Dr. Sem Gorfman and **Prof. U. Pietsch** Department of Physics, University of Siegen



Lecture course on crystallography, 2016

Lecture 1 Part 1 Introduction

Objectives of the course

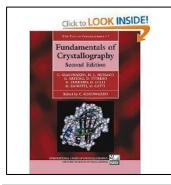
To provide the basic knowledge necessary for the **description**, **understanding** and **investigation** of crystalline materials.

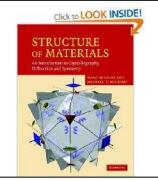
To understand the most important concepts of crystallography such as crystal lattice, unit cell, symmetry, atomic positions

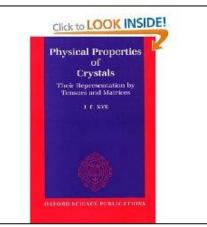
To give a general idea on how the **symmetry** of a material is responsible for the **unique physical properties of crystals**

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

Recommended Books







Fundamentals of Crystallography C. Giacovazzo Oxford University Press, 1992 £49.40 (Amazon) Available in University library

Structure of Materials Marc de Graef, Michael Mc Henry Cambridge University Press, 2007 £42.75 (Amazon) NOT Available in University library

Physical properties of crystals and their representations by tensors and matrices

J.F. Nye

Oxford University Press, 1985.

£42.75 (Amazon) NOT Available in University library

Recommended Books

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



International Tables for Crystallography, Volumes A - D



Material science

CRYSTALLOGRAPHY

CHEMISTRY

Biology



Your mathematical background. What you need to know beforehand

Vector algebra:

- Sum of two vectors
- Dot product of two vectors
- Cross product of two vectors
- Mixed product of three vectors

Basics of linear algebra:

Calculations of determinants

What is a crystal?

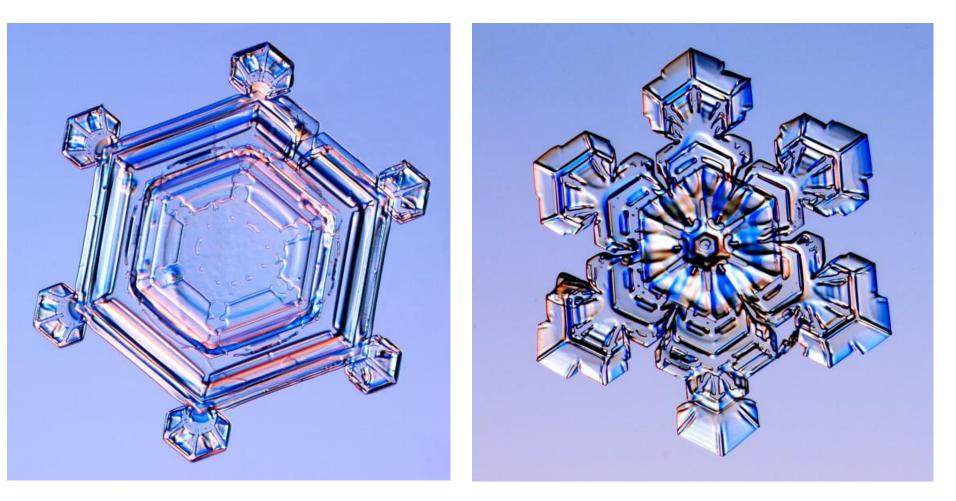
Originally from Greek: CRYSTAL – NATURAL ICE



Visit <u>www.snowcrystals.com</u> for your own pleasure

What is a crystal?

Originally from Greek: CRYSTAL – NATURAL ICE



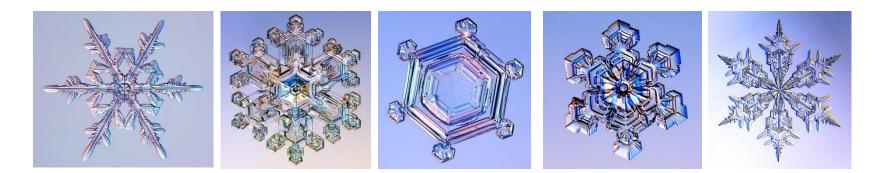
Visit <u>www.snowcrystals.com</u> for your own pleasure

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: H₂O

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



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

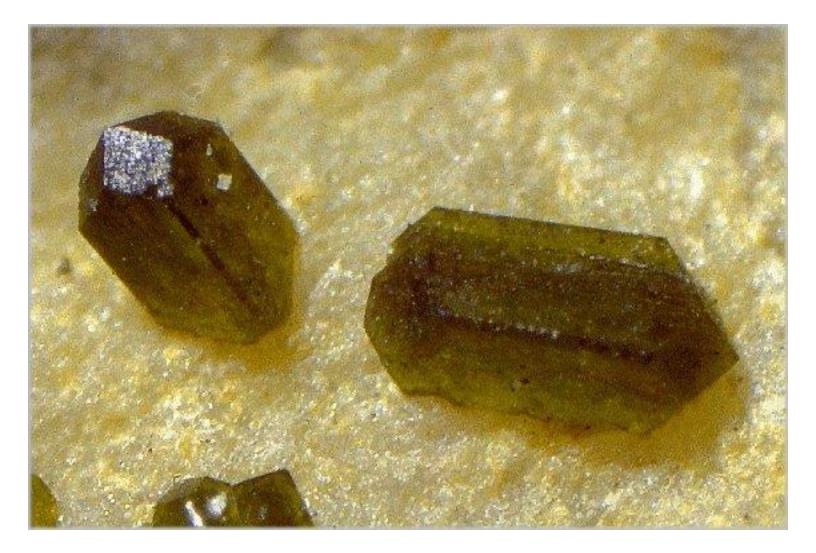






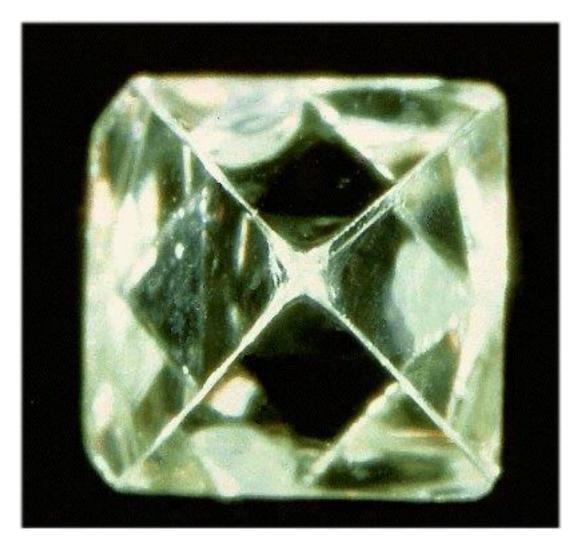
http://webmineral.com





http://webmineral.com





http://webmineral.com

Common features of minerals

Formation of natural facets

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



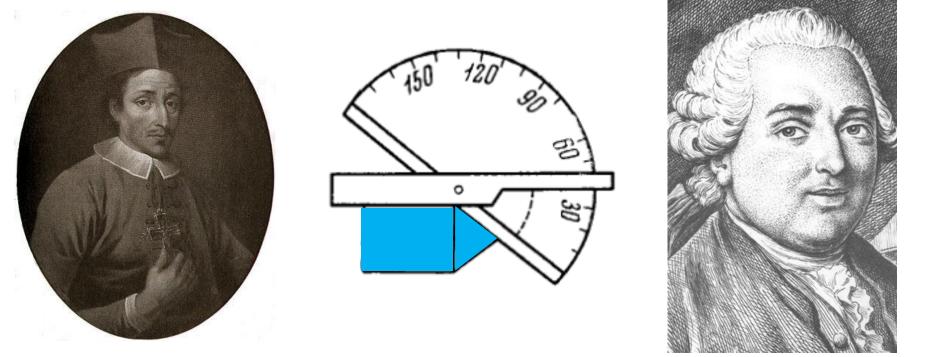
First stage of crystallography

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.

<u>THE BIRTH OF CRYSTALLOGRAPHY : The law of constancy of the</u> <u>interfacial angles</u>

Nicolaus Steno (1638-1686)

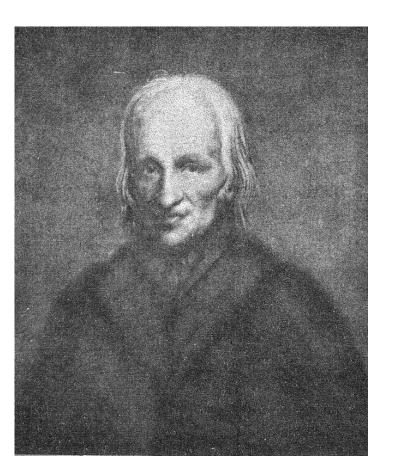
Romé de L'Isle (1736 -1790)



...The angles between the crystal faces of a <u>given species</u> 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

<u>2. Haüy (1743-1822)</u>



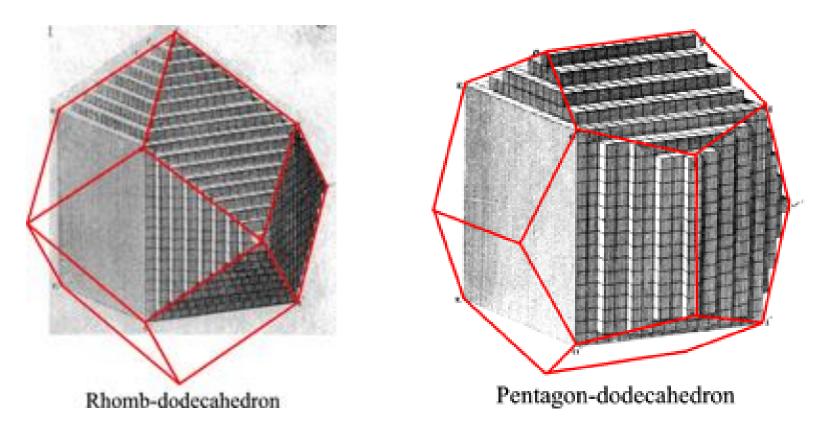
First mathematical approach to the description of the crystal faces in crystals

