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Crystallochemistry

Lecture

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Spis treści

1. Crystallography – science of ordered solids.

Crystallography is an inter-disciplinary science, originated from mineralogy. Considering the description of matter, phenomena coupled with the research, the nature of objects and problems being solved, crystallography is an interdisciplinary science located between physics (research methods), mathematics (formal description), chemistry and biology (relations between the 3D structure and properties or function of molecules and biomolecules).

Foundation of modern crystallography was laid in XVII century. One of the important bases is the law of constancy of angles formulated by Nicolas Steno, which states that angles between faces in the crystals of a given substance obtained under the same physico-chemical conditions (eg. pH, temperature, solvent) are constant. The rational basis for this law was proposed by mineralogist Rene Haüy, who hypothesized that crystals are built up with identical fragments repeated in space. Consider the growth of the crystal containing identical molecules. Due to the chemical assembly, each molecule has the preferred directions of interactions with the surrounding molecules. Energy of these interactions depends on the participating fragments (functional groups). If we let the system reach the thermodynamic equilibrium, we may expect that each molecule forms analogous interactions with the surrounding matter, and the distances between molecules in equivalent directions will be identical (**Fig. 1.1**). Three directions, corresponding to the highest energy of intermolecular interactions, might be chosen in space as the axes of the coordinate system, that will be used for a crystal description. If the surroundings of each molecule is identical, the whole crystal has a periodic structure. Unit translations along the axes (axis unit vectors) correspond to the distances between adjacent molecules. Choice of the system axes might be done based on analysis of the crystal morphology – directions corresponding to the highest energy of the inter-molecular interactions will appear in the crystal morphology as the longest edges (**Fig. 1.2**) and correspond to the highest linear density of matter. The largest faces correspond to the planes with the highest planar density, what also results from the thermodynamic optimum of interactions. If molecules reveal the symmetry of their spatial architecture, the network of their interactions might also reveal such symmetry, and would be reflected in the symmetry of the crystal.

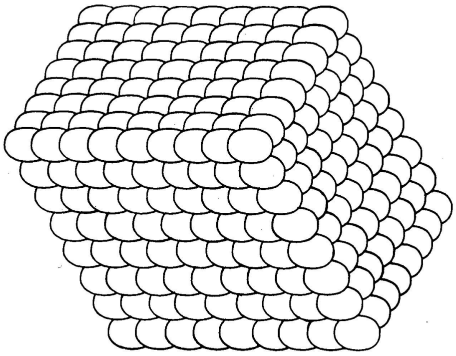


Fig. 1.1.

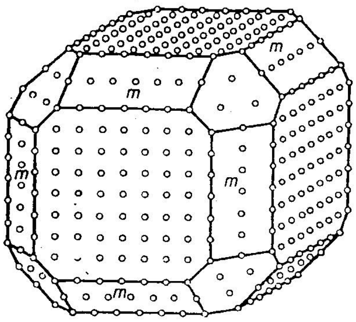


Fig. 1.2

Based on that, a **crystal** can be defined as a chemically homogeneous solid having the ordered internal structure (periodicity, symmetry of the matter distribution), in which the scalar properties are identical in all directions, while the vector properties are identical in directions parallel to each other or those related by symmetry.

Description of the crystal can be done by determination of coordinates of all atoms in the crystal. That corresponds to the **crystal lattice**. However, the description can be simplified, by substitution of molecules (eg. proteins, viruses, molecular associates) by points called nodes or **lattice points**. Such a description is much simpler, and still strictly reflects the geometrical relations between the lattice components, such as distances or the lattice symmetry. This description refers to the **lattice**.

Axes of the coordinate system are selected as three non-coplanar lines defining the right-handed trihedral. Description of coordinates axes and their unit translations are shown on **Fig. 1.3**. **Base vectors** of X, Y and Z axes are called a_0, b_0 and c_0, respectively. If one of the identical lattice points will be chosen as the system origin, the base vectors and their sum will define eight lattice points (molecule representations) in the corners of the parallelepiped. This parallelepiped is called the **unit cell** and corresponds to the basic unit of the crystal, postulated by Rene Haüy. Shape of the unit cell depends on the vectors between the lattice points. The lengths of these vectors correspond to the lengths of the unit cell edges, while the angles correspond to the angles between the coordinate system axes. The lengths of the base vectors and angles between system axes (a_0, b_0, c_0, α, β, γ) are called the **unit cell parameters (cell constants)**. The choice of the unit cell in the periodic lattice can be made in different ways (**Fig. 1.4**). Such choice has to satisfy several conditions:

- Contents of the unit cell is representative for the whole crystal
- Choice must correspond to the minimal volume of the cell, maximal number of the right angles between axes and maximal symmetry

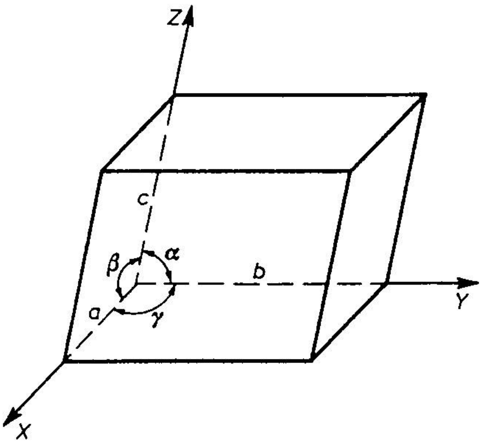


Fig. 1.3.

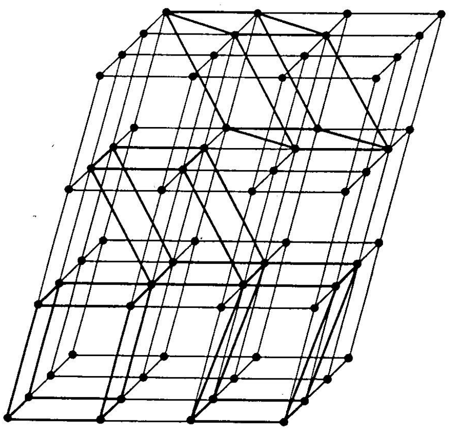


Fig. 1.4

Based on the parameters of the unit cell, all crystals belong to one out of 7 **crystal systems**:

Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	L1
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90 < \beta$	L2

Orthorhombic	a≠b≠c	α=β=γ=90		3L2
Tetragonal	a=b≠c	α=β=γ=90		L4
Trigonal	a=b=c	α=β=γ≠90	(rhombohedral)	L3
	a=b≠c	α=β=90 γ=120	(hexagonal)	
Hexagonal	a=b≠c	α=β=90 γ=120		L6
Cubic	a=b=c	α=β=γ=90		4L3

The above table also contains an information on the symmetry axes (described in the further lectures) characteristic for the given system.

Description of the whole crystal is therefore simplified to the description of a single unit cell and three base vectors a_0, b_0, c_0, the linear combination of which defines the position of other cells in the crystal lattice. That results in the necessity of using the analytical geometry or introducing the notations used by crystallography. Position of the point (e.g. the equilibrium position of atom) is defined by three fractional coordinates x y z. These coordinates are calculated as fractions of the base vectors along X Y Z axes. Therefore, position of the point can be described with the vector staring at the origin:

$$\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$$

The consequence of the above equation is that coordinates for all points belonging to the unit cell belong the range [0,1]. Coordinates of the lattice points are integers.

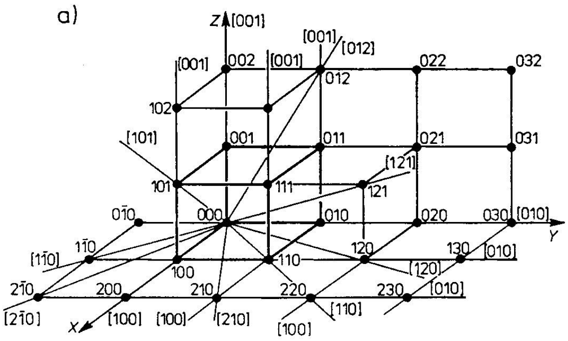


Fig. 1.5.

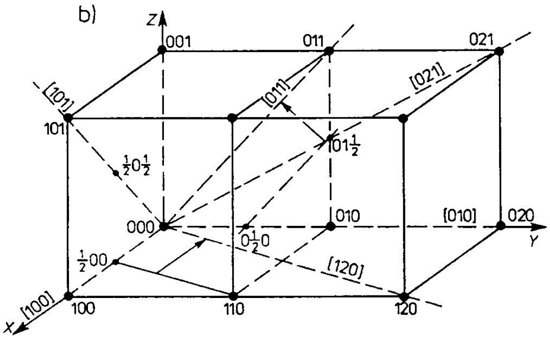


Fig. 1.6

Lattice rows (lines) and planes in the lattice are defined as sets of points (**Figs. 1.5 and 1.6**). In space, direction of the line can be defined by two points x_1 y_1 z_1 and x_2 y_2 z_2 belonging to that line. Indices in the symbol of that lattice row [uvw] can be calculated as the differences of coordinates for the pair of points [Δx Δy Δz]. For example, pair of points 112 and 223 defines the lattice row [111]. Consequently, the lines X Y and Z running through the system origin and the points at the end of each base vector a_0, b_0, c_0 have symbols X [100] Y [010] and Z [001]. Since indices uvw are also integers, the numbers resulting from the subtraction should be multiplied by the appropriate factor (**Fig. 1.6**). All parallel lattice rows in the lattice have an identical symbol [uvw], what is consistent with the crystal definition.

The planes in 3D space can be defined by coordinates of three points. To introduce the plane symbols, one should consider a pair of planes intersecting the coordinate axes at the lattice points point H K L and H_1 K_1 and L_1 (**Fig. 1.7**). Positions of points correspond to the integer multiples of unit vectors a_0, b_0, c_0. That leads to the law of rational indices: quotients of the axis sections cut by two planes are rational numbers OH/OH_1 OK/OK_1 $OL/OL_1 \in W$.

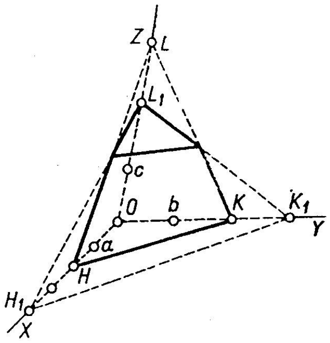


Fig. 1.7.

Based on that, English crystallographer Miller has defined the plane notation. Assuming that OH, OK. and OL sectors correspond to the unit translations $OH=a_0$, $OK.=b_0$, $OL=c_0$, the plane intersecting the axes at H, K and L might be the reference plane, and the orientation of other planes can be described relative to this plane. Converting the rational numbers into integers we obtain the **Miller indices** (hkl) for the H_1 K_1 L_1 plane:

$$h = a_0/OH_1 \quad k = b_0/OK_1 \quad l = c_0/OL_1 \qquad \text{where } h, k, l \in C$$

From the crystal definition, the parallel planes are equivalent to each other since they intersect the system axes in subsequent lattice points. Interpretation of Miller indices is shown in the following example. The unit plane intersects the axes at the ends of the unit vectors (H, K, L), defining the sectors OH=a; OK=b; OL=c. Therefore from the Miller notation for (hkl), the quotient:

$$h : k : l = a/OH_1 : b/OK_1 : c/OL_1$$
$$OH_1 = a/h \quad OK_1 = b/k \quad OL_1 = c/l$$

Therefore, the interpretation is as follows: numbers h, k and l indicate how many identical sections of a_0 b_0 and c_0 are defined by successive parallel grid planes intersecting the axes in the subsequent lattice points. For (421) plane, the lengths of the sections on the coordinate axes are

$$OH_1 = a/4; OK_1 = b/2; OL_1 = c$$

Consider the indices of planes parallel to the crystal system axes. Such planes cut off the infinite sectors on the axis. Based on the Miller definition, the index calculated for X axis is $\lim(a_0/\infty) = 0$.

Four planes (faces) in space describe in a complete way the unit cell and unequivocally determine the crystal system (**Fig. 1.8**). Three of them are defined by the pair of coordinate axes XY, XZ and YZ, while the fourth one intersects all the axes in points defining the unit vector lengths. That set of planes is called a basic tetrahedron. Three faces of that tetrahedron corresponding to the unit cell faces have symbols (100) (010) and (001), while the fourth one, defining the unit vectors has a symbol (111).

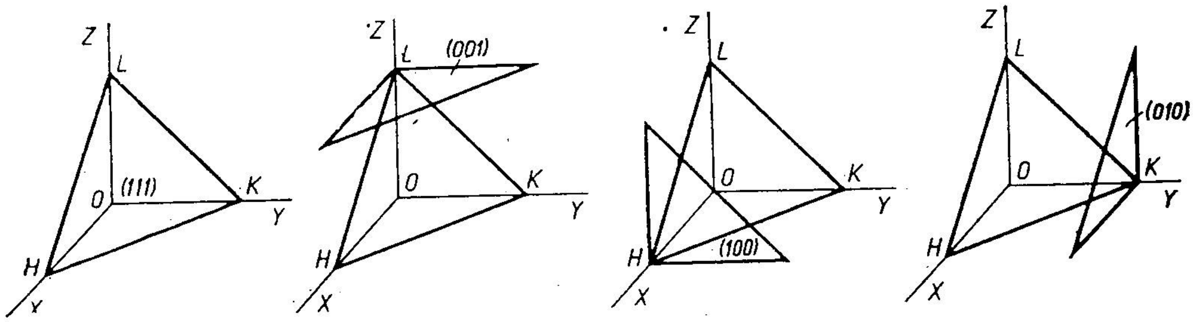


Fig. 1.8.

A face parallel to X and Y axes and intersecting Z axis at the end of c_0 has a symbol (001). Symbols of faces parallel to X,Z and Y,Z are (010) and (100), respectively.

2. Basic crystallography. Zone calculations. Bravais translational groups.

One of the important terms in crystallography is a **zone** – a set of planes parallel to the common line, called the **zone axis**. The zone equation can be derived based on the analytical geometry. Consider the plane in the 3D space as a set of xyz points satisfying the sector equation:

$$\frac{x}{a}+\frac{y}{b}+\frac{z}{c}=1$$ where a,b,c - sectors cut off on X, Y and Z axes

Translation of this plane changing the sectors by the factor d: ad, bd and cd gives:

$$\frac{x}{ad}+\frac{y}{bd}+\frac{z}{cd}=1$$ or

$$\frac{x}{a}+\frac{y}{b}+\frac{z}{c}=d$$

For a plane running through the system origin d=0. Any plane of the Miller symbol (hkl) cuts off the sectors a/h, b/k, c/l giving the equation:

$$\frac{x}{a/h}+\frac{y}{b/k}+\frac{z}{c/l}=1$$ or

$$\frac{hx}{a}+\frac{ky}{b}+\frac{lz}{c}=1$$

Introduce the zone equation. The equation of (hkl) plane running through the system origin:

$$\frac{hx}{a}+\frac{ky}{b}+\frac{lz}{c}=0$$

If (hkl) plane belongs to the [uvw] zone, one can use translations to find a line [uvw] lying in the plane (hkl). Both contain the system origin. For such a line the following proportion is true x : y : z = u : v : w. Points 000, uvw; au bv cw belong to both plane and the line. Substitution gives:

$$\frac{hua}{a}+\frac{kvb}{b}+\frac{lwc}{c}=0$$ or

hx + ky + lz = 0

The above equation is called the **zone equation**. If it is correct, the (hkl) plane and [uvw] line are parallel, therefore the plane belongs to the [uvw] zone. Other meaning is that the [uvw] line is the zone axis for the (hkl) plane. If incorrect, it means that [uvw] and (hkl) are not parallel. Lets analyze the example. Is the line [201] a zone axis for (010) plane? Calculation 2x0 + 0x1 + 1x0 = 0 confirms that thesis.

Based on the appropriate zone equation, one can calculate the general symbol of planes belonging to the zone of the X axis. Since the symbol of X axis is [100], the equation gives:

1x0 + 0xk + 0xl = 0 ⇒ symbol (0kl).

Similarly, the general symbol of the plane belonging to the Y [010] zone is (h0l), and the general symbol of the plane belonging to the Z [001] zone is (hk0). Consequently, the coordinate system axes might be defined not only by the faces of the basic tetrahedron, but also by any pair of planes belonging to the zone of the given axis.

The spatial geometry indicates that intersection of two planes unequivocally defines the line, and two lines define the plane in space. Using the crystallography terms, that conclusions can be reduced to the system of two zone equations. Lets introduce the **zone law**. The zone is a set of all planes parallel to the zone axis. Consider two planes (h_1 k_1 l_1) and (h_2 k_2 l_2) defining the zone axis and running through the origin 000:

$$\frac{h_1 x}{a} + \frac{k_1 y}{b} + \frac{l_1 z}{c} = 0 \quad /h_2 \qquad\qquad /k_2$$

$$\frac{h_2 x}{a} + \frac{k_2 y}{b} + \frac{l_2 z}{c} = 0 \quad /\text{-}h_1 \qquad\qquad /\text{-}k_1$$

After multiplying the first equation by h_2 and the second by ($-h_1$), and adding them:

$$\frac{(k_1 h_2 - k_2 h_1)y}{b} + \frac{(l_1 h_2 - l_2 h_1)z}{c} = 0$$

Similarly, multiplication of the first by k_2 and the second by ($-k_1$) and summation gives:

$$\frac{(h_1 k_2 - h_2 k_1)x}{a} + \frac{(-l_1 k_2 + l_2 k_1)z}{c} = 0$$

After conversion of both, we get:

$$\frac{(l_1 h_2 - l_2 h_1)z}{c} = \frac{(h_1 k_2 - h_2 k_1)y}{b} \qquad\qquad \frac{(h_1 k_2 - h_2 k_1)x}{a} = \frac{(l_1 k_2 - l_2 k_1)z}{c}$$

Further conversion allows to calculate the common expression depending on z/c:

$$\frac{y}{b(l_1 h_2 - l_2 h_1)} = \frac{z}{c(h_1 k_2 - h_2 k_1)} = \frac{x}{a(k_1 l_2 - k_2 l_1)} \quad \Rightarrow \quad \frac{x}{au} = \frac{y}{bv} = \frac{z}{cw}$$

In such a way we get the values u, v and w – the indices in the symbol of the zone axis defined by two planes. The quotient u:v:w can be written as the quotient of three determinants, and the formula below allow to memorize that.

$$u{:}v{:}w = \begin{vmatrix} k_1 & l_1 \\ k_2 & l_2 \end{vmatrix} : \begin{vmatrix} l_1 & h_1 \\ l_2 & h_2 \end{vmatrix} : \begin{vmatrix} h_1 & k_1 \\ h_2 & k_2 \end{vmatrix} \quad \text{or} \quad \begin{array}{c|c|c} h_1 & k_1\ l_1\ h_1\ k_1 & l_1 \\ h_2 & k_2\ l_2\ h_2\ k_2 & l_2 \\ & \mathrm{u}\ \ \mathrm{v}\ \ \mathrm{w} & \end{array}$$

Symbol of the plane belonging to zones [$u_1v_1w_1$] and [$u_2v_2w_2$] can be obtained in a similar way.

Lets go back to the node distribution in the space lattice. In the periodic lattice, molecules are positioned not only around the cell corners, but also around centers of the cell faces or the cell center. Figures **Fig. 2.1** and **Fig. 2.2** present the Pd complex molecule and the corresponding packing of the crystal lattice. It can be noticed that the pair of the complex molecules is positioned at the cell center and defines the node identical to those at the cell corners.

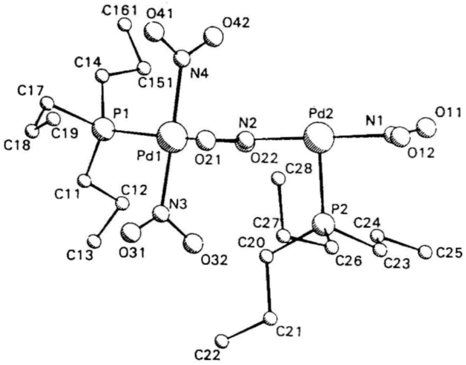


Fig. 2.1

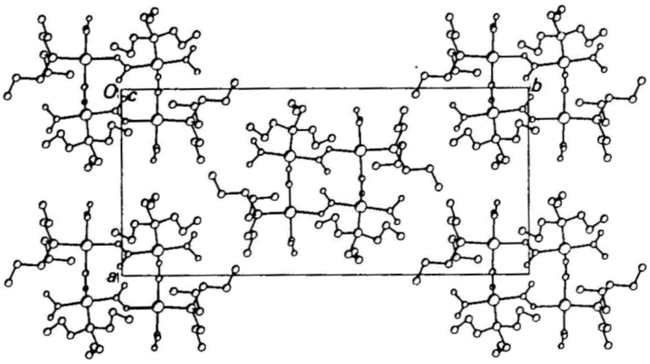


Fig. 2.2

Based on the real distribution of matter in the crystal unit cells, four basic types of the cells are defined: the primitive cell P, base-centered cell C, body-centered I and face-centered F (**Fig. 2.3**). For these cell types the node position is defined as a linear combination of the unit translations (a_0, b_0, c_0) in the P cell, with additional translations: (a+b)/2 and (a+b)/2 + c in C, (a+b+c)/2 for the I cell and (a+b)/2; (a+b)/2 + c; (a+c)/2; (a+c)/2 + b; (b+c)/2; (b+c)/2 + a in the F type cell. Only such node distribution is found in nature. Formed in such a way, 14 types of the translational lattices satisfy the definition of the translation group in space.

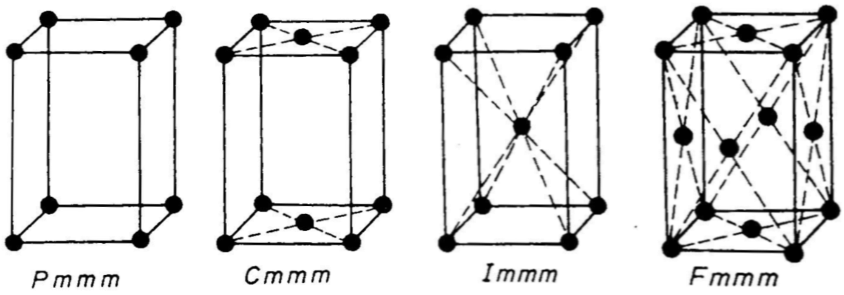


Fig. 2.3.

The translation group is a set of group elements – translations and the group rule – the translation vector summation, defined in the 3D space:

Set of translations and their summation • constitute the group G closed under the • operation, if the following axioms are satisfied:

1. For each $a,b,c \in G$ the associative condition
   $(a\bullet b)\bullet c = a\bullet(b\bullet c)$

2. Identity element. For each $a \in G$, the identity element $e \in G$ exists such that
   $a\bullet e = e\bullet a = a$

3. Invertibility. For each $a \in G$, the inverse element $a^{-1} \in G$ exists such that
   $a\bullet a^{-1} = a^{-1}\bullet a = e$

4. Closure. For each $a,b \in G$ closure exists
   $a\bullet b = b\bullet a$

The node distribution in cells affects the number of nodes (molecules) contained in the cell.

The primitive cell P has nodes only in the cell corners, so their coordinates are: 000, 100, 010, 001, 110, 101, 011, 111.

Three types of the base-centered cells are defined. The A cell has two nodes at the centers of two faces intersecting the X axis. Therefore the node coordinates are as in P type cell and additional pair 0½½ and 1½½. In the B type cell, the faces with additional nodes are those intersecting the Y axis, and their coordinates are as in the P cell plus ½0½ and ½1½. In the C cell, the additional nodes center the faces intersecting Z axis, so their coordinates are as for P cell plus ½½0 and ½½1.

In the F type cell, all faces are centered, so it is a logical sum of A, B and C cells. The node coordinates are as in the P type plus 0½½, 1½½, ½0½, ½1½, ½½0 and ½½1.

The I type cell has the nodes in corners and at the center ½½½.

In crystallography, number of nodes (molecules) in the unit cell is denoted Z. Number of nodes in the primitive cell P related by the translation group $Z = 8\bullet 1/8 = 1$

Number of nodes in the A, B or C cells: $Z = 8\bullet 1/8 + 2\bullet ½ = 2$

For the I cell, number of nodes: $Z = 8\bullet 1/8 + 1 = 2$

Number of nodes in the F cells: $Z = 8\bullet 1/8 + 3\bullet(2\bullet ½) = 4$

French mathematician Auguste Bravais has derived 14 types of the translation lattices in the 3D space, taking into account 7 crystal systems and 4 types of the cell centering. These translation lattices are listed below. Some lattices are missing due to two reasons. The first one is that it is possible to convert the hypothetical lattice into the other one, and maintain the cell parameters for the considered crystal system. The other reason is breaking the symmetry characteristic for the considered crystal system or breaking the requirements for existence of the translation group.

