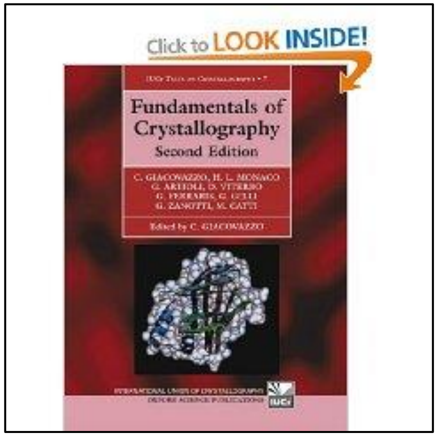
Dr Semën Gorfman
Department of Physics, University of SIegen

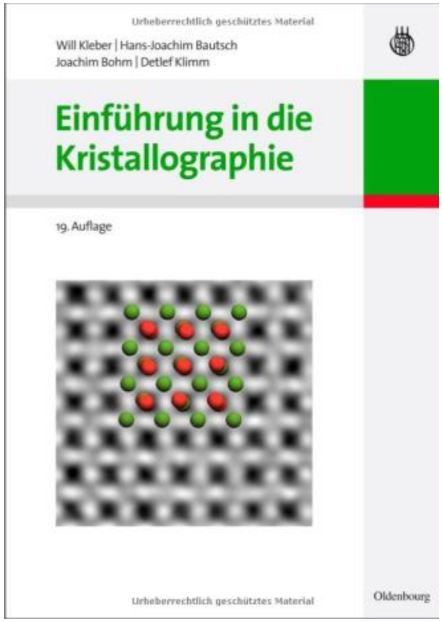
Lecture course on crystallography, 2015

Lecture 1: Introduction to crystallography

Recommended Books

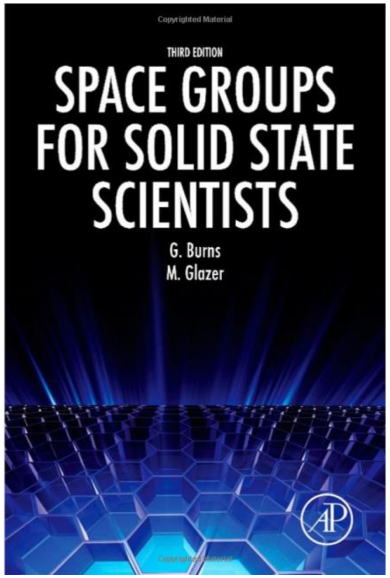


Fundamentals of Crystallography
C. Giacovazzo
Oxford University Press, 1992
~ 70 EURO (Amazon)
Available in University library



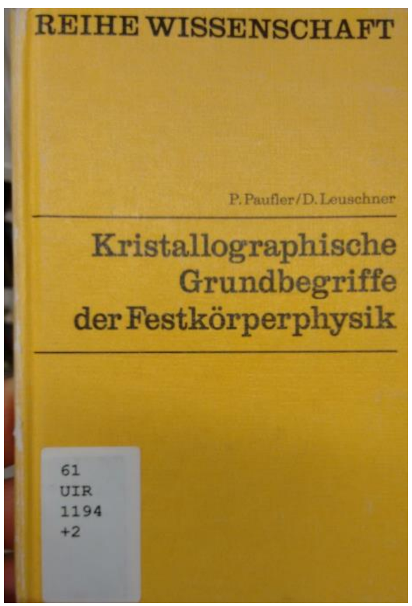
Einführung in die Kristallographie
Kleber, Bautsch, Bohm, Klimm
Available in University library

Recommended Books



Space Groups for Solid State Scientist
G. Burns, A. M. Glazer
Elsevier

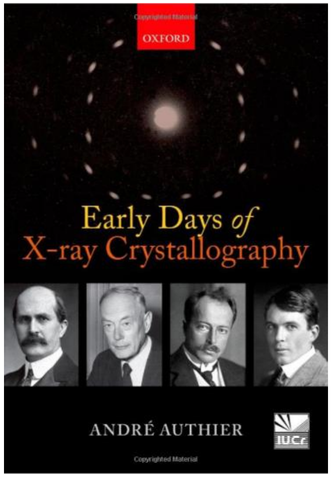
~ 64 EURO (Amazon)
<u>Limited availability</u> in the University library



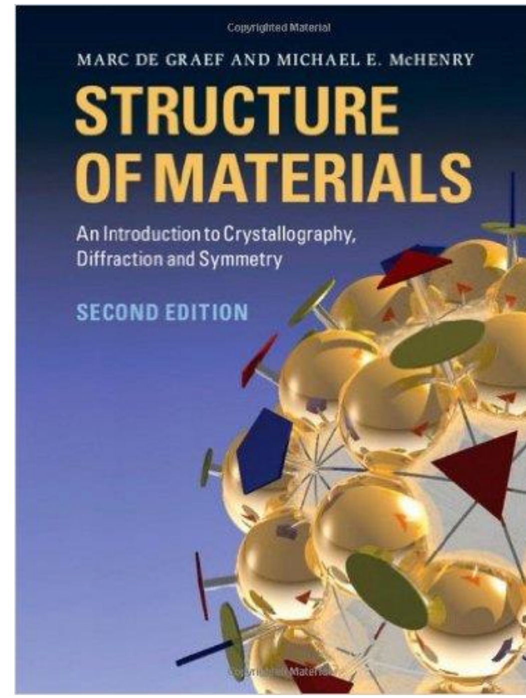
Kristallographische Grundbegriffe der Festkörperphysik
P. Paufler, D.Leuschner

JUST 9 EURO (Amazon)!
<u>Limited availability</u> in the University library

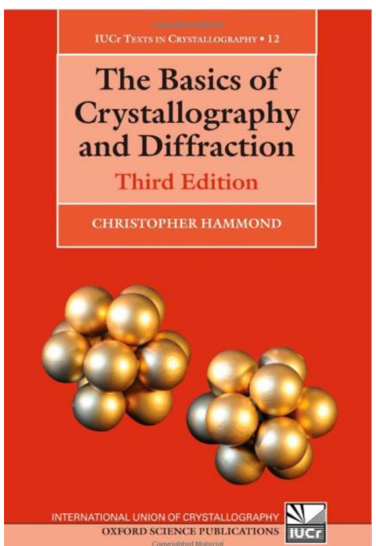
Recommended Books



Early Days of X-ray crystallography
A. Authier
Oxford University Press, 1992
~ 60 EURO (Amazon)
NOT Available in University library



Structure of Materials
Marc de Graef, Michael Mc Henry
Cambridge University Press, 2007
~ 70 EURO (Amazon)
NOT Available in University library



The basics of crystallography and Diffraction
C.Hammond
Oxford University Press, 1992
Very Limited availability in University library

Recommended Books

If you feel advanced and want to know EVERYTHING in MODERN CRYSTALLOGRAPHY

International Tables for Crystallography, Volumes A - D

Objectives of the course

To provide the basic knowledge about the **structure of** crystalline materials.

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

To give an idea about the role of **symmetry** for the description of crystal structures

To provide with the key knowledge for understanding **X-ray and electron diffraction experiement** used to investigate the structure of materials.

2014: International year of crystallography

www.iycr2014.org

Why 2014?

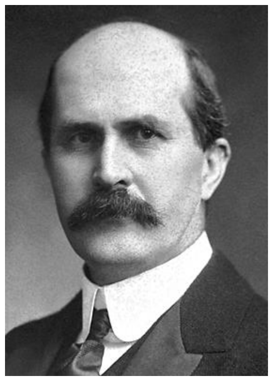
Nobel Prizes, associated with Crystallography

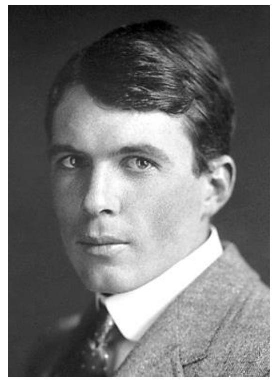
http://www.iucr.org/people/nobel-prize

All together: 29; Physics prizes: 10; Chemistry prizes: 18; Physiology and medicine 1

