

MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
NATIONAL TECHNICAL UNIVERSITY OF UKRAINE
«IGOR SIKORSKY KYIV POLYTECHNIC INSTITUTE»

T. A. Dontsova
S. V. Nahirniak

STRUCTURAL INORGANIC CHEMISTRY

*Approved by the Academic Council of National Technical University of Ukraine
«Igor Sikorsky Kyiv Polytechnic Institute» as Manual for Bachelor students of the specialty
161 «Chemical technologies and engineering», specialization «Chemical technologies of
inorganic substances and water purification»full-time education*

Kyiv
Igor Sikorsky Kyiv Polytechnic Institute
2019

Reviewers: **Ogenko V. M.**, *Dr. Sci. (Chem.), Prof.*
V.I. Vernadsky Institute of General and Inorganic Chemistry,
National Academy of Sciences of Ukraine
Perekos A.O., *PhD (Phys.-Math.), Senior Researcher*
G.V. Kurdyumov Institute for Metal Physics
National Academy of Sciences of Ukraine

Responsible editor **Astrelin I. M.**, *Doctor of Sciences, Professor*

The Grief is provided by the Academic Council of
Igor Sikorsky Kyiv Polytechnic Institute
(Protocol № 7 from 24.06.2019)

Electronic educational edition

Dontsova Tetiana Anatoliivna, PhD, Associate Professor
Nahirniak Svitlana Valeriivna, PhD, Assistant Professor

STRUCTURAL INORGANIC CHEMISTRY

Structural inorganic chemistry [Electronic resource] : Textbook for Bachelor students of the specialty 161 «Chemical technologies and engineering» / Igor Sikorsky Kyiv Polytechnic Institute; the authors: T. A. Dontsova, S. V. Nahirniak – Electronic text data (1 file: 4,89 MB). – Kyiv: Igor Sikorsky Kyiv Polytechnic Institute, 2019. – 194 p.

Annotation

The textbook contains sections: «Introduction to the structural inorganic chemistry», «Geometric crystallography», «Crystal chemistry» and «Structural crystallography». The textbook is considered the importance of the solid state in the inorganic chemistry, the structure of different types of crystals, their symmetry and the connection with the properties of matter, the spatial arrangement and the chemical bond of atoms in crystals, etc. The methodical recommendations for implementation of practical works containing brief theoretical information, examples and tasks for independent performance are given; the recommendations for the control home work and independent study of this discipline are given. The textbook is for providing study of the discipline «Structural inorganic chemistry», which is taught for Bachelor students of the specialty 161 «Chemical technologies and engineering», specialization «Chemical technologies of inorganic substances and water purification».

© Dontsova T. A., Nahirniak S. V., 2019
© Igor Sikorsky Kyiv Polytechnic Institute, 2019

CONTENT

INTRODUCTION	6
CHAPTER 1. INTRODUCTION TO THE INORGANIC STRUCTURAL CHEMISTRY	8
1.1. The emergence of the structural chemistry	8
1.2. General information	13
1.3. General structural chemistry of substances.....	14
1.4. The importance of the solid state in the inorganic chemistry	14
Control questions	15
CHAPTER 2. GEOMETRIC CRYSTALOGRAFY	16
2.1. Crystal and its properties.....	16
2.2. Crystallographic indexing	26
2.3. The crystallographic projections	33
2.4. Symmetry and elements of crystals symmetry	43
2.5. The crystal systems	50
2.6. Symmetry classes, systems of notation and spatial groups	59
2.7. Simple forms	66
Control questions	75
CHAPTER 3. CRYSTAL CHEMISTRY	77
3.1. Types of chemical bonding in crystals.....	77
3.2. Atomic and ionic radius	83
3.3. Coordination numbers and coordination polyhedra.....	88
3.4. Structural and formula units.....	90
3.5. The closest packing in crystals.....	92
3.4. Features of the structure of ionic and covalent crystals.....	97
3.5. Polarization	100
Control questions	101
CHAPTER 4. STRUCTURAL CRYSTALOGRAPHY	102
4.1. Classification of structures and crystals.....	102
4.2. Description of some crystalline structures	107
Control questions	123
PRACTICAL WORKS	124
Practical work 1. The crystallographic indexing	124

Brief theoretical information.....	124
Examples of the crystallographic indexing of nodes, rows and planes ..	128
Tasks for the individual work	129
Practical work 2. Description of crystal models	131
Examples of the description of some crystal models.....	131
Tasks for the individual work	133
Practical work 3. Dimension of the crystals and simple forms	134
Brief theoretical information.....	134
Examples of the crystal's dimension and determining its simple forms.....	145
Tasks for the individual work	146
Practical work 4. Calculation of the crystallochemical radii of compounds	146
Brief theoretical information.....	146
Examples of calculation of the crystallochemical radii	148
Task for the individual work.....	149
Practical work 5. Determination of the coordination numbers and coordination polyhedra	154
Brief theoretical information.....	154
Examples of the determination of coordination numbers and coordination polyhedra.....	156
Tasks for the individual work	158
Practical work 6. Determination of the stoichiometric formula of the substance	160
Brief theoretical information.....	160
Examples of the determination of structural and formula units.....	161
Tasks for the individual work	163
METHODOLOGICAL RECOMMENDATIONS FOR THE IMPLEMENTATION OF THE home test WORK (HTW).....	166
Basis thesis	166
Example of the implementation of the HTW practical part.....	167
Task variants for the HTW.....	172
REFERENCE	173
APPENDICES	175
Appendix 1. Space groups.....	175

Appendix 2. Atomic and ionic radii.....	179
Appendix 3. Important inorganic structures	180
Appendix 4. The values of the internuclear distances in metals.....	189
Appendix 5. Elementary cells of crystalline structures	190

INTRODUCTION

The textbook on the discipline «Structural inorganic chemistry» is developed in accordance with the curriculum of bachelor's training and is intended to provide students with the ability to use basic concepts in the field of structural inorganic chemistry, in particular, crystallography and crystallochemistry, for the successful mastering of disciplines in the technology of inorganic materials from the point of view of material science. The textbook allows to use the acquired knowledge and practical skills to analyze inorganic solids in order to establish the «structure-property» relationship.

The discipline «Structural inorganic chemistry» is the basis for profile disciplines in the curriculum of bachelor's degree in professional direction «Chemical technologies of inorganic substances and water purification» and consists of one credit module. The lecture course and methodical recommendations on practical individual work and home test work are presented.

The course materials contain 4 sections, which consider the emergence of structural chemistry; definition of terminology; features of the crystalline state structure; symmetry of crystals and crystallographic formulas; existing patterns between the type of chemical bond and the structure of crystals; typical inorganic structures. The basics of structural inorganic chemistry, crystallography and crystallochemistry, which are necessary for students understanding the influence of the internal structure on the finite properties of substances, are covered.

The «Structural inorganic chemistry» discipline provides practical classes, which have own peculiarities, they are covered in the textbook in the methodical recommendations for the implementation of practical work. According to the discipline program of «Structural inorganic chemistry» students independently carry out the home control work, therefore, the textbook gives detailed recommendations for its preparation.

Consequently, this textbook allows students to master theoretical knowledge of the substances structure and features of the composition of crystalline substances, general principles of the crystals structure and the classification of crystalline structures, features of the geometry and symmetry of molecules and crystals even during independent study of the discipline. Students will also learn to establish connections between the crystals structure and the nature of the chemical interaction of atoms, the crystalline structure and the physical and chemical properties of crystalline substances.

CHAPTER 1. INTRODUCTION TO THE INORGANIC STRUCTURAL CHEMISTRY

1.1. The emergence of the structural chemistry

In the first half of the XIX century, the fundamentally new concept of chemistry – the structural chemistry was born. It is based on the fact that the matter's properties are determined not only by its composition, but also by the structure, that is, the order of the atomic and spatial locations.

The first structural representations arise with *Dalton's* atomic theory and the electrochemical theory of *Berzelius*. *Dalton* was developing the theory of "complex atoms" formation from "simple atoms", based on empirical stoichiometric laws, *Berzelius* was considering some problems of structural chemistry – adhesive forces, the position of atoms, and others, which later became the fundamental issues of the structural chemistry [1–3].

The appearance of the structural chemistry is referred to the discovery of the isomerism phenomenon in organic chemistry. In 1825, *Johann Justus von Liebig* discovered that the elemental composition of the fulminic acid corresponds to the composition of the cyanic acid, which *Friedrich Wöhler* received a year earlier. Repeated analyzes conducted by *Wöhler* and *Liebig* clearly identified the existence of substances that are identical in composition, but different in properties. In 1830, *Jöns Jacob Berzelius* found that grape and tartaric acid also have the same composition, but differ in their properties.

Berzelius proposed the term «isomerism» (from the Greek $\text{ισοζ\text{ }\mu\text{ε}\text{ρ}\text{ο}\text{ν}}$ – equal measure) for the discovered phenomenon. It soon became clear that this phenomenon is very common in the organic chemistry. The composition of organic substances includes the relatively small number of elements – carbon, hydrogen, nitrogen, oxygen, sulfur and phosphorus, but organic materials have the large variety of

properties. Therefore, during almost the entire XIX century, the structural representations were in demand, above all, in organic chemistry¹.

Theories of the structural chemistry. At that time the *Berzelius* presentation of radicals was the base for the question of the organic matter structure – polar groups of atoms, which are able to transfer from one substance to another without change. *The theory of complex radicals* originated in 1832 and has been actively developed by many chemists, including *Liebig* and *Wöhler*. The number of the described radicals has grown rapidly. The theory of complex radicals proceeded from the assumption that radicals are capable of independent existence, although chemists could not separate them. *Berzelius* wrote about this: «The reason why we can not isolate radicals is not that they do not exist, but that they connect too fast» [2].

A little later, in 1834, French chemist *Jean Baptiste André Dumas*, in studying the reaction to obtain chlorine ($C_2H_3Cl_3O$) from ethanol (C_2H_6O), described the phenomenon of metalepsis², which consists in the fact that at the substitution reactions the preservation of the basic properties of the substance is observed. *Dumas* (co-author of *Liebig* for the article about the radicals) initially did not attach much importance to the discovered phenomenon, but after receiving the chloroacetic acid in 1839, reconsidered own views. The phenomenon of metalepsis was radically contradicted to the *Berzelius* electrochemical dualism; however, it was well coordinated with the *Mitscherlich* law of isomorphism. After this, *Dumas* in his work developed the idea that the properties of compounds are determined only by the arrangement of atoms in the molecule, but not by their nature. Therefore, according to *Dumas*, the chemists should deal with the location of atoms in the molecule [3].

After a while, French chemists *Charles Frederick Gerard* and *Auguste Laurent* developed the new theory. In the 40s of XIX century, *Gerard* and *Laurent* offered the fundamentally new understanding of the molecule of chemical compound as the unitary (single) system. But their assumption that the value of electrostatic forces

¹ It should not be equated the concept of "structural chemistry" and "organic chemistry".

² Replacement of hydrogen with halogens in the organic compounds.

exaggerated caused sharp criticism from *Berzelius* and other supporters of electrochemical dualism. And only in 50s of the XIX century (after the *Berzelius* death) the views of *Gerard* and *Laurent* in the form of unitary theory were recognized. Then, in 1852, *Gerard* formulated the provisions of the new theory of types (the theory of *Gerard-Laurent* types), which, based on the unitary approach, included the idea of the complex radicals and *Dumas* ideas about the molecules types.

New *theory of types* spread in 50s of the XIX century. It allowed to systematize organic compounds, the list of which was rapidly increasing and, most importantly, led to the discovery of many new compounds (in particular, the existence of carboxylic anhydrides was predicted by *Gerard* on the basis of this theory). The new theory of types developed in the works of many scientists, but it also could not fully satisfy chemists [4].

The next stage in the development of structural chemistry was the *theory of valence*, which to the certain extent represented the rejection of unitary representations. However, it is the theory of *Gerard-Laurent* types that led chemists to the idea of the affinity unit of atoms and radicals, based on which the theory of valence was created. The emergence of the valence concept usually associated with the name of English chemist *Edward Frankland*, who was the supporter of the theory of complex radicals, while studying organometallic compounds, he came to the conclusion that it was necessary to reconsider the theory of radicals and recognize certain provisions of the theory of types. Developing the ideas expressed by *Gerard*, *Laurent*, *Odling*, *Williamson* and other ideas about the relationship between the equivalence of atoms and the equivalence of radicals, *Frankland* in 1852 proposed the introduction of the concept of the "connecting force" of atoms. *Friedrich August Kekule* played the decisive role in the creation of the theory of valency. Mitova I. Ya. and Samoilov AM in [4] recall that in 1857, *Kekule* in his article in the new way discovered the theoretical meaning of the three main types of compounds of *Gerard* – hydrogen, water and ammonia: the number of atoms of one element, connected with one atom of another, depends on the basicity or degree of kinship. According to

Kekule, the basicity is the fundamental property of the atom, and it is as constant and unchanging as atomic weight.

In 1858, *Couper's* views were almost identical with *Kekule's* ideas, however, unlike *Kekule*, *Couper* believed that some elements were capable of detecting variable valence: carbon is characterized by two degrees of affinity: lower in CO and higher in CO₂. The theory of valence, in spite of the fact that *Kekule* came to it as the development of the theory of *Gerard-Laurent* types, completely differently interpreted the idea of the molecule integrity, namely, only as the inability to divide it into independently existing radicals. In other words, the theory of valence originally represented the molecule aditically. Already three years later, in September 1861, the Russian chemist *Alexander Butlerov* introduced the most important additions to the theory of valence. In the report «On the chemical structure of matter» read at the Congress of German naturalists and doctors in Speyer, he outlined his theory of chemical structure. Yu. I. Soloviev wrote about this in his «History of Chemistry. The development of chemistry from ancient times to the end of the XIX century» [5]. The main provisions of this theory *Butlerov* formulated as follows:

1. «Considering that for each chemical atom only the certain and limited quantity of chemical force (affinity) with which it participates in the formation of the body is inherent, I would call this chemical bond the chemical structure, or the method of the interconnection of atoms in the complex body»;
2. «The chemical nature of the complex compound is determined by the nature of the elementary components, their number and the chemical structure».

While leaving open the question of the most convenient appearance of the chemical structure formulas, *Butlerov* spoke about their content: «...when the general laws of the dependence of chemical properties of bodies on their chemical structure will become known, then such formula will be an expression of all these properties». At the same time, *Butlerov* was convinced that structural formulas cannot be simply the conditional representation of molecules, but should reflect their real structure. He emphasized that each molecule has the well-defined structure.

The great advantage of the theory of chemical structure was the possibility of the molecule visualization. The history of the graphical image of the valence and chemical bonding itself is extremely interesting.

Stereochemistry. The most important stage in the development of structural chemistry was the discovery of the spatial structure of molecules. The emergence of stereochemistry was due to the number of discoveries that seemed to have no relation to chemistry. For example, in 1801, *Thomas Young* conducted experiments that proved the wave nature of light; *Auguste Jean Fresnel* around 1814 showed that light waves belong to the type of transverse waves, thereby he explained the nature of the plane-polarized light that was discovered in 1808 by *Etienne Louis Malus*; in 1815 the French physicist *Jean-Baptiste Biot* discovered the phenomenon of optical activity of some substances, while the isomeric wine and grape acid (tartaric acid rotates the plane of polarization of light to the right, grape acid – optically inactive), isolated by *Berzelius* in 1832, became the first example of optical isomerism.

Coordination chemistry. For the long time, the theory of valency was used mainly for organic compounds. However, soon enough structural representations were in demand in the inorganic chemistry also, namely, in the chemistry of complex compounds. Theoretical representations of this section of inorganic chemistry were formed on the basis of studying the properties of complexes obtained by the interaction of transition metal salts with ammonia. The first step on the path to coordination chemistry was the ammonia hypothesis of *Thomas Graham* (1840). The next step was the chain theory, which was proposed in 1869 by *Christian Wilhelm Blomstrand*. In 1893, the Swiss chemist *Alfred Werner* published the article «On the structure of inorganic compounds», in which he outlined the main provisions of his coordinating theory. *Werner* was already known for his work on stereochemistry of organic compounds of nitrogen and his theory significantly developed the idea of chemists about the valence of elements [6].

1.2. General information

Structural chemistry is the branch of chemistry, which studies the relationship of physical and chemical properties of substances with their chemical structure (atomic and spatial arrangement) and reactivity. Consequently, structural chemistry research the geometric structure of molecules, examines the lengths of chemical bonds, valence angles, coordination numbers, conformations, and molecular configurations; the effects of their mutual influence, etc.

The subject of structural chemistry is the atomic (spatial) and electronic structure of substances and factors on which it depends, as well as the influence of structure on physical and chemical properties, that is, the regularities of type: composition-structure-properties.

Methods of structural chemistry:

- 1) experimental: diffraction and spectroscopic research methods;
- 2) theoretical: calculations, such as the method of molecular orbitals, the theory of functional electronic density, and others;
- 3) qualitative and semi-quantitative: statistical analysis and generalization of already decrypted structures, analysis and various calculations of volumetric ratios, stabilization energy, molecular orbitals and valence bonds, etc.

Crystallography is the science of crystals, their structure, origin and properties, which is closely related to mineralogy, solid state physics and chemistry. Crystallography is divided into geometric and structural.

Crystal chemistry is the science about crystalline structures and their relationship with the nature of substances. Crystal chemistry studies the spatial location and chemical bonds of atoms in crystals, as well as the dependence of the physical and chemical properties of crystalline substances on their structure. Crystal chemistry is closely related to crystallography.

1.3. General structural chemistry of substances

General structural chemistry of any compound can be represented in the form of the scheme depicted in Figure 1.1. It includes the structure of the substance in various aggregate states, structural changes occurring in the phenomena of melting, evaporation, dissolution, as well as other changes occurring in the solid, liquid or gas state.

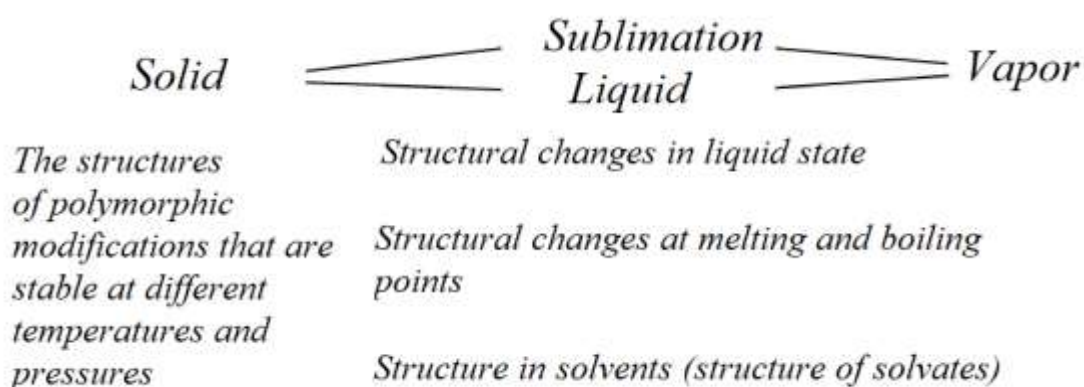


Figure 1.1. General structural chemistry of substances

1.4. The importance of the solid state in the inorganic chemistry

Most of the compounds (almost 90%) are solid under normal conditions; this is also true for the most inorganic compounds. It is known that the significant part of important reagents – liquids, gases or solutions, but in general, they form the small fraction of inorganic compounds. In view of the fact that chemical reactions usually occur in the solution or in the gaseous state, most of the products are solids.

The solid state is characterized by the short-range and long-range orders simultaneously. Under *the short-range order*, it understand the particular environment of the particular structural unit (atom, ion) in the crystal lattice, as well as in the molecule. Under *the long-range order* it understand the spatial arrangement of structural units, their complete (crystalline state) or incomplete (amorphous state) subordination to the laws of the spatial lattice.

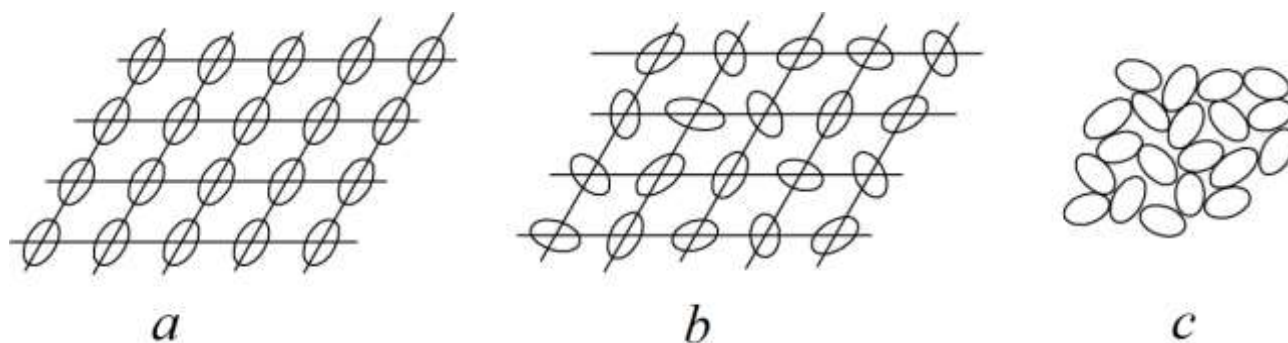


Figure 1.2. The arrangement of particles: completely ordered structure (crystal) (a); structure with the long-range order, but without the short-range order (gas-crystalline state) (b); structure without the order (liquid crystal state) (c) [2]

Control questions

1. Name and describe the main stages of the development of the structural chemistry.
2. Describe the general structural chemistry and methods used to study the substance's structure.
3. Give the definition of the notions «crystallography» and «crystallochemistry».
4. Identify the notion «complete structural chemistry of matter».
5. Justify the importance of the solid state of matter; give its important characteristics.

CHAPTER 2. GEOMETRIC CRYSTALOGRAFY

2.1. Crystal and its properties

Crystals are bodies in which material particles (atoms, ions, molecules) form the ordered periodic structure.

Crystals are divided into monocrystals and polycrystals. Correct polyhedra crystals are monocrystals. Examples of these monocrystals are shown in Figure 2.1 [7]. Most crystalline substances are known as crystalline aggregates (crystallites) – polycrystals.

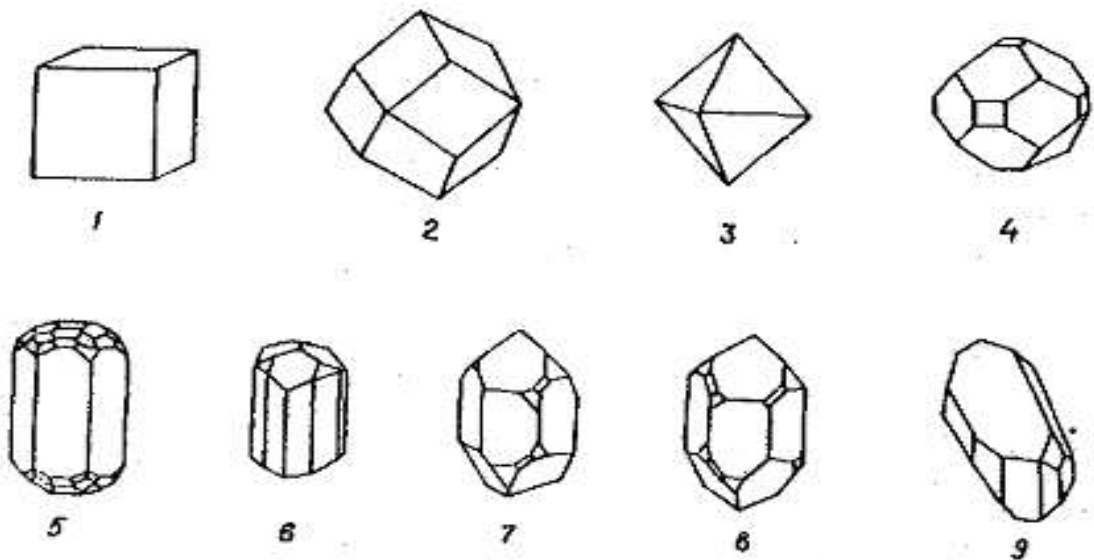


Figure 2.1. Monocrystals: rock salt (1); pomegranate (2); diamond (3); alums (4); beryl (5); tourmaline (6); left quartz (7); right quartz (8); copper sulfate (9) [7]

The ways of growing single crystals include: methods of growing from solutions, melts, from the gas phase, methods of gas transport reactions.

The determining factor of the crystallinity of materials is its internal structure, that is, the character of the arrangement of atoms, ions, or molecules in space. The characteristic feature of the crystalline materials is that atoms, ions, or molecules are placed in the strictly natural way, that is, they form certain types of structures in which the distances between individual structural elements in different directions are

constant (Figure 2.2). Structural elements connect in the certain order, form the spatial lattice (structure) consisting of separate parallelepipeds – elementary Bravais lattices (Table 2.3).

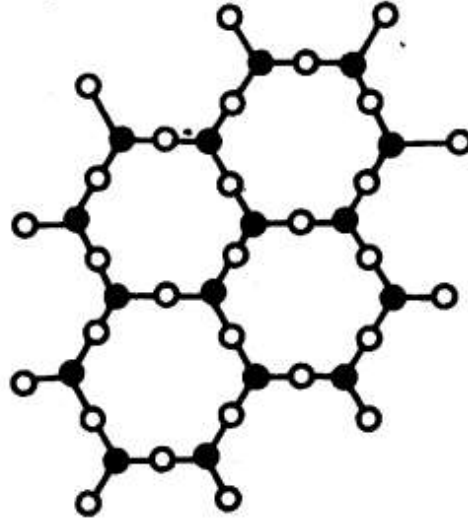


Figure 2.2. The nature of the ions placement in crystalline quartz

The elementary cell is the smallest parallelepiped that retains all the properties of the crystal. Its parallel movement in the space on the integer number of edges allows obtained the entire crystal.

Each elementary cell is characterized by two types of parameters: linear and angular (Figure 2.3).

Linear parameters a , b , c are the distance between the closest spatial nodes of the elementary cell on three axes of coordinates x , y , z . These distances in three-way can be either the same or different. They are measured in angstroms or nanometers.

Angular parameters α , β , γ are the angles of the slope of spatial rows, which coincide with the coordinate axes x , y , z . Theoretically, they can vary from 0° to 180° .

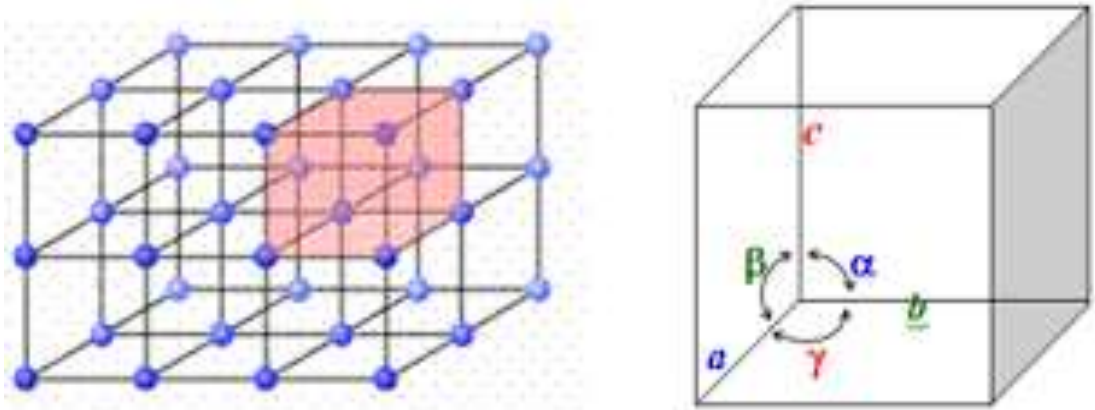


Figure 2.3. Elementary cell and its parameters [8]

The example of cubic elementary cells in substances of different structure is represented by Figure 2.4.

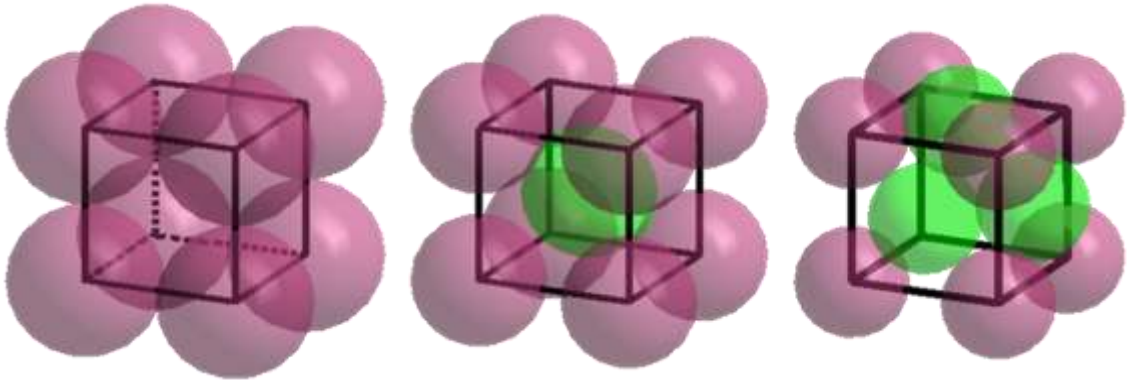


Figure 2.4. Elementary cubic cell in substances [8]

The main components of the elementary cell are [7]: spatial node, spatial row, flat mesh.

Spatial node is the point near the vertex or elsewhere in the elementary parallelepiped, which is filled with atoms, ions or molecules (Figure 2.5, *a*).

Spatial row is the set of unambiguous or diverse nodes placed along the straight line, which are repeated at regular intervals of length (Figure 2.5, *b*, *c*). Accordingly, the number of spatial rows in spatial lattices are very large.

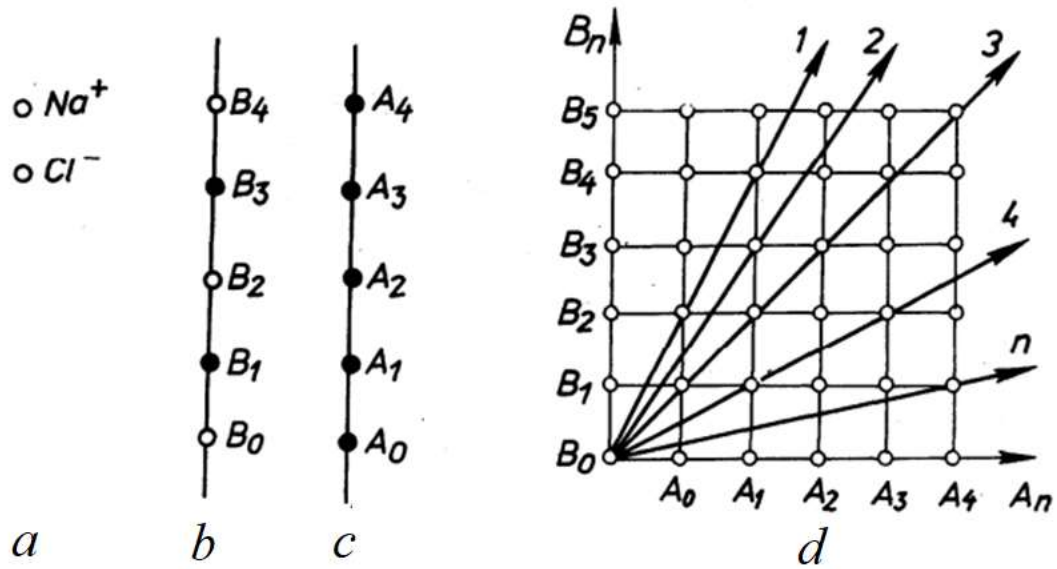


Figure 2.5. Elements of the crystalline structure [7]: spatial nodes (a); spatial row nodes (b) and (c); flat mesh (d)

Flat mesh is a system of spatial units located in one plane at certain distances from each other in two directions (Figure 2.5, d). Flat meshes are placed in different directions of the spatial cell.

All crystalline polyhedra have geometric form, which is characterized by faces, edges and vertices (Figure 2.6), which are called elements of the crystals structure.

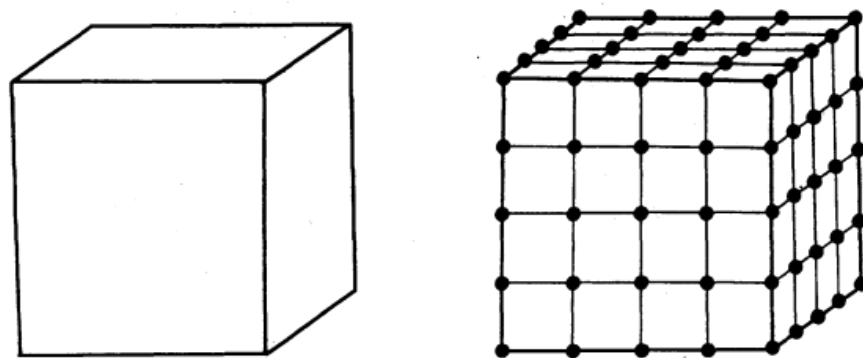


Figure 2.6. Correlation between elements of the crystal display (ribs, vertices, faces) and elements of the spatial lattice (nodes, spatial rows, flat meshes) [7]

In the ideal form *faces* are flat surfaces of various form and sizes and correspond to flat grids of spatial lattices. Based on the fact that flat mesh has two-dimensional structure in space, and atoms, ions or molecules, which form it, lie in the

same mathematical plane, one of the laws of geometric crystallography was formulated. It was the law of plosogonality: "The face corresponds to the flat mesh of the real crystal and it is the ideally equal mirror surface".

Ribs are ideally represented by straight lines formed at the intersection of two faces and at the microlevel corresponding to spatial rows of lattices. The number of ribs and their size are in direct dependence on the internal structure of the crystal.

Tops are places of intersection of the ribs of the crystal. They correspond to spatial nodes.

Between faces, edges and tops there is the certain quantitative interdependence, known as the Euler-Descartes law, which has the following expression: $\sum \text{faces} + \sum \text{tops} = \sum \text{ribs} + 2$. On real crystals, faces, edges and tops are often complicated by various dislocations that acquire the distorted form.

The law of constancy of interfacial angles (XVIII century) is as follows: the corners between the corresponding faces (and ribs) in all crystals of the same substance are constant. This is the fundamental law of crystallography, which is based on diffraction methods of real crystals investigating.

Depending on the crystal's growth conditions, the number, shape and size of the faces vary (Figure 2.7). Only the angles between the corresponding faces remain unchanged with the growth of the crystal.

In accordance with the above law the crystals of the certain substance are characterized by their specific angles, therefore, in most cases, measuring the angles can prove the affinity of the investigated crystal to the certain substance. Hence it is clear what significance is the knowledge of the law of constancy of angles in the history of the crystals study.

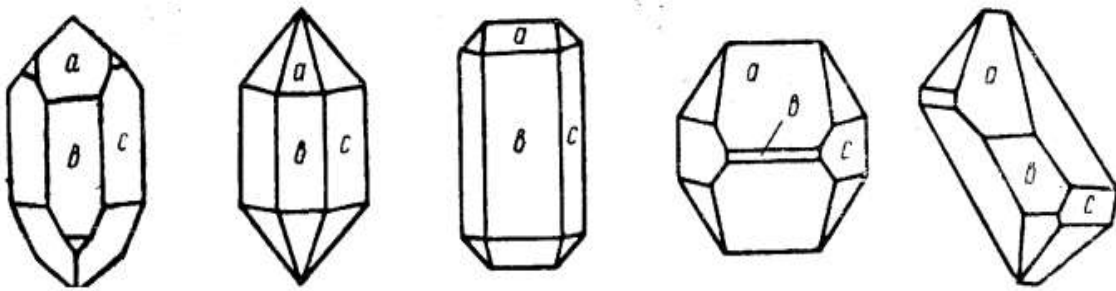


Figure 2.7. The external form of various quartz crystals (a-, b-, c-faces) [7]

Important properties of crystals. The important properties of crystals are *homogeneity* and *anisotropy*. In planes of the asymmetric crystal lattice, atoms are placed at different densities, this heterogeneity leads to the fact that many properties of crystals depend on the direction. Mechanical, optical, electrical and other properties of crystals in different directions are not the same.

Homogeneity is the property of the body characterized by the same physical and chemical properties in the whole volume. Anisotropy is the property of the body in which there is the distinction in the properties of the medium in different directions, while for some properties the medium can be isotropic, for others it is anisotropic (Figure 2.8).

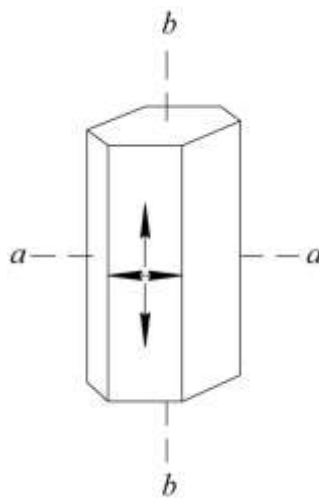


Figure 2.8. Differences in the properties of the crystal in dissimilar directions (in the direction *aa* hardness is greater than in the direction *bb*)

The crystalline structure is inevitably related to anisotropy due to the inequality of the gaps between atoms in different directions. Even in the crystal of sodium chloride (Figure 2.9), which has the shape of the cube, strength in different directions is not the same. If you cut the rods in the different directions shown in the figure, then the force required for their break will be different.

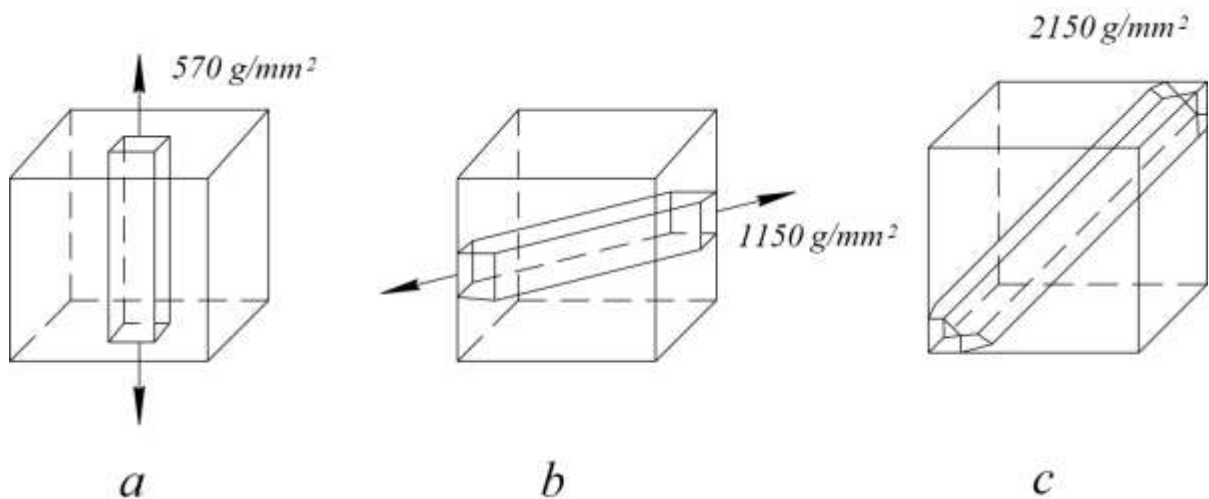


Figure 2.9. The strength of the crystal of NaCl salt in different directions (*a*, *b*, *c*) [9]

This example is illustrative. Crystals of other materials do not have such a characteristic anisotropy, but all crystals have anisotropy to the certain extent.

Generation, growth and destruction of crystals. The location of particles in some simple crystalline structures gives the approximate understanding of the processes that lead to the formation of crystals. For example, NaCl crystals crystallize from aqueous solutions due to the grouping and alternation of positive particles with negative ones. Numerous examples of crystallization from the liquid state (ice is formed from water, pieces of metal from its melt, and others) are also known. There are also known cases of crystals formation from the gaseous state (condensation), for example, ice sheets and rains of salts on chemical dishes. Also, crystalline materials can be formed from solids, for instance, the crystalline glass (transition of amorphous state to crystalline), the obtaining of other modifications (recrystallization).

Under laboratory conditions, the crystals are mostly obtained from solutions, but in this way polycrystals are usually obtained. The monocrystals can also be obtained from solutions, but most often they are obtained from melts or gas phase.

When growing monocrystals from aqueous solutions, you need to follow these guidelines:

- 1) selected for growing crystals, the reagent is crushed;
- 2) the crushed powder is dissolved in 100 ml of water;
- 3) the solution is heated to the full dissolution of the reagent;
- 4) the solution is filtered off from the impurities;
- 5) the filtrate transfer to the crystallizer;
- 6) the best crystals are separated from the solution the next day;
- 7) the old solution to pour, and the new pour;
- 8) selected crystals are placed in the new solution;
- 9) the following sequence of actions repeated several times.

Observing the growth of crystals, you can notice some interesting phenomena. Some of them are visible to the naked eye, some are visible under the microscope. What is this phenomenon? First, growth is due to new layers of matter, which are built parallel to ourselves; secondly, the growth rate of different faces is different; thirdly, due to the growth of the faces parallel to ourselves, the angles between all faces remain constant.

You can also observe how some faces become larger, while others disappear. Figure 2.10 shows how the BC face disappears due to the lower growth rate of this face compared with the AB and CD faces.

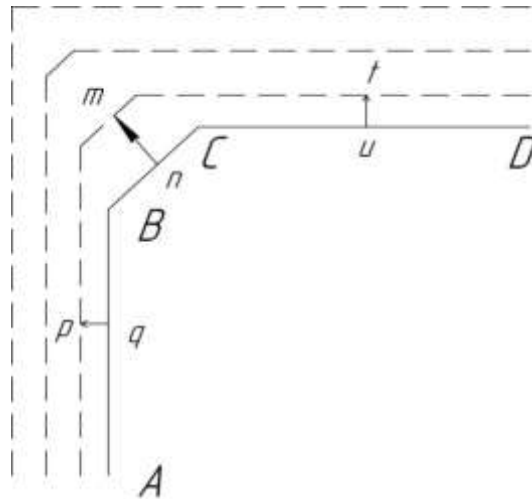


Figure 2.10. The effect of the face disappearance in the process of the crystal's growth [9]

Observing the speed of the faces growth, the law was invented: in the process of crystal growth dominated faces which atomic meshes are densely covered with material particles. On the other hand, the slow growth of the face contributes to the increase of their surface. On this basis, one can notice that the faces, which contain the largest amount of material particles, are likely to have the lowest rate of growth. The latter is due to the fact that the forces between the particles in the plane of the face, on which the largest number of material particles, is greater than the forces between particles of different faces (planes), therefore such faces grow more slowly. However, it should be noted that the growth of crystals affects absolutely everything: concentration, pressure, temperature, the presence of other ions, which eventually leads to the formation of different crystals in the form of various defects (Figure 2.11).

The external shape of crystals, undoubtedly, also dependent on the concentration streams that occur in the formation or dissolution of crystals. This is due to the fact that in the crystallization zone (or dissolution) the density of the solution decreases (or increases), and there is the concentration alignment that causes the formation of these concentration streams.

