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# Introduction to Crystallography

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### **Crystallography:**

It is dedicated to the study of matter on the atomic scale, to the structural characteristics of matter and its relation to physical and chemical properties.

This talk will be limited to crystalline matter,

i.e.to crystals

# Introduction

### Crystal:

A crystal is often associated with a solid of smooth faces and a regular geometric shape.









Virtually all naturally occuring solids, most solid inorganic materials and many solid organic compounds are made up of crystals.

### <u>However:</u>

Most crystals exhibit distorted forms as a result of les-than-ideal growth conditions.

# **Constancy of interfacial angles (Steno, 1669):** The angles between corresponding faces of different species of

the same kind of crystal are the same .

The law of the constancy of interfacial angles by Steno in 1669:

This year is the birth of crystallography as an exact discipline of science. For more than 240 years the studies of crystals have been based on their morphological appearance and their macroscopical properties.

### General characteristic features of a crystal





<u>Anisotropy:</u> A property of the crystal is different in different directions

Homogeneity: In the same direction the crystal has the same property at different points (A and B).

The formation of smooth crystal faces as well as the constancy of interfacial angles can easily be understood by the **internal ordering** of the crystals:

The crystal structure consists of a structural unit of atoms which is repeated periodically in three non-co-linear directions of space.



fictitious molecule



fictitious structure

This periodic repetition can be described by three translation vectors **a**, **b**, **c** (basis vectors) which by repetition form a 3dimensional grid (called lattice).





The parallelepiped formed by **a**, **b**, **c** and the **structural unit** is called **unit cell**.



# Principle of Correspondence

The appearance of a crystal represents the internal ordered arrangements of atoms, molecules or ions.



## Symmetry

Crystals exhibit another characteristic feature: symmetry

A symmetry operation on an object is a displacement, which maps the object onto itself such that the mapped object cannot be distinguished from the object in the original state.

We shall discuss separately the symmetries of macroscopic crystals and of the atomic structures.

# Symmetry of macroscopic crystals

The symmetry operations which may be observed on macroscopic crystals are limited to 5 rotations and 5 roto-inversions

Rotation	2π/1	$2\pi/2$	2π/3	2π/4	2π/6
Symbol for the rotation	1	2	3	4	6
Symbol for the roto- inversion	ī	$\overline{2} \equiv m$	$\overline{3}$	$\overline{4}$	ō

### **Examples**



The axis of a twofold rotation



The axis of a twofold rotoinversion is equal to a mirror plane m

The symmetry operations listed above leave at least one point in space invariant: They are called point symmetry operations.

It became tradition to use the symbol m for  $\overline{2}$ 

Based on the observed symmetry of the external crystal form the forefathers of crystallography categorized all known crystals as members of one of 32 morphological crystal classes.

For this purpose 7 different crystallographic axes systems (crystal system) had to be chosen.

The precondition for an axes system (or basis) is: <u>It must be invariant under the symmetry operations</u> of the crystal to be described



# **Triclinic System**

Length of the axes:  $a_0 \neq b_0 \neq c_0$ Angles:  $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ 



**Monoclinic System** 

Length of the axes:  $a_0 \neq b_0 \neq c_0$ Angles:  $\alpha = \gamma = 90^\circ \quad \beta \neq 90^\circ$ 



# **Orthorhombic System**

Length of the axes:  $a_0 \neq b_0 \neq c_0$ Angles:  $\alpha = \beta = \gamma = 90^{\circ}$ 



# Tetragonal System

Length of the axes:  $a_0 = b_0 \neq c_0$ Angles:  $\alpha = \beta = \gamma = 90^{\circ}$ 



# Cubic System

Length of the axes:  $a_0 = b_0 = c_0$ Angles:  $\alpha = \beta = \gamma = 90^{\circ}$ 



Hexagonal System Length of the axes:  $a_0 = b_0 \neq c_0$ Angles:  $\alpha = \beta = 90^\circ \gamma = 120^\circ$ 

Note: -(a+b) is a symmetrically equivalent axis (green line).



a<sub>tr</sub> b<sub>tr</sub> b<sub>hex</sub> Trigonal System

(also called rhombohedral system) Length of the axes:  $a_0 = b_0 = c_0$ Angles:  $\alpha = \beta = \gamma ~(\neq 90^\circ)$ 

Note: The trigonal symmetry is also compatible with a hexagonal axes system.