Max von Laue
1914

WH Bragg and WL Bragg
1915

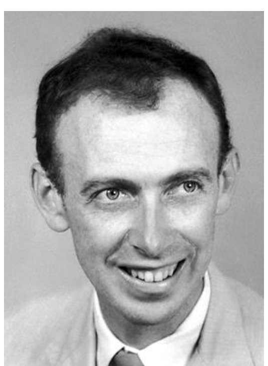




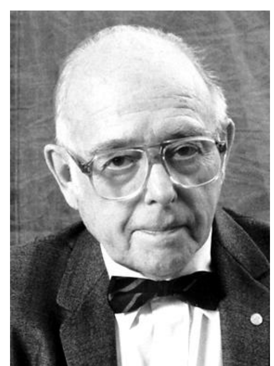
Davisson and GP Thompson
1937

D Hodgkin
1964

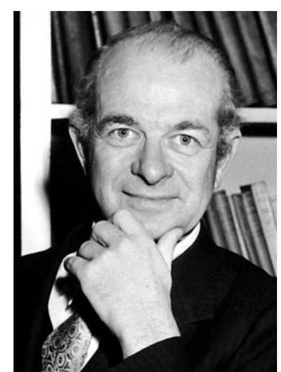
F Crick, J Watson and M Wilkins
1962



C Shull
1994

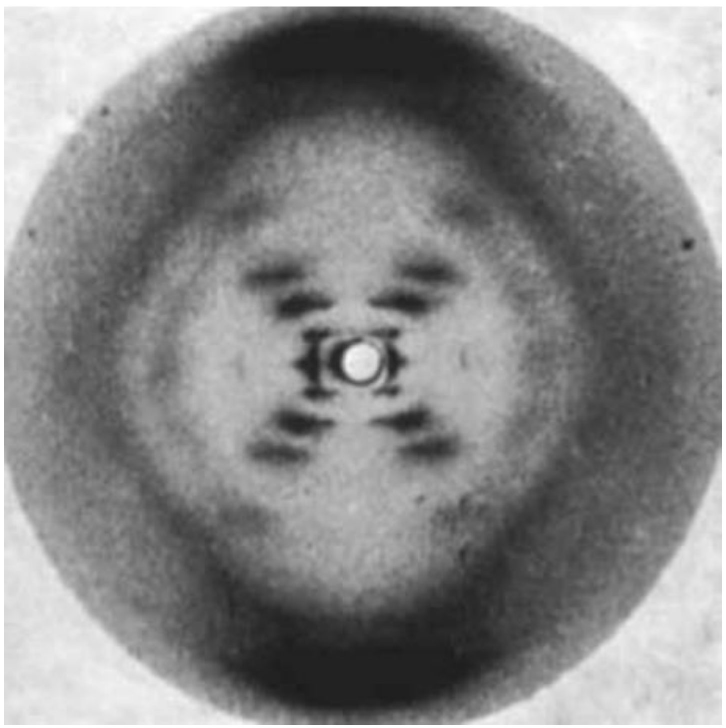


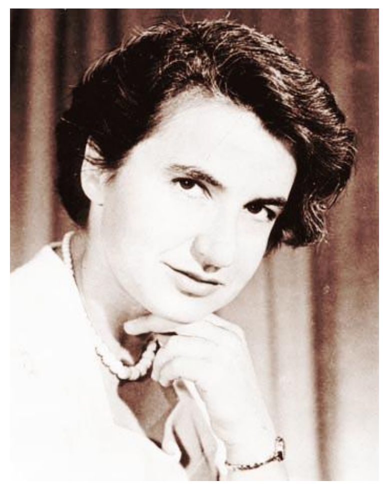
L Pauling
1994



Dan Shechtman
2011

On particular highlight





Rosalind Franklin

Double helix structure of DNA

PHYSICS

Material science

MODERN CRYSTALLOGRAPHY

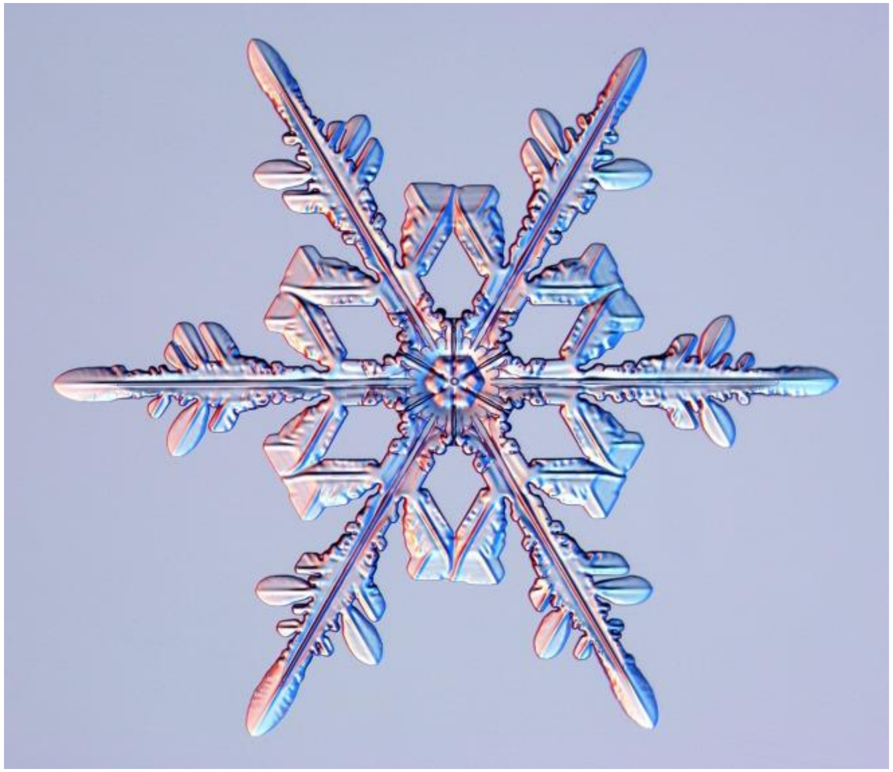
CHEMISTRY

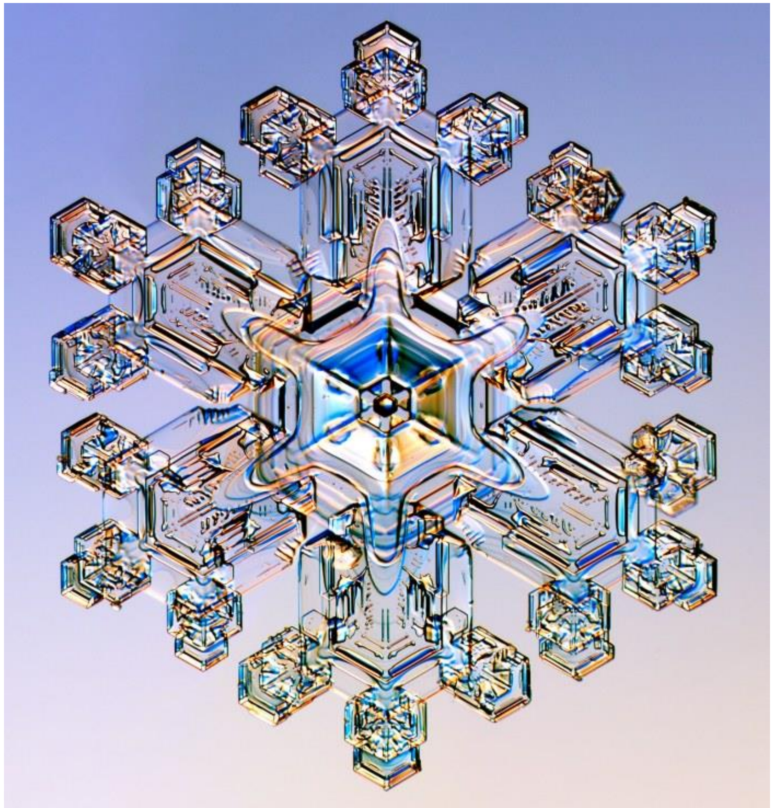
Biology

MATHS

What is a crystal?

Originally from Greek: CRYSTAL – NATURAL ICE





Visit   www.snowcrystals.com for your own pleasure

What is a crystal?