...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

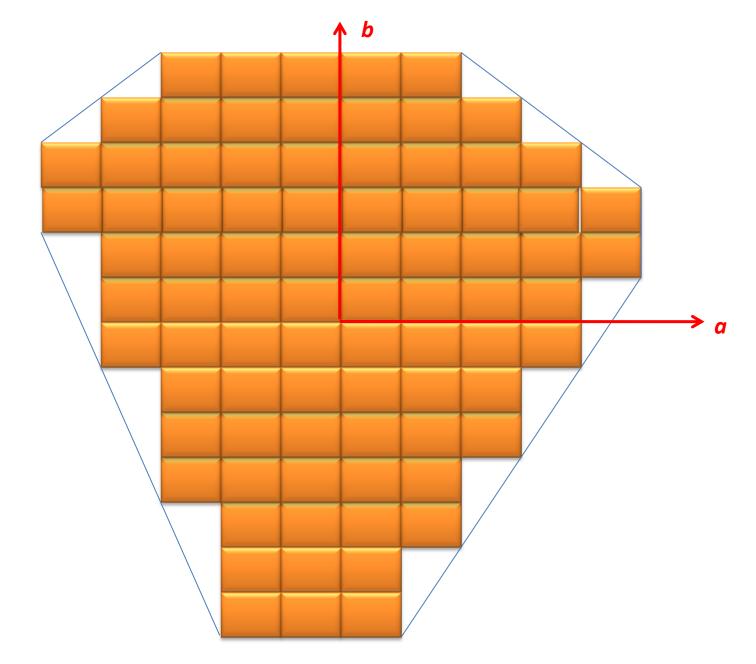
The graphical illustration of the law of rational indices

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



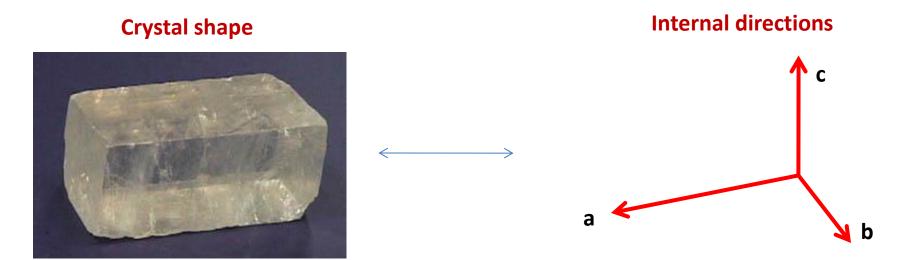
Models from Haüy's Traité de Minéralogie (1801)

The graphical illustration of the law of rational indices



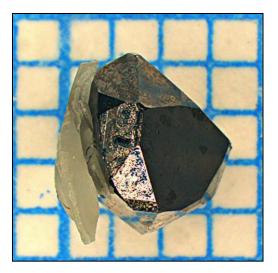
In the works of <u>Nicolaus Steno (1638-1686)</u>, <u>Romé de L'Isle (1736 - 1790)</u> the first systematic studies of crystal shapes were performed. Result – the law of constancy of interfacial angles. This is an important empirical observation, however it does not give any insight into the internal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

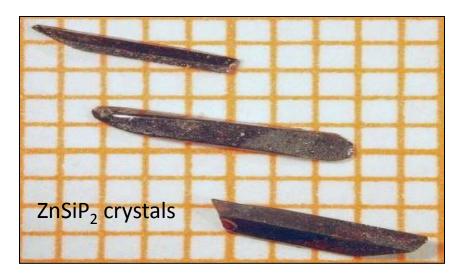
<u>Haüy (1743-1822)</u> was the first who formulated the link between fascinating polyhedral shape and internal structure of crystal. His hypothesis was to explain the crystal shape by the periodic structure of a crystal.



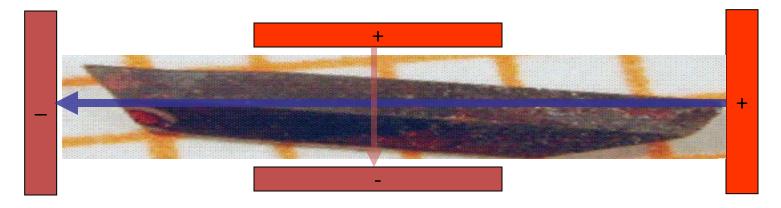
Anisotropy of physical properties

1. Growth velocity (formation of facets)





2. Electrical conductivity

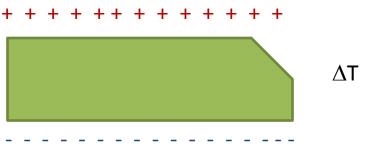


<u>Physical properties of crystals: pyroelectric effect in</u> tourmaline

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



Tourmaline crystal

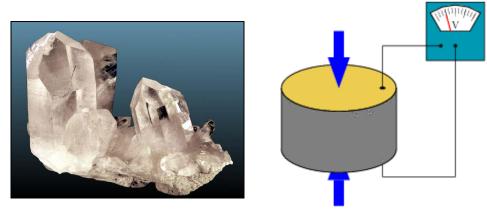


Important: pyroelectric effect is anisotropic, electrical charges develop only in <u>certain directions</u>, i.e. on the certain faces of a crystal.

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

Discovery of piezoelectricity in QUARTZ



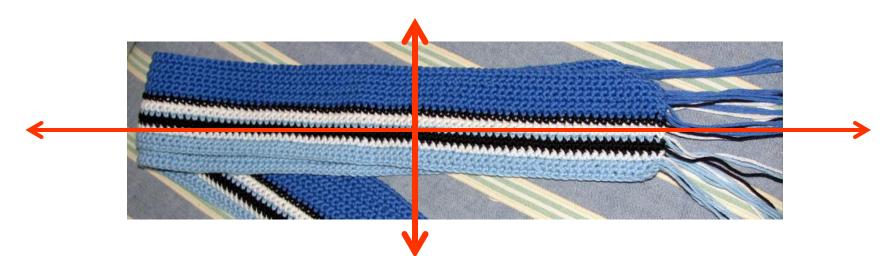


Piezoelectricity is a physical phenomena occurring in some crystals, related to the generation of electric charges by external pressure.

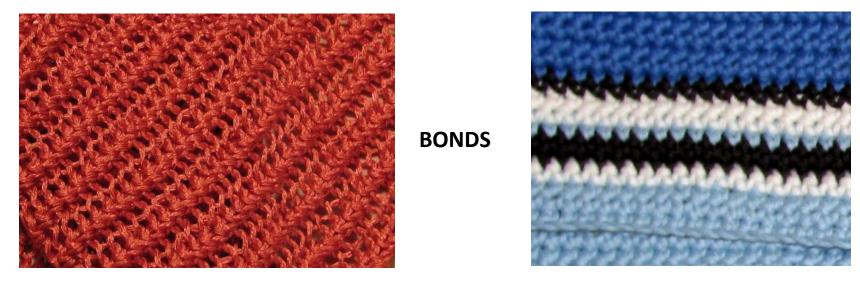
General for crystals – ANISOTROPY of PHYSICAL properties

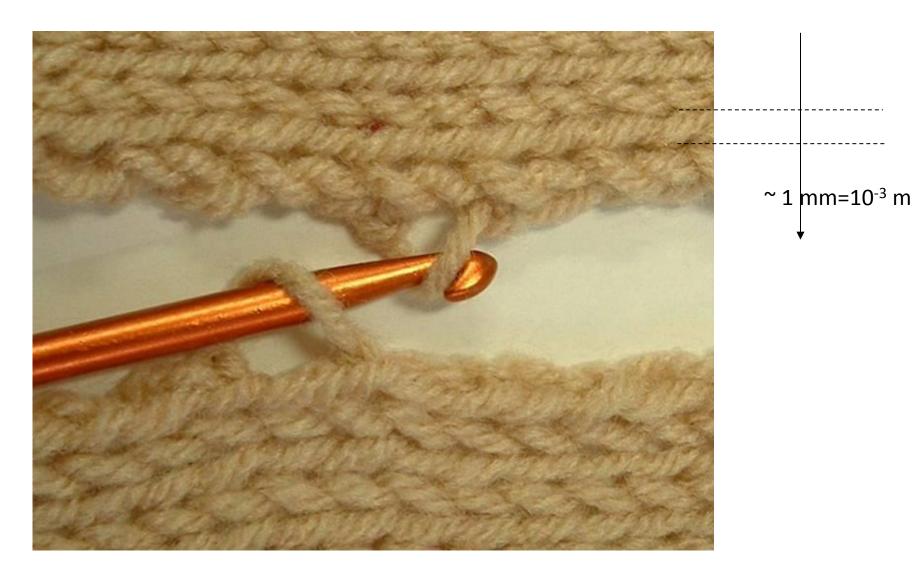
"Life" example of anisotropic physical properties

Cutting a scarf is a typical example of the directional dependence



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





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

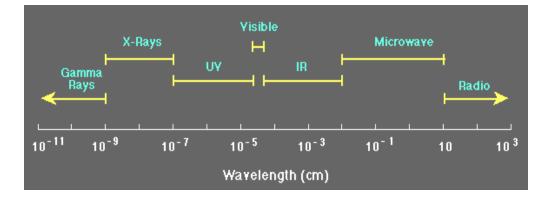
<u>Crystallography -> birth of solid state physics</u>

1912Max von Laue

1914

Nobel prize in physics

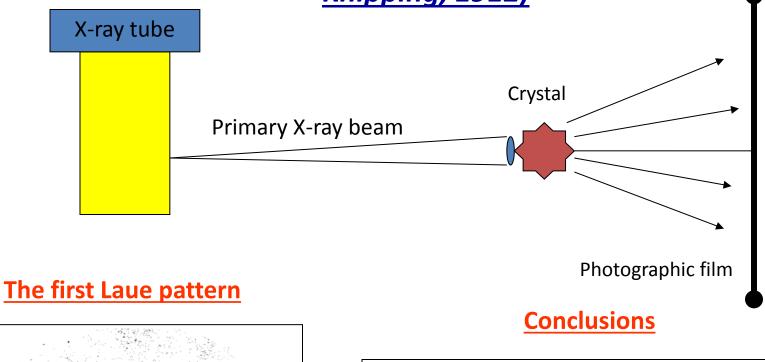
"for his discovery of the diffraction of X-rays by crystals"