Possible Bravais translation groups

Triclinic	P
Monoclinic	P, C
Orthorhombic	P, A(B,C), F, I
Tetragonal	P, I
Trigonal	P, R
Hexagonal	P
Cubic	P, F, I

In the trigonal system, symbol R is used for the primitive cell with the rhombohedral coordinate axes $a=b=c$, $\alpha=\beta=\gamma\neq90$, while symbol P denotes for the hexagonal axis choice $a=b\neq c$, $\alpha=\beta=90$ $\gamma=120$ (identical to the hexagonal system).

3. Symmetry. Elements of the point groups.

Lets begin with the statistics. Considering the unit cell parameters (a, b, c, α, β, γ) all crystals can be classified into 7 crystal systems. The molecule distribution in the unit cell allows to define 4 types of the Bravais cells P, A(B,C), F and I. Possible translation cells in different crystal systems lead to 14 Bravais translation lattices. The detailed analysis of the matter distribution in the three-dimensional space results in 32 groups of symmetry, called the **point groups**. This lecture is focuses on the symmetries and their description.

The crystal morphology reveals that some crystal faces have identical shape and dimensions. Also some crystal edges have the same length. Having a set of identical faces or edges one can define the transformations relating these morphology elements to each other, and these are symmetry operations. Some examples of the symmetry axes revealed by morphology are shown on **Fig. 3.1.**

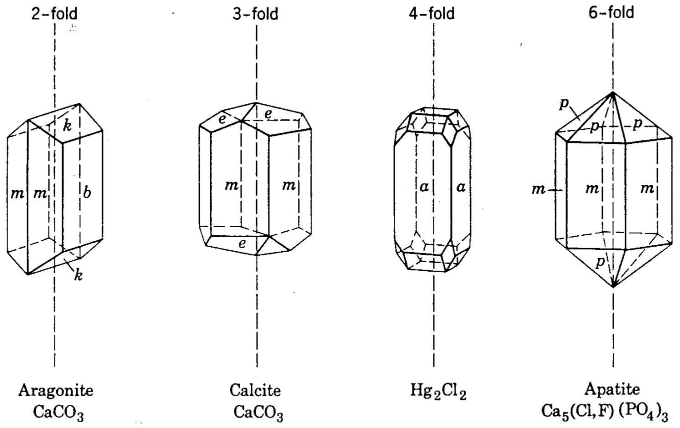


Fig. 3.1

Associating crystal faces and edges with the distribution of molecules or nodes in the crystal (**Fig. 1.1 Fig 1.2**) allows to conclude that the matter distribution in the crystal lattice has a symmetry revealed by the crystal morphology. Similar to translations, the symmetry operations are the isometric transformations – they preserve the distances. Description of symmetry **S** can be done with the matrix operators.

$$\mathbf{S} \begin{pmatrix} s11 & s12 & s13 \\ s21 & s22 & s23 \\ s31 & s32 & s33 \end{pmatrix}$$

transforming point **X** into its symmetry equivalent **X’**

The form of the matrix is easy to derive. Consider the product of matrix **S** and the column matrix describing the ends of the unit vectors a_0, b_0, c_0. For example:

$$\begin{pmatrix} s11 & s12 & s13 \\ s21 & s22 & s23 \\ s31 & s32 & s33 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} s11 \\ s21 \\ s31 \end{pmatrix} \qquad \text{and similar for points 010 and 001}$$

One should consider the symmetries relative to the point, line and plane. Each symmetry has a corresponding symmetry element – a set of points that are invariant for the given symmetry. The point reflection is called the inversion. We introduce the Groth symbolism. The Groth symbol of this symmetry is **C**. The point equivalent to **X** is **X’** positioned on the common line with **X** and the center of symmetry, opposite to **X** and equally distant from the center (**Fig. 3.2**). Therefore, the set of the invariant points has only one element – the center of symmetry. This symmetry involves 2 symmetry-equivalent points.

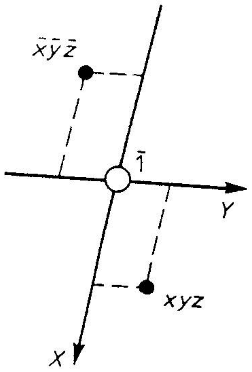


Fig. 3.2.

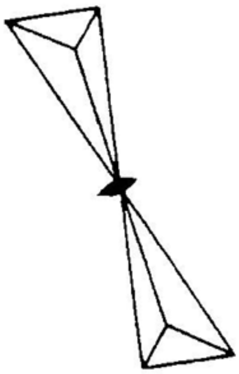


Fig 3.3

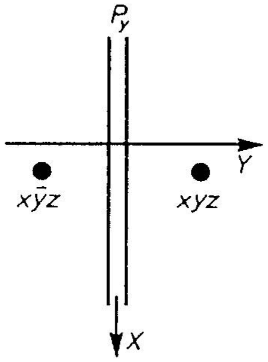


Fig. 3.4

If we assume that the system origin coincides with the center of symmetry, the inversion can be described with the equation:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

The line symmetry is the rotational symmetry (**Fig. 3.3**) which corresponds to the rotation around the two-fold axis by 180^0, and the Groth symbol is L_2. The two-fold symmetry involves 2 symmetry-equivalent points. The set of the invariant points corresponds to the rotation axis. Since this axis is a directional element, its orientation is described with the line symbol [uvw]. The matrix operators for basic two-fold axes are given below:

$$L_2[100] \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad L_2[010] \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad L_2[001] \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The plane symmetry is shown on **Fig. 3.4**. The Groth symbol is P. Since the mirror plane is also a directional element, its orientation is encoded with the Miller symbol (hkl). This symmetry involves 2 symmetry-equivalent points. Description of this symmetry with the matrix operators is given below:

$$\mathrm{P(100)}\begin{pmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}\qquad \mathrm{P(010)}\begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}\qquad \mathrm{P(001)}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{pmatrix}$$

In addition, the identity occurs, for which the Groth symbol is **E**, and the operator is as follows:

$$\mathrm{E}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}$$

Consider the rotation around the n-fold axis parallel to Z by the angle $\beta = \frac{360}{n}$. Position of point x,y can be described with the vector of the length is r and the angle α between the vector and the X axis. The rotation transforms the point x, y into its image x’, y’ (**Fig. 3.5**)

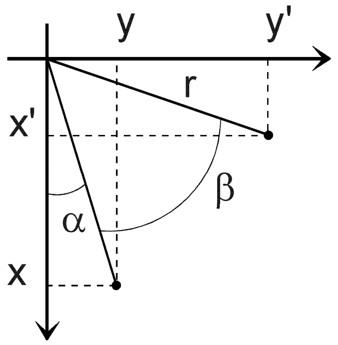


Fig. 3.5

Coordinates x,y can be expressed as a function of r and the angle α. The coordinates of the image can be expressed in a similar way. Simple transformation can relate their coordinates:

$$x = r\cos\alpha \qquad y = r\sin\alpha$$
$$x' = r\cos(\alpha+\beta) = r\cos\alpha\cos\beta - r\sin\alpha\sin\beta$$
$$y' = r\sin(\alpha+\beta) = r\sin\alpha\cos\beta + r\cos\alpha\sin\beta$$

$$x' = x\cos\beta - y\sin\beta$$
$$y' = x\sin\beta + y\cos\beta$$

Therefore, the transformation of x,y point into x’,y’ can be described with the matrix corresponding to the n-fold axis (rotation around Z, examples for the 2-fold and 4-fold axes):

$$\begin{array}{cccc} & & L_2 & L_4 \\ L_n\|z & \begin{pmatrix} \cos\beta & -\sin\beta & 0 \\ \sin\beta & \cos\beta & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

For the axes parallel to Y and X the matrices look as follows:

$$\begin{array}{cccc} L_n\|y & \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ & & & \\ L_n\|x & \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\beta & -\sin\beta \\ 0 & \sin\beta & \cos\beta \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \end{array}$$

Consider the rotation by any angle φ, but take into account the periodicity of the crystal lattice. This leads to the answer for a question of what axes of symmetry can describe the matter distribution in crystals

Consider 4 nodes N_1-N_4 (**Fig. 3.6**). The n-fold axes with the rotation angle $\varphi = 360/n^o$ (Groth symbol L_n) run through nodes N_1 and N_4. Let N_1 and N_4 be the adjacent nodes on the grid line, with the N_1-N_4 distance of a. Since nodes N_2 and N_3 result from the rotation of N_4 and N_1, the N_1-N_2 and N_4-N_3 distances also equal to a. Due to the periodicity of the crystal lattice, the distance N_2-N_3 is a integer multiple of a.

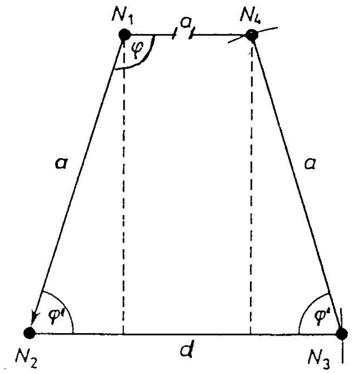


Fig. 3.6

From periodicity of the crystal lattice, $d = ma$, $m \in C$

$d = ma = a + 2a\cos(\varphi')$ /:a

$m - 1 = 2\cos(\varphi')$

$\varphi = 180 - \varphi' \Rightarrow \cos(\varphi') = -\cos(\varphi)$ Therefore:

$1 - m = 2\cos(\varphi)$

$(1-m)/2 = \cos(\varphi)$

Values of cos(φ) belong to range [-1,1]. Therefore for the subsequent integers m:

m	cos(φ)	φ	n = 360/φ	L_n
3	-1	180	2	L_2
2	-0.5	120	3	L_3
1	0	90	4	L_4
0	0.5	60	6	L_6
-1	1	0 (360)	1	L_1

The above calculation proves that in the periodic crystal lattice the only rotations allowed are those of 360/0 180, 120, 90 and 60 degrees, what corresponds to axes: 1-fold $\mathbf{L_1}$, 2-fold $\mathbf{L_2}$, 3-fold $\mathbf{L_3}$, 4-fold $\mathbf{L_4}$ and 6-fold $\mathbf{L_6}$. As can be seen, the index denotes for the axis multiplicity. It has to be emphasized, that the n-fold axis relates n symmetry-equivalent points.

Besides the rotation axes, the inversion axes exist of the general Groth symbol $\mathbf{L_{ni}}$. These transformations are products of rotation and inversion.

Calculations of the respective operator products give:

$$L_1 \bullet C = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = C$$

$$L_2[010] \bullet C = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = P_{(010)}$$

$$L_4[001] \bullet C = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} = L_{4i}$$

$$L_3[001] \bullet C = L_{3i}$$

$L_6[001] \bullet C = L_3 \bullet P_{(001)} = L_{6i}$

The above calculations allow to conclude that L_{1i} corresponds to inversion, and the inversion two-fold axis is the mirror plane perpendicular to the two-fold. Therefore there is no need to use these inversion symmetries. On the other hand, the inversion 3-fold corresponds to the product of the 3-fold axis with the center of symmetry, while the inversion 6-fold axis is a product of the 3-fold axis and the perpendicular mirror plane. Number of the symmetry-equivalent points for the inversion axes is shown on **Fig. 3.7**.

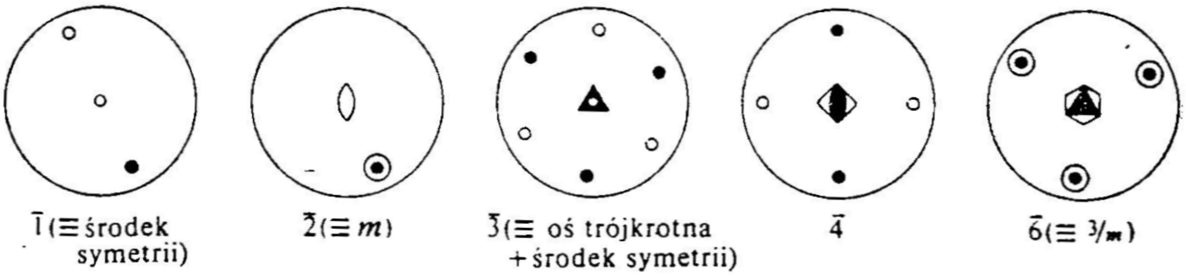


Fig. 3.7.

Black circles denote for points above the projection plane, the open circles denote for points below the plane. Depending on the fold of axis, the number of symmetry-equivalent points is 2, 2, 6, 4 and 6 for the inversion axes L_{1i}, L_{2i}, L_{3i}, L_{4i} and L_{6i}, respectively.

4. Properties of symmetry. Elements of the point groups.

In the tree-dimensional space, the symmetry (transformation) operator S can be formulated as a 3x3 matrix, in which columns describe the equivalents of a_0, b_0 and c_0 unit vectors in this symmetry:

$$\mathbf{S}\begin{pmatrix} s11 & s12 & s13 \\ s21 & s22 & s23 \\ s31 & s32 & s33 \end{pmatrix}$$

Result of several symmetries can be described as:

S1(X) = X’ and S2(X’) = X” what is equivalent to S2*S1 (X) = X”

Notation S2*S1 means the product of matrix symmetry operators describing the combination of S1 and S2 symmetries. It can easily be proven that the combination of inversion, 2-fold axis or a mirror plane with the same symmetry results in the identity:

$$C * C = L2 * L2 = P * P = E$$

So far we described the symmetry axes parallel or mirror planes perpendicular to the system X, Y or Z axes. Other orientations of the symmetry elements are also possible. Consider the 2-fold axis positioned on the diagonal between X and Y, i.e. the grid line with [110] symbol. Such symmetry converts the X axis into Y and Y into X, while Z is transformed into –Z. Symmetry $L_2[1\bar{1}0]$ can be described in a similar way:

$L_2[110]$ involves 2 points: $L_2(x,y,z) = (y,x,-z)$ Therefore matrix $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

$L_2[1\bar{1}0]$ involves points $L_2(x,y,z) = (-y,-x,-z)$ Matrix $\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

Attention has to be paid to symmetry-equivalents of vectors a_0 and b_0 in the above symmetries. Both matrices indicate that the length of both vectors must be identical. Therefore such symmetry is possible only in the systems with $a_0 = b_0$, i.e. in trigonal, tetragonal, hexagonal and cubic systems.

Combination of any two-fold axis with itself results in the identity:

$$L_2 * L_2 = E$$

Description of the mirror planes perpendicular to the system axes was given in Lecture 3. Additionally, we can analyze the mirror planes running along the diagonals between X and Y or X and –Y. The matrix description of these symmetries is given below:

P(110) (x,y,z) = (-y,-x,z) Matrix $\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

$P(1\bar{1}0)$(x,y,z) = (-y,-x,z) Matrix $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Combination of any mirror plane with the same plane also results in the identity:

P * P = E

Does a combination of the symmetry with the same symmetry always result in the identity? We have to negate that statement. Consider the unit rotations of $360/n^o$ around the n-fold axis. Matrices describing such a transformations are called generators. Lets choose the L_4 axis parallel to Z, and shown on **Fig. 4.1**.

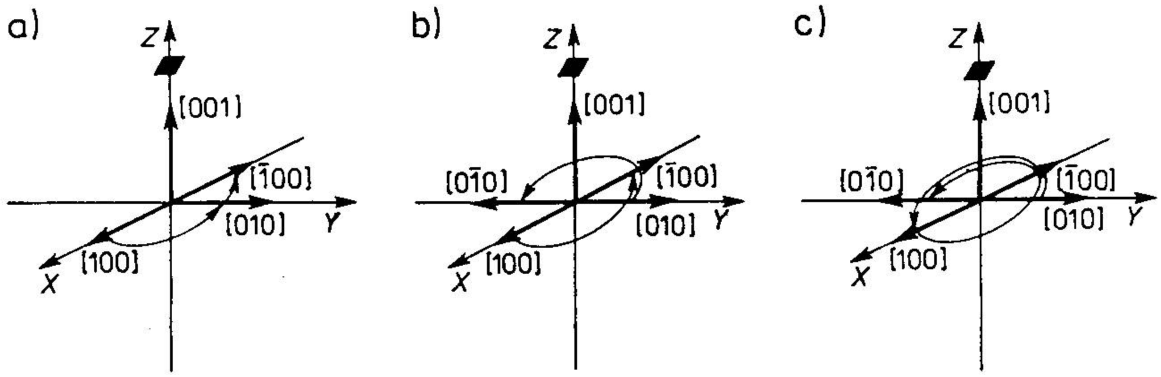


Fig. 4.1

Analysis of 90^0 rotation (**Fig. 4.1.a**) reveals the images of the transformed unit vectors and allows to find the matrix:

Axis L_4 [001] Rotation by 90^0 $\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ - Generator

Calculations performed by subsequent unit rotations give the subsequent images of the starting xyz point and correspond to rotations of 180, 270 and 360^0

$$\text{Rotation of } 180^0 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = L_2$$

$$\text{Rotation of } 270^0 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Rotation of } 360^0 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

The subsequent rotations are show on **Fig. 4.1.b** and **Fig. 4.1.c**. Notice the transformation of c_0 into the same vector. That results from the rotation around Z axis, which constitutes the set of the invariant points. That example causes the comment: rotation $(L_4)^2$ corresponds to L_2 symmetry. Generalizing, for all even L_{2n} symmetry axes, combination of n unit rotations gives the L_2 symmetry. In turn, combination of n unit rotations around L_n results in the identity.

Other generators of axes L_2, L_3, L_6 give:

$L_2 \bullet L_2 = E$
$L_3 \bullet L_3 \bullet L_3 = E$
$L_6 \bullet L_6 \bullet L_6 \bullet L_6 \bullet L_6 \bullet L_6 = E$

Every subsequent combination of the unit symmetry creates a new image of the starting point xyz. Thus, number of generated points plus the starting xyz equals the multiplicity of L_n (**Fig. 4.2**)

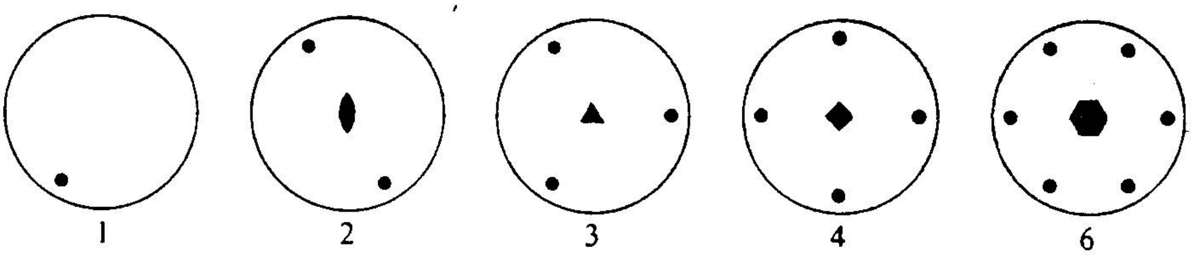


Fig. 4.2

Lets introduce the table of the group product. The first raw and first column contain the symmetries found in the space. The intersection of a raw and a column defines the result of a combination of both symmetries. If the new symmetry is found, the lists in the first raw and column has to be completed, and the whole procedure has to be repeated until the list is consistent with the table contents. In the example below we analyze the three-fold axis with the unit rotation of 120^0 (O_{120}). All the transformations related to L_3 are as follows:

O_{120}, $O_{120} \bullet O_{120} = O_{240}$ $O_{120} \bullet O_{120} \bullet O_{120} = O_{120} \bullet O_{240} = O_{360} = E$

and the table of group products for rotations around L_3 is:

	O_{120}	**O_{240}**	**$O_{360} = E$**
O_{120}	O_{240}	E	O_{120}
O_{240}	E	O_{120}	O_{240}
$O_{360} = E$	O_{120}	O_{240}	E

Constructing the table of the group products allows to obtain the sets of symmetries in space, in which the combination of any two symmetries results in the third symmetry also acting in that space. Such sets of symmetries are called groups.

In mathematics, groups are defined as sets of elements acting in a given space with the • operation defined between the group elements. In space we define the sets of symmetries described with the matrix operators and their product as the group operation. The set of symmetries and their product • constitute the closed group G if the following axioms are satisfied:

1. For all symmetries $a,b \in G$ their combination gives another symmetry c, being a group element
   $a \bullet b = c \in G$
2. For all symmetries $a,b,c \in G$ the associative condition
   $(a \bullet b) \bullet c = a \bullet (b \bullet c)$
3. Identity element. For each symmetry $a \in G$, the identity element $e \in G$ exists such that
   $a \bullet e = e \bullet a = a$
4. Invertibility. For each $a \in G$, the inverse element $a^{-1} \in G$ exists such that
   $a \bullet a^{-1} = a^{-1} \bullet a = e$
5. Closure. For all symmetries $a,b \in G$ closure exists
   $a \bullet b = b \bullet a$

Such sets of symmetries constituting the closed groups are called the point groups (classes). The point groups describe the symmetry of the limited finite space – molecule or the unit cell. Only 32 point groups exist in the E^3 space.

The table of the group products corresponds to all axioms of the closed group. Using such table one can check what transformation is an inverse to any given symmetry or find the identity element. From the table corresponding to L_3 axis, the identity element is the rotation by 360°. The inverse element for the rotation by 120° is the rotation by 240° and so on.

5. Rules for symmetry combination. Point groups of symmetry.

Lets call the definition of a group, assuming that the group elements are symmetries. We define the symmetries described with the matrix operators and their product as a group operation •. The set of symmetries and the operation • will consist the closed group if:

1. For all symmetries $a,b \in G$ their combination gives another symmetry c, being a group element
   $a \bullet b = c \in G$
2. For all symmetries $a,b,c \in G$ the associative condition
   $(a \bullet b) \bullet c = a \bullet (b \bullet c)$
3. Identity element. For each symmetry $a \in G$, the identity element $e \in G$ exists such that
   $a \bullet e = e \bullet a = a$
4. Invertibility. For each $a \in G$, the inverse element $a^{-1} \in G$ exists such that
   $a \bullet a^{-1} = a^{-1} \bullet a = e$
5. Closure. For all symmetries $a,b \in G$ closure exists
   $a \bullet b = b \bullet a$

Lets analyze few symmetries acting in the same space, what corresponds to the axiom 1 of the group of symmetries. The matrix product allows to calculate the result of the symmetry combinations. Also, one can use rules for the symmetry combinations, which give the qualitative information without necessity of any calculations. It has to be emphasized, that the rules of the symmetry combinations are the interpretation of the matrix algebra and are based on the matrix products.

Rule 1.

Lets analyze the action of L_2 axis and an inversion C. Choose axis $L_2\|_y$. Combination is described with the equation:

$$L_2\|_y \bullet C = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = P_{(010)} \perp L_2$$

The result is the mirror plane $P_{(010)}$, perpendicular to the analyzed 2-fold axis. It has to be noted, that for each even symmetry axis, the L_2 is its sub-group. Therefore, for each even rotation axis, eg. $L_4\|_z$ we have:

$$L_4\|_z \bullet L_4\|_z = L_2\|_z \qquad \text{and} \qquad L_4\|_z \bullet C = P_{(001)} \perp L_4$$

Now we calculate the results of all combinations of symmetries from the first equation:

$$P_{(010)} \bullet C = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = L_{2\|y} \perp P_{(010)}$$

$$P_{(010)} \bullet L_{2\|y} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = C$$

We can construct the table of the group products reflecting the above relations. The table below proves that the symmetries from the analyzed example constitute the closed group.

	$L_{2\|y}$	$P_{(010)}$	C	E
$L_{2\|y}$	E	C	$P_{(010)}$	$L_{2\|y}$
$P_{(010)}$	C	E	$L_{2\|y}$	$P_{(010)}$
C	$P_{(010)}$	$L_{2\|y}$	E	C
E	$L_{2\|y}$	$P_{(010)}$	C	E

The Rule 1 might be generalized: the closed group contains the even rotation axis, the perpendicular mirror plane and the center of inversion. According to equations below, the presence of two symmetries implies the presence of the third symmetry. The second equation should be interpreted as follows: combination of the mirror plane and inversion gives the 2-fold axis perpendicular to the mirror plane, but this axis might be a sub-group of the even L_{2n} axis.

- $L_{2n} \bullet C \Rightarrow P \perp L_{2n}$
- $P \bullet C \Rightarrow L_2 \perp P$
- $L_{2n} \bullet P \Rightarrow C$

Rule 2.

We analyzed the combination of the L_{2n} axis with inversion and the mirror plane perpendicular to the axis. Lets consider combination of the L_n axis with the 2-fold axis perpendicular to it. For simplicity lets choose $L_{2\|z}$ in the orthorhombic system:

$$L_{2\|z} \bullet L_{2\|y} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = L_{2\|x}$$

The result of the combination of two symmetries is yet another 2-fold axis, also perpendicular to the main $L_{2\|z}$. This rule can be generalized: combination of the n-fold axis and the 2-fold axis perpendicular to it gives n two-fold axes perpendicular to the main L_n. The appropriate table of the group products will show all relations in such a closed group. This rule has important consequences. If n two-fold axes intersect at a given point in space, this results in a presence of L_n axis perpendicular to these 2-fold axes. Also the presence of the intersecting 2-fold axes with the 180/n° angle between them results in the presence of L_n axis perpendicular to the 2-fold axes

- $L_n \bullet L_2 \perp L_n \Rightarrow nL_2 \perp L_n$
- Angle between adjacent L_2 is 180/n°
- $nL_2 \Rightarrow L_n \perp nL_2$

Rule 3.

