Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Crystallochemistry

Laboratory

Dr Anna Kozakiewicz

UMK Toruń 2014

Lesson 1: Basic terms in crystallography

Issues to be prepared:

- axial ratio,
- symbolism: points, lines and planes,
- zone axis, zone law,
- unit cell, parameters,
- crystal systems,

Introduction:

Tetrahedron composed of four triangular crystal faces. Three of which intersect along the crystallographic axes of coordinates and the fourth one - parametral face. The parametral face intersects the positive parts of the crystallographic axes, defining the unit translations of the unknown absolute value (axial units). These units are used to determine the position of nodes, lines and planes in the lattice. The axial units are marked using symbols a_o, b_o, c_o for the X, Y and Z axes, respectively.

Based on the know shape of unit cell of crystal (axial ratio a:b:c and angles α, β, γ between the crystallographic axes), crystals can be assigned to one of the seven crystal systems:

Crystal systems	**The unit cell parameters**	
Triclinic	$\alpha \neq \beta \neq \gamma \neq \alpha \neq 90^o$	$a_o \neq b_o \neq c_o \neq a_o$
Monoclinic	$\alpha = \gamma = 90^o, \beta \neq 90^o$	$a_o \neq b_o \neq c_o \neq a_o$
Orthorhombic	$\alpha = \beta = \gamma = 90^o$	$a_o \neq b_o \neq c_o \neq a_o$
Tetragonal	$\alpha = \beta = \gamma = 90^o$	$a_o = b_o \neq c_o$
Cubic	$\alpha = \beta = \gamma = 90^o$	$a_o = b_o = c_o$
Trigonal or Rhombohedral cell	$\alpha = \beta = 90^o, \gamma = 120^o$ $\alpha = \beta = \gamma = 90^o$	$a_o = b_o \neq c_o$ $a_o = b_o = c_o$
Hexagonal	$\alpha = \beta = 90^o, \gamma = 120^o$	$a_o = b_o \neq c_o$

Description of the position of the nodes, lines and planes in the lattice requires the use of clear symbols:

- position of the **node** is written as resultant vector (linear combination of unit vectors),

$$\boldsymbol{R} = x\mathbf{a_o} + y\mathbf{b_o} + z\mathbf{c_o}$$

  The symbol of the node is three coordinates **x y z**, giving the number of units of axial on X, Y and Z axes, respectively.

- position of a **lattice row** is written in square brackets **[uvw]**, can be calculated from the known coordinates of two nodes A: $x_1\, y_1\, z_1$ and B: $x_2\, y_2\, z_2$, which lie on this lattice row

$$\mathbf{u} = x_2 - x_1; \quad \mathbf{v} = y_2 - y_1; \quad \mathbf{w} = z_2 - z_1;$$

- position of the **plane** is written in parenthesis **(hkl)** - Miller symbol, Miller indices indicate how many times the line segments cut on axes by the first of the parallel planes are within units of axial a_o, b_o, c_o.

In the symbols of nodes, lines and planes commas are used only when there is a two-digit number in the symbol and there is a possibility of ambiguity. If the negative number is in the symbol, minus is written over the number. The numbers in the symbol of lattice row and plane are integers.

The **zone** is a set of planes that are parallel to the common direction [uvw], called the zone axis. The **zone law of Weiss** indicates that each face of the crystal belongs to two zones at least, and the zone axis is defined by two faces.

Using **zonal equation** one can determine whether the face (hkl) belongs to the zone axis [uvw].

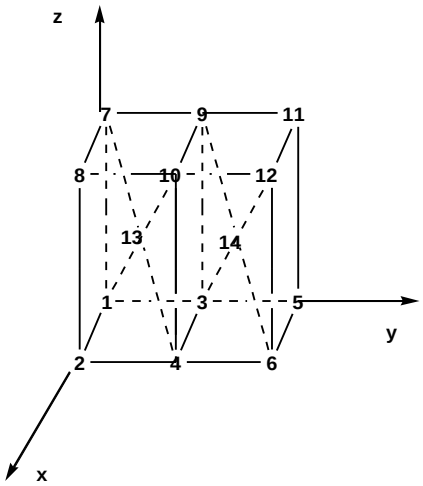
$$hu + kv + lw = 0$$

Knowing the symbols planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$, one can calculate the symbol of zone axis [uvw] to which they belong. Similarly, one can determine the symbol of plane (hkl), which belongs to two axis zones $[u_1v_1w_1]$ and $[u_2v_2w_2]$.

Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

Exercises:

Exercise 1. Determine the coordinates xyz for all marked nodes in the tetragonal lattice, which are shown in Figure:



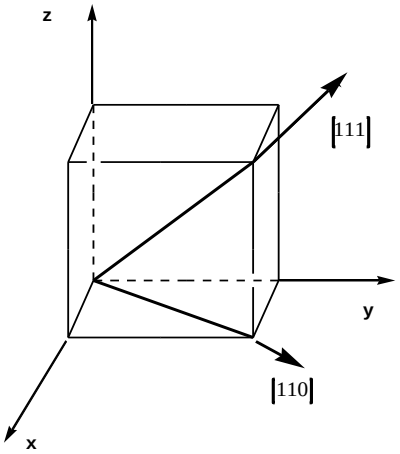
Example:

Node 6 has coordinates: 120, node 11 has coordinates: 021

Exercise 2. Plot the lattice rows [010], [130], [112] and $[\bar{1}\,\bar{2}\,1]$ in crystals from cubic, tetragonal and orthorhombic system.

Example:

Plot the lattice row [110] and [111] in cubic system:



Exercise 3. Calculate the symbol of lattice row [uvw] passing through the points A and B (two nodes in the lattice), if known coordinates of these nodes: node A 0 1 ½, node B ½ 0 ½.

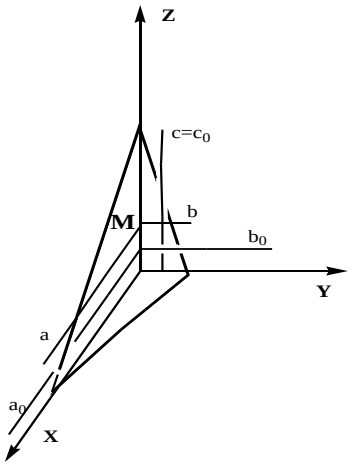
Example:

Calculate the symbol of lattice row [uvw] passing through the points C: 0 1 ½ and D: ½ 1 0:

$u = x_2 - x_1 = ½ - 0 = ½$
$v = y_2 - y_1 = 1 - 1 = 0$
$w = z_2 - z_1 = 0 - ½ = -½$

$[uvw] = [10\bar{1}]$

Exercise 4. Calculate the indices of Miller plane M, whose position in the crystallographic axis system X, Y, Z shown in Figure. Give the symbol (hkl) plane M, a=2Å, a_o=3Å, b=1Å, b_o=4Å, c=c_o=4Å,



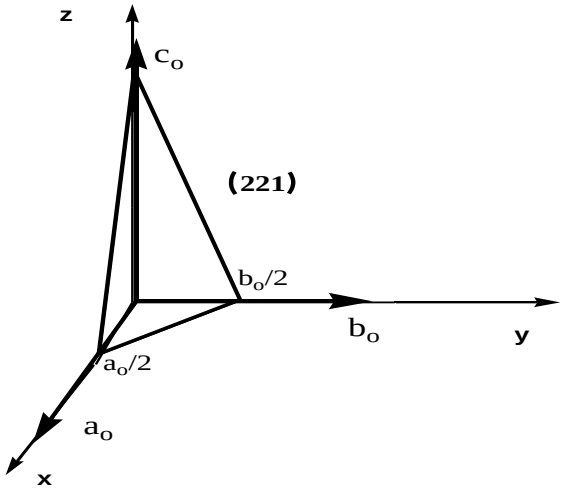
Example:

Calculate the indices of Miller plane M, a=1Å, a_o=3Å, b=2Å, b_o=3Å, c=c_o=2Å.

Axial units a_o, b_o, c_o are respectively 3Å, 3Å, 2Å. M plane intersects on the axes at following points a=1Å, b=2Å, c=2Å. Dividing the values of the axial units (a_o, b_o, c_o) by the values of the corresponding parameters for the plane M (a, b, c), obtained the following values: $h = {}^{ao}/_{a} = 3$, $k = {}^{bo}/_{b} = {}^{3}/_{2}$, $l = {}^{co}/_{c} = 1$, $hkl \in C$, → ***(hkl) = (632)***

Exercise 5. Draw planes (110), (210), (101), (12$\bar{1}$) and ($\bar{2}$10) in the cubic unit cell.

Example:
Draw plane (221) in the cubic unit cell.



Exercise 6. Determine symbols of Miller planes, which cut off following line segments on the crystallographic axes, expressed in axial units:

A: $^1/_2\,a_o$, $^1/_2 b_o$, $1c_o$; B: ∞, $1b_o$, $^2/_5 c_o$; C: $^2/_3 a_o$, ∞, $^1/_6 c_o$; D: $^1/_3 a_o$, $^2/_5 b_o$, ∞;

Exercise 7. Calculate the indices of plane belonging to the axis zones [110] and [001]. Using zonal equation prove that the plane can also belong to the zone, which axis is following lattice row [111].

Exercise 8. Determine the direction of axis zone [uvw], defined by the following planes:

a) $(20\bar{1})$ and $(\bar{6}\,41)$
b) $(41\bar{5})$ and $(1\bar{1}0)$
c) $(\bar{1}1\bar{2})$ and (001)
d) $(20\bar{3})$ and (111)

Example:

Determine the direction of axis zone [uvw], defined by the following planes *(123) and* $(0\bar{1}1)$.

The exercise can be solved using the following scheme:

- *write indices of each planes two times in a row,*
- *discard the first and last column,*
- *calculate [uvw], determining the minors of created matrix.*

Exercise 9. Check whether the planes (-110), (-311) and (-1-32) belong to a common zone. If yes, give the symbol of this zone axis [uvw].

Exercise 10. What is the symbol of the zone axis [uvw], to which the following planes (112) and (341) belong.

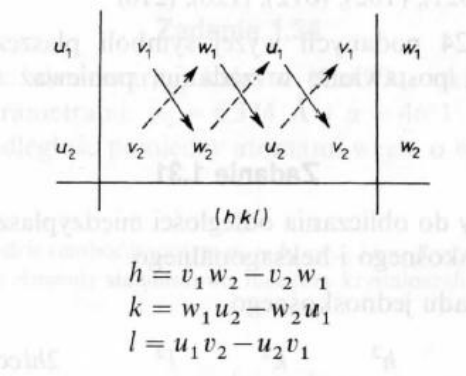
Exercise 11. What are the indices of Miller plane belonging to the axis zones:

a) [123] and $[\bar{1}1\bar{1}]$ b) [101] and $[21\bar{1}]$ c) [012] and $[1\bar{1}0]$

Example:

What are the Miller indices of plane belonging to the pairs of zone axes [113] and [201].

Proceed is the same as in the case of determining the direction [uvw] to which belongs planes with known symbols.



$[u_1v_1w_1] = [113]$, $[u_2v_2w_2] = [201]$

$h = 1 \cdot 1 - 0 \cdot 3 = 1$

$k = 3 \cdot 2 - 1 \cdot 1 = 5$

$l = 1 \cdot 0 - 1 \cdot 2 = -2$

$\boldsymbol{(hkl) = (15\bar{1})}$

Lesson 2: Translation group, Bravais lattices

Issues to be prepared:

- definition of group,
- translation groups,
- Bravais lattices,
- node coordinates in the cell,
- the number of nodes in the cell,

Educational aids: 14 models of Bravais lattices.

Introduction:

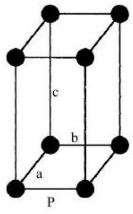
Auguste Bravais proved the existence of 14 types of translation lattices in 3 dimensions, called Bravais lattices. The 14 Bravais lattices are obtained by coupling one of the 7 crystal systems (or axial systems) with one of the lattice centerings.

Not all combinations of the crystal systems and lattice centerings are needed to describe the possible lattices. There are total of $7 \times 6 = 42$ combinations, but it can be shown that several of these are in fact equivalent to each other. For example, the monoclinic I lattice can be described by a monoclinic C lattice with different choice of crystal axes. Similarly, all A- or B-centred lattices can be described either by a C- or P-centering. This reduces the number of combinations to 14 Bravais lattices, shown in the table below.

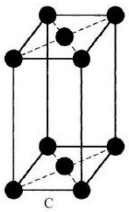
Crystal systems	**Cell types**
Triclinic	**P**
Monoclinic	**P, C**
Orthorhombic	**P, I, F, C** (A, B)
Tetragonal	**P, I**
Cubic	**P, I, F**
Trigonal or Rhombohedral cell	**R**
Hexagonal	**P**

The lattice centerings are:

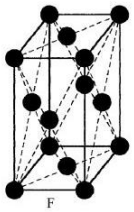
- **Primitive** unit cell (**P**): nodes in the cell corners only. The P-type cell includes $^1/_8$ of each node from the corner, because each node belongs to the eight neighboring cells, so the cell has one node: $N = {}^1/_8 \cdot 8 = 1$.



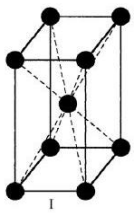
- **Base-centered** unit cell (**A**, **B** or **C**): nodes in the cell corners and in the center of one pair of the parallel cell faces. If the nodes are in the center of the faces which intersect the X axis then unit cell is denoted by A, if the Y axis - type B, Z axis - type C. Such unit cell has two nodes: $N = {}^1/_8 \cdot 8 + {}^1/_2 \cdot 2 = 2$.



- **Face-centered** unit cell (**F**): nodes in the cell corners and in the center of each of the cell faces. The unit cell has four nodes: $N = {}^1/_8 \cdot 8 + 3 \cdot ({}^1/_2 \cdot 2) = 4$.



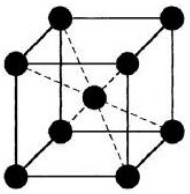
- **Body-centered** unit cell (**I**): nodes in the cell corners and in the center of the cell. The unit cell has two nodes: $N = {}^1/_8 \cdot 8 + 1 = 2$



Exercises:

Exercise 1. Analyze the obtained model: assign a model to one of the seven crystal systems, specify the Bravais lattice. Write down the coordinates of all nodes and the number of nodes belonging to that unit cell. Check whether the conditions are met those for the translational group.