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

Knipping, 1912)

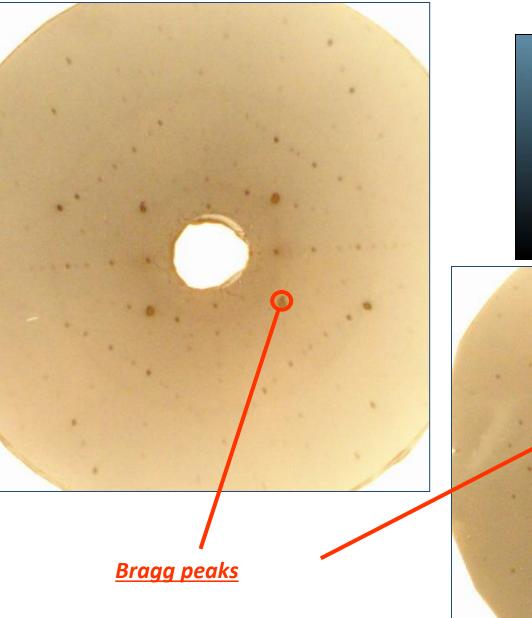


1. X-rays are <u>electromagnetic waves</u>

2. Crystal structures are periodic

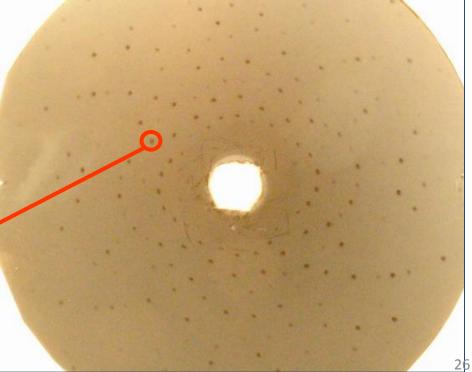
3. The <u>period of crystal lattice</u> has the <u>order of</u> <u>the wavelength of X-rays</u>

Laue diffraction patterns



α -Quartz crystals (SiO₂)





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

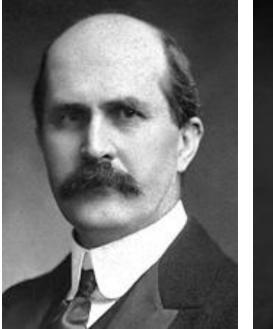
Nowadays X-ray diffraction is the main tool for the solving, determination and characterization of crystal structures

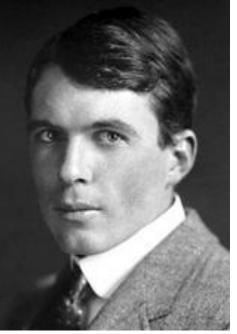
The first REAL crystal structure

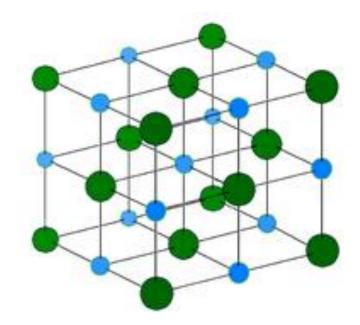
1915



Nobel prize in physics "for their services in the analysis of crystal structures by 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 <u>naturally</u> formed faces	No <u>naturally</u> formed faces
Properties	Anisotropic	Isotropic
<i>Atomic</i> <i>structure</i>	Periodic (long range ordered)	No periodicity. Short-order only
X-ray Diffraction	Well separated diffraction picture with DISTINCT spots	No clearly separated features

CRYSTAL: Official definition



International Union of CRYSTALLOGRAPHY

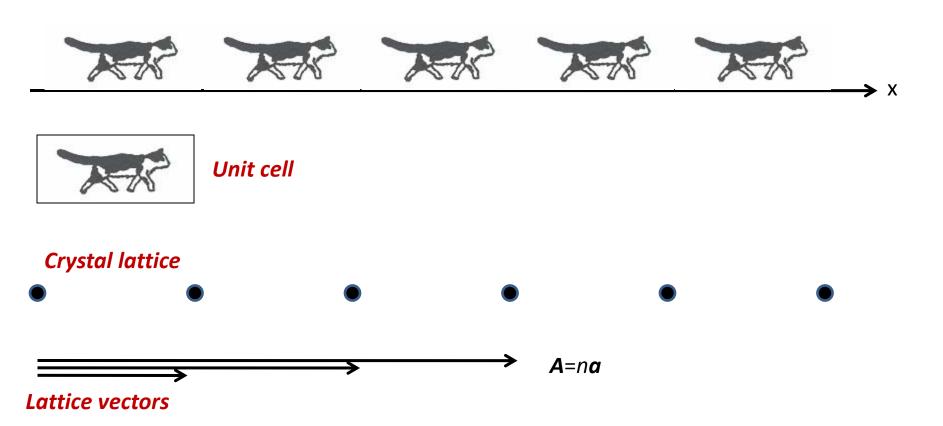
A material is a crystal if it has **essentially** sharp diffraction pattern. The word **essentially** means that most of the intensity of the diffraction is concentrated in relatively sharp **Bragg peaks**, besides the always present diffuse scattering Dr. Sem Gorfman and Prof. U.Pietsch Department of Physics, University of Siegen



Lecture course on crystallography, 2013

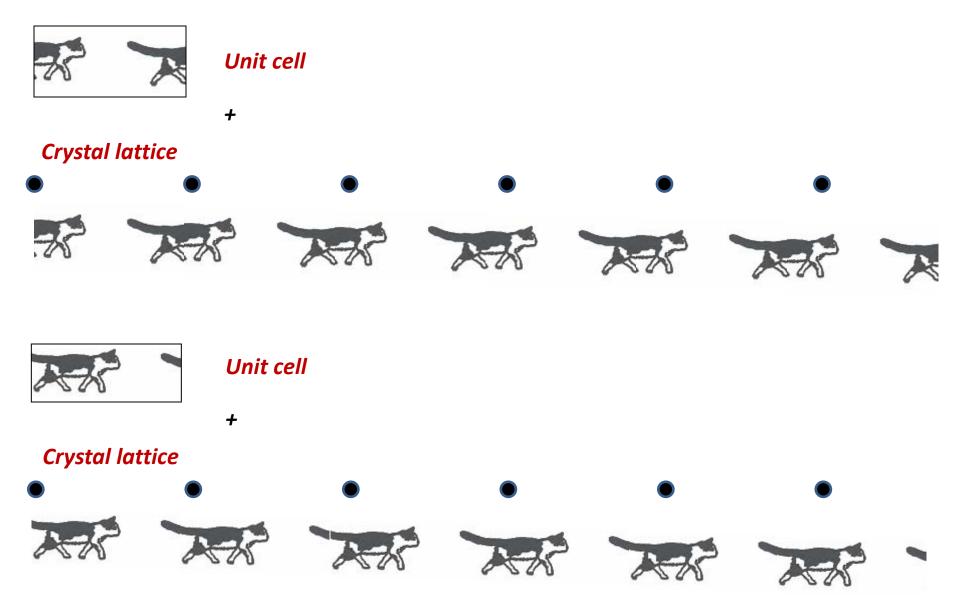
Lecture 1 Part 2 The concept of crystal lattice, properties of crystal lattice, lattice planes and Miller Indices

1 Dimensional crystal (1D periodic structures)

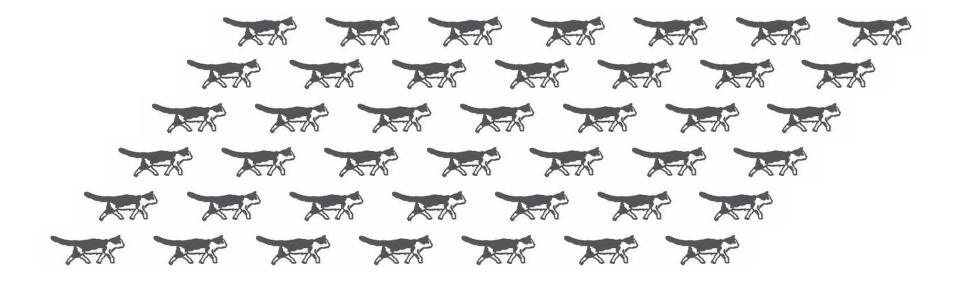


To obtain the whole crystal structure one has to translate the UNIT CELL to each LATTICE POINT

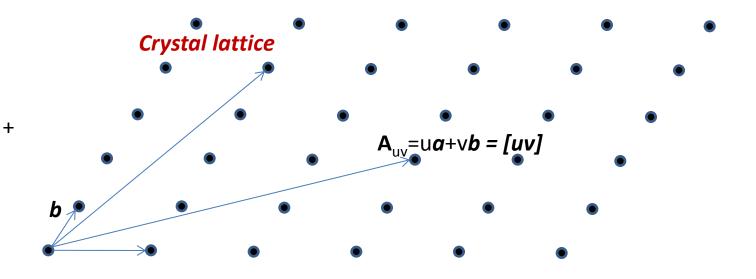
Different choices of unit cell



2 Dimensional crystal (2D periodic structures)



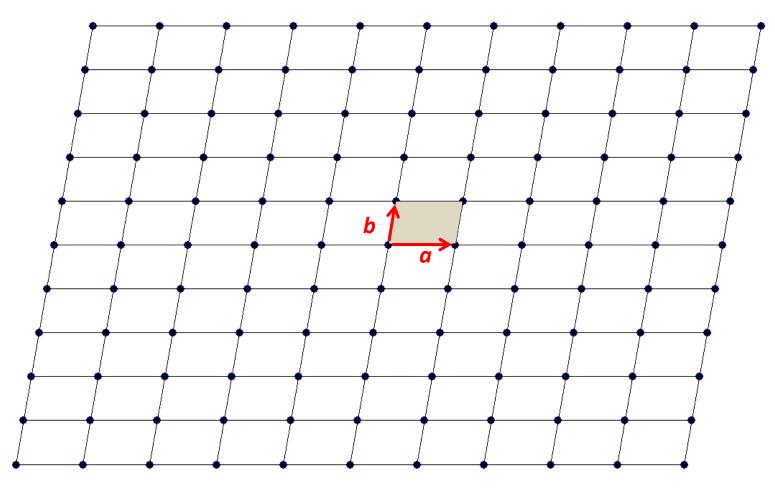




IMPORTANT MESSAGES!!!