Consider the combination of n-fold axis with the parallel mirror plane. Lets choose $L_{2||z}$.

$$L_{2||z} \bullet P_{(100)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = P_{(010)}$$

This combination gives another mirror plane parallel to the axis and perpendicular to the first plane. The group table will prove, that the closed group of symmetry can be constituted by the L_n axis and n mirror planes parallel to it, with the angle of 180/n° between adjacent planes. Presence of two planes intersecting with such angle results in the L_n axis at the line of the plane intersection.

- $L_n \bullet P|| \Rightarrow nP||L_n$
- Angle between adjacent planes is 180/n°
- $nP \Rightarrow L_n || nP$

Rule 4.

Last rule describes the combination of the even inversion L_{2ni} axis, the mirror planes and two-fold axes. The matrix products proves that the closed group of symmetry is constituted by the even inversion L_{2ni} axis, n mirror planes (inversion two-fold axes, see Lecture 3) parallel to it and n two-fold axes perpendicular to the main axis. The 2-fold axes and mirror planes are positioned in a alternating manner, and the angle between the adjacent elements is 180/2n°.

- $L_{2ni} \bullet L_2 \perp \Rightarrow nL_2 \perp L_{2ni} + nP||L_{2ni}$
  Two-fold axes and mirror planes are alternating
- $L_{2ni} \bullet P|| \Rightarrow nL_2 \perp L_{2ni} + nP||L_{2ni}$

Sets of symmetries constituting the closed groups are called point groups (classes). They describe the symmetry of the limited finite space – molecule or the unit cell. Only 32 point groups exist in the E^3 space. All these point groups can be derived using the matrix product or the rules formulated above. To do so, we have to state the assumptions that have been silently used so far. They concern the rules of choice for the origin and the system axes.

The symmetry elements corresponding to symmetries are the sets of points invariant in the given symmetry. Assume that all symmetry elements contain the origin 000. This means that for the point group acting in space, all the symmetry elements run through the origin. The origin is defined as one of points invariant in all symmetries in a given group. Since in groups containing the inversion, symmetry axes and mirror planes at least one such point exists, these groups are called the point groups. As a first rule, the X,Y and Z axes are chosen parallel to the symmetry axes. In case the number of symmetry axes is not enough, the system axes are perpendicular to the mirror planes. Finally, the system axes are selected parallel to the longest crystal edges.

Below (**Fig. 5.1**) the way to derive all 32 point groups of symmetry is shown. Procedure includes the use of the rotation axes allowed in the periodic lattice, their combination with perpendicular 2-fold axes, and mirror planes parallel or perpendicular to the main axis.

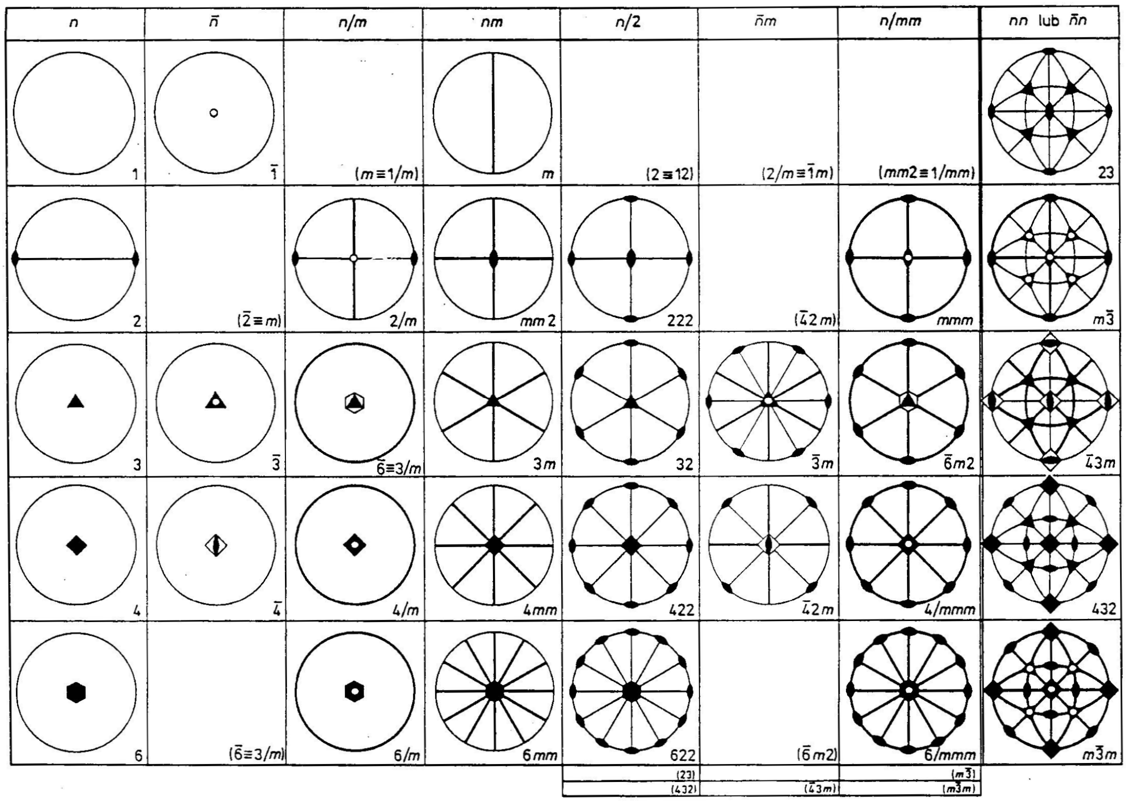


Fig. 5.1

Some graphic notations are used on **Fig. 5.1**, identical to those presented in Lecture 3. The axes of symmetry are denoted as corresponding polygons. Each cell contains the projection of the symmetry elements and the international notation of the group. Introduction of the international notation will be presented in the next lecture. However, for better understanding the figure, some elements are described here. In the international notation, the symbol of the L_n axis is n, $\bar{n}$ denotes for the inversion symmetry axis and m stands for a mirror plane.

Lets introduce two terms. The special position – position corresponding to the invariant point for a symmetry in the group, that means the point belonging to the symmetry element. The general position – position outside the symmetry elements, therefore corresponding to identity only.

6. Point groups. Symbolism.

Sets of symmetries constituting the closed groups are called the point groups of symmetry (classes). They describe the symmetry of the of the limited finite space – molecule or the unit cell. In the E^3 space, only 32 point groups exist. All these point groups can be derived using the matrix product or rules for the symmetry combination and the group product tables. Each of these point groups has its own symbol.

The **Groth symbolism** is the simplest. It is the list of all symmetries consisting the group. The Groth notation uses L_n and L_{ni} symbols for the rotation axes, P for the mirror planes, C for the inversion and E for identity.

The **international symbolism** of Hermann-Mauguin is used in crystallography. Its advantage is an ease to describe the symmetry groups containing the generalized symmetries (combined with translations), which occur in the space groups of symmetry. In the international notation, the symbol for the L_n axis is n, accounting for the fold of the rotation axis. The inversion axes are denoted $\bar{n}$, the mirror planes have the m symbol. The symbol for the point groups has several positions, and each position corresponds to the symmetry of one direction or several directions that are symmetry related. If the axis of symmetry and the mirror plane are perpendicular to each other, they describe the same direction in space, what is accounted for with both symbols separated by slash and occurring at the same position.

	Groth symbol	International symbol
Identity E	L_1	1
Inversion	C	$\bar{1}$
Mirror plane	P	m
n-fold axis	L_n	n
n-fold inversion axis	L_{ni}	$\bar{n}$

The international symbolism is used in the crystallographic or chemical literature, where the crystal data are reported. Therefore, it is important to understand its system-specific rules.

1. Triclinic system. The cell parameters are to $a_0 \neq b_0 \neq c_0$ and $\alpha \neq \beta \neq \gamma$. Since the angles might have any value, no directional symmetry elements occur in this system. However, the identity and inversion (1-fold inversion axis) can act in such space. Therefore, only two point groups can be defined. The international symbol has only one position, and contains an information on the presence or lack of the symmetry center:
   1; $\bar{1}$.

2. Monoclinic system: $a_0 \neq b_0 \neq c_0$ and $\alpha = \gamma = 90^o < \beta$. Besides E and C, the $L_{2\parallel y}$, $P_{\perp y}$ or both symmetries might act in such space, and their matrix product results in the presence of the inversion. That gives three possible point groups. The international symbol has only one position, describing the symmetry of Y direction [010]:

2, m, 2/m

3. Orthorhombic system: $a_0 \neq b_0 \neq c_0$ and $\alpha=\beta=\gamma=90^o$. Each of the axis direction is similar to the monoclinic Y – it is perpendicular to the remaining two axes. Therefore, all these directions can reveal the $L_{2\parallel}$ or $P_{\perp}$ symmetry. Since three directions might have different symmetry, the international symbol consists of three positions, reflecting the symmetry of [100], [010], [001, respectively. The matrix products prove only three point groups:

222, mm2 and 2/m2/m2/m.

The comment is necessary. In the mm2 group, the direction of the 2-fold axis defines the Z axis. In the third group, the 2-fold axes are parallel to X,Y,Z with three mirror planes perpendicular to them, what results in the presence of inversion. According to the rules of symmetry combination for the even rotation axes with the perpendicular mirror planes, to define this group, three mirror planes perpendicular to each other fully define such group. For that, the short symbol mmm is frequently used in the literature.

4. Tetragonal system: $a=b \neq c$; $\alpha=\beta=\gamma=90^o$. Consistently with the system name, the 4-fold axis of symmetry is the leading transformation. The unit cell shape indicates that L_4 or L_{4i} are parallel to the Z axis, X and Y can reveal $L_{2\perp z}$ or $P_{\parallel z}$ symmetry. However, the group product tables indicate that the number of such L_2 or mirror planes has to be equal to 4. Therefore the international symbol has three positions, describing the symmetry of Z, X and Y, [110] and $[\bar{1}10]$. Please, note that X and Y, but also [110] and $[\bar{1}10]$, are related by 90^o rotation around Z. Therefore, these pairs of directions are described in the same position. Considering all symmetry combinations leads to 5 point groups with L_4 and two with the L_{4i} axes:

4; 4/m; 422; 4mm; 4/m2/m2/m; $\bar{4}$; $\bar{4}2m$

The short symbol for group 4/m2/m2/m is 4/mmm.

5. Cubic system: $a=b=c$ $\alpha=\beta=\gamma=90^o$. Each coordinate axis is similar to the tetragonal Z axis and might reveal the L_4 symmetry. Due to identical X,Y,Z, all symmetry groups contain 4 L_3 axes on the cell space diagonals (4 directions [111] and equivalent). Additionally, for each of X,Y,Z direction, one has to account for 4 perpendicular directions having L_2 or P symmetry, as was done for the tetragonal system. The resulting international symbol has three positions, describing symmetry of X,Y,Z, [111] and equivalents, and [110] and equivalents. The first position corresponds to the symmetry of the unit cell edges (3x), the second one to the space diagonals (4x), while the third position to the cell face diagonals (6x). Possible groups:

23; 2/m3; 432; 4/m32/m; $\bar{4}3m$.

Short symbols for groups 2/m3 and 4/m32/m are m3 and m3m, respectively.

6. Trigonal system with the hexagonal coordinate axes $a=b \neq c$ $\alpha=\beta= 90^o$ $\gamma=120^o$ or rhombohedral axes $a=b=c$; $\alpha=\beta=\gamma \neq 90^o$. The system name indicates the leading symmetry of tree-fold along Z axis (hexagonal choice) or along the cell space diagonal (rhombohedral coordinate system). Symbol has two positions: symmetry of Z, and symmetry of X,Y,U perpendicular to Z (hexagonal), or space diagonal (rhombohedral choice) and 3 perpendicular directions. Point groups based on L_3 lub L_{3i}:

3; 32; 3m; $\bar{3}$; $\bar{3}2/m$

For $\bar{3}2/m$ the short symbol is $\bar{3}m$.

7. Hexagonal system: $a=b\neq c$ $\alpha=\beta= 90^o$ $\gamma=120^o$. The system name contains the information about the leading axial symmetry: L_6 or L_{6i}. Consistently with the cell geometry, such symmetry axes can reflect the symmetry of Z axis. Three directions perpendicular to Z and intersecting each other with the angle of 120^o, possessing the symmetry of 2-fold axis or the mirror plane, are chosen as X,Y,U axes, while at diagonals between them additional three exist (consistent with the rules of symmetry combination between L_n and 2-fold axes perpendicular to it). Therefore, the international symbol has three positions. First position reflects the symmetry of Z axis, the second one corresponds to the symmetry of X,Y,U and the third position describes the symmetry of diagonals between X,Y,U. The possible point groups:

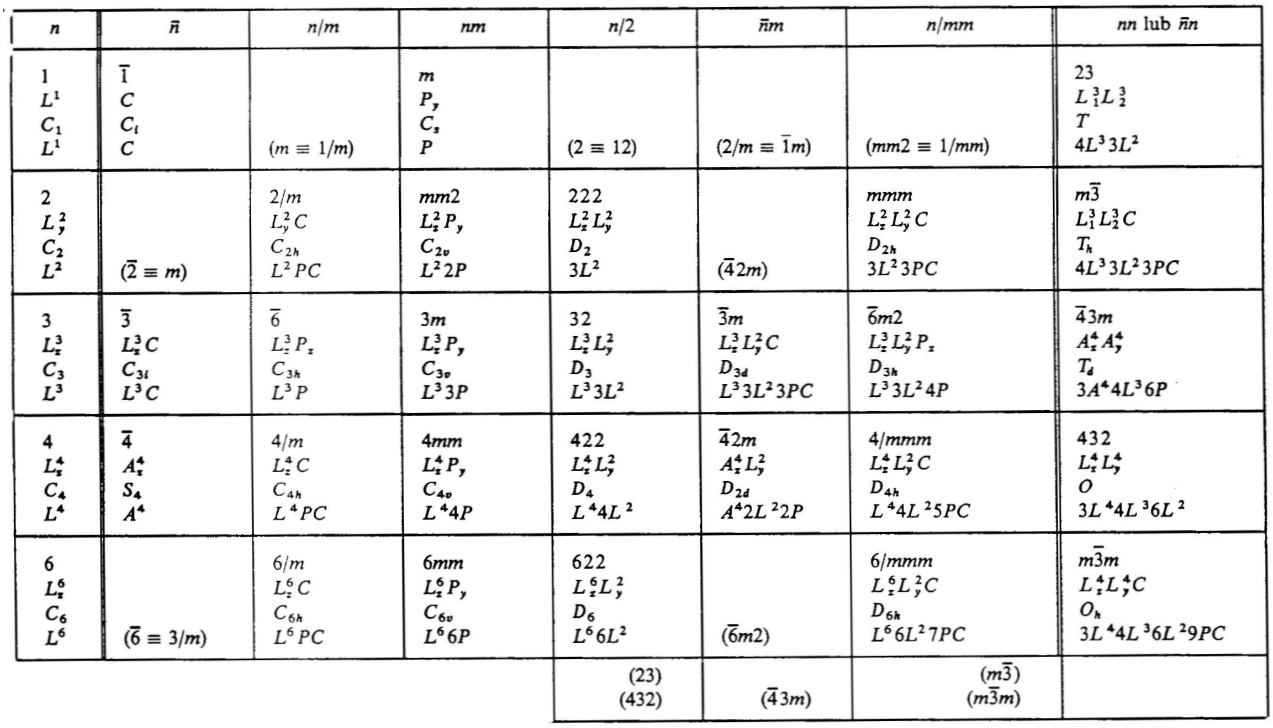
6; 6/m; 622; 6mm; 6/m2/m2/m; $\bar{6}$; $\bar{6}2m$

For group 6/m2/m2/m the short symbol is 6/mmm.

Theoretical chemistry and spectroscopy use the **Schoenflis symbolism**. Basis for this notation is the symmetry axis of the highest fold, and the fundamental assumption is that this axis is vertical. The group containing identity and the n-fold axis L_n is C_n. For the inversion axis L_{ni}, the symbol jest C_{ni} is used. The mirror planes are described by letters in the lower index, which reflect the orientation of the plane relative to the leading axis. The mirror plane perpendicular to this axis (horizontal) is indicated by h, plane parallel is v (vertical) or d (diagonal). The set of the symmetry axes $L_n + nL_2$ is described with the symbol D_n. The special symbols used for the groups with the inversion or a single mirror plane are C_i and C_s. Symbols for the point groups in the cubic system (containing four 3-fold axes) are T, T_h, T_d, O, O_h, for the tetrahedral and octahedral system of symmetry axes (T and O, respectively). These rules are shown in the table below.

1.	L_n	C_n
2.	L_{ni}	C_{ni}
3.	$L_n + n\,L_{2\perp}$	D_n
4.	$L_n + n\,P_{\parallel}$	C_{nv}
5.	$L_n + P_{\perp}$	C_{nh}
6.	$L_n + n\,L_{2\perp} + P_{\perp} + n\,P_{\parallel}$	D_{nh}
7.	P	C_s
8.	L_{1i}	C_i
9.	$3L_2 + 4L_3$	T
10.	$3L_2 + 4L_3 + 3P + C$	T_h
11.	$3L_4 + 4L_3 + 6L_2$	O
12.	$3L_4 + 4L_3 + 6L_2$ $9P + C$	O_h
13.	$3L_{4i} + 4L_3 + 6P$	O_d

The international, Groth and Schoenflis notations for all 32 point groups of symmetry occurring in the 3D space is shown on **Fig. 6.1**. This figure corresponds to **Fig. 5.1** of the previous lecture.



n	$\bar{n}$	n/m	nm	$n/2$	$\bar{n}m$	n/mm	nn lub $\bar{n}n$
1 L^1 C_1 L^1	$\bar{1}$ C C_i C	$(m \equiv 1/m)$	m P_y C_s P	$(2 \equiv 12)$	$(2/m \equiv \bar{1}m)$	$(mm2 \equiv 1/mm)$	23 $L_1^3 L_2^3$ T $4L^3 3L^2$
2 L_y^2 C_2 L^2	$(\bar{2} \equiv m)$	$2/m$ $L_y^2 C$ C_{2h} $L^2 PC$	$mm2$ $L_z^2 P_y$ C_{2v} $L^2 2P$	222 $L_z^2 L_y^2$ D_2 $3L^2$	$(\bar{4}2m)$	mmm $L_z^2 L_y^2 C$ D_{2h} $3L^2 3PC$	$m\bar{3}$ $L_1^3 L_2^3 C$ T_h $4L^3 3L^2 3PC$
3 L_z^3 C_3 L^3	$\bar{3}$ $L_z^3 C$ C_{3i} $L^3 C$	$\bar{6}$ $L_z^3 P_z$ C_{3h} $L^3 P$	$3m$ $L_z^3 P_y$ C_{3v} $L^3 3P$	32 $L_z^3 L_y^2$ D_3 $L^3 3L^2$	$\bar{3}m$ $L_z^3 L_y^2 C$ D_{3d} $L^3 3L^2 3PC$	$\bar{6}m2$ $L_z^3 L_y^2 P_z$ D_{3h} $L^3 3L^2 4P$	$\bar{4}3m$ $A_z^4 A_y^4$ T_d $3A^4 4L^3 6P$
4 L_z^4 C_4 L^4	$\bar{4}$ A_z^4 S_4 A^4	$4/m$ $L_z^4 C$ C_{4h} $L^4 PC$	$4mm$ $L_z^4 P_y$ C_{4v} $L^4 4P$	422 $L_z^4 L_y^2$ D_4 $L^4 4L^2$	$\bar{4}2m$ $A_z^4 L_y^2$ D_{2d} $A^4 2L^2 2P$	$4/mmm$ $L_z^4 L_y^2 C$ D_{4h} $L^4 4L^2 5PC$	432 $L_z^4 L_y^4$ O $3L^4 4L^3 6L^2$
6 L_z^6 C_6 L^6	$(\bar{6} \equiv 3/m)$	$6/m$ $L_z^6 C$ C_{6h} $L^6 PC$	$6mm$ $L_z^6 P_y$ C_{6v} $L^6 6P$	622 $L_z^6 L_y^2$ D_6 $L^6 6L^2$	$(\bar{6}m2)$	$6/mmm$ $L_z^6 L_y^2 C$ D_{6h} $L^6 6L^2 7PC$	$m\bar{3}m$ $L_z^4 L_y^4 C$ O_h $3L^4 4L^3 6L^2 9PC$
				(23) (432)	$(\bar{4}3m)$	$(m\bar{3})$ $(m\bar{3}m)$	

Fig. 6.1

Knowledge on rules of these symbolisms, in particular the international symbols used in crystallography, is important for understanding the literature reports and the structural data included in many papers or in the Cambridge Structural Database (CSD).

It has to be reminded, that all symmetry elements in the point groups run through the system origin at 000. Consider the 222 group. Since there are three positions in the symbol and only 2-fold axes of symmetry, that symbol corresponds to the group from the orthorhombic system. Therefore, the subsequent positions in the symbol describe the symmetry of X,Y and Z of the coordinate system. The set of the invariant points in this group can be specified. The X axis is a set of {x00} points, Y and Z are sets of {0y0} and {00z}, respectively. Each point of such coordinates has the 2-fold axis symmetry. One point exists, which satisfies all the conditions specified above – it is 000. That point always has the highest symmetry possible in a given point group – here the 222 symmetry. The position in space, having a non-identity symmetry defined in a given group is called the **special position**. Consequently, any other point with coordinates xyz different from these mentioned above has only the identity symmetry 1 (E). Such positions are called **general positions**.

7. Point groups of symmetry. The symmetry-equivalent points.

Isometries such as rotation axes, mirror planes and inversion, which preserve the distances, are the elements of the point groups. Transformations corresponding to these symmetry elements are described with 3x3 matrices. Such formalism is used for calculating the coordinates of the symmetry-equivalent points (related by symmetry) according to the equation:

$$\begin{pmatrix} s11 & s12 & s13 \\ s21 & s22 & s23 \\ s31 & s32 & s33 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

It has to be reminded, that the symmetries acting in the crystal can be recognized by analysis of the crystal morphology – the external shape of the crystal (Fig. 3.1 Lecture 3). Crystal faces related by the symmetry have identical shape and size. Look closer to that statement. In 3D space, plane (hkl) is defined by three points of the coordinate axes intersection: H[a_o/h,0,0], K[0,b_o/k,0] and L[0,0,c_o/l] or the equivalent vector **H**[h,k,l]. Symmetry S transforms these points into other, symmetry-equivalent points according to equation: **H’**[h’,k’,l’] = S**H**.

$$h' = \begin{pmatrix} s_{11} \\ s_{21} \\ s_{31} \end{pmatrix} \mathbf{H} \qquad k' = \begin{pmatrix} s_{12} \\ s_{22} \\ s_{32} \end{pmatrix} \mathbf{H} \qquad l' = \begin{pmatrix} s_{13} \\ s_{23} \\ s_{33} \end{pmatrix} \mathbf{H}$$

Calculation of Miller indices of the plane resulting from the (hkl) transformation is show below.

Plane (hkl) has its equivalent in the transformation $L_4 \| z$ $\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

h’= 0h + 1k + 0l = k
k’= -1h + 0k + 0l = -h
l = 0h + 0k + 1l =l

Faces (hkl) (k,-h,l) are related by symmetry, symmetry-equivalent, and they belong to the same form. In crystallography, **form** is defined as the set of planes (faces) related by all symmetries in the given symmetry group.

Consequently, the simpler equation can be given to shorten the calculations:

$$\begin{pmatrix} s11 & s12 & s13 \\ s21 & s22 & s23 \\ s31 & s32 & s33 \end{pmatrix} \begin{pmatrix} h \\ h \\ l \end{pmatrix} = \begin{pmatrix} h' \\ k' \\ l' \end{pmatrix}$$

The same matrix of the axis of symmetry relates planes (hkl) and (k,-h,l), or atoms (points) x,y,z and y,-x,z. Back to **Fig. 5.1** one can see that in many point groups there are number of transformations generating the symmetry-equivalent points. The question raises – how many such points are in each point group.

To answer his question, we have to analyze the number of symmetry-equivalent points for single symmetries. Below, these numbers are given for all symmetries occurring in the point groups. Number of the symmetry-equivalent points (Polish: lprs) includes the starting xyz point and all its images in a given symmetry.