This is obvious in a projection along the body diagonal of the trigonal basis; it becomes the hexagonal c-axis  $c_{hex}$  after a basis transformation.

# Crystal Faces, Miller Indices

In order to denote the flat crystal faces, Miller described the intercepts of each planar crystal form as numbers. The numbers are presented as whole numbers (fractions are not allowed) and are the reciprocal of the actual intercept number, all whole numbers being reduced by their lowest common denominator



The set of all symmetry operations observed on a crystal forms a group in the mathematical sense: the point group (i. e. point symmetry group).

Therefore the axioms for a mathematical group apply:
e. g. <u>the combination of two group elements</u>
(i.e. symmetry operations) generate another element
of the group.
In general a crystal exhibits a combination of several symmetry elements .

The observed point symmetry group of any external crystal form belongs to one of 32 point groups.

In crystallography the symmetries of a point group are denoted by the Hermann-Mauguin symbol (or international symbol) The Hermann-Mauguin symbol . It contains the sequence of symmetry elements according the following hierarchy:

 The unique rotation or roto-inversion axis of the highest order is parallel to a basis vector and it takes the first position in the symbol.

• If additional symmetry elements exist, they are placed in the second and even the third position if necessary.

 If two types of symmetry elements are perpendicular to eachother, they are separated by a "/".

# The 32 Crystallographic Point Groups

triclinic	1	ī					
monoclinic	2	т	2/m				
orthorhombic	222	mm2	mmm				
trigonal	3	<u>3</u>	32	3 <i>m</i>	$\overline{3}m$		
tetragonal	4	$\overline{4}$	4/m	422	4 <i>mm</i>	$\bar{4}2m$	4/mmm
hexagonal	6	ō	6/m	622	6 <i>mm</i>	$\overline{6}2m$	6/ <i>mmm</i>
cubic	23	m3	432	$\overline{4}3m$	m3 m		

Note: In the orthorhombic system there are three  $\frac{2}{2}$  or  $\frac{1}{2}$  axes parallel to the basis vectors.

In the cubic system there are three 2 or  $\overline{2}$  or 4 or  $\overline{4}$  axes parallel to the basis vectors; but in addition three 3 or  $\overline{3}$ must exist in the space diagonal.

Note:  $\overline{2} \equiv m$  therefore m perpendicular to  $\overline{2}$  is used instead of  $\overline{2}$ .

**Summary :**All crystals can be categorized as one of 32 crystal classes or as one of 32 point groups. The notations of a crystal as a member of a crystal class or as a member of a point group are isomorphic.

# Graphic Symbols

Symbol for the rotation	1	2	3	4	6
Graphic symbol		1			
Symbol for the roto-inversion	Ī	$\overline{2} \equiv m$	<u>3</u>	$\overline{4}$	ō
Graphic symbol	•				

# Orientation of the Symmetry Elements in Space

**Important :**The orientation of the symmetry elements in space is restricted by the condition, that the symmetry element must transform the basis vectors into themselves (or into an equivalent set of vectors ).

Example : 4/mmm



# Symmetry of Crystal Structures

### Remember:

The crystal structure consists of a structural unit of atoms which is repeated periodically in three non-co-linear directions of space. This periodic repetition can be described by three basis vectors **a**, **b**, **c** which by repetition form a 3-dimensional lattice.



### 1. Consequence.

There is a new symmetry, which determines the crystal structure: the translation.

### 2. Consequence:

Since there are 7 different axes systems (crystal systems), we must consider 7 different lattices. They are called **primitive lattices**.

### 3. Consequence:

Since translation is a new symmetry element in crystal structures, it might be coupled with a point group symmetry elements.