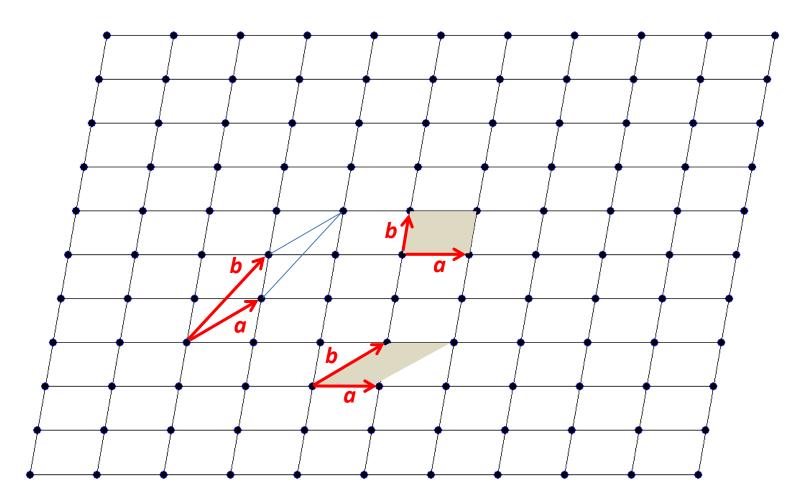
- Crystal lattice is the mathematical object, describing the periodicity of crystal structure.
- Do not confuse <u>crystal lattice</u> with <u>crystal</u> <u>structure</u>
- Crystal structure is <u>UNIT CELL * CRYSTAL LATTICE</u>
- In order to get the whole crystal structure one has to translate the unit cell to the all lattice points

BASIS VECTORS and CRYSTAL LATTICE PARAMETERS



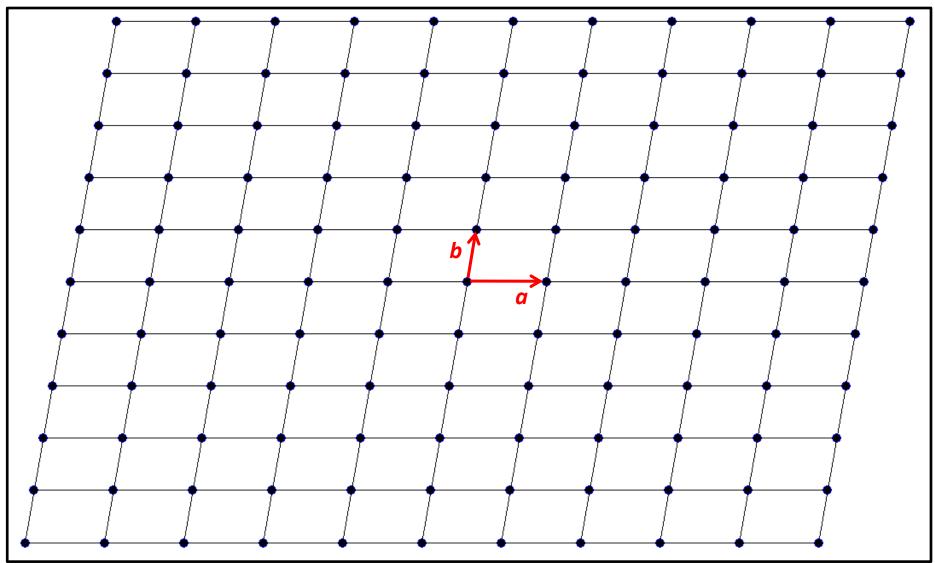
Lattice parameters for two dimensional case: $a = |\mathbf{a}|, b = |\mathbf{b}|, \alpha = \angle (\mathbf{a}, \mathbf{b})$ For the given example: a=1.5, b=1, α =80 deg

Different choices of basis vectors and lattice parameters

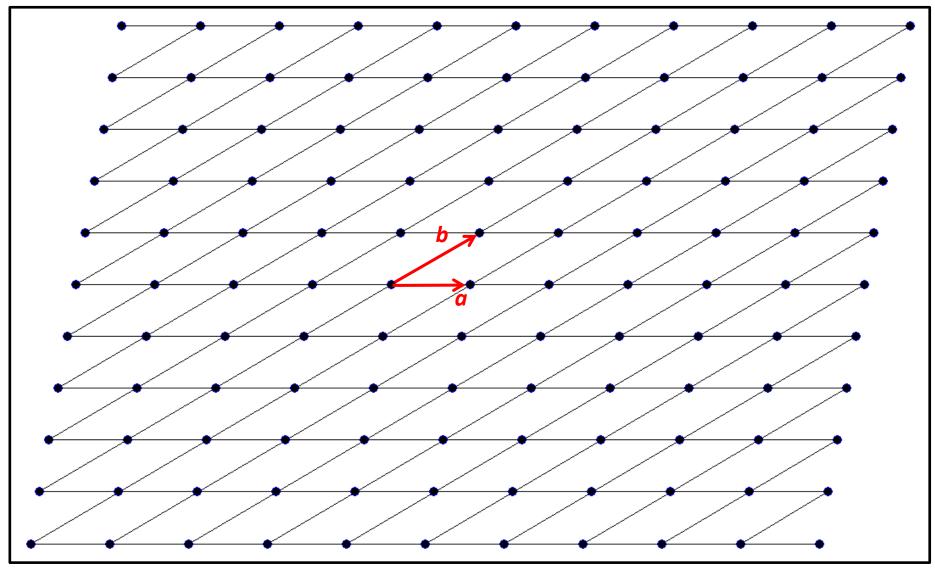


There is a freedom of choice of the lattice basis vectors and therefore lattice parameters

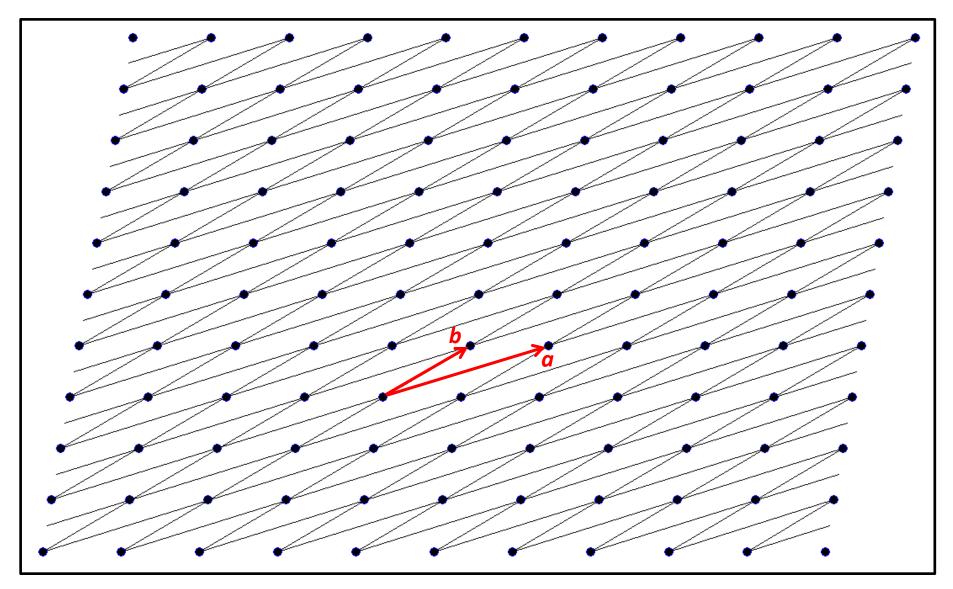
Building a lattice : choice of basis vectors 1



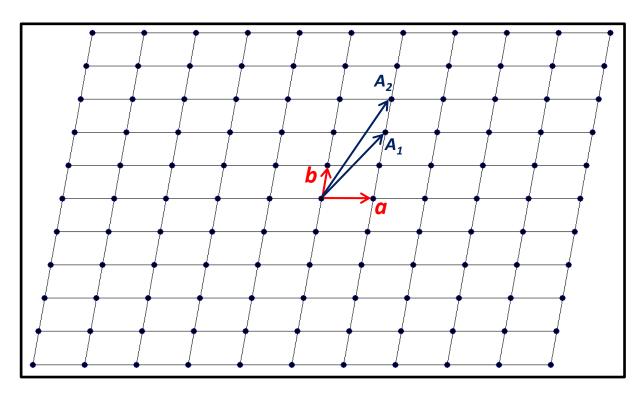
Building a lattice : choice of basis vectors 2



Building a lattice : choice of basis vectors 3



Theorem about the choice of basis vectors



Consider the lattice built with two basis vectors, a and b

Take two other lattice vectors

 $A_1 = [u_1v_1] = u_1 \boldsymbol{a} + v_1 \boldsymbol{b}$ $A_2 = [u_2v_2] = u_2 \boldsymbol{a} + v_2 \boldsymbol{b}$