1. Identity E(x,y,z) = (x,y,z)
   Number of the symmetry-equivalent points: 1
2. Inversion C(x,y,z) = (-x,-y,-z)
   Number of the symmetry-equivalent points: 2
3. Two-fold axis eg. $L_{2[100]}$ (x,y,z) = (x,-y,-z)
   Number of the symmetry-equivalent points: 2
4. Mirror plane eg. $P_{(100)}$ (x,y,z) = (-x,y,z)
   Number of the symmetry-equivalent points: 2
5. The n-fold symmetry axes
   $(L_2)^2 = E$ Number of the symmetry-equivalent points: 2
   $(L_3)^3 = E$ Number of the symmetry-equivalent points: 3
   $(L_4)^4 = E$ Number of the symmetry-equivalent points: 4
   $(L_6)^6 = E$ Number of the symmetry-equivalent points: 6
6. Inversion axes – combination of the n-fold symmetry axes and inversion
   $L_{1i} = C$ Number of the symmetry-equivalent points: 2
   $L_{2i} = P$ Number of the symmetry-equivalent points: 2
   $L_{3i} = L_3C$ Number of the symmetry-equivalent points: 6
   L_{4i} Number of the symmetry-equivalent points: 4
   $L_{6i} = L_3P$ Number of the symmetry-equivalent points: 6

Knowing the action of a single symmetry, one can analyze the point groups. Consider the group 2 (C_2). The only non-identity isometry is the 2-fold axis, which has 2 symmetry-equivalent points. However, adding other symmetries will complicate the case. In group 2/m (C_{2h}) there is an axis L_2 [010], inversion C and a mirror plane P(010) perpendicular to L_2.

Combination of symmetries increases the number of the symmetry-equivalent points. According to the rules, $L_2 * C = P$ or $P * C = L_2$ or $L_2 * P = C$. Lets search for all points that are symmetry-equivalent to xyz. The dependencies are shown on the scheme below.

$$\begin{tikzcd}
x,y,z \arrow[r, "C"] \arrow[d, "L2"'] \arrow[dr, phantom, "P"] & -x,-y,-z \arrow[d, "L2"] \\
-x,y,-z \arrow[r, "C"] & x,-y,z
\end{tikzcd}$$

Transformations in rows correspond to the images related by inversion C. Transformations in columns correspond to the 2-fold axis. Points on the diagonals are related by the mirror plane. However, number of the symmetry-equivalent points is 4 and not 8, as might be expected considering the product of the number of points related by each symmetry in the 2/m group. What is the reason for that? The first combination rule states that the presence of two symmetries results in the presence of the third in the above example. Therefore, only two symmetries are independent, while the third one results from their combination. Number of symmetry-equivalent points can be calculated by multiplying the numbers for the independent symmetries in a given group, and matrix calculations or the combination rules define the dependent symmetries. In the analyzed group:

lprs = 2 x 2 =4.

The asymmetric part of the space is defined as the reciprocal of the number of the symmetry-equivalent points. For the analyzed group, the asymmetric part is 1/4.

In the 422 group, the axis L_4[001] has 4 symmetry-equivalent points, and each of 4 axes L_2 has two symmetry-related points. However, number of the symmetry-related points lprs = 4 x 2 = 8, according to the combination rule ($L_4 \bullet L_2 \Rightarrow 4L_2$).

In group 4/m 3 2/m of the cubic system, the list of symmetries includes 3 L_4, 4 L_3, 6 L_2, 9P and C. However, according to the combination rules for the symmetry axes, parallel planes and the inversion, the independent symmetry elements are a single 4-fold axis, one 3-fold axis, one 2-fold axis and the inversion. Therefore, the number of symmetry-equivalent points is 48.

lprs = 4 x 3 x 2 x 2 = 48

It has to be emphasized, that this is the way of calculating the number of points in general positions. For the special positions, some symmetries might transform the certain point into the same point. The point in the special position, as belonging to the symmetry element, is invariant in the corresponding transformation. Therefore in such case, the number of the symmetry-related points is less than lprs by the factor related to the given symmetry element. For example, in 422 group and a point positioned on the 4-fold axis, number of points related by the group symmetry is 4 x 2 / 4 = 2. For a point on the 3-fold axis in the analyzed group 4/m 3 2/m it is 4 x 3 x 2 x 2 / 3 = 16.

Lets summarize the properties of the point groups.

1. Point groups describe the symmetry of the finite closed space: molecules or a single unit cell.
2. Symmetries relative to the point, line and plane and the group operation satisfies the axioms (associative condition, identity element, invertibility, closure) giving the closed groups.

3. All symmetry elements intersect at least in one point. Consequently at least one point exists that is invariant for all symmetries in the given point group (a point and its image are identical).
4. One of the invariant points for all symmetries defines the system origin 000. In the centrosymmetric groups the origin coincides with the center of symmetry.
5. Special positions – points belonging to the symmetry element corresponding to the symmetry in the given group – the invariant point of this symmetry.
6. General position – points are not invariant for any symmetry in the group – have only C_1 symmetry.
7. The symmetry-equivalent points – point xyz and all its images in all group symmetries.
8. For a description of the whole structure, the description of the asymmetric part (asymmetric unit ASU) is required (one plane from the {hkl} form in a given group, atoms giving all other as the symmetry related images) and the transformations in a given group with their matrix operators.
9. Number of the symmetry-equivalent points is calculated as the product of number of points associated with the independent symmetries in a group, those generating all other symmetries according to the combination rules.

Understanding of rules in the point groups, in particular the possible special positions, allows to hypothesize on the possible molecular architecture. The molecular symmetry corresponds to the symmetry of the point group, or its point sub-group. Analyze few examples.

Complex [$NiCl_2$ $(NH_3)_2$] reveals symmetry $\bar{1}$.

Inversion acts in this group with 2 symmetry-equivalent points. If one knows the unit cell volume, determination of the crystal density allows to calculate the number of molecules in the unit cell. Density is defined as the quotient of mass and volume, and mass of the cell depends on the molecular mass M of the compound and a number of molecules in the unit cell Z:

$$d = \frac{m}{V} = \frac{1.6604ZM}{V} \Rightarrow Z = \frac{1.6604M}{dV}$$

Number 1.6604 is a gram equivalent of the molecular mass unit if the cell volume is given in $Å^3$, what is allowed for the scientific literature, although it is not in the SI system. Lets consider several cases of the calculated Z value:

Z=1 Molecular symmetry $\bar{1}$ with Ni ion at 000. Since only Ni ion is in the molecule, it has to be an invariant point for inversion. The molecular symmetry might be respected only for the trans isomer with the square-planar architecture of the coordination sphere. The center of symmetry excludes the complexes with the tetrahedral architecture. With such molecular symmetry, both Ni-Cl bond lengths are identical and the Cl-Ni-Cl angle is 180^o. The same concerns the Ni-N(imidazole) bonds.

Z=2 Molecular symmetry 1. All atoms, including Ni, are in the general positions, so the molecular architecture is arbitrary.

If the calculated Z value is 4, the asymmetric unit ASU contains 2 complex molecules. Other Z values correspond to the combination of molecules of C_i and C_1 symmetry.

Crystal of difluormethane CH_2F_2 reveals symmetry 2.

This is the monoclinic group with a single L_2 axis, so 2 symmetry-equivalent points exist. The determined crystal density corresponds to Z=2 or Z=1. The molecular symmetry:

Z = 2. Symmetry L_1 – this is the general position

Z = 1. Symmetry of L_2 axis. Since only one carbon atom is in the molecule, it has to be the invariant point, positioned on the 2-fold symmetry axis. Since in the monoclinic system this axis direction is [010] and it runs through the system origin, the C atom coordinates are 0y0. The 2-fold axis runs through the diagonal of H-C-H and F-C-F angles.

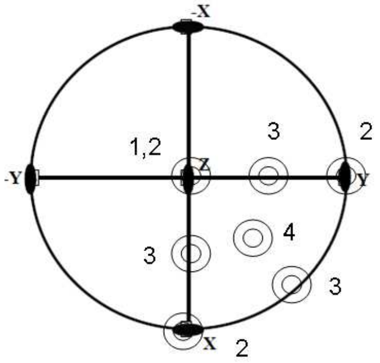


Fig. 7.1

Consider a more complicated example. Crystal containing water molecules crystallize in the mmm group. What is the molecular architecture?

In the orthorhombic group mmm, with the full symbol 2/m 2/m 2/m, the symmetries are: $3L_2$, 3P, C. As in all point groups, the symmetry elements intersect in a common point, which is the system origin (**Fig. 7.1**).

Several special positions and general position exist in this group. The possible positions corresponding to the points shown on **Fig. 7.1** reveal different symmetry:

- Point 1: molecule is positioned around 000. Such molecule has the mmm symmetry. Calculations would prove that each symmetry relates this point to the same point, what means that in this group a number of points (molecules) with the mmm symmetry in the unit cell Z=1.

- Points 2: molecule is positioned on one of the 2-fold axes. However, that means the mm2 symmetry, since molecule must have the symmetry of two perpendicular mirror planes intersecting along this L_2 axis. The special position of such symmetry corresponds to coordinates x00, 0y0 or 00z. It can be shown that for all these positions, the number of the symmetry-equivalent points in the unit cell Z=2.

- Points 3: the special position on the mirror planes, but not the 2-fold axes. That corresponds to coordinates 0yz ($P\perp X$), x0z ($P\perp Y$) or xy0 ($P\perp Z$). The point symmetry is m, and only for this symmetry this point is invariant. For all these possible positions, the number of symmetry-related points is Z=4.

- Point 4: the general position with no local symmetry, therefore corresponding to L_1 symmetry. Number of the symmetry-equivalent points in the unit cell Z=8.

Number of the symmetry-equivalent points (in the general position) can be calculated as a product of lprs for the independent symmetries. In the analyzed group these are three out of 7 symmetries { 3L2, 3P, C }. Therefore for this group, lprs = 2 x 2 x 2 = 8. The asymmetric unit ASU is defined by the independent symmetries and be calculated as the reciprocal of the number of symmetry-equivalent points. Determination of the crystal density would allow to calculate the number of molecules in the unit cell giving Z=8, Z=4, Z=2 or Z=1. What are the consequences for the water architecture?

Z=8. Molecule in the general position – we do not know its position, and the molecule cannot reveal the non-identity symmetry. (Point 4 **Fig. 7.1**)

Z=4. Molecule in the special position. The quotient Z/lprs = 4/8 results in half of the molecule in ASU. Considering all possibilities in the mmm group, molecule can reveal only the m symmetry. Therefore the coordinates for the oxygen atom are O[0,y,z] or O[x,0,z] or O[x,y,0] (Point 3 **Fig. 7.1**). There might be two orientations of the molecule relative to the mirror plane. The first one: all atoms are positioned on the plane, and are invariant in this symmetry. No symmetry relates the positions of H atoms, and two O-H bonds are different. Second: the mirror plane is perpendicular to the plane defined by the water molecule and runs through the diagonal of H-O-H angle. Position of oxygen atom is invariant in this mirror plane symmetry. However, two H atoms are related by the mirror plane, so both O-H bonds are identical. The question raises if both these possibilities might occur simultaneously? That is exactly the next point.

Z=2. The special position with the symmetry of two perpendicular mirror planes, the combination of which results in the L_2 symmetry – symmetry mm2. The oxygen atom coordinates O[x,0,0] O[0,y,0] or[0,0,z], and is invariant in all these symmetries. However, the H atoms are positioned only in one mirror plane consistent with the molecule plane. Their coordinates are related by the other symmetries of the sub-group i.e. H1 [0yz] and H2 [0,-y,z].

Z=1. The special position around 000 origin – symmetry mmm, therefore including the inversion. There is only one O atom in the molecule, so O[0,0,0] would be possible. However, the H-O-H valence angle is not 180^o, what excludes the inversion symmetry for water molecule. This position is not allowed, until there is a statistical disorder of the water position.

Such analysis can be performed for all groups of symmetry. If the quotient Z/lprs is 1 or other natural number, the molecule is in the general position. In such case, the atomic positions and the molecular symmetry cannot be determined for the investigated crystal. If the density determination gives the number of molecules Z smaller that lprs, that results in the special position and consequently the internal symmetry of the molecule. Then, having the possible symmetry for the special positions, one can count the atoms of all elements and consider if they must be the invariant points in the symmetries, as was done in the examples above, or have to be related by the symmetries, as carbon atoms in the benzene molecule of the L_6 symmetry.

8. Translation symmetry elements. Space groups.

Symmetries constituting the point groups were described with the matrix operator 3x3:

$$\mathbf{X' = S \bullet X} \qquad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{pmatrix} \bullet \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Real crystals are the periodic objects, with the translational repetition of the unit cell. Therefore, to describe the matter distribution in the whole crystal, one has to account for translations. One element of such description is the cell centering and the Bravais translation lattices (Lecture 2). However, there are also other translations associated with the translation symmetry elements, which are the generalization of the symmetry elements discussed previously. The translation symmetry elements correspond to the transformation composed of the symmetry and translation by a fractional vector parallel to the symmetry element. Two kinds of such symmetries are defined – the screw axes and the glide planes.

The matrix operators for such symmetries (transformations) in the space groups can be given as a combination of symmetry S and translation T:

$$\mathbf{X' = S \bullet X + T} \qquad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{pmatrix} \bullet \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} t_x \\ t_y \\ t_x \end{pmatrix}$$

For convenient multiplication of such operators and formulation of the symmetry groups, these transformations are described with the 4x4 operator S’. The 3x3 block corresponds to the symmetry component, the last column contains the components of the translation vector, and the matrix is completed with the fourth row in order to define the 4x4 matrix:

$$\mathbf{X' = S' \bullet X} \qquad \mathbf{S'=} \begin{pmatrix} s_{11} & s_{12} & s_{13} & t_x \\ s_{21} & s_{22} & s_{23} & t_y \\ s_{31} & s_{32} & s_{33} & t_z \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Based on the definition of translation symmetry, the translation vector is parallel to the symmetry component of the translation symmetry element. Therefore, the translation equivalent of the inversion is not defined – there is no translation vector parallel to the point.

Lets introduce the international symbolism used for the translation symmetry elements and corresponding transformations. The translational equivalents of the symmetry axes L_n are the screw axes. The screw axes n_m are defined as a combination of the rotation of $360^0/n$ and translation by the vector m/n of the unit lattice translation along the symmetry axis, with m defined by the lower index.

For example, symbol 6_5[001] corresponds to the rotation of 60^0 combined with the translation of 5/6 c_0. In the monoclinic system the 2_1 axis is a combination of the 180^o rotation around Y and translation of $b_o/2$ vector. If the 3_1[111] axis is considered in the cubic system, it means the rotation of 120^0 combined with the translation of $1/3(a_0 + b_0 + c_0)$. Such translation results from the unit lattice translation linking two closest points on the grid line - 000 and 111 on the cell space diagonal. Notice that m is the natural number and its value ranges from 1 to n-1. If m=0, the translation of the zero vector combines with rotation, and the transformation is a normal rotation. Value m=n corresponds to the unit lattice translation to the equivalent point in the adjacent cell, what also corresponds in the periodic crystal lattice to the normal rotation axis.

The glide planes are described with the letter symbols. Planes a, b and c correspond to the combination of the mirror plane symmetry with the translation of a/2, b/2 or c/2 vector parallel to the mirror plane. Planes n are the combinations of the mirror planes and translations of (a+b)/2, (b+c)/2, (a+c)/2 or (a+b+c)/2 vector. Planes called d are the combinations of the mirror planes and translations of a+b)/4, (b+c)/4, (a+c)/4 or sometimes (a+b+c)/4.

Lets analyze the action of the screw axes. **Fig. 8.1** shows the comparison of axes 2 and 2_1. For axis 2, rotation of point a_1 by 180^0 results in point a_2, which in turn is transformed back to a_1. These two points are symmetry equivalent. The unit lattice translation **t** gives the images of these points in subsequent cells (a_3 and a_4, a_5 and a_6) also related by the 2-fold axis. Look at the screw axis 2_1. Point a_1 is transformed into a_2 after the rotation coupled with the translation of 1/2**t**. That point in turn is transformed into a_3, shifted by t/2 relative to a_2 and by **t** relative to a_1. Such transformation is an open transformation – we cannot get the starting point a_1 as a result of its subsequent transformations by 2_1 axis. The reason for that is a non-zero translation coupling with the rotation axis. The other consequence of the action of such elements is a formation of additional layers of nodes (molecules) of the coordinates 0, 1/2, 1/, 3/2 and so on when compared to the layers with coordinates 0, 1, 2 and so on for the normal rotation axes. It has to be stated that for both 2 and 2_1 the direction of rotation is not important. Both right-handed and left-handed rotations give the identical matter distribution

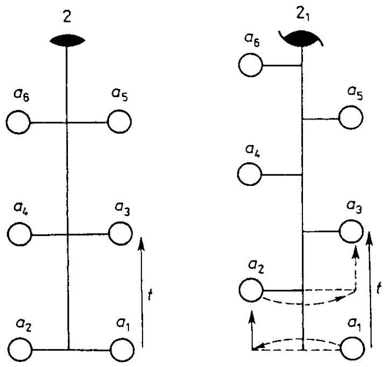


Fig. 8.1

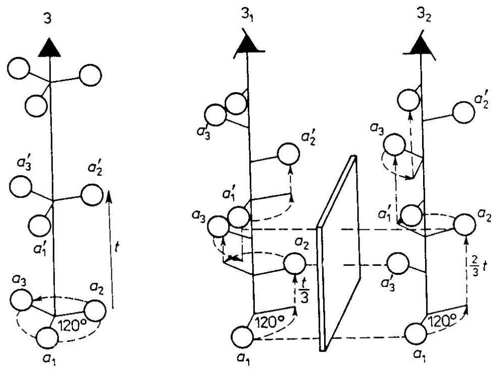


Fig. 8.2

There is also another important difference between these transformations. Consider the matrices describing both these symmetries, choosing the [010] direction of the rotation axis. Lets assume both axis run through the system origin.

$$2[010]\begin{pmatrix}-1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 1\end{pmatrix} \quad \text{and} \quad 2_1[010]\begin{pmatrix}-1 & 0 & 0 & 0\\ 0 & 1 & 0 & 1/2\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 1\end{pmatrix}$$

The simple calculation allows to determine the coordinates of the xyz image in both transformations. These points are –x,y,-z and –x,½+y,-z, respectively. Lets transform the 0y0 point positioned on the rotation axis. Its image in the 2 symmetry is the same point –invariant for this symmetry. Calculation for the 2_1 axis gives the coordinates 0,1/2+y,0. This result can be generalized for all screw axes – such symmetries do not have the invariant points, even if the points are positioned on the rotation axis. Therefore, the screw axes cannot reflect the molecule symmetry.

Consider the screw axes related to L_3 as shown on **Fig. 8.2**. The normal 3-fold axis has three symmetry-equivalent points in the cell, forming the layer analogous to those in the 2 axis, while the other layers are shifted by the unit translation **t** or its integer multiple. Contrary, the 3_1 axis with the marked rotation direction of the high-handed (clockwise) rotation forms 3 layers of the symmetry related points in the cell, with coordinates z, 1/3+z and 2/3+z. The other equivalent layers correspond to the shifts by the integer multiple of **t**. The right-handed 3_2 axis results in layers of the coordinates z, 2/3+z, 4/3+z and so on. Since the unit translations **t** act in the crystal lattice, the latter one has its equivalent at coordinate z+4/3-3/3 being 1/3+z. The careful analysis of the figure indicates that this axis can be in fact the left-handed 3_1 axis, since its matter distribution is identical to that of the right-handed 3_2 axis. Therefore, it is enough to use only the right-handed axes. The other consequence – the right-handed 3_1 axis and left-handed 3_1 (being right-handed 3_2) are enantiomorphs. The pairs of the enantiomorphic screw axes consist of n_m and n_{n-m} axes. Therefore, such pairs are 3_1 and 3_2, 4_1 and 4_3, 6_1 and 6_5, 6_2 and 6_4. Axes 2_1, 4_2 or 6_3 are enantiomorphic to themselves – for these axes the rotation direction is not important since the matter distribution would be identical.

Similarly, the glide planes do not have the invariant points and cannot reflect the molecule symmetry. Comparison of the sets of the symmetry-equivalent points for the m mirror plane and the glide plane (**Fig. 8.3**) indicates that the latter forms the additional node layers separated by t/2.

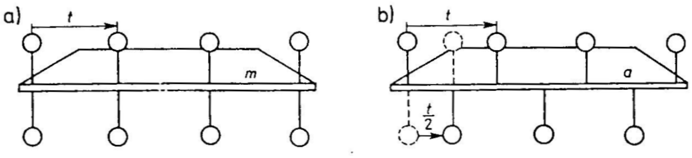


Fig. 8.3

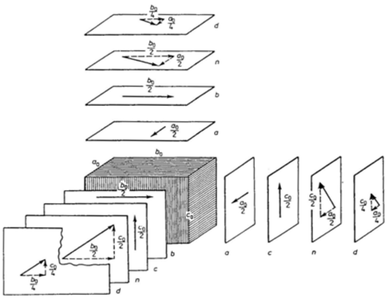


Fig. 8.4

Presence of glide planes in different orientations is illustrated on **Fig. 8.4**. If we consider the glide planes perpendicular to XYZ axes of the coordinate system, the limitation is the required for translation parallel to the symmetry plane. The glide plane perpendicular to X has the (100) symbol. According to definition, the translation vector must be parallel to this plane, so its fractional components must be parallel to Y or Z. Therefore, the possible (100) glide planes can be b, c, n($\frac{b+c}{2}$) or d ($\frac{b+c}{4}$). For (010) glide planes perpendicular to the Y axis, the possible planes are a, c, n($\frac{a+c}{2}$) and d ($\frac{a+c}{4}$). Analogously, for the (001) orientation excluding the z component of the translation vector, the possible glide planes are a, b, n and d.

The symmetry groups, **space groups**, can be formulated from these generalized symmetries. The complete list o the group elements can be obtained by applying all the axioms in the definition of the closed group and the matrix algebra (or the combination rules). The combination rules are identical with those introduced for the point groups. Also the number of symmetry-equivalent points for the translation symmetries is the same as for the non-translation symmetries.

The international symbol of the space groups consists of two elements: the symbol of the Bravais cell and the symmetry (translation or non-translation). Rules of the international symbolism are the same as for the point groups. Number of the symmetry-equivalent points is calculated as for the point groups, taking into account the independent symmetries. The multiplier associated with the number of the translation-equivalent points in the Bravais group has to be used. For the P, A(B,C) I and F it is 1, 2, 2 and 4, respectively, and is equal to the number of nodes within the cell of the given type. Two examples illustrate the space group specificity.

Consider the space group P2_1/c. Symbol P denotes for the primitive cell. The group belongs to the monoclinic system, what becomes obvious after skipping all the translations in the symbol, not used in the point group symbol. The associated point group is 2/m. Therefore, the orientation of the symmetry elements is as follows: axis 2_1||y has a symbol [010], the plane c || x,z has a Miller symbol (010). The respective translations are 1/2 b_0 for 2_1 and 1/2 c_0 for the plane c. The combination rules suggest that the result of the symmetry combination is the inversion. Position of the inversion center can be determined by the matrix product: $2_1 \bullet c = P'$:

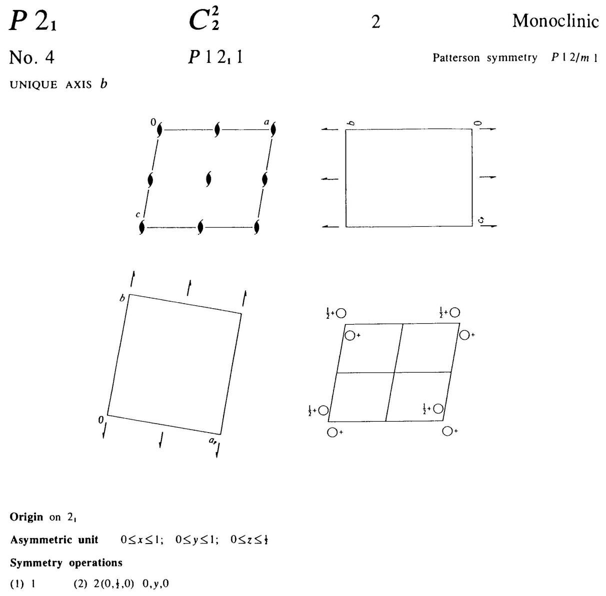
$$P' = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \bullet \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & -\frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Interpretation is as follows: P’ is the inversion center C. The fourth column corresponds to the translation T[0,1/2,-1/2]. This translation is divided into components parallel to the generated symmetry element and others. In our case, for the inversion center the whole translation is not parallel. Half of this translation is related to the position of the generated element - it corresponds to the shift from the point or line of intersection of the combined symmetries to the final position. In this example T = T||[0,0,0] + T⊥[0,1/2,-1/2], and the inversion center is at point [0,1/4,-1/4].

Another example allows to answer the question what results from the combination of the symmetries. Consider the group Pna2? The question mark reflects the ambiguity – axis 2 or 2_1. Omitting the translations make the interpretation straightforward – the associated point group is mm2 and belong to the orthorhombic system. Therefore the n plane is perpendicular to X, has a (100) symbol and translation $\frac{b+c}{2}$. The a plane is perpendicular to Y, the Miller symbol is (010) and the translation is $\frac{a}{2}$. The matrix product gives:

$$P' = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix} \bullet \begin{pmatrix} 1 & 0 & 0 & \frac{1}{2} \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & -\frac{1}{2} \\ 0 & -1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Interpretation: the resulting symmetry is the axis L_2||z + T||[0,0,1/2] + T⊥[-1/2,1/2,0]. The parallel component of the translation is $\frac{c}{2}$ what corresponds to the 2_1 axis. The space group is Pna2_1. This axis is shifted by 1/2 T⊥[-1/2,1/2,0] so by [-1/4,1/4,0] relative to the line of the planes intersection. If the z component of translation would be zero or other integer, the resulting element would be a normal 2 axis. Such analysis can be performed for all 230 space groups giving the spatial positions of the symmetry elements, sets of the invariant points and positions of the symmetry-equivalent points. Results of such analysis are published in the crystallographic literature, in particular in the *International Tables for X-ray Crystallography*, a fragment is shown on **Fig.8.5**.