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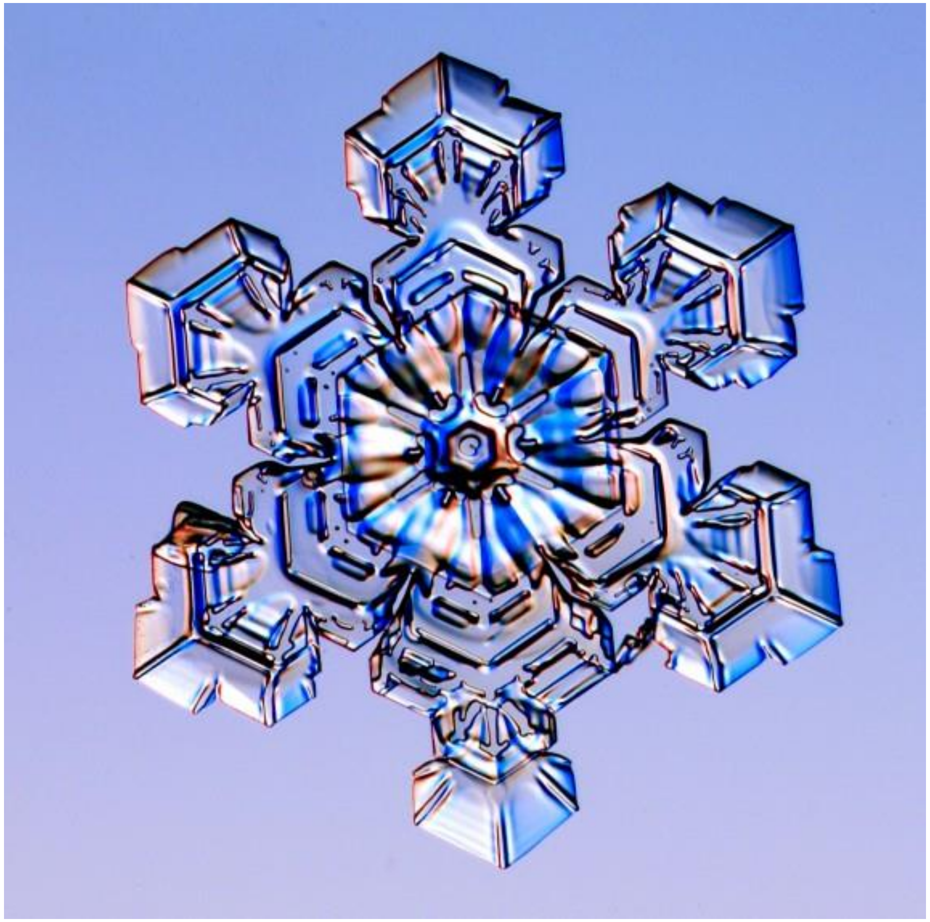
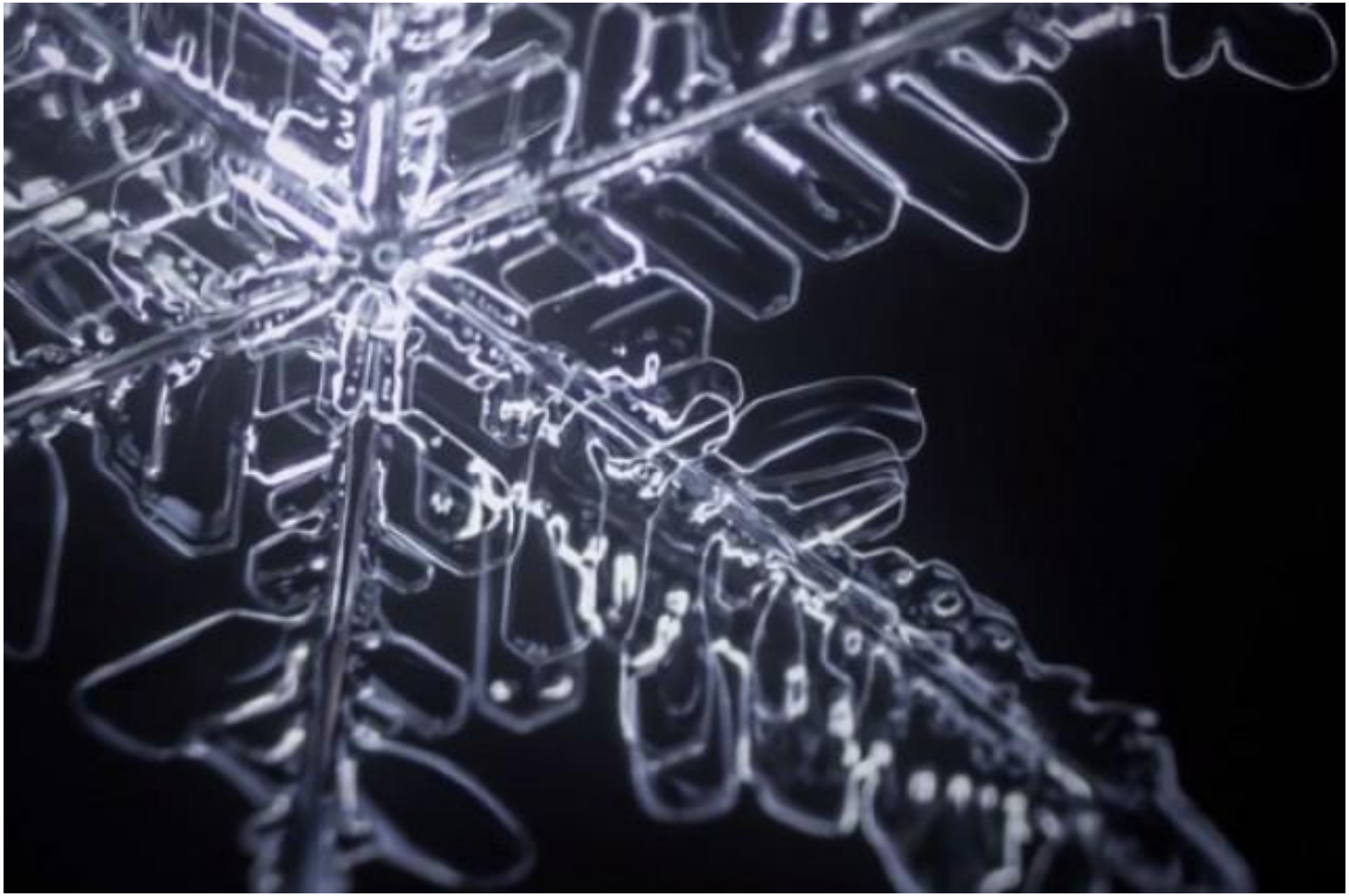


Visit   www.snowcrystals.com for your own pleasure

The growth of an ice crystal

http://www.iflscience.com/chemistry/watch-snowflake-form-your-eyes



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

Minerals

Minerals are natural solids formed as a result of the certain geological processes

Minerals are the largest source of naturally formed crystalline solids

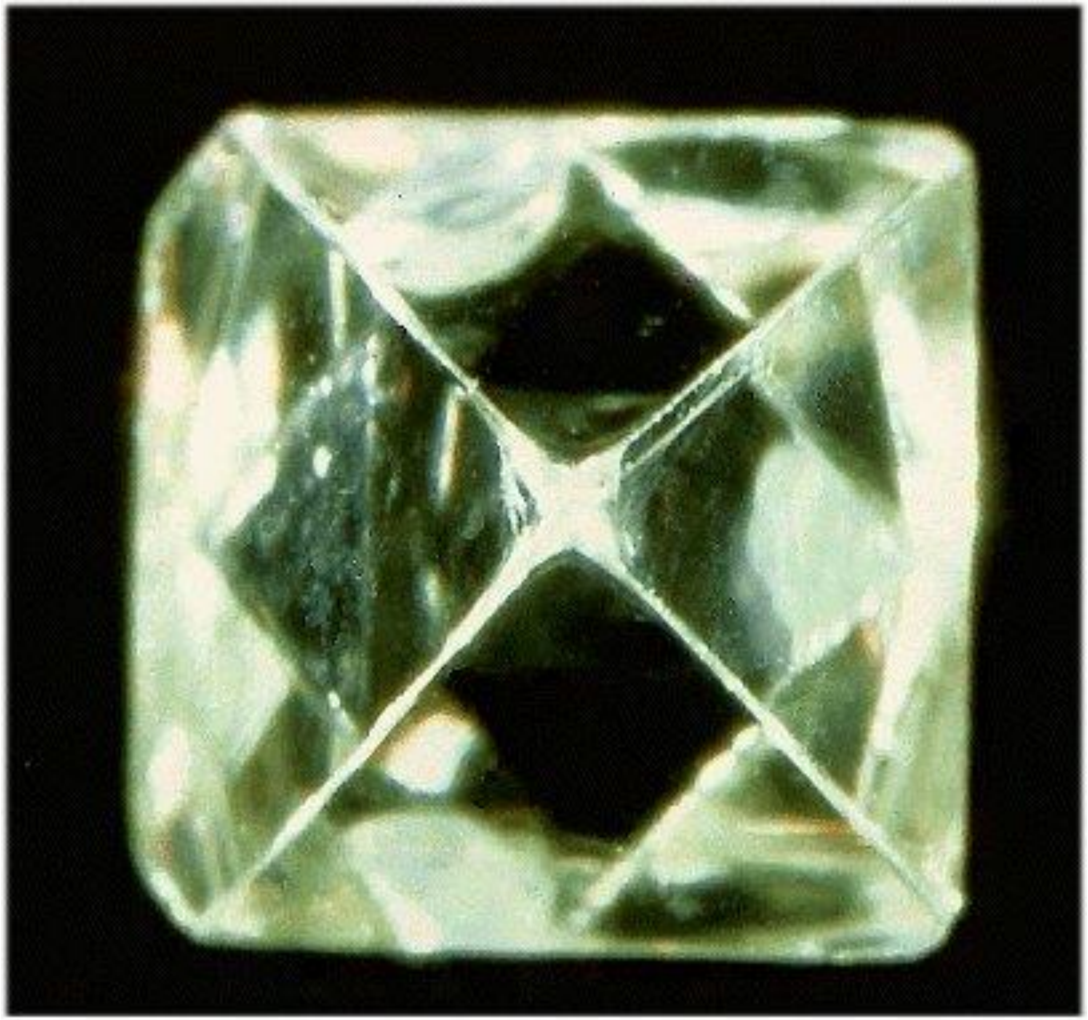
QUARTZ, SiO_2

http://webmineral.com

Mackayite, $Fe_3Te_2O_5(OH)$

http://webmineral.com

DIAMOND, C

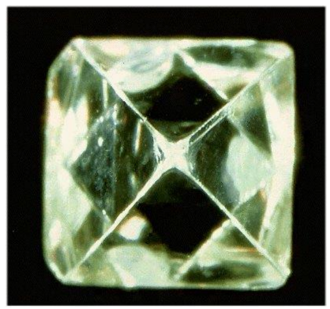


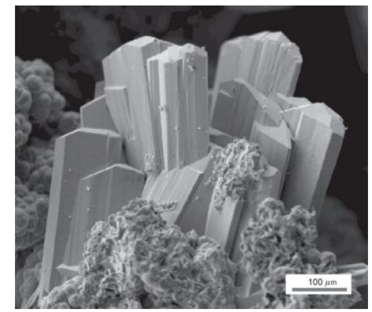
http://webmineral.com

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.