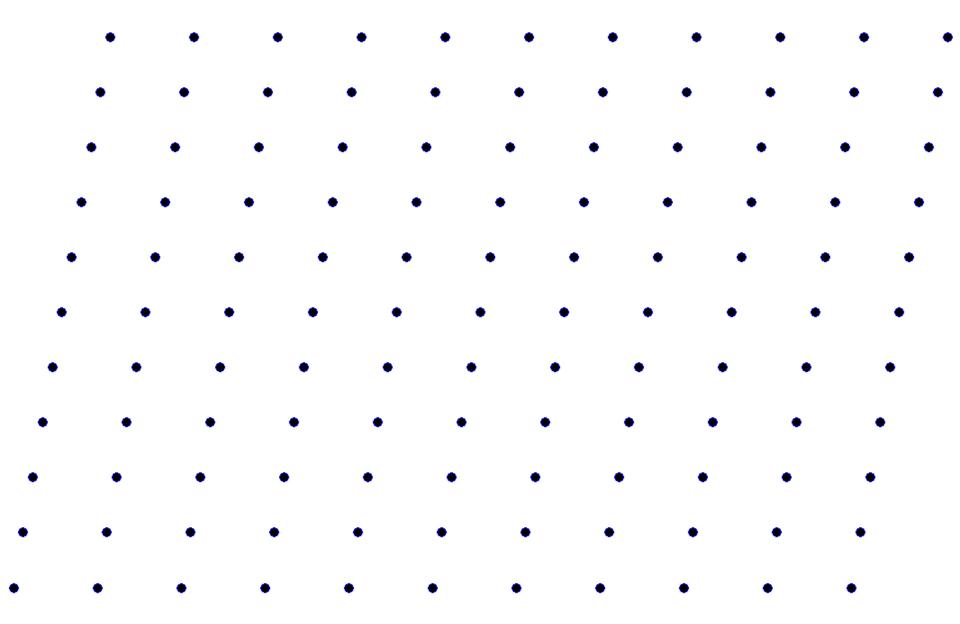
 u_1, u_2, v_1 and v_2 are integer

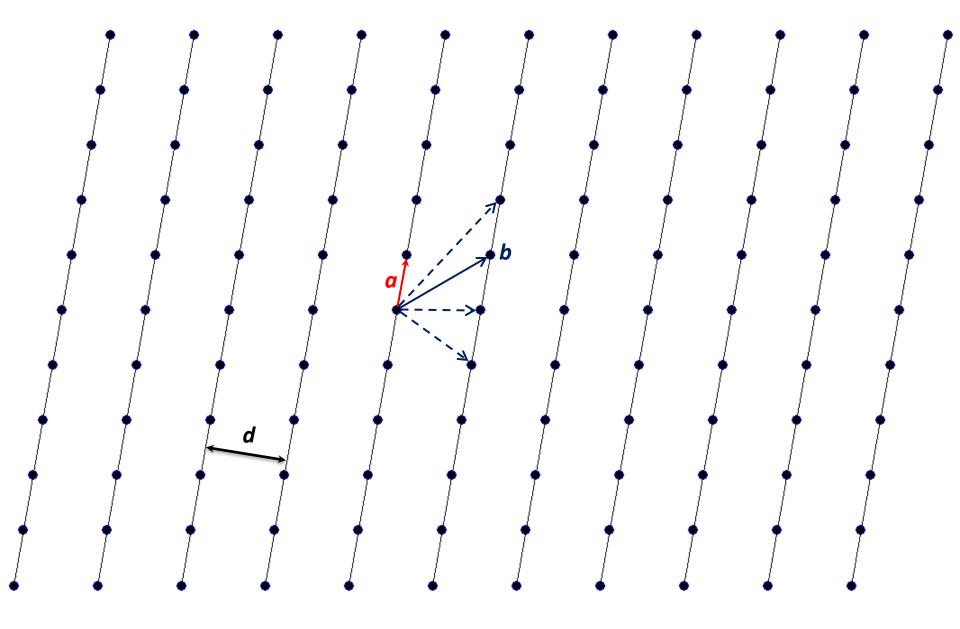
Does this new pair of vectors build the same lattice???

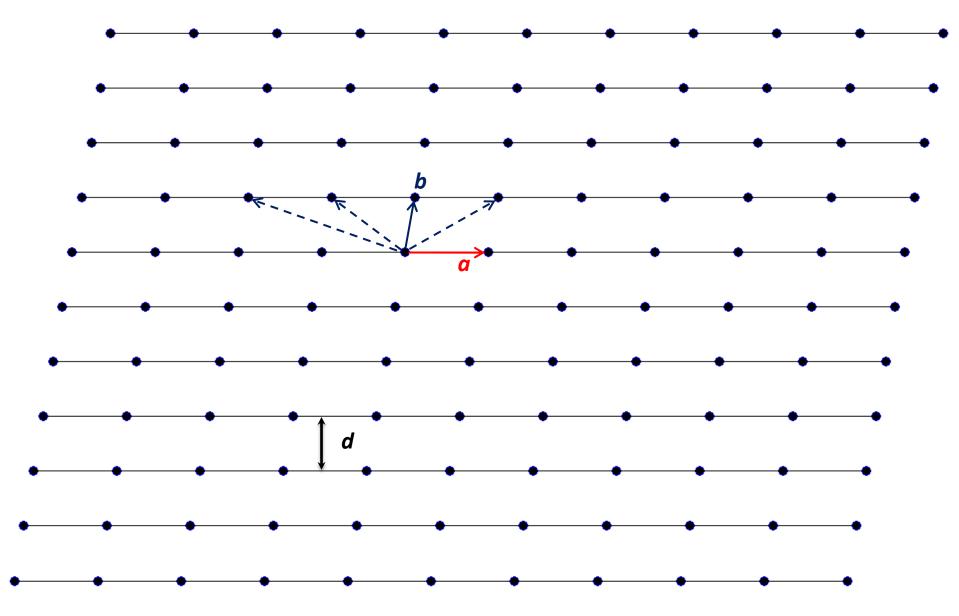
It is necessary to provide that the area, **S** of the parallelogram built on **a** and **b** is the same as the area of parallelogram built on A_1 and A_2

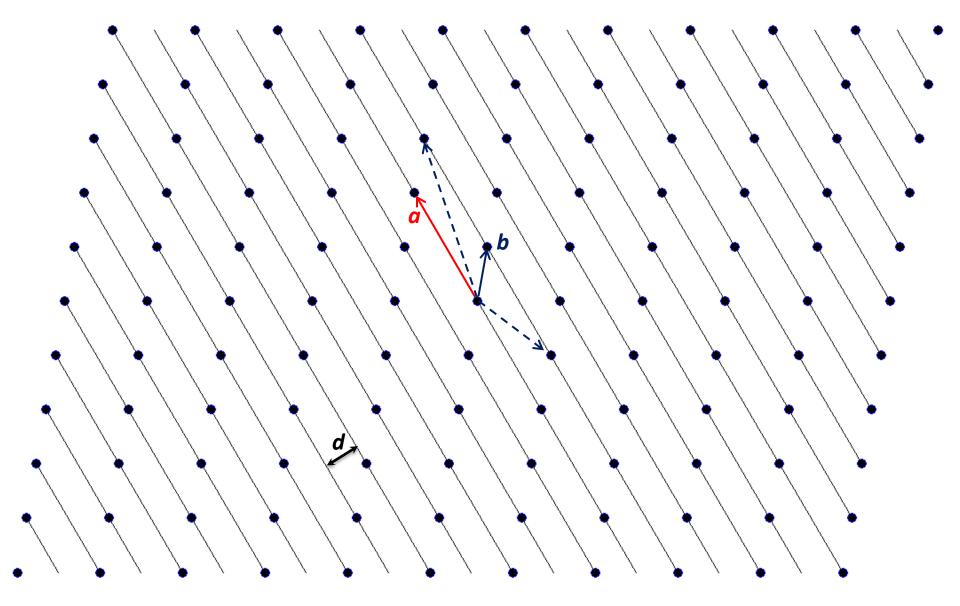
$$S(\mathbf{A}_{1}, \mathbf{A}_{2}) = \pm \begin{vmatrix} u_{1} & v_{1} \\ u_{2} & v_{2} \end{vmatrix} S(\mathbf{a}, \mathbf{b}) \qquad \longrightarrow \qquad \begin{vmatrix} u_{1} & v_{1} \\ u_{2} & v_{2} \end{vmatrix} = \pm 1 \qquad (1)$$

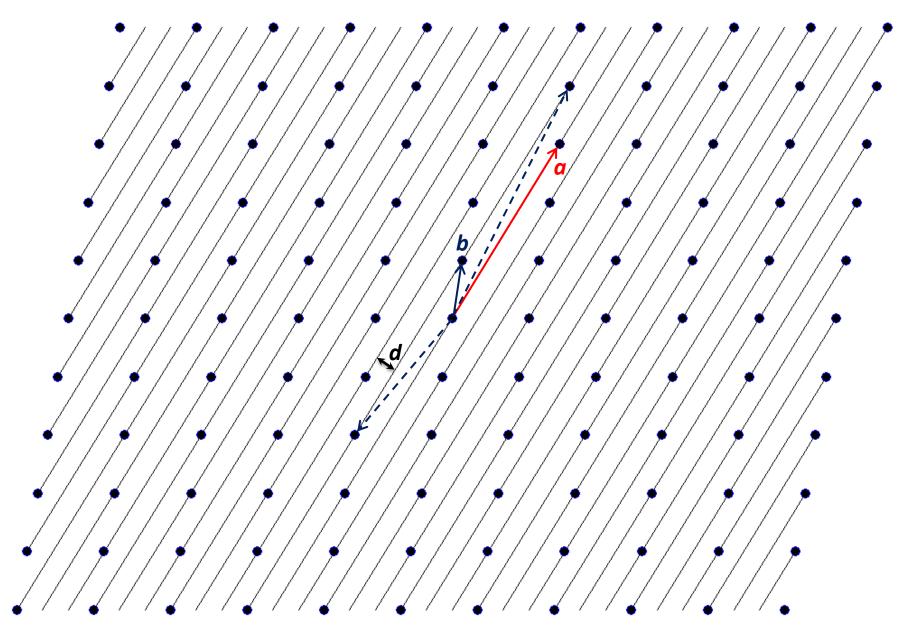
If equation (1) is fulfilled the pair of vectors A_1 and A_2 can be chosen as basis vectors for the SAME LATTICE