$P\,2_1$ C_2^2 2 Monoclinic

No. 4 $P\,1\,2_1\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS *b*

Origin on 2_1

Asymmetric unit $0 \leq x \leq 1$; $0 \leq y \leq 1$; $0 \leq z \leq \frac{1}{2}$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)$ $0,y,0$

Fig.8.5

9. Diffraction of X-rays. The powder method.

Chemists face the question what is the substance they deal with. It can be answered by the elemental analysis and spectroscopic methods. Frequently there is a need to determine the molecular geometry or the network of intermolecular interactions. This is a domain of crystallography.

Analysis of the crystal morphology, spatial relations between identical faces or edges, reveals the symmetry and allows to assign the point group. The helpful tools are the stereographic projection with its ability to measure angles and determine zones, rules of the group symbolism, as well as the matrix algebra or equivalent rules of symmetry combinations.

Symmetry of the crystal lattice is a translation symmetry (screw axes, glide planes) and the Bravais translation groups. Here again the rules of symmetry combinations and relations between the point groups and the space groups are necessary. However, the geometric crystallography lacks the tool to determine which symmetry from the morphology corresponds to the translation symmetry in the crystal space. To analyze the molecule geometry and intermolecular interactions, one needs the crystal lattice geometry, including the unit cell constants and cell volume, and positions of molecules. Also for that, the rules for the choice of the coordinate axes are needed, combination of symmetries and determination of the crystal density. The key role is played by the X-ray crystallography, which allows to determine the cell parameters, as well as the space group from so called systematic absences.

The X-rays can be generated in several ways. In the laboratory, the simple way is to use the X-ray tubes. The electric potential is applied between the tube anode and cathode. The electrons pulled out from cathode are accelerated and collide with the anode atoms, resulting in knock out of electron from the anode atom inner shell. In this process, the rule of the energy conservation can be written:

$$E_{el} = E_1 + E_2 + h\nu$$

Energy of the incident electron equals the energy after collision (E_1, E_2) and its excess is released as the radiation photons. If the appropriate potential difference is used, the lamp generates the X-rays. This radiation has enough energy for atom excitation. This process results in a continuous X-ray spectrum. Subsequently, the vacancies in the atom electronic shell are filled by the spontaneous transfer of electrons from the outer shells. This process is accompanied by emission of the radiation of the energy corresponding to the energy difference between shells, what is characteristic for the anode material. In this way the spectrum characteristic for the anode elements is generated. The obtained X-rays directed towards the crystal have the appropriate energy and interact with crystal atoms by interacting with their electrons and causing internal transfers between the excited and basic states. The spectrum of X-rays generated in the tube is the superposition of the continuous spectrum and characteristic emission lines corresponding to K, L, M series (Lyman, Balmer and other) . (**Fig. 9.1**). This radiation can be monochromatized in several ways. The simplest method is to run the beam through a metal foil prepared from the metal differing by 1 atomic number from the anode material. In this case the maximum absorption occurs between the characteristic lines, decreasing also the intensity in the range of the continuous spectrum. The X-rays of the wavelength λ 0.5 - 2.5Å, comparable with the inter-atomic distances, are diffracted on the crystal and are useful in the crystallographic research. Depending on the method, the used radiation is monochromatic or has the continuous spectrum.

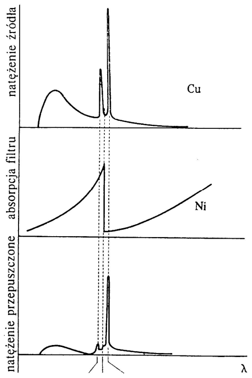


Fig. 9.1.

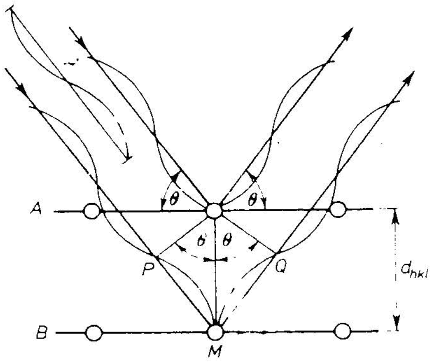


Fig. 9.2

The incident beam is reflected on the crystal and the resulting beams interfere with each other. This phenomenon can be described using the reflection formalism of Bragg or the diffraction formalism of Laue. Lets use the former one.

The monochromatic beam is directed towards the set of parallel (hkl) lattice grid planes distant by d_{hkl} and interacts with atoms of the molecules represented by the grid points (**Fig. 9.2)**. Both the incidence and the reflection angles for the beam equal θ. The interference with the amplification occurs if the difference of the optical way Δ for the parallel beams equals the integer multiple of the used wavelength λ. That can be formulated as the **Bragg law**:

$$\Delta = 2\,PM = n\lambda = 2d_{hkl}\sin\theta \quad \text{or} \quad \frac{d}{n} = \frac{\lambda}{2\sin\theta}$$

The integer n is the reflection order. Angle θ, at which the amplified beam is observed (equal to the incidence angle), is called the Bragg angle. The Bragg law relates the crystal lattice geometry, described with the inter-planar spacing d_{hkl}, with the corresponding Bragg angles, descriptors of the diffraction pattern geometry. The equation also indicates that for the (hkl) family of parallel planes and a given wavelength λ, the series of reflected beams is observed corresponding to the subsequent integers n (**Fig. 9.3**). The equation independent from n is obtained by transforming the Bragg equation to the form containing the d_{hkl}/n ratio.

In the diffraction experiment, when the reflection angles are measured and the known wavelength λ is used, the ratios d_{hkl}/n can be calculated. For the known inter-planar spacing d_{hkl} and wavelength λ, the geometry of the diffraction pattern θ for the crystal can be calculated.

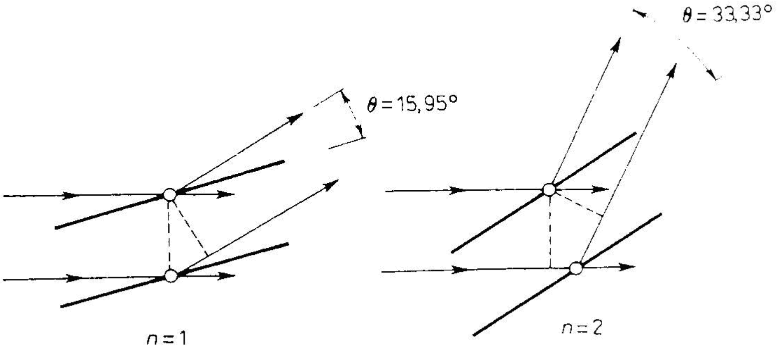


Fig. 9.3

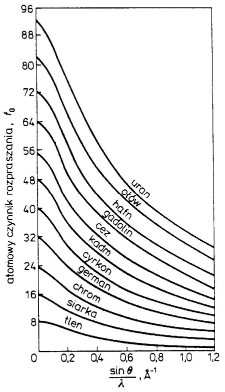


Fig. 9.4

Consider the intensity of beams diffracted by crystals. X-rays interact with the atom electrons. The ability of the electron to interact with X-rays can be formulated as the electron scattering power. Since the effect is additive, the power of interaction of each atom is a sum over all its electrons. Therefore the atomic scattering factor f_i is introduced, which is identical for all atoms of a given element and proportional to the atomic number Z_i. The atomic scattering factor f_i is given:

$f_i = f_0 \exp(-K\sin^2\theta/\lambda^2)$ where
f_0 – atomic scattering factor for a non-oscillating atom
K – temperature factor, depends on the amplitude of oscillations around the equilibrium position
λ – radiation wavelength
θ – incident angle, angle for the observed reflected beam

Fig. 9.4 presents a plot of the f_0 dependence on the quotient sinθ/λ. The atomic scattering factor f_0 is proportional to the atomic number of the element, so different curves do not intersect. The decrease in the scattering factor depends exponentially on sinθ, therefore for high reflection angles the light atoms (C, H) have a minor contribution. If atoms have a large oscillation amplitude or large K, as for molecular fragments of large conformational flexibility or revealing a disordered in the crystal lattice, their contribution decreases comparing to atoms of small dynamics in the lattice. The effect of the wavelength is also important. The atom ability to interact with the radiation is larger for the longer wavelengths. In practice, the most frequently used radiation is Cu λ = 1.54178 Å and Mo λ = 0.71073 Å. For crystals containing only light atoms, the copper radiation is more useful.

Intensity I_{hkl} of the beam diffracted by the (hkl) plane family of the crystal depends on the structure factors F_{hkl}, which can be calculated as a sum of contributions of all atoms in the structure:

$$I_{hkl} \sim F_{hkl} = \sum_{i=1}^{N} f_i \ \exp 2\pi i(hx_i + ky_i + lz_i)$$

F	structure factor, ~ $\sqrt{I_{hkl}}$
fi	atom scattering factor
h,k,l	Miller indices of the reflecting plane I_{hkl}
x,y,z	coordinates of the i-th atom in the unit cell

Expression for the structure factor indicates that F_{hkl} (and intensity I_{hkl}) of the diffracted beam depends on the kind of atom (f_i) and its position (xyz) or the matter distribution in the crystal lattice. Geometry of the diffraction pattern described with the Bragg law depends on the cell parameters (d_{hkl}, a,b,c,α,β,γ), which in turn are related to the sizes of atoms and molecules constituting the crystal lattice and interactions between them. Therefore, the diffraction pattern obtained in the experiment and interpreted in means of $\{I_{hkl}, \theta_{hkl}\}$ pairs is a basis for the substance identification – the diffraction pattern is characteristic for the crystal of a given compound.

The simplest method for the diffraction experiment is the powder method of Debye-Scherrer-Hull (DSH). In this method, the monochromatic beam is diffracted by the crystalline powder sample, containing a large number of randomly oriented small single crystals. The sample is rotated to make the lattice planes reach the θ angle satisfying the Bragg law (**Fig. 9.5**). The pattern can be recorded in the cylindrical camera.

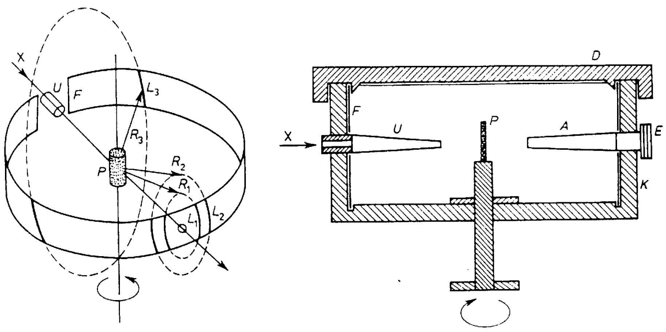


Fig. 9.5

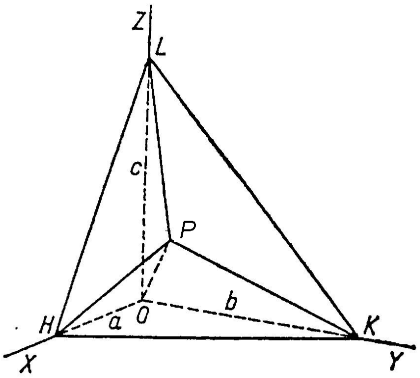


Fig. 9.6

The beams are diffracted with the Bragg angles, so are distributed on the side surfaces of the co-axial diffraction cones with the beam angle $2\theta_{hkl}$ to the incident beam and the cone angle $4\theta_{hkl}$. The axis of all cones is the incident beam. The measured distances between the diffraction rings (lines) allow to calculate the Bragg angles. The powder diffractometers record the diffractograms $I = I(\theta)$.

Beams recorded for Bragg angles should be related to the (hkl) reflecting planes, what means the indexing of the pattern lines with hkl. For that the quadratic form has to be used. The adjacent planes (hkl) run through points H=a/h, K = b/k, L = c/l and the system origin 000 (**Fig. 9.6**). Lets draw the OP line perpendicular to the (hkl) planes and running through the system origin.

For each axis the expression can be formulated $\cos \delta_X = OP/OH = d_{hkl}/(a/h)$

For the orthogonal systems (normal equation of a plane) $\cos^2\delta x + \cos^2\delta y + \cos^2\delta z = 1$
Combining these equations gives the quadratic form:

$$1/d^2_{hkl} = h^2/a^2 + k^2/b^2 + l^2/c^2$$

For the tetragonal system a=b $1/d^2_{hkl} = (h^2+k^2)/a^2 + l^2/c^2$

For the cubic system $a=b=c$ $1/d^2_{hkl} = (h^2+k^2+l^2)/a^2$

Summarizing, the Bragg equation relates geometry of the lattice d_{hkl} with the diffraction geometry θ_{hkl}. The inter-planar distances depend on the cell constants a,b,c and Miller indices h,k,l (quadratic form). In turn, cell parameters depend on the size of atoms and molecules.

Indexing is based on the Bragg equation and the quadratic form. Lets use the simplest form for the cubic system. The Bragg equation will be used in a form independent from the reflection order $d' = d/n$.

$$n\lambda = 2d_{hkl}\sin\theta; d_{hkl}/n = d' \Rightarrow 1/d' = 2\sin\theta/\lambda$$

$$1/d'^2_{hkl} = (h^2+k^2+l^2)/a^2 = Q/a^2$$
$$1/d'^2_{hkl} = (h^2+k^2+l^2)/a^2 = 4\sin^2\theta/\lambda^2$$

For all beams (reflections) $\sin^2\theta = \lambda^2 Q/4a^2 = kQ$ where k=const for the experiment

$$\sin^2\theta_i/Q_i = \lambda^2/4a^2 = \text{const}; Q_i \in N$$

For the beam of the smallest θ angle, Q will be the smallest. The diffraction experiment gives θ_i and one can find numbers Q_i giving in the constant values of quotients $\sin^2\theta_i/Q_i$. Some Q values are forbidden (see below). In such case, different Q has to be assigned to the beam of the smallest angle

$Q = 1 \Rightarrow hkl = 100$ or 010 or 001	the same form in the cubic system
$Q = 2 \Rightarrow hkl = 110$	
$Q = 3 \Rightarrow hkl = 111$	
$Q = 7 \Rightarrow hkl = ???$	also Q = 15, 23, 28, 31...
$Q = 9 \Rightarrow hkl = 300$ or 221	that is the reflection superposition!

Knowing the reflection indices, one can analyze the diffraction pattern symmetry. Besides periodicity, the crystal lattice reveals the symmetry. Consider the diffraction from two symmetry related planes. Lets assume the symmetry is the $L_2[010]$ axis. Two planes (hkl) and (-hk-l) are symmetry related, therefore the plane spacing d_{hkl} and d_{-hk-l} are equal. The Bragg law indicates that the Bragg angles for both plane families are identical:

$$2\sin\theta / \lambda = d'_{hkl} = d'_{-hk-l} = 2\sin\theta / \lambda$$

The diffraction pattern will show the symmetry related to the symmetry of the crystal lattice. On the other hand, intensity I_{hkl} of the beam diffracted on (hkl) crystal planes is related to the structure factors F_{hkl}, that can be calculated as the sum of contributions of all atoms constituting the structure. Structure factors can be calculated for the example above, using $L_2[010]$ symmetry. The symmetry-equivalent atoms have coordinates xyz and –xy-z. The structure factors for the symmetry related planes, F_{hkl} and F_{-hk-l} are expressed as sum of contributions of of atoms related by symmetry:

$$F_{hkl} = f_i [\exp 2\pi i\{hx + ky + lz\} + \exp 2\pi i\{h(-x) + ky + l(-z)\}]$$
$$F_{-hk-l} = f_i [\exp 2\pi i\{(-h)x + ky + (-l)z\} + \exp 2\pi i\{(-h)(-x) + ky + (-l)(-z)\}] = F_{hkl}$$

Both geometry of the diffraction pattern and the beam intensities reveal the symmetry, that is related to the that of the matter distribution in the crystal – the lattice symmetry. However, the formalism of the diffraction description is affected by the Friedel law. Consider the structure factors originated by (hkl) and (-h-k-l) planes, with no assumptions on the crystal symmetry. We use the Euler theorem for the exponential function with the imaginary index: $\exp(i\alpha) = \cos\alpha + i \sin\alpha$ and the evenness of the trigonometric functions.

$$F_{hkl} = \Sigma fi \exp 2\pi i(hx+ky+lz) = \Sigma fi[\cos 2\pi (hx+ky+lz) + i\sin 2\pi (hx+ky+lz)]$$
$$F_{hkl} = \Sigma fi \cos 2\pi (hx+ky+lz) + i\Sigma fi \sin 2\pi (hx+ky+lz) = A_{hkl} + i B_{hkl}$$
$$I_{hkl} \sim F_{hkl}\ F_{hkl}^{*} = (A + iB)(A - iB) = A_{hkl}^{2} + B_{hkl}^{2}$$

$$F_{-h-k-l} = \Sigma fi \exp 2\pi i(-hx-ky-lz) = \Sigma fi[\cos 2\pi (-hx-ky-lz) + i\sin 2\pi (-hx-ky-lz)]$$
$$F_{-h-k-l} = \Sigma fi \cos 2\pi (hx+ky+lz)\ i\ i\Sigma fi \sin 2\pi (hx+ky+lz) = A_{hkl} - i B_{hkl}$$
$$I_{-h-k-l} \sim F_{-h-k-l}\ F_{-h-k-l}^{*} = (A_{hkl} - i B_{hkl})(A_{hkl} + i B_{hkl}) = A_{hkl}^{2} + B_{hkl}^{2}$$

Hence $I_{hkl} = I_{-h-k-l}$

The Friedel law indicates that intensities of hkl and –h-k-l reflections are identical, and the diffraction pattern is centrosymmetric (has an inversion symmetry), despite the real symmetry of the crystal lattice. Consequently, the diffraction pattern symmetry corresponds to 32 point groups but supplemented by the inversion, what limits the possible symmetry to 11 **Laue diffraction groups**:

Point group	Laueg diffraction group
1, $\bar{1}$	$\bar{1}$
2, m, 2/m	2/m
222, mm2, mmm	mmm
3, $\bar{3}$	$\bar{3}$
32, 3m, $\bar{3}$m	$\bar{3}$m
4, $\bar{4}$, 4/m	4/m
422, 4mm, 4/mmm, $\bar{4}$2m	4/mmm
6, $\bar{6}$, 6/m	6/m
622, 6mm, 6/mmm, $\bar{6}$2m	6/mmm
23, m3	m3
432, $\bar{4}$3m, m3m	m3m

10. Systematic absences. Determination of the space group.

How to determine the space group reflecting the matter distribution in the crystal,, if the morphology analysis gives an information about the point group only, and the symmetry of the diffraction pattern allows to recognize one out of 11 Laue diffraction groups? That can be accomplished with the use of so called **systematic absences**: some classes of reflections have intensity, and consequently the structure factor F_{hkl}, of zero, independent from the kind and position xyz of atoms in the structure.

To understand the rules of systematic absences, consider the expression of the structure factor for atoms related by a transformation in the space group. To calculate the structure factor, summation will be performed over only those atoms that are related by the analyzed transformation

Lets start with the Bravais translation lattice P. Let the atom have a general position with coordinates xyz. Positions of the equivalent atoms in this translation group correspond to the linear combination of the unit vectors a_0, b_0 and c_0. Therefore, the equivalent atoms have the xyz coordinates in the adjacent unit cells. Consequently, the structure factor can be calculated as the contribution of a single atom:

$$F_{hkl} = f_i \exp 2\pi i(hx+ky+lz)$$

Since the obtained expression depends on the coordinates xyz, we cannot define the systematic absences related to the analyzed transformation – there are no systematic absences for general position xyz. It has to be noted that this calculation can give the zero value of the structure factor, but that would result from the arithmetic only, and is not a systematic effect for any reflection group. The next example will explain it in more details.

Analyze the Bravais lattice C. It corresponds to the lattice translation $\frac{a+b}{2}$ centering faces (001). Coordinates of atoms equivalent in this transformation are xyz and 1/2+x,1/2+y,z. For all reflections hkl, the structure factor can be calculated, and moving the first sum component ahead of the square bracket:

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(1/2+x)+k(1/2+y)+lz)]$$
$$F_{hkl} = f_i\,[\exp 2\pi\,(hx+ky+lz) + \exp 2\pi i(hx+ky+lz)\exp 2\pi i(h/2 + k/2)]$$
$$F_{hkl} = f_i \exp 2\pi i(hx+ky+lz)\,[1 + \exp 2\pi i(h/2 + k/2)]$$
$$F_{hkl} = f_i \exp 2\pi i(hx+ky+lz)\,[1 + \exp \pi i(h+k)]$$
$$F_{hkl} = f_i \exp 2\pi i(hx+ky+lz)\,[1 + \cos\pi\,(h+k) + i \sin\pi(h+k)]$$

Since h and k are the Miller indices in the plane symbol, the imaginary part is zero:
$h+k \in I \Rightarrow \sin\pi\,(h+k) = 0$

- for $h+k=2n+1$ $1+\cos\pi\,(h+k)=0 \Rightarrow F_{hkl}=0$
- for $h+k=2n$ $1+\cos\pi\,(h+k)=2 \Rightarrow F_{hkl}=2fi\exp 2\pi i(hx+ky+lz) = 2\,F_{hkl}\,(P)$

For any reflections hkl, these with the odd sum h+k will not be observed, since their structure factors and intensities are zero. However, the observed reflections will have the structure factors of a value two times larger than those for the hypothetic primitive lattice P. What is a difference between the discussed P and C lattices? The difference is associated with the fractional translation $\frac{a+b}{2}$ in the C lattice. That resulted in the exponential function with sum h+k in its index and leaded to the systematic absences independent from the atom position.

Other Bravais lattices can also be analyzed. For the F lattice, translations $\frac{a+b}{2}$ $\frac{a+c}{2}$ $\frac{b+c}{2}$ occur. Coordinates of the equivalent points are: x,y,z; 1/2+x,1/2+y,z; 1/2+x,y,1/2+z; x,1/2+y,1/2+z.

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(\tfrac{1}{2}+x)+k(\tfrac{1}{2}+y)+lz) +$$
$$\exp 2\pi i(h(\tfrac{1}{2}+x)+ky+l(\tfrac{1}{2}+z)) + \exp 2\pi i(hx+k(\tfrac{1}{2}+y)+l(\tfrac{1}{2}+z))]$$
$$F_{hkl}=f_i \exp 2\pi i(hx+ky+lz)[1+\exp 2\pi i(\tfrac{h}{2}+\tfrac{k}{2})+\exp 2\pi i(\tfrac{h}{2}+\tfrac{l}{2})+\exp 2\pi i(\tfrac{k}{2}+\tfrac{l}{2})]$$
$$F_{hkl}(F) = F_{hkl}(P)[1+\cos\pi\,(h+k) + \cos\pi\,(h+l) + \cos\pi\,(k+l)]$$

- $h+k,\ h+l,\ k+l = 2n \Rightarrow F_{hkl}(F) = 4F_{hkl}(P)$
- $h+k=2n+1 \Rightarrow F_{hkl}(F) = 0 \quad \Rightarrow \quad h$ or $k=2n+1$ therefore for any l
  $[1+\cos\pi\,(h+k) + \cos\pi\,(h+l) + \cos\pi\,(k+l)] = 1-1+1-1=0$

As a result, the F lattice can be recognized by the observed reflections only with the same parity of all indices hkl.

For I lattice, the translation $\frac{a+b+c}{2}$ relates points x,y,z and 1/2+x,1/2+y,1/2+z.

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(\tfrac{1}{2}+x)+k(\tfrac{1}{2}+y)+l(\tfrac{1}{2}+z)]$$
$$F_{hkl}=fi\exp 2\pi i(hx+ky+lz)[1+\exp 2\pi i(\tfrac{h}{2}+\tfrac{k}{2}+\tfrac{l}{2})]$$
$$F_{hkl}(I) = F_{hkl}(P)[1+\cos\pi\,(h+k+l)]$$

- $h+k+l = 2n \Rightarrow F_{hkl}(I) = 2_{hkl}(P)$
- $h+k+l = 2n+1 \Rightarrow F_{hkl}(I) = 0$

Summary of his analysis is a table below.

Type of Bravais translation lattice	Systematic absences
P	none
A	k+l=2n+1
B	h+l=2n+1
C	h+k=2n+1
F	h+k=2n+1, h+l=2n+1, k+l=2n+1
I	h+k+l=2n+1

Systematic absences have been caused by the presence of fractional translations in the centered Bravais groups. That suggests the analogous possibility of detecting the translation symmetry elements as components of the space groups.