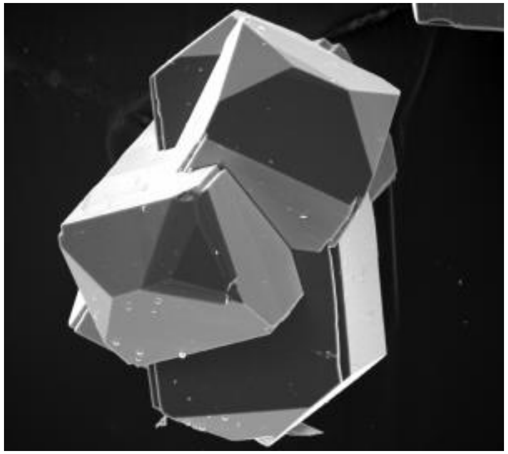



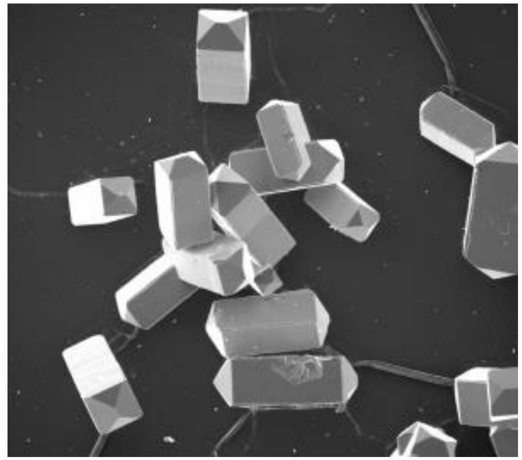


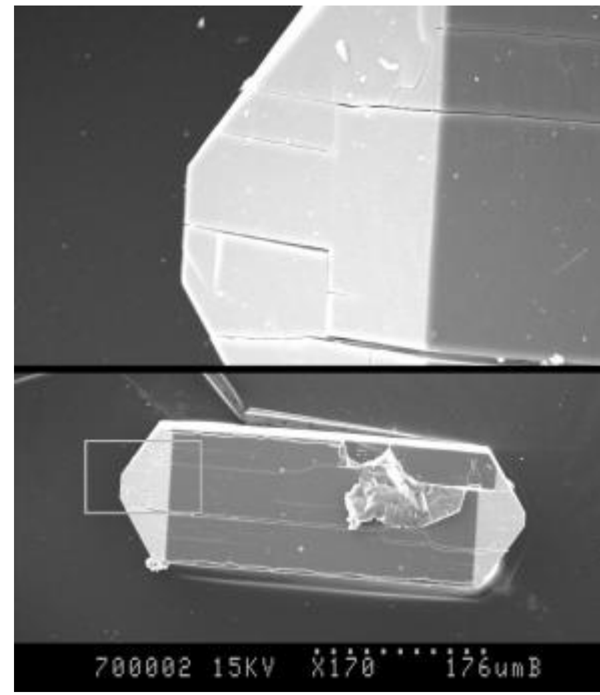
First stage of crystallography

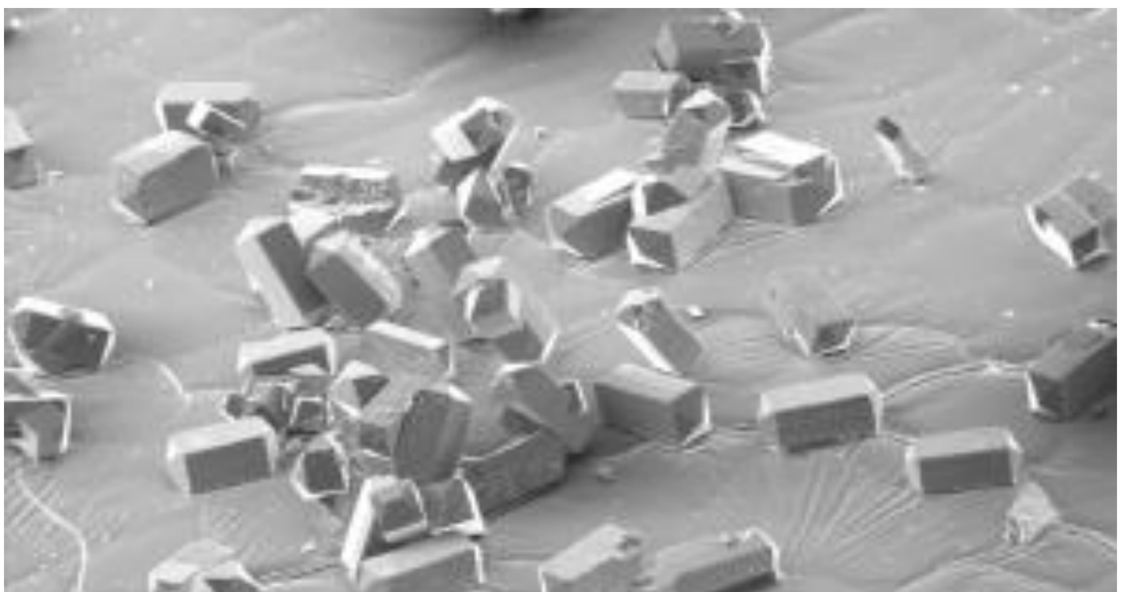
Investigating of crystal morphologies, i.e. external shapes of natural minerals. However it was more difficult to find the common features of external shapes of minerals.

Some electron microscopy images of natural faces



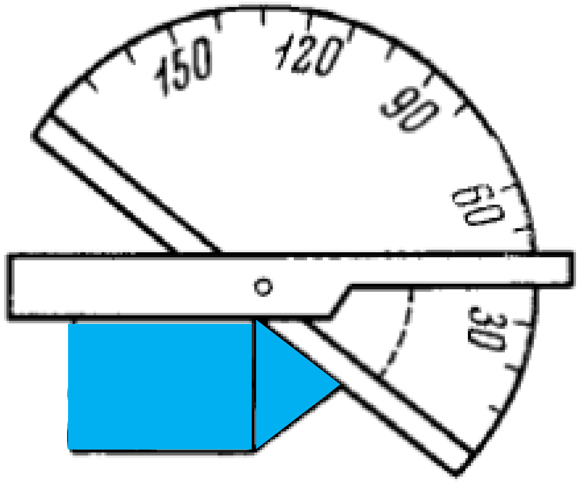






THE BIRTH OF CRYSTALLOGRAPHY : The law of constancy of the interfacial angles

Nicolaus Steno (1638-1686)

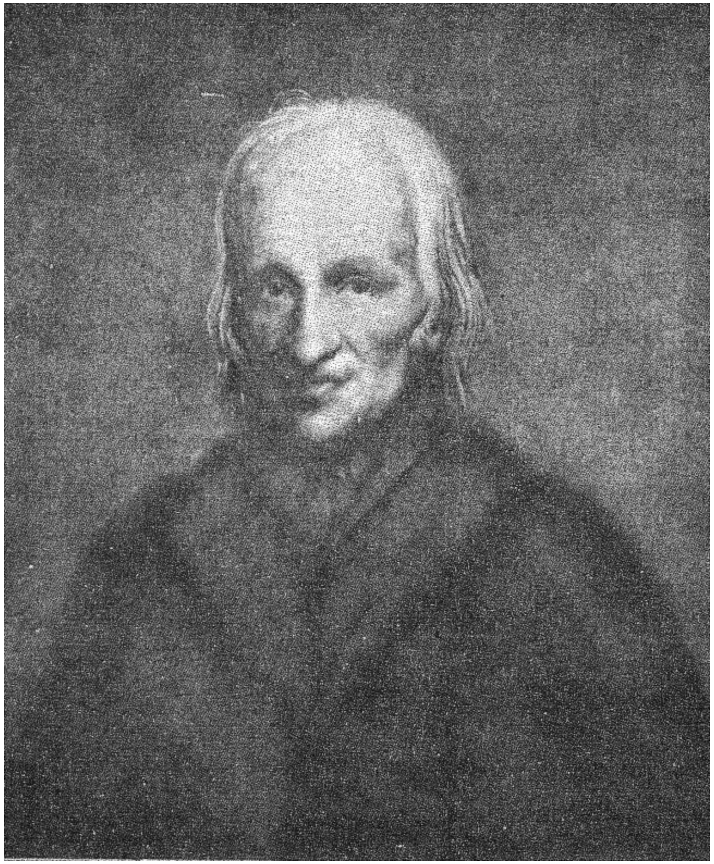


Romé de L'Isle (1736 -1790)

...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)



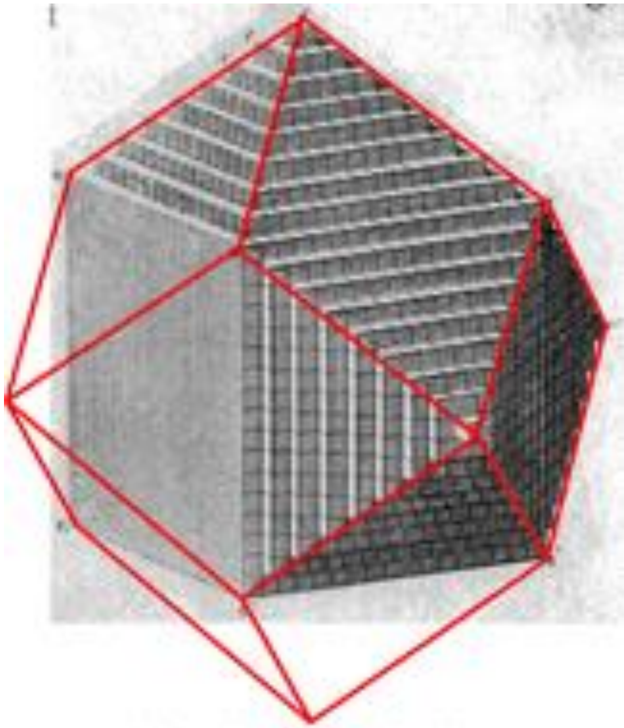
First mathematical approach to the description of the crystal faces in crystals

...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 ...