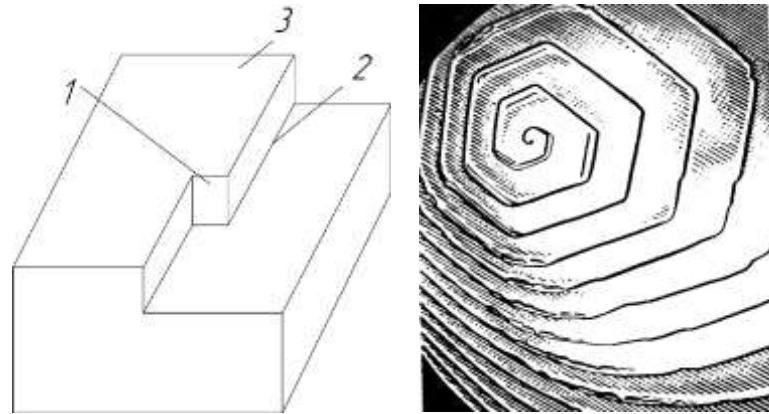


Figure 2.11. Examples of layer growth: 1, 2, 3 – possible cases of rising faces [10]

The decreasing of concentration flows can be achieved by mixing the solution or movement of the crystal itself, then the crystal will grow or dissolve more or less evenly.

The industry uses the dynamic method of growing crystals for obtaining the large homogeneous crystal (Figure 2.12). The essence is as follows: the crystal is evenly displaced at the appropriate speed, which provides the constant uniform supply of matter to the entire surface of the crystal. Also, already grown crystal can change its shape if it placed in other conditions.

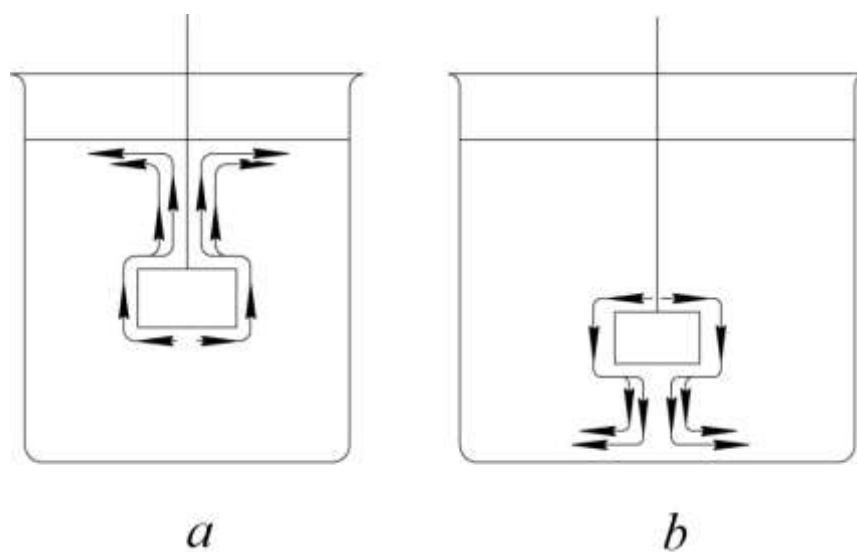


Figure 2.12. Installation of crystal growth and dissolution; appropriate streams concentrations in solutions: when growing (a); when dissolved (b)

The influence of physical and chemical factors on the diversity of crystals is illustrated by various forms of minerals (Figure 2.13), which are obtained under different conditions.

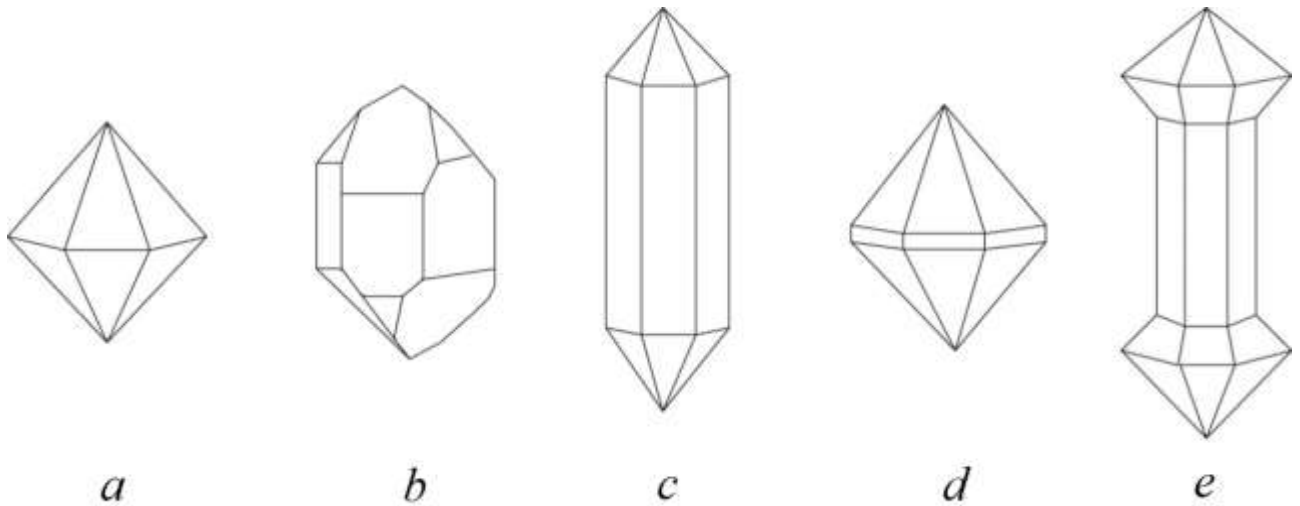


Figure 2.13. Crystals of quartz, formed under different conditions [11]: from melt (a); from solutions at high temperatures (b); from solutions at low temperature and different concentrations (c, d); from solution in the presence of ferum ions (e)

2.2. Crystallographic indexing

The symbols of nodes. If one of the nodes of the lattice is chosen as the origin of the coordinate, then any other node of the lattice is determined by the radius vector, which is calculated as follows: $R = ma + nb + pc$, where m, n, p – three numbers. The set of numbers m, n, p (written in double square brackets $[[m\ n\ p]]$), called *node symbol*. Numbers are written in a row, without commas, read singly. Commas are only applied in cases where the index is ambiguous.

In the case of the negative coordinate of the index, the minus sign is written above the number. Example, $[[1\ 3\ 0]]$ are reading «one, three, zero», $[[0\ \bar{2}\ 3]]$ – «zero, minus two, three».

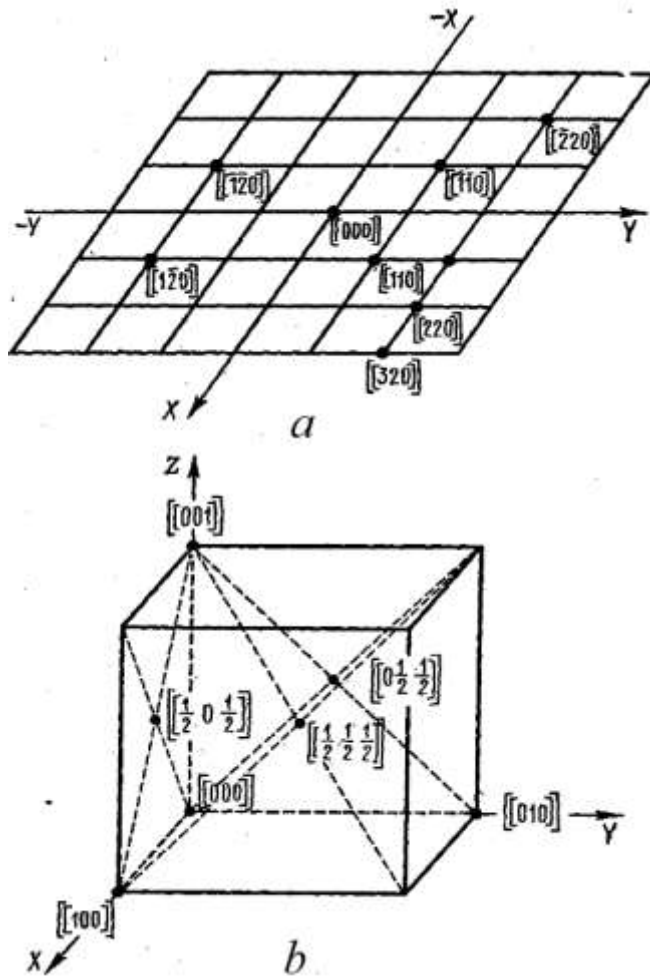


Figure 2.14. The signed nodes on the flat mesh (a) and symbols of tops (b) [12]

Figure 2.14 *a* shows the symbols of several nodes in the flat mesh with the slanting angle (the index on the third axis is zero), and Figure 2.14 *b* displays the tops, the faces centers and the centers of the elementary cell, if one of the cell tops is taken as the origin of the coordinate.

Symbols of rows (edges). The row, or nodular line, as well as the edge of the crystalline polyhedron, are characterized by the slope in the chosen coordinate system. If the series does not pass through the origin, it is necessary to move it mentally in parallel to itself so that it passes through the origin of the coordinate. Then the direction of the row will be determined by two points: the origin of the coordinates and any node in the row. The character of this node is taken as the series symbol and is written in square brackets $[m\ n\ p]$. Obviously, this symbol

characterizes the system of parallel rows, as well as the parallel edges of the crystalline polyhedron.

The set of crystal faces intersecting along parallel ribs form zone and the general direction of these edges is called the axis of the zone. The symbol $[m\ n\ p]$ characterizes the axis of the zone. From Figure 2.15 a, it can be seen that the line $[1\ 1\ 0]$ can be characterized by symbols $[2\ 2\ 0]$ and $[3\ 3\ 0]$, and so on, but to determine the character of the line, the node closest to the coordinate should be chosen. If the indexes in the character of line are multiple, they can be reduced to the positive number. Axis coordinates OX, OY, OZ have symbols $[1\ 0\ 0], [0\ 1\ 0], [0\ 0\ 1]$ respectively (Figure 2.15 b).

Symbols of planes (faces). The flat meshes in spatial lattices and the corresponding faces of the crystalline polyhedron are also characterized by the slope in the given coordinate system. Any facet of the crystal is parallel to any flat mesh, therefore, to the infinite number of parallel layers of it.

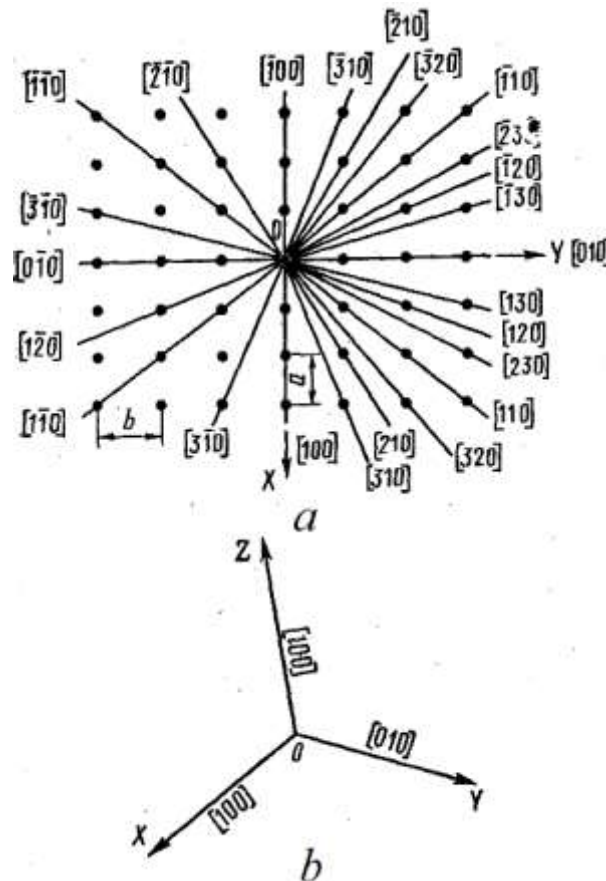


Figure 2.15. The symbols of directions in the flat mesh (a) and symbols of the coordinate axes (b) [12]

Consider set of planes 1, 2, 3, which are parallel to the Z axis (Figure 2.16), where for plane 1 along the axes X, Y, Z have the following coordinates $a/2, b/3, \infty$ respectively, and for the plane 2 – $a, 2/3b, \infty$ etc.

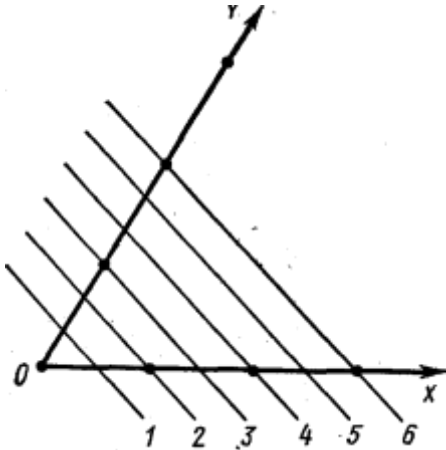


Figure 2.16. Definition of symbols of parallel planes the system

Consequently, for the set of planes in Figure 2.16 we have the coordinates of the planes, which are given in the table 2.1.

Table 2.1. The planes coordinates

Plane number	Segments on the axes			m : n : p	Weiss Parameters			Miller's Indices		
	X	Y	Z		p	q	r	h	k	l
1	a/2	b/3	∞	1/2:1/3: ∞ =3:2: ∞	3	2	∞	2	3	0
2	a	2b/3	∞	1:2/3: ∞ =3:2: ∞	3	2	∞	2	3	0
3	3a/2	b	∞	3/2:1: ∞ =3:2: ∞	3	2	∞	2	3	0
4	2a	4b/3	∞	2:4/3: ∞ =3:2: ∞	3	2	∞	2	3	0

Weiss's Parameters and Miller's Indices. The series of relations of rational numbers $m: n: p$ can be applied to all parallel planes as the ratio of integers of relatively prime numbers $p: q: r$ of the Weiss's parameters. In the example above (Table 2.1) $1/2 : 1/3: \infty = 1:2/3: \infty = 3/2:1: \infty = 2:4/3: \infty = p : q : r$, so $p : q : r = 3 : 2 : \infty$.

In crystallography it is customary to characterize the planes (or the normals to them) not by the Weiss's parameters, but by the Miller's indices. The Miller's indices

are values that are inverse to the Weiss's parameters, summed up to integers. If the plane parameters are p, q, r , then the Miller's indices are determined from the ratio $1/p : 1/q : 1/r = h : k : l$. In the example below (Figure 2.17) we have $h : k : l = 2 : 3 : 0$.

The numbers h, k, l called plane indices; indices written in succession and taken in round brackets $(h k l)$ called the plane symbol; in our example (Table 2.1 and Figure 2.16) it is $(2 3 0)$. And as one can see, the symbol $(h k l)$ characterizes the whole set of parallel planes. This symbol means that the system of parallel planes intersects the segment a on h parts, b on k parts and c on l parts, that is, it cuts off the segments $a/h, b/k, c/l$ on the axes. So, for building the plane $(h k l)$, it is necessary to designate on these segments the axes of coordinates and to draw the plane through them.

In the general form, the plane equation $(h k l)$ and the family of planes parallel to it will be $hx + ky + lz = N$, where N – always the integer; h, k, l are relatively simple integers. For the plane passing through the origin of coordinates – $N = 0$; for the plane closest to the coordinates – $N = 1$.

Figure 2.17 shows the planes and their symbols in the cubic system. From this Figure it can be seen that if the plane is parallel to the coordinate axis, that is, it is intersected with this axis in infinity, then the plane index on this axis will be $1/\infty = 0$. The symbols of coordinate planes, regardless of the angles between the axes, will always be $XOY = (001)$, $XOZ = (010)$, $YOZ = (100)$.

The method of describing the faces and edges of the crystal with the help of indices and symbols was established long before the crystal lattice structure was proven by the experimental method. It is based on the empirical law of crystallography: the law of rational indices.

The law of rational indices, which is brought out R.-J.Haüy (1783 year), says: *for any two faces of the real crystal, the double ratios of the parameters are equal to the ratio of small integers, that is $OA'/OA : OB'/OB : OC'/OC = p : q : r$, de p, q, r – entire, are relatively simple and small numbers for real crystals. This law is also*

called the law of rational relations, or the law of rationality of parameters and explains the internal structure of the crystal.

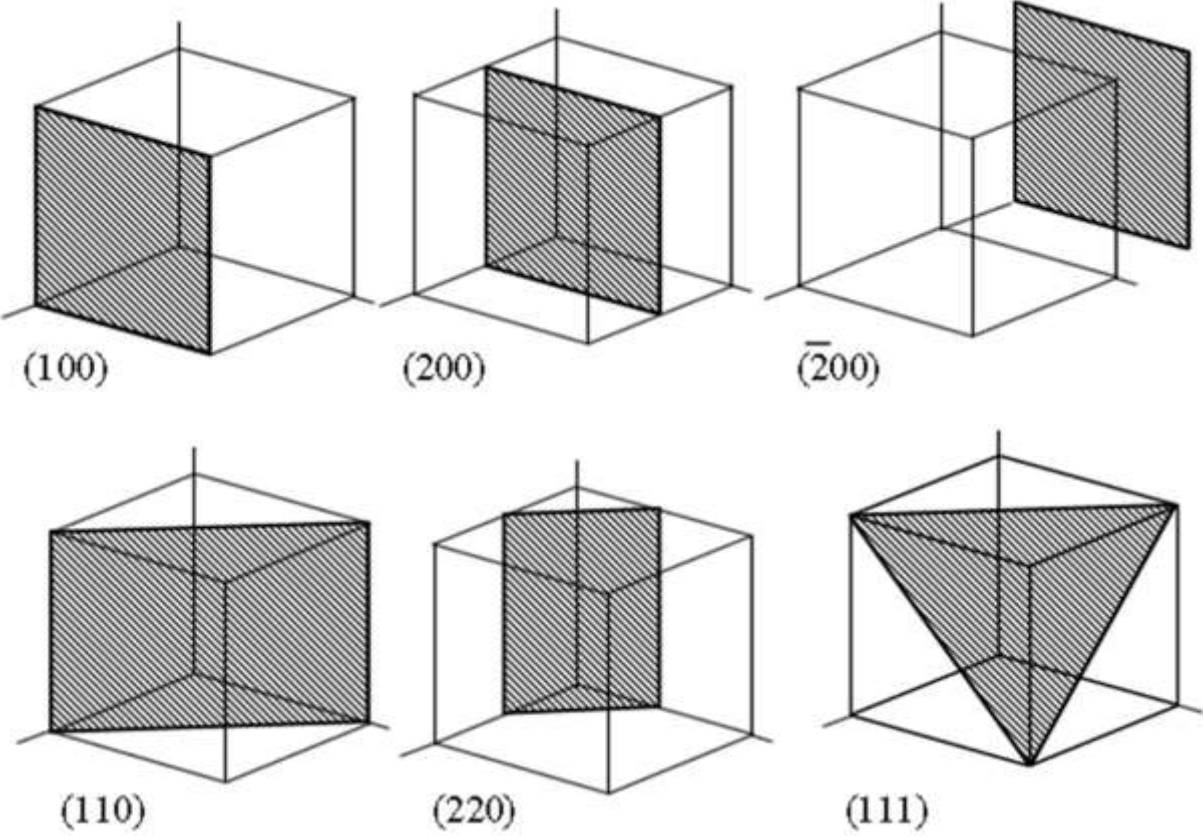


Figure 2.17. Symbols of planes in the cubic system [13]

To explain the law, two non-parallel faces should be taken $A_1B_1C_1$ та $A_2B_2C_2$ (Figure 2.18) which cut off by 3 ribs OA_1, OB_1, OC_1 та OA_2, OB_2, OC_2 accordingly. These lengths correspond Weiss's parameters.

If to divide the parameters of one face are divided by the parameters of another, and take the relation between them, the relatively small and integers numbers can be obtain:

$$OA_1/OA_2 : OB_1/OB_2 : OC_1/OC_2 = p : q : r.$$

Let's denote $OA_1 = ua, OB_1 = vb, OC_1 = wc$ and $OA_2 = ra, OB_2 = sb, OC_1 = tc$, where u, v, w, r, s, t – integers or fractional, but necessarily rational numbers, a, b, c – cell parameters. Then: $ra/ua : sb/vb : tc/wc = r/u : s/v : t/w$, having brought to the

common denominator and taking the relation between them, we always have the integers.

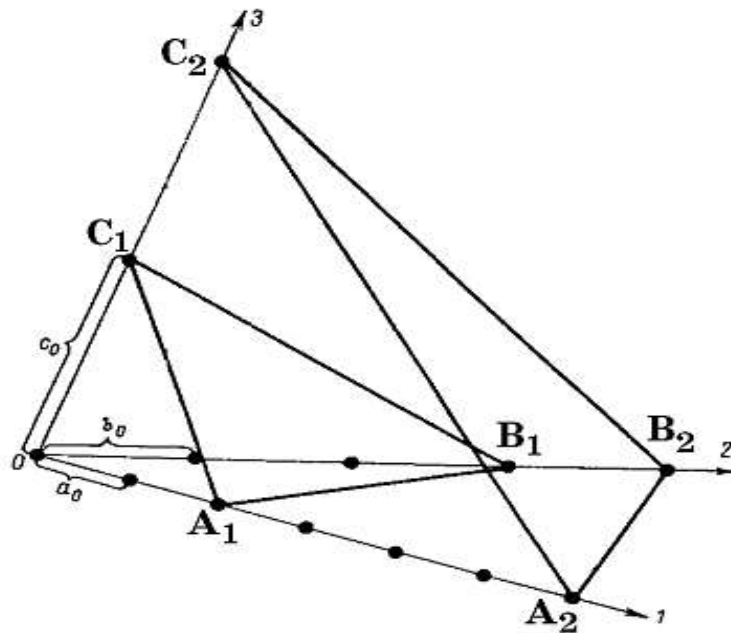


Figure 2.18. Scheme of explanation to the Haüy law [7]

Figure 2.19 shows the symbols of some planes in the flat mesh (the index along the Z-axis is zero). It is easy to see the characteristic feature, common to any structures: *the simpler the symbol of the plane* (that is, the smaller the value of the indexes), *the greater the reticular density of this plane*. The planes with larger indexes have small reticular density. Since the total number of nodes per unit volume for each given structure is constant, the distances between parallel planes will be larger with greater reticular density of these planes. Consequently, the planes with small indexes have greater reticular density and larger interplanar distances. These planes are most often encountered in real crystals (Brave's law). This explains that the integers in the law of rational relations are small.

Consequently, any crystallographic plane and any facet of the crystal can be determined by three integer Miller-number indices that is:

- 1) the coefficients in plane equation, written in parametric form (provided that the coordinates are expressed in relative units x/a , y/b , z/c), or,
- 2) the values are inversely proportional to the length that are cut off by the

plane on the coordinate axes, or,

3) the values proportional to the double relation of the axial length in accordance with the law of rational indices.

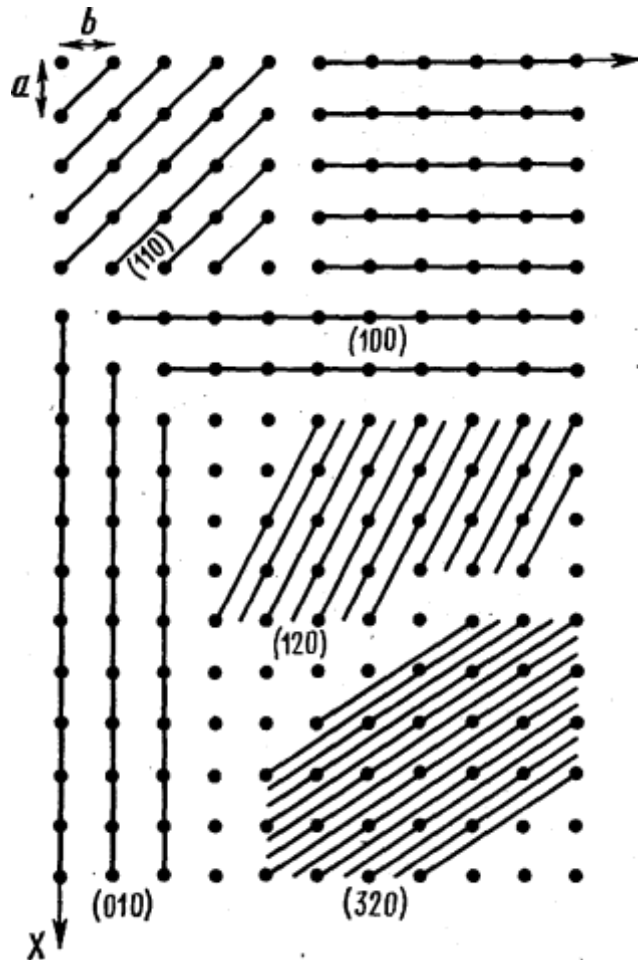


Figure 2.19. Traces of planes with different symbols in the simple cubic lattice [9]

2.3. The crystallographic projections

For study crystals except to measuring the angles also their image draw, which is also one of the essential tasks of crystallography. To do this two methods use:

- 1) shaped or perspective (axonometric ta orthographic projections (Figures 2.20 *a* and 2.20 *b* respectively);
- 2) graphic (graphical projections).

Image design does not allow to determine fully the actual values of the angles between the faces, in contrast to the graphic projections. According to the graphic

method, the crystal is projected either to the surface of the sphere (spherical projection) or to the equatorial plane of the sphere (stereographic and gnomostereographical projection), or to the plane tangent to the northern (upper) pole of the sphere (gnomonical projection).

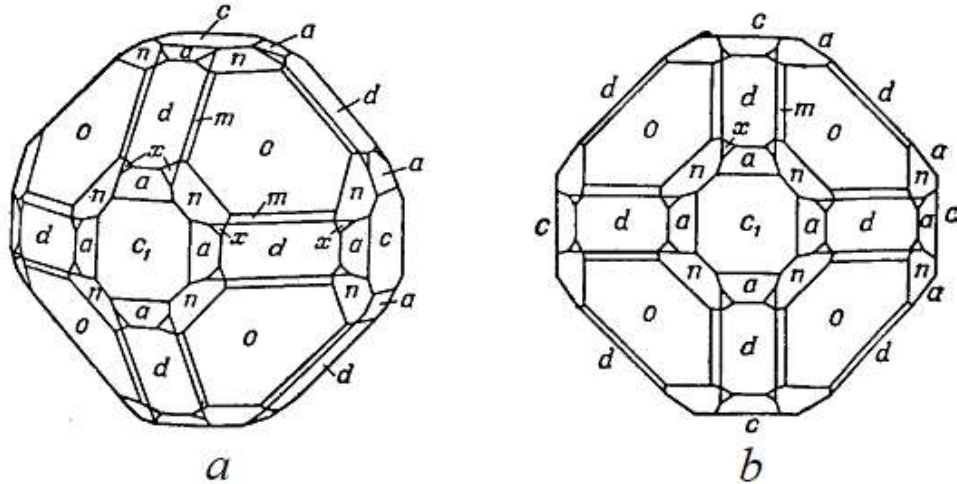


Figure 2.20. Projection of fluorite crystal (CaF_2): axonometric (a); orthographic (b) [12]

For this, the crystal is represented as either the direct (crystalline) complex (Figure 2.21 a), or in the form of the reverse (polar) complex (Figure 2.21 b). In the latter case, each facet of the projected crystal is replaced by normal.

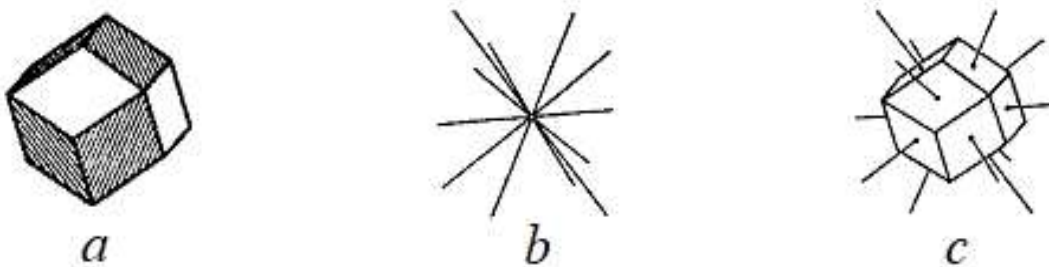


Figure 2.21. Crystalline polyhedron (a); reverse (polar) complex (b); normal to the faces of the polyhedron (c)

Spherical projection. The spherical projection is constructed by following way: there is holding straight lines (Figure 2.22 b) from the sphere centre through the face center (Figure 2.22 c). The obtained normals are intersected with the sphere and the

obtained points are their spherical projection. (Figure 2.22 *e*). So, each normal is projected onto the surface sphere in the form of the point. Thus, the each point of the projection corresponds to one of the crystal's faces. The points obtained on the sphere are called the poles of the faces of the crystal (Figure 2.22 *f*).

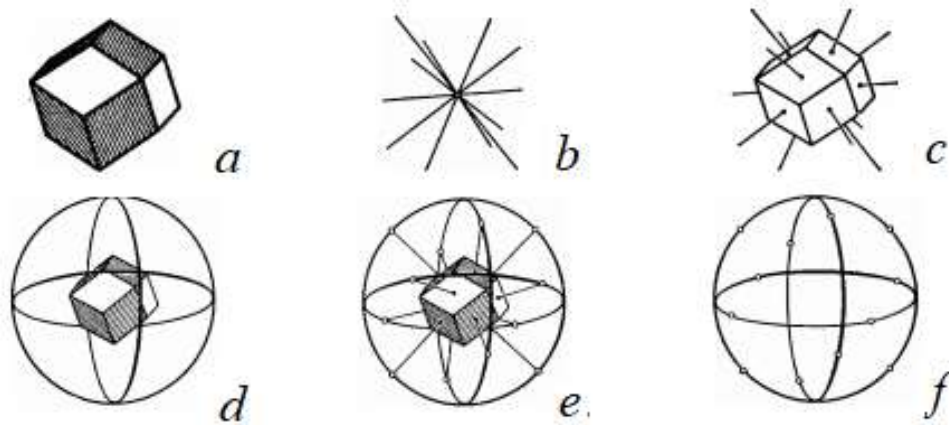


Figure 2.22. Crystalline polyhedron: rhombic dodecahedron (*a*); its polar complex (*b*); normal to its faces (*c*); projection of sphere (*d*); spherical projection (*e*); complete spherical projection of rhombic dodecahedra (*f*)

The spherical projection of the crystal can be constructed without replacing the crystal faces by normals. In this case, all crystal faces through the parallel transfer are moved towards the sphere and at the point of intersection of the face with the sphere there is the projection of the face (Figure 2.23). The position of each of these points is determined by their spherical coordinates: latitude $0 < \rho < 180^\circ$ (it changes from the north to the south pole) and longitude φ (is calculated on the equator from the meridian taken as zero) (Figure 2.24).

The spherical projection of the crystal is visual, but it is volumetric and it is convenient to project it on the plane for the practical usage, therefore stereographic, gnomostereographic and gnomonic projections are used.

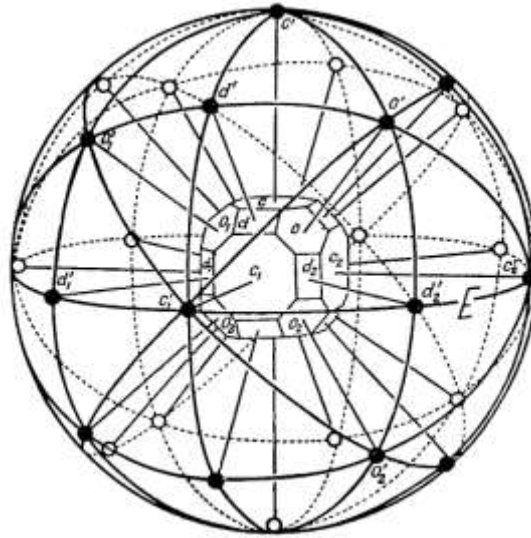


Figure 2.23. Spherical projection of fluorite crystal

Stereographic projection. In harmony to the law of constancy of interfacial angles, the characteristic constants in crystals between faces or edges are the angles. The most accurate values of the angular values are the stereographic projection (stereo – spatial (in Greek)). The stereographic projection is based on the spherical projection.

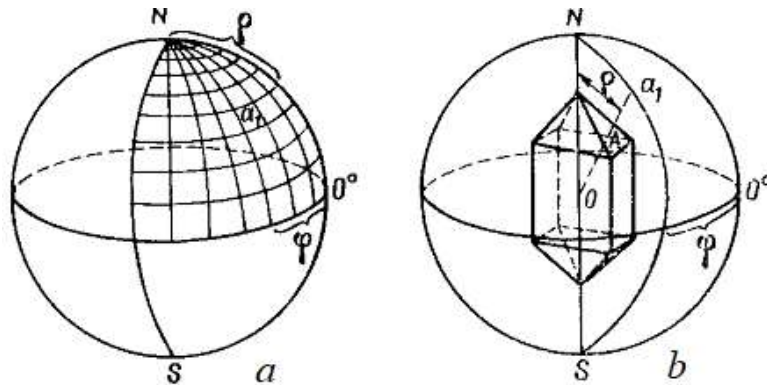


Figure 2.24. Image of the face a_1 with spherical coordinates ρ and φ

According to the plane of the stereographic projection, the equatorial plane P should be chosen, on which is projected the spherical projection of crystal (Figure 2.25), i.e., the crystalline complex is projected.

To design a point a inside a sphere with a certain radius on the surface of the sphere, the center of O and point a should be connected by straight line to the intersection with the sphere. The obtained point a' is a spherical projection. By

connecting the point a with the southern pole S we obtain the point a_1 on the plane P . It is the stereographic projection of the point a (Figure 2.25).

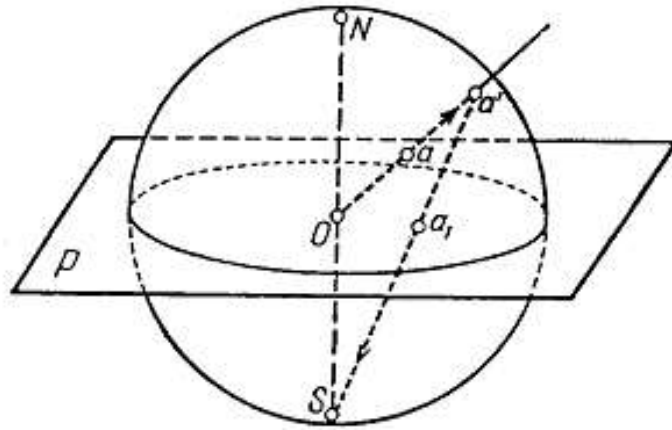


Figure 2.25. Stereographic point projection

If the direction is vertical, it is depicted as a point on the projection circle of the stereographic projection (Figure 2.26 a), horizontal direction is depicted as two dots on the equator (Figure 2.26 b). The spherical projection of the point passing at an angle is represented by the point inside the circle of projections. It is the point of intersection of a vector with pole S (Figure 2.26, c).

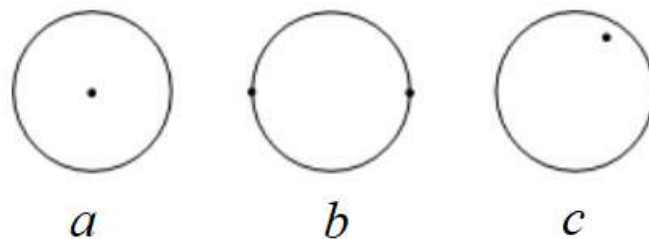


Figure 2.26. Stereographic projection of directions

The stereographic projection of the vertical axis is represented by two overlapping points in the center of the projection circle, one of which corresponds to the upper one, the other fits to the lower end of the symmetry axis (Figure 2.27 a). The stereographic projection of the horizontal axis of symmetry is depicted by two diametrically opposite points corresponding to the points of the stereographic

projection (Figure 2.27 *b*). The directions that pass at the angle are characteristic only for the axes of the second L_2 and the third L_3 orders.

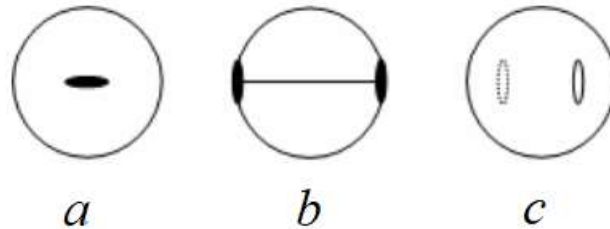


Figure 2.27. Stereographic projections of the second order axis:

L_2 perpendicular to the projection plane (*a*); L_2 parallel to the projection plane (*b*);

L_2 is at an angle to the projection plane (*c*)

For designing the straight line (direction) AB (Figure 2.28), which passes through the center of the sphere and intersects its surface at points n and m , first is finding the projections of these points on the equatorial plane P using southern and northern poles. The points found n' , m' connect and get the direct projection nm . Since the Om length is in the upper part, and the On length is in the bottom, then the line $m'O$ depicted as the solid line, and the line On' is as a dotted line.

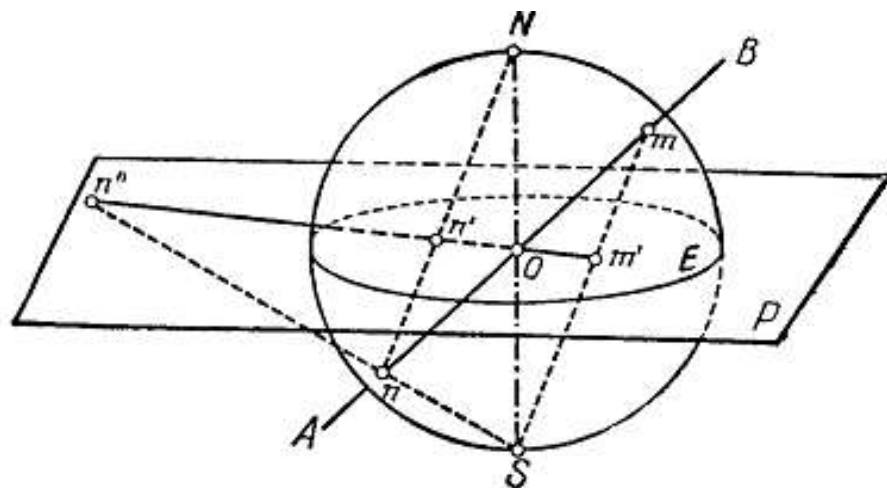


Figure 2.28. Stereographic projection of an arbitrary line

The stereographic projections of the planes are represented by arcs within the circle of projections (Figure 2.29).

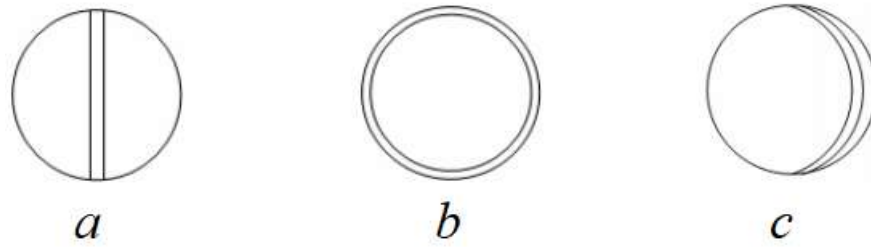


Figure 2.29. Stereographic projections of the plane that are located:
perpendicular to the projection plane (vertical plane) (a);
parallel (horizontal plane) (b); at the angle (inclined plane) (c)

The stereographic projection has the following properties:

- 1) any circle held on the sphere is depicted on a stereographic projection as well as a circle;
- 2) angular ratios are not distorted on this projection;
- 3) the angle between the poles of the faces on the sphere, measured along the arcs of the large angles, is equal to the angle between the stereographic projections of the same arcs.

The stereographic projection is used to represent the symmetry elements of the crystal, the image of symmetric transformations and the external shape of the crystal, as well as to determine the anisotropy of physical properties of the crystal, etc (Figure .30).

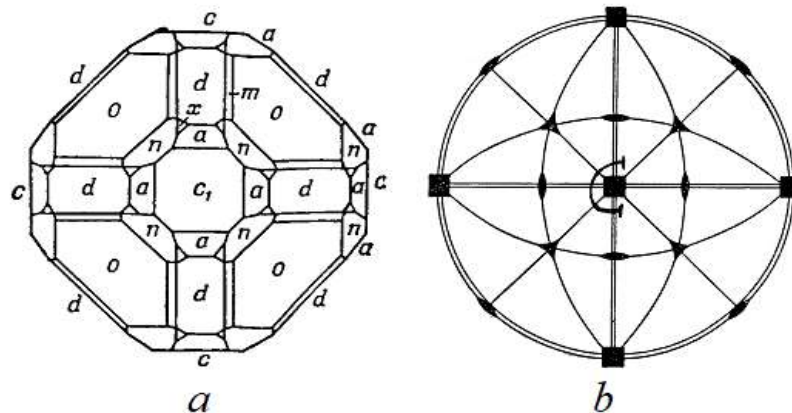


Figure 2.30. Orthogonal (a) and stereographic (b) projections of the crystal

Gnomostereographic projection. This type of projection is used to represent polyhedra. It is under construction in the same way as the stereographic projection, but the normals are projected to the crystal faces, so, the polar complex is projected. The plane for designing of the gnomostereographic projection is also the equatorial plane of the projection sphere. A gnomostereographic projection is a set of stereographic projections of normal to the crystal faces (Figure 2.31).

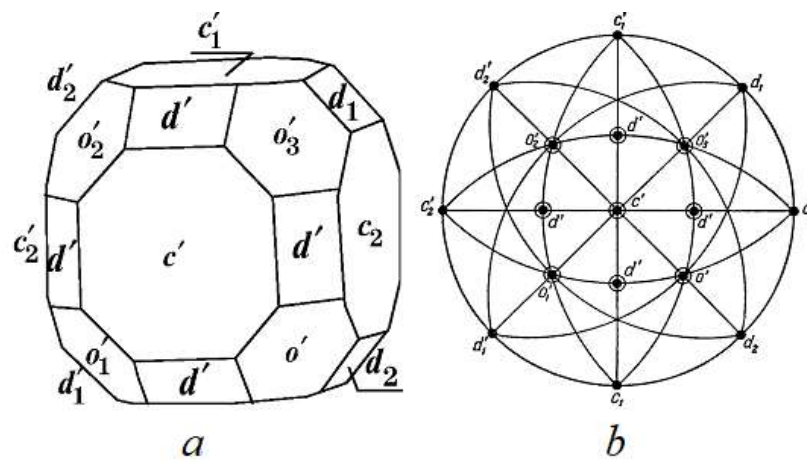


Figure 2.31. Axonometric (a) and gnomostereographic (b) projection of the crystal

Gnomonic projection. The possibilities of using gnomonic projection are somewhat less than stereographic, but under certain conditions it is more visible. For example, belts can be easily recognize on it as well as symbols of the faces belonging to one belt can be easily read without usage of additional networks.

The plane of the gnomonic projection is parallel to the plane of stereographic and gnomostereographic projections, but it is not equatorial, but tangent to the north pole of the surface. A gnomonic projection represents the result of the transfer of a point from the sphere of projections on a tangent to ray, conducted from the center of the sphere (Figure 2.32 a).