Lets calculate the structure factor for atoms related by the $L_2 \| y$ symmetry axis. Coordinates of the symmetry-equivalent atoms are x,y,z and -x,y,-z.

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(-x)+ky+l(-z))]$$

There are no systematic absences since there is no expression independent from the coordinates.

Consider the screw axis 2_1. Since axes are directional elements – lets choose the axis $2_1 \| y$ with the translation $\frac{b}{2}$. Coordinates of the symmetry-related atoms : x,y,z -x,1/2+y,-z. Sum over these atoms gives:

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(-x)+k(1/2+y)+l(-z))]$$
$$F_{hkl} = f_i \exp 2\pi i(hx+ky+lz)[1 + \exp 2\pi i(-2hx+\tfrac{k}{2}-2lz)]$$

For any xyz coordinates, one has to consider reflections 0k0 (axial) for which the components -2hx and -2lz in the index equal zero. Notice that the presence of these components results from the direction of the screw axis:

$$Fhkl = f_i \exp 2\pi i(hx+ky+lz)[1 + \cos k\pi]$$

- $Fhkl = 0$ when $\cos k\pi = -1 \Rightarrow k=2n+1$
- $Fhkl \neq 0$ when $\cos k\pi = 1 \Rightarrow k=2n$

If we change the axis for $2_1 \| x$ with the translation $\frac{a}{2}$, calculations will be performed for a pair of the related atoms x,y,z 1/2+x,-y,-z::

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(1/2+x)+k(-y)+l(-z))]$$
$$F_{hkl} = fi \exp 2\pi i(hx+ky+lz)[1 + \exp 2\pi i(\tfrac{h}{2}-2ky-2lz)]$$

Equation will be independent from coordinates only for h00 reflections:

$$F_{hkl} = f_i \exp 2\pi i(hx+ky+lz)[1 + \cos h\pi]$$

- $Fhkl = 0$ when $\cos h\pi = -1 \Rightarrow h=2n+1$
- $Fhkl \neq 0$ when $\cos h\pi = 1 \Rightarrow h=2n$

Again, type of reflections affected by the absences is related to the direction of the screw axis, while the systematic absences condition is derived from the fractional translation.

Analyze the action of the glide planes. Similar to rotation axes, normal mirror planes do not have the coupled translation. Consider the glide plane c perpendicular to Y, which relates points x,y,z and x,-y,1/2+z :

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(hx)+k(-y)+l(1/2+z))]$$
$$F_{hkl} = f_i\,\exp 2\pi i(hx+ky+lz)[1 + \exp 2\pi i(-2ky+\tfrac{l}{2})]$$

For any x,y,z and reflections h0l (zone of Y axis)

$$F_{hkl} = f_i\,\exp 2\pi i(hx+ky+lz)[1 + \cos\pi l]$$

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

For the plane n⊥x, translation is $\frac{b+c}{2}$. Coordinates of two symmetry-equivalent points are x,y,z and -x,1/2+y,1/2+z. Condition for the systematic absences:

$$F_{hkl} = f_i\,[\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(-x)+k(1/2+y)+l(1/2+z))]$$
$$F_{hkl} = f_i\,\exp 2\pi i(hx+ky+lz)[1 + \exp 2\pi i(-2hx+\tfrac{k}{2}+\tfrac{l}{2})]$$

Hence for any x,y,z and for reflections 0kl (zone of X axis):

$$F_{hkl} = f_i\,\exp 2\pi i(hx+ky+lz)[1 + \cos\pi\,(k+l)]$$

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

Summarizing, the selected systematic absences related to translation symmetry elements are tabulated below:

Orientation	Symmetry element	Systematic absences
any	m, 2, 3, 4, 6	no
[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+k=2n+1

Systematic absences contain the information only on the translation symmetry elements and the translation Bravais lattices. However, coupled with the rules of the symmetry combination, they frequently allow to overcome the limitation superimposed by the Friedel law and determine the true space group.

For example, compound (1R,2R)- $C_{28}H_{26}N_2O_2$ crystallizes in the orthorhombic system and the systematic absences for groups of reflections are h00 for h=2n+1, 0k0 k=2n+1, 00l l=2n+1, with the lack of other absences. If the space group would have 3 planes of symmetry, they would intersect along the axis directions, and therefore would be the glide planes. Therefore, the analyzed crystal reveals only $P2_12_12_1$ symmetry and consists of the optically pure compound!

Another crystal from the monoclinic system reveals only absences for reflections 0k0 k=2n+1 and h0l l=2n+1, describing the rotation axis parallel to Y and the plane perpendicular to it. Conclusion – the space group is centrosymmetric $P2_1/c$.

11. Single crystal methods. Laue equation.

The powder method DSH allows to investigate the polycrystalline samples. Result of the experiment is the diffraction pattern giving the one-dimensional data with the beams diffracted on all the lattice planes. Such pattern results from the random orientation of the large number of microcrystals. Only use of the monochromatic beam allows the interpretation of the obtained results.

Different possibilities result from the use of a single crystal sample. Knowledge on the crystal orientation allows the interpretation of the diffraction pattern, including the obtained 3-dimensional data leading to the determination of the pattern symmetry, the relative orientation of the symmetry elements in the Laue diffraction group, the reflection indexing, easy determination of the space group and also the unit cell parameters.

The Laue theory applied for the single crystal methods is based on the diffraction formalism. The basic assumptions are as follows: the motionless atoms are located in the nodes of the lattice; these are the point atoms with all electrons located at the atom position – in the grid point of the lattice; the atom ability to diffract is described as the atomic scattering factor f_i proportional to its atomic number Z_i; The X-ray beam causes the electron oscillations and the emission of the radiation of the same frequency (ν/λ) as the incident beam; the diffracted beam is emitted as the spherical wave; the diffracted beam has the same amplitude as the incident beam; amplitude depends on f_i (Z_i); the spherical waves interfere and are amplified in the directions of the observed diffracted beams.

Consider the radiation beam of the λ wavelength directed to the one-dimensional crystal lattice of the constant a (the grid line in the crystal lattice) with the incidence angle of α_o and the reflection angle α (**Fig. 11.1**).

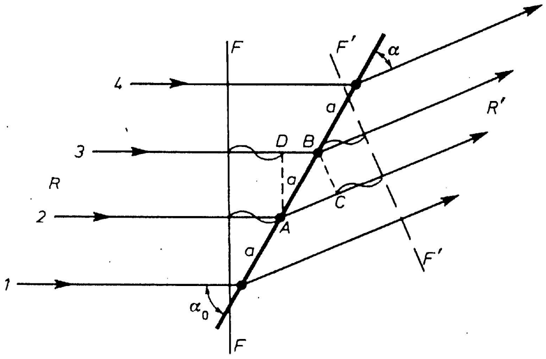


Fig. 11.1

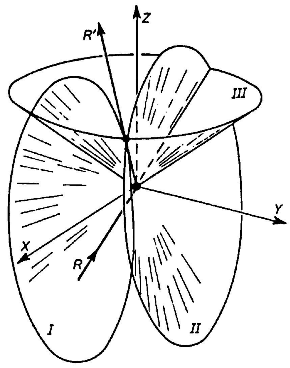


Fig. 11.2

Amplification will occur if the difference of the optical way AC-BD will be equal to the integer multiple of the wavelength λ. Hence:

$$AC\text{-}BD = a(\cos\alpha - \cos\alpha_o) = h\lambda \qquad \text{where } h \in \mathrm{C}$$

The above is the **Laue equation**. Its consequence is that the deflection of the diffracted beam from the incident beam direction, expressed with the difference is ($\cos\alpha$ - $\cos\alpha_o$), is proportional to the interference order h, proportional to the wavelength λ of the incident beam, and inversely proportional to the lattice constant a. The amplified reflections will be positioned on the side surface of the cone co-axial with the grid line with the cone angle equal to the reflection angle α (**Fig. 11.1**).

For the three-dimensional lattices, the system of 3 Laue equations has to be satisfied (**Fig. 11.2**)

$a(\cos\alpha - \cos\alpha_o) = h\lambda$
$b(\cos\beta - \cos\beta_o) = k\lambda$
$c(\cos\gamma - \cos\gamma_o) = l\lambda$

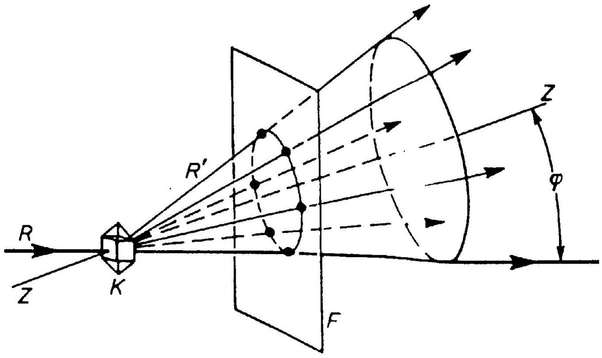


Fig. 11.3

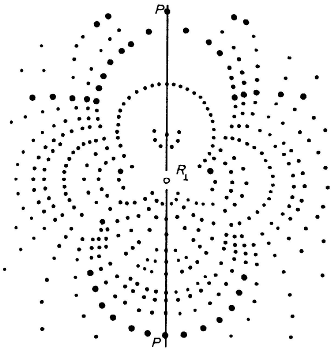


Fig. 11.4

There is a remote probability that the radiation of the wavelength λ will satisfy the system of 3 equations for a fixed crystal orientation. To increase this probability, the experiment is performed with the polychromatic radiation or with the changing crystal orientation.

There are several methods of the single crystal investigations. Lets start with the Laue method. The polychromatic beam is directed towards the motionless single crystal (**Fig. 11.3**). Usually, the flat detector is positioned behind the crystal. The observed reflections originated from the planes belonging to the same zone are located on the same zonal curve (circle, ellipse, parabola, hyperbola). Position of the zone axis Z can be determined by analysis of the zonal curves. If the zonal curves of X,Y,Z system axes will be identified, the cell parameters can be determined. The Laue method allows to simultaneously record many beams diffracted by the crystal. The clear advantage of the method is also the ability to determine the symmetry. If the incident beam runs along the symmetry element, the zonal curves resulted from the symmetry-related zones will give the symmetric diffraction pattern (**Fig. 11.4**). One has to remember about the limitations imposed by the Friedel law – the diffraction pattern will always be centrosymmetric. The example below illustrates this case.

The symmetry of the diffraction pattern for the monoclinic crystal is analyzed. Possible point groups of symmetry are 2, m and 2/m. In group 2, the incident beam along the 2-fold axis will result in the 2-fold symmetry of the diffraction pattern, but the incident beam perpendicular to the axis will result in the m symmetry. In group m, the incident beam parallel to the mirror plane will give such symmetry of the diffraction pattern, while the beam perpendicular to the mirror plane will result in the 2-fold symmetry of the pattern. Finally, for the 2/m group there will be a combination of both cases analyzed above. Such analysis leads to 10 types of symmetry of the diffraction pattern recorded with the Laue method (**Fig. 11.5**).

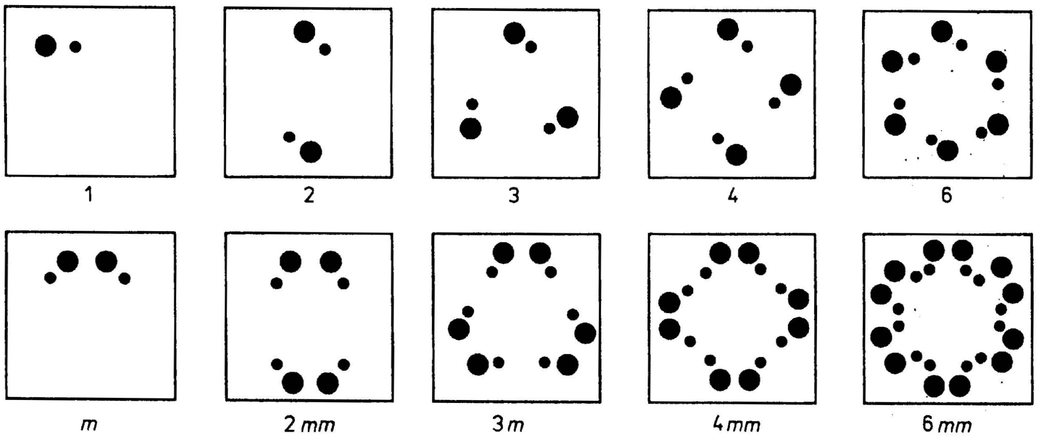


Fig. 11.5

Another method is called the rotation method. The single crystal is rotated around the chosen grid line. That requires the precise crystal alignment. In this method, the monochromatic incident beam is directed with the incidence angle of $90^{0,}$ towards the grid line being the axis of the crystal rotation in camera (**Fig. 11.6**). In this method the detector is on the inner surface of the cylindrical camera co-axial with the axis of crystal rotation'. Reflections from the grid line are distributed on the side surfaces of the co-axial diffraction cones (**Fig. 11.7**), and after the film (detector) is unrolled, their traces are visible as the parallel lines called layers.

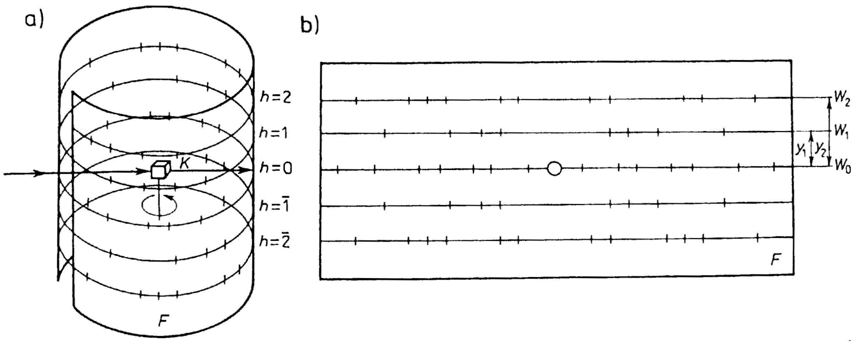


Fig. 11.6

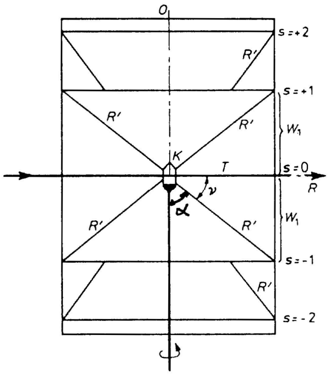


Fig. 11.7

The observed layers correspond to different diffraction orders h=0,1,2 and so on. The incident beam, crystal and the transient beam are positioned in the plane of the zero layer h=0. The layer distribution is symmetrical relative to the zero layer (**Fig. 11.7**), what is the consequence of satisfying the Laue equation for identical diffraction angles above and below the plane of the zero layer. In the rotation method both wavelength and the camera radius R are known. Therefore, the lattice constant can be calculated with high precision. Notice, that the first order layers on both sides of the zero layer (h=1 and h=-1) have the same cone angle – so called layer angle ν. The sum of the layer angle and the diffraction angle is 90^0. The distance between layers of the same order h and –h is $2W_h$.

$$\nu + \alpha = 90^o \qquad \text{hence } \alpha = 90 - \nu \qquad \cos\alpha = \sin\nu$$

In the rotation method $\alpha_o = 90^o$. For the layer of the h order, the Laue equation:

$$a(\cos\alpha - \cos\alpha_o) = h\lambda$$
$$a\cos\alpha = h\lambda$$
$$a = h\lambda / \cos\alpha = h\lambda / \sin\nu = h\lambda\sqrt{\frac{1}{\sin^2\nu}}$$

Since $\sin^2\nu + \cos^2\nu = 1$:

$$a = h\lambda\sqrt{1+ctg^2\nu} \qquad \text{where } ctg\nu = 2R/2W$$

The rotation method allows to precisely calculate the lattice constant, but also the length of any vector of the unit translation for the adjacent nodes positioned on the rotation axis (the grid line). Determination of all unit cell parameters a_o, b_o and c_o requires the precise alignment of the crystal, with the coordinate axes positioned parallel to the rotation axis. Usually, the rotation method is combined with the Laue method, since the latter gives the angular relations between different zone axes (**Fig. 11.3**). Identification of directions of the coordinate axes can also be done based on the crystal morphology combined with the rules for the choice of the system axes XYZ relative to the symmetry elements in an investigated crystal system.

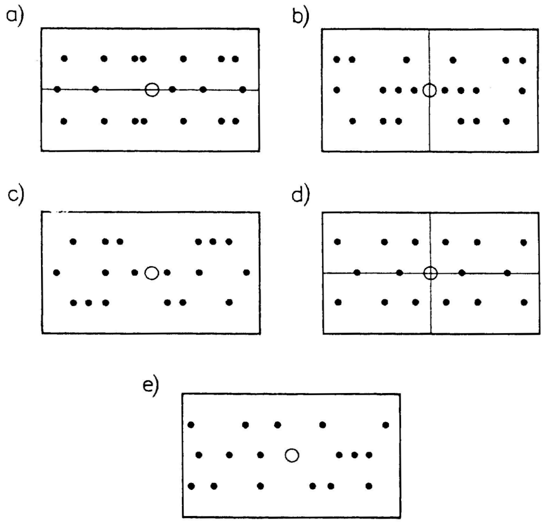


Fig. 11.8

The rotation method can also give the information on the symmetry of the incident beam direction or the crystal rotation axis (**Fig. 11.8**). If the incident beam is directed to a crystal having the mirror plane perpendicular to the axis of rotation, the h and –h layers will reveal the identical distribution and intensities of reflections, and the diffraction pattern will have the top-bottom symmetry relative to the zero layer (**Fig. 11.8a**). If the mirror plane parallel to the axis of rotation will pass through the direction of the incident beam, the right-left symmetry of the diffracted pattern will be seen (**Fig. 11.8b**). If both these cases occur simultaneously, the diffraction pattern will reveal the mm2 symmetry (**Fig. 11.8d**). For the incident beam parallel to the lattice 2-fold axis, the diffraction pattern will reveal such symmetry (**Fig. 11.8c**). If, however, the incident beam will be directed in any other direction, the diffraction pattern will have no symmetry (**Fig. 11.8e**).

Lets summarize the methods of crystal investigations leading to the determination of the matter structure.

1. The Laue diffraction group (lattice symmetry) and the crystal system can be determined with the Laue or rotation methods (single crystal methods).
2. The unit cell geometry a,b,c,α,β,γ,V can be determined with the rotation, Laue or DSH (powder) methods
3. Number of molecules in the unit cell can be calculated based on the crystal density measurement
   $d = m_k/V_k = 1.6604\ ZM_{cz} / V_k \qquad Z = 0.6023\ dV_k / M_{cz}$
4. Indexing of the diffraction pattern in all methods (rotation, Laue, DSH)
5. Bravais lattice from the systematic absences of hkl reflections. The observed reflections:
   P: all A: k+l=2n B: h+l=2n C: h+k=2n F: h+k, h+l, k+l=2n I: h+k+l=2n
6. The space group from the systematic absences. For the screw axes absences occur for reflections h00 (X) 0k0 (Y) 00l (Z), for the glide planes perpendicular to X,Y and Z absences for the reflection classes 0kl, h0l and hk0
7. Amplification of the diffracted beams occurs if the equations are satisfied:
   Bragg $n\lambda = 2d_{hkl} \sin\theta$
   Laue $a(\cos\alpha - \cos\alpha_o) = hc$
8. Intensity of the diffracted beam for the (hkl) planes is expressed:
   $I_{hkl} \sim F_{hkl} = \sum_i fi\ \exp 2\pi i(hx_i + ky_i + lz_i)$
9. Each atom diffracts the radiation proportional to its atomic number. The atom scattering factor $f_i = f_o \exp(-K\sin^2\theta/\lambda^2)$
10. Intensity of the diffracted beam is affected by polarization p, detection time (the experiment geometry) L and the radiation absorption A:
    $I = LpA\ F^2 = \theta \bullet \frac{1+\cos^2(2\theta)}{2} \bullet \frac{1}{V}\int \exp -\mu l\ dV \bullet F^2$

12. Theory of the structure factors. The phase problem.

Three-dimensional periodic crystal lattice is described with the use of the basis of the unit vectors **a**, **b** and **c**, coupled with the selected crystal system. However, in space the infinite number of such bases can be defined and one basis can be transformed into another. In particular, for basis **a**, **b** and **c** in the real space, one can construct the basis of vectors **a***, **b*** and **c*** defining the reciprocal space. Vectors of the reciprocal space can be defined in a following way: for (100), (010) and (001) planes the perpendicular lines are constructed from the point chosen as the system origin, the sectors $1/d_{100}$ is selected as **a*** and analogous sectors for other axes. The (hkl) plane (real space) has the corresponding hkl point in the reciprocal space defined by the vector $\mathbf{h} = h\mathbf{a^*} + k\mathbf{b^*} + l\mathbf{c^*}$.

Function G(**h**) is a Fourier transform of function g(**x**), when the equation is satisfied:

$$G(\mathbf{h}) = T[g(\mathbf{x})] = \int_{Vx} g(\mathbf{x})\cdot\exp(2\pi i\mathbf{h}\cdot\mathbf{x})dV_x$$

Vector **x** is defined in the real space of **a**, **b** and **c** vectors, while vector **h** in the reciprocal space **a***, **b*** and **c***. Function f(**x**) is derived from the inverse Fourier transform of the G(**h**) function:

$$g(\mathbf{x}) = T^{-1}[G(\mathbf{h})] = k\int_{Vh^*} G(\mathbf{h})\cdot\exp(-2\pi i\mathbf{h}\cdot\mathbf{x})dV_h{}^*$$

Several important theorems concern the transforms. Transform of the sum of functions is a sum of their transforms. Transform of the function convolution is the product of their transforms:

$$T[g(\mathbf{x}) \otimes q(\mathbf{x})] = G(\mathbf{h}) \cdot Q(\mathbf{h})$$

Transform of the inverse function is $G^*(\mathbf{h}) = T\,[g^*(-\mathbf{x})]$. It can be shown that:

$$P(\mathbf{x}) = \int_{Vh^*} G(\mathbf{h})\cdot G^*(\mathbf{h})\cdot\exp(-2\pi i\mathbf{h}\cdot\mathbf{x})dV_h{}^* = \int_{Vh^*} |G(\mathbf{h})|^2\cdot\exp(-2\pi i\mathbf{h}\cdot\mathbf{x})dV_h{}^*$$

In the unit cell, the electron density distribution can be described as a sum of distributions for atoms $a(x) = \Sigma a_i(x-x_i)$. Transform of the sum of functions is a sum of their transforms. If the transform $T[a_i(x-x_i)] = f_i(h)$, then the transform of function a(x) can be written as:

$$T[a(x)] = \Sigma f_i(h)\cdot\exp(2\pi ih\cdot x_i)$$

In crystallography, function g(**x**) is the function of the electron density distribution ρ(**x**), while function G(**h**) is the structure factor F(**h**). Hence:

$$F(\mathbf{h}) = \int_{Vx} \rho(\mathbf{x})\cdot\exp(2\pi i\mathbf{hx})dV_x$$

For a discrete distribution of the point atoms:

$$F(\mathbf{h}) = \Sigma f_i \cdot \exp(2\pi i \mathbf{hx})$$

The inverse Fourier transform allows to calculate the function of the electron density distribution $\rho(\mathbf{x})\cdot$in a point of coordinates **x**:

$$\rho(\mathbf{x}) = V^{-1}\sum_{h} F(\mathbf{h})\cdot\exp(-2\pi i\mathbf{hx})$$

The Fourier transform of the structure factors allows to calculate the electron density distribution in the crystal $\rho(xyz)=V^{-1}\Sigma F(hkl)\cdot\exp[-2\pi i(hx+ky+lz)]$. The direct use of this formula is impossible. The structure factors are complex values with the amplitude $|F(hkl)|$ and phase $\varphi(hkl)$: $F(hkl)=|F(hkl)|\cdot\exp[i\varphi(hkl)]$. The diffraction experiment provides only the information on the reflection intensity $I(hkl)$, which is proportional to the square of the amplitude $|F(hkl)|^2$. The amplitude can easily be calculated as a square root of the intensity measured in the diffraction experiment $|F(hkl)|=\sqrt{I(hkl)}$, but there is no information on the phase. It is the phase, what has a decisive effect on the quality of the obtained function of the electron density distribution.