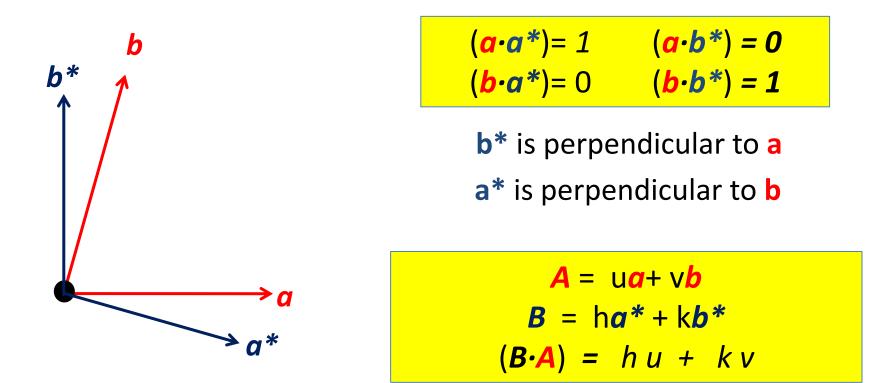






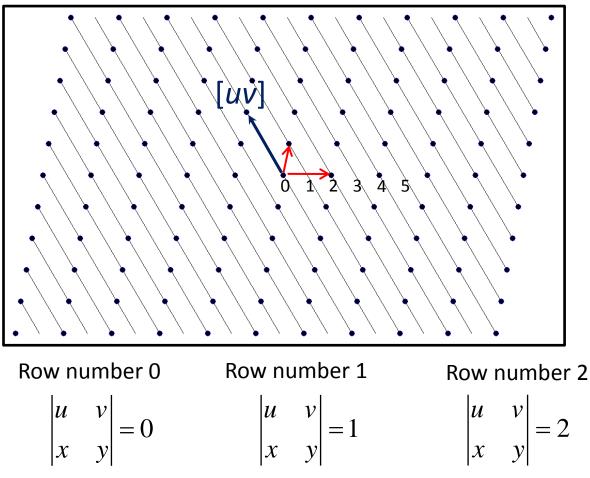
Reciprocal basis vectors

Consider a lattice built on the pair of vectors, *a* and *b*. The pair of reciprocal basis vectors, *a** and *b** is introduced according to the following dot products



The lattice based on the vectors **a*** and **b*** is a RECIPROCAL LATTICE

Description of the lattice planes



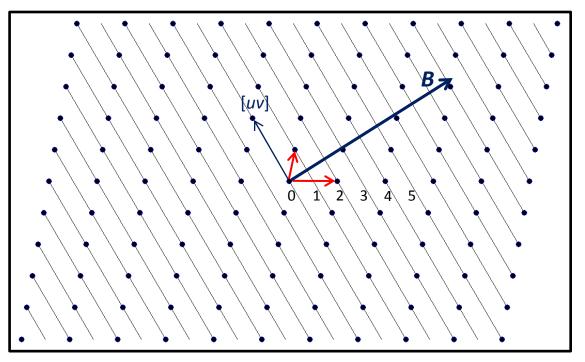
Suppose the pair of basis vectors, *a* and *b* is chosen and the lattice is built.

We split the lattice into the system of rows parallel to the lattice vectors A_1 =[uv]. We aim to formulate the equation for the point within row N

The equation of the row number N

hx + ky = N with *h=-v and k=u*

Equation of planes in terms of reciprocal basis vectors



The equation of the lattice rows: h x + k y = N

can now be rewritten as simply with the dot product

 $(\boldsymbol{B} \boldsymbol{R}) = N$

with $\mathbf{R} = \mathbf{x}\mathbf{a} + \mathbf{y}\mathbf{b}$ and $\mathbf{B} = \mathbf{h}\mathbf{a}^* + \mathbf{k}\mathbf{b}^*$

For the row number 0 (plane going through the origin) we get

$$(\boldsymbol{B} \boldsymbol{R}) = \boldsymbol{0}$$

i.e. the row is perpendicular to the vector **B**.

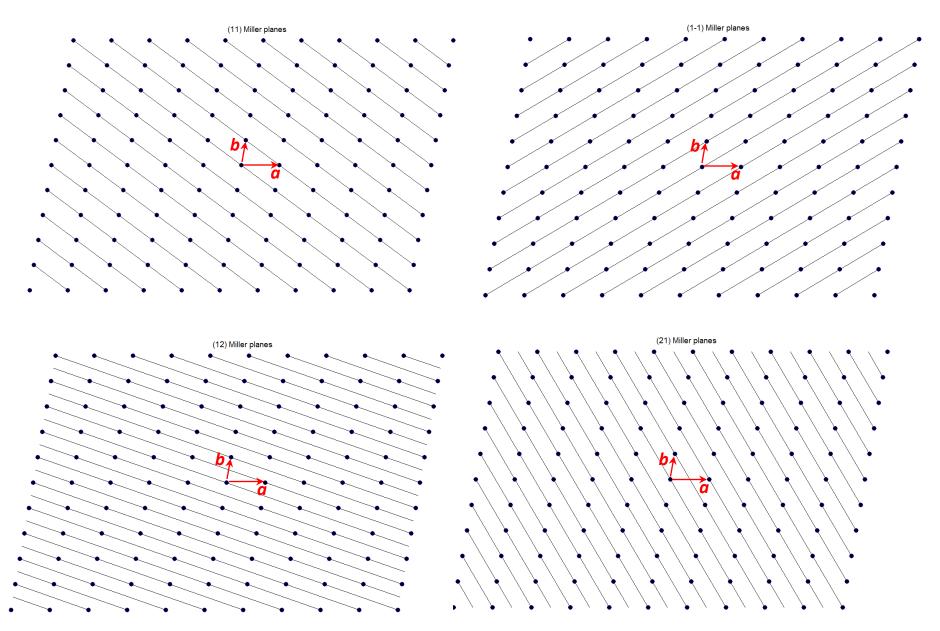
For the first plane (B R) = 1.

Each set of lattice rows is described by the INTEGER NUMBERS *h* and *k* known as **MILLER INDICES**

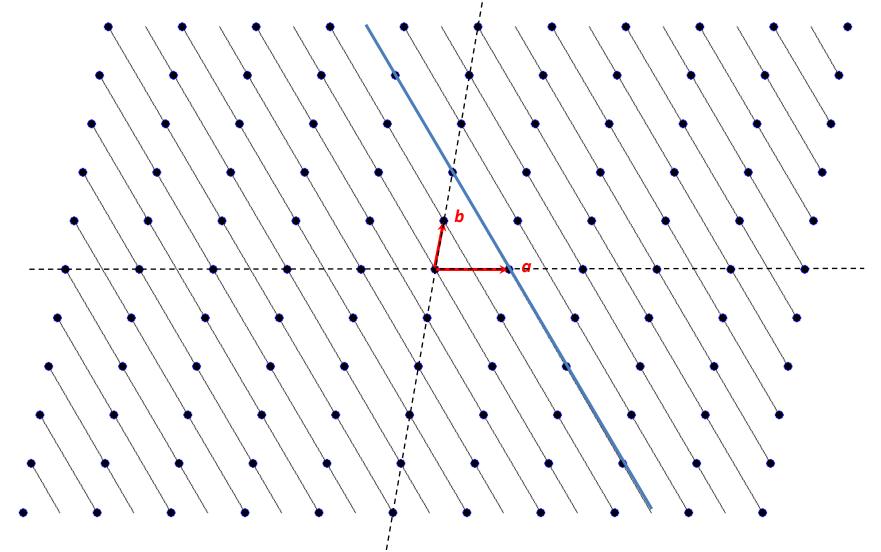
The properties of lattice planes with MILLER INDICES h and k

- 1. The equation of planes are h x + k y = N (with N integer)
- 2. According to the definition the numbers h and k are mutually prime
- 3. The set of planes is perpendicular to the reciprocal lattice vector B = ha* + kb*
- 4. The distance between the neighbouring planes is given by d = 1 / |B|
- 5. The plane intersect the lattice basis vectors in the points [N/h, 0] and [0, N/k]
- 6. The distance between two lattice point within single plane is
 I_{hk} = |B|*S(*a,b*)

Examples. MILLER INDICES AND LATTICE PLANES



How do you calculate the Miller indices of the given set of lattice planes?

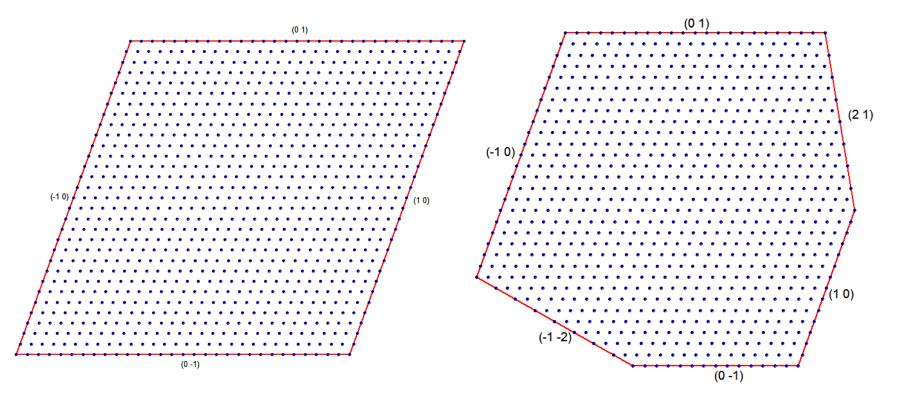


- 1. There is a plane (number N) intersecting the main axes **a** and **b** in points [1,0] and [0,2].
- 2. According to equation of this plane h=N and k=N/2.
- 3. The mutually prime h and k are obtained by taking N=2. We get h=2 and k=1.