However: The translations coupled with point group symmetry elements must be consistent with the lattice, i.e. <u>they must not</u> <u>destroy the lattice.</u>

Example The coupling between a mirror plane and a translation:

Glide plane



### The glide plane in a lattice:



# The translation vector **t** must lead to a lattice point after two translations

Example: Glide planes in an orthorhombic system Glide planes may exist instead of mirror planes

The convention which is used to name glide planes. Arrows and letters indicate the gliding directions and the corresponding symbols. A glide plane parallel to a diagonal of the unit cell is in some cases denoted with the letter **d**.



### The coupling between a rotation and a translation:

Screw axis (helicoidal axis)

Example : A threefold screw axis with a translation of 1/3 and 2/3. The subscript quantifies the translation along the axis



Note: The translation vector must be parallel to the axis of rotation

### The screw axis in a lattice:

The translation vector **t** must lead to a lattice point after two translations, **t** must be parallel to the axis.



### The rotation axes coupled with the possible translations and the symbols of the screw axes.

Axis	Translation	num. Symbol	graph. Symbol
2	1/2	$2_1$	ý
3	1/3, 2/3	$3_{1,}3_{2}$	
4	1/4, 1/2, 3/4	4 <sub>1</sub> , 4 <sub>2</sub> , 4 <sub>3</sub>	┮ <u>↓</u> _ <u></u>
6	1/6, 1/3, 1/2, 2/3, 5/6	$6_1, 6_2, 6_3, 6_4, 6_5$	

# **Translation Lattices, Bravais Lattices**

### Remember:

The periodic repetition of the three basis vectors **a**, **b**, **c** form a 3-dimensional point lattice, which is called a **primitive lattice**. Since there are 7 basis systems , we can distinguish 7 primitive lattices.

Each lattice has the property that a translation of the lattice to any lattice point leaves the lattice invariant. Beside the 7 primitive lattices there are other lattices conceivable,

which have the property: The lattices are centered

### Example: Centered lattice in an orthorhombic cell

The translation **t** is also a lattice translation. However: It depends on the basis system, whether a centering will yield a new translation lattice



#### Convention :

The face not containing the **c** basis vector is called the **C-face**, the cell is called the **C-cell**, the lattice is called a **C-lattice** accordingly.

Centering	A-face	<b>B-face</b>	C-face	Body center	All faces centered
Lattice	А	В	С	Ι	F
Position of the center	$(0, 0, 0) (0, \frac{1}{2}, \frac{1}{2})$	(0, 0, 0) (1/2, 0, 1/2)	$(0, 0, 0) (\frac{1}{2}, \frac{1}{2}, 0)$	$(0, 0, 0) (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1)$	See A-,B-,C- face

The 7 primitive and the 7 centered lattices are called the 14 Bravais lattices.

Note: The primitive trigonal lattice is called the R lattice, it can also be described in the hexagonal basis.

The trigonal primitive R- lattice in the hexagonal setting is twofold centered, i. e. threefold primitive



### **Space Groups**

The symmetry of a crystal structure is a combination of the lattice symmetry and of the symmetry derived from the point group symmetry. The space group symmetry characterized by the space group symbol. It has the general form:

# Lcccc

L is the reference to the lattice type, cccc stands for the up to 4 point symmetry operation or the point symmetry operation coupled with translations (i. e. glide planes or screw axes)

# Examples :

Pccm

**ccm** is derived from the orthorhombic point group **mmm**, where two mirror planes have been replaced by two c glide planes.

 $\begin{array}{c} {\bf P} \ \mbox{refers to the orthorhombic primitive lattice.} \\ {\bf Cmm2} \end{array}$ 

mm2 is the orthorhombic point group mm2,C refers to the orthorhombic C-centered lattice.

# I4cm

**4cm** is derived from the tetragonal point group **4mm**, where one mirror plane has been replaced by a c glide plane.

I refers to the tetragonal body centered lattice.

## X-ray Diffraction

Since 1669 (Steno's law) crystals have been studied based on their macroscopical properties.