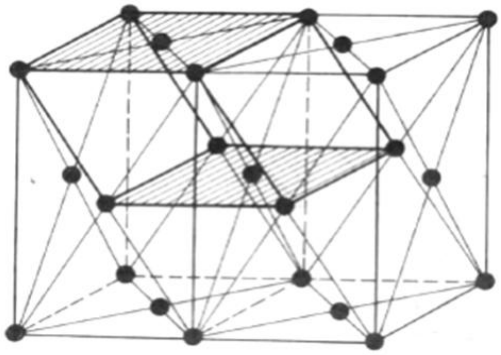
Example:



Crystal system	*Cubic*
Bravais lattices	*Body-centered unit cell (I)*
Node coordinates	$[0\vec{0}0][1\vec{0}0][0\vec{1}0][0\vec{0}1][1\vec{1}0][0\vec{1}1][1\vec{0}1][1\vec{1}1]\left[\frac{1}{2}\frac{\vec{1}}{2}\frac{1}{2}\right]$
The number of nodes in the cell (N)	*2*
Check whether the conditions are met for translational group: **1. closure property: a • b = b • a** **2. existence of identity property: a • e = e • a = a** **3. existence of inverse property: $a \bullet a^{-1} = a^{-1} \bullet a = a$** **4. associative property: (a • b) • c = a • (b • c)** Symbol • denotes for summation of vectors.	*1.* a $[0\vec{1}0]$ b $[1\vec{0}0]$ $[0\vec{1}0] \bullet [1\vec{0}0] = [1\vec{1}0]$ $[1\vec{0}0] \bullet [0\vec{1}0] = [1\vec{1}0]$ *2.* $e = [0\vec{0}0]$ *3.* a $[0\vec{1}0]$ a^{-1} $[0\vec{-}10]$ *4.* a $[1\vec{1}0]$ *b* $[1\vec{0}0]$ *c* $\left[\frac{1}{2}\frac{\vec{1}}{2}\frac{1}{2}\right]$ $([1\vec{1}0] \bullet [1\vec{0}0]) \bullet \left[\frac{1}{2}\frac{\vec{1}}{2}\frac{1}{2}\right] = \left[\frac{5}{2}\frac{\vec{3}}{2}\frac{1}{2}\right]$ $[1\vec{1}0] \bullet ([1\vec{0}0] \bullet \left[\frac{1}{2}\frac{\vec{1}}{2}\frac{1}{2}\right]) = \left[\frac{5}{2}\frac{\vec{3}}{2}\frac{1}{2}\right]$

Exercise 2. Show in the drawing, why the monoclinic I and F lattices do not exist.

Example:
Putting together the two face-centered unit cell (F), the new unit cell can be selected in other way to give the base-centered unit cell (C).



Exercise 3. Show in the drawing, why the tetragonal system C and F lattices do not exist.

Lesson 3: Symmetry in crystal morphology

Issues to be prepared:

- symmetry elements in the point groups, Groth symbols,
- 3x3 matrixes for the symmetry elements,
- submission rules of the symmetry operations,
- selection rules of crystallographic axes XYZ,
- point groups (triclinic, monoclinic and orthorhombic systems), international and Schoenflis symbols,

Introduction:

The symmetry of a molecule can be described by 3 main types of symmetry elements:

- **center of symmetry**,
- **symmetry axis**,
- **plane of symmetry**.

Center of symmetry, abbreviated C_i. A molecule has a center of symmetry when, for any atom in the molecule, an identical atom exists diametrically opposite to this center at equal distance from it.

Symmetry axis - an axis around which a rotation by 360°/n results in a molecule indistinguishable from the original. This is also called an n-fold rotational axis and abbreviated Cn. A molecule can have more than one symmetry axis; the one with the highest n is called the principal axis.

Plane of symmetry - a mirror plane through which an identical copy of the original molecule is given. A symmetry plane parallel to the principal axis is dubbed vertical (v) and one perpendicular to it horizontal (h). A third type of symmetry plane exists: If a vertical symmetry plane additionally bisects the angle between two 2-fold rotation axes perpendicular to the principal axis, the plane is dubbed dihedral (d).

Submission rules of the symmetry operations**:**

1. $\mathbf{L_{2n} \bullet C = P \perp L_n}$
   $\mathbf{P \bullet C = L_2 \perp P}$
   $\mathbf{P \bullet L_{2n} = C}$
2. $\mathbf{L_n \bullet L_2 \perp L_n = n L_2 \perp L_n}$ the two L_2 at an angle of 180°/n
3. $\mathbf{L_n \bullet P_{||} = n P \,||\, L_n}$ the two P at an angle of 180°/n

Symmetry element	*Groth symbol*	*Graphic symbol*	*Matrix*
Identity	E	none	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
Center of symmetry	**C**	•	$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}$
Plane of symmetry	$\mathbf{P}\perp\mathbf{x}$ or $\mathbf{P}_{(100)}$	| or ‖	$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
	$\mathbf{P}\perp\mathbf{y}$ or $\mathbf{P}_{(010)}$		$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$
	$\mathbf{P}\perp\mathbf{z}$ or $\mathbf{P}_{(001)}$		$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}$
Symmetry axis	$\mathbf{L_2}\|\|\mathbf{x}$ or $\mathbf{L}_{\mathbf{2[100]}}$	⬯	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}$
	$\mathbf{L_2}\|\|\mathbf{y}$ or $\mathbf{L}_{\mathbf{2[010]}}$		$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}$
	$\mathbf{L_2}\|\|\mathbf{z}$ or $\mathbf{L}_{\mathbf{2[001]}}$		$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Exercises:

Exercise 1. Derive a point groups for the three systems: triclinic, monoclinic and orthorhombic. Use the multiplication table for groups and submission rules of the symmetry operations.

1. **Triclinic system** – all symmetry elements {E, C}

Symmetry elements	**Multiplication table for groups**
{E}	| | **E** | | **E** | |
{E, C}	| | **E** | **C** | | **E** | | | | **C** | | |

Example:

Create a multiplication table for a group by typing in the row and column symmetry elements that are included in a point group.

	C
C	

In order to complete a multiplication table for a group, matrixes for the symmetry elements should be multiplied. Take a matrix for one symmetry element from row (C) and one from column (C), then specify what kind of the symmetry element is obtained.

$$\mathbf{C \bullet C = E} \qquad \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \bullet \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The obtained matrix corresponds to the identity E. The new symmetry element (E) is to be typed in the row and column of the table. Proceed as above - in order to complete the whole table.

	C	**E**
C	*E*	*C*
E	*C*	*E*

Point groups of triclinic system:

Symmetry element of point group	International symbol	Schoenflis symbol
{E}	**1**	C_1
{E, C}	**-1**	C_i

2. **Monoclinic system** – All symmetry elements {E, C, $P_{(010)}$, $L_{2[010]}$}

Symmetry elements	**Multiplication table for groups**
{E, $P_{(010)}$}	
{E, $L_{2[010]}$}	
{E, $L_{2[010]}$, C, $P_{(010)}$} Use the I submission rule of the symmetry operations	

	E	**$P_{(010)}$**
E		
$P_{(010)}$		

	E	**$L_{2[010]}$**
E		
$L_{2[010]}$		

	E	**$L_{2[010]}$**	**C**	**$P_{(010)}$**
E				
$L_{2[010]}$				
C				
$P_{(010)}$				

Example:

*Symmetry elements belong to a point group: {E, $L_{2[010]}$, C, $P_{(010)}$}. Create a multiplication table for a group by typing all symmetry elements in columns and rows. Complete the table. To do this, one should multiply matrixes of symmetry elements from rows by the matrixes of symmetry elements from columns. For example: choose an element, which is located in row 2 (**$L_{2[010]}$**) and another located in column 3 (**C**), then multiply and specify what kind of the symmetry element is obtained. The obtained matrix corresponds to the plane of symmetry (**$P_{(010)}$**).*

$$\mathbf{L_{2||y} \bullet C = P_{(010)} \perp L_{2||y}} \qquad \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \bullet \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Complete the multiplication table for a group. Proceed as above - in order to complete the whole table. If the new symmetry element is obtained one should add it in the row and column of the table.

	E	**$L_{2[010]}$**	**C**	**$P_{(010)}$**
E				
$L_{2[010]}$			$P_{(010)}$	
C		$P_{(010)}$		
$P_{(010)}$				

Point groups of monoclinic system:

Symmetry element of point group	International symbol	Schoenflis symbol
{E, $P_{(010)}$}	**m**	C_s
{E, $L_{2[010]}$}	**2**	C_2
{E, $L_{2[010]}$, C, $P_{(010)}$}	**$^2/_m$**	C_{2h}

3. **Orthorhombic system** – all symmetry elements {E, C, $P_{(010)}$, $P_{(100)}$, $P_{(001)}$, $L_{2[010]}$, $L_{2[100]}$, $L_{2[001]}$}

Symmetry elements	**Multiplication table for groups**
{E, $L_{2[100]}$, $L_{2[010]}$, $L_{2[001]}$} Use the II submission rule of the symmetry operations	

	E	**$L_{2[010]}$**	**$L_{2[100]}$**	**$L_{2[001]}$**
E				
$L_{2[010]}$				
$L_{2[100]}$				
$L_{2[001]}$				

{E, $P_{(010)}$, $P_{(100)}$, $L_{2[001]}$}

Use the III submission rule of the symmetry operations

	E	**$P_{(010)}$**	**$P_{(100)}$**	**$L_{2[001]}$**
E				
$P_{(010)}$				
$P_{(100)}$				
$L_{2[001]}$				

{E, $L_{2[010]}$, $L_{2[100]}$, $L_{2[001]}$, C, $P_{(010)}$, $P_{(100)}$, $P_{(001)}$}

	E	**$P_{(010)}$**	**$P_{(100)}$**	**$P_{(001)}$**	**C**	**$L_{2[001]}$**	**$L_{2[010]}$**	**$L_{2[010]}$**
E								
$P_{(010)}$								
$P_{(100)}$								
$P_{(001)}$								
C								
$L_{2[001]}$								
$L_{2[010]}$								
$L_{2[010]}$								

Point groups of orthorhombic system:

Symmetry element of point group	International symbol	Schoenflis symbol
{E, $L_{2[010]}$, $L_{2[100]}$, $L_{2[001]}$}	**222**	D_2
{E, $P_{(010)}$, $P_{(100)}$, $L_{2[001]}$}	**mm2**	C_{2V}
{E, C, $P_{(010)}$, $P_{(100)}$, $P_{(001)}$, $L_{2[010]}$, $L_{2[100]}$, $L_{2[001]}$}	$^{2}/_{m}\,^{2}/_{m}\,^{2}/_{m}$	D_{2h}

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Lesson 4: Stereographic projection

Issues to be prepared:

- standard projection,
- spherical coordinates,
- projection,
- rules of measuring angles,
- graphic symbol: lattice rows and planes,
- symmetry elements – graphic symbol and projection,

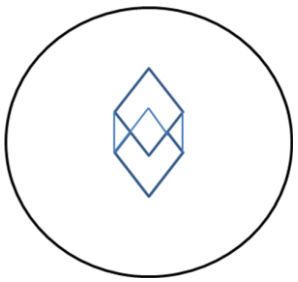
Educational aids: A4 tracing paper, Wulff net, pencil and eraser.

Introduction:

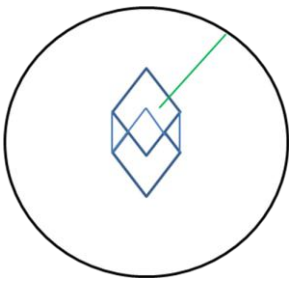
In the crystal geometry, the most important aspect of the lattice is the angular relationship between various planes and symmetry elements, not the relative translational position of planes. We need to be able to describe these angular relationships in an easily understandable manner, and so we use the stereographic projection, which presents a 3D structure on the surface of a sphere (spherical projection) and subsequently projected on a plane. Such a projection allows direct measurement of angles between various rotational axes or normals to planes, and this is very useful.

Rules of stereographic projection

The crystal is placed in the center of the sphere.



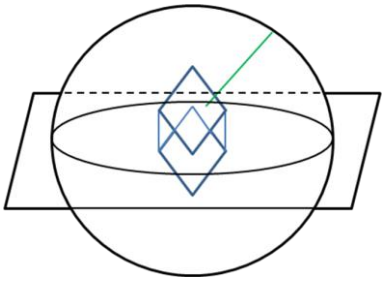
Draw normal to the crystal face (perpendicular), which we want to project - get a point on the sphere.



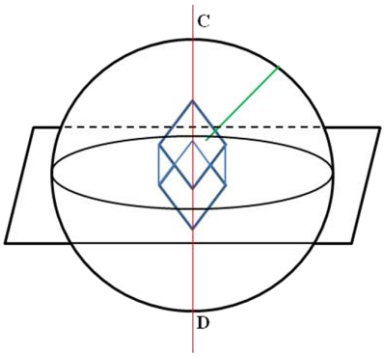
Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Draw the plane through the center of the sphere.

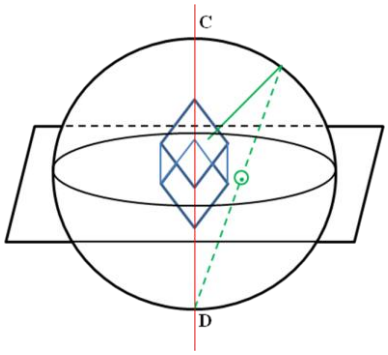


Draw perpendicular to this plane - we get two poles C and D (so-called ocular points)



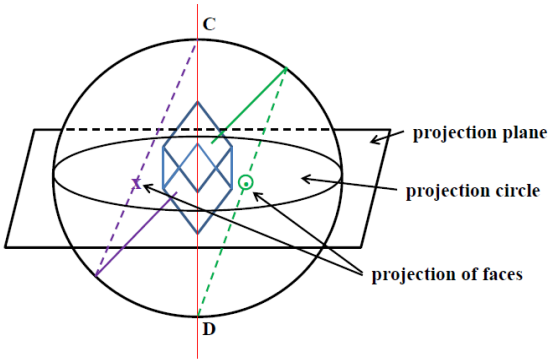
Points from the upper hemisphere are combined with the lower D pole - the face is marked on the projection in the following way:

⊙



Points from the lower hemisphere are combined with the upper C pole - the face is marked on the projection in the following way:

x



The parallels and meridians grid can be imposed on the surface of the sphere, what allows you to specify the exact position of each face, for which two angular coordinates are given: azimuth **φ** and pole distance **ρ**. The azimuth (**φ**) is measured according to the clockwise direction

Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

(0-360°). The pole distance (**ρ**) is measured from the center of the projection circle towards the edge (0-180°) (Figure 1). Measuring grid formed in such way can be represented as a two-dimensional grid. If the projection plane for such grid is a plane of one of the meridians, that this grid is called the **Wulff net** (Figure 2). The Wulff net is a tool using for the crystallographic calculations and geometric construction with the use of a stereographic projection. A typical Wulff net has a diameter of 20cm, and great and small circles are conducted every 2°, so measurements can be done with a precision of 1°.