The **phase problem** indicated above is shown on **Fig. 12.1**. The structure factor $|F_{hkl}|\exp i\varphi$ can be expressed as the vector sum of the real and imaginary parts:

$$F_{hkl} = |F_{hkl}|\exp i\varphi = |F_{hkl}|(\cos\varphi + i\sin\varphi) = A_{hkl} + iB_{hkl}$$

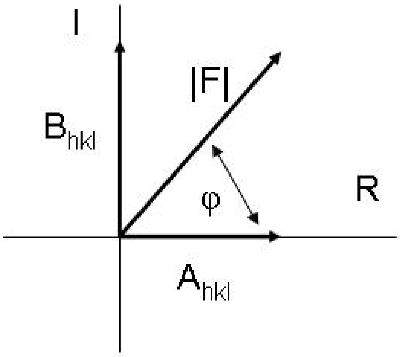


Fig. 12.1

Intensity measured in the diffraction experiment is $I_{hkl} \sim |F_{hkl}|^2 = FF^* = A^2+B^2$. The unknown phase can be calculated from the known positions of atoms in the structure:

$$F_{hkl} = |F_{hkl}|(\cos\varphi + i\sin\varphi) = A_{hkl} + iB_{hkl}$$
$$\mathrm{tg}\varphi_{hkl} = B_{hkl} / A_{hkl}$$

Then the experimental $F_{hkl} = |F_{hkl}| \exp i\varphi$
or model-based $F = \Sigma f_i \exp 2\pi i(hx_i + ky_i + lz_i)$

The function of the electron density distribution at the point of coordinates xyz:

$$\rho_{xyz} = V^{-1} \sum_{hkl} F_{hkl} \exp -2\pi i(hx+ky+lz)$$

or if the kind and position x_i, y_i, z_i of atoms in the cell are known:

$$\rho_{xyz} = V^{-1} \sum_{hkl} \left[\sum_{i} fi \exp 2\pi i(hx_i+ky_i+lz_i)\right] \exp -2\pi i(hx+ky+lz)$$

The essence of the phase problem is that the phase necessary for determination of the atomic positions can be calculated from the known atomic positions!

It has to be noted, that in many cases position of some atoms in the structure can be deduced from the comparison of the number of symmetry-equivalent points in a given space group (lprs) and the number of molecules in the unit cell Z, determined from the experimental crystal density d. Density can be expressed as a quotient of mass and volume of the unit cell:

$$d = m_k/V_k = 1.6604 \; Z \; Mcz \;/\; V_k$$
$$Z = 0.6023 \; dV_k \;/\; Mcz$$

Number of the symmetry-equivalent points is calculated for each space group as the product of numbers of points related by the Bravais translation group and number of points related by the symmetries in the group. The reminder: number of the symmetry-equivalent points for the translation symmetry is identical with that for the non-translation symmetry.

If Z>lprs, the asymmetric part of the structure (ASU) contains more than 1 molecule. If Z=lprs, the asymmetric unit contains one molecule in a general position. In both cases, molecules have only C_1 symmetry and nothing can be deduced about the molecule position. For Z<lprs, fraction of the molecule equal to the quotient Z/lprs is in the asymmetric unit, and the molecule has an internal symmetry. Both translation and non-translation symmetries exist in the space groups, but only the latter (rotation axes, mirror planes, inversion center) can reflect the molecule symmetry. Therefore, if the molecule contains an atom that has to be invariant in a certain symmetry, its coordinates are strictly defined. The examples below will explain this deduction method.

Complex $[Pt(NH_3)_2Cl_2]$ crystallizes in the orthorhombic space group Pbca. Therefore, the whole list of symmetries include three glide planes, three screw axes 2_1 and the inversion. Number of symmetry-equivalent points in this group lprs = 8. The density measurement indicated that 8 molecules are in the unit cell. Thus the asymmetric unit contains 8/8 = 1 molecule, and that means the molecule has no internal symmetry. If the measured density indicate Z=4, then the asymmetric unit contains 4/8 or half of the molecule. The other half can be obtained by using the symmetry relating 2 symmetry-equivalent points. All symmetries in the analyzed space group (glide planes, screw axes, inversion center) satisfy that requirement. However, only the non-translation symmetry, an inversion, can describe the symmetry of the investigated complex molecule. Since only one central ion is in the molecule, it has to be the invariant point of the inversion, so its coordinates are identical to those of the inversion center. Thus we know the ion position Pt(0,0,0).

Crystal of [$Pt(NH_3)_2Cl_2$] was obtained in the space group $P2_1/c$ with Z=2. Two translation symmetry elements exist in this group – the screw axis and the glide plane, and the non-translation inversion. Only the non-translation symmetry can reflect the molecule symmetry. Therefore, in this example, the molecule must posses the inversion symmetry, and the only Pt ion must be positioned on the inversion center. The system origin has to coincide with one of the common invariant points of the group symmetries. If the group is centrosymmetric, the system origin coincides with the inversion center. Therefore, the coordinates of Pt ion are 0,0,0.

The same complex [$Pt(NH_3)_2Cl_2$] crystallizes in the space group Pnn2. It is a group from the orthorhombic system, so tree positions in the international symbol characterize the symmetry of X,Y,Z system axes. Thus the 2-fold axis direction is Z. There are 4 symmetry-equivalent positions in that group. The measured crystal density indicates Z=2, what corresponds to 1/2 molecule in the asymmetric unit and consequently the C_2 symmetry of the molecule. The 2-fold axis is a set of points {00z}, with coordinate z having any value. The analyzed group is polar, and any z value can be assigned for one atom, defining in this way its position relative to the system origin or assigning the origin position in space! That allows to calculate the phase and the electron density distribution.

In similar cases, deduction of atom coordinates allows to calculate the approximate value of the phase angle and subsequently the function of the electron density distribution. Such deduction of the structure is one of the methods for solving the phase problem.

For the deduced or known position of one or several atoms, the structure factor can be calculated according to the equation:

$$F = \Sigma f_i \exp 2\pi i(hx_i + ky_i + lz_i) = A_{hkl} + iB_{hkl}$$

Phases calculated for all reflections are only approximate, since are based on the contribution of only few atoms. However, if this contribution is significant (for heavy atoms f_i is large), the obtained values are good estimations of the true phases. In such case, maxima on the electron density distribution reveal positions of other atoms, and their contribution to the calculated structure factor and the phase is accounted for in the further calculation. Thus, in the subsequent iterations, all non-hydrogen atoms can be located, correcting the calculated phases for all reflections. Location of hydrogen atoms is performed after refining the structure with the least-squares method fitting the non-hydrogen atom coordinates and their oscillation amplitudes to the experimental data (intensities or structure factors).

13. Solving the phase problem. The Patterson method.

The nature of the phase problem is that the diffraction experiment gives only the intensities I_{hkl} of the diffracted beams. They can be converted into the structure factor amplitudes $|F_{hkl}|$. However, these experimental data do not enable the calculation of the inverse Fourier transform

$$\rho_{xyz} = V^{-1} \sum_{hkl} F_{hkl} \exp -2\pi i(hx+ky+lz)$$

since we do not know the phase necessary for calculating $F_{hkl} = |F_{hkl}| \exp i\varphi$. The phase can be calculated from the known atomic positions x_i,y_i,z_i in the cell and their atomic scattering factor f_i.

$$\rho_{xyz} = V^{-1} \sum_{hkl} \left[\sum_{i} fi \exp 2\pi i(hx_i+ky_i+lz_i) \right] \exp -2\pi i(hx+ky+lz) \quad \text{and}$$

$$tg\varphi_{hkl} = B_{hkl} / A_{hkl}$$

Importance of phase for obtaining the proper function of the matter distribution is illustrated on **Fig. 13.1**. Pictures of two crystallographers, Jerome Karle and Herbert Hauptmann, the Nobel prize laureates, have been converted into sets of structure factors F (color saturation) and phases. Then the distribution maps have been calculated, or pictures have been re-calculated for the proper combination of phases and amplitudes, giving the correct images of both laureates. The use of F from the Karle picture combined with phases from the picture of Hauptmann resulted in the deformed picture of Hauptmann, and the opposite combination – the picture of Karle. That experiment reveals that the phase value is decisive for the quality of the calculated map of the matter distribution!

Fig. 13.1

Besides deduction of the structure (practically impossible for proteins or nucleic acids!) there are several formally elegant methods of the phase problem solution.

The Patterson method is based on the inverse Fourier transformation of the reflection intensities measured in the experiment (**Patterson function P**). Previously, the experimental data have to be corrected for the geometric and physical factors affecting the measured intensity and accounted for in the Lorentz L, polarization p and absorption A corrections.

$$I = LpA\,|F|^2 = LpA\,FF^*$$

Referring to the introduction, the transform value at the uvw point can be expressed as:

$$Puvw = V^{-1}\sum_{hkl} FF^*\,\exp\text{-}2\pi i(hu+kv+lw)$$

The transform of the convolution of functions equals the product of transforms of these functions. Both F and F* are Fourier transforms of the function of the matter distribution. Thus the above expression corresponds to the convolution of the function of the electron density distribution ρ_{xyz} and the distribution function shifted by a vector [uvw]:

$$Puvw = \int \rho_{xyz} \otimes \rho_{x-u,y-v,z-w}\,dV$$

The value of the Patterson function at the uvw point is proportional to $\rho_{xyz} \otimes \rho_{x-u,y-v,z-w}$. If the uvw vector corresponds to the inter-atomic vector between atoms of a large atomic number, the electron density ρ associated with these atoms is large and the Patterson function P_{uvw} is also large. If uvw is not an inter-atomic vector, then in either (xyz) point, (x-u,y-v,z-w) or in both density is close to zero, and the Patterson function value is small or zero (**Fig. 13.2** and **Fig. 13.3**).

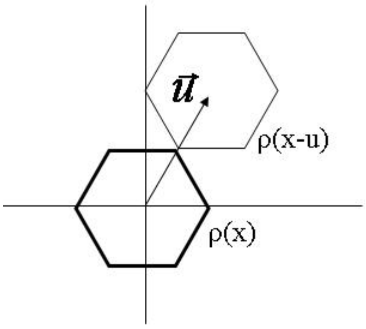


Fig. 13.2

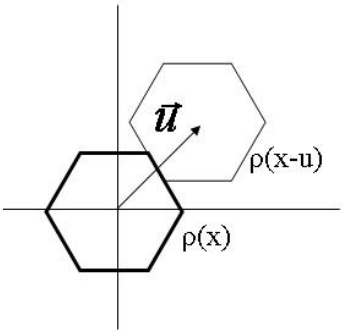


Fig. 13.3

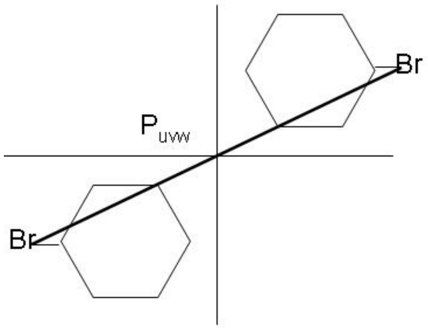


Fig. 13.4

If uvw are the components of an inter-atomic vector, then Puvw ~ Z(at1) ● Z(at2) or the product of two atomic numbers, and the components are $u=x_2-x_1$ $v=y_2-y_1$ $w=z_2-z_1$ (**Fig. 13.4)**. For bromobenzene, the Patterson peaks corresponding to vectors Br-Br, Br-C and C-C are proportional to 1225, 210 and 36, respectively. Therefore, after calculation of the Patterson function, it would be easy to identify the peaks corresponding to the Br-Br vectors. It should be noted, that for the N-atom structure, the N(N-1) Patterson peaks can be found. Interpretation is even more complicated, since the Patterson function is centrosymmetric, and contains vectors 1-2 and 2-1.

The significant simplification of the interpretation is offered by so called **Harker sections**, defined as vectors between atoms related by symmetries in a space group. After identification of the group based on the symmetry of the diffraction pattern and systematic absences, the Harker sections can be defined. For example, in the C2/c space group, the Harker sections will be associated with the translation group C, the inversion, 2-fold axis and the glide plane c. In this group, the section associated with the C centering corresponds to a vector ½½0, the one related to the inversion center is 2x,2y,2z (**Fig. 13.4**), it is 2x,0,2z for the 2-fold axis [010] and 0,2y,½ for the glide plane c.

The question raises, when the elegant Patterson method can be used for solving the phase problem. The obvious answer is - for structures with atoms heavier than the other. How heavy is heavy? That is described by the Sim ratio $\Sigma Z^2_{heavy} / \Sigma Z^2_{light}$ ~0.5. However, even for the ratio value of 0.1 the solution might be possible. This method can be used efficiently for solving the structure of organic compounds containing sulfur atoms or heavier. Presence of the bromine atom practically guaranties that the determined position of Br will result in phases and electron density maps revealing the whole molecule or its recognizable fragment. On the other hand, the Patterson method cannot be used for normal organic compounds, which do not have atoms significantly heavier from the other – it is difficult to distinguish between Harker sections O-O (~64), O-C (~48) and C-C (~36) on the Patterson function with N(N-1) peaks.

It has to be emphasized, that the Patterson method is relatively resistant to the systematic errors affecting the experiment. The important part is to get the true values of $|F|^2$ by correcting the intensities with the Lorentz, polarization and absorption factors. Also, necessity of using the Harker section requires the determination of the correct space group.

Use of Harker sections is simple and gives the information on heavy atom positions. Presence of the transformations in the space group can also be confirmed. Examples below illustrate that.

Crystal of UF_6 reveals the P-1 symmetry, a=b=c=10 Å, α=β=γ=90. The inter-atomic peaks U-U will be proportional to $92^2 = 8464$ U-F ~ 92 x 9=828 F-F ~ $9^2 = 81$. Positions of the symmetry related atoms are xyz and –x-y-z. In the UF_6 structure, the largest Patterson peaks correspond to vectors U-U: P(U-U) = P(uvw) = P(2x, 2y, 2z). Analysis of lower peaks frequently enables the location of light atoms, giving the lower peaks:

P	u(Δx)	v(Δy)	w(Δz)	
850	0.10	0.34	0.02	U-U: U(x=0.05 y=0.17 z=0.01)
80	0.23	0.17	0.01	U-F: F1(0.18,0,0) U-F1 1.8 Å
80	0.05	0.35	0.01	U-F: F2(0,0.18,0) U-F2 1.8 Å
10	0.18	0.18	0.00	F1-F2 : F2-F1 2.54 Å

Crystal of UF_6 has the $P2_1/c$ symmetry, a=b=c=10 Å, α=β=γ=90. The symmetry-equivalent positions are: (1) x,y,z; (2)(C) -x,-y,-z; (3)(2_1) -x, 0.5+y, 0.5-z; (4)(c) x, 0.5-y, 0.5+z. The Harker sections for the screw axis allow to determine the x and z coordinates, those for the c glide plane give only the y coordinate. How to match them? The proper localization gives the 2x,2y,2z section related to the inversion, what should confirm the correct solution.

2_1	P(3-1), P(2-4)	2x, 1/2, 1/2-2z
c	P(4-1)	0, 1/2-2y, 1/2
C	P(2-1)	2x, 2y, 2z

P	u(Δx)	v(Δy)	w(Δz)		
850	0.10	0.50	0.20	U-U (2_1):	U(x=0.05 y z=0.15)
850	0.00	0.10	0.50	U-U(c):	U(x y=0.20 z)
850	0.10	0.40	0.30	U-U (C):	u(0.05, 0.20, 0.15)

The Harker sections in the $P2_1/c$ group unequivocally locate the U atom, but all possible sections have to be combined, and the results have to be internally consistent. One comment is necessary – position of the symmetry element in the cell is not important, what matters is the distance between atoms and the symmetry element giving the section. Therefore, calculation of the positions of symmetry-related atoms for a given symmetry can be performed as a product of the matrix operator and the matrix describing the atom position xyz.

The non-translation symmetry elements also give the Harker sections, so their presence in the space group can be verified. This information is not available from the analysis of the systematic absences, because they occur only for transformations associated with the fractional translations.

The highest Patterson peak will correspond to the zero vector of translation between all atoms $P(000)\sim\Sigma(Z)^2$ (heavy and light). Identical peaks result from the Bravais translation lattices, what enables an identification of the cell type from the Fourier transform of F^2:

P	translations a,b,c	peaks uvw: 1,0,0 0,1,0 0,0,1
A	$\frac{b+c}{2}$	0, 1/2, 1/2
B	$\frac{a+c}{2}$	1/2, 0, 1/2
C	$\frac{a+b}{2}$	1/2, 1/2, 0
F	$\frac{b+c}{2}, \frac{a+c}{2}, \frac{a+b}{2}$	0, 1/2, 1/2; 1/2, 0, 1/2; 0, 1/2, 1/2
I	$\frac{a+b+c}{2}$	1/2, 1/2, 1/2

The calculated Patterson function $P(\mathbf{u})$ is the inverse transform of experimental reflection intensities measured in the diffraction experiment. Use of the Harker sections enables the determination of the heaviest atoms positions. In most cases we do not get the complete structural information, or coordinates of all atoms. The question raises if such method is useful for solving the phase problem. Contribution of each atom into the structure factor F depends on its atomic scattering factor, or its atomic number Z. Therefore, in the structure containing the heavy atom, contribution of this atom is the largest. Location of this atom with the Patterson method enables the calculation of phase values, which are good approximations of the true phases. Use of these phases for calculation of the matter distribution function allows to locate other atoms, subsequent phase improvement and to locate all atoms in the asymmetric unit of the structure in the following iterations. It has to be emphasized that special variants of the Patterson method (MIR, MAD) are best methods used to solve the phase problem by the protein crystallography.

14. Solving the phase problem. Direct methods.

What can be done, if the structure cannot be deduced (requirement Z<lprs is not satisfied), or the structure does not contain atoms significantly heavier from the other (what disables the use of the Patterson method)? For structures composed of ‘equally light’ atoms, the **direct methods** are used. In 1985 Jerome Karle and Herbert Hauptmann have won the Nobel prize in medicine for derivation of direct methods. These methods are based on the statistical relations between values of the **normalized structure factors** E_{hkl}. The first step is the scaling of reflections and determination of the overall temperature factor by the Wilson method. It is necessary to know the scale factor and the overall temperature factor B for all atoms to obtain normalized E from the structure factors F.

$F_{rel} = t\,|F| = \sqrt{\dfrac{I}{LpA}}$ is calculated from the experimental data I_{hkl}

$F_{rel} = t\,|\Sigma\, f_{i0} \exp 2\pi i(hx+ky+lz) \exp(-B_i \sin\theta^2/\lambda^2)|$

where f_{i0} – atom scattering factor for the motionless atom

Assuming that the atomic oscillations are spherical (isotropic) and have identical amplitudes (the temperature factor $B_i = B$), the equation is simplified:

$$F_{rel} = t \exp(-B \sin\theta^2/\lambda^2)\, |\Sigma\, f_{i0} \exp 2\pi i(hx+ky+lz)| = t \exp(-B \sin\theta^2/\lambda^2)\, |F|$$

$$|F|^2 = F^2_{\ rel} / t^2 \exp[-2B \sin^2\theta / \lambda^2]$$

Assuming $s = \sin\theta/\lambda$ and for average values of F and F_{rel}, the Wilson equation is derived:

$$\ln t^2 - 2Bs^2 = \ln K(s)$$

In practice, the ranges of $s=\sin\theta/\lambda$ are chosen, for which the average values $<F_{rel}^2>$ and experimental $<F^2> = I / LpA$ and $f_i = f_0 \exp(-B\sin^2\theta/\lambda^2)$ are calculated. Then, the plot of lnK as a function of s^2 is prepared and approximated with the straight line (**Fig. 14.1**). The scale factor (ln t2) is calculated from the line equation for $s^2 = 0$. The line slope gives the value of -2B.

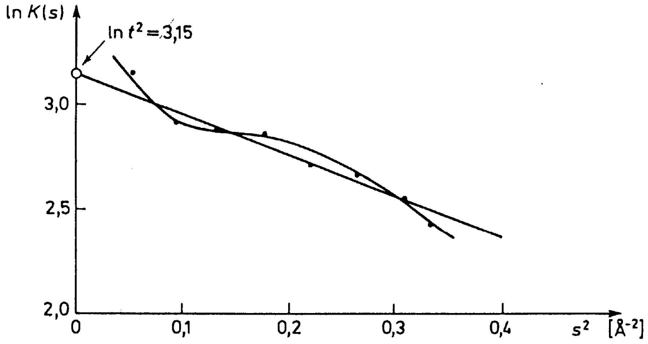


Fig. 14.1

After calculating the scale factor t and the average value of the temperature factor B for all atoms in the structure, the normalization of the structure factors is performed according to the equation, in which the numerator contains the obtained squared structure factor and the denominator contains the sum of the atomic scattering factors taking into account B and the factor accounting for changes in the intensities related to the systematic absences.

$$E^2_{hkl} = |F_{hkl}|^2 / \Sigma f_i^2\ \varepsilon$$

Average value of the squared normalized structure factors E_{hkl}, is $\langle E^2 \rangle = 1$. Analysis for different structures revealed, that distribution of the normalized structure factors E for structures crystallizing in the centrosymmetric groups differs significantly from that describing the non-centrosymmetric groups (Table below). In particular, the average value $\langle E^2-1 \rangle$ in most cases enables to decide if the structure possess the inversion center, since for the centrosymmetric structures the value 0.968 is significantly larger than that of 0.736 found for the non-centrosymmetric structures. Table below includes the data for two structures. The structural research revealed, that complex cudmtp was in fact the centrosymmetric dimer $[Cu_2Cl_4(dmtp)_2]$. Compound be2 is the optically pure terpene derivative with tree chiral centers in the molecule. Therefore, if the normalization process is carefully performed, the statistical analysis of the E distribution enables to overcome the limitations imposed by the Friedel law.

	Centro	Non-centro	cudmtp	be2
$\langle E^2 \rangle$	1.0	1.0	0.806	0.870
$\langle E \rangle$	0.798	0.886		
$\langle E^2-1 \rangle$	0.968	0.736	0.950	0.792
Amount of $\lvert E\rvert > 1.0$	31.7%	36.8	31.5	33.5
Amount of $\lvert E\rvert > 2.0$	4.6	1.8	5.1	2.9
Amount of $\lvert E\rvert > 3.0$	0.3	0.01	0.5	0.1
			Centro	Non-centro

Lets go back to the phase problem. For Fourier transforms of the electron density G(h), relation in the reciprocal space exists $G(h) = \int G(h')G(h-h')dV^*$. The theoretical basis of the direct methods is the Sayre equation, in which the integral is replaced by a sum over all h’ indices (reflections).

$$E(h) = T\ \Sigma\ E(h')E(h-h')$$

For the centrosymmetric structures, the solution is relatively straightforward. It can be shown that for such structures the phase can have only two values - : 0 or π. That leads to the equation:

$$E(h) = |E(h)|\cos\alpha = |E(H)|\, s(h) \quad \text{where } s(h) \text{ is } +1 \text{ or } -1$$

The Sayre equation for the large values of the normalized structure factors E and a triplet of reflections with indices h, h’ and h-h’ leads to the Σ_2 relationship:

$$s(h) = s(h')s(h-h'),$$

The special case of the above is the Σ_1 relationship, when = 2h’ : s(h) = s(h’)s(h’). This relationship indicates that despite the phase of reflection h’, the phase of reflection h is 0.

For the N-atom structure, probability of the correct phase assignment from the Σ_2 relationship is:

$$p = 1/2 + 1/2 \text{ tgh } [1/N^{1/2} \; | E(h_1)E(h_2)E(h_3)|]$$

Probability increases for reflections with large $E(h_1)$, $E(h_2)$, $E(h_3)$ values, decreases for the large N. That indicates, that direct methods can be used for relatively small structures, but not for proteins. However, for proteins two diffraction experiments can be performed – for the native protein and for the protein derivatized with the heavy ions. If no changes of the protein conformation, the unit cell size and the lattice symmetry occur, the difference between corresponding structure factors F(hkl), resulting from the presence of the heavy atoms, can be calculated. Normalization of these differential structure factors enables the phase determination and localization of the heavy ions.

For the non-centrosymmetric structures, there is no limit for the phase value. The tangent formula of Karle-Hauptmann is used:

$$\text{tg } \alpha(\text{h}) = \frac{\Sigma | E(h')E(h-h')\sin[\alpha(h)+\alpha(h-h')]}{\Sigma | E(h')E(h-h')\cos[\alpha(h')+\alpha(h-h')]}$$

This method of the reflection phase determination can be used for both organic and metal-organic compounds. It should be noted, that the basis of the direct methods is the assumption that all atoms in the structure are identical and have the identical oscillations around the equilibrium positions. If this assumption is too drastic, the method might fail. The other limitation is the normalization, which requires the knowledge of the compound composition in the investigated crystal. Introducing errors at this stage might make the solution of the phase problem difficult or even impossible. The incorrect symmetry might cause averaging of the structure factors not related by the true symmetry, and this can also make the structure solution impossible.

The normalized structure factors E_{hkl} have the same properties as structure factors F_{hkl}. Their inverse transformation leads to the maps of the electron density distribution. In the practice of direct methods, the starting reflections are selected with large values, say E(h) > 2.5, and satisfying the Σ_2, relationships, the initial phases α(h) for these reflections are assigned, then phases of reflections involved in Σ_2 are estimated using the arbitrary probability limit of 99%. Based on the obtained phases, the electron density maps are calculated using E.

$$\rho_{xyz} = \frac{1}{V}\sum_{hkl} |E_{hkl}| \exp i\alpha_{hkl} \exp -2\pi i(hx+ky+lz)$$

After locating atoms on the ρ_{xyz} maps, new phases and better maps are calculated, completing the structure.

$$\rho_{xyz} = \frac{1}{V}\sum_{hkl} |F| \exp 2\pi i\alpha \exp -2\pi i(hx+ky+lz)$$

Considering the type of the structure factors used, we obtain different functions describing the electron density distribution. In all cases, phases φ are calculated based on the coordinates of the localized atoms (direct methods, Patterson).