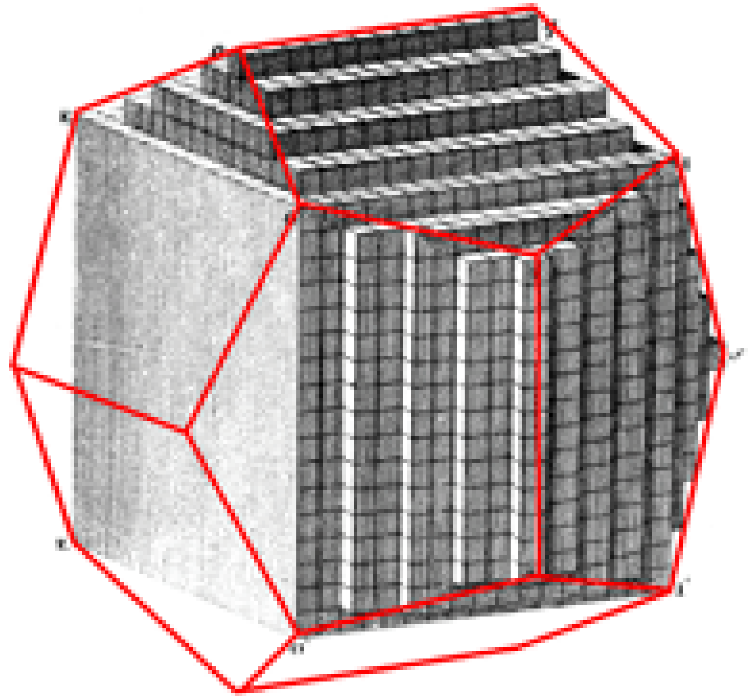
The exact meaning of these three integer numbers will be explained later

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



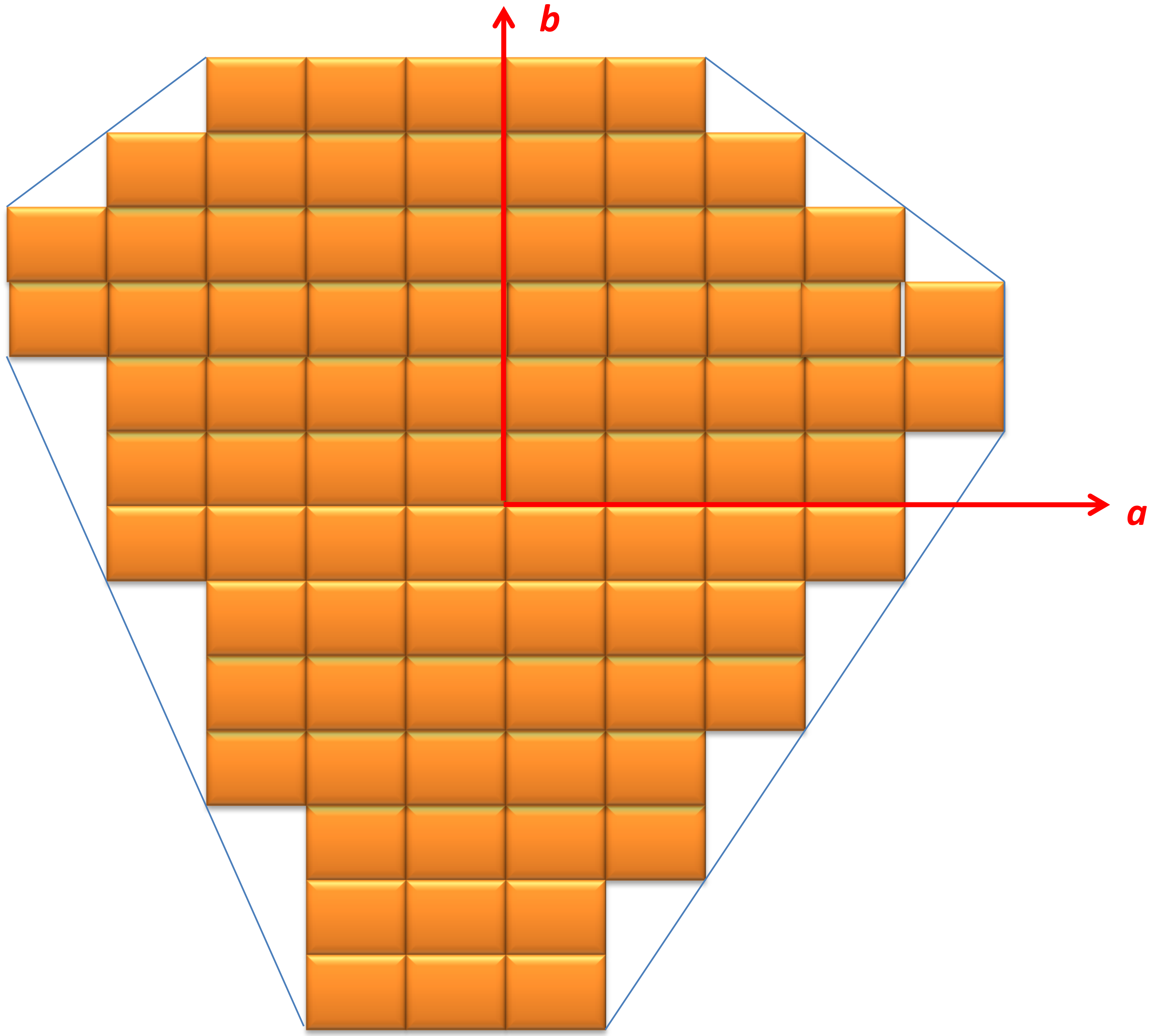
Rhomb-dodecahedron



Pentagon-dodecahedron

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

The graphical illustration of the law of rational indices

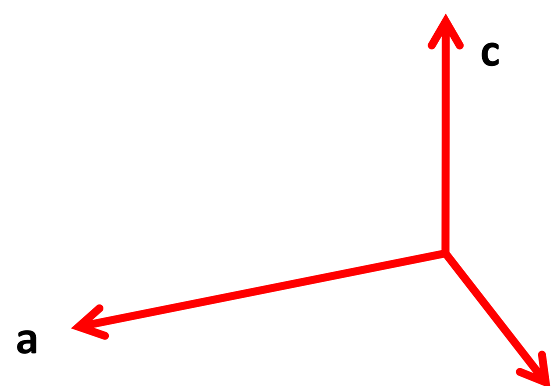


In the works of *Nicolaus Steno (1638-1686)* , *Romé de L'Isle (1736 - 1790)* the first systematic studies of crystal shapes were performed. Result – the law of constancy of interfacial angles. This is an important empirical observation, however it does not give any insight into the internal structure.

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.