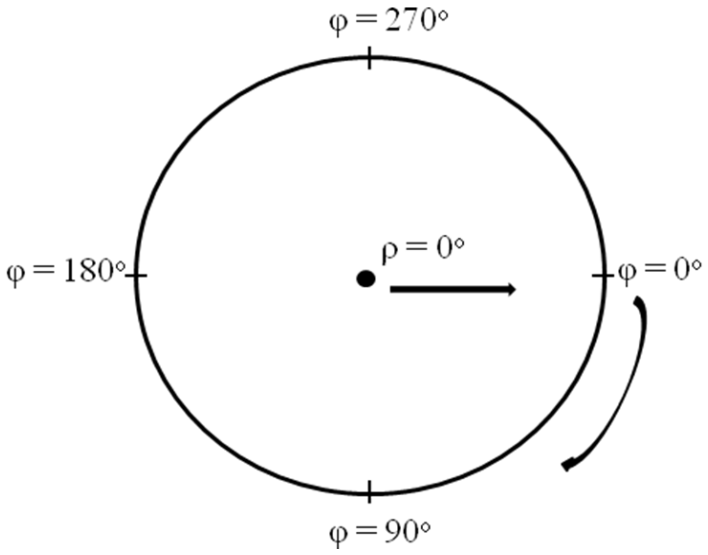


Fig. 1.

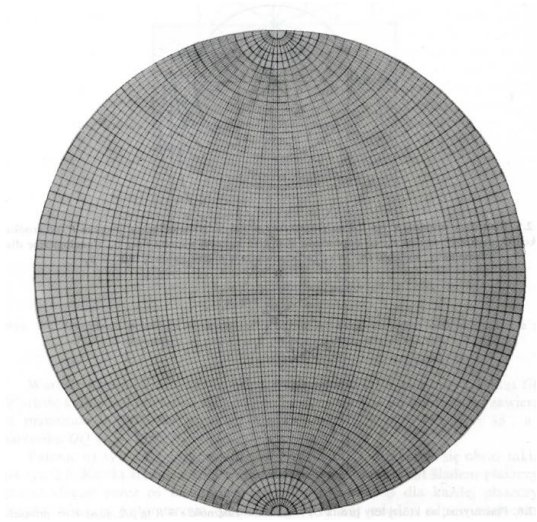


Fig. 2 Wulff net

Exercises:

Exercise 1. Make a projection of points on the projection plane A_1 (**φ**= 30°, **ρ**= 52°) and A_2 (**φ**= 170°, **ρ**= 130°).

Example:

In order to construct stereograms with the help of the Wulff net, a student is expected to work on the tracing paper over the net. Put a transparent tracing paper over the Wulff net and draw a projection circle by the continuous line, mark the values of azimuth (φ): 0°, 90°, 180° and 270° and mark the center of the net, from which we measure the pole distance (ρ). Figure 1 shows the tracing paper prepared to work on the Wulff net.

*Stereographic projection of **A_1 point**: on the tracing paper mark the auxiliary point that corresponds to the azimuth of this point (φ = 30°). Next, move only the tracing paper (the Wulff net is at the same*

position) until the auxiliary point will be on a straight of the net (e.g. at the equator). Along this line, from the center of the net we measure the value of pole distance (ρ = 52°). Point A_1, in the spherical projection, is located on the upper hemisphere, therefore this point in the projection plane is marked with a dot in a circle.

*Stereographic projection of **A_2 point**: the value of pole distance for the A_2 point is > 90 °. The value of this angle is measured from the center of the Wulff net along the radius defining the value of the azimuth to the circumference of a projection circle (ρ = 90°), and then back along the same radius towards the center of the net, measuring the missing 40°. Point A_2, in the spherical projection, is located on the lower hemisphere, therefore this point in the projection plane is marked with a cross. Stereographic projection of points A_1 and A_2 is shown in Figure 3.*

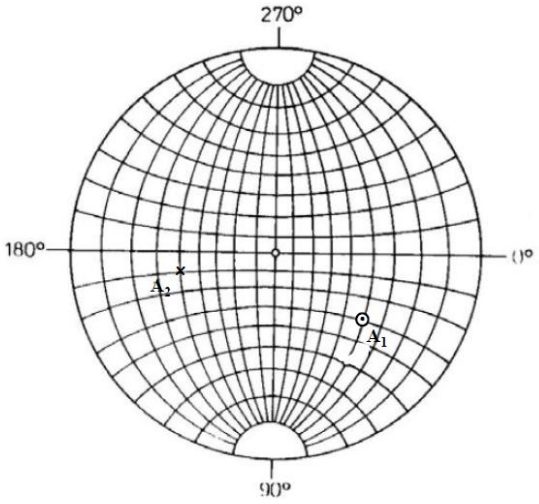


Fig. 3

Exercise 2. Measure the angular distance between the points: A1 and A2 (exercise 1) on the projection plane.

Example:

Prepare the tracing paper to work on the Wulff net (Fig. 1). Point A_1,in the spherical projection, is located on the upper hemisphere, and the point A_2 on the lower hemisphere. Angular distance between these points is measured along one great circle. First points should be put on the same great circle, which is located symmetrically on both sides of the diameter NS. The measure of the angular distance between the points A_1 and A_2 is the distance measured along the common great circle (Fig. 4). Angular distance between the points A_1 and A_2 is 140°.

Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

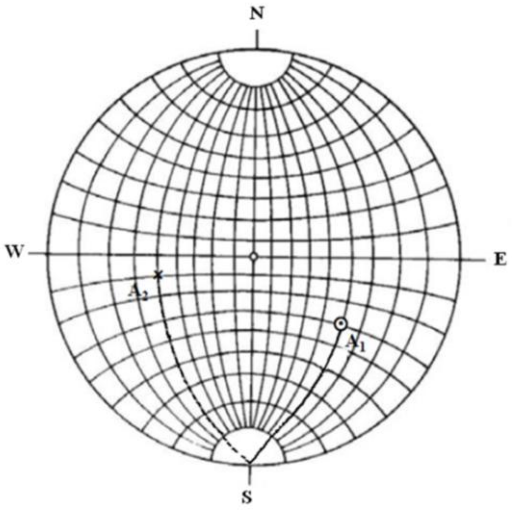


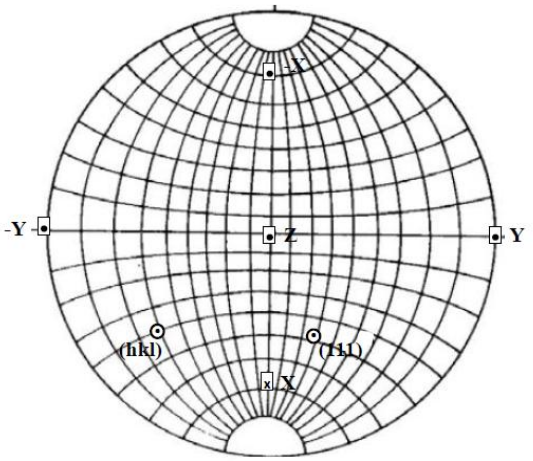
Fig. 4

Exercise 3. Make a projection of following points P_1: ($\varphi_1 = 57°$ and $\rho_1 = 71°$), P_2 ($\varphi_2 = 130°$ and $\rho_2 = 56°$), P_3 ($\varphi_3 = 200°$ and $\rho_3 = 116°$), P_4 ($\varphi_4 = 220°$ and $\rho_4 = 108°$), P_5 ($\varphi_5 = 80°$ and $\rho_5 = 90°$) and P_6 ($\varphi_6 = 260°$ and $\rho_6 = 90°$). Measure the angles between all possible pairs of these points.

Exercise 4. Make a projection of normal to parametral face on the projection plane (111) ($\varphi = 61{,}5°$, $\rho = 60°$) and normal to P face ($\varphi = 138°$, $\rho = 66°$). Make a projection of XYZ axes in the monoclinic system. Calculate the Miller indices (hkl) for unknown P face.

Example:

Prepare tracing paper to work on the Wulff net (Fig. 1). Make a projection of following faces: (111), (hkl) and XYZ axes (monoclinic system: $\alpha = \gamma = 90^o$, $\beta \neq 90^o$).



$\rho > 90°$ x

$\rho < 90°$ or $= 90°$ •

Fig. 5

Miller indices of crystal face (hkl) can be determined by measuring the angles between the normal to the face and the XYZ axes, and then use a following formula,

$$h:k:l=\frac{\cos P_x}{\cos(111)_x}:\frac{\cos P_y}{\cos(111)_y}:\frac{\cos P_z}{\cos(111)_z}$$

in which P_x, P_y, P_z are the angles formed by the normal to the P face of unknown Miller indices (hkl) and XYZ crystallographic axes; whereas the $(111)_x$ $(111)_y$, $(111)_z$ - the angles formed by the normal to the parametral face (111) and XYZ axes.

We measure the angles between:

- *the normal to the face (hkl) and the XYZ axes, these angles have values: 61°, 132° and 66° respectively,*
- *the normal to the parametral face (111) and the XYZ axes, these angles have values: 54 °, 66 ° and 60 ° respectively.*

$$h:k:l=\frac{\cos 61°}{\cos 54°}:\frac{\cos 132°}{\cos 66°}:\frac{\cos 66°}{\cos 60°}$$

$$h:k:l=0{,}82:(-1{,}64):0{,}81$$

Dividing the obtained quotients by 0.81 we obtain the following Miller indices for P face:

$$(hkl)=(1\bar{2}1)$$

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Lesson 5: Triclinic, monoclinic and orthorhombic systems

Issues to be prepared:

- point groups (submission rules) - triclinic, monoclinic and orthorhombic systems,
- stereographic projection: XYZ axes, zonal circle, symmetry elements,
- projection and indexing of faces (hkl),

Introduction:

Knowledge of the symmetry group provides the full information about all the possible symmetry operations that can be used on the object. The set of all point symmetry operations and operation of submission of these symmetry operations define a point group.

Rules of creating international symbols of point groups:

1. Triclinic system – there is no need to make arrangements.
2. Monoclinic system – one place in the symbol, that corresponds to the symmetry related to Y axis.
3. Orthorhombic system – three places in the symbol, that correspond to the symmetry related to X, Y, Z axis respectively.

Crystal systems	The unit cell parameters	Point groups	
		International symbol	Schoenflis symbol
Triclinic	$\alpha \neq \beta \neq \gamma \neq \alpha \neq 90^o$ $a_o \neq b_o \neq c_o \neq a_o$	1	C_1
		$\bar{1}$	C_i
Monoclinic	$\alpha = \gamma = 90^o, \beta \neq 90^o$ $a_o \neq b_o \neq c_o \neq a_o$	2	C_2
		m	C_s
		$^2/_m$	C_{2h}
Orthorhombic	$\alpha = \beta = \gamma = 90^o$ $a_o \neq b_o \neq c_o \neq a_o$	222	D_2
		mm2	C_{2v}
		$^2/_m\,^2/_m\,^2/_m$	D_{2h}

Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

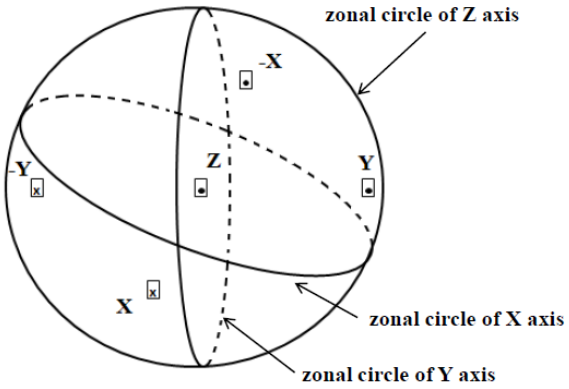
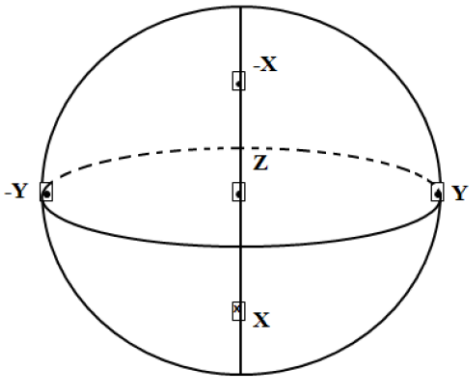
Hierarchy of rules for the choice of crystallographic axes XYZ:

1. C 000
2. $L_n \parallel XYZ$
3. $P \perp XYZ$
4. Edges $\parallel$ XYZ

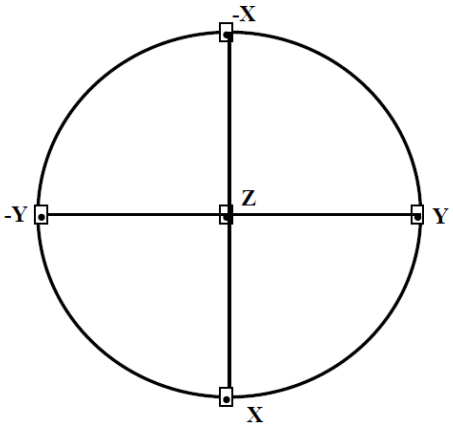
Selection of the crystallographic axis in triclinic, monoclinic, orthorhombic systems:

Triclinic	Monoclinic	Orthorhombic
XYZ $\parallel$ edges in crystal	Y $\parallel$ L_2 or $\perp$ P XZ $\parallel$ edges in crystal $\beta > 90^o$	XYZ $\parallel$ L_2 or $\perp$ P

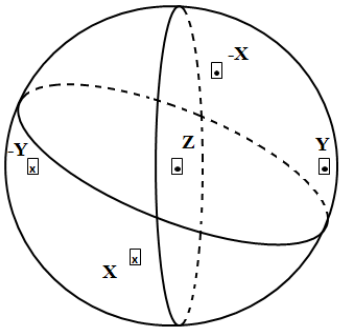
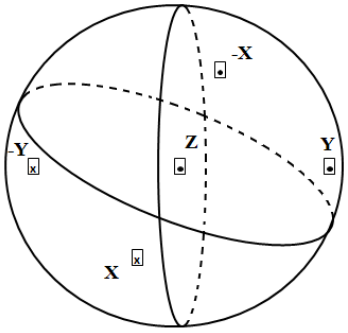
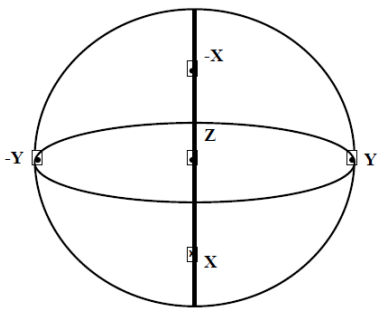
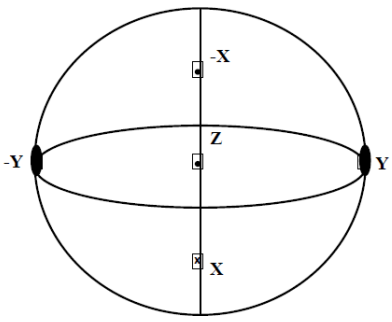
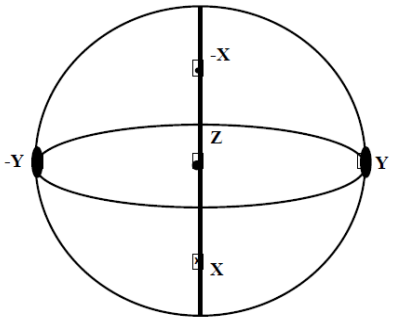
Stereographic projection of axes and zonal circles:

Crystal system	Angles	Projection of axes and zonal circles
Triclinic	$\alpha \neq \beta \neq \gamma \neq \alpha \neq 90^o$ eg. α (YZ) = 80^o β (XZ) = 120^o γ (XY) = 110^o	
Monoclinic	$\alpha = \gamma = 90^o$, $\beta \neq 90^o$ e.g. β (XZ) = 120^o	

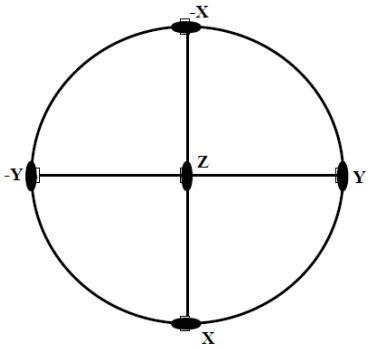
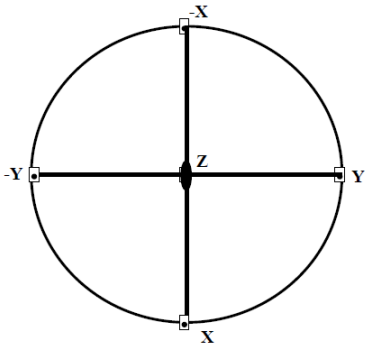
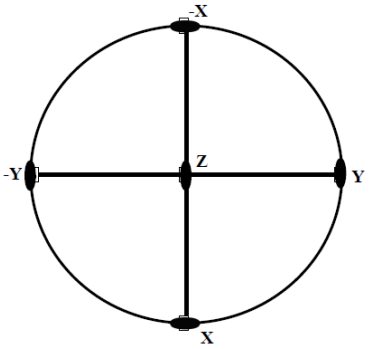
Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Orthorhombic	$\alpha = \beta = \gamma = 90^o$	

Projection of symmetry elements in point groups:

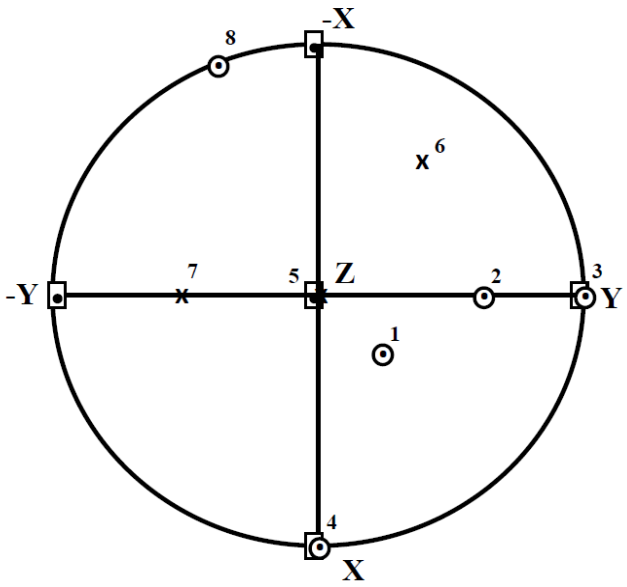
Triclinic	
 **1**	 **-1**
Monoclinic	
 **m**	 **2**
 **$^2/_m$**	

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Orthorhombic		
		
222	**mm2**	$^{2}/_{m}\,^{2}/_{m}\,^{2}/_{m}$

Exercises:

Exercise 1. Determine the Miller symbol (hkl) of crystal faces (1-8) for the orthorhombic system, which are located on the stereographic projection.



Example:

Signs of Miller indices in (hkl) symbol can be defined using the following formula,

$$h = a_o \cos(hkl)_x$$
$$k = b_o \cos(hkl)_y$$
$$l = c_o \cos(hkl)_z$$

in which a_o, b_o and c_o mean the axial unit, whereas the $(hkl)_x$, $(hkl)_y$, $(hkl)_z$ - mean angles between the normal to the face of unknown symbol (hkl) and the XYZ axes.

Face 1:

- *the angle between the normal to the face 1 and the X axis is <90 ^{o}, the cos of the angle <90 ^{o} has a positive value, therefore* ***h*** *index has a positive value,*
- *the angle between the normal to the face 1 and the Y axis is <90 ^{o}, the cos of the angle <90 ^{o} has a positive value, therefore* ***k*** *index has a positive value,*
- *the angle between the normal to the face 1 and the Z axis is <90 ^{o}, the cos of the angle <90 ^{o} has a positive value, therefore* ***l*** *index has a positive value,*

Miller symbol of face 1: ***(hkl)****.*

Face 2:

- *the angle between the normal to the face 2 and the X axis = 90 ^{o}, the cos90 ^{o} = 0, so* ***h*** *index equals 0,*
- *the angle between the normal to the face 1 and the Y axis is <90 ^{o}, the cos of the angle <90 ^{o} has a positive value, therefore* ***k*** *index has a positive value,*
- *the angle between the normal to the face 1 and the Z axis is <90 ^{o}, the cos of the angle <90 ^{o} has a positive value, and* ***l*** *index has a positive value,*

Miller symbol of face 2: ***(0kl)****.*

Face 5:

- *the angle between the normal to the face 5 and the X axis = 90 ^{o}, the cos90 ^{o} = 0, so* ***h*** *index equals 0,*
- *the angle between the normal to the face 5 and the Y axis = 90 ^{o}, the cos90 ^{o} = 0, so* ***k*** *index equals 0,*
- *the angle between the normal to the face 5 and the Z axis is >90 ^{o}, the cos of the angle >90 ^{o} has a negative value, therefore* ***l*** *index has a negative value,*

Divide by l, thus shift the plane and give the following Miller symbol of face 5: $\boldsymbol{(00\bar{1})}$*.*

Lesson 6: Identification and description of models from the triclinic, monoclinic and orthorhombic systems

Issues to be prepared:

- point groups (submission rules) - triclinic, monoclinic and orthorhombic systems,
- stereographic projection: XYZ axes, zonal circle, symmetry elements,
- projection and indexing of faces (hkl),
- form {hkl},
- symmetrically equivalent points,
- molecules,

Educational aids: models of point groups from triclinic, monoclinic and orthorhombic systems.

Introduction:

Symmetrically equivalent points are the points associated by the symmetry operations in the space with a point xyz. Symmetry matrixes are very useful for determining the positions of the symmetrically equivalent points. The positions of all the points we get by the action of a matrix on a point xyz and next equivalent points as long as we get back to the starting point.

Exercises:

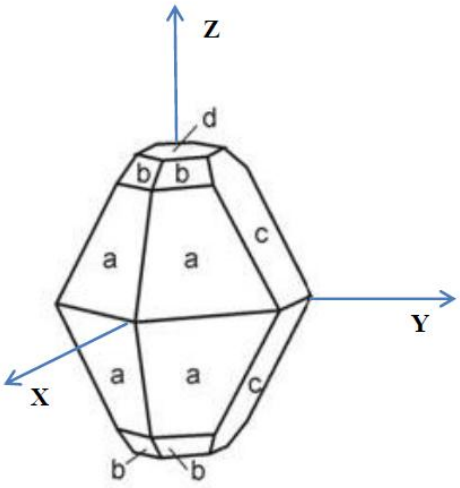
Exercise 1. Identify and describe the received model.

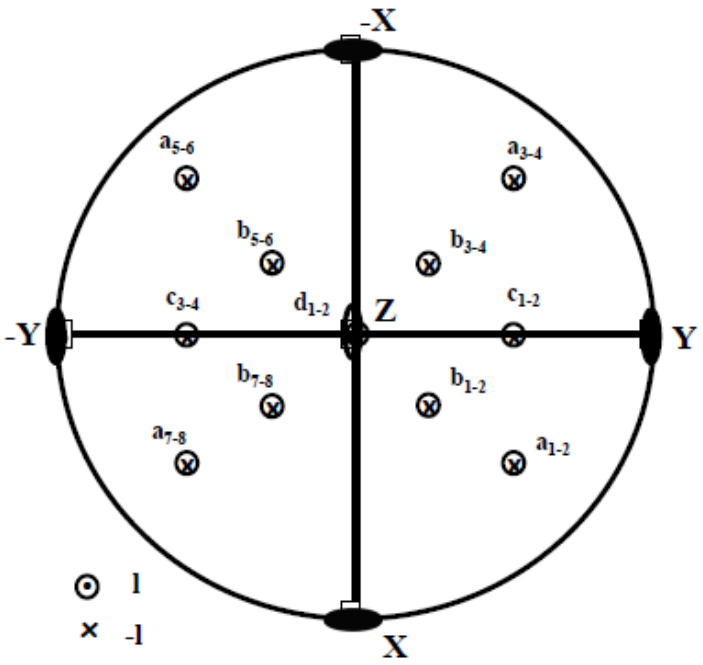
Identification and description of the model:

1. Symmetry elements {Groth symbol} > submission rules.
2. Crystal system (selection of XYZ axes).
3. Point group – International symbols and Schoenflis symbol.
4. Stereographic projection: XYZ axes, zonal circle, symmetry elements, faces.
5. Indexing of faces (hkl).
6. Form {hkl}.

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Example:



Symmetry elements {Groth symbol}	*{ E, C, $L_{2[010]}$, $L_{2[100]}$, $L_{2[001]}$, $P_{(010)}$, $P_{(100)}$, $P_{(001)}$}*
Crystal system	*orthorhombic*
Point group – International symbols and Schoenflis symbol	*mmm, D_{2h}*
Stereographic projection: XYZ axes, zonal circle, symmetry elements, faces	

Indexing of faces (hkl)	*a1 (hkl)* *a2 (hk-l)* *a3 (-hkl)* *a4 (-hk-l)* *a5 (-h-kl)* *a6 (-h-k-l)* *a7 (h-kl)* *a8 (h-k-l)*	*b1 (hkl)* *b2 (hk-l)* *b3 (-hkl)* *b4 (-hk-l)* *b5 (-h-kl)* *b6 (-h-k-l)* *b7 (h-kl)* *b8 (h-k-l)*	*c1 (0kl)* *c2 (0k-l)* *c3 (0-kl)* *c4 (0-k-l)*	*d1 (001)* *d2 (00$\bar{1}$)*
Form (form in crystal is a set of symmetrically equivalent faces, i.e. associated to each other by the symmetry elements)	*{hkl}*	*{hkl}*	*{0kl}*	*{001}*

Exercise 2. Give coordinates of points and number of symmetrically equivalent points in the following point groups: $^{2}/_{m}$, mm2, 222, $^{2}/_{m}{}^{2}/_{m}{}^{2}/_{m}$.

Example:
Give coordinates of points and number of symmetrically equivalent points in the mm2 point group.
First, write the matrixes for symmetry elements for mm2 point group: $m \perp x$, $m \perp y$ and $2 \parallel z$.

$$m \perp x \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad m \perp y \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad 2 \parallel z \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The positions of all the points we get by the action of a matrix on a point xyz and next equivalent points as long as we get back to the starting point:

$$m \perp x \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ y \\ z \end{bmatrix} \qquad m \perp y \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ \bar{y} \\ z \end{bmatrix} \qquad 2 \parallel z \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix}$$

$$m \perp y \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} \bar{x} \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix} \qquad 2 \parallel z \quad \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} \bar{x} \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ \bar{y} \\ z \end{bmatrix}$$

$$m \perp x \quad \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} x \\ \bar{y} \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix} \qquad 2 \parallel z \quad \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} x \\ \bar{y} \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ y \\ z \end{bmatrix}$$

Number of symmetrically equivalent points: 4

Coordinates of symmetrically equivalent in mm2 point group: xyz, $\bar{x}yz$, $x\bar{y}z$, $\bar{x}\bar{y}z$.

Exercise 3. Suggest a molecule, which has the following symmetry: C_1, C_i, C_{2h}, C_{2v}, C_2, C_s, D_{2h}.

Example:

C₁ *CFBrClH*	***Cᵢ*** *$C_2Br_2Cl_2H_2$*	***Cs*** *CBr2ClH*	***C₂*** *H_2S*
C₂ₕ *trans-$C_2H_2Cl_2$*	***C₂ᵥ*** *cis-$C_2H_2Cl_2$, H_2O*	***D₂ₕ*** *C_2H_4*	

Lesson 7: Crystal systems: tetragonal and cubic

Issues to be prepared:

- point groups (submission rules) – tetragonal and cubic systems,
- stereographic projection: XYZ axes, zonal circle, symmetry elements,
- projection and indexing of faces (hkl),

Introduction:

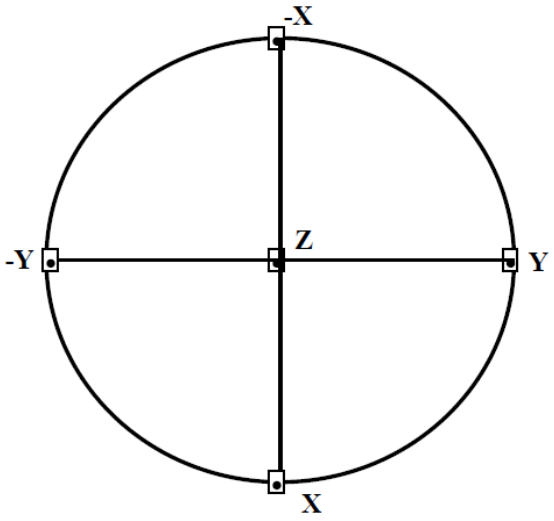
Rules of creating international symbols of point groups:

1. Tetragonal system – three places in the symbol: symmetry of Z axis takes first place, XY - second, two directions [110] - third place.
2. Cubic system – three places in the symbol: symmetry of XYZ axes takes first place, four directions [111] - second, six directions [110] - third place.