Function ρ_{calc} describing the calculated distribution of the electron density reflects the current model of the real crystal structure. It is calculated as the inverse Fourier transformation of the calculated structure factors $F_{c,hkl}$ being the sum of the atomic contributions for the known atoms:

$$F_{c,hkl} = \Sigma f\,[\cos 2\pi\,(hx+ky+lz) + i\sin 2\pi\,(hx+ky+lz)] = A + iB$$

$$\rho_{calc} = V^{-1}\sum_{hkl} F_{c,hkl} \exp -2\pi i(hx+ky+lz)$$

Structure factor $F_{o,hkl}$ (F_{hkl} observed) is calculated using the experimental $|F_{hkl}|$ and phase φ_c calculated from the currently known partial structure:

$$Fo = |F| \exp i\varphi_c \qquad \text{where} \quad \varphi_c = tg^{-1}\,[\Sigma f \sin 2\pi\,(hx+ky+lz) \,/\, \Sigma f \cos 2\pi\,(hx+ky+lz)]$$

The observed electron density ρ_{obs} is the inverse Fourier transform of F_o. It is the map of the experimental distribution of the electron density, which originated the diffraction pattern.

$$\rho_{obs} = V^{-1}\sum_{hkl} Fo \exp -2\pi i(hx+ky+lz)$$

Important and very useful is the transform from the difference F_o and F_c, corresponding to the difference $\rho_{obs} - \rho_{calc} = \Delta\rho$ in the density distribution functions. That is called the difference map. The difference of structure factors is calculated as:

$$F_o - F_c = |F| \exp i\varphi_c - \Sigma f_i \exp 2\pi i(hx_i + ky_i + lz_i)$$

$$\Delta\rho(xyz) = V^{-1}\sum_{hkl} (Fo-Fc) \exp -2\pi i(hx+ky+lz) = \rho_{obs}(xyz) - \rho_{calc}(xyz)$$

The difference function is used for completing the structure and correcting the errors. Value $\Delta\rho(xyz) < 0$ indicates that $\rho_{obs} < \rho_{calc}$. Hence in the xyz point of the model, the electron density ρ_{calc} has too high value relative to the real density – the atom too heavy or in the false position. If $\Delta\rho(xyz) > 0$ then $\rho_{obs} > \rho_{calc}$, there is a missing atom at the xyz point of the model or the current atom has too small atomic number. Interpretation of the difference electron density maps allows to find the missing atoms, change of the incorrect atom type, locate hydrogen atoms or correct the molecular conformation

To estimate the solution quality, the discrepancy index is used $R = \dfrac{\Sigma \| F_o | - | F_c \|}{\Sigma | F_o |}$

At initial stages of the model building, R~30%. Well refined small molecular structure have R~2-6%, while for well determined protein structures R should be 10-20%

15. Basic crystallochemistry. Basic types of structures.

The crystal lattice is formed due to interactions between its components. In crystals, one or several different interactions occur – we refer to them as homodesmic and heterodesmic structures. Structures can be single-component (elements) or multicomponent (compounds). Interactions between components in the crystal lattice affect the physical and chemical properties of crystals. Ionic interactions are strong and directionless, satisfying the Coulomb law, and crystals revealing such interactions should dissolve in the polar solvents. The covalent interactions are directional and strong, and crystals having such interactions are usually stable. The metallic interactions can be either strong or weak, but are directionless. Hydrogen bonds are weak and directional. The van der Waals forces are weak, occur in many structures, eg. crystals of gases, but they are the only interactions in crystals of noble gases. Depending on their composition, crystals can also be classified as types A (elements) and crystals of compounds of stoichiometry AB, AB_2 and so on.

Basic types of structures can be derived from structures composed of atoms of the same element. In the most compact two-dimensional crystal lattice, every atom will be tangent to six identical atoms (**Fig. 15.1**). Identity of interactions between atoms results in the formation of the two-dimensional **close packed structure**. Such layer has the hexagonal 6mm symmetry. There are free spaces between atoms, called **interstices**, in which identical atoms of the next layer can be positioned. Interstices are located between three atoms and reveal the 3m symmetry. Size and distances between the interstices in the first layer are such, that only three out of six can be filled with the next layer atoms. So the next layer arrangement can be in one set of interstices of the first layer. The third layer can be oriented on the interstices of the second layer. The layer orientations can be coded with A for the first and B for the second one. The third might be arranged in either A or new C position. Thus periodic crystal can be arranged into ABAB or ABCABC patterns. Energy of interactions between such hexagonal layers is identical for both arrangements, since interstices in each layer are identical. Therefore the possibility raises for irregularities in the orientation of layers, eg. ..ABABCABAB.. with no loss in the interaction energy in the structure. Such phenomenon is known as modulation and is relatively frequent.

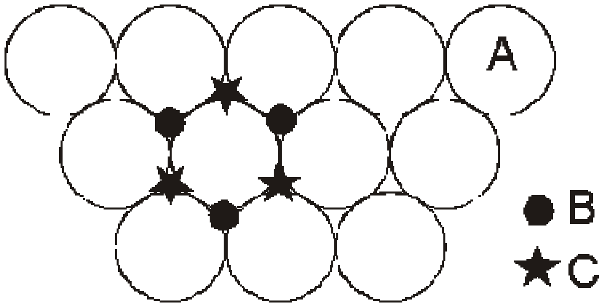


Fig. 15.1

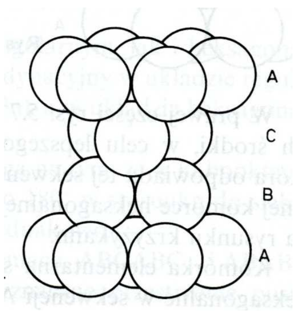


Fig. 15.2

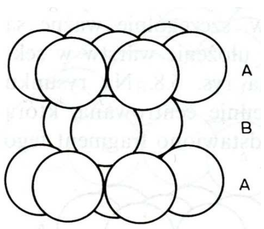


Fig. 15.3

Three-dimensional close packed structures are built up with the hexagonal layers arranged ABAB.. or ABCABC.. (**Fig. 15.2** and **Fig. 15.3**) and reveal the hexagonal or cubic symmetry, respectively. Crystals of metals or noble gases have such structure. In both kinds of structures, the tetrahedral and octahedral interstices occur, the name refers to the symmetry of their environment

(**Fig. 15.4** and **Fig. 15.5**). Many crystal structures are composed of the hexagonal close packed layers formed by one component and atoms of the other component occupying the interstices in the first sub-lattice.

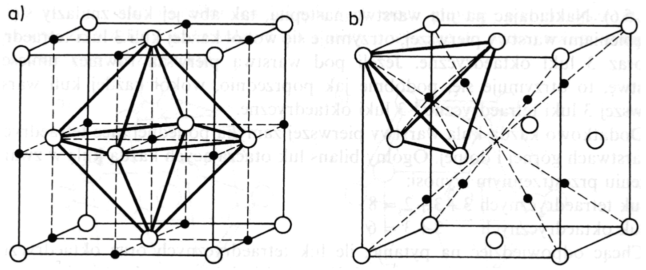


Fig. 15.4.

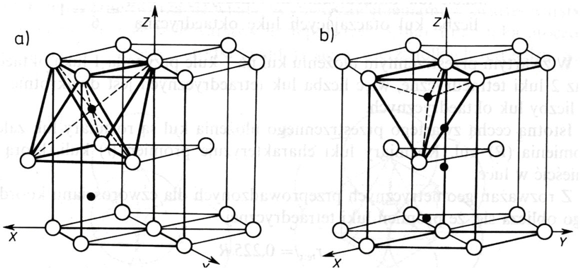


Fig. 15.5.

First type of the close packed structure is the copper type structure. In crystal, the metallic interactions occur. The structure is cubic F, with the layer arrangement ABC (**Fig. 15.6**). Coordinates of Cu atoms are as in the F cell, the space group is Fm3m. The three-fold axes are perpendicular to the hexagonal layers and correspond to the cell space diagonals. The coordination number for Cu atoms is 12 (4+4+4) and the coordination polyhedron is a cubic cubooctahedron. The strongest inter-atomic interactions occur along the face diagonal ([110] and equivalent). Hence for the cell parameter $a_o = 3.615$ Å the length of the metallic Cu-Cu bond is $d_{Cu\text{-}Cu} = a_o\sqrt{2}/2$ and the copper metallic radius is $r_{Cu} = a_o\sqrt{2}/4$. This type of the structure is found for Ag, Au, Ne, Ar.

The **degree of the space filling** can be defined as the quotient of the volume of atoms in the cell and the unit cell volume. Simple calculation (F lattice) gives $V_{at} / V_{cell} = \pi\sqrt{2}/6 = 74\%$

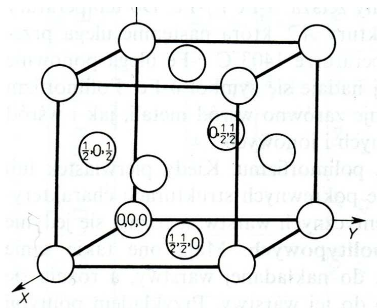


Fig. 15.6.

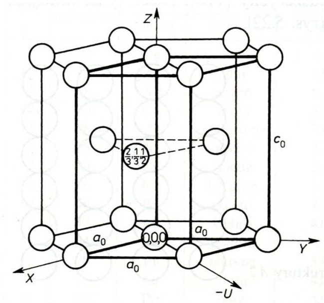


Fig. 15.7.

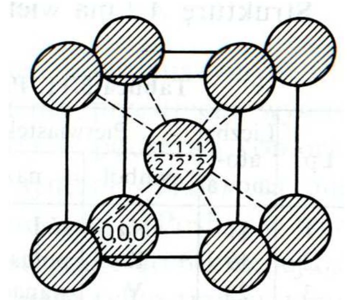


Fig. 15.8

Next type of the close packed structure is the magnesium type with the layer arrangement ABAB (**Fig. 15.7**) and the hexagonal P cell. The coordination number for all atoms is 12 (3+6+3) and the polyhedron is the hexagonal cubooctahedron. The shortest distance between Mg atoms is along the cell edge a_o, the calculated length of the metallic Mg-Mg bond is $d_{Mg\text{-}Mg} = a_o$ and the Mg metallic radius is $r_{Mg} = a_o/2$. Since this is also a close packed structure, the degree of the space filling is identical as for Cu – 74%. Such type of structure is found for H, He, Be, Co, Zn.

The tungsten type structure (**Fig. 15.8**) is not a close packed structure. The inter-atom interactions are metallic. The coordination number for each atom is 8, and the atom distribution is that of the cubic I cell. For the cell parameter $a_o = 3.165$ Å, the W-W bond length can be calculated as $d_{W\text{-}W} = a_o\sqrt{3}/2$ and the metallic radius $r_W = a_o\sqrt{3}/4$. The degree of the space filling (I lattice) gives $V_{at} / V_{cell} = \pi\sqrt{3}/8 = 68\%$. The tungsten type structure has more space for inserting another components modifying the properties, than the Cu or Mg types. This type structure is found for Na, K, Mo, α-Cr, α-Fe.

Lets compare Cu and W metallic radii calculated from the cell parameters and the literature data on their van der Waals radii. For Cu these values are 1.278 and 1.280 Å, and for W they are 1.370 and 1.410 Å. Calculated ratios $r_{Cu}/r_{vdW} = 0.998$ and $r_W/r_{vdW} = 0.972$ indicate the significant differences in the inter-atomic interactions. For the copper structure, shortening of the bond relative to the weak van der Waals interaction is very small, indicating only insignificant interference of atom cores with the electron gas. For tungsten, this shortening is more pronounced, the interference and consequently the electric resistance is much higher than that of Cu. The careful analysis of the structural data can reveal reasons for differences in the physical or chemical properties. This is an important tool for chemistry, physics or the material sciences.

Other structures of elements are structures of diamond (**Figs. 15.9-15.10**) and graphite (**Fig. 15.11**). The diamond structure can be described as a composition of two F lattices shifted relative to each other by ¼ of the cell space diagonal. Distribution of atoms in the first sub-lattice is that of the cubic F lattice, while atoms of the second sub-lattice fill the tetrahedral interstices in the first sub-lattice. Consequently, the coordination number for each C atom is 4, and the polyhedron is a tetrahedron. The structure is homodesmic, formed by the covalent bonds. Thus the hybridization of carbon atoms is sp^3. The C-C bond length is $d_{C\text{-}C} = a_o\sqrt{3}/4$ and can be a standard for a single C-C bond. The covalent radius of C is $r_C = a_o\sqrt{3}/8$. The whole structure reveals the cubic F symmetry. The systematic absences should be calculated in a way that can easily be generalized. The two-atom scattering factor is defined for atom at 000 point and that shifted by ¼ of the space diagonal, which then is used in a calculation for the F lattice:

$$f_{C\text{-}C} = f_C \exp 2\pi i(h0+k0+l0) + f_C \exp 2\pi i(h\tfrac{1}{4} +k\tfrac{1}{4} +l\tfrac{1}{4})$$
$$F_{hkl} = f_{C\text{-}C} [\exp 2\pi i(hx+ky+lz) + \exp 2\pi i(h(\tfrac{1}{2}+x)+k(\tfrac{1}{2}+y)+lz) +$$
$$+ \quad \exp 2\pi i(h(\tfrac{1}{2}+x)+ky+l(\tfrac{1}{2}+z)) + \exp 2\pi i(hx+k(\tfrac{1}{2}+y)+l(\tfrac{1}{2}+z))]$$

The degree of the space filling can be calculated. Apparently, the diamond structure is composed of two close packed cubic structures (F lattices). Number of atoms in the unit cell Z = 4+4. However, calculation gives only $V_{at} / V_{cell} = \pi\sqrt{3}/16 = 34\%$.

The graphite structure is heterodesmic, with the covalent interactions in the grapheme layers and van der Waals interactions between the layers. The coordination number for each atom in the layer is 3, what corresponds to the hybridization sp^2 and results in the aromatic properties of the layer. Distance C-C is approximately 1.42 Å. The inter-layer distance is approximately 3.4 Å, what corresponds to the sum of van der Waals radii. Difference in the interactions inside and inter the layers affects the physical properties. Delocalization and transport of electrons along layers causes the excellent electric and heat conductivity. Such conductivity in the direction perpendicular to the layers is much smaller. Therefore the graphite elements can be either the electric conductors (graphite electrodes) and insulators (electric and heat). Also, the low energy required for the shift of one layer against others causes that graphite is used as a solid lubricant or in pencils. Analyzing the graphite structure, the attention should be paid to the **polymorphism**. That means occurrence of in different crystal forms, with different internal architecture, different unit cell and symmetry for the same substance. The hexagonal graphite has an identical orientation of the 1-st, 3-rd, 5-th layers and so on (AB type arrangement). The ABC arrangement of layers results in the rhombohedral cell of the trigonal system.

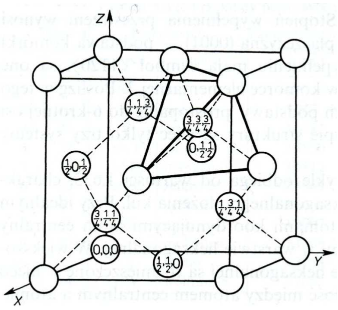


Fig. 15.9

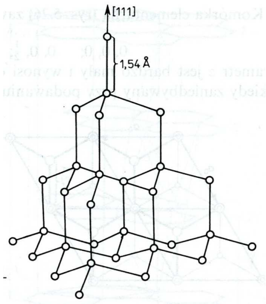


Fig. 15.10

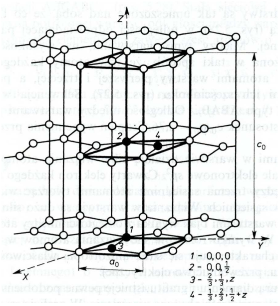


Fig. 15.11

Consider the chemical compounds. One of the basic structure types is that of sodium chloride NACl. It is a homodesmic AB structure with the ionic interactions (**Fig. 15.12**) built up with two cubic F sub-lattices formed by ions of the same charge, shifted relative to each other by ½ of the unit vector. The cubic F structure can be described as the regular F sub-lattice formed by Cl anions, in which the octahedral interstices are filled with Na^+ ions. The coordination number for both Cl and Na is 6, and coordination polyhedron is the cube. The radii of both components can be calculated. Sum of 4 ionic Cl^- radii equals the cell face diagonal, while sum of Cl and Na radii is $a_o/2$. The system of two equation gives $r_{Cl} = a_0\sqrt{2}/4$ and $r_{Na} = a_0/2 - r_{Cl} = a_0/2\ (1 - \sqrt{2}/2)$. For this type of structure, the geometric **condition for stability** can be derived as the ratio of the atom radii:

$$r_k / r_a = a_0/2\ [(1 - \sqrt{2}/2)] / [\sqrt{2}/2] = \sqrt{2} - 1 = 0.41$$

Other compounds crystallizing in the NaCl type structure: KCl, CaO, AgCl, LiF, FeO, MgO

Systematic absences can be derived from the di-atomic scattering factor, used subsequently in the F lattice calculation:

$$f_{NaCl} = f_{Cl} \exp 2\pi i(h0+k0+l0) + f_{Na} \exp 2\pi i(h/2 +k0 +l0) = f_{Cl} + f_{Na} \exp \pi ih$$

Having the ionic radii, one can calculate the degree of the space filling as $V_{Na} + V_{Cl} / V_{cell}$, accounting for 4 ions of each kind present in the cell.

Other type of the structure is the cesium chloride type (**Fig. 15.13**). Structure is cubic P and can be described as the P sub-lattice formed by anions and another P sub-lattice formed by cations, shifted relative to each other by ½ of the cell space diagonal. For each component the coordination number is 8 and the coordination polyhedron is the cube. The structure is homodesmic with the ionic interactions. The bond distance is calculated as $d_{Cs\text{-}Cl} = r_{Cl} + r_{Cs} = a_o\sqrt{3}/2$. :The ionic radii

$r_{Cl} = a_o/2$ and $r_{Cs} = a_o\sqrt{3}/2 - r_{Cl} = a_o/2(\sqrt{3}-1)$

The geometric condition for stability for the CsCl type structure can be derived as:

$r_k/r_a = [a_o/2\,(\sqrt{3}-1)] / [a_o/2] = \sqrt{3}-1 = 0.73$

Such type of structure is fund for: NH_4Cl, CsBr, TlCl, LiAg, LiGa, CuZn

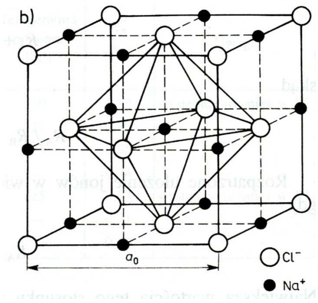


Fig. 15.12

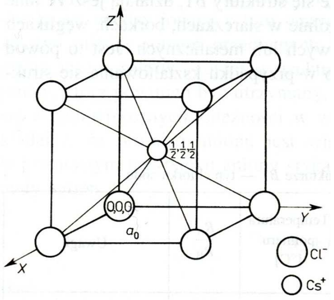


Fig. 15.13.

Another types are the sphalerite type – the cubic form of ZnS (**Fig. 15.14**) and wurtzite – the hexagonal form (**Fig. 15.15**). Thus, crystals of ZnS reveal the polymorphism mentioned previously

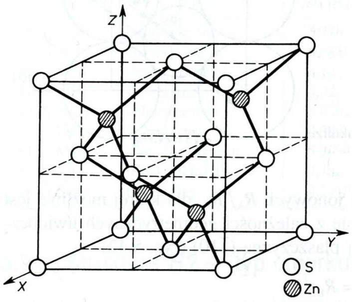


Fig. 15.14

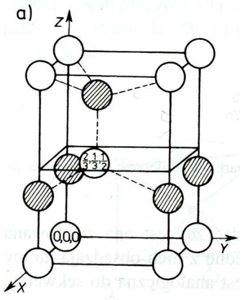


Fig. 15.15.

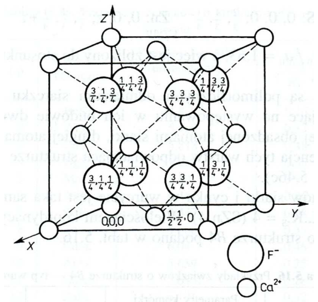


Fig. 15.16.

Both structures are homodesmic. The sphalerite structure is a two-component analogue of the diamond, with the cubic F cell. Tetrahedral interstices of S^{2-} sub-lattice are filled with the Zn^{2+} cations. For both ions, the coordination number is 4 and the corresponding polyhedron is the tetrahedron. The bond length is $d_{Zn\text{-}S} = a_0\sqrt{3}/4$, while the ionic radii:

$r_S = a_o\sqrt{2}/4$ i $r_{Zn} = a_o\sqrt{3}/4 - r_S = a_o/4\,(\sqrt{3}-\sqrt{2})$

Hence, the geometric condition for stability for sphalerite is :

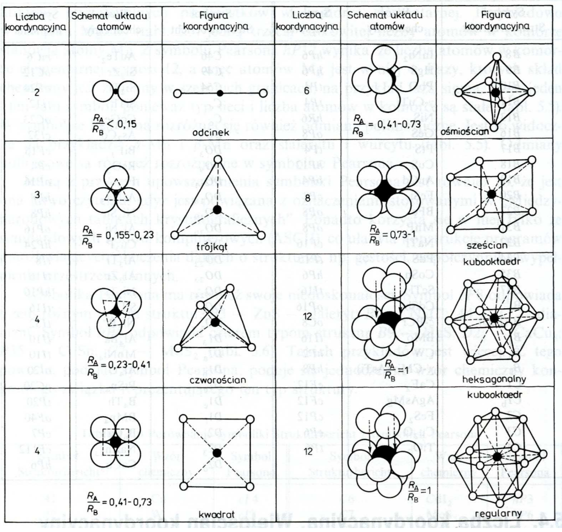
$r_k/r_a = [a_0\sqrt{3}/4)] / [a_0\sqrt{2}/4] = (\sqrt{3}-\sqrt{2})/\sqrt{2} = 0.225$

The wurtzite structure can be treated as the one similar to the Mg structure. It is formed by two P lattices shifted by $u = 1/8\ c_0$ (sub-lattices Mg). The hexagonal layers are formed by Zn or S. The surrounding and the coordination number are identical to those in the sphalerite. The Zn-S interaction is along the Z axis, while the S-S is along the cell a_o edge.

Lets analyze one structure of the AB_2 type – the fluorite CaF_2 structure (**Fig. 15.16**), since it gives few additional aspects to the structure analysis. First, the way of the component identification. One component forms the cubic F sub-lattice, so the unit cell contains 4 such atoms. The second component fills all tetrahedral interstices of the first sub-lattice, thus the cell contains 8 atoms of that type. The fluorite stoichiometry unequivocally indicates that the first sub-lattice is formed by Ca^{2+}, while the second with F^-. Surrounding of each type ion is different. For Ca^{2+} cations, the coordination number is 8 with the cube as the coordination polyhedron. For anions, the coordination number 4 corresponds to the coordination tetrahedron. The Ca-F bond distance can be calculated as $d_{Ca\text{-}F} = r_{Ca} + r_F = a_0\sqrt{3}/4$, while the ionic radii:

$$r_F = a_0\sqrt{2}/4 \qquad r_{Ca} = a_0\sqrt{3}/4 - r_F = a_0/4\,(\sqrt{3} - \sqrt{2})$$

Notice another conclusion derived from the structure comparison. Comparison of the geometric condition for stability with the coordination number indicates, that the larger difference between the component radii occurs, the smaller coordination number and different coordination polyhedron are found (**Fig. 15.17**). This dependence enables to certain degree to anticipate the matter distribution, at least in the simple structures.



Liczba koordynacyjna	Schemat układu atomów	Figura koordynacyjna	Liczba koordynacyjna	Schemat układu atomów	Figura koordynacyjna
2	$\frac{R_A}{R_B} < 0,15$	odcinek	6	$\frac{R_A}{R_B} = 0,41\text{-}0,73$	ośmiościan
3	$\frac{R_A}{R_B} = 0,155\text{-}0,23$	trójkąt	8	$\frac{R_A}{R_B} = 0,73\text{-}1$	sześcian
4	$\frac{R_A}{R_B} = 0,23\text{-}0,41$	czworościan	12	$\frac{R_A}{R_B} = 1$	kubooktaedr heksagonalny
4	$\frac{R_A}{R_B} = 0,41\text{-}0,73$	kwadrat	12	$\frac{R_A}{R_B} = 1$	kubooktaedr regularny

Concluding, the above analysis of the basic structure types illustrates only few conclusions that can be derived from the structural data. In practice, for each investigated structure, the most important geometrical features have to be defined and discussed in context of chemical or physical properties. Author hopes, that this course of crystallochemistry helped the participants in preparation for such task.

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