The point in which the normal intersects with the plane is called the center of gnomonical projection. Projections of horizontal and inclined faces are depicted in the form of points. There is the point of intersection of their normal with the

projection plane for each face. The stronger the slope of the face, the farther its projection is located from the center.

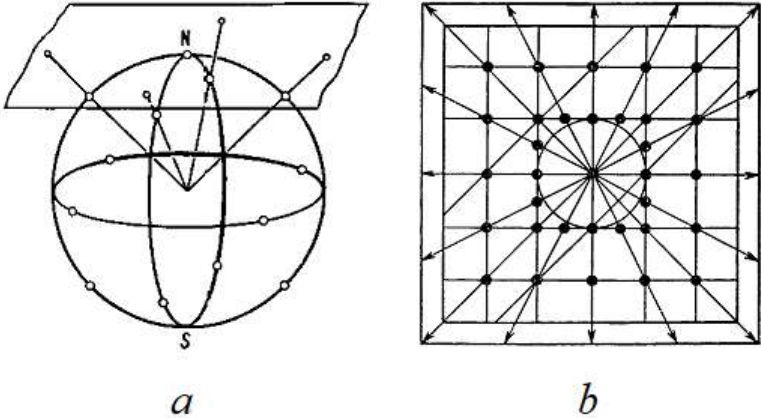


Figure 2.32. The structure of the gnomonic projection (a) and the typical gnomogram (b)

Vertical faces are projected into infinity and their position on gnomonic projection is indicated in the form of arrows. The direction of the arrow corresponds to the orientation of the normal on this vertical line (Figure 2.32, b). Consequently, the vertical faces of the crystal do not have gnomonic projections (only, as shown in Figure 2.32, b, directions), since the corresponding rays, which conducted from the center of the sphere, are parallel to the plane of the gnomonic projection (Figure 2.33).

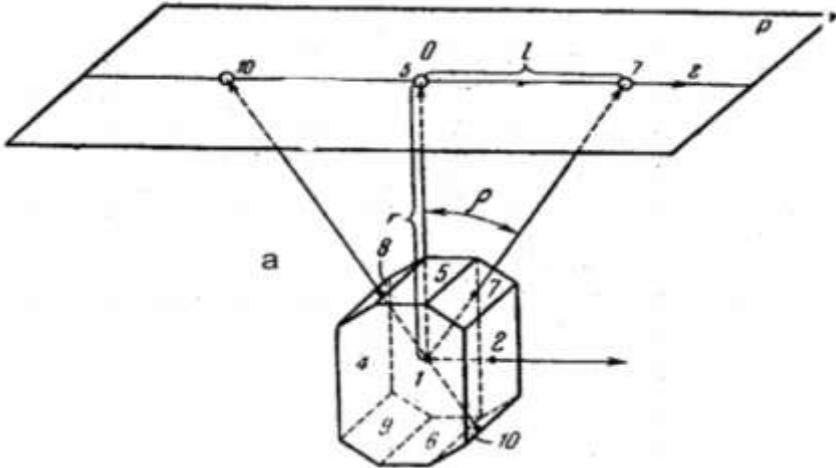


Figure 2.33. The principle of constructing of gnomonic projection of a crystal

Gnomonic projection is used to decipher the structure of a crystal in a structural analysis. The advantage of this projection is that the coordinates of the points are directly proportional to the Miller's indices. The disadvantages include the fact that angular ratios are not stored.

On Figure 2.34 orthogonal, gnomostereographic and gnomonic projections of the topaz crystal are depicted. On this Figure we can follow the reflection of the same faces on different projections.

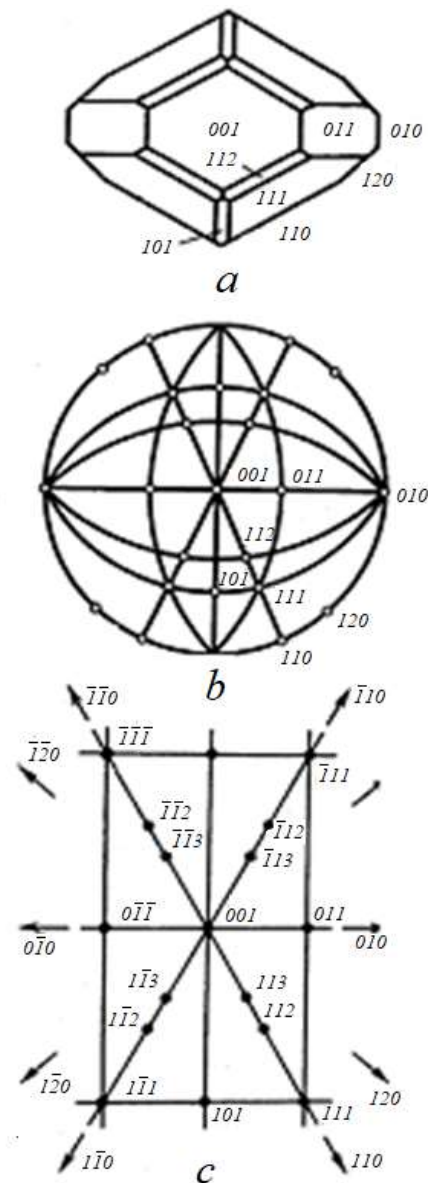


Figure 2.34. Orthogonal (a), gnomonic-stereographic (b) and gnomonic (c) projection of the topaz crystal [12]

2.4. Symmetry and elements of crystals symmetry

Symmetry is the ability of geometric figures to repeat their similar parts some integer number of times. Symmetry of geometric bodies has two concepts: geometric and physical. If from the geometric point of view symmetrical bodies include bodies that consist of the same external shape and size of parts, then physical symmetry implies not only geometric equivalence, but also physical – color, hardness, etc.

Elements of symmetry are called auxiliary geometric images (points, straight lines, planes), by which symmetry of a figure or a polyhedron is determined.

Elements of symmetry of crystals are:

- 1) inversion center C ;
- 2) plane of symmetry P ;
- 3) rotary axes of symmetry L ;
- 4) inversion axes of symmetry L_i ;
- 5) single directions SD .

Inversion center (C). Inversion center is called the point inside the crystal, through which similar parts of the crystal on straight lines at the same distances are cut off. As can be seen from Figure 2.35 *a*, the conducted straight lines AA_1 , BB_1 and DD_1 at identical distances from the point C on both sides have similar parts of the triangles ABC and $A_1B_1C_1$. In this case, the upper triangle ABC rotated relative to the lower triangle $A_1B_1C_1$ on 180° . This phenomenon is called inversion, and the C point itself, through which the reflection of the triangle passes ABC in the triangle $A_1B_1C_1$, – inversion center. On Figure 2.35 *b* we can see two parallelograms, the faces of which are also linked by the inversion center.

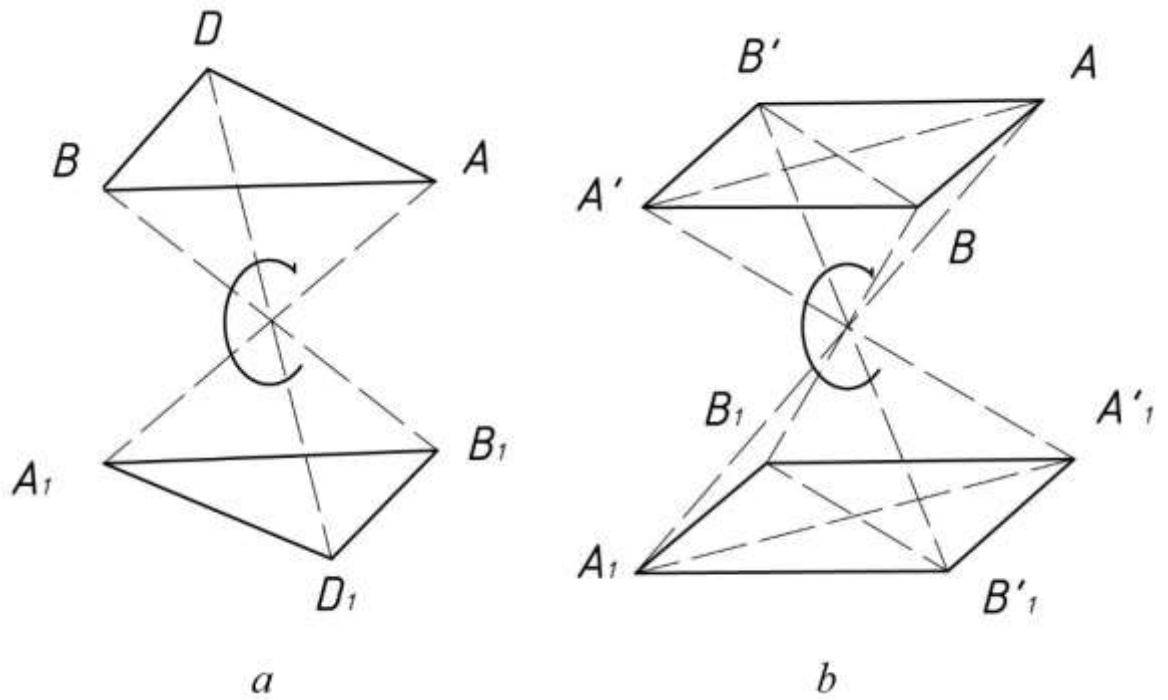


Figure 2.35. Two triangles (a) and two parallelograms (b) interconnected by center of inversion C [7]

The presence of the inversion center in bulk model is shown on Figure 2.36 a. As can be seen, any line drawn through the center of this polyhedron on both sides of the point *O* at similar distances crosses similar parts of the figure, that is, if on one side of the point *C* placed vertex *A*, respectively, on the other side at the same distance there is the similar apex *A*₁. This applies to any points that can be placed both at the edges and on the faces of the crystal.

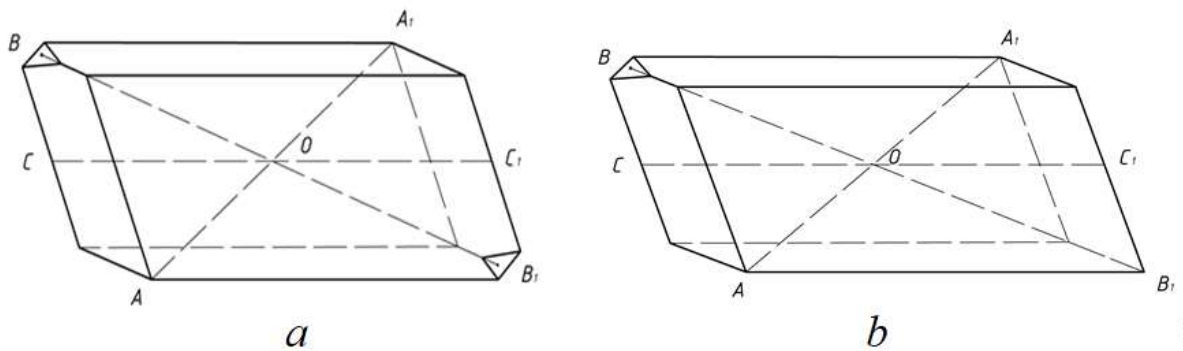


Figure 2.36. Illustration to explain the presence (a) and absence (b) the inversion center in bulk crystal models [7]

Unlike Figure 2.36 a, which shows polyhedron with the inversion center, Figure 2.36 represents the polyhedron in which the inversion center is absent. This is due to the fact that although straight lines AA_1 and CC_1 on both sides of the point O have the same parts of the figure (apex – apex, ribs – ribs), straight line BB_1 on both sides of the point O crosses different parts of the crystal: OB – face, OB_1 – apex. Thus, the necessary condition for the presence of the center of inversion in crystals is the presence of pairwise-parallel faces. *If in the crystal there is at least one face that does not have a parallel face, then the inversion center is absent.*

Plane of symmetry (P). Plane of symmetry called the imaginary plane dividing figure into two equal parts and when one part is the mirror image of another.

To determine the symmetry planes, the model of the polyhedron must be set to the certain position so that the same plane is not taken into account several times. The symmetry planes pass through the middle of the faces, ribs, parallel to the ribs or through opposite apexes. For example: in the rectangular parallelepiped (Figure 2.37 a) there are three symmetry planes (two vertical ones P_1 , P_2 and one horizontal P_3), and in the cube (Figure 2.37 b) – nine (four vertical P_1 , P_2 , P_3 , P_4 , four inclined P_5 , P_6 , P_7 , P_8 i and one horizontal P_9).

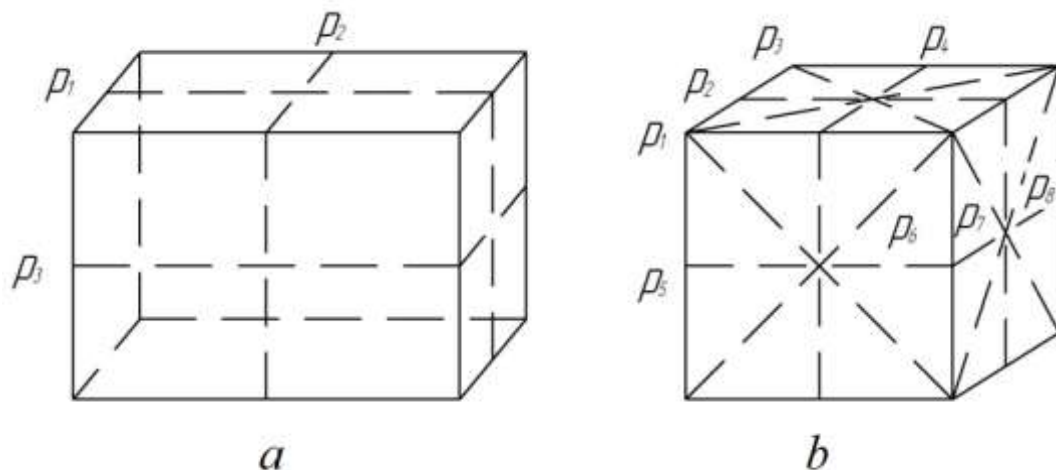


Figure 2.37. Plans of symmetry in polyhedra [7]:

rectangular parallelepiped (a); cube (b)

Rotary axis of symmetry (L). Rotary axes of symmetry is the straight line at rotation around which on 360° the crystal repeats the integer number of times « n ».

In this case, the parts of crystal are arranged so that, by rotating around the axis at the certain angle, the crystal has the same look as it was before the turn, only on the place of one part of crystal there are others similar to them. It is coincide not only individual parts, but the whole body itself. For example, on Figure 2.38 three prisms (a, b, c) and one pyramid (d) are shown.

If to conduct the axis perpendicular to their bases, then when rotation around the selected axis by 360° in the first prism (L_2) there are two similar parts, in the second – three (L_3), in the third (L_6) – six; in the pyramid (L_4) – four can be seen. So, in order to obtain the characteristic of the axis of symmetry, it is necessary to find the smallest angle of rotation, which will allow to obtain similar parts of the crystal. This angle is called *the elementary angle of rotation α* . Accordingly, the order of the axis of symmetry corresponds to the number indicating how many times the elementary angle α is repeated at the rotation of the crystal around the axis of symmetry by 360° .

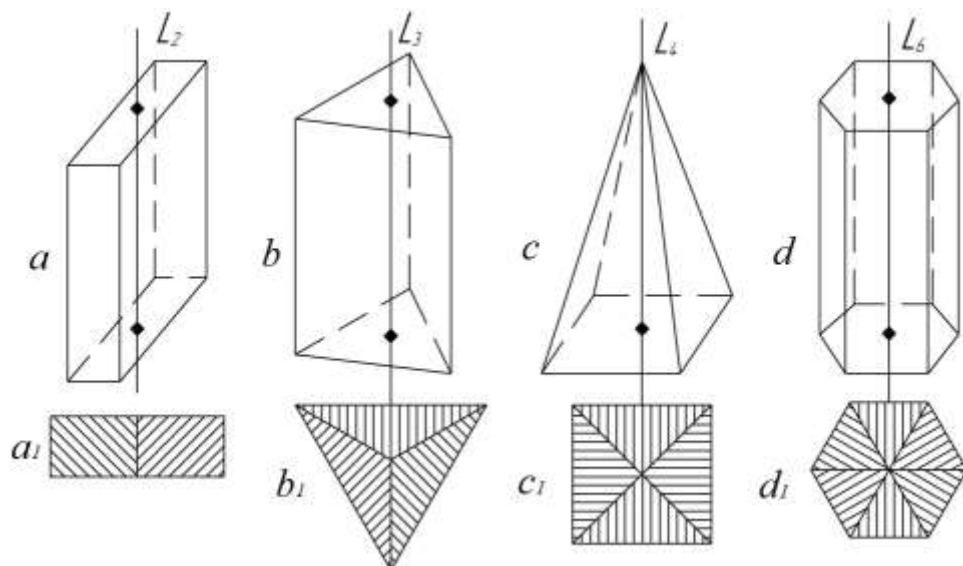


Figure 2.38. Examples of polyhedra with rotary axes of symmetry [7]:

L_2 (a); L_3 (b); L_4 (c); L_6 (d)

In crystalline polyhedra there are rotary axes of symmetry of the second (L_2 , $\alpha = 180^\circ$), the third (L_3 , $\alpha = 120^\circ$), the fourth (L_4 , $\alpha = 90^\circ$) and the sixth (L_6 ,

$\alpha = 60^\circ$) orders (Figure 2.35). The axis of the first order (L_1 , $\alpha = 360^\circ$) available in all crystals in unlimited quantities and do not have the decisive value for the systematics of crystalline bodies. The unpaired axes of the fifth, the seventh and more, and also paired axes of the eighth, the twelfth and other orders in crystals are absent.

The axes of rotoinversion (L_i). Inversion axis of symmetry is called direct, in the case of rotation around which to 360° with the corresponding displacement (inversion) through the center of the crystal, similar parts are joining by themselves an integer number of times «n». In crystals there can be inversion axes of the fourth L_{i4} and the sixth L_{i6} orders, other axes correspond to the elements of symmetry considered earlier: $L_{i1} = C$; $L_{i2} = P$; L_{i3} corresponds to the third-order symmetry axis (L_3) in the presence of the center of inversion.

To determine the inversion axes of symmetry, it is recommended that the crystal be oriented so that L_{i4} or L_{i6} is arranged vertically. In the future, with this orientation, the crystal turns on 60° or on 90° , and the elements of the crystal (tops, ribs, faces) are transferred through its center on opposite sides. If after turning around the given axis (L_{i4} or L_{i6}), the specified elements of the cut (top, rib, face) of the upper part of the crystal will be a reflection-inversion through the center of the lower part then this axis is indeed the axis of inversion of the particular order. If there is no reflection-inversion then there is no inversion axis. The order of the axis is determined by the number of the parts of the crystal, which are repeated at its rotation on 360° .

Consider the inversion axis and define the order in the polyhedron depicted on Figure 2.39. It has the third order axis L_3 (straight line LL), which is simultaneously the inverse symmetry axis of the sixth order (L_{i6}). When turning all parts of the polyhedron around the axis LL on 60° the subsequent reflection at the central point of the figure will combine with itself.

So, after turning the rib AB around LL on 60° , the rib will take position A_1B_1 , which by means of reflection through the center combines A_1B_1 with rib HE . At full

turn 360° such combinations will be six. So the axis LL is the inverse axis of the sixth order.

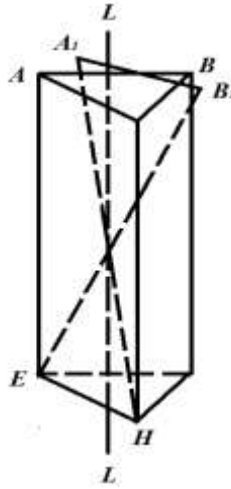


Figure 2.39. An example of the polyhedron with the third-order inversion axis

Single directions (SD). Single direction is called the direction (straight line) in crystals, which does not have the same direction, that is, it is not repeated. In crystals there can be one single direction or three (Figure 2.40), or plural.

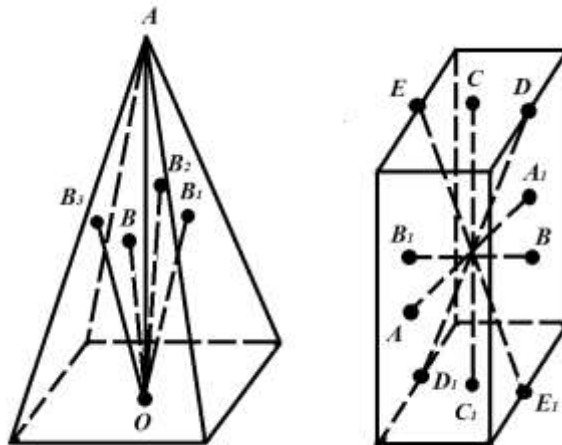


Figure 2.40. Examples of polyhedra with different number of single directions

Regarding the placement of single directions on symmetry elements, they can pass through the center of inversion (Figure 2.41 a), coincide with the planes and axes of symmetry or placed perpendicular to them (Figure 2.41 b, 2.41 c; 2.41 d; 2.41 e).

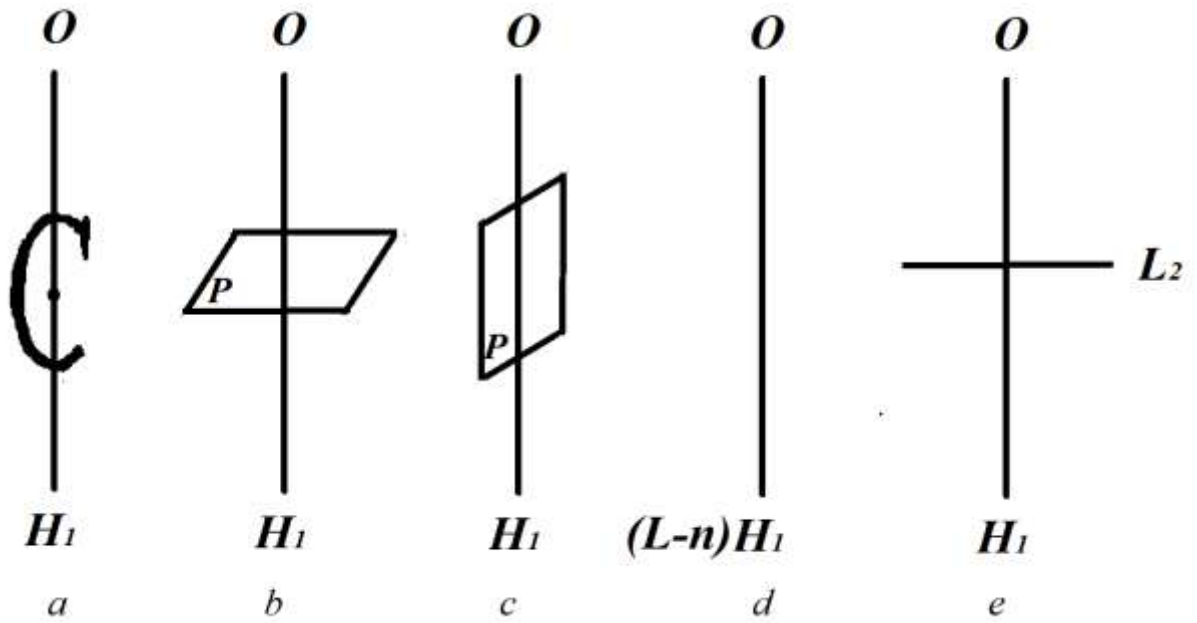


Figure 2.41. Possible variants of placement of single directions relative to symmetry elements

Directions that are repeated in a crystal and are related to symmetry elements are called symmetrically equal. In the cube any direction is repeated several times. For example, the axis of the third order presents four times ($4L_3$), the axis of the fourth order is three times ($3L_4$) etc. This is due to the fact that there are no single directions in the cube, and there are only symmetrically equal directions. For an example, define the symmetry elements of the cube (Figures 2.42 and 2.43).

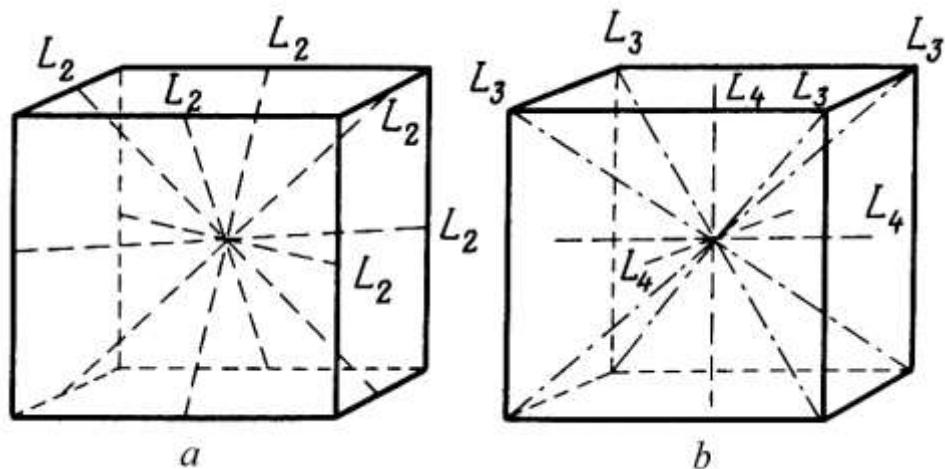


Figure 2.42. Elements of the cube symmetry: symmetry axis 2 order (a); symmetry axis 3 and 4 orders (b)

In the cube the inversion center C , three axes of the fourth order $3L_4$, passing through the middle of the faces; four axes of the third order $4L_3$, passing through the top of the cube; six axes of the second order $6L_2$, passing through the middle of the ribs; and nine planes of symmetry can be determined. All of them can be expressed by the formula $3L_44L_36L_29PC$.

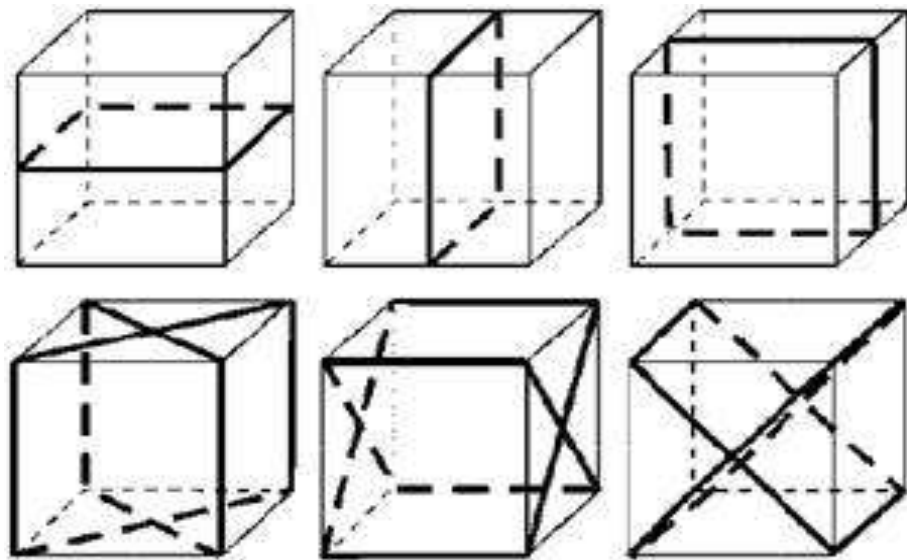


Figure 2.43. Cubic symmetry plane

2.5. The crystal systems

The crystals systems is the group of symmetry types that have one or more similar elements of symmetry with the same number of individual directions.

The classification of crystals by the crystal system is determined by the choice of the crystallographic coordinate system or the elemental cell of the crystal. Each elementary parallelepiped is characterized by three linear parameters a , b , c , which are equal to the sides of the elementary cell (called the lattice periods), and three angular parameters α , β , γ between its coordinate axes. All six parameters are called constant lattices. Based on these parameters, there are 7 crystal systems in the parallelepipeds (Table 2.2).

Table 2.2. Characteristics the crystal systems of parallelepipeds according to linear and angular parameters

The crystal system	Characteristic of the crystal system (parameters)	Number of classes in the crystal system
Triclinic	$a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$	2
Monoclinic	$a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$	3
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	3
Trigonal	$a = b = c; \alpha = \beta = \gamma \neq 90^\circ$	5
Tetragonal	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$	7
Hexagonal	$a = b \neq c; \alpha = \beta = 90^\circ; \gamma = 120^\circ$	7
Cubic	$a = b = c; \alpha = \beta = \gamma = 90^\circ$	5
Total		32

Characteristics of elementary parallelepipeds by their form and the typical examples of crystals in the crystal systems are given below.

1. *Triclinic crystal system.* It includes two classes of symmetry L_1 and C , in which there are no axes and planes (Table 2.2). All three angles between the ribs of the elementary parallelepiped in this crystal system of the spatial lattice are acute or obtuse. All directions in crystals are single.

2. *Monoclinic crystal system.* It belongs to three classes of symmetry, which have either one plane P , or one axis L_2 , or the following combination L_2PC (each of the simplest elements of symmetry is available only in singular). Between the ribs of the elementary parallelepiped there is only one angle and it is acute. Crystals of this crystal system contain a set of single directions. All directions that are oblique to L_2 or P , correspond symmetrically equal way. All the directions that lie in the plane of symmetry or in the plane, perpendicular to L_2 , and also coincide with L_2 or with normal which perpendicular to P , it is single.

3. *Orthorhombic crystal system* also combines three classes of symmetry. They are characterized by the presence of combination of three or four simple elements of symmetry, but do not include axis higher that second order. All the corners between the ribs of the elementary parallelepiped are right. In crystals of orthorhombic crystal system there are three single directions that coincide with $3L_2$ or with normal which perpendicular to P .

4. *Trigonal crystal system* contains five classes that have one single direction, which coincides with the only one L_3 . This crystal system can also be viewed as the special case of hexagonal crystal system. The elementary parallelepiped of the crystals spatial lattice of this crystal system is rhombohedron.

5. *Tetragonal crystal system* consists of seven classes, which have the single direction, which coincides with the only axis L_4 or L_{i4} .

6. *Hexagonal crystal system* combines seven classes, which are characterized by the single direction which is identical with axis L_6 or L_{i6} .

7. *Cubic crystal system*. Always it has several axes of higher order in excess of L_2 and must be present $4L_4$. There are no single directions.

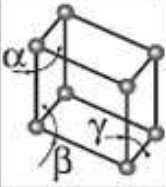

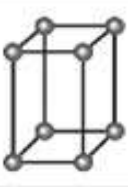


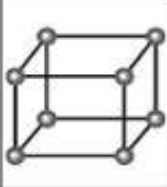
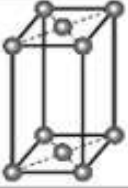
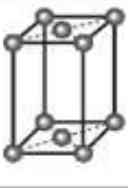
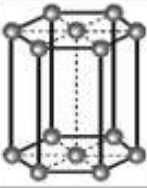

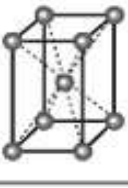
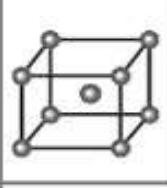
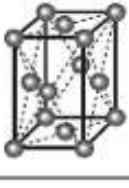
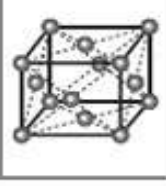
The crystal systems are grouped into three categories: the lower one (triclinic, monoclinic and orthorhombic); the middle one (trigonal, tetragonal and hexagonal); the higher one (cubic).

Bravais lattice is called the group of broadcasts that characterize the position of material particles in space. Bravais lattice are chosen in the following way:

- 1) their symmetry remained the same as the symmetry of the entire lattice;
- 2) quantity of right angles and equal ribs is maximal;
- 3) lattice volume is minimal.

According to these conditions the Bravais lattices may be primitive, base-centered, body-centered and face-centered. In the Table 2.3 the fourteen Bravais lattices are listed. Vertically designated types of lattice: 1 – primitive; 2 – base-centered; 3 – body-centered; 4 – face-centered. Horizontally marked the crystal systems: 1 – triclinic (all the angles and ribs are different, there are no right angles); 2 – monoclinic (all ribs are different, but two of three angles are right); 3 – orthorhombic (all ribs are different, all angles are right); 4 – tetragonal (the two ribs are the same, all the angles are right); 5 – trigonal (all the ribs are equal, the two angles are equal, but both are not right angles); 6 – hexagonal (the two ribs are identical and form the angle between them 120° , two other angles are right); 7 – cubic (all ribs are equal, all angles are right).

Table 2.3. The fourteen Bravais lattices

	1	2	3	4	5	6	7
1							
2							
3							
4							

In the primitive lattice, these material particles are found only in its nodes (at the vertices of elementary parallelepipeds). The primitive Bravais lattices are the main cells that characterized the crystal systems. For defined ratios between a , b , c , α , β , γ it is convenient to use non-primitive but complex lattices, since they better reflect the symmetry of the structure.

In non-primitive lattices, particles are placed not only in its nodes, but also at the intersection of the diagonals of two opposite faces (base-centered), or in the center of the lattice (body-centered), or in the center of each face (face-centered).

In the hexagonal crystal system the primitive elementary cell is the prism with rib parallel to the axis L_6 and the base in the form of rhombus ($a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). The cell is determined by two parameters a and c , but it does not correspond to the symmetry of the entire lattice. Therefore, the hexagonal prism imagine as the combination of three primitive cells. Consequently, the prism is already non-primitive, but base-centered.

For the tetragonal crystal system the primitive elemental cell, which satisfies the conditions for choosing Bravais lattices, is the rhombus that has $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$ (Table 2.4). Consequently, any of the fourteen Bravais lattices is the collection of all equivalent crystalline lattice nodes that can be combined with each other through the translation. Bravais lattices exhaust all possible variants of simple lattices, which consist of atoms of the same sort, which can be constructed on the basis of seven crystal systems.

Consider the above crystal system in more detail.

Triclinic crystal system ($a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$). In this crystal system all three angles between the ribs of the elementary parallelepiped of the spatial lattice are acute or obtuse. The primitive cell in this crystal system is asymmetric, that is the oblique parallelepiped. In triclinic crystals, there are no axes and planes of symmetry. All directions in crystals are single. The coordinate axes are not specified by the elements of symmetry, but are chosen along the ribs of the crystal under the condition $c < a < b$. One rib is installed vertical (axis Z); from two others shorter is taken for the axis X and longer one for the axis Y (Figure 2.44). Characteristic symmetry: $\bar{1}, 1$.

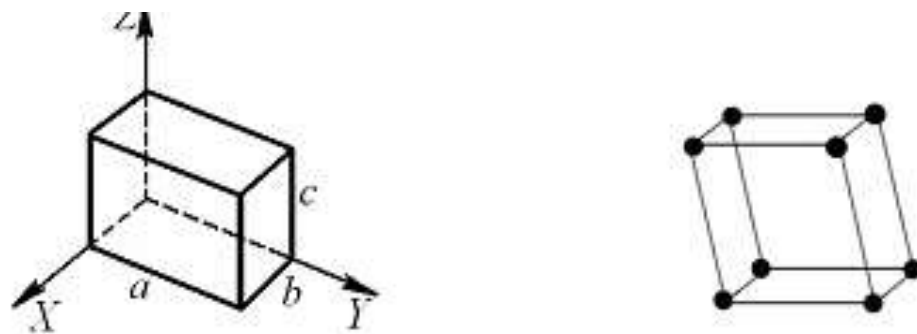


Figure 2.44. Elementary cell of the triclinic system

Monoclinic crystal system ($a \neq b \neq c$; $\alpha = \gamma = 90^\circ \neq \beta$). Two axes (X and Z) intersect at acute or obtuse angle. The third axis (Y) perpendicular to the axes X and Z. Between the indicated ribs there is only one indirect angle (two others are right angles). The crystal is set so that the axle is tilted forward. The elementary cell is the direct prism, based on parallelogram (Figure 2.45). In monoclinic crystals there is

only one axis of the second order L_2 or just the plane P , or L_2PC . Crystals of this crystal system have many single directions, which pass in the plane perpendicular to L_2 , and also corresponds with L_2 , or normal is parallel to P , and many symmetrically equal lines, passing at the angle to L_2 and P .

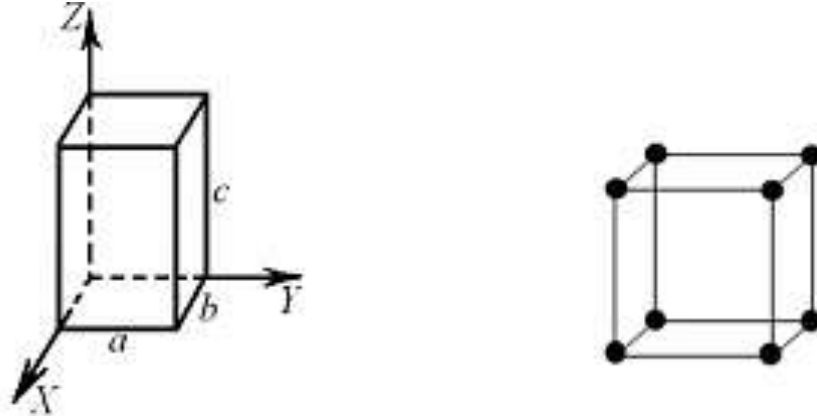


Figure 2.45. Elementary cell of the monoclinic crystal system

Orthorhombic crystal system ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$). Simple forms that belong to it, very often have the form of rhombus in the section. This system corresponds to the rectangular coordinate system, but the axis distance are different $c < a < b$. It does not matter which of the three crystallographic axes is taken as the axis X , Y or Z . When placing rhombic crystal it is assumed that axis X corresponds to the smallest axial distance, and axis Y is with the largest axial length. The elementary cell is the rectangular parallelepiped, so called «brick» (Figure 2.46).

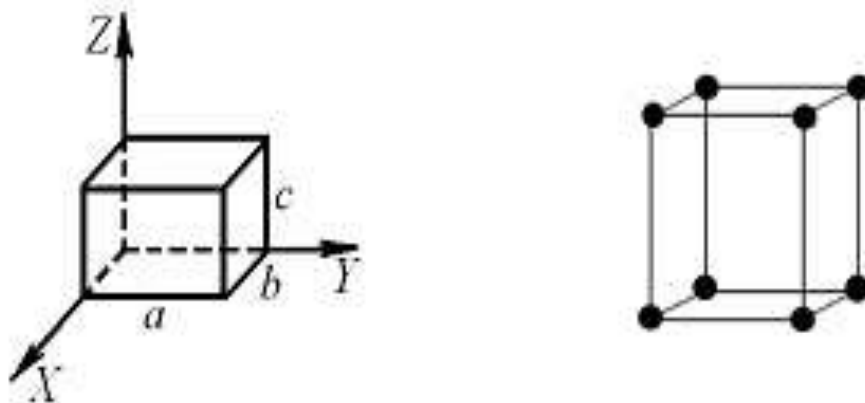


Figure 2.46. Elementary cell of the orthorhombic crystal system

For the rhombic system, the presence of three mutually perpendicular L_2 axes is characteristic. Characteristic symmetry: three axes L_2 or three planes P . In crystals of the rhombic crystal system, there are three single directions that match up with $3L_2$ or with normal to P .

Trigonal crystal system ($a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$) (Figure 2.47). This system is actually the subsystem of the hexagonal system. Crystals of the trigonal system have single axis L_3 . In these crystals there is one single direction, which coincides with a single axis L_3 . All directions relative to L_3 are symmetrically equal and repeat at least three times. Characteristic symmetry: 3 and $\bar{3}$.

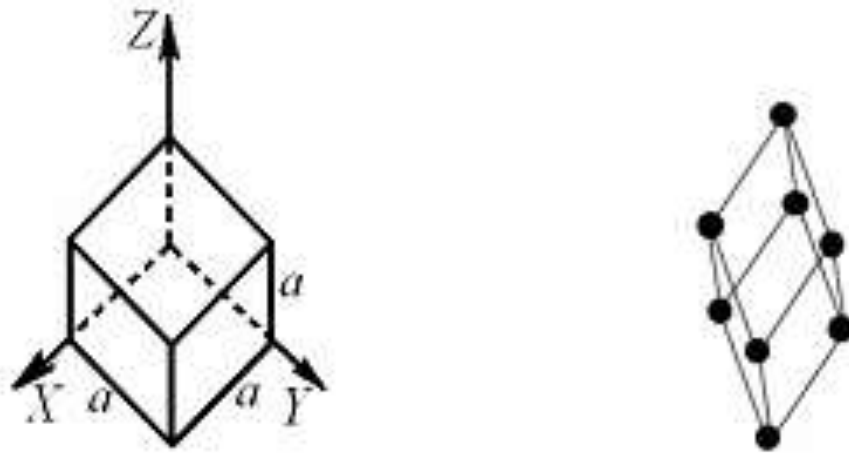


Figure 2.47. Elementary cell of the trigonal crystal system

Tetragonal crystal system ($a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$) (Figure 2.48). In this crystal system three mutually perpendicular crystallographic axes are present. Axis unit along the axis Z not equal to the axial units along the axes X and Y . For this crystal system is characteristic the L_4 axis, which coincides with the axis Z . The elementary parallelepiped is the square-shaped prism. Characteristic symmetry: 4 or $\bar{4}$. So, this system owns one single direction, which coincides with the single axis L_4 or L_4^- . All directions are relative to L_4 (or L_4^-) symmetrically equal directions that are repeated at least 4 times. For this crystal system are introduced relationship c/a , which is called the material constant of matter.

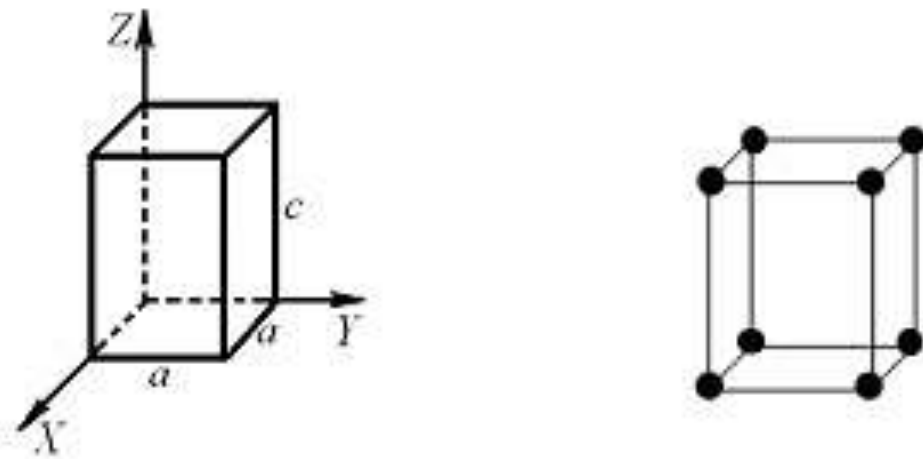


Figure 2.48. Elementary cell of the tetragonal crystal system

Hexagonal crystal system ($a = b \neq c$; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$). Four axes are used to describe the hexagonal system (Figure 2.49).

