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## 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 X-ray and neutron diffraction techniques used to investigate the atomic structure of crystals will also be gained.

## Recommended Books



Click to LOOK INSIDE!
Physical Properties
of
Crystals

feisw
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

## PHYSICS

## 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 www.snowcrystals.com for your own pleasure

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## 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: $\mathrm{H}_{2} \mathrm{O}$
2. Symmetry of the shapes. Independent on the particular morphology the snowflake always appear as 6 folded. There are no 4-fold, 5 -fold, 7fold, 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

http://webmineral.com

## Mackayite, $\mathrm{Fe}_{3} \underline{T e}_{2} \underline{O}_{5}(\mathrm{OH})$


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.

## 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


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

$\Delta \mathrm{T}$

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

## 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



Photographic film 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



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 $\AA=10^{-10} \mathrm{~m}$

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 $\mathrm{NaCl}, \mathrm{KCl}$, 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 <br> naturally formed faces | No naturally formed faces |
| Properties | Anisotropic | Isotropic |
| Atomic <br> structure | Periodic (long range <br> ordered) | No periodicity. Short-order <br> only |
| X-ray <br> Diffraction | Well separated diffraction <br> picture with DISTINCT spots | No clearly separated <br> 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

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## 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)



Crystal lattice


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


Un s Unit cell
Crystal lattice


2 Dimensional crystal (2D periodic structures)
 $x x_{x}^{x} x+\infty x$ $x x_{0} x+x$ x $x$ $x x_{x} x \in x \in x$
 $x x_{x} x$ x $x$


## 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: $a=|\boldsymbol{a}|, b=|\boldsymbol{b}|, \alpha=\angle(\boldsymbol{a}, \boldsymbol{b})$
For the given example: $a=1.5, b=1, \alpha=80$ 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

$$
\begin{aligned}
& \mathrm{A}_{1}=\left[\mathrm{u}_{1} \mathrm{v}_{1}\right]=\mathrm{u}_{1} a+\mathrm{v}_{1} b \\
& \mathrm{~A}_{2}=\left[\mathrm{u}_{2} \mathrm{v}_{2}\right]=\mathrm{u}_{2} a+\mathrm{v}_{2} b
\end{aligned}
$$

$$
\mathrm{u}_{1}, \mathrm{u}_{2}, \mathrm{v}_{1} \text { and } \mathrm{v}_{2} \text { are integer }
$$

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

It is necessary to provide that the area, $\boldsymbol{S}$ of the parallelogram built on $\boldsymbol{a}$ and $\boldsymbol{b}$ is the same as the area of parallelogram built on $A_{1}$ and $A_{2}$

$$
S\left(\mathbf{A}_{1}, \mathbf{A}_{2}\right)= \pm\left|\begin{array}{ll}
u_{1} & v_{1}  \tag{1}\\
u_{2} & v_{2}
\end{array}\right| S(\mathbf{a}, \mathbf{b}) \longrightarrow\left|\begin{array}{ll}
u_{1} & v_{1} \\
u_{2} & v_{2}
\end{array}\right|= \pm 1
$$

If equation (1) is fulfilled the pair of vectors $A_{1}$ and $A_{2}$ can be chosen as basis vectors for the SAME LATTICE


## Lattice rows (2D) / Lattice planes (3D)



Lattice rows (2D) / Lattice planes (3D)


Lattice rows (2D) / Lattice planes (3D)


Lattice rows (2D) / Lattice planes (3D)


## Reciprocal basis vectors

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


$$
\begin{array}{ll}
\left(a \cdot a^{*}\right)=1 & \left(a \cdot b^{*}\right)=0 \\
\left(b \cdot a^{*}\right)=0 & \left(b \cdot b^{*}\right)=1
\end{array}
$$

b* is perpendicular to a
$a *$ is perpendicular to $b$

$$
\begin{gathered}
A=u a+v b \\
B=h a^{*}+k b^{*} \\
(B \cdot A)=h u+k v
\end{gathered}
$$

The lattice based on the vectors $\boldsymbol{a}^{*}$ and $\boldsymbol{b}^{*}$ 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 $A_{1}=[u v]$. We aim to formulate the equation for the point within row N

$$
\left|\begin{array}{cc}
u & v \\
x & y
\end{array}\right|=0 \quad\left|\begin{array}{ll}
u & v \\
x & y
\end{array}\right|=1 \quad\left|\begin{array}{ll}
u & v \\
x & y
\end{array}\right|=2
$$

The equation of the row number N

$$
\begin{gathered}
h x+k y=N \\
\text { with } h=-v \text { and } k=u
\end{gathered}
$$

## 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

$$
(B R)=N
$$

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

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

$$
(B R)=0
$$

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

For the first plane $(\boldsymbol{B R})=1$.
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 hand $k$

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 $\mathrm{B}=h \mathbf{a}^{*}+k \mathbf{b}^{*}$
4. The distance between the neighbouring planes is given by $d=1 /|B|$
5. The plane intersect the lattice basis vectors in the points [ $\mathrm{N} / \mathrm{h}, 0]$ and $[0, \mathrm{~N} / \mathrm{k}]$
6. The distance between two lattice point within single plane is
$I_{\mathrm{hk}}=|\mathrm{B}|^{*} \mathrm{~S}(\boldsymbol{a}, \boldsymbol{b})$

## Examples. MILLER INDICES AND LATTICE PLANES




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

## Examples. MILLER INDICES AND CRYSTAL MORPHOLOGY

According to the original idea of $\underline{\text { Haüy }}$ 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 $B=[h k l]^{*}=h \boldsymbol{a}^{*}+\mathrm{k} \boldsymbol{b}^{*}+\mid c^{*}$