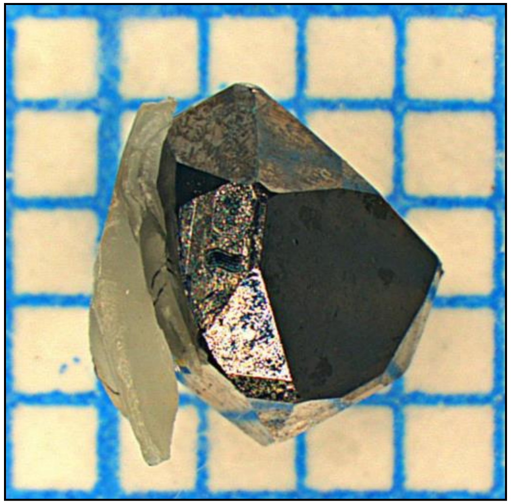
Crystal shape

Internal directions

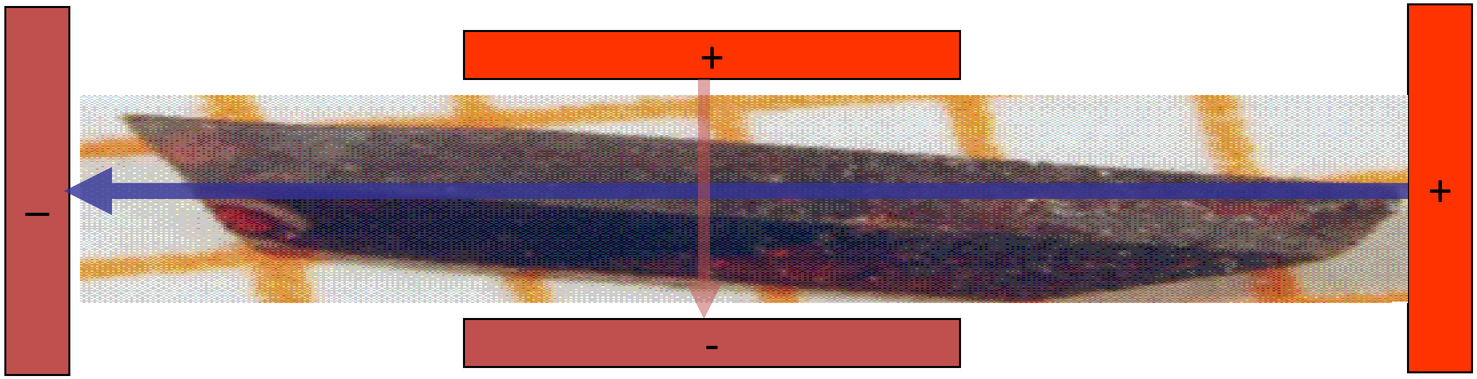


Anisotropy of physical properties

1. Growth velocity (formation of facets)



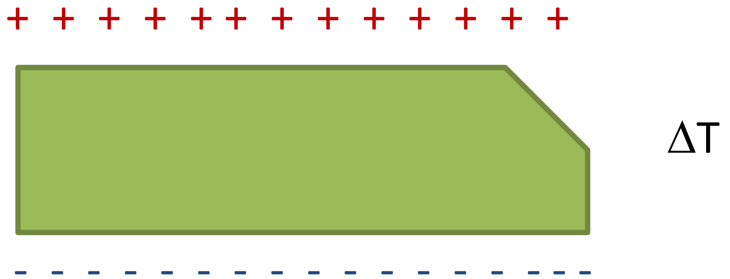
2. Electrical conductivity



Physical properties of crystals: pyroelectric effect in tourmaline

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

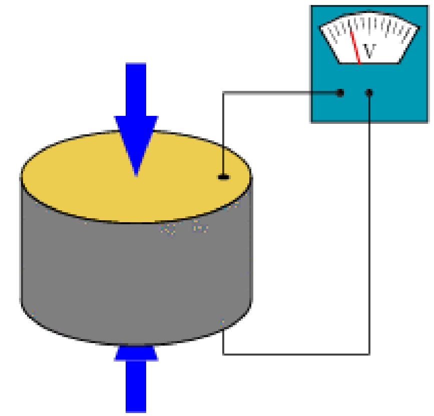
Tourmaline crystal



Important: pyroelectric effect is anisotropic, electrical charges develop only in <u>certain directions</u>, 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

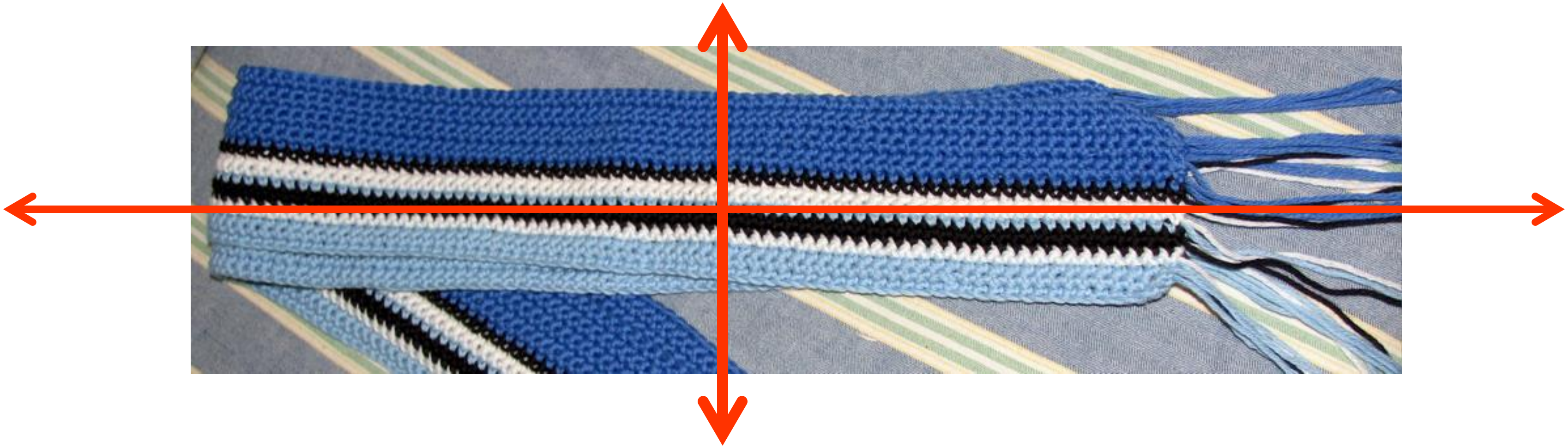


Piezoelectricity is a physical phenomena occurring in some crystals, related to the generation of electric charges by external pressure.

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

~ 1 mm=10^{-3} m

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

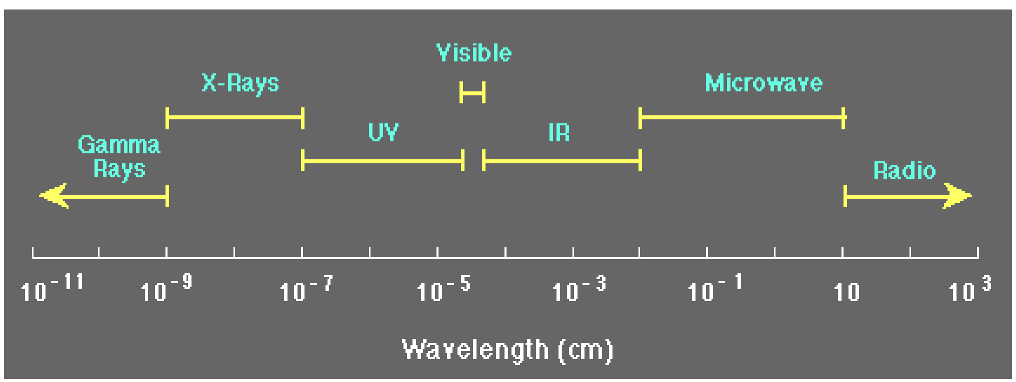
Crystallography -> birth of solid state physics

1912 **Max von Laue**

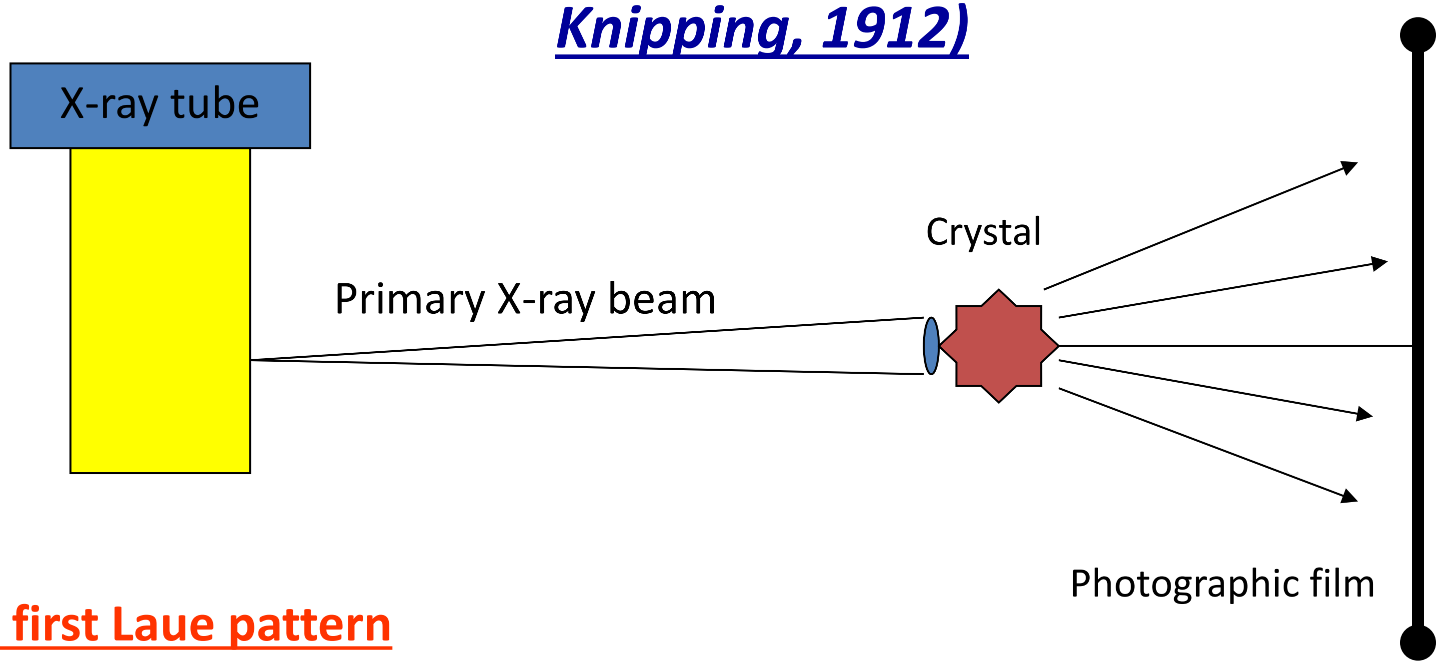
1914

Nobel prize in physics

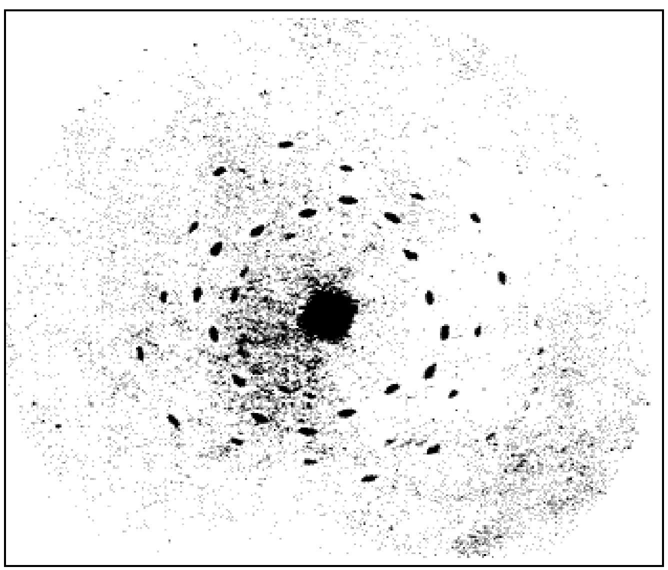
"for his discovery of the diffraction of X-rays by crystals"