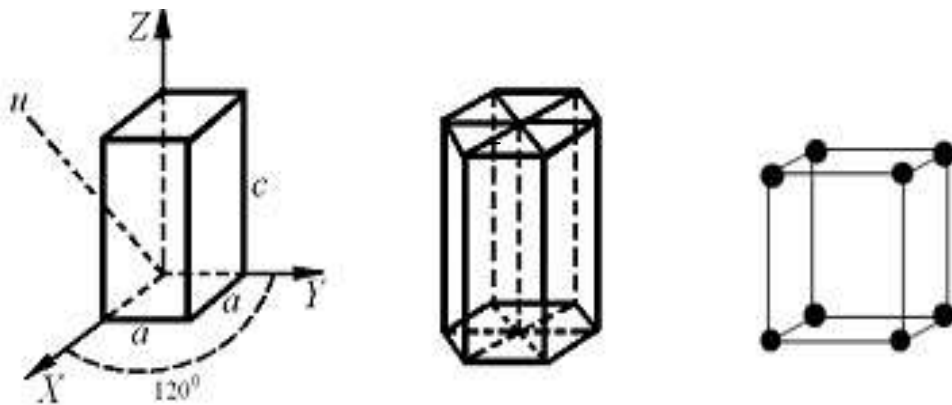


Figure 2.49. Elementary cell of the hexagonal crystal system

(three primitive lattice together make the hexagonal prism; so in this case it is convenient to add the fourth coordinate axis U in the XY)

Three of them (axis X , U , Y) are in the horizontal plane and intersect at the angle 120° and 60° , and the fourth (axis Z) perpendicular to this plane. The ratio of axial units in the hexagonal crystal $a:c$ may be larger or less than one. The axis L_6^- (or L_6) is characteristic to this crystal system. The elementary parallelepiped in this case is a prism, which is based on the rhombus with angle 120° . Three such prisms together form the hexagonal prism, which is not primitive. Characteristic symmetry: 6 or $\bar{6}$. This crystal system is characterized by the single direction, which coincides

with L_6 (or L_6). All directions are relative to L_6 (or L_6) are symmetrically equal directions, which are repeated 6 times.

Cubic crystal system ($a = b = c$; $\alpha = \beta = \gamma = 90^\circ$). Crystals of this system are projected onto three mutually perpendicular crystallographically equivalent axes (Figure 2.50). Crystals of the cubic system have spatial lattices and elementary parallelograms, which have the cubic shape. In the crystals of this system must be $3L_4$ and several order axes are higher L_2 . There are no single directions. Characteristic symmetry: $4L_3$.

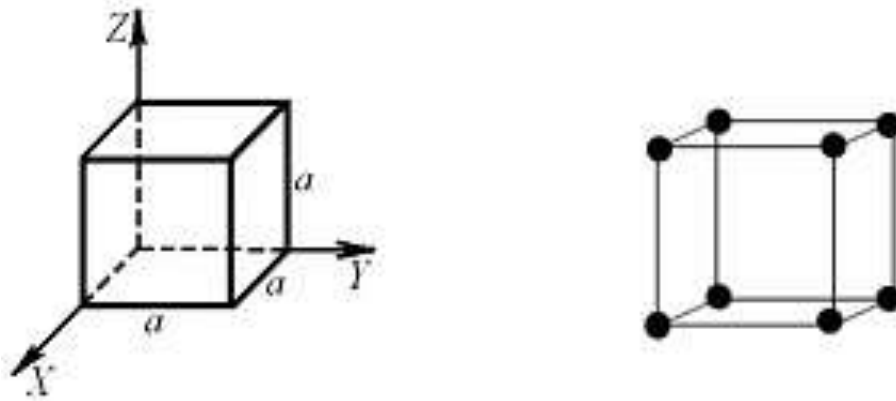


Figure 2.50. Elementary cell of the cubic crystal system

By symmetry and the number of unidirectional crystals are divided into three categories:

1. The lower category, which includes the triclinic, monoclinic, and rhombic crystal systems, is characterized by the presence of several single directions (in the number of at least 3) and the absence of axes of symmetry of order more than two. These are the least symmetric crystals with pronounced anisotropy properties.

2. The middle category, which combines trigonal, tetragonal, hexagonal crystal system. It is characterized by the presence of one single direction, which coincides with the single axis of the order above two. Anisotropy of physical properties is less than the lower category. It is particularly noticeable difference in properties along and perpendicular to the main axis. Characteristic forms of crystals are prisms, pyramids.

3. The higher category consist the cubic system. There are no single directions here. There are always several order axes above two. These are highly symmetrical

crystals. All directions in the crystal corresponds to other symmetrically equivalent directions. The properties of the anisotropy are very small, since in the symmetrically equivalent directions the physical properties must be the same.

2.6. Symmetry classes, systems of notation and spatial groups

Symmetry classes is called the complete set of elements of a crystal polyhedron. Each class is characterized by the certain complex of symmetry elements, which can be expressed by the corresponding crystallographic formula (Table 2.4). The symmetry formula consists of all symmetry elements of the crystal written consecutively. The axes of symmetry from the higher to the lower are written in the first position, planes of symmetry – on the second position, then the center of symmetry. So, the symmetry formula of the cube $3L_44L_36L_29PC$.

Used till this notations by E. E. Flint is the listing of all available symmetry elements, but they are very cumbersome. They can be simplified by using theorems on the combination of symmetry elements. E. E. Flint uses the following notation of symmetry: *axis of rotary* L_1, L_2, L_3, L_4, L_6 , *axis of rotoinversion* L_2^4, L_6^3 або L_{i4}, L_{i6} , *plane of symmetry* P and *center of symmetry* C .

In crystallography there is the international system of notation called *Hermann–Mauguin*. The point group symbol contains only such set of symmetry elements, by which it is possible to find the complete set according to known rules. They are more compact and you can set the symmetry symbols on the character record. To do this, the theorems on the combination of symmetry operations (Euler's theorem) and rules for setting each system should be taken into account. In the international symbol of each class not all simbol have written, but only the main or so-called "generating" elements of symmetry. The «generated» elements of symmetry, which can be deduced from the combinations of «generating» elements, are not written.

The international system gives only the initial symmetry elements for this class. In the literature there are full notations and abbreviations. They show the initial

elements of symmetry in certain dominant geometric directions, which run parallel to the axes of symmetry, normals, symmetry planes, that is, associated with the placement of crystals. The rotary axis of symmetry denoted by numbers that correspond to the order of the axes (2, 3, 4 and 6), the planes are marked with the letter m . In this system, inversion rotary axes are introduced 1, 2, 3, 4, 6. Classes denote different combinations of numbers and letters m .

Basic designations:

n – the n th order axis of rotation;

\bar{n} – the n th order axis of rotoinversion;

m – mirror plane;

nm – axis of rotation of the n th order and n symmetry planes passing along it;

n/m – the n th order axis of rotation and the plane of symmetry perpendicular to it;

$n2$ – the n th order axis of rotation and n axes of the second order, which are perpendicular to it;

n/mm – the n th order axis of rotation and parallel and perpendicular to their of plane m .

International characters are written according to the rules of crystallographic placement and the order of the record: the position of a digit or letter, which means the element of symmetry, depends on which position in the symbol it is put. In international symbols distinguish the «coordinate» elements of symmetry that pass along coordinate planes, and «diagonal» – along the bisector of the corners between them. *Warning! Replace a letter or a digit in a character from one position to another completely changes the meaning of the character. Example, $m3 = 4L_33L_23PC$ – cubic crystal system, $3m = L_33P$ – trigonal crystal systems.*

Table 2.4. Thirty-two classes of symmetry

Category	The crystal system	The classes of symmetry						
		Primitive	Center	Plane	Axis	Plane and axis	Inversion-primitive	Inversion-plane
The lower	Triclinic	L_1	C	–	–	–	–	–
	Monoclinic	–	–	P	L_2	L_2PC	–	–
	Orthorhombic	–	–	L_2P	$3L_2$	$3L_23PC$	–	–
The middle	Trigonal	L_3	L_3C	L_33P	L_33L_2	L_33L_23PC	–	–
	Tetragonal	L_4	L_4PC	L_44P	L_44L_2	L_44L_25PC	$L_{i4}=$ L_2^*	$L_{i4}=$ $(L_2^*)=$ $2L_22P$
	Hexagonal	L_6	L_6PC	L_66P	L_66L_2	L_66L_27PC	$L_{i6}=$ L_3P	$L_{i6}3L_23P$ $=$ L_33L_2 $4P$
The higher	Cubic	$4L_33L_2$	$4L_33L_23PC$	$3L_{i4}4L_36P$	$3L_44L_36L_2$	$3L_44L_3$ $6L_29PC$	–	–

In determining the symmetry classes, the following data are taken into account:

1. The presence or absence of single directions (crystals with single directions belong to the lower or middle categories and constitute 27 classes; crystals that do not have single directions refer to the higher category and they form 5 classes).






2. In accordance with the theorems on the combination of symmetry elements:
 a) the intersection line of the mirror planes of symmetry is the axis of rotation. The order of axis is determined by the angle divided by two between the planes of symmetry what is intersecting; b) the number of mirror planes of symmetry passing through the axis of rotary is equal to the order of this axis; c) in the presence of the center of symmetry and the pair axes of symmetry, the mirror plane of symmetry is located perpendicularly to them; d) the number of 2-order axis of rotary placed parallel to the axis of rotary of the n th order is numerically equal to the order of this axis n .

According to this the distribution on the symmetry classes can be considered. Let consider classes in which there are single directions.

1. *Primitive class of symmetry.*

Indication: the only axis of rotation of the n th order, which coincides with the single direction. 5 classes of symmetry are belong to this type of symmetry. According to the international classification, the formulas take the form: for $L_1 - 1$; $L_2 - 2$; $L_3 - 3$; $L_4 - 4$; $L_6 - 6$. According to the symmetry elements stereographic projections are given (Table 2.5).






Table 2.5. Characteristic of the primitive class of symmetry

Brave Symbolics	L_1	L_2	L_3	L_4	L_6
International notation (Hermann–Mauguin)	1	2	3	4	6
Projection of symmetry elements					

2. *Center class symmetry.*

Indication: The center of symmetry is added to the single direction. The single direction may coincide with the axis of rotation. According to the 1st Euler's theorem, the plane perpendicular to the axis of the pair order appears. So, to this type of symmetry belong 5 classes of symmetry with formulas: $C - \bar{1}$; $L_2PC - 2/m$; $L_3C - \bar{3}$; $L_4PC - 4/m$; $L_6PC - 6/m$. Stereographic projections are induced in Table 2.6.






Table 2.6. . Characteristics of center symmetry class

Brave Symbolics	C	L_2PC	L_3C	L_4PC	L_6PC
International notation (Hermann–Mauguin)	$\bar{1}$	$2/m$	$\bar{3}$	$4/m$	$6/m$
Projection of symmetry elements					

3. Plane symmetry class.

Indication: to the original single direction the symmetry plane passing along the direction is added. The single direction coincides with the axis of rotation. According to the 4th Euler's theorem such planes appear in quantity n . To this type of symmetry belong 5 classes of symmetry with formulas: $P - 2$; $L_22P - 2mm$; $L_33P - 3m$; $L_44P - 4mm$; $L_66P - 6mm$. Stereographic projections are shown in Table 2.7.

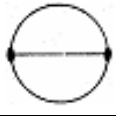

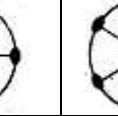
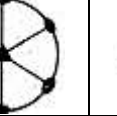
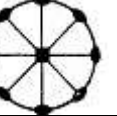
Table 2.7. Characteristics of plane symmetry class

Brave Symbolics	P	L_22P	L_33P	L_44P	L_66P
International notation (Hermann–Mauguin)	$\bar{2}$	$2mm$	$3m$	$4mm$	$6mm$
Projection of symmetry elements					

4. Axis symmetry class.

Indication: to the n th order axis of rotary, which coincides with the single direction, the axis of the 2nd order is added. According to the 3rd Euler's theorem n such axes are present. Thus, the following classes of symmetry belong to this symmetry type: $L_2 - 2$, $3L_2 - 222$, $L_33L_2 - 32$, $L_44L_2 - 422$, $L_66L_2 - 622$. Projections are presented in Table 2.8.


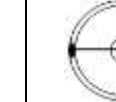



Table 2.8. Characteristics of axis symmetry class

Brave Symbolics	L_2	$3L_2$	L_33L_2	L_44L_2	L_66L_2
International notation (Hermann–Mauguin)	2	222	32	422	622
Projection of symmetry elements					

5. The plane and axis symmetry class.

Indication: to the n th order axis of rotating, which coincides with the single direction, parallel planes and perpendicular the 2nd order axes are added. According to 4th Euler's theorem, the number of parallel planes and axes of the second order is equal to the order of the axis and, according to the 2nd Euler's theorem, there is also the transverse plane. That is, the following symmetry classes appear: $L_2PC - 2/m$, $3L_23PC - mmm$, $L_33L_23PC - 32/m$, $L_44L_25PC - 4/mmm$, $L_66L_27PC - 6/mmm$. The corresponding stereographic projections are given in Table 2.9.

Table 2.9. Characteristics of plan and axis symmetry class

Brave Symbolics	L_2PC	$3L_23PC$	L_33L_23PC	L_44L_25PC	L_66L_27PC
International notation (Hermann–Mauguin)	$2/m$	mmm	$32/m$	$4/mmm$	$6/mmm$
Projection of symmetry elements					

6. Inversion-primitive and inversion-plane symmetry classes.

Indication: inversion primitive class of symmetry: the single direction coincides with the single axis of rotoinversion: $L_{4i}^- - 4$, $L_3\bar{P} - 6$. The sign of the inversion-plane symmetry class: to the original single direction, which coincides with the single axis of rotoinversion, the axis of the 2nd order and the symmetry plane are added. It follows from the 5th Euler's theorem that the number of axes of the second order is equal to the order of the higher axis: $\bar{L}_{i4}2L_22P - 42m$, $L_3P - 6m2$. Stereographic projections are shown in Table 2.10.

Table 2.10. Characteristics of inversion-primitive and inversion-plane symmetry class

Brave Symbolics	L_{4i}	L_3P	$L_{i4}2L_22P$	$L_{i6}3L_24P=L_33L_24P$
International notation (Hermann–Mauguin)	$\bar{4}$	$\bar{6}$	$\bar{4}2m$	$\bar{6}m2$
Projection of symmetry elements				

7. Classes of symmetry that have no single directions.

Consider cases without single directions (Table 2.11). For each direction, arbitrary axes are repeated several times. These include cubic system with the 5 classes of symmetry: the primitive – 23 (combination the axes of rotation), the center – $m\bar{3}$ (combination the axes of rotation and the axes of rotoinversion), the plane – $4\bar{3}m$ (combination the axes of rotation and the axes of rotoinversion), the axis – 432 (combination the axes of rotation) ta the plane and axis – $m\bar{3}m$ (combination the axes of rotation and the axes of rotoinversion).

Table 2.11. Characteristics of symmetry class of the higher category

Brave Symbolics	$4L_33L_2$	$3L_44L_36L_2$	$4L_33L_2$	$3L_44L_36L_2$	$4L_33L_2$
International notation (Hermann–Mauguin)	23	432	23	432	23
Projection of symmetry elements					

The interaction of the symmetry elements (point groups) and the 14 Brave lattices leads to the appearance of 230 spatial groups (Fedorov groups). A set of these groups must be regarded as the constant of nature.

Point groups characterize the symmetry of the external shape of the crystal and its physical properties. Spatial groups characterize the crystal symmetry structure. They are the main criterion that distinguishes crystalline structures from other formations. Typically, Brave cell type is used to determine spatial groups (it is indicated by the corresponding letter, see Table 2.12) and the international symbol of the point group.

Table 2.12. **Brave cell type and the corresponding designation**

Brave cell type	
Base-centreted	<i>C</i>
Face-centreted	<i>F</i>
Body-centered	<i>I</i>
Rhombohedral	<i>R</i>
Primitive	<i>P</i>

2.7. Simple forms

The crystal cut is the important characteristic of a crystalline substance that distinguishes crystals of one substance from crystals of another. Crystallography was formed as a science during the process of study of the outer shape of crystals that.

In nature, the crystals of one substance can have a variety of forms, at the same time, some faces occur more often, others are less often. The presence of the same faces in different crystals of the same substance became the basis for the discovery of the first fundamental law of crystallography – law of constancy of interfacial angles.

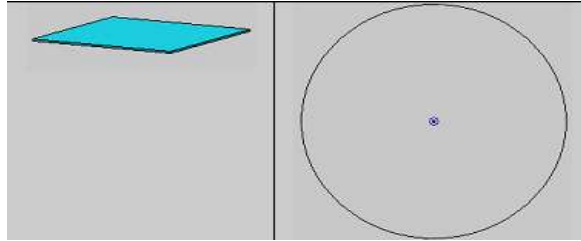
The each crystal cut strictly is responsible own symmetry, that is, one of the point groups. The uniform development of a crystalline polyhedron contribute the crystal gets an ideal shape, but there is almost no ideal growth condition, therefore the shape of real crystals is distorted. However, the fact during the crystal growing, the faces (edges) move in parallel to themselves, allows to determine their faces by normals, through that the crystal any shape, receives a single description.

Simple form of a crystal is called the set of faces, which are connected with each other by operations of the exact group of symmetry.

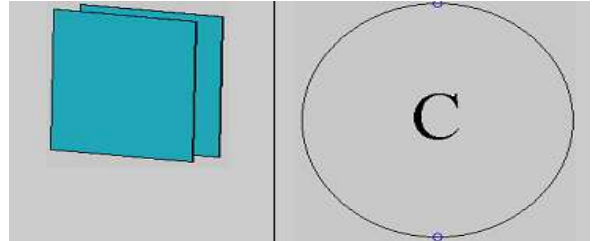
In the fringing of the crystal, the faces of one simple form or several may participate, forming a combination polyhedron. In this case, distinguish closed simple forms (those that completely close the space, for example – the cube), and open (those that do not close the space, for example, prism and pinacoid). The open simple can not shape the closed polyhedron.

There are 47 simple forms in total, among them 32 forms belong to the lower and the middle category, and 15 to the higher category.

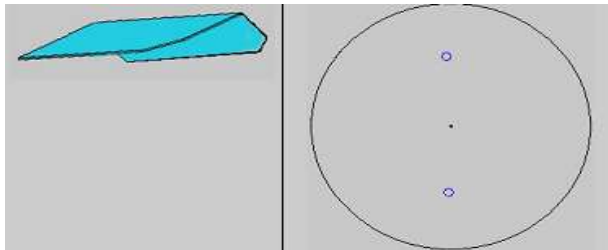
Simple forms referring to the lower and middle categories are shown in Figures 2.51–2.57.



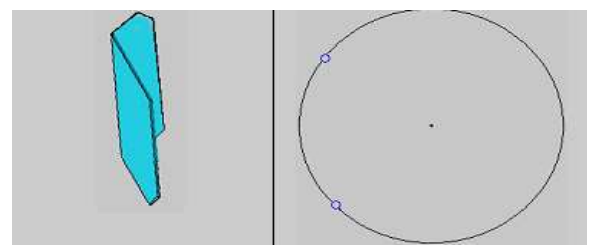
Pediton



Pinacoid

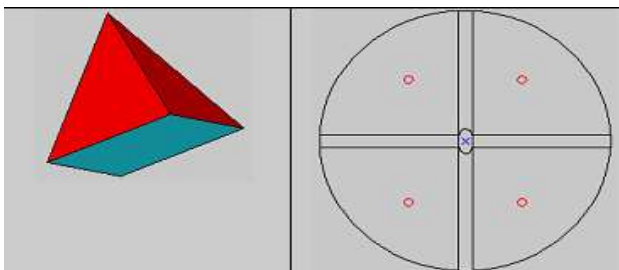


Dome

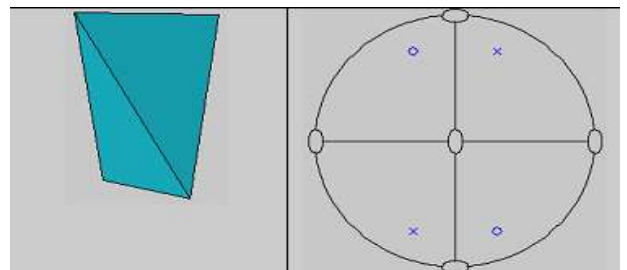


Shenoid

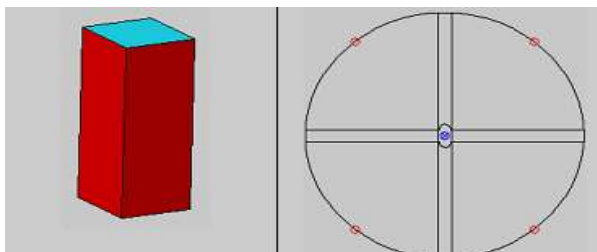
Figure 2.51. Types of open simple forms



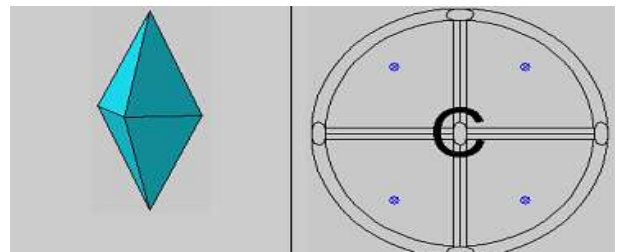
Rhombic pyramid + pediton



Rhombic tetrahedron

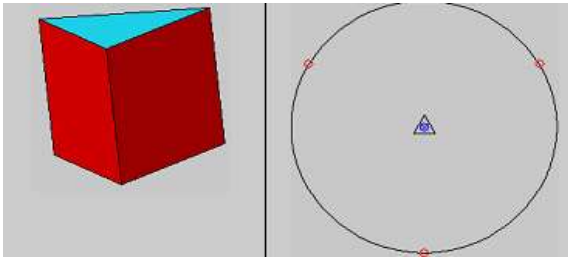


Rhombic prism + pinacoid

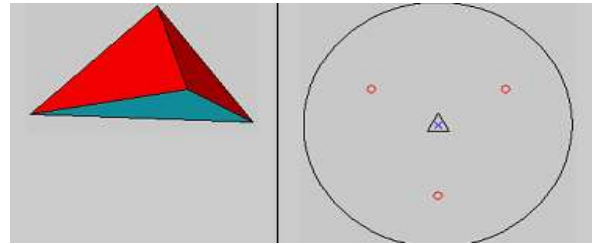


Rhombic bipyramide

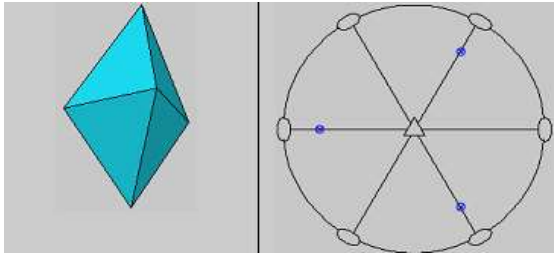
Figure 2.52. Types of rhombic simple forms



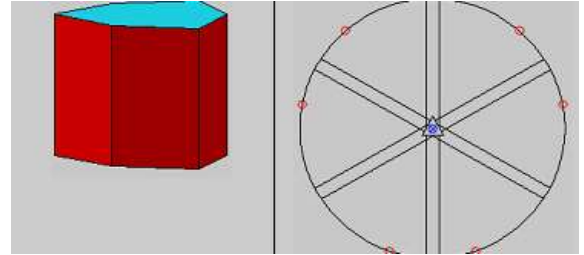
Trigonal prism + pinacoid



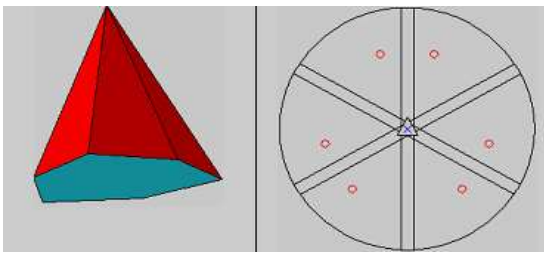
Trigonal pyramide + pedion



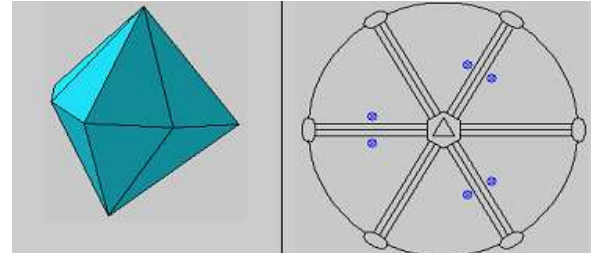
Trigonal bipyramide



Ditrigonal prism + pinacoid



Ditrigonal pyramide



Ditrigonal bipyramide

Figure 2.53. Types of trigonal simple forms

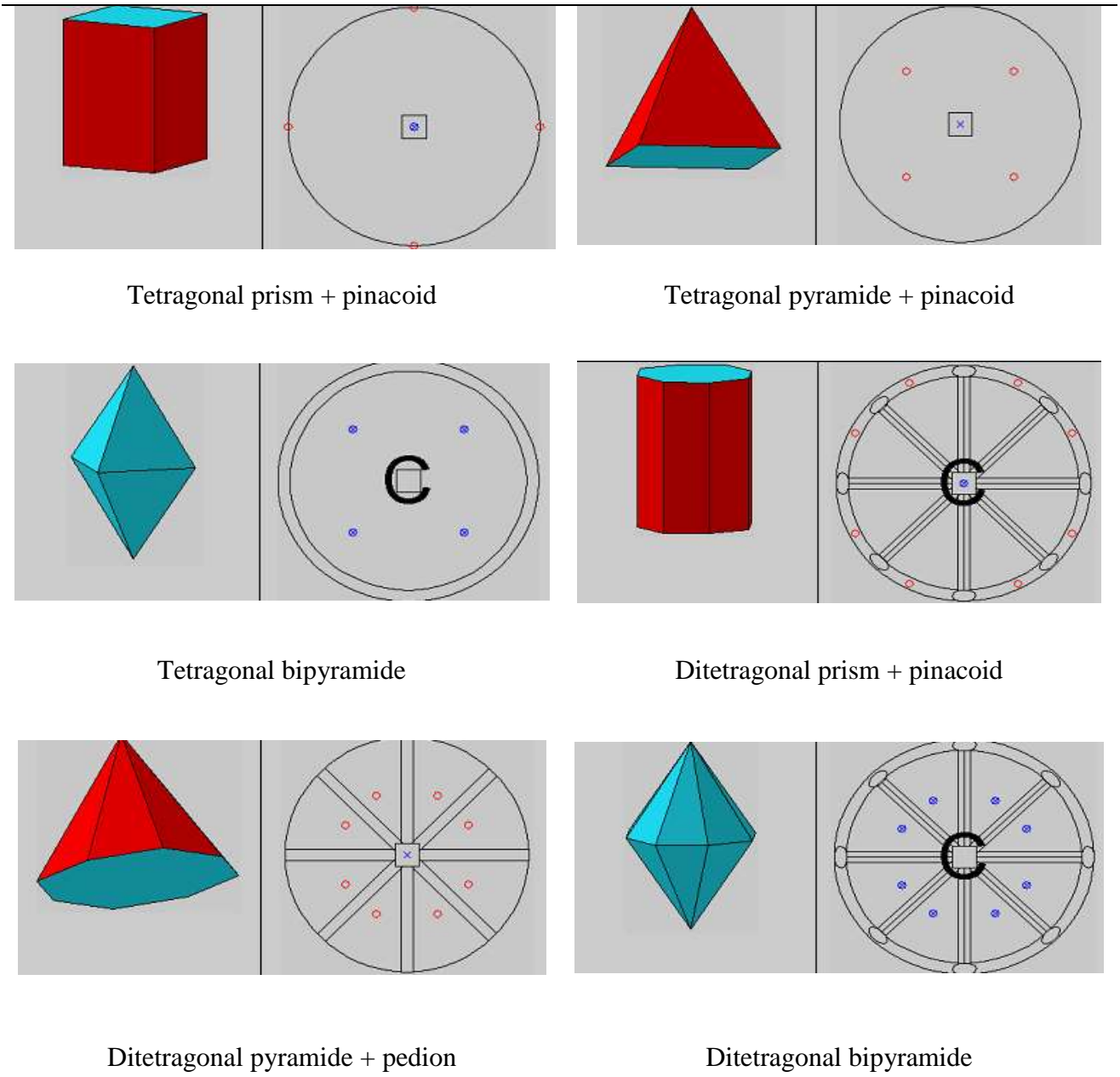
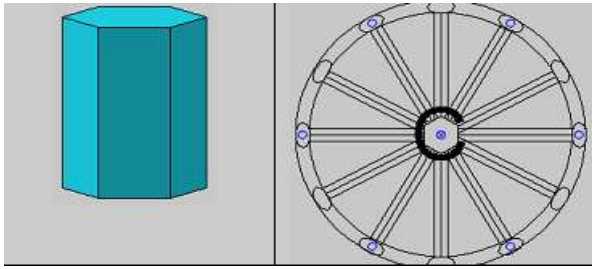
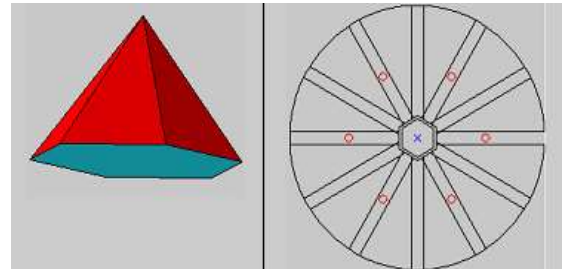


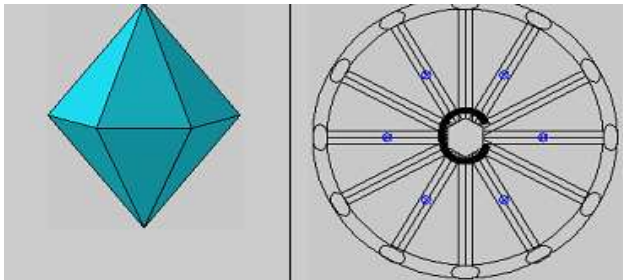
Figure 2.54. Types of tetragonal simple forms



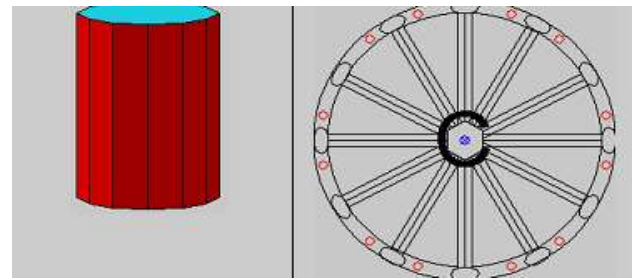
Hexagonal prism + pinacoid



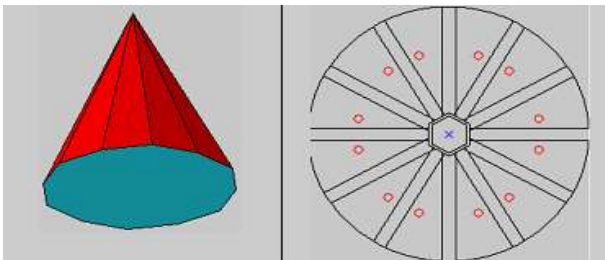
Hexagonal pyramide + pinacoid



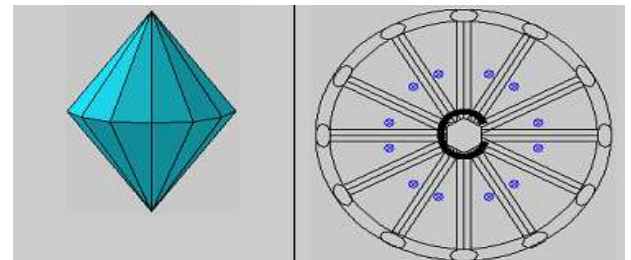
Hexagonal bipyramide



Dihexagonal prism + pinacoid



Dihexagonal pyramide + pediom



Dihexagonal bipyramide

Figure 2.55. Types of hexagonal simple forms

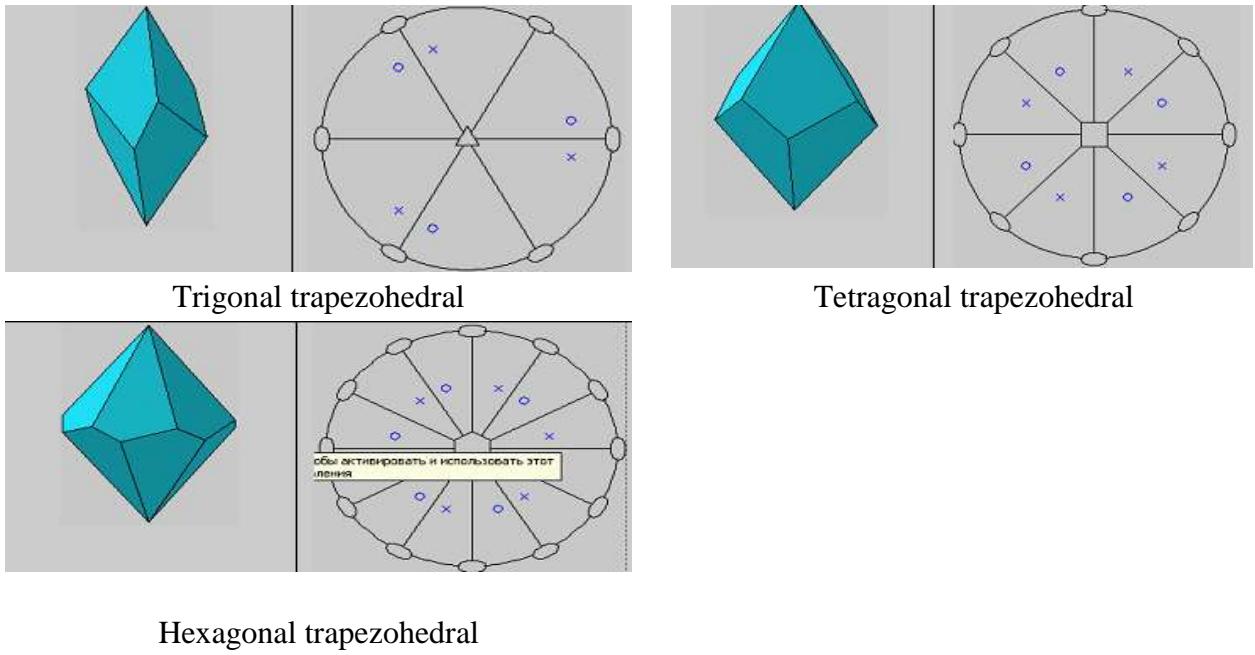


Figure 2.56. Types of simple forms for the trapezohedral

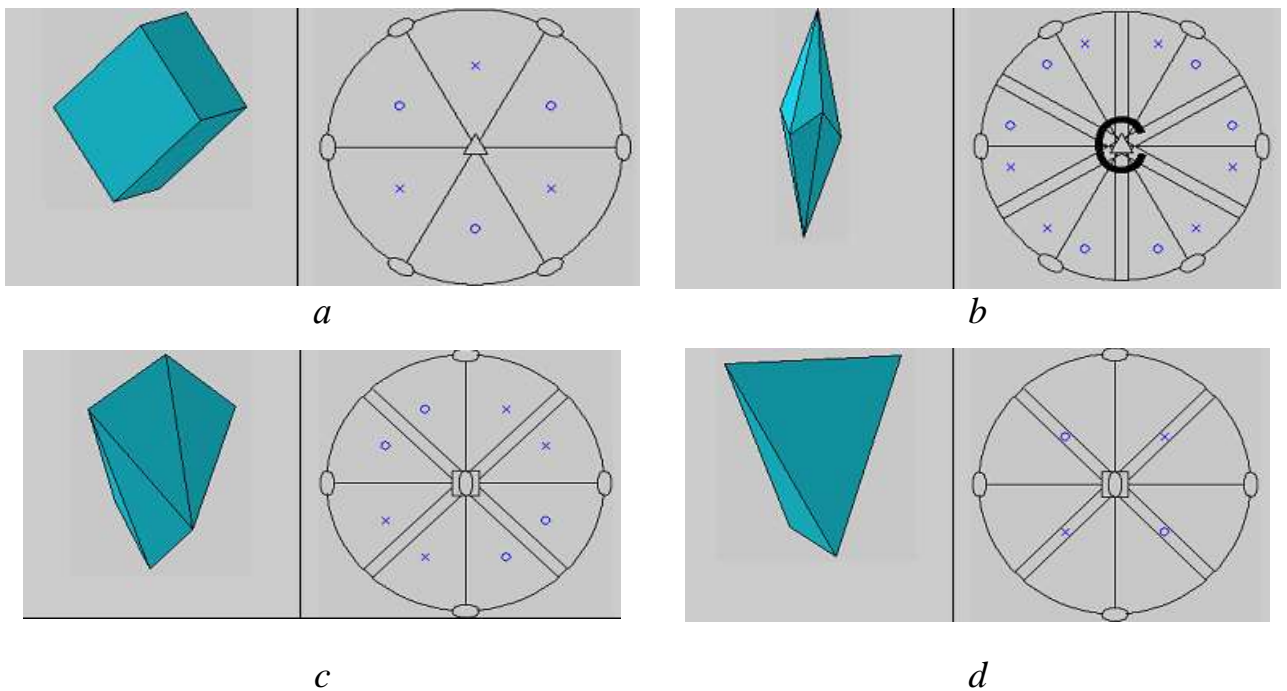
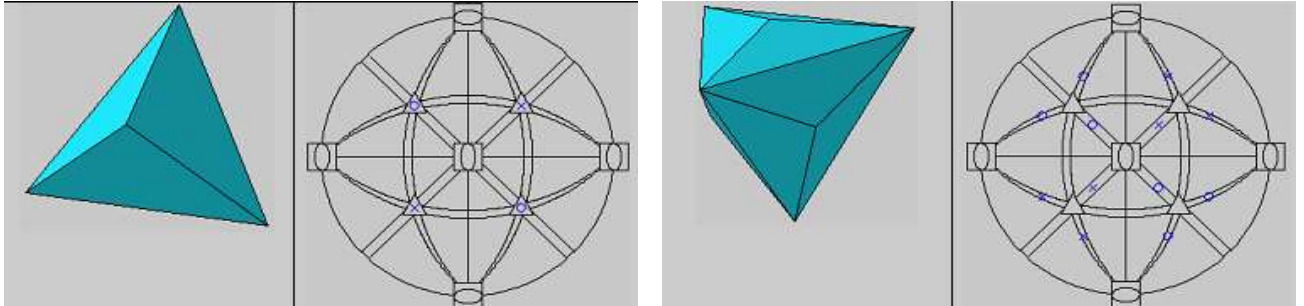


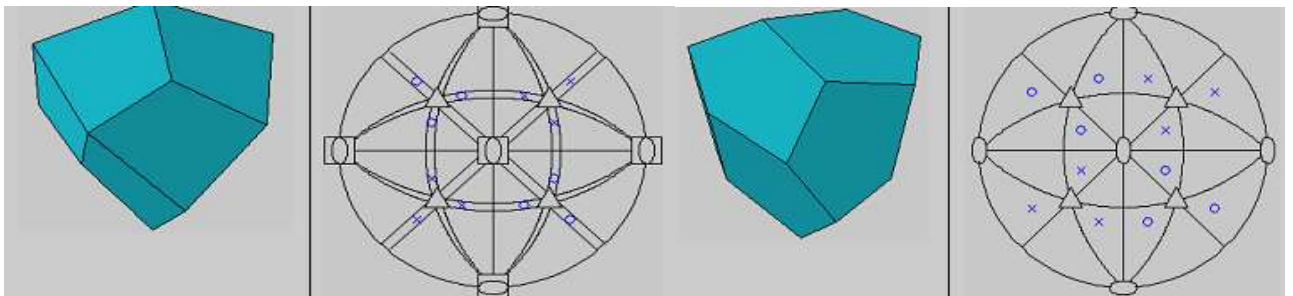
Figure 2.57. Types of simple forms: rhombohedral (*a*); trigonal scalenohedron (*b*); tetragonal scalenohedron (*c*); tetragonal tetrahedron (*d*)

Simple forms referring to the higher category or cubic system are shown in the Figures 2.58–2.60 [7].



