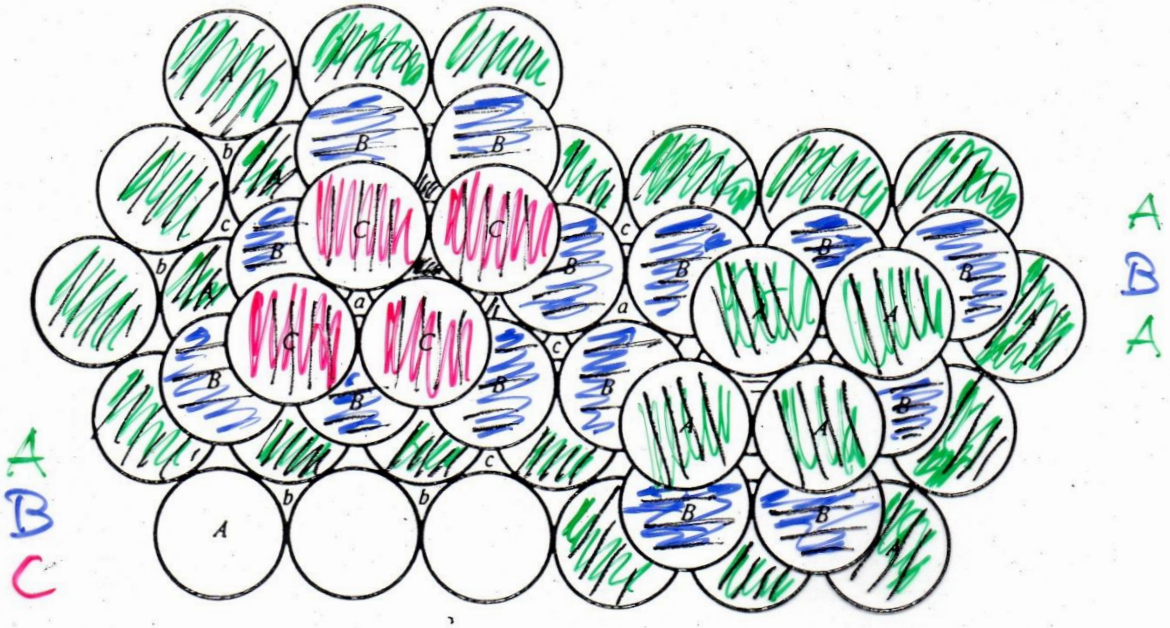


Fig. 1.62. Two principal variants of the formation of three-dimensional closest packing of spheres made up of the layers *A*, *B*, *C* stacked over the interstices in the lower layer *a*, *b*, *c*; *ABC* (*left*) and *ABAB* (*right*)

Dense packing of rigid sphers

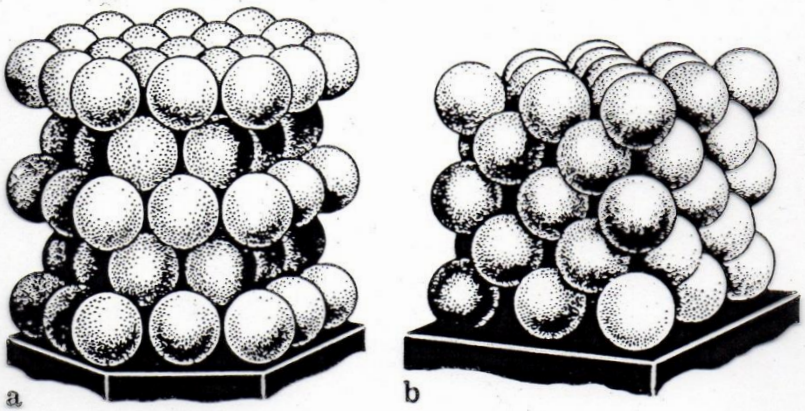
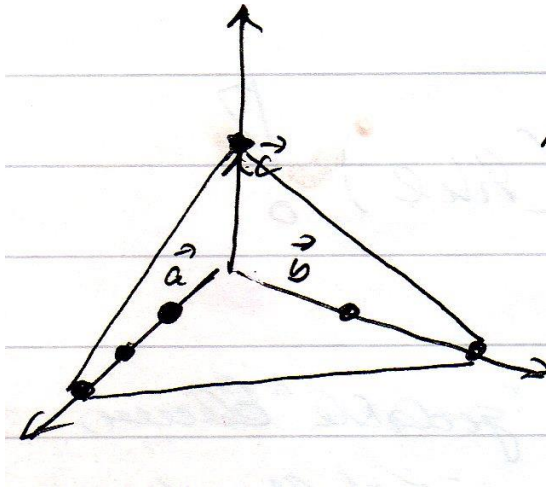


Fig. 1.63a, b. Hexagonal (a) and cubic (b) closest packing. In the cubic packing the closest-packed layers can be singled out in four planes perpendicular to the body diagonals of the cube

Indexation of lattice planes (Miller indicees)

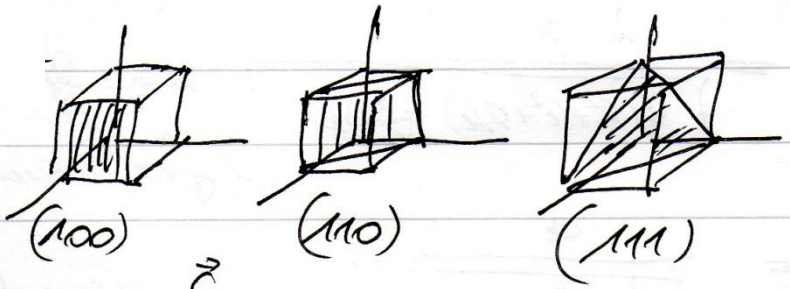


Net planes cut axes at 3a,2b and 1c → (3 2 1)

Takes reciprocals

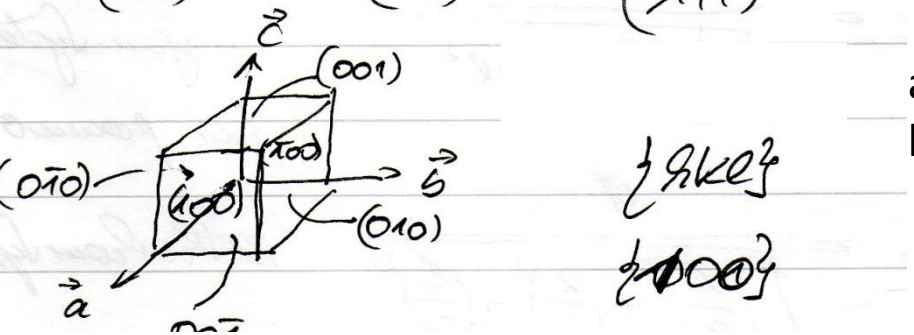
1/3 : ½ : 1/1 → * 6 → 6/3 : 6/2 : 6:1 → (2 3 6)

Defines Miller indicees : characteristics of a set of lattice planes in reciprocal space



K = ha* + kb* + lc*

vector in reciporcal space pointing from origin towards reciprocal lattice point (hkl)



a*, b*, c* , axes in reciprocal space
h , k, l , Miller indicees

Direct and reciprocal space