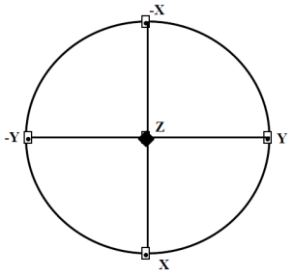
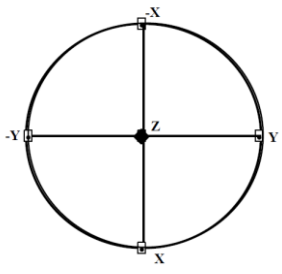
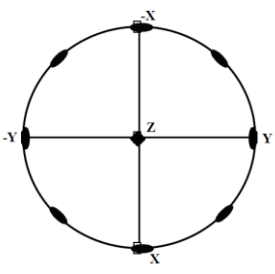
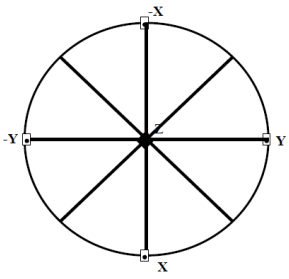
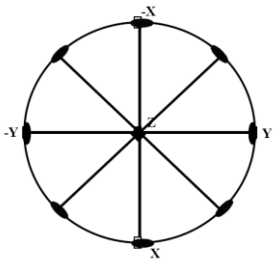
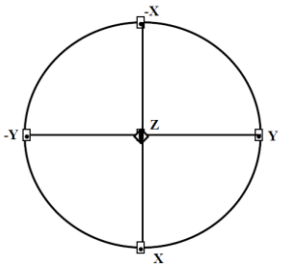
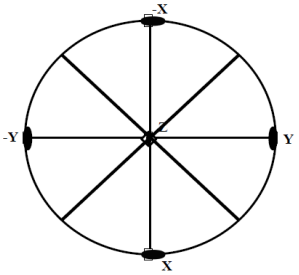
Crystal system	The unit cell parameters	Point groups	
		International symbol	Schoenflis symbol
Tetragonal	$\alpha = \beta = \gamma = 90^o$ $a_o = b_o \neq c_o$	4	C_4
		$^4/_m$	C_{4h}
		422	D_4
		4mm	C_{4v}
		$^4/_m\,^2/_m\,^2/_m$	D_{4h}
		$\bar{4}$	S_4
		$\bar{4}2m$	D_{2d}
Cubic	$\alpha = \beta = \gamma = 90^o$ $a_o = b_o = c_o$	23	T
		$\frac{2}{m}\bar{3}$	T_h
		432	O
		$\bar{4}3m$	T_d
		$\frac{4}{m}\bar{3}\frac{2}{m}$	O_h

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

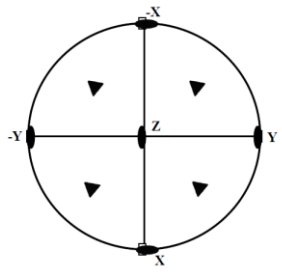
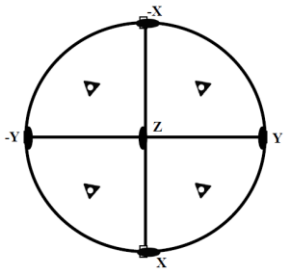
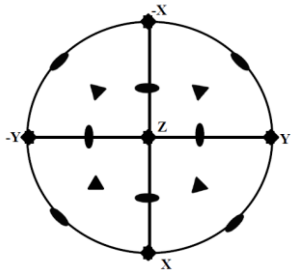
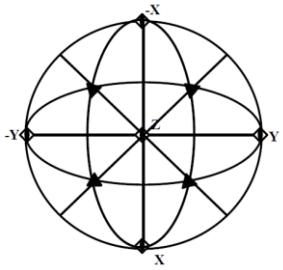
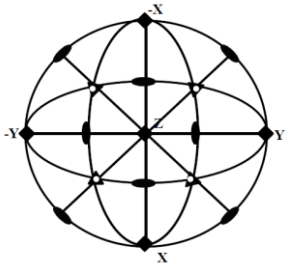
Stereographic projection of axes and zonal circles:

Crystal system	Angles	Projection of axes and zonal circles
Tetragonal Cubic	$\alpha = \beta = \gamma = 90^o$	

Projection of symmetry elements in point groups:

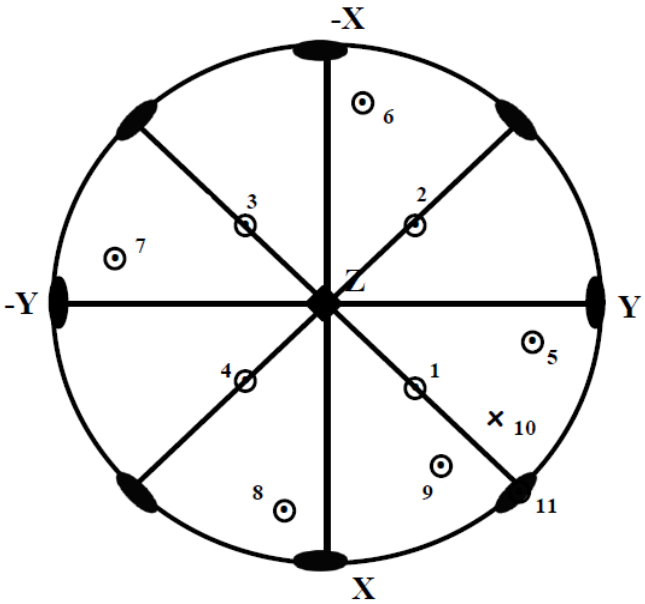
Tetragonal			
 **4**	 $^{4}/_{m}$	 **422**	 **4mm**
 $^{4}/_{m}\,^{2}/_{m}\,^{2}/_{m}$	 $\bar{4}$	 $\bar{4}2m$	

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Cubic		
 **23**	 $\frac{2}{m}\bar{3}$	 432
 $\bar{4}3m$	 $\frac{4}{m}\bar{3}\frac{2}{m}$	

Exercises:

Exercise 1. Determine the Miller symbol (hkl) of crystal faces (1-11) for the tetragonal system, which are located on the stereographic projection.



Example:

Signs of Miller indices in (hkl) symbol can be defined using the following formula,

$$h = a_o \cos(hkl)_x$$
$$k = b_o \cos(hkl)_y$$
$$l = c_o \cos(hkl)_z$$

in which a_o, b_o and c_o mean the axial unit, whereas the $(hkl)_x$, $(hkl)_y$, $(hkl)_z$ - mean angles between the normal to the face of unknown symbol (hkl) and the XYZ axes.

Face 1:

- *angle $(hkl)_x = 45^o$ - **h** index has a positive value,*
- *angle $(hkl)_y$ has the same value as angle $(hkl)_x$, because this face is located on the plane, which bisects the angle between X and Y axes – therefore **k** index = h index,*
- *angle $(hkl)_z < 90^o$ - so **l** index has a positive value.*

*Miller symbol of face 1: **(hhl)**.*

Face 5:

- *angle $(hkl)_x < 90^o$ - therefore **h** index has a positive value,*
- *angle $(hkl)_y < 90^o$ - therefore **k** index has a positive value,*
- *angle $(hkl)_z < 90^o$ - therefore **l** index has a positive value.*

*Miller symbol of face 5: **(hkl)**.*

Faces 6-8:

Faces 6-8 are related to the face 5 by action of the 4-fold axis parallel to Z. In order to determine the Miller symbol of faces 6-8 the symmetry matrix should be used. We create a matrix of $L_4 \| z$:

$$L_{4\|z} = \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Then, Miller symbol of faces 6-8 we get by the action of a matrix on a face (hkl) and next equivalent faces as long as we get back to the starting face:

Face 6: $$\begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} h \\ k \\ l \end{bmatrix} = \begin{bmatrix} \bar{k} \\ h \\ l \end{bmatrix}$$

Face 7: $$\begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} \bar{k} \\ h \\ l \end{bmatrix} = \begin{bmatrix} \bar{h} \\ \bar{k} \\ l \end{bmatrix}$$

$(\bar{k}hl)$ $(\bar{h}\bar{k}l)$

Face 8: $\begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} \bar{h} \\ \bar{k} \\ l \end{bmatrix} = \begin{bmatrix} k \\ \bar{h} \\ l \end{bmatrix}$ *Face 5:* $\begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} k \\ \bar{h} \\ l \end{bmatrix} = \begin{bmatrix} h \\ k \\ l \end{bmatrix}$

$(k\bar{h}l)$ (hkl)

Miller symbols of faces: 6 ($\bar{k}$ ***hl)**, 7 **(**$\bar{h}$ $\bar{k}$ **l)**, 8 **(k**$\bar{h}$ **l)**.*

Lesson 8: Identification and description of models from the tetragonal and cubic systems

Issues to be prepared:

- point groups (submission rules) – tetragonal and cubic systems,
- stereographic projection: XYZ axes, zonal circle, symmetry elements,
- projection and indexing of faces (hkl),
- form {hkl},
- symmetrically equivalent points,
- molecules,

Educational aids: models of point groups from tetragonal and cubic systems.

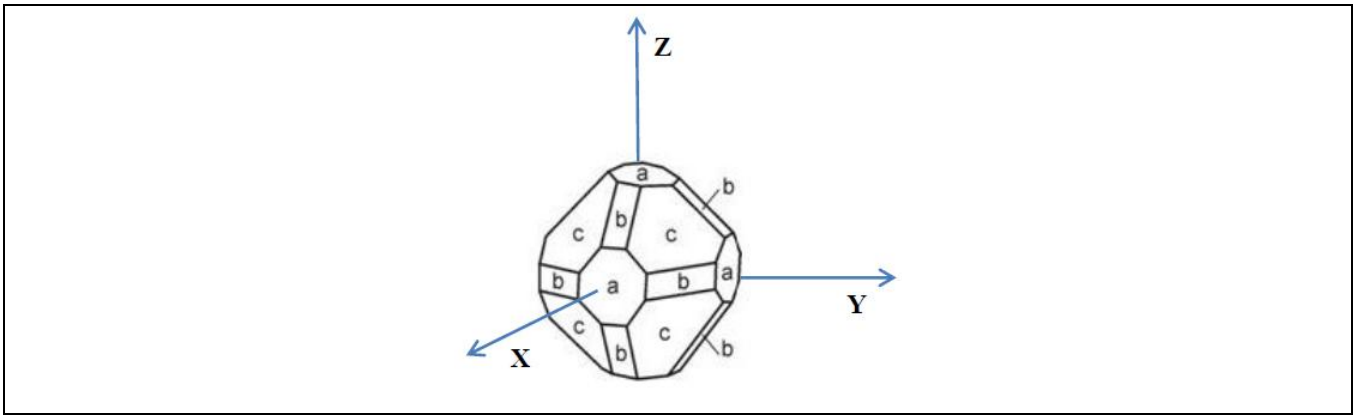
Exercises:

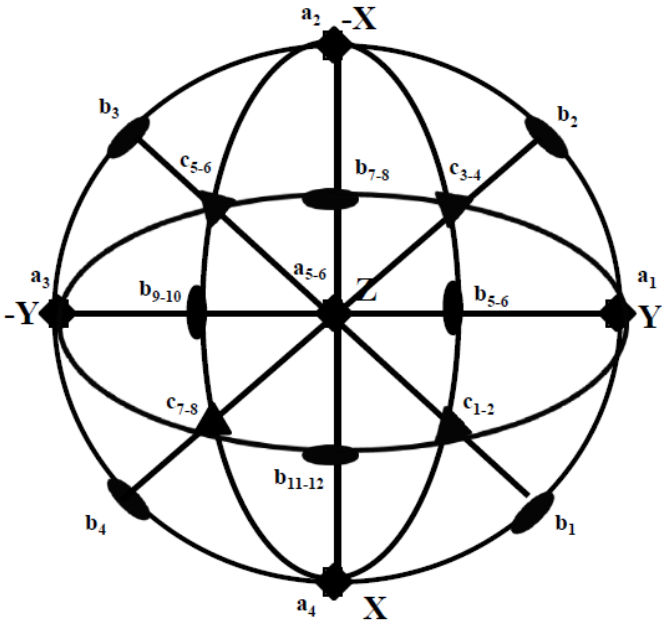
Exercise 1. Identify and describe the received model.

Identification and description of the model:

1. Symmetry elements {Groth symbol} > submission rules.
2. Crystal system (selection of XYZ axes).
3. Point group – International symbols and Schoenflis symbol.
4. Stereographic projection: XYZ axes, zonal circle, symmetry elements, faces.
5. Indexing of faces (hkl).
6. Form {hkl}.

Example:



<table>
<tr><td>Symmetry elements {Groth symbol}</td><td colspan="3">{ E, C, $L_{4[010]}$, $L_{4[100]}$, $L_{4[001]}$, $P_{(010)}$, $P_{(100)}$, $P_{(001)}$, 4 x $L_{3[111]}$, 6 x $L_{2[110]}$, 6 x $P_{(110)}$}</td></tr>
<tr><td>Crystal system</td><td colspan="3">cubic</td></tr>
<tr><td>Point group – International symbols and Schoenflis symbol</td><td colspan="3">$\frac{4}{m}\bar{3}\frac{2}{m}$, O_h</td></tr>
<tr><td>Stereographic projection: XYZ axes, zonal circle, symmetry elements, faces</td><td colspan="3"> 
</td></tr>
<tr><td>Indexing of faces (hkl)</td><td>a1 (010)
a2 (-100)
a3 (0-10)
a4 (100)
a5 (001)
a6 (00-1)</td><td>b1 (110)
b2 (-110)
b3 (-1-10)
b4 (1-10)
b5 (011)
b6 (01-1)
b7 (-101)
b8 (-10-1)
b9 (0-11)
b10 (0-1-1)
b11 (101)
b12 (10-1)</td><td>c1 (111)
c2 (11-1)
c3 (-111)
c4 (-11-1)
c5 (-1-11)
c6 (1--1-1)
c7 (1-11)
c8 (1-1-1)</td></tr>
<tr><td>Form</td><td>{010}</td><td>{110}</td><td>{111}</td></tr>
</table>

Exercise 2. Give coordinates of points and number of symmetrically equivalent points in the following point groups: 4, $^4/_m$, 422, 23.

Example:

Give coordinates of points and number of symmetrically equivalent points in the $^4/_m$ point group. First, write the matrixes for symmetry elements for $^4/_m$ point group: $4 \| z$, $m \perp z$:

$$4 \| z \begin{bmatrix} \bar{0} & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad m \perp z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}$$

The positions of all points we get by the action of a matrix on a point xyz and subsequently the equivalent points as long as we get back to the starting point:

$$4 \| z \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{y} \\ x \\ z \end{bmatrix} \qquad 4 \| z \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} \bar{y} \\ x \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix} \qquad 4 \| z \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix} = \begin{bmatrix} y \\ \bar{x} \\ z \end{bmatrix}$$

$$4 \| z \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} y \\ \bar{x} \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \qquad m \perp z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \bullet \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ \bar{z} \end{bmatrix} \qquad m \perp z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \bullet \begin{bmatrix} \bar{y} \\ x \\ z \end{bmatrix} = \begin{bmatrix} \bar{y} \\ x \\ \bar{z} \end{bmatrix}$$

$$m \perp z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \bullet \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \\ \bar{z} \end{bmatrix} \qquad m \perp z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \bullet \begin{bmatrix} y \\ \bar{x} \\ z \end{bmatrix} = \begin{bmatrix} y \\ \bar{x} \\ \bar{z} \end{bmatrix}$$

Number of symmetrically equivalent points: 8

Coordinates of symmetrically equivalent in $^4/_m$ point group: xyz, $\bar{y}xz$, $\bar{x}\bar{y}z$, $y\bar{x}z$, $xy\bar{z}$, $\bar{y}x\bar{z}$, $\bar{x}\bar{y}\bar{z}$, $y\bar{x}\bar{z}$.