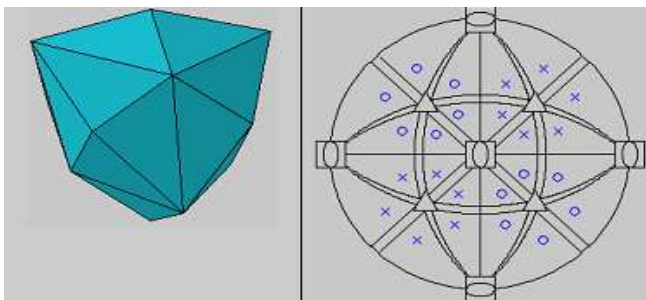
Tetrahedron

Trigon-3-tetrahedron



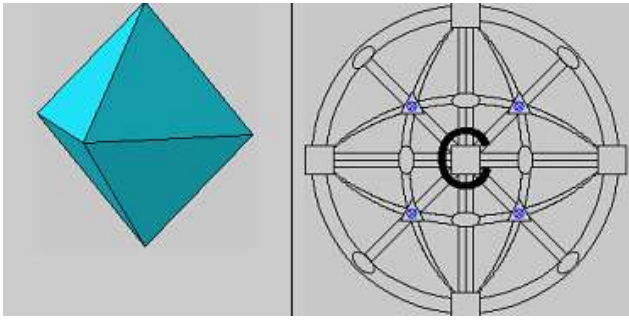
Tetra-3-tetrahedron

Pentagon-3-tetrahedron

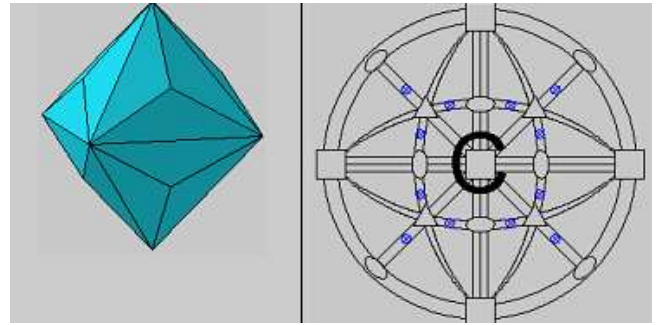


Hexatetrahedron

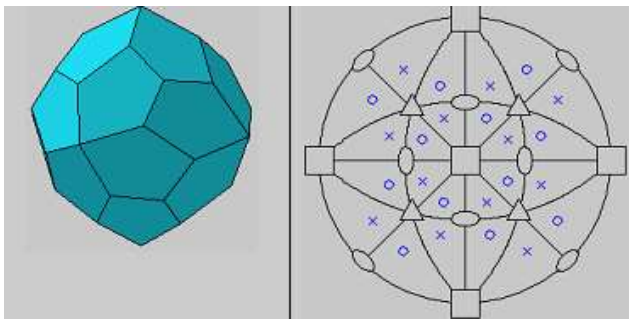
Figure 2.58 . Types of simple forms for tetrahedra shapes



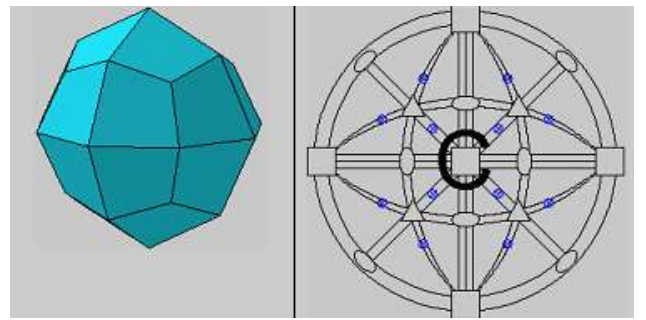
Octahedron



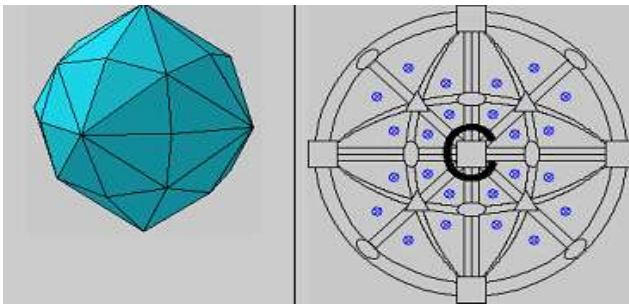
Trigonal octahedron



Tetragonal octahedron

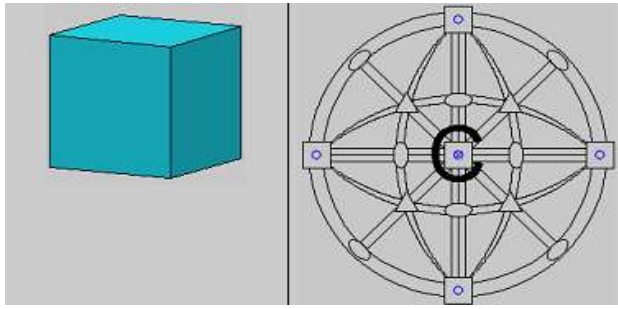


Pentagonal octahedron

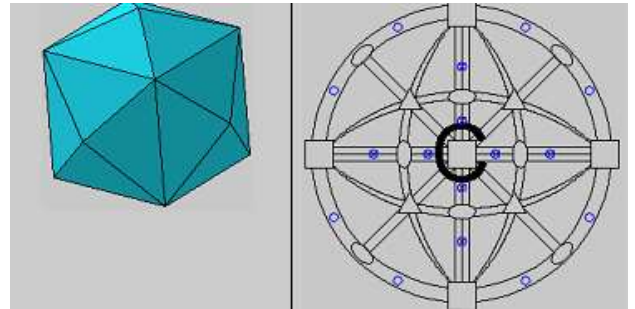


Hexagonal octahedron

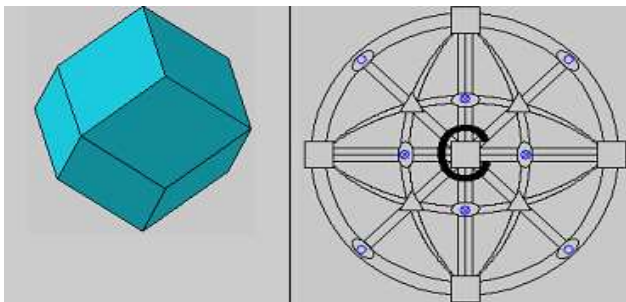
Figure 2.59. Types of simple forms for the octahedron-based bodies



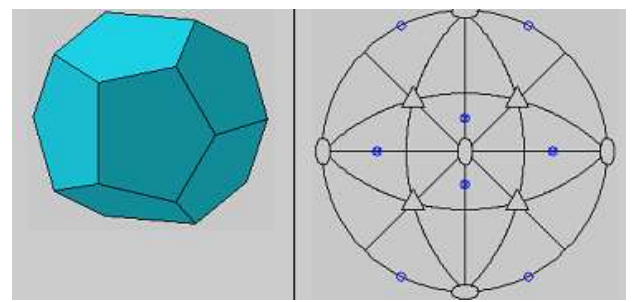
Hexahedron (cube)



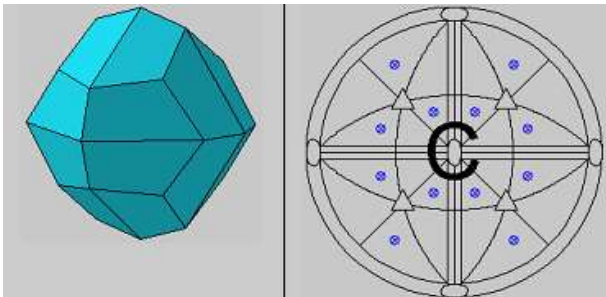
Tetragonal hexahedron



Rhomboid dodecahedron



Pentagonal dodecahedron



Dodecaedro

Figure 2.60 . Types of simple forms for Hexahedron shapes

Control questions

1. Give the definition of crystals, name their elements.
2. Give the definition of the elementary cell and its elements.
3. Give the definition of the law of constancy of interfacial angles for the crystals.
What is follow from this?
4. Provide nodes indexing principles.
5. Give the principles of indexing the crystal faces.
6. Explain Weiss's parameters and Miller's indices.
7. What are the principles of plotting planes symbols?
8. Give the definition and the value of the integers law.
9. What methods of crystal projections are used in crystallography?
11. How to build the spherical projection of a crystal?
12. How to build the stereographic projection of a crystal?
13. What are elements depicted on the stereographic projection?
14. How are elements of symmetry depicted on the stereographic projection?
15. How to build the gnomostereographic projection of a crystal?
16. How to build the gnomonic projection of a crystal?
17. What kind of projection use for image the symmetry elements?
18. What is the inversion center and its features? What is the plane of symmetry?
19. What is the axis of rotation and how is it determined?
20. Give the definition of the axis of rotoinversion.
21. What is the single direction?
22. What are the crystal systems? Provide their types
23. What are Bravais lattices?
24. How are the elements of symmetry and plane depicted on the stereographic projection?
25. Give the definition of symmetry.
26. Name the symmetry elements and point classes.

27. Describe the lower category.
28. Describe the middle category.
29. Give the description of the higher category.
30. What is the symmetry class? Name the symbols of symmetry elements.
31. Describe the primitive symmetry classes.
32. Describe the central symmetry classes.
33. Describe the planetary symmetry classes.
34. Describe the axial symmetry class.
35. Describe the planaxial symmetry classes.
36. Describe the inversion symmetry classes.
37. Give characteristic of the symmetry class that does not have *SD*.
38. What are simple forms of the crystal ? What and how many simple forms exist?

CHAPTER 3. CRYSTAL CHEMISTRY

Crystallochemistry studies the connection between the laws of the internal structure of crystalline substances, whose reflection is the geometrically correct external shape of the crystals, and their chemical, physical and geometric properties [13]. Thus, crystallochemistry occupies the intermediate position between chemistry and crystallography and is inextricably linked with geological sciences, as well as with the chemistry and physics of the solid state.

3.1. Types of chemical bonding in crystals

Determination of the chemical bond type. By chemical bond mean forces that unite atoms in (crystalline) structure and hold them in the certain positions. Its various manifestations are called «types» or «species» of chemical bonding. Each type of connection imposes certain requirements on the structure geometry, on the physical and chemical properties of the crystal. Depending on which elementary particles are placed in the nodes of crystal lattices, there are four basic types of chemical bonding: ionic, covalent, metallic, and molecular. However, in most crystalline compounds there are bonds of several types, which are conventionally described as mixed bonds. Ionic, covalent and metallic are strong chemical bonds, the molecular is the weak bonding.

The main characteristics of the chemical bond are:

1) *bond length* – the distance between the centers of the atomic nuclei in the crystal molecule. It depends on the interacting atoms nature, and on the multiplicity of the bonding. With increasing multiplicity, the length of bond decreases, and, as a result, increases its strength. For example: the length of the C-bond in the ethane molecule is 0.154 nm; the length of the C=C bond in the ethen molecule is 0.134 nm; the length of the C≡C bond in the molecule of ethin is 0.120 nm;

2) the *bond multiplicity* is determined by the number of electron pairs that bind two atoms. With increasing multiplicity, the bonding energy is increasing;

3) the *angle of bond* is the angle between the imaginary straight lines passing through the nuclei of two chemically interconnected neighboring atoms (Figure 3.1);

4) *the bond energy* is the energy that is released when the bond is formed and spent for its break. This is the measure of the bond strength. The higher the energy, the stronger the bond. For example: the formation of bonds in 1 mole of hydrogen is accompanied by the release of 432.1 kJ of heat, that is, the energy of the H-H bond is 432.1 kJ/mol.

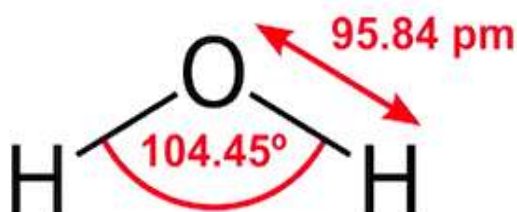


Figure 3.1. The structure of the water molecule

The conclusion about belonging to each type of bonding is based on the indirect data, by the comparing various physical properties of the compound under investigation (Table 3.1).

The ionic (heteropolar) bond is present in ionic crystalline structures and occurs between two differently charged ions. In essence, it is the Coulomb interaction between different ions (cations and anions) in the crystal formed by the transition of external valence electrons from one atom to another (from metal to nonmetal). The interaction of electrostatic forces of attraction and repulsion keeps the ions at the certain distance from each other. The linkage forces are non-directional, each ion is bound by equal forces with all adjacent ions. In the crystal, you cannot isolate a single molecule. The entire crystal can be regarded as a molecule.

The most closely packaging is characteristic for compounds with ionic bonding type. Ionic crystals are fragile, have low thermal and electrical conductivity. Most of them are dielectrics, whose conductivity is 20 orders of magnitude lower than the

electrical conductivity of typical metals. Compounds with ionic bonds are easily dissociated in the aqueous solution (i.e., they are well soluble). They have the high melting point, glass gloss, light color. The ionic bond energy is significant. Its value is within (5-17) eV/molecule.

Table 3.1. Comparative characteristics of chemical bond types [14]

Characteristic	Bond			
	Covalent	Ionic	Metallic	Molecular
Crystallochemical	Saturated Directed Small coordinate numbers (1, 2, 3, 4, 6)	Unsaturated Non-directional Large coordinate numbers (12, 8, 6, 4) Closest packaging		
Interatomic distance*, nm	0,1-0,15*	0,1-0,15*	0,1-0,15*	0,37-0,38*
Conductivity	Insulators	Medium insulators in solid state; ionic conductivity in liquid state	Conductors, electronic conductivity	Insulators in solid and liquid state
Melting point	High	High	Different	Low
Temperature expansion factor	Low	Low	Significant, different values	Large
Energy, kJ/mole	Hundreds	Hundreds	Tens	Less 0,5
Optical	n** large. Absorb in the UV, visible and infrared regions of the spectrum	n** different. UV and visible area does not absorb, the maximum absorption in the IR region. In most cases, absorption in the solid state is similar to absorption in the liquid state	Opacity Metallic shine	n** different
			Absorption in the solid state is similar to absorption in the liquid state	
Mechanical	Linkage is strong, high hardness	Linkage is strong, high hardness, fragility	Tensile strength is different, plasticity	Linkage is weak, soft crystals
Solubility	In nonpolar solvents with small ϵ^{***}	In polar solvents with large ϵ^{***}	Not soluble or chemically interact	Soluble in polar solvents

* for elements of period 2, **refractive index of light, *** dielectric constant.

Ionic bond is the most simple and most common in inorganic compounds – halides, nitrates, carbonates, sulfates. An example of minerals with ionic bond type can be NaCl (Figure 3.2).

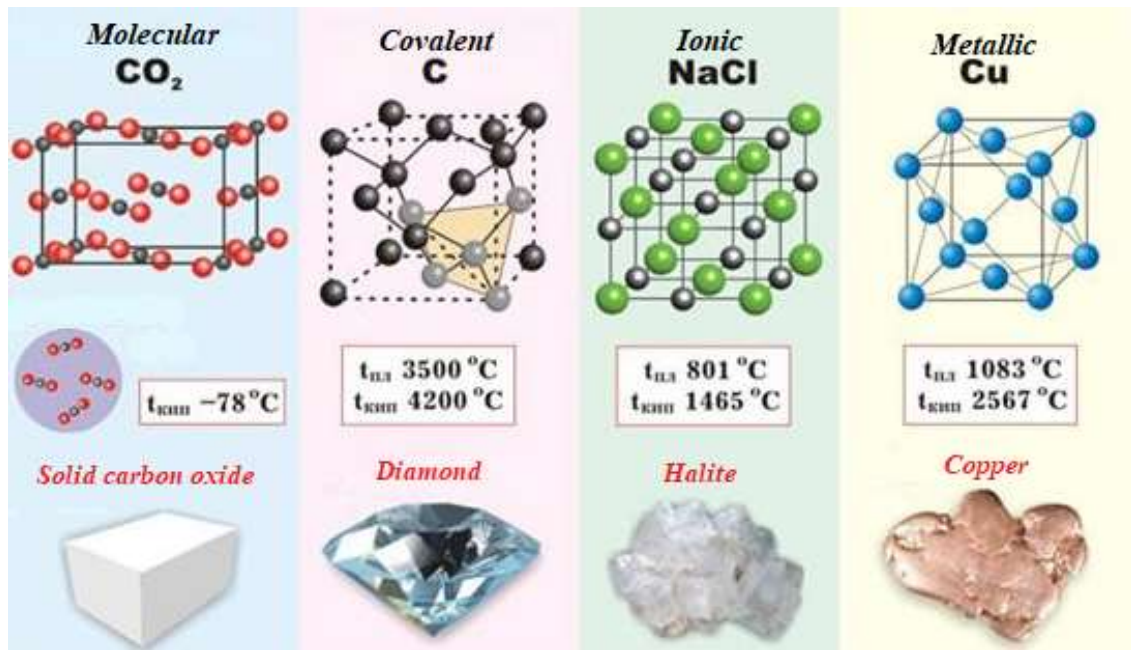


Figure 3.2. Examples of substances with different types of chemical bonding

The covalent (homopolar, atomic) bond is carried out in atomic and partially ionic crystalline structures. The characteristic feature of the covalent bond is the formation of one or more (two, three) common electron pairs that are in common use of the atoms that formed the bond. The two atoms or ions appear to be "constricted" together due to the appearance of common electronic shells. This bond is very strong, which explains the increased hardness of minerals with covalent bonding.

The main properties of covalent bond:

1) *orientation* (orientation of electronic shells one relative to another) characterizes the chemical structure and form of substances and determines the spatial structure of molecules, that is, their geometric form;

2) *saturation* – the property of atoms to form the strictly defined number of covalent bonds. Due to the bonds saturation, the molecules have the certain composition. The number of bonds that can form atoms is called valence;

3) the bond *polarity* arises due to the uneven distribution of the electronic density between two atoms with different electronegativity. Covalent bonds are divided into polar and nonpolar;

4) *polarizability* – the ability of the electrons of the bond to be displaced under the action of the external electric field (in particular, the electric field of another particle). Polarization depends on the mobility of electrons. The further the electron is from the core, the more it moves, respectively, and the molecule is more polarized.

All covalent crystals follow the rule that the coordinate number is equal to $(8-N)$, where N is the number of the periodic group (*Hume-Rothery Rule*). In fact, the coordination number is equal to the number of electrons that the atom can attach .

Covalent crystals are characterized by small coordination numbers, the absence of closely packings, the significant influence of impurities and temperature on photographic and electrical conductivity, and high melting temperatures. Covalent bonding is the sign of semiconductor crystals. The conductivity of covalent crystals varies in very broad ranges: from insulators to conductors. All minerals with covalent bonding are insoluble in water, most of them have diamond shine, high hardness, bright or light color. The bond energy – (3-12) eV/particle. The typical example of minerals with covalent bonding is diamond (Figure 3.2).

The metallic bond is carried out by the interaction of free electrons and positively charged atomic nuclei. Metallic crystal can be represented as the grid of positively charged atomic nuclei (atomic skeleton) immersed in the negatively charged «gas» («electronic gas»).

The atomic skeleton is the core with internal, tightly connected electron shells.

«Electronic gas» – are electrons, weakly connected with the atomic skeleton.

Each atom of the crystal lattice gives its electrons and becomes the positively charged ion (atomic skeleton). The given electrons are not fixed by any atom, but are «in general use» in the form of the electron gas.

Free movement and mobility of electrons lead to the high electrical and thermal conductivity. The metallic bond is spherically symmetric, and therefore not

directional. Metallic bonding characterized by large coordination numbers, closely particle packing, low band gap width, small compression and thermal expansion coefficients, ductility, opacity, dark color and metallic luster. The characteristic binding energy of metallic crystals is 3 eV/atom. Substances with the metallic type of bonding – copper, gold, silver (Figure 3.2).

The molecular (Van der Waals) bond is characteristic of molecular crystals. In molecular crystalline lattices, the bond between two molecules is made at the expense of the so-called residual forces (or Van der Waals bonds). Structures with this bond type consist of the neutral molecules, but the latter may have the slight excess of positive charge from one end of the molecule with the corresponding lack on its other end (e.g., the molecular structure of Cl₂). Thus, the center of gravity of all positively charged particles in the molecule does not coincide with the center of gravity of all negatively charged particles. Such molecules interact as weakly charged dipoles, and as the result of dipole-dipole interactions there are weak bonds called Van der Waals.

Crystal structures with the molecular bond are dielectrics (low heat and electrical conductivity), differing in their low hardness, fragility, low melting and boiling temperatures.

The characteristic energy of the molecular bond is 0.2 eV/atom, that is, it is the weak bond. With the slightest external influence (heating, pressure, etc.), the molecules are easily disconnected. Molecular crystals include O₂, H₂, HCl, CH₄ and organic crystals (Figure 3.2).

In some crystals, sometimes, the *hydrogen bond* is isolated, which has electrostatic character and occurs due to the attraction of neighboring electrons by hydrogen. Most often it occurs between the hydrogen atom and strongly electronegative atoms F, O, Cl, N. Usually, the hydrogen bond appears as an addition to the basic bond in the crystal. The energy of hydrogen bond – (0,1-0,5) eV/atom.

3.2. Atomic and ionic radius

The radius of the atom is not constant, but depends on the type of chemical bond and the valence state of the atom. Due to the attraction created by the chemical bond, the connected atoms are approaching ("squeezed" to each other). Thus, the radius of the atom in the compound (molecule, crystal) will be less than the radius of the free atom (Figure 3.3).

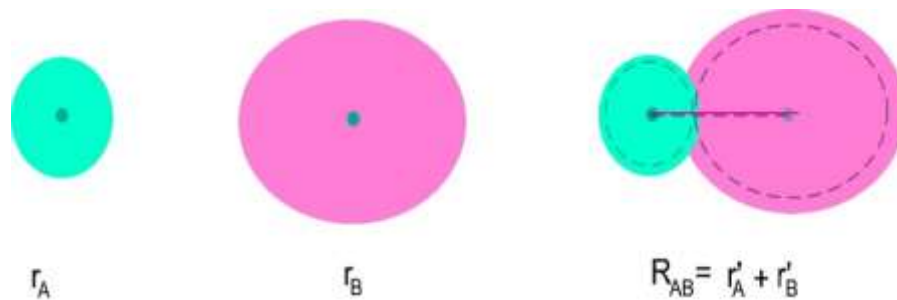


Figure 3.3. Calculation of the crystal-chemical radius

The effective radius of the atom or ion is the radius of its sphere of action. The atom is represented as the nucleus around which electrons rotate on orbits. The effective radius of the ion depends on the filling of the electron shells, but does not equal the radius of the outer orbit. To determine the effective radius, atoms (ions) in the structure represent as rigid balls touching such that the distance between their centers is equal to the sum of their radii [15].

The atomic (ionic) radii actually determine the distance between the nodes of the lattice, thus, the nature of the structure of this crystalline substance. The atomic (ionic) radii of different chemical elements have different magnitudes.

The value of the atomic (ionic) radius depends on [7]:

- 1) ion charge. Negatively charged anions are characterized by large radii due to excessive of electrons;
- 2) the polarization ability of the atom or ion, that is, the ability of the atom or ion to change its configuration under the influence of the external electric field;
- 3) thermodynamic conditions. The higher temperature and lesser pressure the greater ion radius.

There is no direct method for determining the radii of atoms (ions). Atomic and ionic radii are determined experimentally by X-ray measurements of the interatomic distances and are calculated theoretically based on the quantum-mechanical representations.

For close-packed metallic-type structures, atomic radii are calculated by dividing in half the distance between two identical atoms. For example, the interplanar spacing for magnesium is 0.32 nm, hence, the corresponding atomic radius is 0.16 nm. For compounds with the residual bonding type, calculations of radii are carried out in the same way as for metals.

The most difficult is to determine the radii of particles in crystals with ionic type of bond. The values of the ionic radii of the various elements differ significantly, but the same element can have different values of the ionic radii due to its different valencies. Nowadays, there are three systems of radii of chemical elements - Goldschmidt, Pauling and Belov-Bokiy. All three systems are based on the reference value of the oxygen ionic radius. Goldschmidt used the oxygen ionic radius of 0.132 nm, obtained from refractometric measurements. Pauling found the theoretical value of the oxygen ionic radius of 0.140 nm by quantum mechanical calculations. Since further research has led to the conclusion that for the oxygen ion radius the Goldschmidt value is small, and Poling is large, Belov and Bokiy compiled the table of ionic radii taking into account the average value of oxygen ionic radius of 0.136 nm (Appendix 2) [14].

Regularities of atomic (ionic) radii changes in the Mendeleev table:

- 1) decrease to the right (increase the nucleus charge and the oxidation degree);
- 2) jump-like increase in the transition from cations to anions;
- 3) increase to the down (increase the number of electronic shells).

The calculation of crystallochemical radii in compounds with the metallic bonding type depends on the lattice type (close packing). As is known, most metals form one of the following high-symmetric lattices with the close packing of atoms: cubic body-centered close packing (Figure 3.4) and cubic face-centered close packing (Figure 3.5).

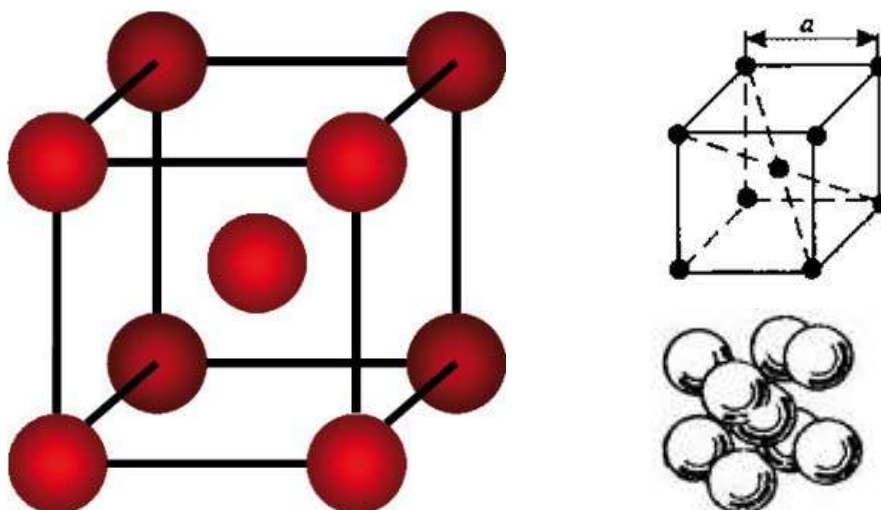


Figure 3.4. Cubic body-centered close packing

Cubic body-centered close packing (BCC) – atoms are located at the vertices of the cube and one atoms in the center of the cube's volume. Examples: K, Na, Li, β -Ti, β -Zr, Ta, W, V, α -Fe, Cr, Nb, Ba.

In this case, the calculation of the crystallochemical radius is reduced to measuring the internuclear distance in the corresponding metal, which then should be divided into two.

Exapmle. Determine the crystallochemical radius of sodium. Type of close packing – cubic body-centered. The value of internuclear distance is 3,716 Å.

Solving. Proceeding from the fact that sodium has cubic body-centered close packing type, then $r = a / 2 = 3,716 \text{ \AA} / 2 = 1,858 \text{ \AA}$.

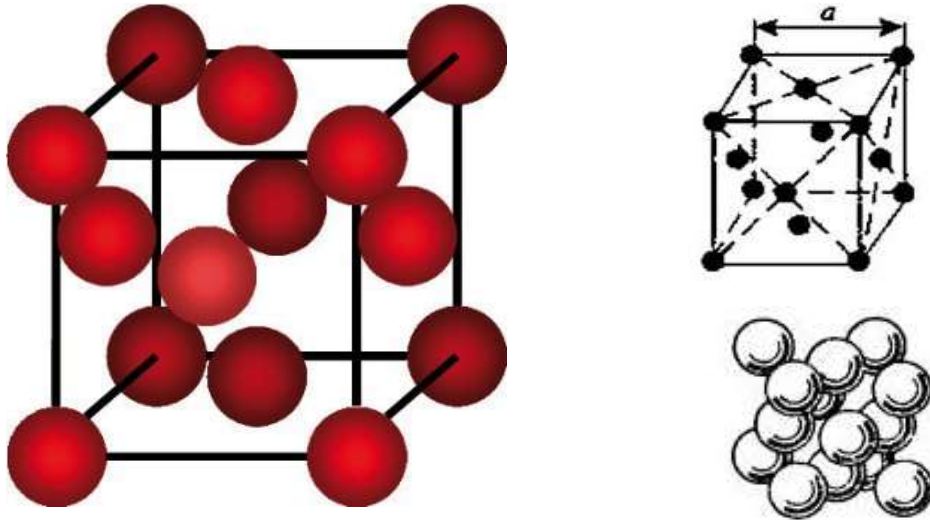


Figure 3.5. Cubic face-centered close packing

Cubic face-centered close packing (FCC) – atoms are located at the vertices of the cube and in the center of the each face. Examples: α -Ca, Ce, α -Sr, Pb, Ni, Ag, Au, Pd, Pt, Rh, γ -Fe, Cu, α -Co.

Example. Determine the crystallochemical radius of copper. Type of close packing – cubic face-centered. The value of internuclear distance is 2,556 Å.

Solving. The crystallochemical radius is equal to the half the diagonal of the isosceles right triangle (Figure 3.6). In this case the length of the diagonal is calculated by the Pythagorean theorem.

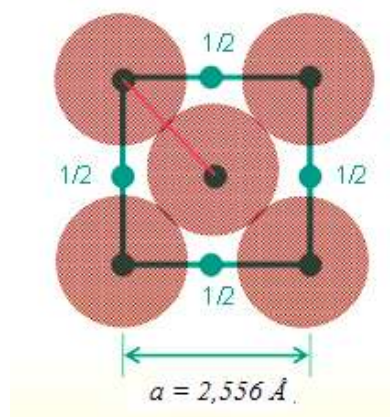


Figure 3.6. Determination of the crystallochemical radius in cubic face-centered close packing

Accordingly, the radius will be:

$$r = \frac{\sqrt{\left(\frac{1}{2}a\right)^2 + \left(\frac{1}{2}a\right)^2}}{2} = \frac{\sqrt{\frac{1}{4}a^2 + \frac{1}{4}a^2}}{2} = \frac{\sqrt{2}}{4} \cdot a = \frac{\sqrt{2}}{4} \cdot 2,556 = 0,904 \text{ \AA}.$$

In the *hexagonal close packing (HCP)* atoms are located at the vertices and in the center of the hexagonal prism bases, and three atoms – in the middle plane of the prism (Figure 3.7). Examples: Mg, α -Ti, Cd, Re, Os, Ru, Zn, β -Co, Be, β -Ca.

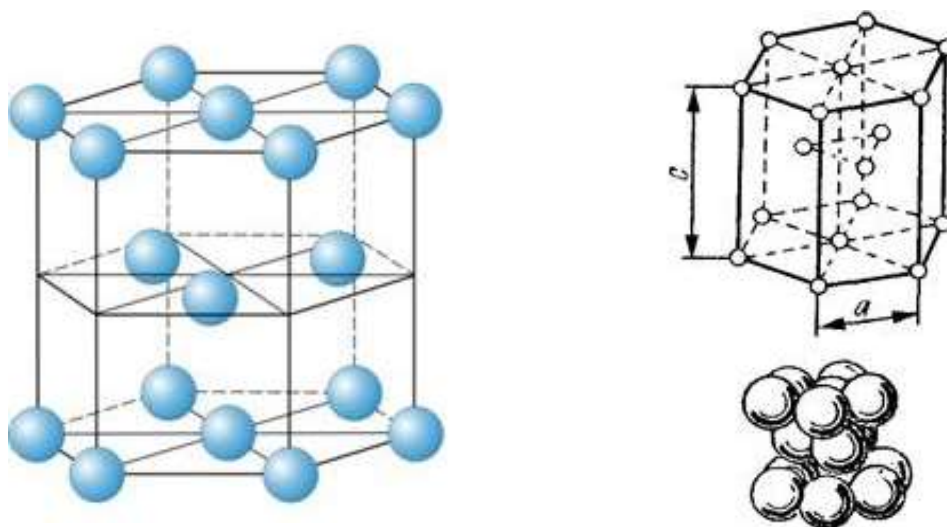


Figure 3.7. Hexagonal close packing

In the case of hexagonal close packing, the determination of the crystallochemical radius is carried out analogously to the cubic body-centered packing.

Determination of the crystallochemical radii in compounds with ionic bonding type is possible, only if the the radius of the at least one ion is known. Calculation in this case is realized from the expression: $a = 2r_a + r_k$, where r_a – anion radius, r_k – cation diameter.

Example. There is compound RbJ, which has structure of the NaCl. Radius of J is 2,20 Å. Determine the radius of the Rb^+ , assuming that the structure of the ionic crystal is the bond between the iones with opposite charges. The value of internuclear distance is $a = 7,33 \text{ \AA}$.

Solving: Figure 3.8 represents the RbJ crystal model, where the anion is the green ball, cation – the purple ball.

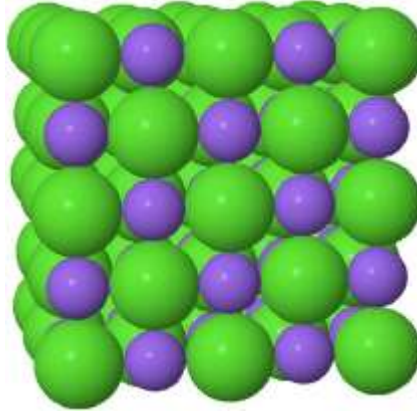


Figure 3.8. The structure of RbJ

The figure shows that the internuclear distance is:

$a = 2 \cdot R_{J^-} + d_{Rb^+} = 2 \cdot R_{J^-} + 2 \cdot R_{Rb^+}$, where cation radius:







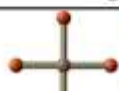
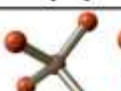
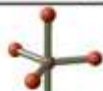

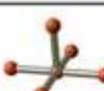














$$R_{Rb^+} = \frac{a}{2} - R_{J^-} = \frac{7,33}{2} - 2,2 = 1,46\overset{0}{A}.$$

3.3. Coordination numbers and coordination polyhedra

The number of the same type neighboring atoms (ions of the opposite sign) from the nearest environment in the crystalline structure of the atom (ion) is called the *coordination number (CN)* of the atom (ion). The geometric figure formed by connection the centers of these atoms (ions) by straight lines is called the *coordination polyhedron (CP)* [7,15].

Typical coordinate numbers and their corresponding coordinate polyhedra are shown in Table. 3.2.

Table 3.2. Coordinate numbers and corresponding coordination polyhedra

CN	Coordination polyhedra			
1				
2	 <i>dumb-bell</i>			
3	 <i>triangle</i>	 <i>triangular polyhedron</i>		
4	 <i>square</i>	 <i>tetrahedron</i>		
5	 <i>trigonal pyramid</i>	 <i>tetragonal pyramid</i>	 <i>tetragonal pyramid (half octahedron)</i>	
6	 <i>octahedron</i>	 <i>trigonal prism</i>		
7	 <i>pentagonal bipyramide</i>	 <i>octahedron</i>	 <i>one-vertex trigonal prism</i>	
8	 <i>cube</i>	 <i>Thompson cube (square antiprism)</i>	 <i>disphenoid</i>	 <i>two-vertex trigonal prism</i>
9	 <i>one-vertex Thompson cube</i>	 <i>three-vertex trigonal prism</i>		
12	 <i>cuboctahedron</i>	 <i>hexagonal analog of cuboctahedron</i>	 <i>icosahedron</i>	

Example: Determine the coordination numbers and coordination polyhedra of sodium and chlorine ions in the structure of rock salt (Figure 3.9).

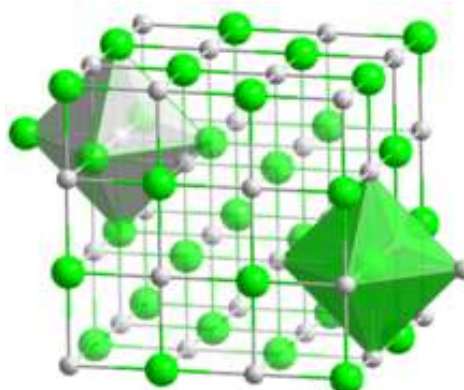


Figure 3.9. NaCl structure for determination CN and CP

Solving. In the structure of rock salt, each sodium ion is surrounded by six chlorine ions, i.e., $CN = 6$. Chlorine ions are located at the vertexes of the octahedron, that is, the coordinate polyhedron is octahedron. The same environment is characteristic for chlorine ions in relation to sodium ions.

3.4. Structural and formula units

The number of structural units (SO) shows how many atoms (or molecules) of this chemical compound must be taken to build one elementary cell. The number of SO is always greater than one and acquires only integer values [7].

For *simple substances* that consist of atoms of one element (Cu, Fe, Se), the number of structural units corresponds to the number of atoms in the elementary cell. For *simple molecular substances* (I_2 , S_8) and molecular compounds (CO_2), the number of SO is equal to the number of molecules in the cell. In the vast majority of *inorganic compounds* (NaCl, CaF_2 , CuAu), instead of the term «number of molecules», the term "number of formula units" (Z) is used.

Example. There is structure NaCl (Figure 3.10). Determine the number of structural and formula units, indicate the position of atoms in the structure and their number.

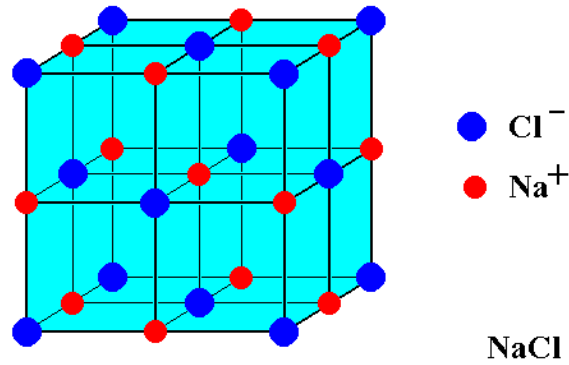


Figure 3.10. NaCl structure for calculating structural and formula units

Solving. In the NaCl structure, which is typical for the ionic crystals of AB type (where A are atoms of one type, B of the another), in the construction of the elementary cell 27 atoms of two types are involved, of which 14 A atoms (chlorine ions) and 13 B atoms (sodium ions). However, fully included in the cell, only one atom at the center. The atom located in the center of the facet of the elementary cell, belongs simultaneously to two cells – to this one and adjacent to it. Therefore, only half of this atom belongs to this cell. 8 cells converge at the same time at each of the vertices of the cell, so only 1/8 of the atom located at the top belongs to this cell. The elementary cell contains the 1/4 of every atom located on the cell's rib.

Table 3.3. The total number of atoms per unit of the NaCl cell

Atom location	Volume that enters the cell	Number of atoms	Total number of atoms per cell
At the vertex	1/8	8	1 (chlorine)
In the middle of rib	1/4	12	3 (sodium)
In the center of facet	1/2	6	3 (chlorine)
In the center of cell	1	1	1 (sodium)
Total		27	8

Thus, NaCl cell contains only 8 atoms instead of 27 atoms: 4 sodium atoms and 4 atoms of chlorine. That is, for the crystal of AB type, which includes NaCl, one cell contains four atoms A and four atoms B. The number of structural units (the number of atoms of both types) is equal to 8. In the structure of NaCl, 8 atoms (4 sodium atoms and 4 chlorine atoms) participate in the formation of the elementary

cell, which form 4 structural units of NaCl. Consequently, the number of formula units $Z = 4$.

In the simplest structures, coordinate numbers can be used to confirm the chemical formula of the compound. Thus, in the structure of sodium chloride (coordinate number NaCl = 6), the ratio of coordination numbers $6:6 = 1:1$, which leads to the stoichiometric formula AB (NaCl).

3.5. The closest packing in crystals

The stability of the crystalline structure can be achieved with the minimum value of its potential energy. Reducing of potential energy is observed at the maximum convergence of structural units, that is, with their close packing. In this case, each particle must interact with as many other particles as possible.

The tendency toward the close packaging is inherent in all types of crystalline structures, but it is most pronounced in metal and ionic structures, where the bonds are not directed, atoms or ions can be considered spherical.

In the case of the closest packing of spheres (atoms, ions) of the same sort, each sphere touches up to six spheres and is surrounded by six gaps, and each of the gaps – by three spheres (Figure 3.11).

The larger number of the same type neighboring atoms, the larger and the compactness coefficient in the structure, which is determined by the ratio:

$$K = \frac{\text{Volume of spheres}}{\text{Total volume (spheres+gaps)}}. \quad (3.1)$$

An elementary layer cell is the rhomb with a side equal to the sphere diameter. The elementary cell contains one sphere and two gaps, that is, the number of gaps in the layer is twice the number of spheres. Gaps differ in orientation in the plane of the layer: triangles with vertices upwards (gaps B) and triangles with vertices down (gaps C) (Figure 3.11).

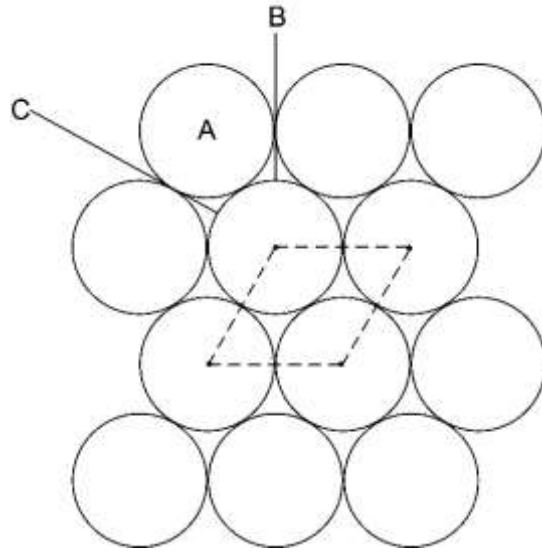


Figure 3.11. Scheme of the closest packing of spheres of the same size on the plane [8]

To obtain the structure of close packing it is necessary to put on the first layer the same close packed second layer, then the third, etc. (Figure 3.12). Obviously, when applying the second layer, it makes no sense to lay the sphere on the sphere (alternation A - A), because the packing will not be close; spheres A of the second layer should be placed in the gaps B or C.

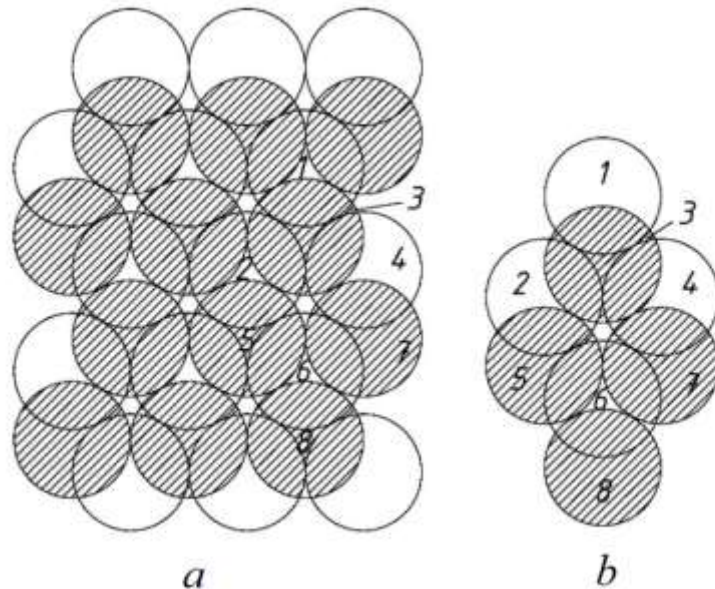


Figure 3.12. Close packing of two layers of spheres (a) and the fragment of this packing (b).

Spheres of the upper layer are shaded [7]

The gaps of the first layer differ only in the direction of the layer plane, and their coordination environment is the same. In the second layer, gaps of two types are formed, differing in coordination environment. The first type includes gaps formed by three spheres of the first layer and one sphere of the second layer, or by one sphere of the lower layer and three spheres of the upper layer. That is, the sphere of the second layer is located above the gap of the first layer (or the gap of the second layer above the sphere of the first layer). The gap in both layers is surrounded by four spheres, the centers of which form the right tetrahedron (Figure 3.13 *a*). Such gaps are called *tetrahedral T*.

The second type includes gaps formed by three spheres of the first layer and three spheres of the second layer. In this case, the gap of the second layer is above the gap of the first layer. The gap is surrounded by six spheres placed at the vertices of the octahedron (Figure 3.13 *b*). Accordingly, gap is called *octahedral O*.

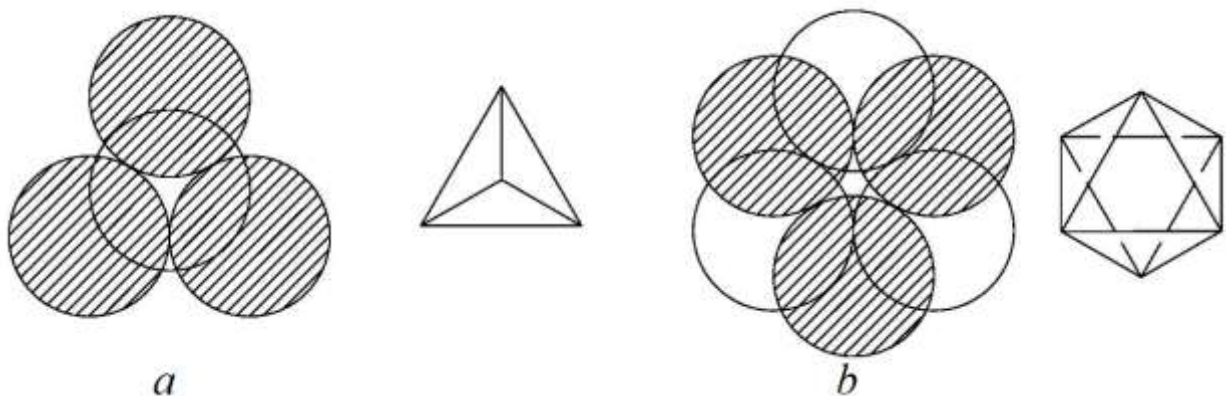


Figure 3.13. The gaps of close packing: tetrahedral (*a*); octahedral (*b*) [7]

The number of gaps *O* is equal to the number of spheres, and the number of gaps *T* is twice that. The dimensions of the gaps between the spheres are characterized by the radius of the sphere, which can be placed in them. If the radius of the main sphere equal one, then the radii of spheres that can be placed in O-type gaps are 0.41, in T-type gaps – 0.22 [7].