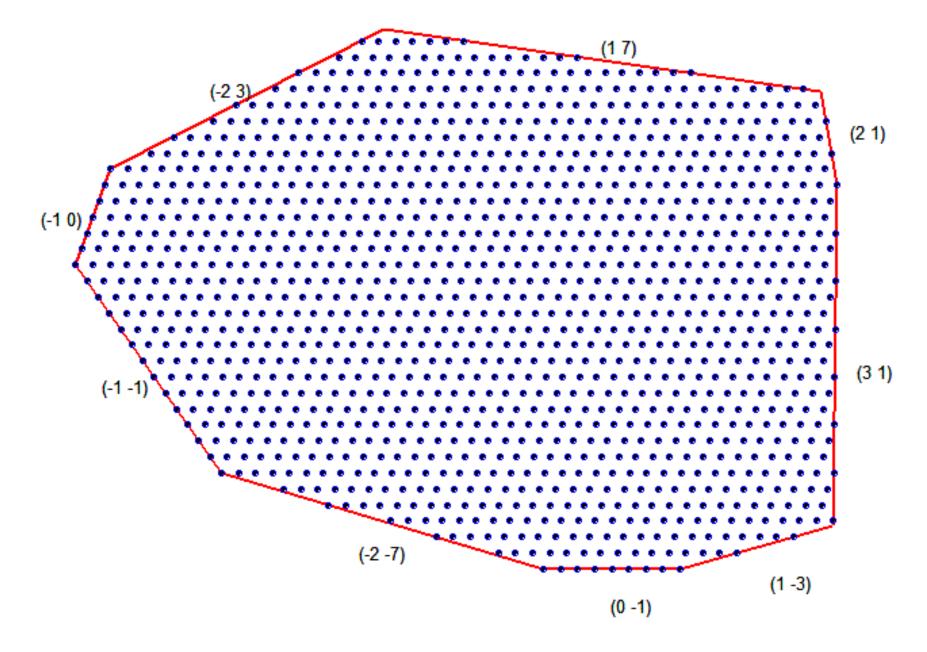
Examples. MILLER INDICES AND CRYSTAL MORPHOLOGY

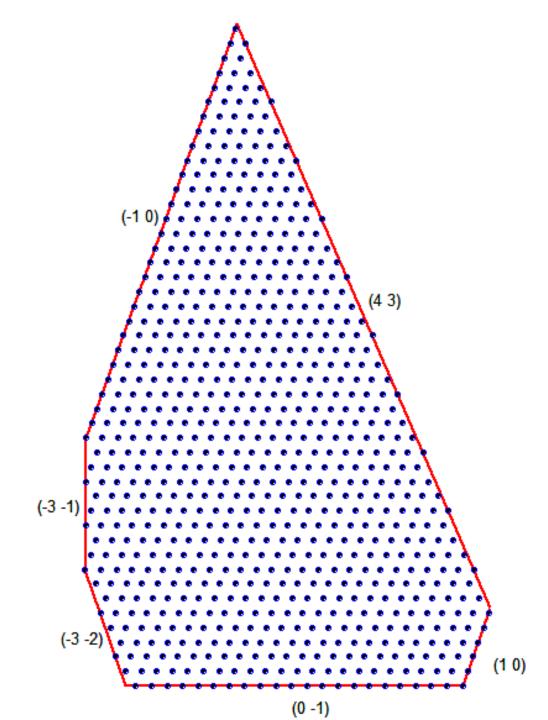
According to the original idea of <u>Haüy</u> the faces of a crystal are parallel to the lattice planes. Now we can characterize the crystal faces in terms of the Miller indices.

We take a lattice and construct a polyhedron from the different number of faces

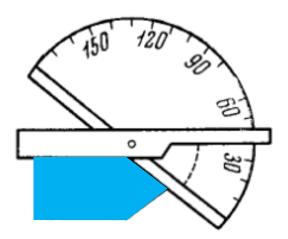


Examples. MILLER INDICES AND CRYSTAL MORPHOLOGY

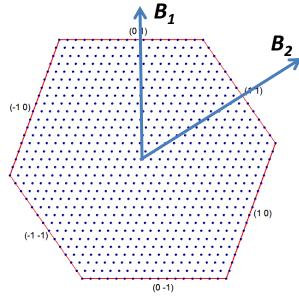




The angles between faces: how do they depend on the crystal lattice



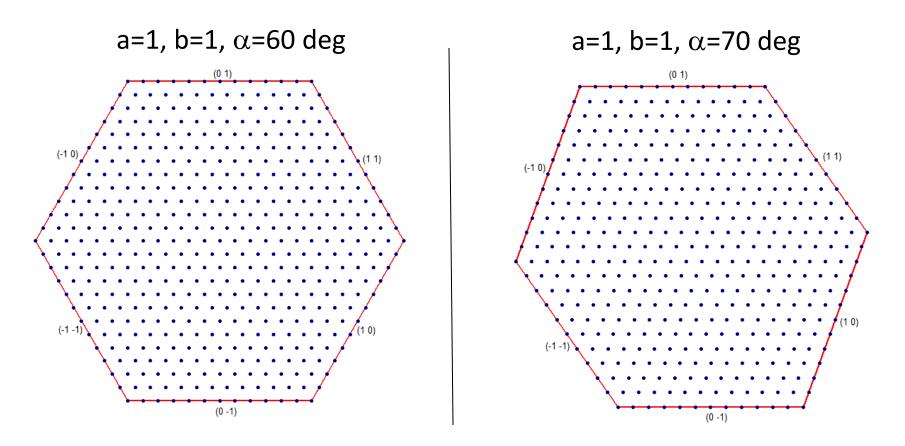
The face with the Miller indices (hkl) is perpendicular to the reciprocal lattice vector B=[hkl]*=h**a***+k**b***+l**c***



The angle between faces $\alpha_{12} = \langle (B_1, B_2) \rangle$

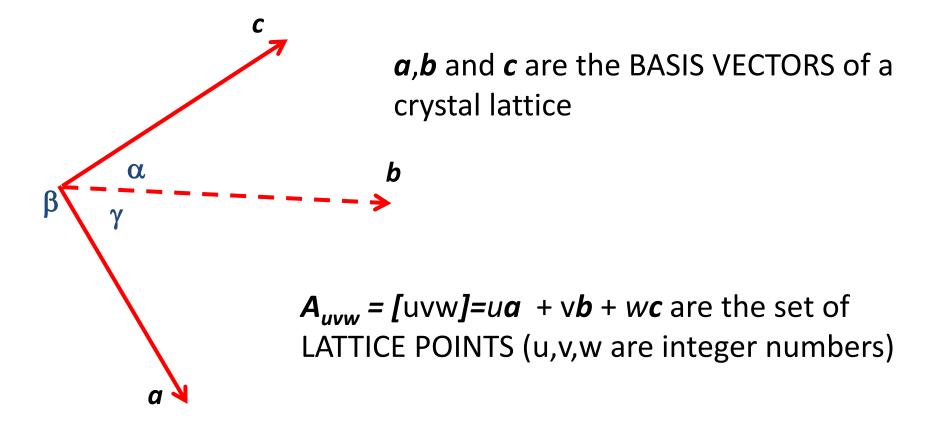
$$\cos \alpha_{12} = \frac{(\mathbf{B}_1 \mathbf{B}_2)}{|\mathbf{B}_1||\mathbf{B}_2|}$$

Example: the polyhedral shape of a 2D for two different crystal lattices



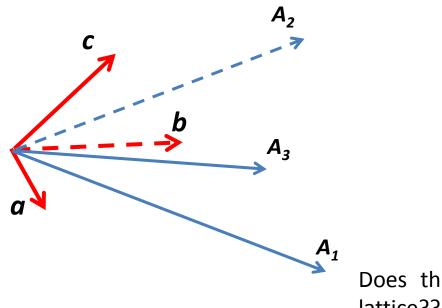
The angles between the natural faces of a crystals are defined by the crystal lattice parameters. This is the background for the law of constancy of the interfacial angles

BASIS VECTORS and CRYSTAL LATTICE PARAMETERS in 3D



The set of lattice parameters for the 3D lattice $a=|a|, b=|b|, c=|c|, \alpha=\angle(b,c), \beta=\angle(a,c), \gamma=\angle(a,b)$

Theorem about the choice of basis vectors, 3D case



Consider the lattice built with three basis vectors, *a* and *b* and *c*

Take three other lattice vectors

 $A_{1} = [u_{1}v_{1}w_{1}] = u_{1}a + v_{1}b + w_{1}c$ $A_{2} = [u_{2}v_{2}w_{2}] = u_{2}a + v_{2}b + w_{2}c$ $A_{3} = [u_{3}v_{3}w_{3}] = u_{3}a + v_{3}b + w_{3}c$

u_i,v_i and w_i are integer numbers

Does this new triple of vectors build the same lattice???

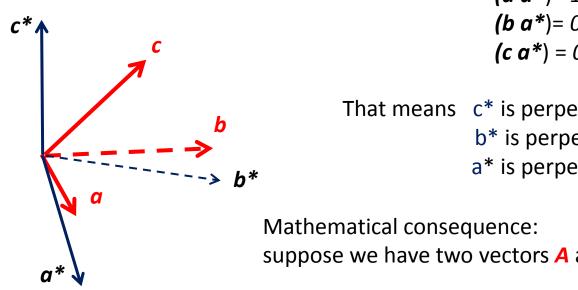
It is necessary to provide that the volume of the parallelepiped built on **a**, **b** and **c** is the same as the area of parallelogram built on A_1 , A_2 and A_3

$$V(\mathbf{A}_{1}, \mathbf{A}_{2}, \mathbf{A}_{3}) = \pm \begin{vmatrix} u_{1} & v_{1} & w_{1} \\ u_{2} & v_{2} & w_{1} \\ u_{3} & v_{3} & w_{3} \end{vmatrix} V(\mathbf{a}, \mathbf{b}, \mathbf{c}) \longrightarrow \begin{vmatrix} u_{1} & v_{1} & w_{1} \\ u_{2} & v_{2} & w_{1} \\ u_{3} & v_{3} & w_{3} \end{vmatrix} = \pm 1 \quad (*)$$

If equation is fulfilled if the vectors A_1 , A_2 and A_3 can be chosen as basis vectors for the SAME LATTICE

Reciprocal basis vectors (3D case)

Consider the crystal lattice and the pair of lattice basis vectors *a*, *b* and *c*. The pair of reciprocal basis vectors, **a***, **b*** and **c*** is introduced according to the following dot products



 $(a a^*) = 1$ $(a b^*) = 0$ $(a c^*) = 0$ $(b a^*) = 0$ $(b b^*) = 1$ $(b c^*) = 0$ $(c a^*) = 0 (c b^*) = 0 (c c^*) = 1$

That means c* is perpendicular to the (*ab*) plane b* is perpendicular to the (ac) plane a* is perpendicular to the (bc) plane

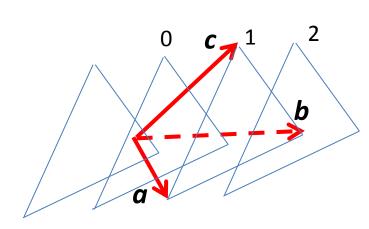
suppose we have two vectors **A** and **B** so that