Exercise 3. Suggest a molecule, which has the following symmetry: C_4, C_{4h}, C_{4v}, D_4, D_{4h}, D_{2d}, T_d, O_h

Example:

C_4/C_{4h}/C_{4v}/D_4/D_{4h} *$[Cu(H_2O)_4]$*	***C_4/C_{4h}/C_{4v}*** *$[Cu(NH_3)_4]$*
D_{2d}/T_d *CH_4*	***O_h*** *SF_6*

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Lesson 9: Crystal systems: trigonal and hexagonal

Issues to be prepared:

- point groups (submission rules) - trigonal and hexagonal systems,
- stereographic projection: XYZ axes, zonal circle, symmetry elements,
- projection and indexing of faces (hkil),

Introduction:

Rules of creating international symbols of point groups:

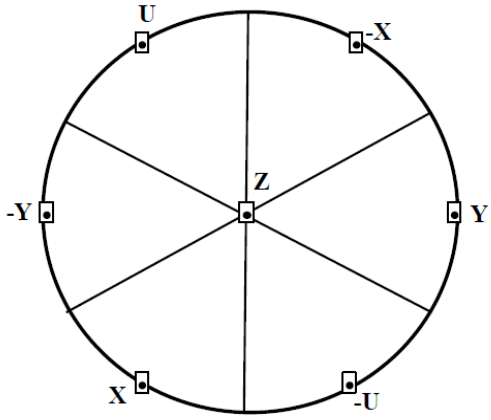
1. Trigonal and hexagonal system – three places in the symbol: symmetry of Z axis takes first place, XYU - second place, three directions [01$\bar{1}$0] - third place.

Crystal systems	The unit cell parameters	Point groups	
		International symbol	Schoenflis symbol
Trigonal or Rhombohedral cell	$\alpha = \beta = 90^o, \gamma = 120^o$ $a_o = b_o \neq c_o$ or $\alpha = \beta = \gamma = 90^o$ $a_o = b_o = c_o$	3	C_3
		$\bar{3}$	C_{3i}
		32	D_3
		3m	C_{3v}
		$\bar{3}\frac{2}{m}$	D_{3d}
Hexagonal	$\alpha = \beta = 90^o, \gamma = 120^o$ $a_o = b_o \neq c_o$	6	C_6
		$^6/_m$	C_{6h}
		622	D_6
		6mm	C_{6v}
		$^6/_m\,^2/_m\,^2/_m$	D_{6h}
		$\bar{6}$	C_{3h}
		$\bar{6}2m$	D_{3h}

Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

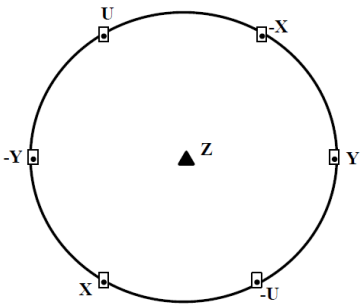
Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Stereographic projection of axes and zonal circles:

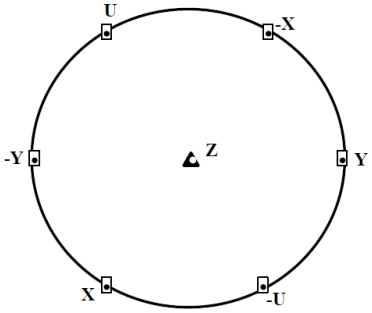
Crystal system	Angles	Projection of axes and zonal circles
Trigonal Hexagonal	$\alpha = \beta = 90^o, \gamma = 120^o$	

Projection of symmetry elements in point groups:

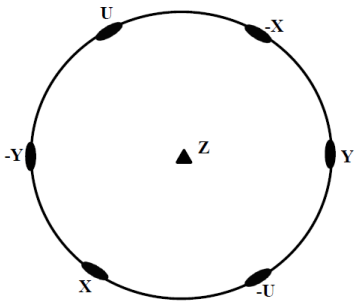
Trigonal



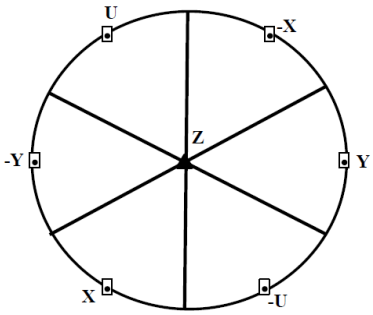
3



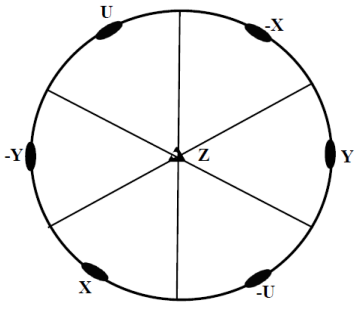
$\bar{3}$



32

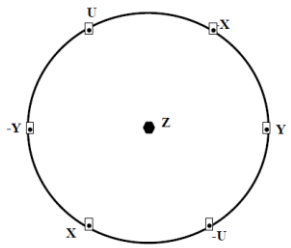
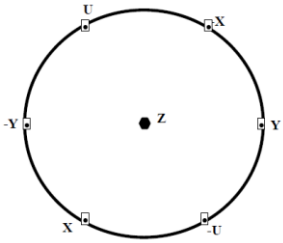
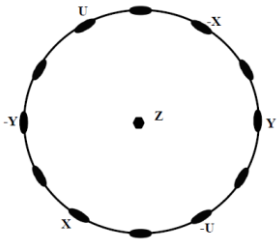
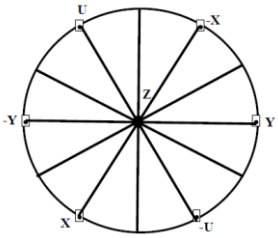
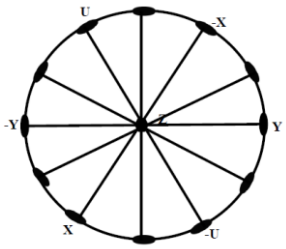
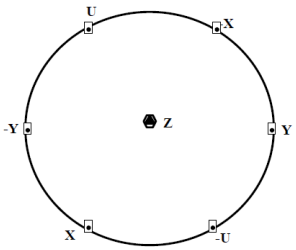
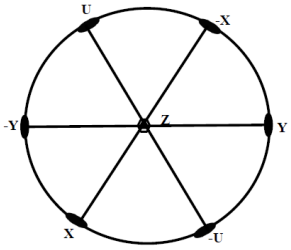


3m



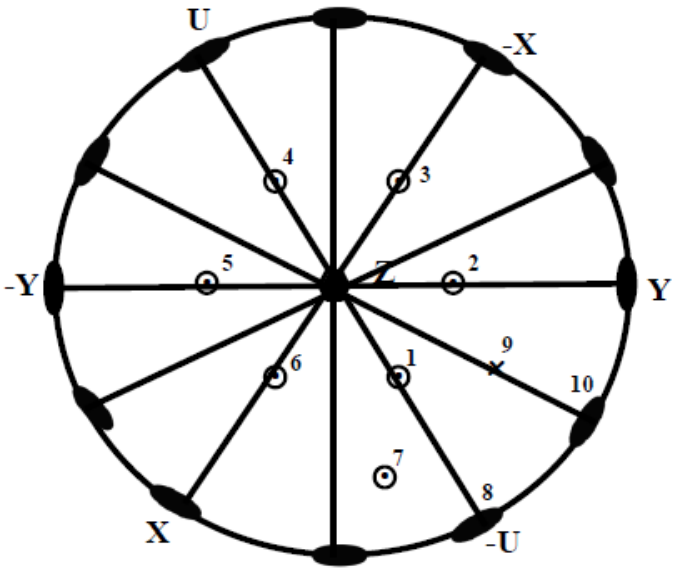
$\bar{3}\frac{2}{m}$

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Hexagonal			
 **6**	 $^{6}/_{m}$	 **622**	 **6mm**
 $^{6}/_{m}\,^{2}/_{m}\,^{2}/_{m}$	 $\bar{6}$	 $\bar{6}2m$	

Exercises:

Exercise 1. Determine the Miller symbol (hkl) of crystal faces (1-10) for the hexagonal system, which are located on the stereographic projection



Example:

The general symbol of crystal face for trigonal and hexagonal systems has (hkil) form, because there are four axes XYUZ. Indices h, k, i and l corresponds to the axes X, Y, U, and Z. Indices of faces in these systems have a special property:

$$h + k + i = 0$$
$$i = -(h + k)$$

Face 1:

- *angle* $(hkil)_x < 90^o$ *- so* ***h*** *index has a positive value,*
- *angle* $(hkil)_y$ *has the same value as angle* $(hkil)_x$*, because this face is located on the plane, which bisects the angle between X and Y axes – therefore* ***k*** *index = h index,*
- *angle* $(hkil)_z < 90^o$ *- so* ***l*** *index has a positive value,*
- ***i*** *= -(h + k), i = -(h + h) = -2h.*

Miller symbol of face 1: $\boldsymbol{(hh\bar{2}hl)}$.

Face 7:

- *angle* $(hkil)_x < 90^o$ *- therefore* ***h*** *index has a positive value,*
- *angle* $(hkil)_y < 90^o$ *- therefore* ***k*** *index has a positive value,*
- *angle* $(hkil)_z < 90^o$ *- therefore* ***l*** *index has a positive value,*
- ***i*** *= -(h + k),*

Miller symbol of face 7: $\boldsymbol{(hk\bar{i}l)}$.

Face 8:

- *angle* $(hkil)_x < 90^o$ *- so* ***h*** *index has a positive value,*
- *angle* $(hkil)_y$ *has the same value as angle* $(hkil)_x$*, because this face is located on the plane, which bisects the angle between X and Y axes – therefore* ***k*** *index = h index,*
- *angle* $(hkil)_z = 90^o$ *- so* ***l*** *= 0,*
- ***i*** *= -(h + k), i = -(h + h) = -2h.*

Divide by h, thus shift the plane and give the following Miller symbol of face 8: $\boldsymbol{(11\bar{2}0)}$.

Face 10:

- *angle* $(hkil)_x = 90^o$ *- so* ***h*** *= 0,*
- *angle* $(hkil)_y < 90^o$ *- therefore* ***k*** *index has a positive value,*
- *angle* $(hkil)_z = 90^o$ *- so* ***l*** *= 0,*
- ***i*** *= -(h + k), i = -(0 + k) = -k*

Divide by h, thus shift the plane and give the following Miller symbol of face 10: $\boldsymbol{(01\bar{1}0)}$.

Lesson 10: Identification and description of the models from the trigonal and hexagonal systems

Issues to be prepared:

- point groups (submission rules) – trigonal and hexagonal systems,
- stereographic projection: XYZ axes, zonal circle, symmetry elements,
- projection and indexing of faces (hkil),
- form {hkil},
- molecules,

Educational aids: models of point groups from trigonal and hexagonal systems.

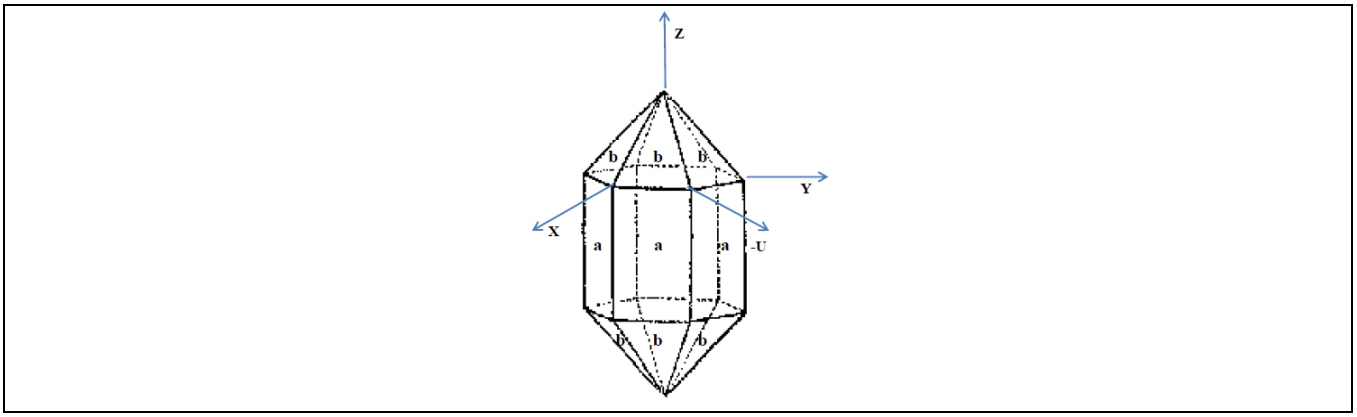
Exercises:

Exercise 1. Identify and describe the received model.

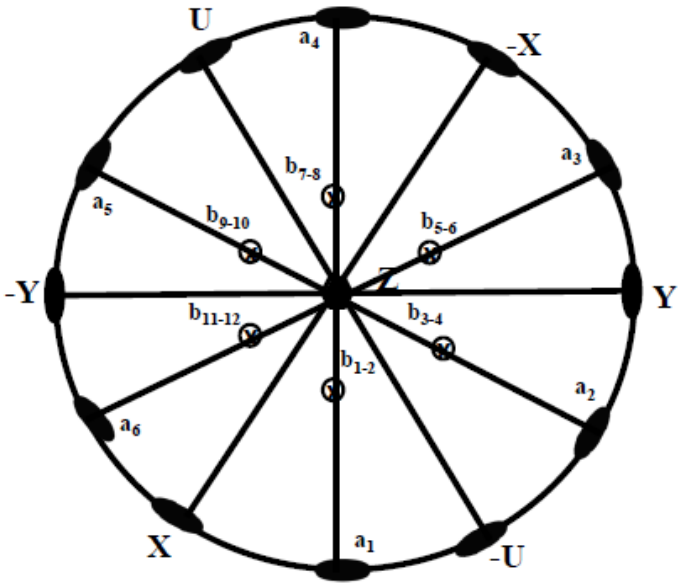
Identification and description of the model:

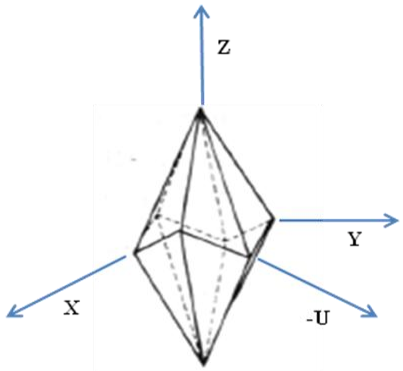
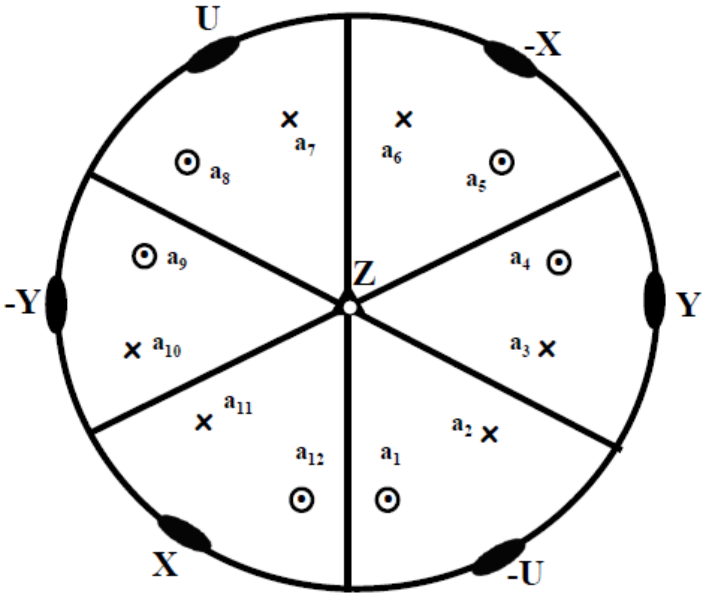
1. Symmetry elements {Groth symbol} > submission rules.
2. Crystal system (selection of XYZ axes).
3. Point group – International symbols and Schoenflis symbol.
4. Stereographic projection: XYZ axes, zonal circle, symmetry elements, faces.
5. Indexing of faces (hkil).
6. Form {hkil}.