Since the second layer is characterized by two types of gaps, there are two variants of stacking the spheres of the third layer: either into the gaps T, or into the

gaps O. In this case, depending on the laying variant, two different types of packing can be obtained.

If the spheres of the third layer are placed in the gaps T , that is, each sphere of the third layer is over the sphere of the first layer, then the third layer repeats the the first layer. Correspondingly, we receive packaging ... ABABAB (Figure 3.14). In a double-layer close packing ... ABABAB ... the coordination number is equal to 12, that is, each sphere is surrounded by 12 spheres: six in the same plane, three on the bottom and three on the top. Octahedral gaps are repeated in each layer, forming through continuous channels. The diffusion of impurities in the crystal may occur in these channels.

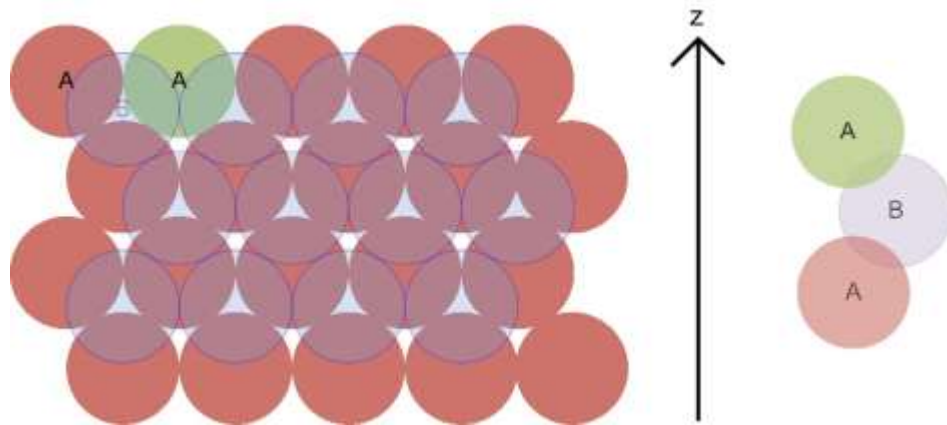


Figure 3.14. Scheme of the close packing of type ...ABABAB....

If the spheres of the third layer are laid in the gaps O, that is, the third layer does not repeat the first layer and the spheres of the fourth layer can be placed above the first layer, then we receive the package ... ABCABC (Figure 3.15). In the three-layer close packing ... ABCABC ... the gap T is located over the gap O and vice versa. There are no through columns of gaps in structures.

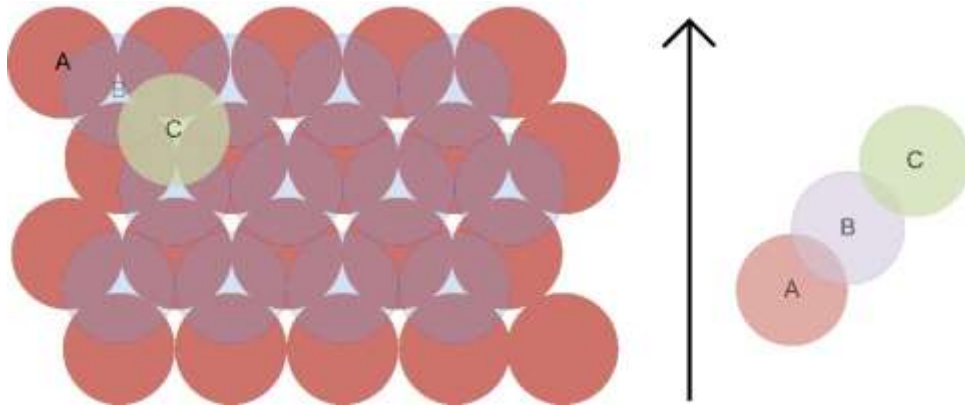


Figure 3.15 The close packing of type ...ABCABC....

Further layers can be stacked in the same way, getting any alternation without repeating the two letters. There are structures with multilayer close packing, which consist of 80 or more layers (polytype). As the number of layers grows, the number of variants of each n-layer packing is also increases. However, only two of them form close packing: two-layer (hexagonal – HCP) ... ABABAB ... and three-layer (cubic – CCP)ABCABCABC ... (Figure 3.16). Compactness coefficient for these packings $K = 74,05\%$.

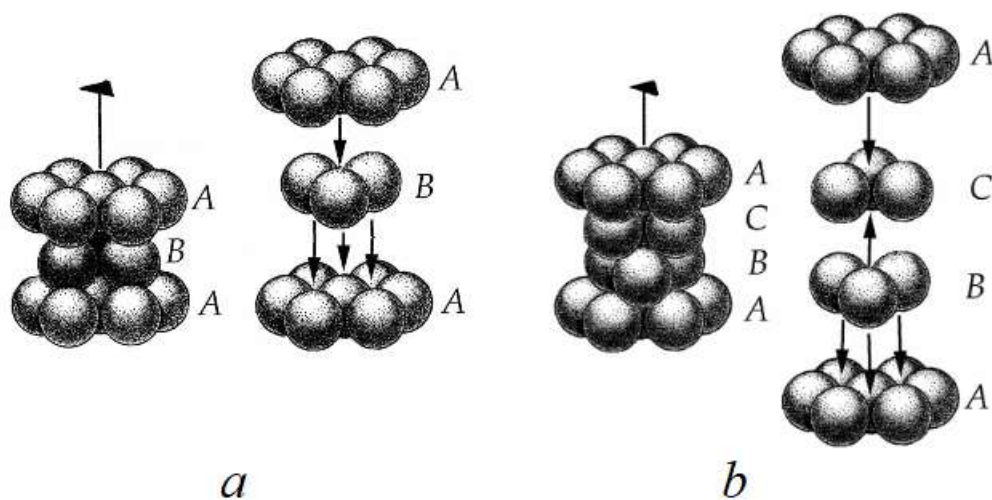


Figure 3.16. Scheme of the close packings: two-layer hexagonal ...ABABAB... (a); three-layer cubic ...ABCABC... (b) [15]

In the gaps between spheres of close metal packings, atoms of Si, C, O, H, N can be located, forming silicides, carbides, oxides, hydrides, nitrides. The principle of close packing remains fair for ionic compounds: anions form the close packing, and cations are placed in gaps

3.4. Features of the structure of ionic and covalent crystals

The *ionic crystals* are formed by particles, the adhesion of which is mainly due to ionic bonds. The example of the ionic crystal is the usual rock salt (Figure 3.17).

Each chlorine ion is surrounded by 6 ions of sodium, and each sodium ion – by 6 ions of chlorine. Such ordered packing of ions is called the ion crystal. If to allocate the separate chlorine atom in the crystal, then among the surrounding sodium atoms it is impossible to find the one with which chlorine reacted.

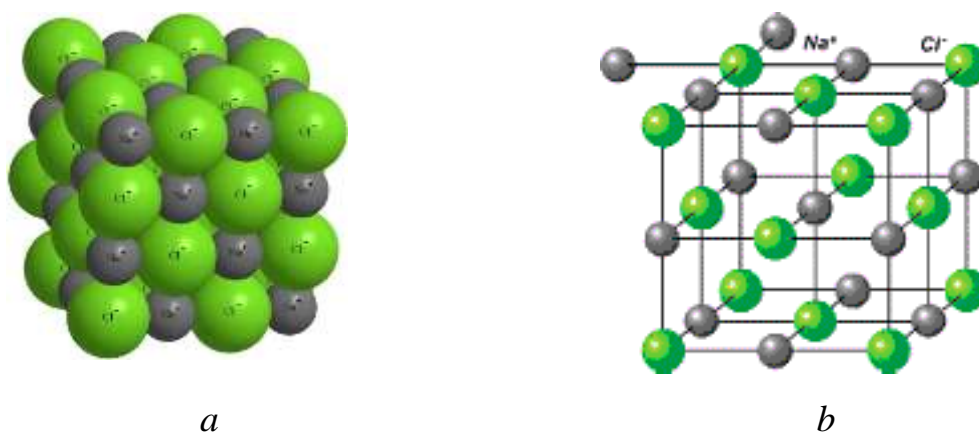


Figure 3.17. Ion crystalline structure of sodium chloride:
packing of ions in the crystal (a); elementary cell (b)

Attracted to each other by electrostatic forces, ions are extremely difficult to change their location under the influence of external force or temperature increase. But if to melt sodium chloride and to continue its heating in the vacuum, it evaporates with forming the diatomic NaCl molecule, indicating that the forces of covalent bonding never disappear.

Crystals in which the atoms in the lattice are held by strong covalent bonds are called *covalent frame crystals* or *atomic crystals*. The smallest structural particles in them are single atoms, bound by covalent or polar covalent bonds into the «infinite» three-dimensional framework. Due to this substances with atomic crystalline grate have high mechanical strength, no odor and are insoluble in the water.

Figure 3.18 shows the fragment of the atomic crystal lattice of silicon oxide SiO_2 (sand, quartz). The atoms of silicon and oxygen are interconnected by strong polar covalent bonds.

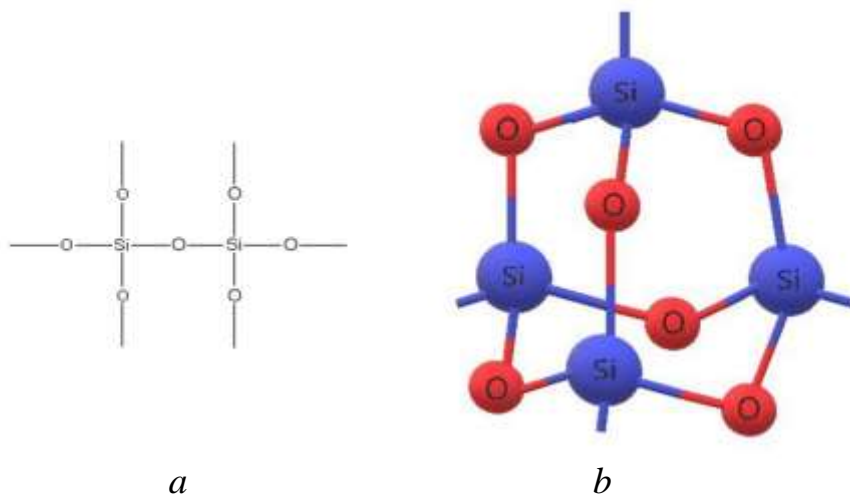


Figure 3.18. Silicon oxide SiO_2 : fragment of the structural formula (a); structure of the atomic crystal (b)

Another very famous atomic crystal is diamond (Figure 3.19). In the diamond, each 4-valence carbon atom is linked to another carbon atom by the covalent bond, and the number of such atoms connected in the framework is extremely high. If the molecules were not required to have the permanent composition diamond could be called the giant molecule. Carbon atoms form curved six-membered rings. In this case, each carbon atom is located in the center of the correct tetrahedron, at the vertices of which are other carbon atoms, connected with it by covalent bonds. Angles between bonds make up 109° – as in the mathematical tetrahedron.

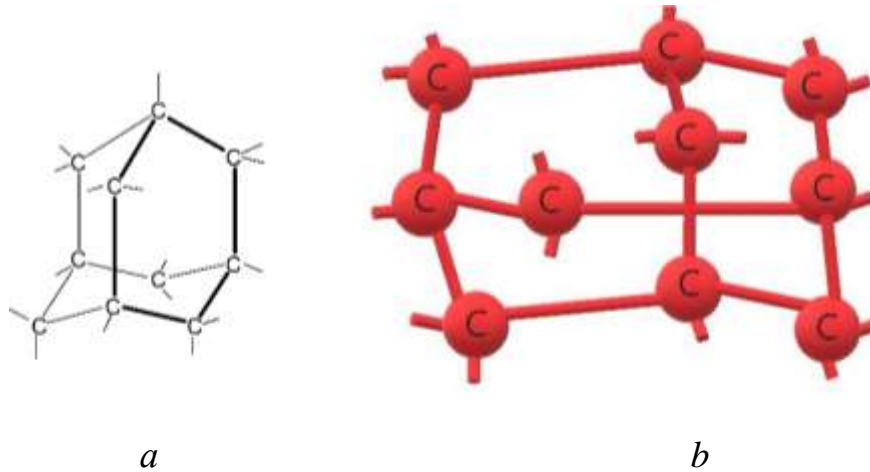


Figure 3.19. The structural formula of the diamond (a) and the structure of its atomic crystal (b).

In the graphite crystal carbon atoms are linked in the different way (Figure 3.20). They are combined into layers consisting of flat hexagons. In the first approximation it can be imagined that carbon atoms are interconnected by simple and dual interchangeable bonds in these hexagons. The distance between the individual layers in the graphite is quite large, and the forces of interaction between them are very weak. Inside the layers, carbon atoms are bound together by strong covalent bonds, and between the layers by the significantly weaker forces of intermolecular interaction.

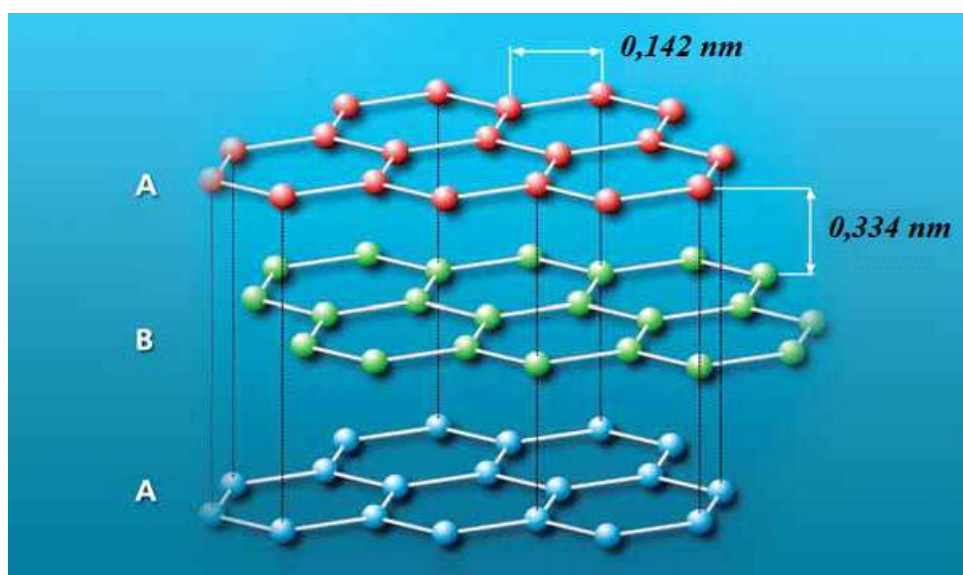


Figure 3.20. Spatial placement of atoms in the graphite crystal lattice

When the chemical element forms two or more simple substances, different in structure and properties, such the phenomenon is called allotropy. Graphite and diamond – two allotropic modifications of carbon [16]. Allotropic modifications can pass one into another under certain conditions. For example, at very high pressures and temperatures graphite can pass into diamond. In such way the artificial diamonds can be obtained from graphite. The emergence of natural diamonds in the depths of the Earth, probably, also occurs under the influence of enormous temperatures and pressures, but over the longer time period.

3.5. Polarization

To consider the ions to be non-compressible spheres can only be the rough approximation. In fact, electronic shells of atoms are deformed during their interaction and their exact radii change. This phenomenon is called *polarization* [7].

The following regularities of ions polarization (*Fajans' rules*) are established:

1) the larger radius of anion, the greater its polarization. In large anions, the outer orbits are screened from the positively charged atomic nucleus by several completely built-up shells, so they are relatively easily polarized;

2) the smaller radius of the cation and greater its charge, the more intense its polarizing effect, since in the small cation the positive charge is concentrated on the small surface. Cations with small sizes and large charges have the higher polarizing power than anions, but almost non-polarized by themselves;

3) the polarizing capacity of the cation will be higher if it does not have the electronic configuration of noble gas, since the latter effectively shields the charge of the nucleus, which prevents polarization.

Atoms of the same element in different compounds exhibit different polarization depending on the bonding types. Polarization can reduce the distance between the particles and cause the change in the coordination number and type of the structure.

Control questions

1. What is chemical bond? Name the types of chemical bond, indicate which ones belong to the strong and weak ones.
2. What are the main characteristics of the different types of chemical bonding?
3. What is the effective radius of the atom (ion)? Describe methods of its determination.
4. What is the condition for the crystalline structure stability? Give the definition of the compactness coefficient in the structure.
5. Identify the types of gaps that occur when the second layer is overlaid.
6. What is the coordination number of the atom (ion) and the coordination polyhedron?
7. What are the ionic and atomic crystals?
8. Identify the definition of allotropy and allotropic modifications of the carbon.
9. What is polarization? Identify the Fajans' rules.

CHAPTER 4. STRUCTURAL CRYSTALLOGRAPHY

4.1. Classification of structures and crystals

International classification of structures by chemical bond (stoichiometric classification of structures). Many different inorganic compounds have the same structure in topology, as opposed to organic or coordination compounds, which, as a rule, have the unique crystalline structure. The same topology of the structures has not the absolute size of atomic groups or lattice parameters, and only their relative values. Therefore, only the topological characteristics of the crystals structure (symmetry, the presence or absence of bonds, the mutual arrangement of atoms) combine into the so-called stoichiometric classification of structures, where inorganic substances refer to certain structural types [19].

A specific spatial arrangement of material particles (atoms, ions, molecules and their groups) is understood under the structure of the crystal (crystalline structure). These particles are also called structural particles or units. The positions of the particles coincide with the nodes of the lattice in a crystalline structure, and the particles are arranged around the nodes with symmetric groups.

Let's recall the spatial model of the three-layer packaging of crystal ...ABCABC... and face-centered cubic cell, which corresponds to it, on the example of copper (Figure 4.1). This model characterizes the structure of not only copper, but also silver, aluminum, and others. However, to show the copper model it is necessary to determine the distance between the atoms in its structure, i.e. to add the scale.

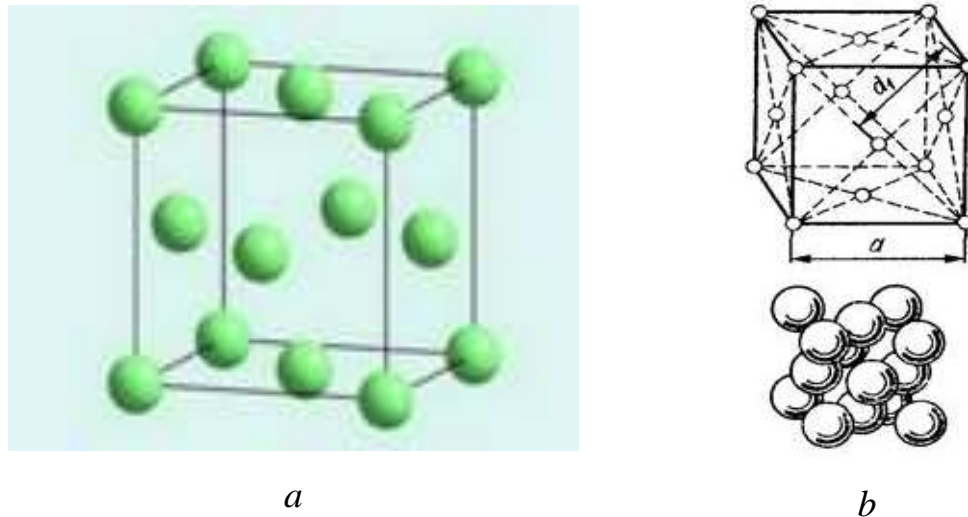


Figure 4.1. Elementary unit cell of copper: architecture (a); geometric parameters (b)

Consequently, the spatial structures of copper, gold, silver and other metals are represented identically in appearance; but they are characterized by different interatomic distances.

The classification of structures is based on the image of the relative arrangement of particles, i.e. the scale is rejected (Figure 4.1). At the same time, the concept of a characteristic structure or structural type for the certain number of substances with a qualitatively similar structure is introduced. The tables attached to the structural type image indicate the crystallographic parameters (a , b , c) and (α , β , γ) of the specified substances. Structural type is denoted by the name of one of the substances, for example: the structural type of copper. However, there are substances that do not have structural analogues. For example, the structural type of graphite is graphite only.

The spatial group, the basis (coordinates of particles in cell), as well as coordination numbers and coordination polyhedra are given for each structural type.

Consequently, crystalline structures are classified into such groups [19]:

- 1) the structure of simple elements: *A*-substances (all simple elements);
- 2) the structure of AB type compounds: *B*-substances (for example, NaCl, CsCl);
- 3) the structure of AB₂ type compounds: *C*-substances (TiO₂, CaF₂);

4) the structure of A_nB_m type compounds: *D*-substances (Al_2O_3);

5) the structure of complex compounds: *E*-substances ($CuFeS_2$), *F*-substances ($NaHF_2$), *G*-substances ($CaCO_3$), *H*-substances ($CaSO_4 \cdot 2H_2O$), і рядкі *I*-substances, *J*-substances, *K*-substances;

6) the structure of alloys: *L*- substances;

7) the structure of silicates: *S*- substances.

Often, compounds of one stoichiometry (for example, AB) form different structures. So, each of these structural (stoichiometric) groups contains a series of numbered structural types. Some structural types are subdivided into sub-types that represent the lower small digit index. Thus, according to classification each crystalline structure has specific symbol that consisting of a large Latin letter (structural group), a number (structural type) and numeric index (subtype).

At present, the classification of structures by stoichiometric formula type lost its meaning, but it is still used.

Classification by the Pearson symbol. The symbol of Pearson is the set of signs used in crystallography as a tool for describing the crystalline structure proposed by W.B. Pearson. The symbol consists of two letters (one small, second one is large) and number, for example: for the diamond structure, the Pearson symbol is *cF8*, for the structure of the rutile is *tP6*. The first two letters point to Bravais lattice, while the first letter shows the crystal system or the symmetry class (Table 2.25), and the second letter represents the type of lattice (Table 2.14). The number indicates the number of atoms (structural units) in the elementary unit cell.

The Pearson symbol defines the structure of the crystal and its spatial group ambiguously. For example, three different crystalline structures – $NaCl$ (spatial group *Fm3m*), diamond (*Fd3m*) and sphalerite (*F43m*) – have different spatial groups, but the same Pearson symbol – *cF8*. So, together with the structural group, as a symbol of Pearson the spatial group also indicated.

Table 4.1. The crystal system and its marking

triclinic	a
monoclinic	m
orthorhombic	o
trigonal	r
tetragonal	t
hexagonal	h
cubic	c

Crystallochemical classification of crystals. The stoichiometric classification is not the only systematization of crystals. At first it was convenient to distribute the crystals by the type inherent in their chemical bond. However, such classification is ambiguous and complicates the classification of crystals, in which there is more than one type of chemical bond. According to this, the modern crystallochemical classification of all crystalline substances, including minerals, is based on two main factors: the physico-chemical bond and nature of coordination in crystals. Thereafter, all crystalline structures are divided into: coordination, layer, chain, island and frame groups.

In coordinating crystals, all atoms (ions) are joined by identical chemical bonds and create the spatial lattice. They are characterized by large coordinate numbers and correct coordination polyhedra, hence the name. The crystals of the other four groups are constructed from structural fragments, in which the particles are joined by strong (often covalent) bonds, and the fragments are tied together weaker. Fragments may be layers, chains, finite groupings of atoms («islets»), frames. It gives the corresponding names to the crystals.

The examples of these groups are given bellow.

1. *Coordinating structures* are structures with three-dimensional spatial coordination of particles, that is, with the uniform distribution of atoms throughout the crystalline space, and atoms do not form any finite or infinite groupings. Such structures are characterized by identical distances between adjacent atoms, which indicates practically one type of chemical bond in them. The example of coordinating structures is the NaCl structure with ionic bond; with the covalent bond is diamond;

with Van der Waals bond are crystals of noble gas elements; with metallic bond are Cu, Mg, Fe, and the like.

2. The layered crystals consist of valence-saturated layers and include following structures: α -graphite (graphite 2H), where covalent (with metal admixtures) bonds are implemented inside the layer, and Van der Waals are between layers; brucite $\text{Mg}(\text{OH})_2$ and CdJ_2 , the geteropolar is determined by ion-covalent bonds in the layer of Mg-octahedrons and Van der Waals bonds between layers.

Since there are molecular coupling forces between the layers, each layer can be regarded as a plane molecule limited by the size of the crystal. Layered crystals have parallelism in layers. There are lamellar, tabular and leafy formations in nature.

3. *Chain structures* consist of groupings of particles in the form of parallel long chains. The distances between the atoms or ions in the chain (preferably the covalent bond) are much smaller than between the chains. The latter can be formed by particles of one or more types. As in layered structures, intermolecular forces operate between parallel chains. Each chain can be considered individual molecule that is limited by the size of the crystal. The chain structure is characteristic of one of the selenium modifications, in which the atoms are connected in a spiral, and also for tellurium, asbestos, and others. Such crystals in nature often look like prisms or fibers.

4. *Island structures* consist of the individual finite groups (often molecules). For example, in the island structure of crystalline chlorine, constructed of separate two-atom molecules, the shortest distance between the two atoms in the molecule ($d_1=2 \text{ \AA}$) corresponds to the covalent bond, while the minimum distance between the atoms of chlorine from different molecules ($d_2=3,56 \text{ \AA}$) reflects intermolecular interaction, that is Van der Waals bond. Crystalline rhombic sulfur is constructed of eight-atomic molecules. These eight atoms form the closed molecule – «islets».

In addition to the valence-saturated, that is neutral, «islets» the cationic or anionic groups in molecular structures Cl_2 , S_8 , CO_2 , O_2 are present. So, in calcite CaCO_3 there is ionic bond between covalently bound atoms in the carbonate group

CO_3^{2-} and Ca^{2+} ions ionic. Similar groups are in the compounds $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{NO}_3$ and some other inorganic substances.

5. *Frame structures* have no distinct linear or layered configurations, but form a three-dimensional frame structure with sufficiently large voids inside. An example is the perovskite CaTiO_3 . The atoms Ti and O in it combined with covalent bonding and forming the laced frame, in cavities are Ca^{2+} , which are connected to the framework by the ionic bond.

There are frame structures in which the structural fragments of different types coexist, for example, constructed of "islets" and chains. Often there are frame crystals with incomplete ordering in which individual atoms or structural fragments statistically occupy several possible positions.

In some frame structures, at a sufficiently high temperature, individual groups of atoms or even entire molecules are in the state of free or retarded rotation.

4.2. Description of some crystalline structures

Among the structures of simple substances, five structural types are considered as the most important [7,19]: the structures of copper, α -iron, magnesium, diamond and graphite, which were identified the first and received the ordinal *A1*, *A2*, *A3*, *A4* and *A9* respectively.

A-elements.

Structural type of copper (A1). Spatial group – *Fm3m*. The structure of the elementary unit cell is the face-centered cubic, $a = 3,6153 \text{ \AA}$, the densest three-layer packaging of atomsABCABC....., the crystalline structure – coordination. Coordinates of atoms in unit cell (the basis): $[[0 \ 0 \ 0]]$, $[[\frac{1}{2} \ 0 \ \frac{1}{2}]]$, $[[0 \ \frac{1}{2} \ \frac{1}{2}]]$, $[[\frac{1}{2} \ \frac{1}{2} \ 0]]$.

The number of atoms *Z* in unit cell are 4; CN = 12 (CuCu_{12}); CP – right cube octahedron (Figure 4.2).

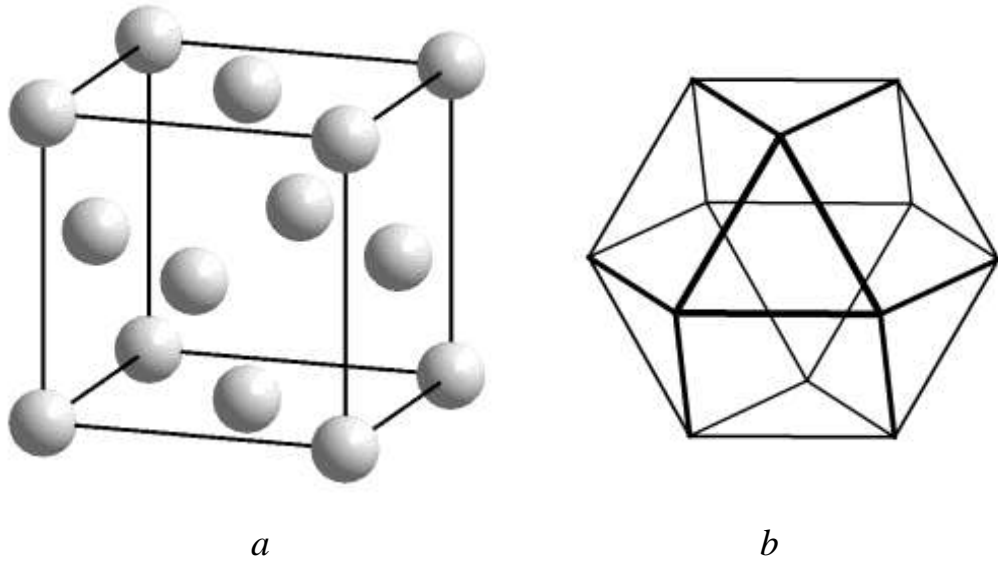
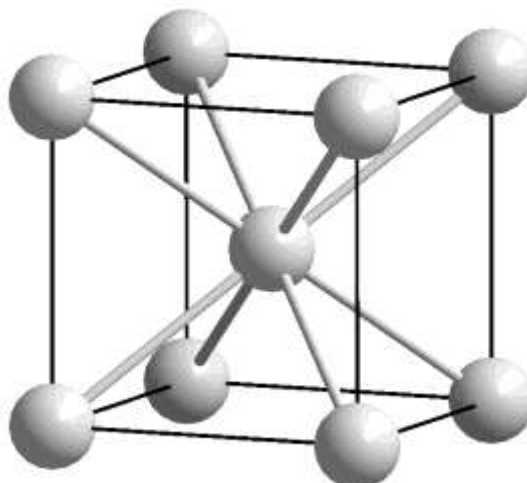


Figure 4.2. Elementary unit cell and coordination polyhedron of structural type of copper

many metals crystallize in the structural type of copper: gold, silver, nickel, calcium, aluminum, β -Co, γ -Fe etc. All these metals are relatively soft, plastic, easy to handle. Many of them form solid solutions. The structure of copper also possesses intermetallic compounds, such as AuSb, Au₂Bi, Au₂Pb, Cu₂Mg, Bi₂K, ZrH, TiH and other.

Structural type of α -iron (A2). Spatial group – $Im\bar{3}m$. Structure of elementary unit cell is the body-centred cubic, $a = 2,8665 \text{ \AA}$, dense packing of atoms, crystalline structure – coordination. Coordinates of atoms in unit cell (the basis): $[[0\ 0\ 0]]$, $[[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]]$.

The number of atoms Z in unit cell is 2; CN = 8 (WW₈); CP – right cube (Figure 4.3).



Puc. 4.3. Elementary unit cell of the α -iron structural type

Li, Na, K, V, Cr, δ -Fe, Rb, Nb, Mo, Cs, Ba, Eu, Ta, α -W, Fr, Ra and polymorphic modifications of other metals belongs to this type.

Structural type of magnesium (A3). Spatial group – $P6_3/mmc$. The structure of the elementary unit cell is the hexagonal, $a = 3,2093$, $c = 5,2116$ Å. It is the densest hexagonal packing of atoms, crystalline structure is coordination. Coordinates of atoms in unit cell (the basis): $[[0\ 0\ 0]]$, $[[1/3\ 2/3\ 1/2]]$.

The number of atoms Z in unit cell is 2; CN = 12 ($MgMg_{12}$); CP – hexagonal cube octahedrol (Figure 4.4).

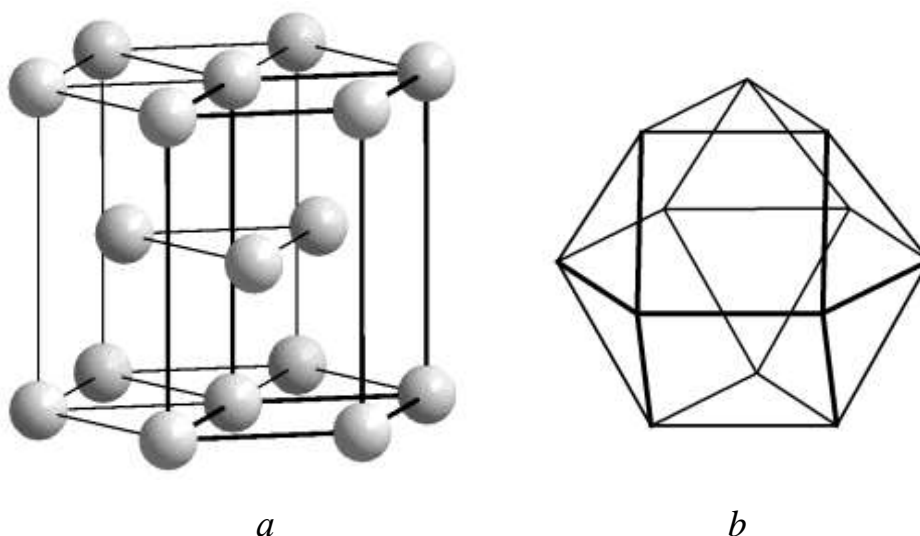


Figure 4.4. Elementary unit cell (*a*) and coordination polyhedron (*b*) of structural type of magnesium

This type includes Be, β -Ca, Sc, α -Ti, α -Co, α -Ni, Zn, Y, α -Zr, Tc, Ru, Cd, α -Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Re, Os, Tl and polymorphic modifications of other metals, as well as the structure of solid helium.

Structural type of diamond (A4). Spatial group – $Fd\bar{3}m$. The structure of the elementary unit cell is the face-centred cubic, $a = 3,559 \text{ \AA}$, another kind of the densest packing of atoms, the crystalline structure is coordination. Coordinates of atoms in unit cell (the basis): $[[0\ 0\ 0]]$, $[[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]]$, $[[\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}]]$, $[[\frac{3}{4}\ \frac{1}{4}\ \frac{1}{4}]]$.

The number of atoms Z in unit cell is 4; CN = 4 (CC_4); CP – right tetrahedral (Figure 4.5). The degree of filling the space is 34,01%.

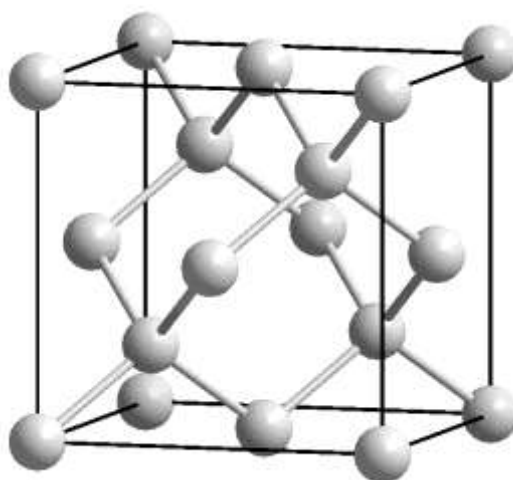


Figure 4.5. Elementary unit cell of structural type of diamond

This structural type also includes silicon, germanium and α -Sn. In addition to the cubic diamond, its hexagonal variation, lonsdaleite, is also known for. Their structure also relates as the structures of sphalerite and wurtzite.

Structural type of graphite (A9). Spatial group – $P6_3/mmc$. The structure of the elementary unit cell is the hexagonal, $a = 2,461$, $c = 6,708 \text{ \AA}$, Carbon atoms form hexagonal layers parallel to the plane (001) , where the broadcast is two layers, a structure with a motive ...ABAB... Crystal structure is layered. Coordinates of atoms in unit cell (the basis): $[[0\ 0\ 0]]$, $[[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]]$, $[[\frac{2}{3}\ \frac{1}{3}\ u]]$, $[[\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2}\ u]]$, where the parameter u is very small (less than $(1/60)c$).

The number of atoms Z in unit cell is 2; CN = 3 (CC_3); CP – equilateral triangle (Figure 4.6). The degree of filling the space is 16,9%.

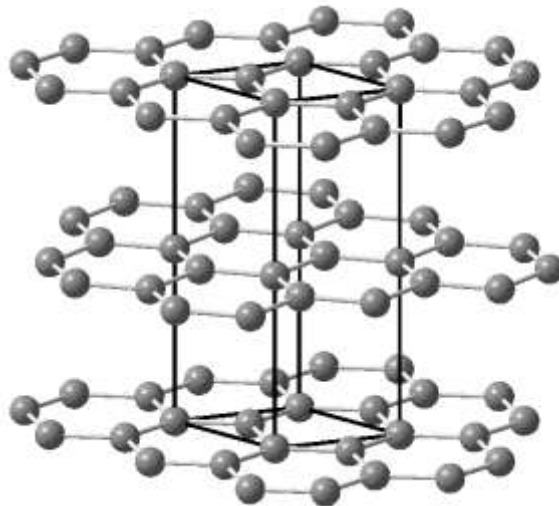


Figure 4.6. Elementary unit cell of structural type of graphite

Graphite is the unique structure. The closest to this structure is rhombohedral modification of β -graphite (14 % of total graphite) and hexagonal form BN.

Among the structure of binary, triple and more complex compounds, there are twelve basic structural types [7,19]: NaCl, CsCl, ZnS (sphalerite and wurtzite), nickelin NiAs, fluorite CaF_2 , pyrite FeS_2 , rutile TiO_2 , CdI_2 , corundum $\alpha\text{-Al}_2\text{O}_3$, perovskite CaTiO_3 , spinel MgAl_2O_4 .

Structural type of NaCl (B1). Spatial group – $Fm\bar{3}m$. The structure of the elementary unit cell is the faced-centred cubic, $a = 5,6287 \text{ \AA}$. It is the densest cubic packaging. Crystal structure is coordination. Coordinates of atoms in unit cell (the basis): $[[0\ 0\ 0]]$, $[[\frac{1}{2}\ 0\ \frac{1}{2}]]$, $[[0\ \frac{1}{2}\ \frac{1}{2}]]$, $[[\frac{1}{2}\ \frac{1}{2}\ 0]]$.

The number of atoms Z in unit cell – 4; CN = 4; CP – octahedral (Figure 4.7).

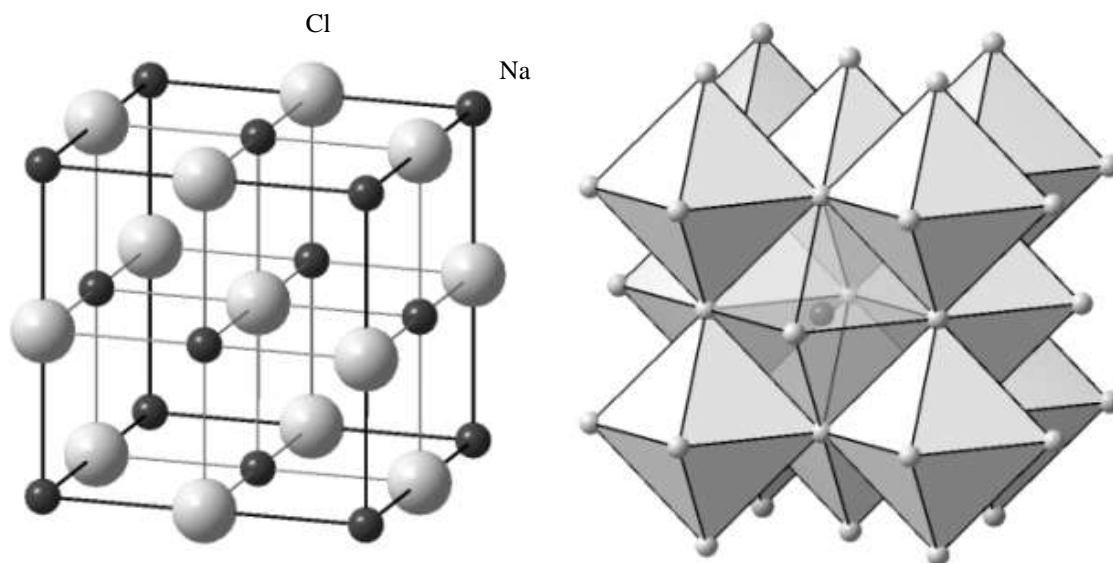


Figure 4.7. Elementary unit cell and coordination polyhedron of structural type of sodium chloride

This type includes:

- all hydrides and alkali metal halides (except CsCl, CsBr, CsI), AgF, AgCl, AgBr;
- oxides of bivalent metals – MnO, CoO, NiO, FeO;
- chalcogenides of alkaline earth elements and some actinides;
- MnS (green), MnSe, PbS, PbSe, β -PbTe etc. [20].

Structural type of CsCl (B2). Spatial group – $Pm\bar{3}m$. The structure of the elementary unit cell is the cubic, $a = 4,123 \text{ \AA}$. It is the densest cubic packaging. Crystal structure is coordination. Coordinates of atoms in unit cell (the basis): chloride ions $[[0\ 0\ 0]]$, cesium ions $[[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]]$.

The number of atoms Z in unit cell is 1; CN = 8; CP – right cubes (Figure 4.8).

The structure of the CsCl type has CsBr, CsI, TlCl, CuPd, chlorides, bromides and potassium iodides and rubidium at high pressures, as well as other compounds and alloys.

Structural type of ZnS (B3). Spatial group – $F\bar{4}3m$. The structure of the elementary unit cell is the faced-centred cubic, $a = 5,406 \text{ \AA}$. It is the densest cubic packaging. Crystal structure is coordination.

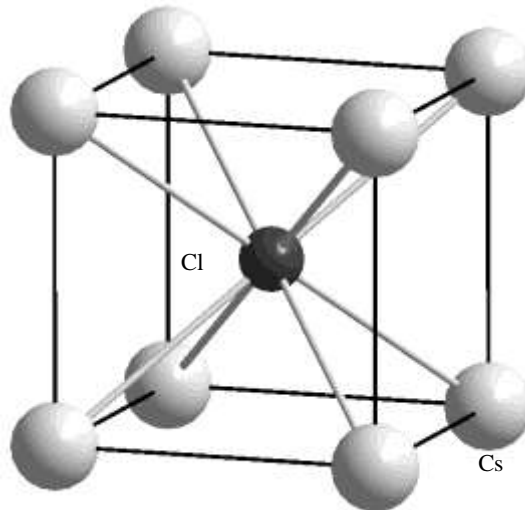


Figure 4.8. Elementary unit cell of structural type of chloride cesium

Coordinates of atoms in unit cell (the basis): Sulfur $[[0\ 0\ 0]]$, $[[\frac{1}{2}\ \frac{1}{2}\ 0]]$, Zinc $[[\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]]$, $[[\frac{3}{4}\ \frac{3}{4}\ \frac{1}{4}]]$.