The detection of X-ray diffraction on crystals by M. v. Laue and co-workers (1912) inaugurates a **new era** in this discipline: The determination of crystal structures. Amplitude of the scattered wave :

 $A = exp(i\Phi)$ 

Path difference of a wave scattered at point **r** with respect to O :  $r(s-s_0)$ The phase angle is :  $F=2p r(s-s_0) / l$ s vector of the diffracted beam  $\mathbf{s}_{\mathbf{o}}$  vector of the incident beam  $(s-s_0) / | = r^*$  $A = \exp(2pi r r^*)$ 



### Diffraction by a periodic structure.

$$\mathbf{A} = \mathbf{\Sigma} \mathbf{f}_0 \exp(2\pi \mathbf{i} \mathbf{r} \mathbf{r}^*)$$



 $\mathbf{r} = \mathbf{r}_{uvw} + \mathbf{r}_{j}$   $\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$   $\mathbf{r}_{j} = x_{j}\mathbf{a} + y_{j}\mathbf{b} + z_{j}\mathbf{c}$ 

 $A = \sum \exp(2\pi i (\mathbf{u}\mathbf{a} + \mathbf{v}\mathbf{b} + \mathbf{w}\mathbf{c})\mathbf{r}^*) f_{0j} \exp(2\pi i (\mathbf{r}_j\mathbf{r}^*))$ 

$$\mathbf{A} = \mathbf{G} \bullet \mathbf{F}$$

G = lattice factor

F = structure factor

### The lattice factor.

$$G = \sum_{u,v,w}^{N} \exp(2\pi i (\xi u + \eta v + \varsigma w))$$



$$|\mathbf{G}| = \delta(\xi - \mathbf{h})$$



### Laue's approximation for $N \rightarrow \infty$



### Laue's equations in vector notation



$$(s-s_0)/l = r_{hkl}^* = ha^* + kb^* + lc^*$$
  
In the basis  $(a^*, b^*, c^*)$ 

### Three properties of **r**\*<sub>*hkl*</sub>

- r\*<sub>hkl</sub> is normal to a lattice plane (h, k, l) or a crystal face, respectively. (h, k, l) are the Miller indices, if they have no common denominator.
- 2.  $\mathbf{r}^*_{hkl}$  represents the set of parallel lattice planes with the distance d The length of  $\mathbf{r}^*_{hkl}$  (also module or norm) :

$$\left\|r_{hkl}^*\right\| = 1/d$$

3. If the indices have a common denominator n,  $\mathbf{r}^*_{hkl} = (nh, nk, nl)$  represents the set of fictitious parallel lattice planes with the distance d/n The length of  $\mathbf{r}^*_{hkl}$  is in this case:

$$\left\|r_{hkl}^*\right\| = n \,/\, d$$

The basis  $(\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*)$  of  $\mathbf{r}^*_{hkl}$ :

 $\mathbf{r}^*_{hkl}$  only has the integer values (h, k, l) if the appropriate basis is chosen:

$$r_{hkl}^{*} = h \frac{\left[b \times c\right]}{V} + k \frac{\left[c \times a\right]}{V} + l \frac{\left[a \times b\right]}{V}$$

$$V = c[a \times b] = a[b \times c] = b[c \times a]$$

V = Volume of the parallelepiped (**a**, **b**, **c**)

$$a^* = \frac{[b \times c]}{V} \quad b^* = \frac{[c \times a]}{V} \quad c^* = \frac{[a \times b]}{V}$$

# Example: a monoclinic lattice



### **Ewald's** interpretation

Crystal at the centre M of a sphere with the radius 1/l.

The origin of the reciprocal lattice is on the sphere with M-0 equal to  $s_0/l$ .



Diffraction occurs in the direction of **s** if a point of the reciprocal lattice intersects the **Ewald-sphere**.

### Bragg's law



Bragg interprets the diffraction of X-rays as a "reflection" on lattice planes.

$$2d\sin\vartheta = n\lambda$$

### Final comment:

The concept of the reciprocal lattice and its application to the diffraction of X-rays not only holds for X-rays but also for all electromagnetic waves, e.g. electrons as well as neutrons.