A = ua + vb + wc and $B = ha^* + kb^* + lc^*$

The dot product of these two vectors is reduced to

(**BA) =** hu + kv+lw

Mathematical description of lattice planes (3D case)



Suppose the triple of main basis vectors, *a*, *b* and *c* is chosen and the lattice is built

We split the lattice into the system of planes so that the plane is defined by the lattice vectors $A_1 = [u_1, v_1, w_1]$ and $A_2 = [u_2, v_2, w_2]$. Similar to the 2D case we can use the theorem about the choice of basis vectors to construct the equations of planes

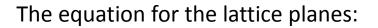
 Plane number 0
 Plane number 1
 Plane number 2

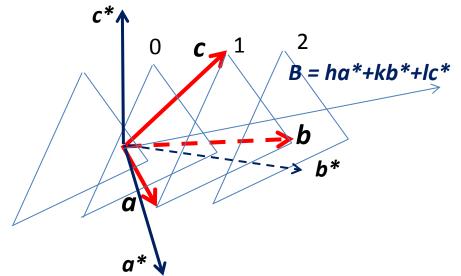
 $\begin{vmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ x & y & z \end{vmatrix} = 0$ $\begin{vmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ x & y & z \end{vmatrix} = 1$ $\begin{vmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ x & y & z \end{vmatrix} = 2$

In general the equation of the plane number N from the origin

$$hx + ky + lz = N$$
 with $h = \begin{vmatrix} v_1 & w_1 \\ v_2 & w_2 \end{vmatrix}$ $k = -\begin{vmatrix} u_1 & w_1 \\ u_2 & w_2 \end{vmatrix}$ $l = \begin{vmatrix} u_1 & v_1 \\ u_2 & v_2 \end{vmatrix}$

Equation of planes in terms of reciprocal basis vectors (3D)





hx + ky + lz = N

can now be rewritten as simply with the dot product

 $(\boldsymbol{B} \boldsymbol{R}) = N$

with $\mathbf{R} = \mathbf{x}\mathbf{a} + \mathbf{y}\mathbf{b} + \mathbf{z}\mathbf{c}$ and $\mathbf{B} = \mathbf{h}\mathbf{a}^* + \mathbf{k}\mathbf{b}^* + \mathbf{l}\mathbf{c}^*$

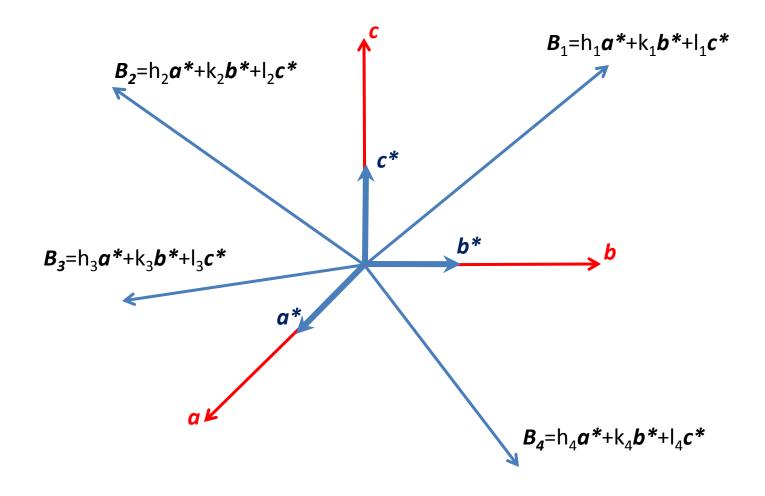
For the plane number 0 (plane going through the origin) we get (**B** R) = O, that means the plane is perpendicular to the vector B. For the first plane (B R) = 1.

Each set of lattice plane is given by the INTEGER NUMBERS *h k and l* known as MILLER INDICES

The properties of lattice planes with MILLER INDICES h k l

- 1. The equation of planes are hx + ky + lz = N (with N integer)
- 2. According to the definition h, k and l are MUTUALLY PRIME
- 3. The set of planes is perpendicular to the reciprocal lattice vector
 B = ha* + kb*+ lc*
- 4. The distance between the neighbouring planes is given by d = 1 / |B|
- 5. The plane intersect the lattice basis vectors in the points [N/h, 0, 0], [0, N/k,0], [0,0,N//]
- 6. The area of 2D lattice between four lattice point within single plane is $S_{hk} = |B| * V(a,b,c)$

<u>3D crystal morphologies. Crystal shapes corresponding to</u> the cubic lattice (lattice constants a=b=c, $\alpha = \beta = \gamma = 90$ deg)

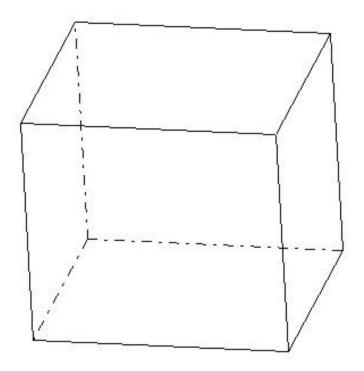


Simple shapes corresponding to the cubic lattice (lattice

constants a=b=c, $\alpha = \beta = \gamma = 90 \text{ deg}$)

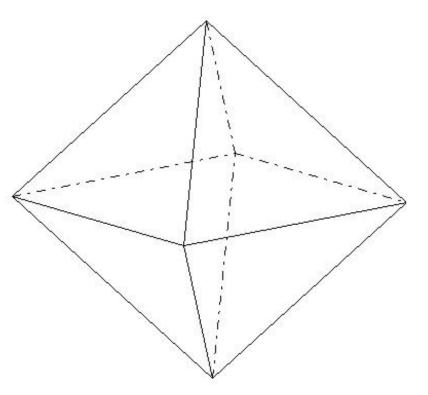
Cube

Octahedron



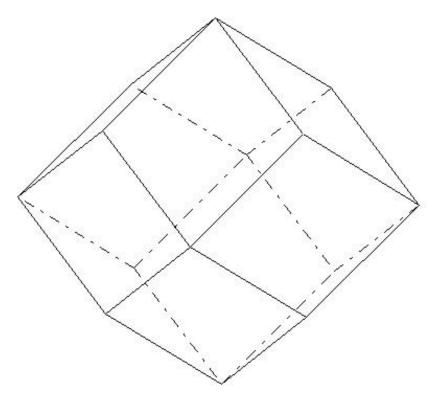
The list of faces for a cube:

(100)	(010)	(001)
(100)	$(0\overline{1}0)$	$(00\bar{1})$



The list of faces for an octahedron: (111) ($\overline{1}11$) ($\overline{1}\overline{1}1$) ($\overline{1}\overline{1}1$) (11 $\overline{1}$) ($\overline{1}1\overline{1}$) ($\overline{1}\overline{1}\overline{1}$) ($\overline{1}\overline{1}\overline{1}$)

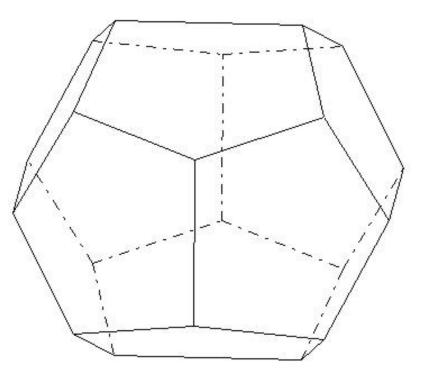
Rhombododecahedron



The list of faces :

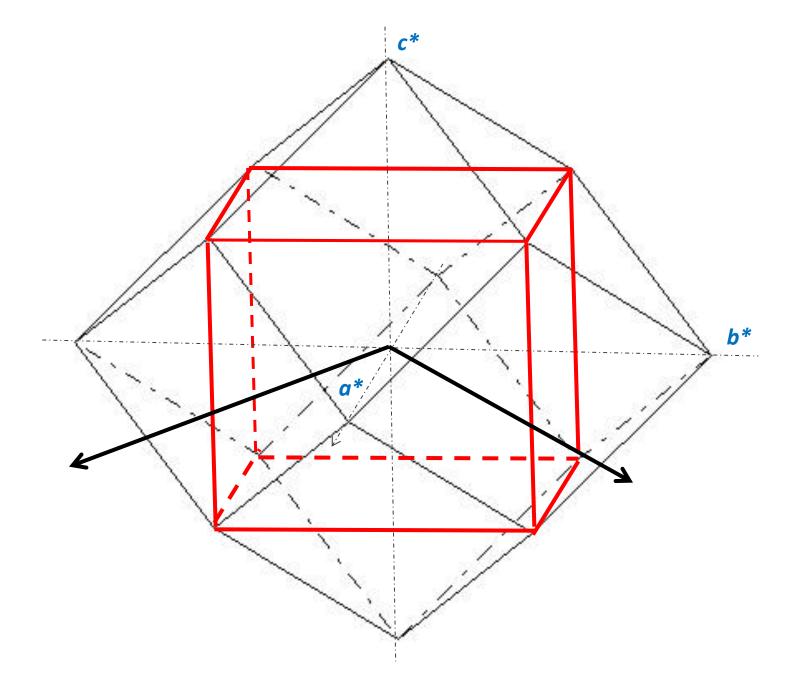
(110)	(110)	(110)	$(\overline{1}\overline{1}0)$
(101)	$(10\overline{1})$	(101)	$(\overline{1}0\overline{1})$
(011)	$(01\overline{1})$	$(0\overline{1}1)$	$(0\overline{1}\overline{1})$

Pentagondodecahedron



The list of faces :

(120)	$(1\overline{2}0)$	(120)	$(\bar{1}\bar{2}0)$
(201)	$(20\overline{1})$	(201)	$(\overline{2}0\overline{1})$
(012)	$(01\overline{2})$	$(0\overline{1}2)$	$(0\overline{1}\overline{2})$



LOOK THROUGH THE LECTURE AND ANSWER THE FOLLOWING QUESTIONS

What is the difference between CRYSTALLINE solid and amorphous SOLID?

What are the evidences for the **periodic structure of a crystal**?

Give your explanation of the term <u>long-range order</u> and <u>short range</u> <u>order</u>?

What is reciprocal lattice basis and reciprocal lattice?

How can the lattice be separated in the planes and how are the planes described?

Answer additional questions in the Exercise 1!