The number of atoms Z in unit cell is 4; $CN = 4$; CP – right tetrahedrons (Figure 4.9).

Such structure is inherent in many widely used semiconductors CdS, CdSe, CdTe, GaP, GaAs and others, as well as in number of alloys (AlMg, AlSb), CuF, CuCl, CuBr, CuI, BeS, BeSe, BeTe, MnS (red), MnSe, ZnSe, ZnTe, HgS, HgSe, HgTe, AlP, AlAs, AlSb, GaSb, InP, InAs, InSb, SiC.

Structural type of ZnS (B4). Spatial group– $P6_3mc$. The structure of the elementary unit cell is the hexagonal, $a = 3,811$, $c = 6,234$ Å. It is the densest hexagonal packaging of Sulfur ions (by Mg (A3) type). Crystal structure is coordination. Coordinates of atoms in unit cell (the basis): Sulfur $[[0\ 0\ 0]]$, $[[\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}]]$, Zinc $[[\frac{2}{3}\ \frac{1}{3}\ u]]$, $[[0\ 0\ \frac{1}{2}\ u]]$, where the parameter $u = \frac{1}{8} c$.

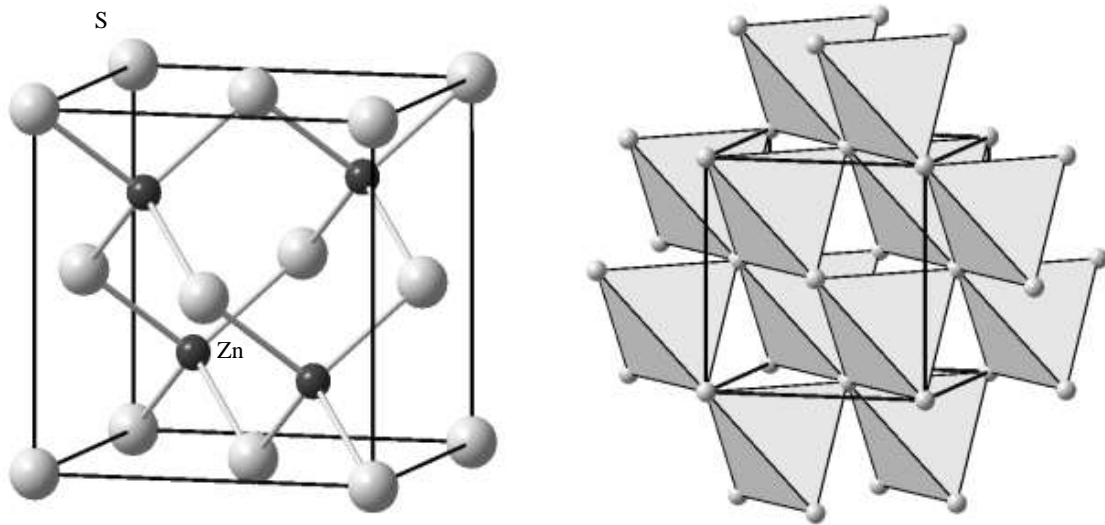


Figure 4.9. Elementary unit cell and coordination polyhedron of structural type of zinc sulfide (sphalerite)

The number of atoms Z in unit cell is 2; $CN = 4$; CP – right tetrahedrols (Figure 4.10).

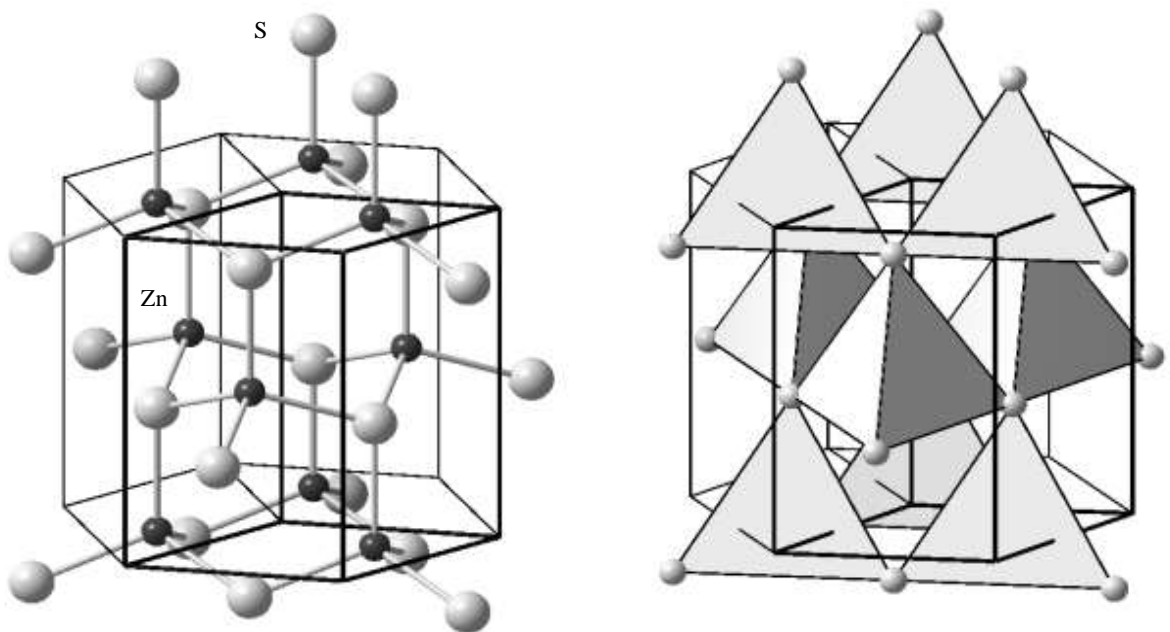


Figure 4.10. Elementary unit cell and coordination polyhedron of structural type of zinc sulfide (wurtzite)

In this type AgI, BeO, MgTe, MnS (pink), MnSe, ZnO, AlN, GaN, InN and some other compounds are crystallized [21].

Structural type of nickelin NiAs (B8). Spatial group – $P6_3/mmc$. The structure of the elementary unit cell is the hexagonal, $a = 3,602$, $c = 5,009$ Å. It is the densest hexagonal packing of Mg ions (by Mg(A3) type). Crystal structure is coordination.

The number of atoms Z in unit cell is 2; CN = 6 (Ni), 6 (As); CP – octahedrol (Ni), right trigonal prism (As) (Figure 4.11).

This type includes chalcogenides Ti, V, Cr, Fe, Co, Ni, and also MnTe, PdTe, PtTe, MnAs, some intermetallics. Pyrrhotin $Fe_{1-x}S$ and a number of other chalcogenides 3d-metals have defective cations structure such as nickel, due to the oxidation of some metal atoms.

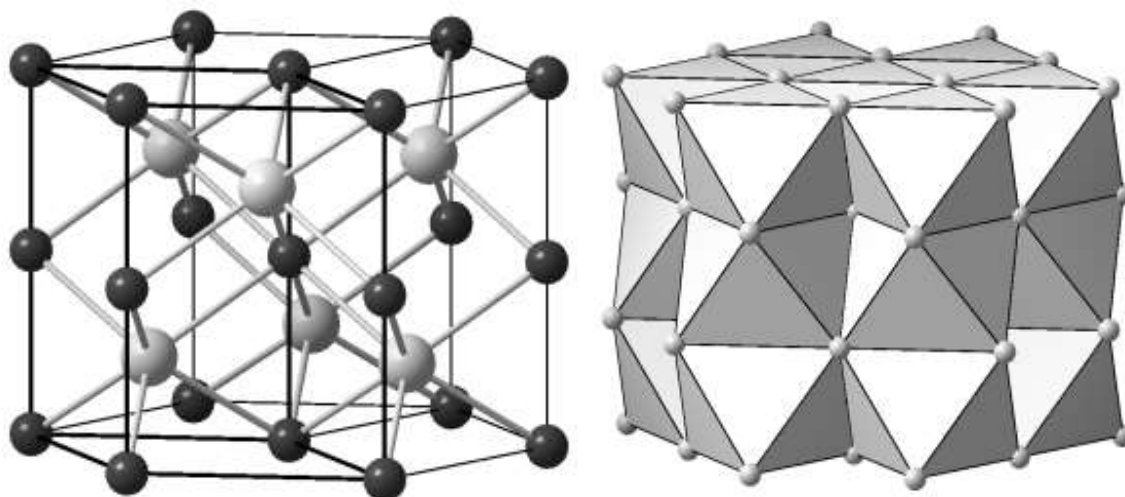


Figure 4.11. Elementary unit cell and coordination polyhedron of structural type of nickelin

Structural type of fluorite CaF₂ (C1). Spatial group – $Fm\bar{3}m$. The structure of the elementary unit cell is the face-centered cubic, $a = 5,462$ Å. It is the densest cubic packing. Crystal structure is coordination. Coordinates of atoms in unit cell (the basis): Calcium $[[0\ 0\ 0]]$, $[[\frac{1}{2}\ \frac{1}{2}\ 0]]$, Fluorine $[[\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]]$, $[[\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}]]$, $[[\frac{3}{4}\ \frac{3}{4}\ \frac{1}{4}]]$, $[[\frac{1}{4}\ \frac{1}{4}\ \frac{3}{4}]]$.

The number of atoms Z in unit cell is 4; CN = 8 (Ca), 4 (F); CP – right cube(Ca), right tetrahedrol (F) (Figure 4.12).

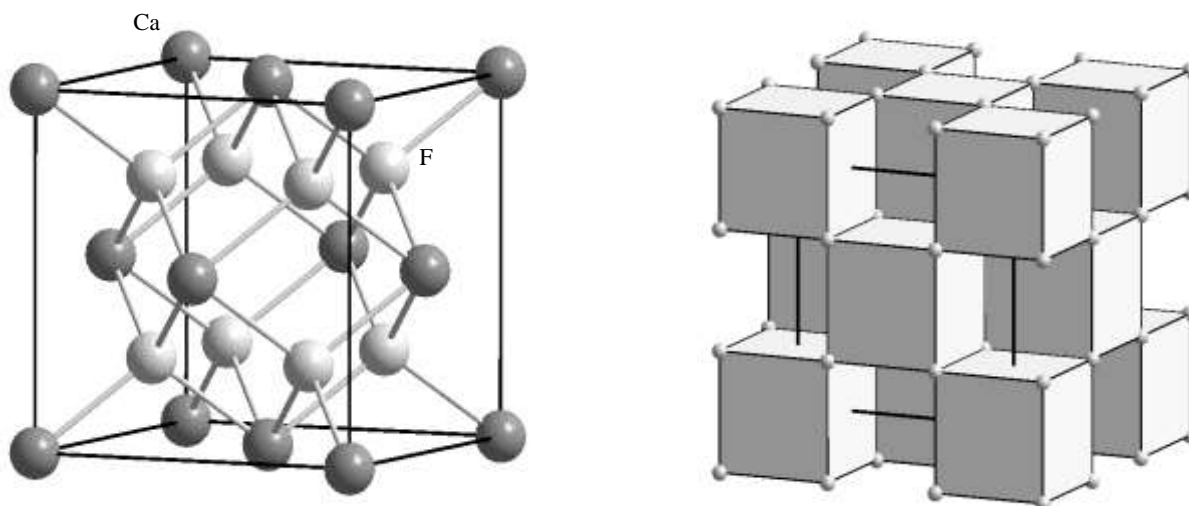


Figure 4.12. Elementary unit cell and coordination polyhedron of structural type of fluorite

In this structural type, many different substances are crystallized, in particular, SrCl_2 , ZrO_2 , HfO_2 , UN_2 , fluorides of alkaline earth metals.

There are packages of fluorite type, but in it cations and anions change places. This is the so-called anti-fluorite structure. It is peculiar, for example, Li_2O , Na_2O , K_2O , Na_2S , K_2S , that is, for compounds in which the stoichiometry of cation and anions are mainly related to ionic radiuses.

Structural type of pyrite FeS_2 ($C2$). Spatial group – $Pa\bar{3}$. The structure of an elementary unit cell is the cubic, $a = 5,418 \text{ \AA}$. It is the densest cubic packing. Crystal structure is frame. The number of atoms Z in unit cell are 4; CN = 6 (Fe), 4 (S); CP – octahedrol (Fe), tetrahedrol (S) (Figure 4.13).

Disulfide groups of S_2^{2-} occupy the middle of the ribs and the center of the elementary cell and, together with the atoms of the ferrum, form the NaCl structure. This structural type is also characteristic for manganese dichalcogenide, CoS_2 , NiS_2 , NiSe_2 , RhS_2 [22].

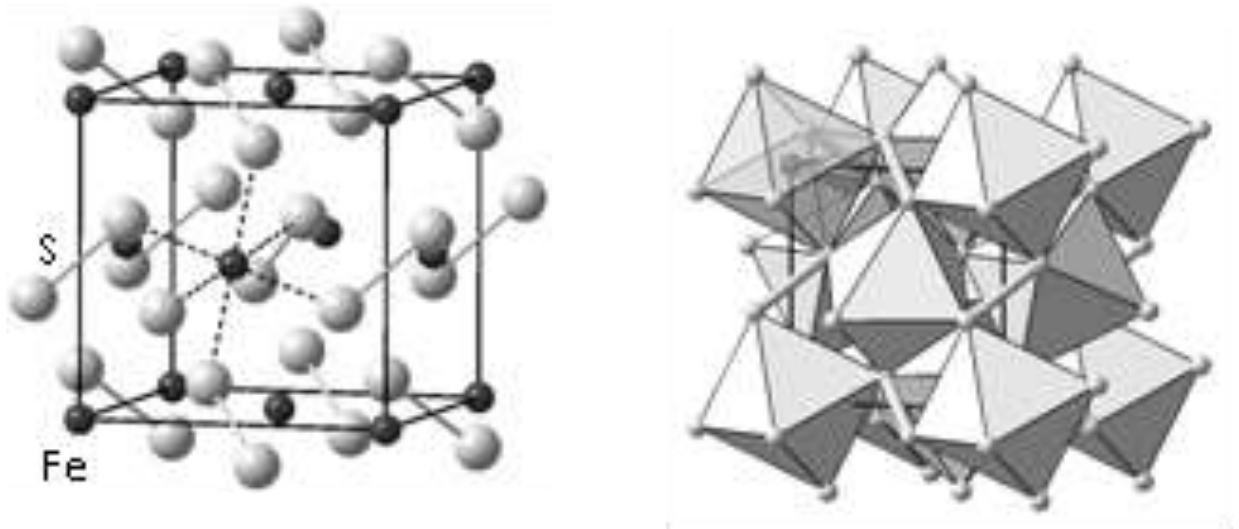


Figure 4.13. Elementary unit cell and coordination polyhedron of structural type of pyrite

Structural type of rutile TiO_2 ($C4$) (Figure 4.14). Spatial group – $P4_2/mnm$. The structure of the elementary unit cell is the tetragonal, $a = 4,594$, $c = 2,958$ Å. It is the densest hexagonal packing of Oxygen atoms (Figure 4.14). The crystalline structure is frame, but close to coordinating through almost equal lengths of ties Ti–O. Coordinates of atoms in unit cell (the basis): Titanium $[[0\ 0\ 0]]$, $[[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]]$, Oxygen $[[0\ \frac{1}{2}+u\ \frac{1}{2}-u\ \frac{1}{2}]]$, where $u = 0,31$.

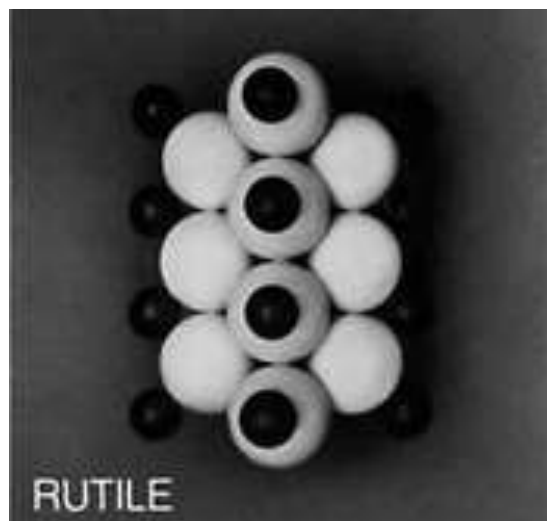


Figure 4.14. Structural type of rutile

The number of atoms Z in unit cell is 2; CN = 6 (Ti), 3 (O); CP – deformed octahedron (Ti), equilateral triangle (O) (Figure 4.15).

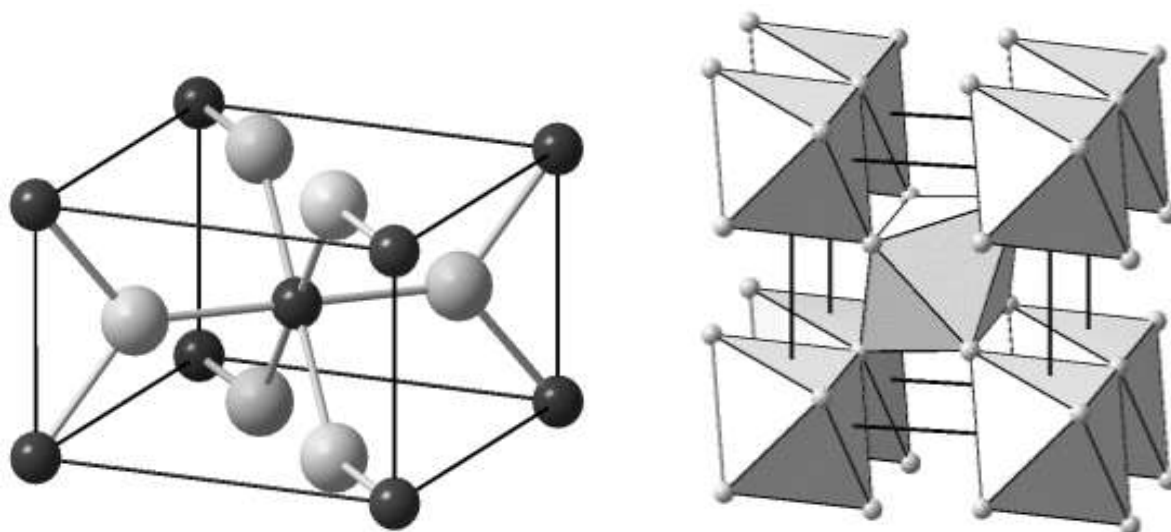


Figure 4.15. Elementary unit cell and coordination polyhedron of structural type of rutile

The projection of the elementary cell of rutile is depicted in Figure 4.16. The unit cell parameters of rutile $a = 4,594$, $c = 2,958$ Å, the number of atoms in the cell is 6, their coordinates (the basis): Ti (0, 0, 0), O (0.3053, 0.3053, 0).

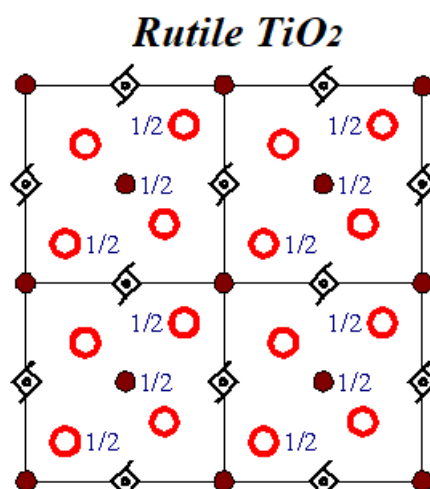


Figure 4.16. Projection of elemental unit cell of rutile

This type of structure also belongs to difluorides Mg, Mn, Fe, Co, Ni, Zn, Pd, dioxides V, Cr, Mn, Ge, Nb, Ir, Ru, Os, Sn, Pb.

Structural type of CdI_2 ($C6$). Spatial group – P_3^2m1 . The structure of the elementary unit cell is the hexagonal, $a = 4,25$, $c = 6,84$ Å. It is the densest three-layer hexagonal packaging of iodine ions. Crystal structure is layered. Coordinates of

atoms in unit cell (the basis): Cadmium $[[0\ 0\ 0]]$, Iodine $[[1/3\ 2/3\ z]]$, $[[2/3\ 1/3\ z]]$ where $z = 0,25$.

The number of atoms Z in unit cell is 1; $CN = 6$ (Cd)/3 (I); CP – (Cd) octahedron (Figure 4.17).

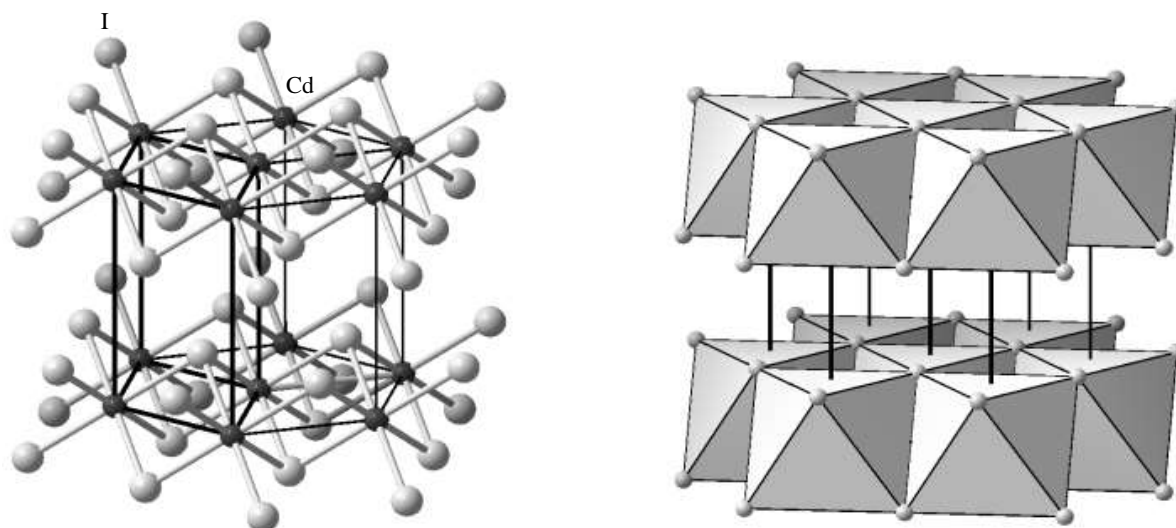


Figure 4.17. Elementary unit cell and coordination polyhedron of structural type of cadmium iodide

Structure of the CdI_2 type is inherent for $Ca(OH)_2$, $Fe(OH)_2$, $NiTe_2$, ZrS_2 , $ZrSe_2$, VSe_2 , TaS_2 , ReS_2 , $CoSe_2$, $CoTe_2$, $PdTe_2$, SnS_2 , dichalcogenides of titanium and platinum.

Structural type of corundum $\alpha-Al_2O_3$ ($D5_1$). Spatial group – $R\bar{3}c$. The structure of the elementary unit cell is the rhombohedral (trigonal), $a = 4,754$, $c = 12,99$ Å. It is the densest deformed hexagonal oxygen packing. The crystalline structure is frame, but close to the coordination through almost equal lengths of bonds Al–O. Coordinates of atoms in unit cell (the basis): Aluminum $[[0\ 0\ z]]$, $[[0\ 0\ -z]]$, $[[0\ 0\ 1/2 - z]]$, $[[0\ 0\ 1/2 + z]]$, Oxygen $[[x\ 0\ 1/4]]$, $[[0\ 3/4\ 0]]$.

The number of atoms Z in unit cell is 2 (in hexagonal installation $Z = 6$); $CN = 6$ (Al) / 4 (O); CP – octahedron (Al), tetrahedron (O) (Figure 4.18).

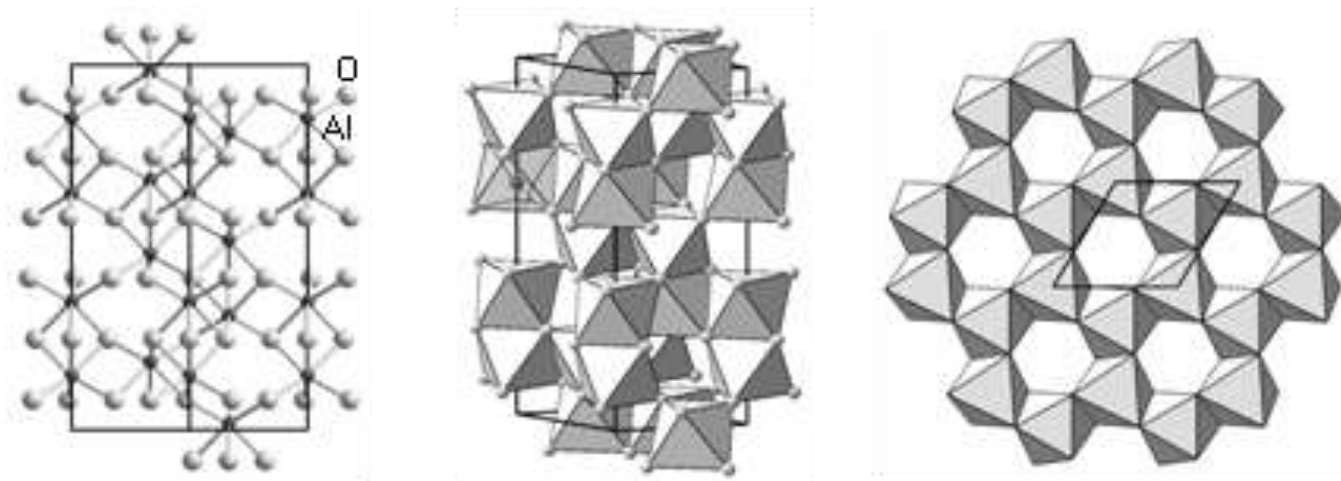


Figure 4.18. Elementary unit cell and coordination polyhedron of structural type of corundum

The type of corundum include hematite $\alpha\text{-Fe}_2\text{O}_3$, Ti_2O_3 , V_2O_3 , Cr_2O_3 , $\alpha\text{-Ga}_2\text{O}_3$, Rh_2O_3 . The structure of ilmenite is close to the structure of the corundum FeTiO_3 . It differs only in the fact that ions Fe and Ti alternate in cationic layers.

Structural type perovskite CaTiO_3 ($E2_1$). Spatial group – $Pm\bar{3}m$. The structure of the elementary unit cell is the cubic, $a = \approx 3,8\text{--}3,9 \text{ \AA}$. It is the densest cubic packing. Crystal structure is frame: titanium forms a three-dimensional framework, and all cubo-octahedral cavities are occupied by calcium atoms.

The number of atoms Z in unit cell is 1; CN = 6 (Ti) / 12 (Ca); CP – right orthohedron (Ti), cube octahedron (Ca), oxygen atoms have wrong octahedral coordination (Figure 4.19).

BaTiO_3 , SrZrO_3 , KTaO_3 , KFeF_3 , SrLiH_3 , Ag_3SBr («anti-perovskite») and many other compounds are crystallizes in the structure of the cubic perovskite.

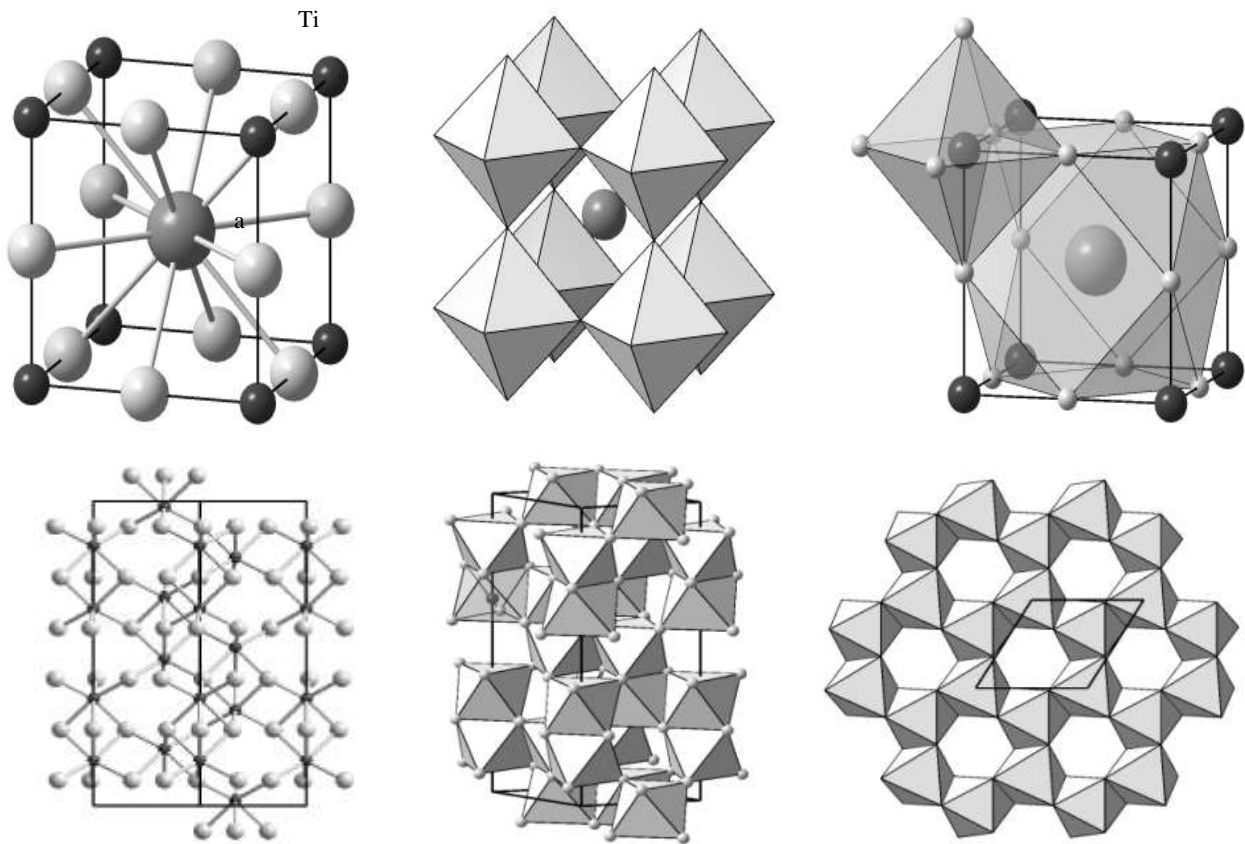


Figure 4.19. Elementary unit cell and coordination polyhedron of structural type of perovskite

Structural type of spinel MgAl_2O_4 (H11). Spatial group – $Fd3m$. The structure of the elementary unit cell is the cubic, $a = 8,081 \text{ \AA}$. It is the densest cubic packing.

Coordinates of atoms in unit cell (the basis): Magnesium $[[0\ 0\ 0]]$, $[[1/4\ 1/4\ 1/4]]$, Aluminum $[[5/8\ 5/8\ 5/8]]$, Oxygen $[[x\ x\ x]]$.

This structural type includes ZnAl_2O_4 , Fe_3O_4 , Na_2MoO_4 , Zn_2SnO_4 , CuCr_2S_4 and large number of other compounds – oxides and less often sulphides – with the general chemical formula AB_2X_4 , where A, B – most often two- and trivalent metals (Mg, Al, Cr, Fe, Mn, Zn etc.).

The number of atoms Z in unit cell is 8; CN = 4 (Mg) / 6 (Al); CP – right octahedron (Mg), practically right octahedron (Al), Oxygen atoms have wrong octahedral coordination (Figure 4.20).

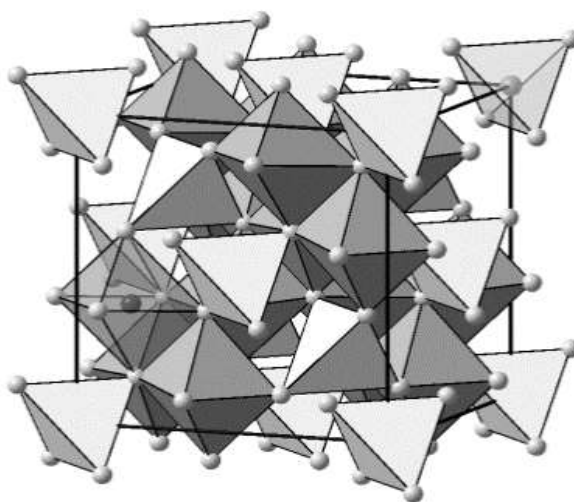


Figure 4.20. The coordination polyhedron of structural type spinel

In MgAl_2O_4 and other oxide *normal spinels* with a crystallochemical formula $A^{IV}B^{VI}_2O_4$ various small and medium cations A^{2+} i B^{3+} (other options are cations A^{4+} and B^{2+} , A^{6+} and B^+) orderly occupy the tetrahedral and octahedral positions respectively, for example, $\text{Fe}^{2+}\text{Cr}^{3+}_2\text{O}_4$, $\text{Ge}^{4+}\text{Co}^{2+}_2\text{O}_4$, $\text{Mo}^{6+}\text{Ag}^+_2\text{O}_4$. Instead, in reverse spinels (for example, $\text{Ni}^{2+}\text{Fe}^{3+}_2\text{O}_4$, $\text{Ti}^{4+}\text{Mg}^{2+}_2\text{O}_4$) the distribution of cations is obey to the formula $B^{IV}(A_{1/2}B_{1.2})^{VI}_2O_4$. Both forms are rare and in real most intermediate variants are implemented in most spinel $(A_{1-x}B_x)^{IV}(A_xB_{2-x})^{VI}O_4$, where the parameter x characterizes the degree of reversibility of the spinel. For normal spinels $x = 0$, but for reversible ones $x = 1$, so at values $0 < x < 1$ (for example, $x = 0,2$ for $\text{Mn}^{2+}\text{Fe}^{3+}_2\text{O}_4$ and $x = 0,8$ for $\text{V}^{4+}\text{Mn}^{2+}_2\text{O}_4$) both types of cations are statistically divided by T - and O -emptiness. The degree of reversibility can vary greatly with temperature: so, at normal and elevated temperatures, magnetite Fe_3O_4 has a reversible structure $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$, but below 120 K the ordering of cations is carried out.

There are also defective spinels, for example: cubic high-temperature modification $\gamma\text{-Al}_2\text{O}_3$, in which the position of magnesium in MgAl_2O_4 are occupied only on 2/3 by Al^{3+} cations.

Typical structures of important inorganic compounds are given in the Appendix 3.

Control questions

1. Give and justify the international classification of the chemical compounds structures.
2. Give classification of structures by the Pearson symbol.
3. What is the basis of the crystal chemical classification of crystalline structures?
4. Describe the structural type of copper.
5. Give characteristic of the α -ferrum type.
6. Describe the structural type of magnesium.
7. Give the graphite and diamond types.
8. Give description of the NaCl and CsCl types.
9. Give the structure types of sphalerite and wurtzite.
10. Describe the structural type of nickel (NiAs).
11. What is difference between fluorite, pyrite and rutile types?
12. Give description of the structural type of CdI_2 .
13. What are the features of the compounds belonging to the structural type of corundum ($\alpha\text{-Al}_2\text{O}_3$)?
14. Describe the triple complex compounds.

PRACTICAL WORKS

Practical work 1. The crystallographic indexing

Purpose of work: indexing of nodes, directions and planes in crystalline figures by methods of crystallographic indexing.

Brief theoretical information

Crystals are solids that have the natural form of the polyhedron and are characterized by the logical arrangement of elementary particles (atoms, ions, molecules) in the space. These include natural crystals of minerals formed in the earth's crust, and synthetic crystals obtained in laboratories. The crystal may not have the shape of the polyhedron, but as the fragment of any crystal it has the number of macroscopic physical properties that are also characteristic of the well-shaped crystal. Separate integral crystals are called single crystals, while aggregates of chaotically oriented small crystals of different sizes and irregular shapes are called polycrystals.

The ideal crystal can be constructed using the infinite regular repetition in the space of identical structural units. The three-dimensional periodic arrangement of the material particles, which is characteristic for crystals, can be clearly depicted by the spatial lattice. The spatial lattice is the abstract mathematical image that allows to fix the location of the material particles in space. In the structure of the ideal crystal, all homologous (equally spaced) points are located by infinitely regular symmetric rows.

The line, which passes through the crystalline lattice between two randomly selected, but identical nodes, also passes through other nodes of the lattice and forms then infinite one-dimensional row (Figure 1 *a*). The distance between the homologous points in the infinite row *a* is called the translational period, the parameter or the interval of the row.

The set of two systems of parallel rows with parameters *a* and *b* allows to obtain the set of homologous points in the form of the plane grid (Figure 1 *b*).

Consequently, the two-dimensional plane grid is determined by two parameters (broadcasts) a and b or by three nodes which do not lie in one straight line. The cell, the sides of which are elementary broadcasts (lattice periods), is called the elementary cell of the plane grid. Thus, the plane grid is completely defined by two rows and is the system of identical plane elementary cells, which are parallel oriented, adjacent to each other and fill the plane without spaces.

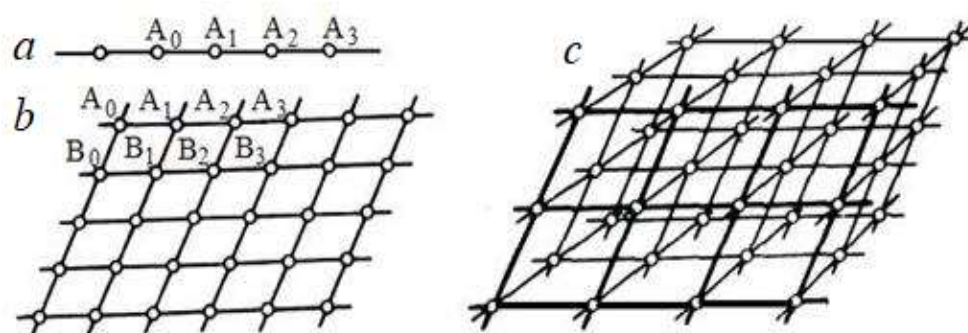


Figure 1. Space lattice (c) and its elements:
one-dimensional row (a), plane grid (b)

In the case if to draw another infinite row with the space c which lies outside the plane of the drawing, it is possible to construct three systems of parallel planes through three systems of parallel rows with parameters a , b and c . This gives the spatial lattice, that is, the three-dimensional system of homologous points (Figure 1 c). Thus, the spatial lattice can be presented as three systems of parallel grids with parameters (a and b), (a and c) and (b and c); these systems, mutually intersecting, form the set of parallelepipeds, which are parallel oriented and adjacent to whole faces.

The spatial lattice of the crystal should be regarded as the mathematical abstraction, with the help of which it is convenient (mathematically) to describe the periodicity of the crystalline structure. The grid reflects the symmetry of the structure, regardless of whether the node coincides with the atom of the certain type or is the gap between the atoms. The concept of «crystal lattice» is inadmissible to be confused with the notion of «crystal structure».

Thus, the main property of crystalline substances is the regular ordered arrangement of material particles in the nodes of the crystal lattice. The nodes of the lattice correspond to the vertices of the real crystals; rows densely covered with material particles – to the ribs of crystals; and plane grids with the large reticular density – to the faces of crystals.

Under the structure of the crystal the specific location of material particles in space, symmetry and the laws of this arrangement are understood. The special symbolism, the same for all syngony, is used for this.

The symbols of nodes. The nodes are indexed by the radius vector, which is calculated as: $R = ma + nb + pc$, where m, n, p – three numbers, called indexes of the given node.

Figure 2 shows the indexing of the nodes located at the vertices, in the center of the faces and in the center of the cube.

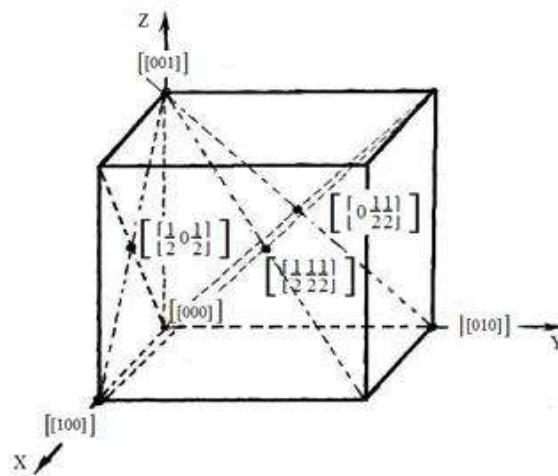


Figure 2. The symbols of nodes located at the vertices, in the center of the faces and in the center of the cube

The set m, n, p written in square brackets, is called the node symbol (Figure 2). Numbers in symbols are written in succession and reading separately. Sign minus is writing above number.

Symbols of rows (directions). The direction of the row passing through the origin is determined by two points: the origin of the coordinates and any node of the row. To determine the symbol of the row it is necessary:

- 1) move the row parallel to itself to the origin;
- 2) determine the coordinates of any point in this direction, taking the lattice period as unit of measure;
- 3) reduce the ratio of the obtained values to the ratio of the three smallest numbers, which are written in square brackets.

Figure 3 shows the symbols of some directions in the plane grid. If it is necessary to designate the set of all crystallographic-equivalent directions, the indices are enclosed in the broken brackets $\langle m n p \rangle$, in particular the set of edges of the cube is denoted as $\langle 1 0 0 \rangle$, the diagonals of faces – $\langle 1 1 0 \rangle$, the volume diagonals – $\langle 1 1 1 \rangle$.

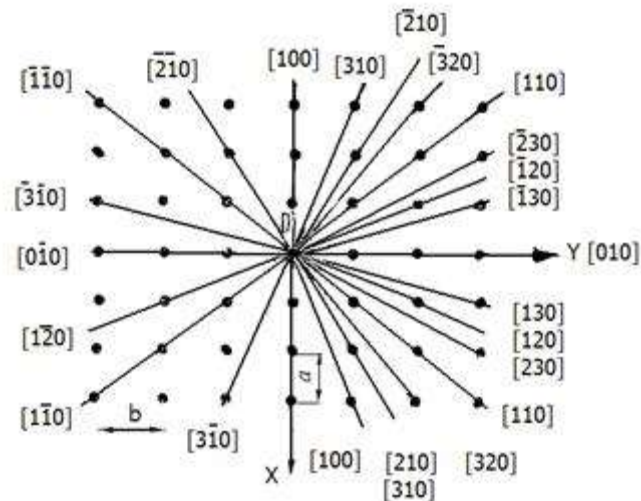


Figure 3. Symbols of some directions on the plane grid

Symbols of planes. In crystallography the planes are characterized by Miller indices. For the indices determination it is necessary:

- 1) to find the segments that this plane cut off on the crystallographic axes (period along each axis is taken as the unit of measurement);
- 2) to take the inverse values of these segments;
- 3) to bring the ratio of the obtained values to the ratio of three integers. These three numbers taken in parentheses $(h k l)$ represent the plane symbol.

The symbols $(h k l)$ and (\overline{hkl}) characterize the orientation of families of parallel planes in the space (Figure 4).

The set of all non-parallel crystallographically equivalent planes, having the same atomic structure, is marked with symbols taken in curly brackets. Thus, the totality of the six faces of the cube is denoted by the symbol $\{1\ 0\ 0\}$, of the eight planes of the octahedron – $\{1\ 1\ 1\}$ and of the twelve planes of the rhombic dodecahedron – $\{1\ 1\ 0\}$.