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



The first Laue pattern



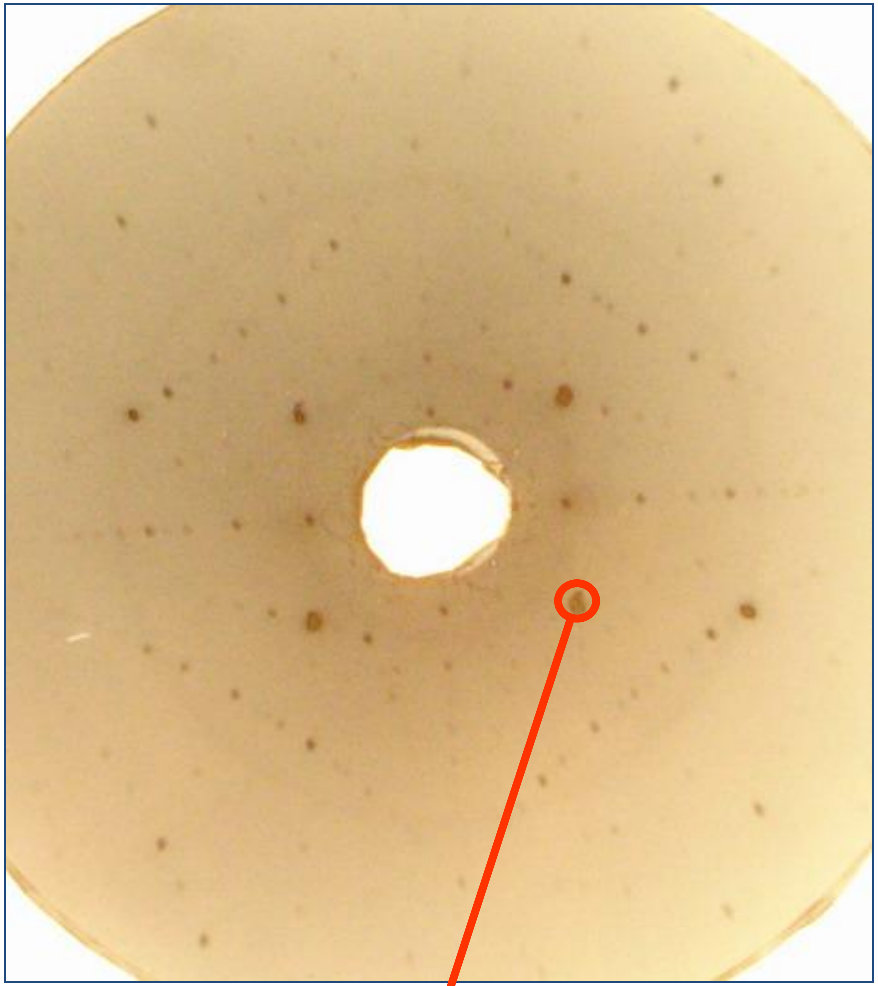
Conclusions

1. X-rays are electromagnetic waves

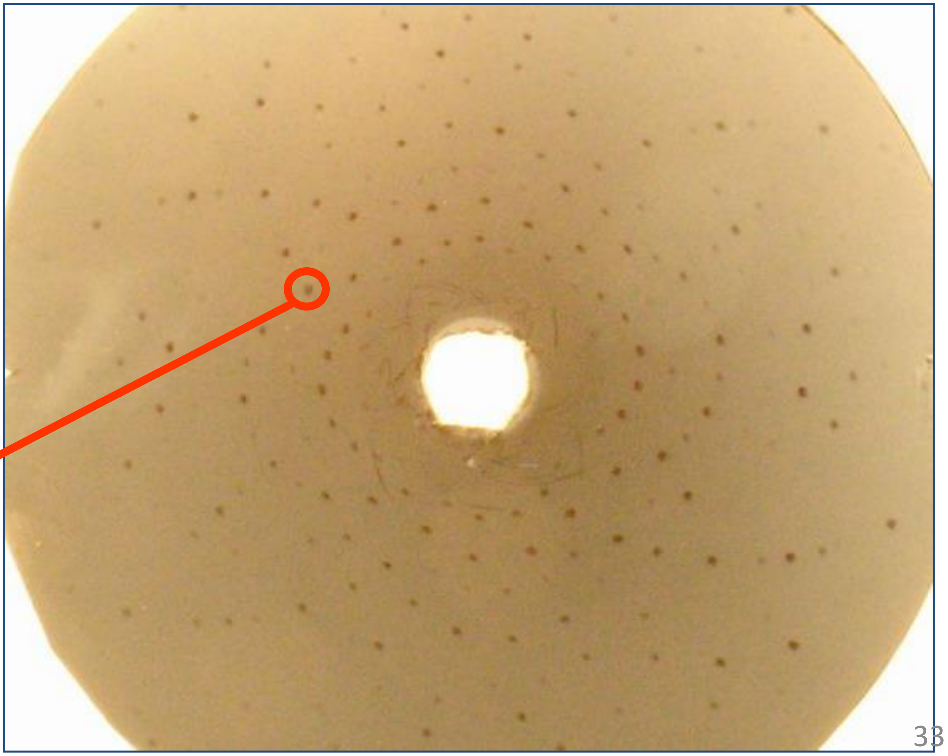
2. Crystal structures are periodic

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 $\mathring{A} = 10^{-10}\ m$

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

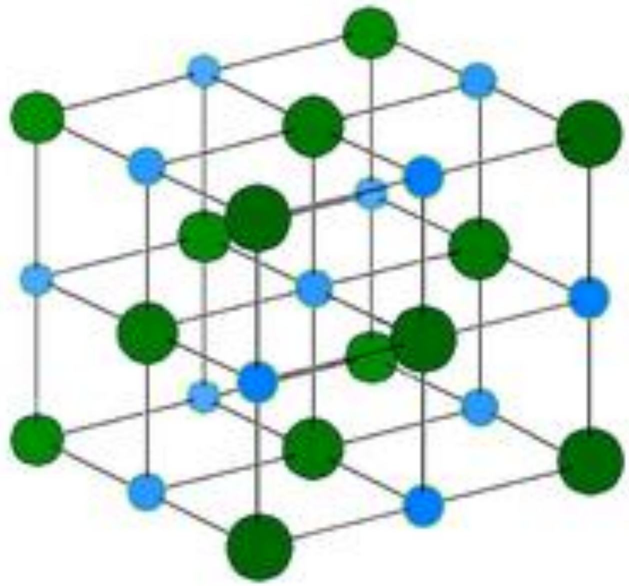
The first REAL crystal structure

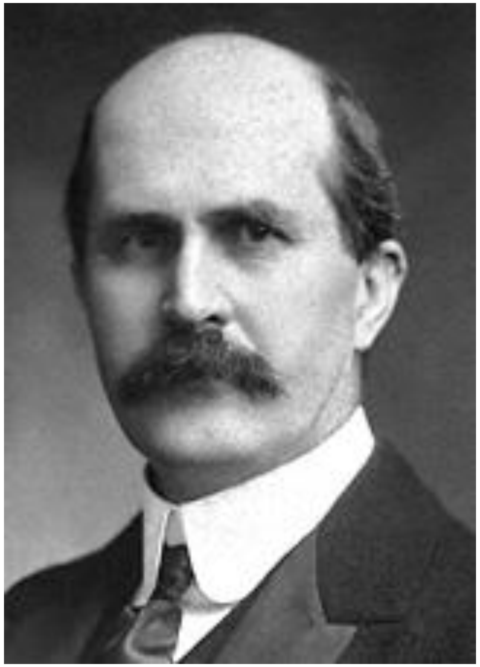
1915

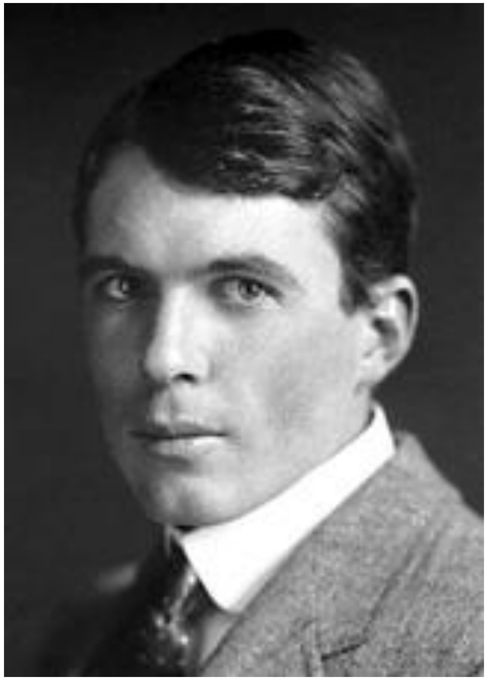
Nobel prize in physics

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

Atomic structure of NaCl, KCl, LiF was established







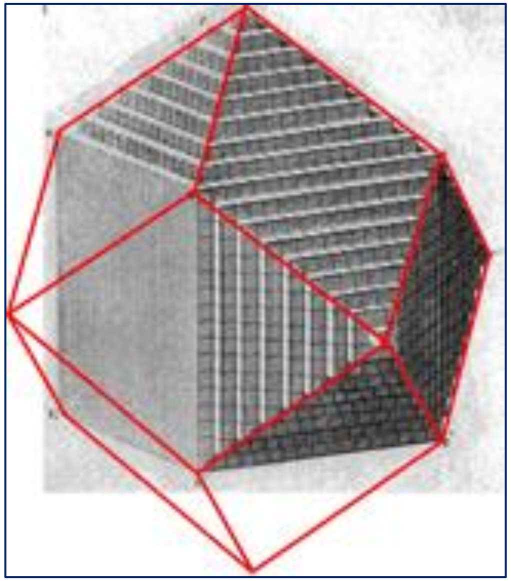
Sir William Henry Bragg ***William Lawrence Bragg***