Example:



Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Symmetry elements {Groth symbol}	*{ E, C, $L_{6[0001]}$, $L_{2[1000]}$, $L_{2[0100]}$, $L_{2[0010]}$, $P_{(0001)}$, $P_{(1000)}$, $P_{(0100)}$, $P_{(0010)}$, 3x$L_{2[10-10]}$, 3x $P_{(10-10)}$}*	
Crystal system	*hexagonal*	
Point group – International symbols and Schoenflis symbol	$^{6}/_{m}\,^{2}/_{m}\,^{2}/_{m}$, D_{6h}	
Stereographic projection: XYUZ axes, zonal circle, symmetry elements, faces		
Indexing of faces (hkil)	*a1 (10-10)* *a2 (01-10)* *a3 (-1100)* *a4 (-1010)* *a5 (0-110)* *a6 (1-100)*	*b1 (h0-hl)* *b2 (h0-h-l)* *b3 (0h-hl)* *b4 (0h-h-l)* *b5 (-hh0l)* *b6 (-hh0-l)* *b7 (-hh0l)* *b8 (-hh0-l)* *b9 (0-hhl)* *b10 (0-hh-l)* *b11 (h-h0l)* *b12 (h-h0-l)*
Form	*{10$\bar{1}$0}*	*{h0$\bar{h}$l}*

<table>
<tr><td colspan="2"> 
</td></tr>
<tr><td>Symmetry elements {Groth symbol}</td><td>{ E, C, $L_{3i[0001]}$, $L_{2[1000]}$, $L_{2[0100]}$, $L_{2[0010]}$, $P_{(0001)}$, $P_{(1000)}$, $P_{(0100)}$}</td></tr>
<tr><td>Crystal system</td><td>trigonal</td></tr>
<tr><td>Point group – International symbols and Schoenflis symbol</td><td>$\bar{3}\frac{2}{m}$, D_{3d}</td></tr>
<tr><td>Stereographic projection: XYUZ axes, zonal circle, symmetry elements, faces</td><td> 
</td></tr>
<tr><td>Indexing of faces (hkil)</td><td>a1 (hk-il)
a2 (kh-i-l)
a3 (-ki-h-l)
a4 (-hi-kl)
a5 (-ihkl)
a6 (-ikh-l)
a7 (-h-ki-l)
a8 (-k-hil)
a9 (k-ihl)
a10 (h-ik-l)
a11 (i-h-k-l)
a12 (i-k-hl)</td></tr>
<tr><td>Form</td><td>{ $hk\bar{i}l$ }</td></tr>
</table>

Exercise 2. Suggest a molecule, which has the following symmetry: C_{3v}, D_{6h}, D_{3d}, D_{3h}.

Example:

$\boldsymbol{C_{3v}}$ NH_3	$\boldsymbol{D_{3d}}$ BF_3	$\boldsymbol{D_{6h}}$ C_6H_6	$\boldsymbol{D_{3h}}$ C_2H_6

Lesson 11: Space groups

Issues to be prepared:

- ordinary and translational symmetry elements (the screw axes, the glide planes),
- 4x4 matrixes,
- Bravais lattices,
- symmetrically equivalent points,
- space groups,

Introduction:

The space groups in three dimensions are made from combinations of the 32 crystallographic point groups with the 14 Bravais lattices, each of the latter belonging to one of 7 lattice systems. This results in a space group being a combination of the translational symmetry of a unit cell including lattice centering, the point group symmetry operations and the screw axis and glide plane symmetry operations. The combination of all these symmetry operations results in a total of 230 different space groups describing all possible crystal symmetries.

Comparison of point groups with space groups:

Point groups	**Space groups**
- ordinary symmetry elements: {C, P, L_n}	- ordinary symmetry elements: {C, P, L_n} - translational symmetry elements: {the screw axes: n_m, the glide plane: a, b, c, n, d}
3x3 matrixes: $\mathbf{X' = S \bullet X}$ $\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{pmatrix} \bullet \begin{pmatrix} x \\ y \\ z \end{pmatrix}$	4x4 matrixes: $\mathbf{X' = S' \bullet X} = \begin{pmatrix} s_{11} & s_{12} & s_{13} & t_1 \\ s_{21} & s_{22} & s_{23} & t_2 \\ s_{31} & s_{32} & s_{33} & t_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$
none	- lattice centering (P, A, B, C, I, F)
number of symmetrically equivalent points = „independent symmetry”	number of symmetrically equivalent points = „independent symmetry” • „ lattice centering”

The rules of creating the symbol of the space group:

1. First place: lattice centerings:
   - **Primitive** unit cell (**P**);
   - **Base-centered** unit cell (**A**, **B** or **C**);
   - **Face-centered** unit cell (**F**);
   - **Body-centered** unit cell (**I**);
   - **Rhombohedral** cell (**R**).

2. Second place: ordinary symmetry elements {C, P, L_n} and translational symmetry elements {screw axes: n_m, glide plane: a, b, c, n, d}.

Translational symmetry elements:

1. A **screw axis** is a rotation about an axis, followed by a translation along the direction of the axis. The general symbol of screw axis is $\mathbf{n_m}$, a number **n** means fold axis and $^{m}/_{n}$ is a translation vector. So, 2_1 is a two-fold rotation followed by a translation of $^{1}/_{2}$ of the lattice vector.

Screw axis	International symbol	Translation vector
Two-fold screw axis	$\mathbf{2_1 \parallel x}$ $\mathbf{2_1 \parallel y}$ $\mathbf{2_1 \parallel z}$	$a_o/2$ $b_o/2$ $c_o/2$

2. A **glide plane** is a reflection in a plane, followed by a translation parallel to that plane. This is noted by **a**, **b** or **c**, depending on which axis the glide is along. There is also the **n** glide, which is a glide along the half of a diagonal of a face, and the **d** glide, which is a fourth of the way along either a face or space diagonal of the unit cell. The latter is called the diamond glide plane as it features in the diamond structure.

Glide plane	International symbol	Translation vector
axial glide plane	**a** **b** **c**	$a_o/2$ $b_o/2$ $c_o/2$
diagonal glide plane	**n**	$(a_o+b_o)/2$, $(a_o+c_o)/2$, $(b_o+c_o)/2$, $(a_o+b_o+c_o)/2$
diamond glide plane	**d**	$(a_o+b_o)/4$, $(a_o+c_o)/4$, $(b_o+c_o)/4$, $(a_o+b_o+c_o)/4$

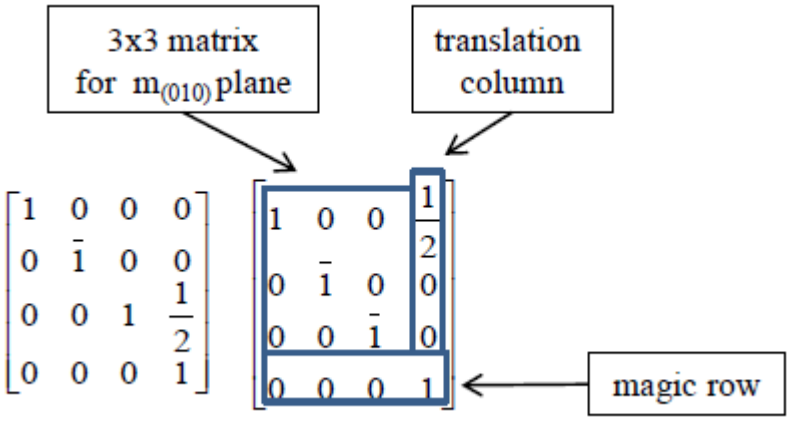
Exercises:

Exercise 1. Write the matrixes for the following symmetry elements: $\mathbf{2_1 \| x}$, $\mathbf{2_1 \| y}$, $\mathbf{b_{(100)}}$, $\mathbf{c_{(010)}}$, $\mathbf{n_{(001)}}$, $\mathbf{d_{(110)}}$.

Example:

Write the matrixes for the following symmetry elements: $\boldsymbol{2_1 \| x}$, $\mathbf{c_{(010)}}$.

The transformation to the screw axis $\boldsymbol{2_1 \| x}$ *consists of two operations: rotation by 180° about the X axis and parallel translation* $a_o/2$. *This information can be used to form a 4x4 matrix for this screw axis. This matrix consists of 3x3 matrix corresponding to the ordinary axis* $2 \| x$ *and translation of* $a_o/2$ *vector.*



The transformation to the glide plane $\mathbf{c_{(010)}}$ *consists of two operations: a reflection in a plane* $m_{(010)}$ *and translation* $c_o/2$. *This information can be used to form a 4x4 matrix for this glide plane. This matrix consists of 3x3 matrix corresponding to the ordinary plane* $m_{(010)}$ *and translation of* $c_o/2$ *vector.*

Exercise 2. Complete the symbol of the space group: Pna, Pmc, Pca.

Example:

Replace the symbol of space group Pca with the symbol of the point group: remove type of the Bravais cell and replace translational symmetry elements by ordinary symmetry elements:

Pca $\Rightarrow$ mm

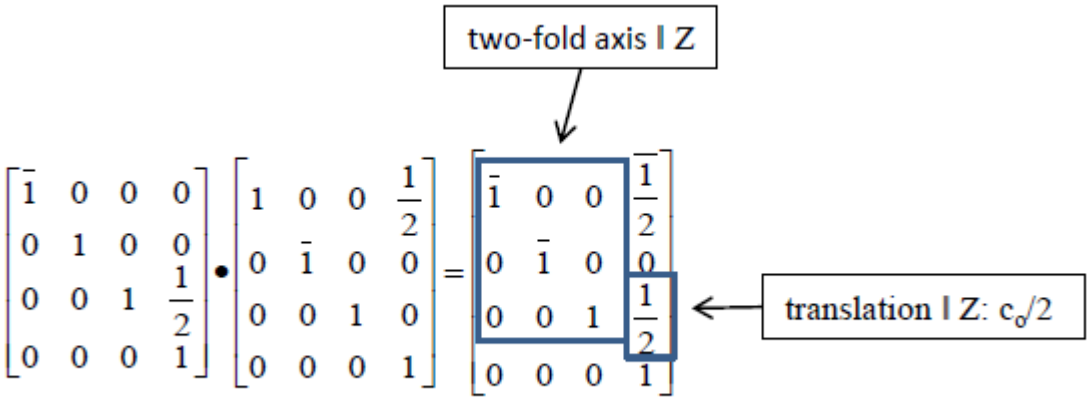
Then specify the crystal system, to which this point group belongs:

Orthorhombic system

Using rules of creating an international symbolism of point groups for orthorhombic system, specify the orientation of the symmetry elements that are part of the this group

c *(100)* *and* ***a*** *(010)*

*In order to complete the symbol of the space group Pca, matrixes for the translational symmetry elements (****c*** *(100)* *and* ***a*** *(010))* *should be multiplied. Then we interpret the obtained matrix.*



Completed symbol of space group: ***Pca2$_1$***

Exercise 3. Complete the symbol of the space group: Pbam, Pnnn, Pcab, Fddd, Pmma.

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Lesson12: Substance identification by the DSH method

Issues to be prepared:

- the Debye-Scherrer-Hull method (DSH),
- calculation of d/n - the Bragg condition,
- calculation of θ angle from the distance between diffraction lines l,
- substance identification: pre identification - based on 5 diffraction lines, then analysis of all lines,

Educational aids: powder diffraction pattern, slide caliper, ruler, calculator.

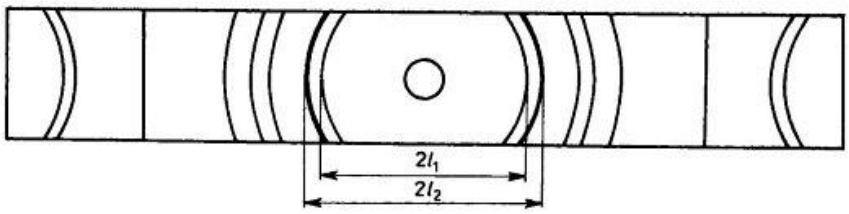
Introduction:

The Debye-Scherrer-Hull method is the basic method of study polycrystalline materials, in which monochromatic radiation is used. The object of study is a sample, which consists of big amounts of crystallite with 10-0.1 microns size. These crystallites are randomly oriented, so the angle of incidence rays θ on individual crystallites is different. Reflections are obtained from these crystal planes, which are set at an angle that satisfies the Bragg equation:

$$n\lambda = 2d_{(hkl)} \sin\theta_{(hkl)}$$

in which: d – is the spacing between the planes in the atomic lattice, θ – is the angle between the incident ray and the scattering planes, λ – is the wavelength of incident wave, n – is an integer.

Example of diffraction pattern obtained by DSH method:



Measured distance between diffraction lines (l) can be used to calculate the Bragg angle (θ):

$$\theta = \frac{90}{2\pi R} \bullet 2l$$

in which: 2R – diameter of camera, which usually amounts 57.3 and 114.6 mm, 2l – distance between symmetrical diffraction lines [mm].

Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

The aim of the exercise is substance identification with using of powder diffraction pattern obtained by DSH method.

Student receives diffraction pattern:

- diameter of camera amounts 64mm or 114.6 mm,
- wavelength of the incident wave: λ_{Cu} = 1.54178 Å or λ_{Co} = 1.79021 Å.

Measurement of the distance between the symmetrical diffraction lines (l) allows to determine the characteristic quantity of the crystal lattice, namely the interplanar distance $d_{(hkl)}$.

The distance between the symmetrical lines (l) should be measured with the use of a slide caliper or a ruler with an accuracy of 0.02 or 0.1 mm. Intensity of line (I) is assessed visually on a scale of 1 to 10: 10 means the strongest line, 1 means the weakest line. The diffraction angle (θ) can be determined using the value of diameter of camera (2R). Then, using the Bragg equation, the interplanar distances $d_{(hkl)}$ for all lattice planes should be calculated.

The obtained data should be placed in the following table:

Lp.	**I (1-10)**	**l**	**θ_{Br}**	**$\sin\theta_{Br}$**	**d/n**	**$I_{theor.}$**	**$d/n_{theor.}$**

The obtained values of interplanar distance $d_{(hkl)}$ and the intensity of the lines I should be compared with literature data in order to identify the substance. At the beginning the pre identification is made based on 5 most intense lines. The next step is comparison of all values of interplanar distance and intensity of lines.