The angle between faces $\alpha_{12}=<\left(B_{1}, B_{2}\right)$

$$
\cos \alpha_{12}=\frac{\left(\mathbf{B}_{1} \mathbf{B}_{2}\right)}{\left|\mathbf{B}_{1} \| \mathbf{B}_{2}\right|}
$$

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

 crystal lattices

$$
a=1, b=1, \alpha=70 \mathrm{deg}
$$



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

$$
\begin{aligned}
& \mathrm{A}_{1}=\left[u_{1} v_{1} w_{1}\right]=u_{1} a+v_{1} b+w_{1} c \\
& \mathrm{~A}_{2}=\left[u_{2} v_{2} w_{2}\right]=u_{2} a+v_{2} b+w_{2} c \\
& \mathrm{~A}_{3}=\left[u_{3} v_{3} w_{3}\right]=u_{3} a+v_{3} b+w_{3} c
\end{aligned}
$$

$u_{i}, v_{i}$ 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 $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ is the same as the area of parallelogram built on $A_{1}, A_{2}$ and $A_{3}$

$$
V\left(\mathbf{A}_{1}, \mathbf{A}_{2}, \mathbf{A}_{3}\right)= \pm\left|\begin{array}{lll}
u_{1} & v_{1} & w_{1}  \tag{*}\\
u_{2} & v_{2} & w_{1} \\
u_{3} & v_{3} & w_{3}
\end{array}\right| V(\mathbf{a}, \mathbf{b}, \mathbf{c}) \longrightarrow\left|\begin{array}{lll}
u_{1} & v_{1} & w_{1} \\
u_{2} & v_{2} & w_{1} \\
u_{3} & v_{3} & w_{3}
\end{array}\right|= \pm 1
$$

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, $\boldsymbol{a}^{*}, \boldsymbol{b}^{*}$ and $c^{*}$ is introduced according to the following dot products


$$
\begin{array}{lll}
\left(a a^{*}\right)=1 & \left(a b^{*}\right)=0 & \left(a c^{*}\right)=0 \\
\left(b a^{*}\right)=0 & \left(b b^{*}\right)=1 & \left(b c^{*}\right)=0 \\
\left(c a^{*}\right)=0 & \left(c b^{*}\right)=0 & \left(c c^{*}\right)=1
\end{array}
$$

That means c* is perpendicular to the (ab) plane $b^{*}$ is perpendicular to the (ac) plane $a^{*}$ is perpendicular to the ( $b c$ ) plane

Mathematical consequence:
suppose we have two vectors $A$ and $B$ so that

$$
A=u a+v b+w c \text { and } B=h a^{*}+k b^{*}+\mathrm{l} c^{*}
$$

The dot product of these two vectors is reduced to
$(B A)=h u+k v+l w$

## Mathematical description of lattice planes (3D case)

Suppose the triple of main basis vectors, $\boldsymbol{a}, \boldsymbol{b}$ 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 $\boldsymbol{A}_{1}=\left[\mathrm{u}_{1}, \mathrm{v}_{1}, \mathrm{w}_{1}\right]$ and $\boldsymbol{A}_{\mathbf{2}}=\left[\mathrm{u}_{2}, \mathrm{v}_{2}, \mathrm{w}_{2}\right]$. 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
$\left|\begin{array}{ccc}u_{1} & v_{1} & w_{1} \\ u_{2} & v_{2} & w_{2} \\ x & y & z\end{array}\right|=0$

Plane number 1

$$
\left|\begin{array}{lll}
u_{1} & v_{1} & w_{1} \\
u_{2} & v_{2} & w_{2} \\
x & y & z
\end{array}\right|=1
$$

Plane number 2

$$
\left|\begin{array}{lll}
u_{1} & v_{1} & w_{1} \\
u_{2} & v_{2} & w_{2} \\
x & y & z
\end{array}\right|=2
$$

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

$$
h x+k y+l z=N \quad \text { with } \quad h=\left|\begin{array}{ll}
v_{1} & w_{1} \\
v_{2} & w_{2}
\end{array}\right| \quad k=-\left|\begin{array}{ll}
u_{1} & w_{1} \\
u_{2} & w_{2}
\end{array}\right| \quad l=\left|\begin{array}{ll}
u_{1} & v_{1} \\
u_{2} & v_{2}
\end{array}\right|
$$

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

The equation for the lattice planes:


$$
h x+k y+I z=N
$$

can now be rewritten as simply with the dot product

$$
(B R)=N
$$

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

For the plane number 0 (plane going through the origin) we get $(\boldsymbol{B} \boldsymbol{R})=\mathbf{0}$, that means the plane is perpendicular to the vector $\boldsymbol{B}$. For the first plane $(\boldsymbol{B} \boldsymbol{R})=1$.

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

## The properties of lattice planes with MILLER INDICES h k I

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

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


# Simple shapes corresponding to the cubic lattice (lattice constants $a=b=c, \alpha=\beta=\gamma=90 \mathrm{deg}$ ) 

Cube


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

Rhombododecahedron


The list of faces :

Pentagondodecahedron


The list of faces :

| $(120)$ | $(1 \overline{2} 0)$ | $(\overline{1} 20)$ | $(\overline{12} 0)$ |
| :--- | :--- | :--- | :--- |
| $(201)$ | $(20 \overline{1})$ | $(\overline{2} 01)$ | $(\overline{2} 0 \overline{1})$ |
| $(012)$ | $(01 \overline{2})$ | $(0 \overline{1} 2)$ | $(0 \overline{12})$ |

(201) (20 $\overline{1}) \quad(\overline{2} 01) \quad(\overline{2} 0 \overline{1})$
(012) (01 $\overline{2}) \quad(0 \overline{1} 2) \quad(0 \overline{12})$


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 long-range order and short range order?

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!