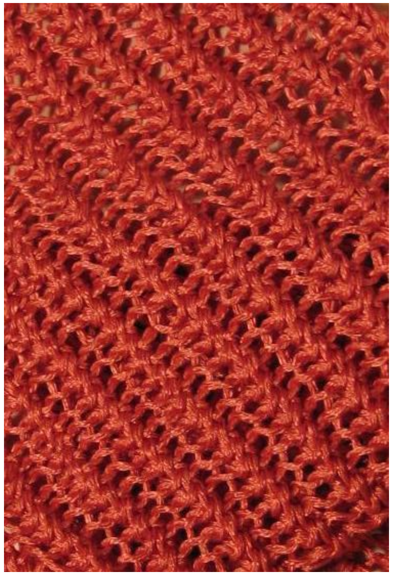
Take home message: what is a crystal

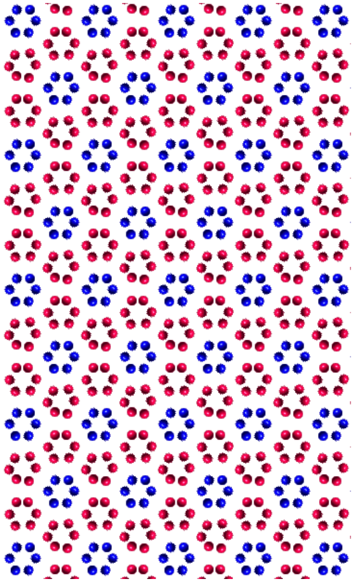
	Crystalline solid	Amorphous solid
Shape	**Polyhedral shape with naturally formed faces**	**No naturally formed faces**
Properties	**Anisotropic**	**Isotropic**
Atomic structure	**Periodic (long range ordered)**	**No periodicity. Short-order only**
X-ray Diffraction	**Well separated diffraction picture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

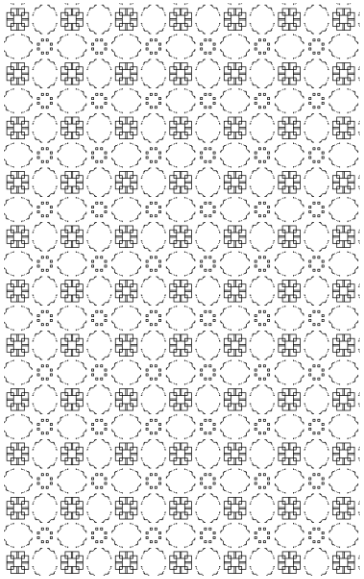
The concept of long-range order

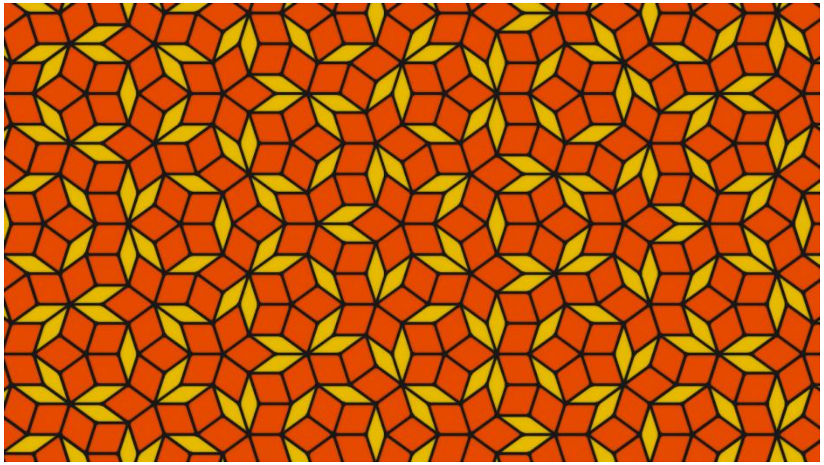
Long-range order is the geometrical law of expansion maintained over long (in comparison to interatomic) distances!





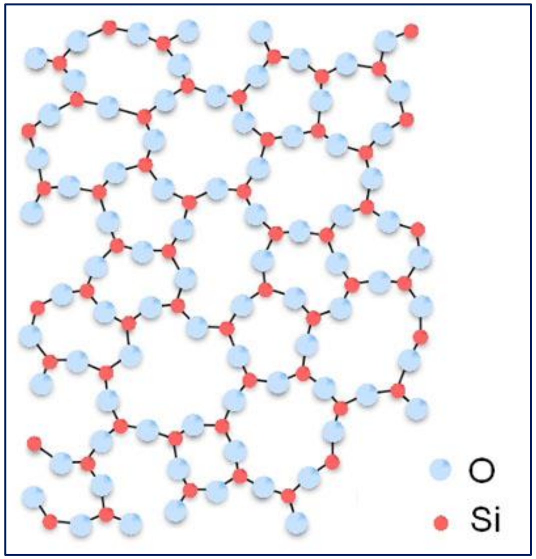


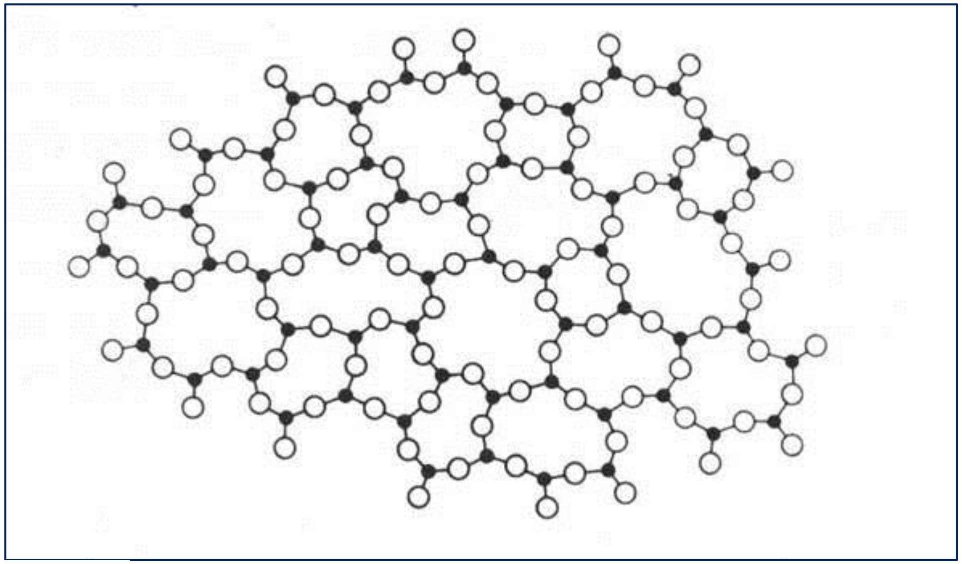


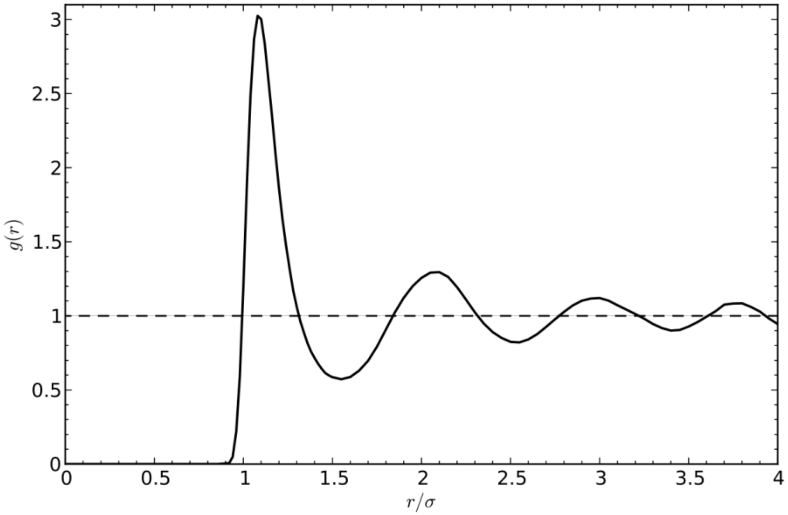


The concept of short-range order

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.

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