Lesson 13: Indexing of the DSH diffractogram for crystals from the cubic system

Issues to be prepared:

- the lattice quadratic equation,
- indexing,
- calculation of the lattice constant a_o,
- systematic absences,
- determination of the Bravais lattice.

Educational aids: powder diffraction pattern, slide caliper or ruler, calculator.

Introduction:

Compounds can be identified using the polycrystalline sample with no used of indexing the powder diffraction pattern. However, in order to determine lattice parameters and a type of Bravais lattice, indexing of the diffraction lines is necessary. This is more difficult if the symmetry of the crystal is lower, because the number of unknown parameters rise from one for the cubic system (a) to six for triclinic system (a, b, c, α, β, γ).

The lattice quadratic equation for cubic system has the form:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

The sum of the squares of indices $Q = h^2 + k^2 + l^2$ is an integer number, what limits the number of possible solutions.

The transformation of the Bragg equation to determine d^2 gives the following equation:

$$\frac{1}{d_{hkl}^2} = \frac{4\sin^2\theta}{n^2\lambda^2}$$

Comparison of the obtained expression to the lattice quadratic equation for cubic system gives:

$$\frac{h^2 + k^2 + l^2}{a^2} = \frac{4\sin^2\theta}{n^2\lambda^2}$$

Using this so-called modified lattice quadratic equation and measurement of the distance between the symmetrical diffraction lines, we can calculate the lattice constant for the cubic system.

Because Q is an integer number, the indexing is based on finding the sequence of integer numbers. Values of $\sin^2\theta$ are divided by these integer numbers giving the constant values. If we know the set of these natural numbers (set of Q) we can determine hkl indices, which are used to determine type of the Bravais lattice. Certain integer numbers, such as 7, 15, 23, 28, 31, etc., are forbidden because they can not be the sum of squares of three integer numbers.

The aim of the exercise is calculation of the lattice constant a_o for substance from the cubic system and determination of the Bravais lattice using the powder diffraction pattern obtained by the DSH method.

Student receives the diffraction pattern:

- diameter of camera is 64mm or 114.6 mm,
- wavelength of incident wave: λ_{Cu} = 1.54178 Å or λ_{Co} = 1.79021 Å.

The distance between the symmetrical lines (l) should be measured with a slide caliper or a ruler with an accuracy of 0.02 or 0.1 mm. Intensity of line (I) is assessed visually on a scale of 1 to 10: 10 means the strongest line, 1 means the weakest line. The diffraction angle (θ_{Br}) can be determined using the diameter of camera (2R). Then, student determines the value of Q, hkl indices for all diffraction lines and type of Bravais lattice. Using modified quadratic lattice equation students calculate the lattice constant a_o for the cubic system

The obtained data should be placed in the following table:

Lp.	**I (1-10)**	**l**	**θ_{Br}**	**$\sin\theta_{Br}$**	**$\sin^2\theta_{Br}$**	**Q**	**hkl**	**a_o**

Projekt pn. „*Wzmocnienie potencjału dydaktycznego UMK w Toruniu w dziedzinach matematyczno-przyrodniczych*”
realizowany w ramach Poddziałania 4.1.1 Programu Operacyjnego Kapitał Ludzki

Lesson 14: Determination of the lattice constant from images obtained by rotation method

Issues to be prepared:

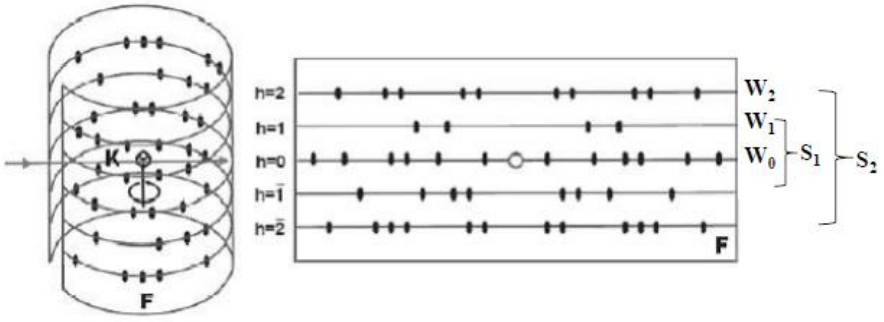
- rotation method,
- Laue equations,
- determination relation between the symmetry of the image and the symmetry of the crystal,
- calculation of the the lattice constant a_o,

Educational aids: diffraction pattern obtained by rotation method, slide caliper or ruler, calculator.

Introduction:

In the rotation method, a single crystal is mounted with an axis normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis. As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point the incident beam will be diffracted.

X-ray beams, which are diffracted at the nodes of the lattice planes, give (cylindrically surrounding single crystal) reflections laying along parallel lines on the film called layer line.



The diffraction pattern obtained by rotation method with the setting of crystallographic axis perpendicular to the incident X-rays: rolled up in a cylindrical camera and developed. K – single crystal, W_o, W_1, W_2 – layer lines, h – integer number, number of layer line, S_1, S_2 – layer line separation, which are situated symmetrically with respect to the layer line W_o.

In the rotation method, Laue equations are used for interpreting the diffraction geometry of X-ray:

Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego

$$a_0(\cos\alpha - \cos\alpha_0) = h\lambda$$
$$b_0(\cos\beta - \cos\beta_0) = k\lambda$$
$$c_0(\cos\gamma - \cos\gamma_0) = l\lambda$$

in which: a_o, b_o, c_o – axial unit; α_o, β_o, γ_o – the angles between the incident beam of rays and the corresponding crystallographic axis XYZ; h, k, l – integer numbers, indices of diffraction reflections.

The transformation of the Laue equation, allow to calculate the lattice constant a_o:

$$a_0 = h\lambda\sqrt{1+\left(\frac{2R}{S_h}\right)^2}$$

in which: λ – is the wavelength of incident wave, h – number of layer line, 2R - diameter of camera, S_h – layer line separation.

The aim of the exercise is calculation of the lattice constant a_o using the rotation method, determination of the symmetry of the image and the symmetry of the crystal.

Student receives the diffraction pattern:

- diameter of camera amounts 64mm or 57.3 mm,
- wavelength of incident wave: λ_{Cu} = 1.54178 Å or λ_{Mo} = 0,71069Å.

The layer line separation (S_h) should be measured using a slide caliper or a ruler with an accuracy of 0.02 or 0.1 mm. The lattice constant a_o can be determined with using the value of diameter of camera (2R), the layer line separation (S_h) and Laue equations. Then, student analyzes the diffraction pattern and determines the symmetry of the image and crystal.

The obtained data should be placed in the following table:

h	**S_h**	**2R/ S_h**	$\sqrt{1+\left(\frac{2R}{S_h}\right)^2}$	**a_o**

Lesson 15: Systematic absences

Issues to be prepared:

- Bravais lattice,
- translational symmetry elements,
- structure factor,
- systematic absences,

Introduction:

The **structure factor** ($\mathbf{F_{hkl}}$) is a mathematical function describing the amplitude and phase of a beam diffracted from the crystal lattice planes characterized by Miller indices hkl. The structure factor may be expressed as

$$F_{hkl} = F_{hkl}\exp(i\alpha_{hkl}) = \sum_{n=1}^{N} f_n \exp\left[2\pi i(hx_n + ky_n + lz_n)\right]$$

where the sum is over all atoms in the unit cell, x_n, y_n, z_n are the positional coordinates of the n-th atom, f_n is the atomic scattering factor of the n-th atom, and α_{hkl} is the phase of the diffracted beam.

The intensity of a diffracted beam is directly related to the amplitude of the structure factor, but the phase must normally be deduced by indirect means.

One speaks of systematic absences when the structure factor is zero, due either to the centering of the lattice or to the presence of glide or screw symmetry elements.

The systematic absences for centred lattices:

Bravais lattices	Systematic absences
P	none
A	k+l = 2n+1
B	h+l = 2n+1
C	h+k = 2n+1
I	h+k+l = 2n+1
F	k+l = 2n+1, h+l = 2n+1, h+k = 2n+1

The systematic absences for chosen symmetry elements:

Orientation	Symmetry elements	Systematic absences
any	m, 2, 3, 4, 6	none
[100]	2_1	h00; h = 2n+1
[010]	2_1	0k0; k = 2n+1
[001]	2_1	00l; l = 2n+1
(100)	b	0kl; k = 2n+1
	c	0kl; l = 2n+1
	n	0kl; k+l = 2n+1
(010)	a	h0l; h = 2n+1
	c	h0l; l = 2n+1
	n	h0l; h+l = 2n+1
(001)	a	hk0; h = 2n+1
	b	hk0; k = 2n+1
	n	hk0; h+l = 2n+1

Exercises:

Exercise 1. Derive the condition for the systematic absences for centred lattices: A, I, F.

Example:

Derive the condition for the systematic absences for centred lattices: C, I.

*Bravais lattice **C**: atoms coordinates: xyz; $^1/_2$+x, $^1/_2$+y, z, translation: (a+b)/2*

$F_{hkl} = fi\ [exp2\pi i\ (hx + ky + lz) + exp2\pi i\ (h\ (^1/_2+x) + k\ (^1/_2+y) + lz)]$

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + exp2\pi i\ (^h/_2 + {}^k/_2)]$

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + exp\pi i\ (h + k)]$

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + cos\pi\ (h + k) + isin\pi\ (h + k)]$

$h + k \in C \Rightarrow sin\ \pi\ (h+k) = 0$

- *for h + k = 2n+l* $\quad l + cos\ \pi\ (h+k) = 0 \Rightarrow F_{hkl} = 0$
- *for h + k = 2n* $\quad l + cos\ \pi\ (h+k) = 2 \Rightarrow F_{hkl} = 2\ fi\ exp2\pi\ (hx+ky+lz) = 2\ F_{hkl}(P)$

*Bravais lattice **I**: atoms coordinates: xyz; $^1/_2$+x, $^1/_2$+y, $^1/_2$+z, translation: (a+b+c)/2*

$F_{hkl} = fi\ [exp2\pi i\ (hx + ky + lz) + exp2\pi i\ (h\ (^1/_2+x) + k\ (^1/_2+y) + l\ (^1/_2+z))]$

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + exp2\pi i\ (^h/_2 + {}^k/_2 + {}^l/_2)]$

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + exp\pi i\ (h + k + l)]$

$F_{hkl} = F_{hkl}(P)\,[1 + \cos\pi\,(h + k + l)]$

- *for* $h + k + l = 2n + l \Rightarrow F_{hkl}(I) = 0$
- *for* $h + k + l = 2n \qquad F_{hkl}(I) = 2\,F_{hkl}(P)$

***Exercise* 2.** Derive the condition for the systematic absences for symmetry elements: a⊥y, n⊥z and $2_1||z$.

Example:

Derive the condition for the systematic absences for symmetry elements: c⊥y and n⊥x.

- *The glide plane* ***c*⊥*y***: *atoms coordinates: x,y,z; x,-y,* $^1/_2$*+z, translation: c/2*

$F_{hkl} = fi\,[exp2\pi i\,(hx + ky + lz) + exp2\pi i\,(hx + k\,(-y) + l\,(^1/_2 + z))]$

$F_{hkl} = fi\,exp2\pi i\,(hx + ky + lz)\,[1 + exp2\pi i\,(-2ky + {}^1/_2)]$

for any xyz consider of h0l reflections (zone of Y axis)

$F_{hkl} = fi\,exp2\pi i\,(hx + ky + lz)\,[1 + \cos\pi l]$

$F_{hkl} = 0$ *when* $\cos l\pi = -1 \Rightarrow l = 2n + 1$

$F_{hkl} \neq 0$ *when* $\cos l\pi = 1 \Rightarrow l = 2n$

- *The glide plane* ***n*⊥*x***: *atoms coordinates: x,y,z; -x,* $^1/_2$*+y,* $^1/_2$*+z, translation: (b + c)/2*

$F_{hkl} = fi\,[exp2\pi i\,(hx + ky + lz) + exp2\pi i\,(h(-x) + k\,(^1/_2 + y) + l\,(^1/_2 + z))]$

$F_{hkl} = fi\,exp2\pi i\,(hx + ky + lz)\,[1 + exp2\pi i\,(-2hx + {}^k/_2 + {}^l/_2)]$

for any xyz consider of 0kl reflections (zone of X axis)

$F_{hkl} = fi\,exp2\pi i\,(hx + ky + lz)\,[1 + \cos\pi(k + l)]$

$F_{hkl} = 0$ *when* $\cos\pi(k + l) = -1 \Rightarrow k + l = 2n + 1$

$F_{hkl} \neq 0$ *when* $\cos\pi(k + l) = 1 \Rightarrow k + l = 2n$

***Exercise* 3** Derive the condition for the systematic absences for symmetry element: $2_1||z$.

Example:

Derive the condition for the systematic absences for symmetry element: $2_1||y$.

- *The screw axis* $\boldsymbol{2_1||y}$: *atoms coordinates: x,y,z; -x,* $^1/_2$*+y,-z, translation: b/2*

$F_{hkl} = fi\,[exp2\pi i\,(hx + ky + lz) + exp2\pi i\,(h(-x) + k\,(^1/_2 + y) + l\,(-z))]$

$F_{hkl} = fi\,exp2\pi i\,(hx + ky + lz)\,[1 + exp2\pi i\,(-2hx + {}^k/_2 - 2lz)]$

for any xyz consider of 0k0 reflections (axial)

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + cos\pi k]$

$F_{hkl} = 0$ *when* $cos k\pi = -1 \Rightarrow k = 2n + 1$

$F_{hkl} \neq 0$ *when* $cos k\pi = 1 \Rightarrow k = 2n$

- *The screw axis* $\mathbf{2_1||x}$: *atoms coordinates:* $x,y,z;\ {}^{l}/_{2}+x,-y,-z$, *translation:* $a/2$

$F_{hkl} = fi\ [exp2\pi i\ (hx + ky + lz) + exp2\pi i\ (h({}^{l}/_{2}+x) + k\ (-y) + l\ (-z))]$

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + exp2\pi i\ ({}^{h}/_{2} - 2ky - 2lz)]$

for any xyz consider of h00 reflections (axial)

$F_{hkl} = fi\ exp2\pi i\ (hx + ky + lz)\ [1 + cos\pi h]$

$F_{hkl} = 0$ *when* $cos h\pi = -1 \Rightarrow h = 2n + 1$

$F_{hkl} \neq 0$ *when* $cos h\pi = 1 \Rightarrow h = 2n$

Literature:

1. Z. Bojarski, M. Gigla, K. Stróż i M. Surowiec, Krystalografia. Podręcznik wspomagany komputerowo, Wydawnictwo Naukowe PWN, Warszawa 2001.
2. Z. Kosturkiewicz, Metody krystalografii, Wydawnictwo Naukowe UAM, Poznań 2004.
3. Z. Trzaska-Durski i H. Trzaska-Durska, Podstawy krystalografii, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 2003.
4. Z. Trzaska-Durski i H. Trzaska-Durska, Podstawy krystalografii strukturalnej i rentgenowskiej, Wydawnictwo Naukowe PWN, Warszawa 1994.