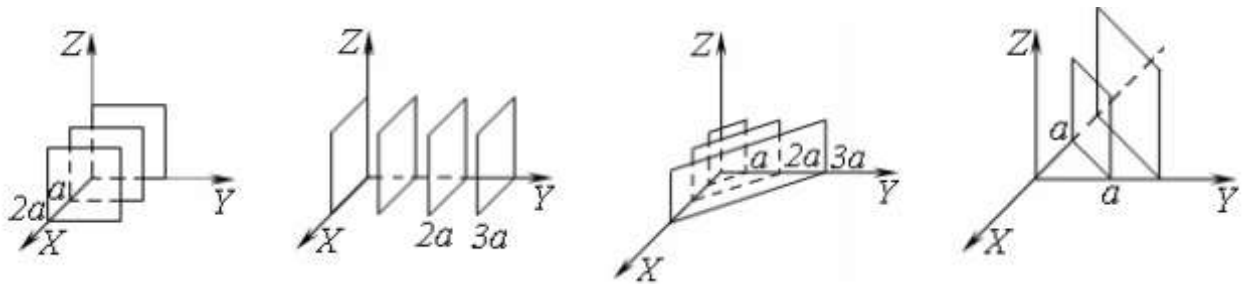


Figure 4. Families of the parallel planes

Examples of the crystallographic indexing of nodes, rows and planes

Nodes, directions, and planes should be indexed in the reverse sequence of defining these indices: first the origin of the coordinates should be selected, while taking into account that the positive (+) and negative (–) directions of the axes relative to the coordinates are carried out as follows:

- 1) the first axis (I or X) – horizontally forward (+) and back (–);
- 2) the second axis (II or Y) – horizontally to the right (+) and to the left (–);
- 3) the third axis (III or Z) – vertically up (+) and down (–).

Choosing the origin of the coordinates takes into account that the origin of the coordinates can coincide with any crystal vertex.

To construct the given plane with indices $(h\ k\ l)$ it is necessary:

- 1) to choose the origin of the coordinates for constructing the plane;
- 2) to write the values which are inverse to the plane indexes – these indices determine the segments that the plane cut off on three coordinate axes;

3) to connect the received three ends of the cuts with straight lines – this will be given the plane with indices $(h\ k\ l)$.

As an example Figure 5 shows symbols of the most important nodes, directions and planes in the cubic lattice.

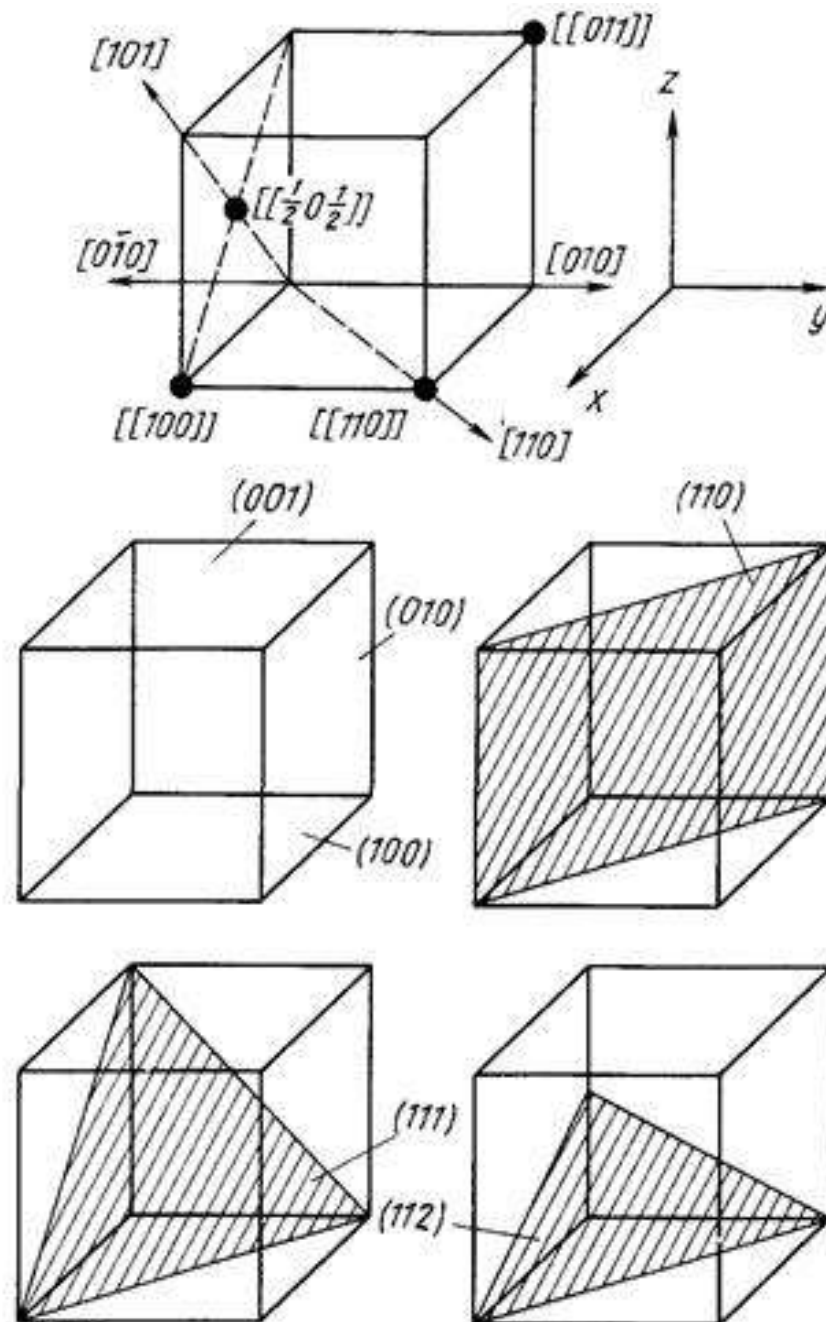


Figure 5. Symbols of the most important nodes, directions and planes in the cubic lattice

Tasks for the individual work

1. Index all nodes of Bravais lattices shown in Figure 6.
2. Index the planes of the cube shown in Figure 7.

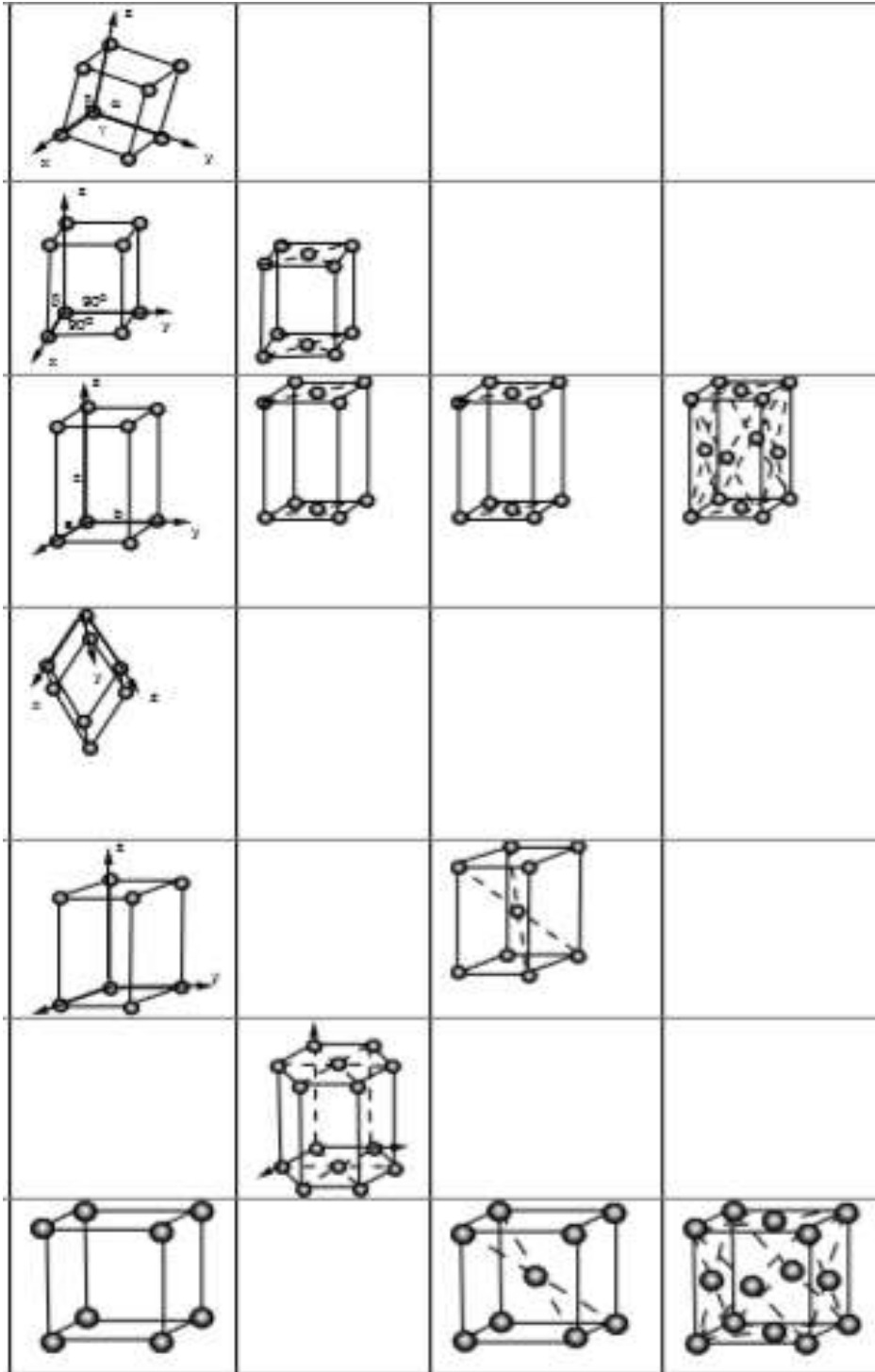


Figure 6. The fourteen Bravais lattices

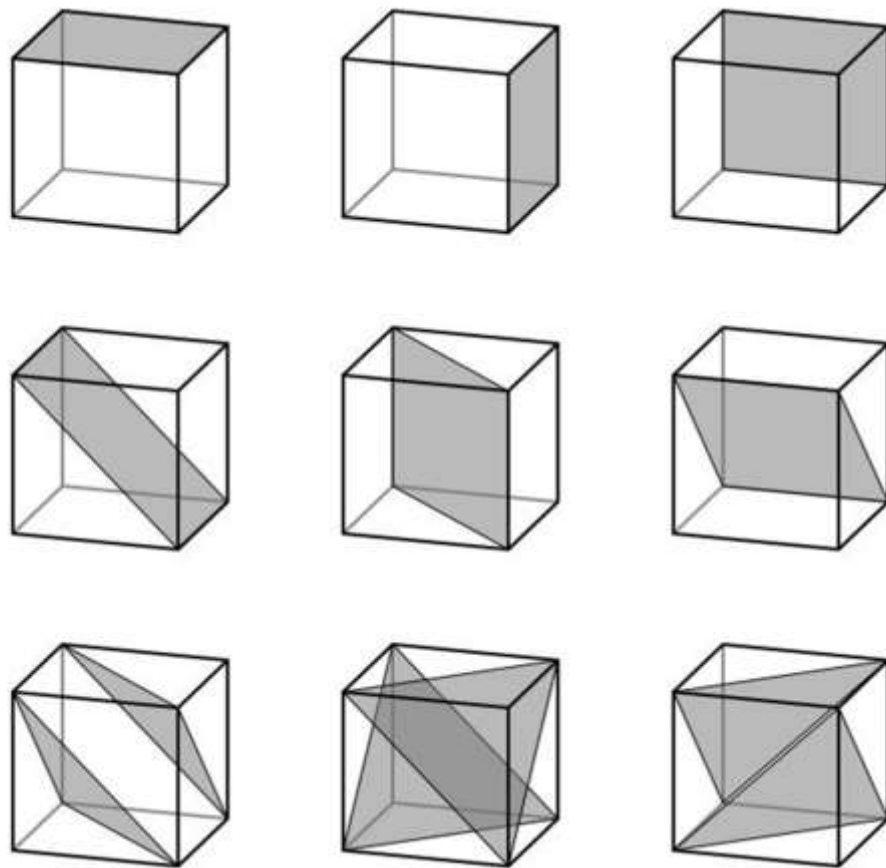


Figure 7. Some planes of the cube

Practical work 2. Description of crystal models

Purpose of work: determination of the symmetry elements and, accordingly, the syngony, the categories and the class of symmetry, the stereographic projection of the crystal.

Examples of the description of some crystal models

Example 1: to determine the elements of the crystal's symmetry, the type of symmetry, the syngony and the category (according to Table 2.5, Chapter 2), to give the stereographic projection of the crystal depicted in Figure 8.

Practical work 3. Dimension of the crystals and simple forms

Purpose of work: determination of simple forms in models of crystals for detection of their symbols and dimension of the crystal according to its syngony.

Brief theoretical information

Differences in the internal structure of crystalline and amorphous bodies determine the differences in their properties. For example, the crystalline state of the substance is characterized by anisotropy: the properties of the crystalline body remain unchanged in all parallel directions and can change only in nonparallel. Physical properties of amorphous bodies remain unchanged in all directions. The bodies whose properties do not change depending on the direction are called *isotropic*.

Outside, crystals are in the form of various polyhedra – cubes, prisms, pyramids (Figure 10) and characterized by symmetry or crystalline syngony, that is, the regular repetition of identical edges, angles, and faces of the crystal in the space.

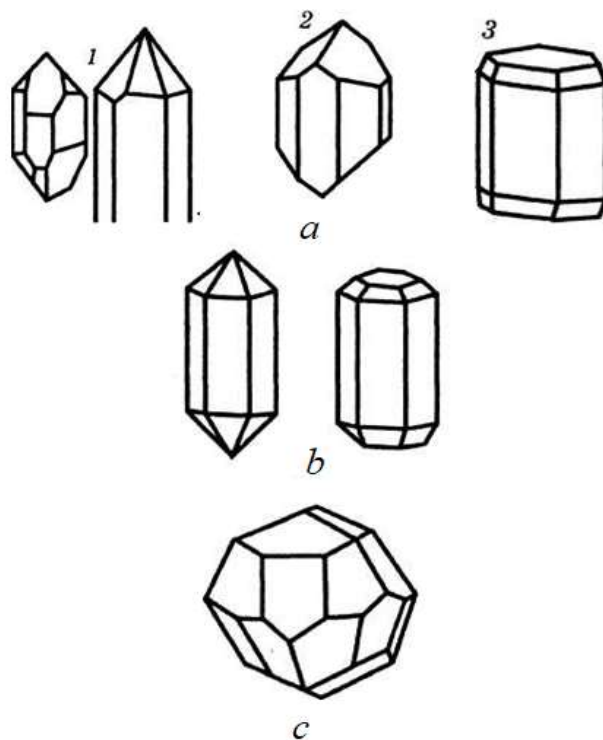


Figure 10 . Forms of common crystals: silicates (1 – quartz, 2 – augite; 3 – nepheline) (a); phosphates (b); oxides (hematite) (c)

The symmetry of crystals is expressed in the correct repetition of the limiting elements – faces, edges and vertices. There are such elements of crystals symmetry: the center (C), axis (L), planes (P).

The center of symmetry (C) is the imaginary point inside the crystal, in which all the diagonals intersect and divide in half.

The axis of symmetry (L) is the imaginary straight line, with the rotation around which at the certain angle all elements of the crystal restriction are combined. Depending on the number of such combinings in the case of the 360° crystal rotation, the axes can be of the 2nd, 3rd, 4th and 6th order. For example, if during the crystal rotation on 360° , the elements of the restriction are combined with their starting position twice, then the crystal has the symmetry axis of the 2nd order, if three times – axis of the 3rd order, etc.

The plane of symmetry (P) is the imaginary plane that divides the crystal into two identical and oppositely inverse parts, each of which is the mirror image of another.

In crystals, all symmetry elements are interconnected. Due to the dependence of symmetry elements on the each other, their mutual combination is rather limited. Russian scientist O.V. Gadolin in 1869 proved that there are 32 different combinations (classes) of symmetry elements in crystals (Chapter 2, Table 2.4). By the degree of complexity, all classes of symmetry elements are conventionally grouped into seven crystallographic syngons: cubic, tetragonal (square), hexagonal, trigonal, orthorhombic monoclinic, triclinic (Figure 11). The triclinic, monoclinic, and Orthorhombic syngony belong to the low symmetric category, trigonal, hexagonal and tetragonal – to the medium, cubic syngony – to the high.

Each syngony is characterized by the certain number of axes and planes of symmetry, by the presence or absence of the symmetry center C. The same crystallographic syngony may have crystals with the different number of planes and axes of symmetry, but which does not exceed the certain maximum number of

symmetry elements. To get the stereographic projection, all elements of symmetry of the crystal depict on the circle.

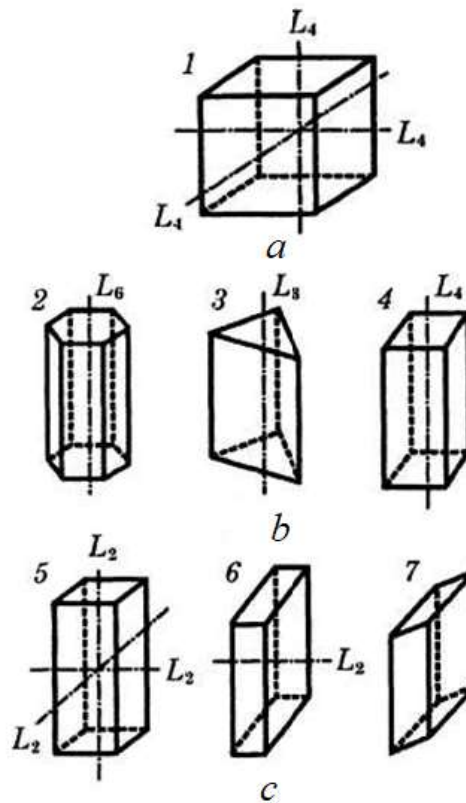


Figure 11. Crystallographic syngony: high (more than one axis of the higher order) (a); medium (one axis of the higher order) (b); low (no axis of the higher order) (c); cubic (1); hexagonal (2); trigonal (3); tetragonal (4); orthorhombic (5); monoclinic (6); triclinic (7)

Figure 12 shows the most common forms of crystals, which are characteristic of various syngony.

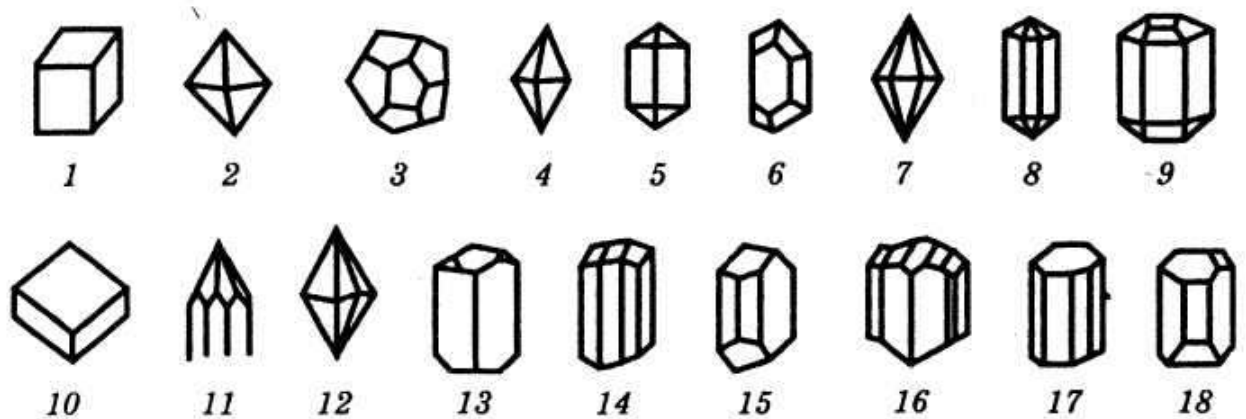


Figure 12. The most common crystal forms of cubic (1-3), tetragonal (4-6), hexagonal (7-9), trigonal (10-12), orthorhombic (13,14), monoclinic (15,16) and triclinic (17,18) syngony

The *simple form* of the crystal is the set of faces, which are connected among themselves by all symmetric operations of the point symmetry group.

There are *closed* simple forms (those that completely enclose space, for example, cube), and *open* (those that do not completely enclose the space, for example, prism and pinacoid).

To determine the form of the particular simple form, it is necessary to establish the appearance of its faces and mentally extend them to the intersection with each other. The name of the simple form is defined by the appearance of the formed polyhedron. Most names of the simplest forms of the low and medium categories are formed by the simple scheme – two signs should be indicated: the form of the basis of the corresponding figure and its general name, such as: prism, pyramid and dipyrmaid. The appearance of these simple forms is shown in Figures 13 and 14.

One of the right plane polygons can serve the basis of the prism, the pyramid and the dipyrmaid: diamond, equilateral triangle – trigon (Figure 13, *d*), dithrion is a double triangle obtained from the equilateral triangle by doubling its sides (Figure 14, *d*), tetragon is the square (Figure 13, *h*), ditetragon is the double square (Figure 14, *h*), hexagon is the correct hexagon (Figure 13, *l*), dihexagon – double hexagon (Figure 14, *l*). The combination of both signs defines the full name of the

simple form. For example, trigonal prism, rhombic pyramid, tetragonal pyramid, dihexagonal dipyramid.

A special position is the family of trapezohedrons (from the Greek word «trapezoid» – quadrangle). Figure 15 shows the trapezohedrons of three syngonies.

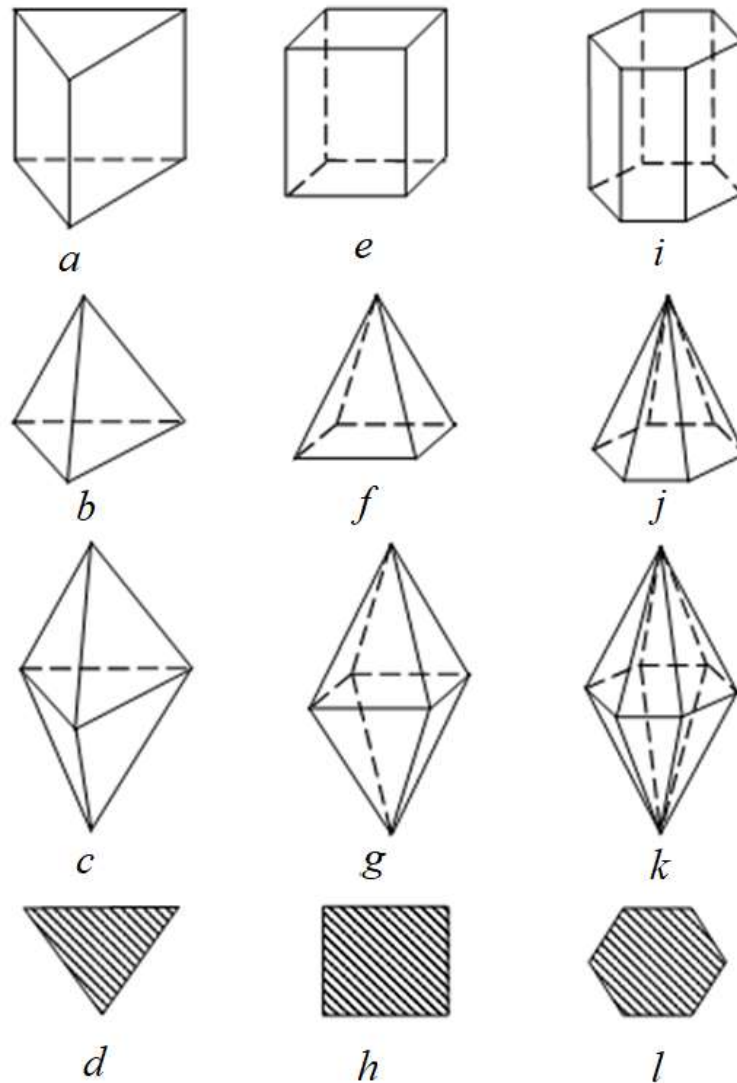


Figure 13. Prisms, pyramids, dipyramids and their cross sections

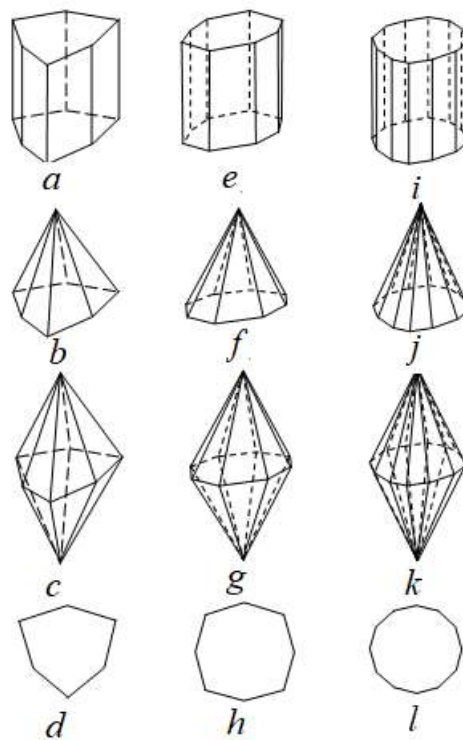


Figure 14. Bipyramids, bipyramids, bidipyramids and their cross sections

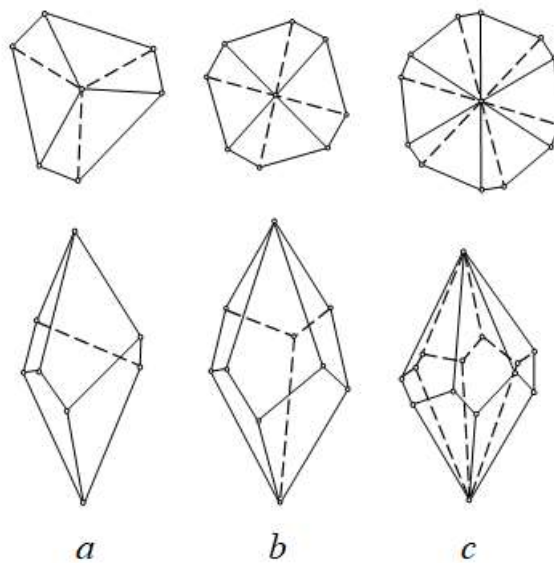


Figure 15. Trapezohedrons

Each of them is formed by quadrangular faces in the form of the non-isosceles trapezoid. Among the simplest forms of the low and medium categories, it is necessary to designate the rhombic (Figure 16, *a*) and tetragonal (Figure 16, *b*) tetrahedra. The rhombic tetrahedron is formed by four faces in the form of oblique

triangles. The tetragonal tetrahedron is formed by four faces in the form of isosceles triangles.

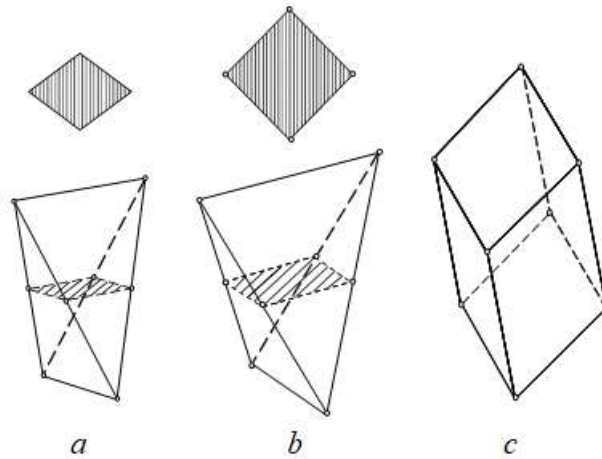


Figure 16. Tetrahedron and rhombohedrons

Another simple form of the low and medium syngony is the rhombohedron (Figure 16, c). Rhombohedron can be depicted as the cube compressed (or stretched) on one of the volume diagonals that consists of six faces in the form of regular diamonds that can form the triangular vertex, joined by either sharp angles (forming the elongated rhombohedron) or dull angles (forming the compressed rhombohedron). The third-order symmetry inversion axis goes through this triangular vertex.

Scalenohedrons are distinguished by the original external facade (Figure 17). There are trigonal (Figure 17 a) and tetragonal (Figure 17 b) scalenohedrons. The trigonal scalenohedron is depicted as the rhombohedron with double number of faces (the number of faces of the trigonal scalenohedron is twice the number of edges of the rhombohedron). The tetragonal scalenohedron is depicted as the tetragonal tetrahedron with double faces.

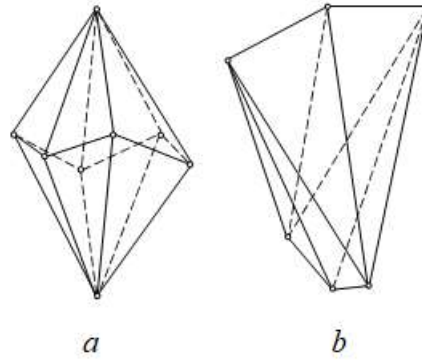


Figure 17. Scalenohedrons

Simple forms of the high category can be divided into three groups of five simple forms in each: tetrahedron group, hexahedron group (cube), octahedron group. The names of these fifteen simple forms of the high category appear to be complex at first sight. However, most of these names are composed of three parts: a) in the first part the form of the face is indicated (trigon, tetragon, pentagon); b) in the second – the number of these faces, formed as a result of the division of one face of the original simple form (tetrahedron, octahedron or cube) – three, four (tetra) or six (hexa); c) in the last – the name of the original simple form (tetrahedron, octahedron or hexahedron). The tetrahedron group (Figure 18) includes such derivative forms as trigonthreetetrahedron, tetragonthreetetrahedron, pentagonthreetetrahedron and hexatetrahedron.

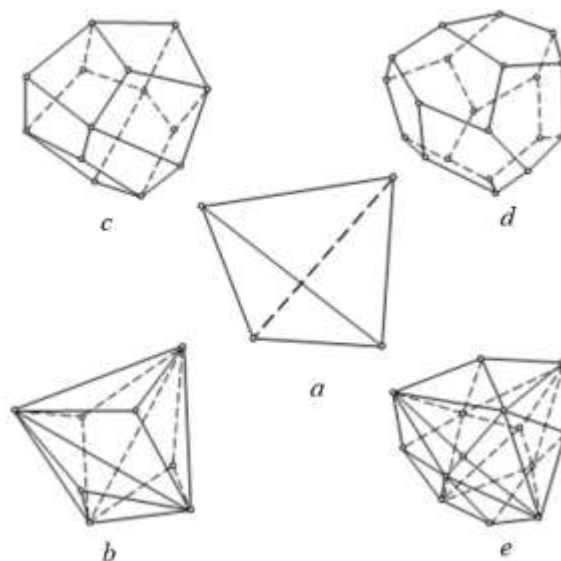


Figure 18. Tetrahedron group

The octahedra group (Figure 19) contains trigonthreeoctahedron, tetragonthreeoctahedron, pentagonthreeoctahedron and hexaoctahedron.

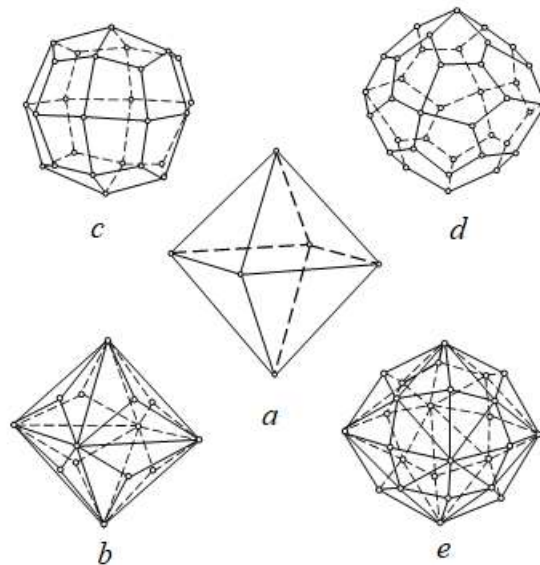


Figure 19. Octahedron group

The group of hexahedra (cube) (Figure 20) contains rhombododecahedron, which has 12 facets in the form of diamonds, pentagonododekaedr (12 faces in the form of pentagons), didodecahedron (doubledodecahedron) and tetrahexahedron.

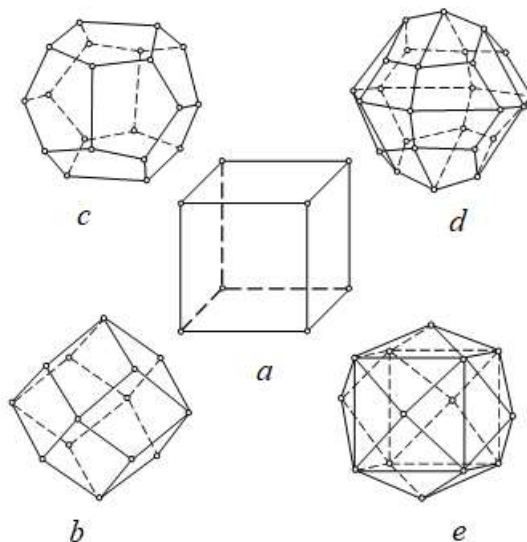


Figure 20. Hexahedron group

The installation dimension of crystals can be arbitrary and standard (Figure 21). In the standard dimension, the international rules of choosing the coordinate

system and the unit face, taking into account the symmetry and the crystal syngony, are kept. Systems of coordinate axis in crystallography can be triaxial and four-axial, depending on the symmetry of the crystal.

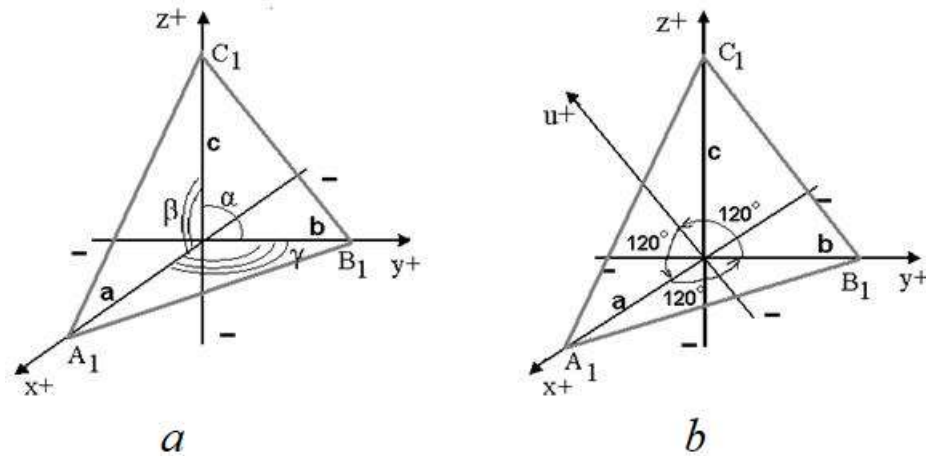


Figure 21. Three- and four-coordinate systems

The right coordinate system is chosen for triaxial system, that is, positive directions are considered: for the X axis – forward to the observer, Y – to the right of the observer, Z to the top. In the four-coordinate system the axis X, Y, U, lie in one plane, the angle between them is 120° , the Z – axis is perpendicular to them.

The single face is taken in such way that it intersects either all of the coordination axes, or their maximum number. In this case, the scale sections cut off by it, as the measurement unit on the corresponding coordinate axis.

The angles between the coordinate axes are characteristic for each syngony: between X and Y – α , between Z and X – β , between X and Y – γ and scale segments (unit parameters) on the coordinate axes: on the X-axis the segment is denoted by a , on the Y-axis – b , on the Z-axis – c .

So, the rules for choosing coordinates in crystals:

1. The axes of the coordinates should be combined with the axes of symmetry, giving priority to the axes of higher order. The only axis of higher order should be combined with the Z axis. In crystals of the monoclinic syngony, L_2 should be combined with the Y axis.

2. If there are no axes of symmetry, the crystals should be located $\perp P$.
3. If there are no axes and symmetry planes, the coordinate axes should be layed on throught to the most advanced faces.
4. The coordinate axes must intersect in the geometric center of the crystal.

Table 1 lists the rules for the crystals dimensions according to the syngony as well as the characteristics of the coordination systems. In fact, each syngony has its own coordination system, which differs from the coordination system of another syngony by the angles coordination and unit parameters. Only in the trigonal and hexagonal syngony the single four-coordinate system is used.

Table 1. Characteristic of the coordinate system depending on the syngony

Dimension	Syngony	Choice of coordinate axes	Choice of the single face
Triaxis 1 – X, 2 – Y, 3 – Z.	Cubic	$\alpha = \beta = \gamma = 90^\circ, a = b = c,$ X, Y, Z on L_4, L_2, L_{i4}	The faces of the octahedron, the tetrahedron
	Tetragonal	$\alpha = \beta = \gamma = 90^\circ, a = b \neq c,$ Z on $L_4, L_{i4},$ X, Y on $L_2, \perp P,$ to the edges	The faces of the pyramid, bipyramid, tetrahedron
	Orthorhombic	$\alpha = \beta = \gamma = 90^\circ, a \neq b \neq c,$ Z on L_2, X, Y on $L_2, \perp P,$ to the edges	The faces of the pyramid, bipyramid, tetrahedron
	Monoclinic	$\alpha = \gamma = 90^\circ \neq \beta, \beta \neq 120^\circ,$ $a \neq b \neq c, Y$ on $L_2 \perp P,$ X, Z to the edges	The faces of the rhombic prism
	Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ, a \neq b \neq c,$ X, Y, Z to the edges	The faces of the pedion, pinacoid
Four-axis 1 – X, 2 – Y, 3 – U, 4 – Z.	Hexagonal	$\alpha = \gamma = 90^\circ, a = b \neq c,$ $\gamma = 120^\circ,$ Z on $L_6, L_{i6},$ X, Y, U on $L_2, \perp P,$ to the edges	The faces of the pyramid, bipyramid
	Trigonal	$\alpha = \beta = 90^\circ, a = b \neq c,$ $\gamma = 120^\circ,$ Z on $L_3, L_{i3},$ X, Y, U on $L_2, \perp P,$ to the edges	The faces of the pyramid, bipyramid, rhombohedron

Solving:

- 1) hexahedron;
- 2) octahedron;
- 3) rhomboid decahedron.

All forms are closed.

Tasks for the individual work

1. Determine simple forms of 5-10 crystal models.
2. Indicate the dimension of 5-10 models of crystals of different categories.
3. Specify the indexes of the invented simple forms.

Practical work 4. Calculation of the crystallochemical radii of compounds

Purpose of work: studying the regularities of the calculation of crystallochemical radii in the compounds with different bonding types.

Brief theoretical information

During the formation of chemical compounds, the output radii of elements are usually deformed and there is the atoms overlapping. The main types of atoms overlapping are given in Figure 24

In determining the crystallochemical radii in the compounds proceed from the simplest reasoning, so introduce the concept of "effective" radius. To this end, atoms (ions) in the crystal structure are presented as rigid touched spheres, so that the distance between their centers equals the sum of their radii.

Determination of crystallochemical (effective) radii of compounds will be considered on the example of compounds with metallic and ionic types.

In the compounds with the metallic bonding type, the calculating method of the crystallochemical radius depends on the type of lattice (close packing). As is known, most metals form one of the following high-symmetric lattices with the close packing of atoms.

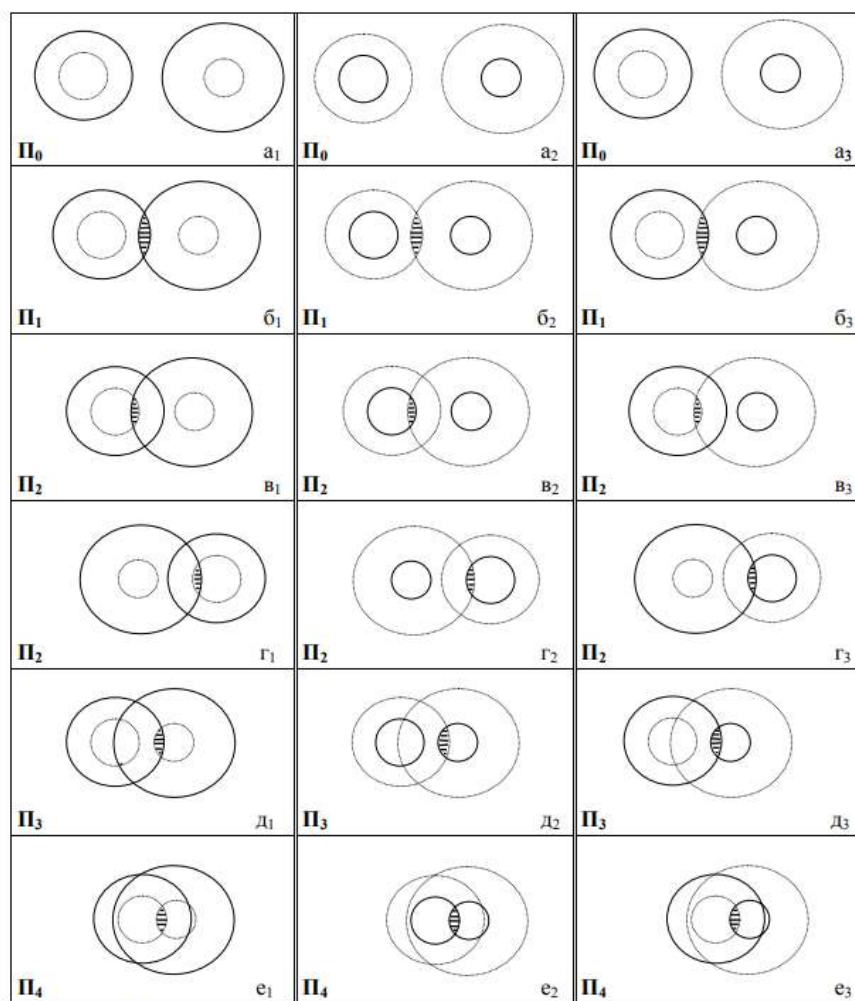


Figure 24. Schematic representation of the main types of overlapping atoms

Crystal lattices, characteristic of compounds with the metallic bonding type, are shown in Figure 25.

Cubic body-centered close packing – atoms are located at the vertices of the cube and one atoms in the center of the cube's volume. In this case, to calculate the crystallochemical radius, it is necessary to measure the inter-nuclear distance in the corresponding metal and divide it by two.

Cubic face-centered close packing – atoms are located at the vertices of the cube and in the center of the each face. In this case, the Pythagorean theorem is used to calculate the crystallochemical radius.

Hexagonal close packing – atoms are located at the vertices and in the center of the hexagonal prism bases, and three atoms – in the middle plane of the prism. In

the case of the hexagonal close packing the definition of the crystallochemical radius is carried out similar to the cubic body-centered close packing.

To calculate the radii in the ionic compounds, it is necessary to determine the radius of the at least one ion and then using the additivity rule $R_{ab} = r_a + r_b$, to calculate all others, subtracting the value of the known radius from the value of the interatomic distance. According to the W. Kossel's ion model, negative particles – electrons, separating from one atom and thereby converting it into cation (K), transfer to another atom, giving it the negative charge (making it the anion (A)) and thereby increasing its size.

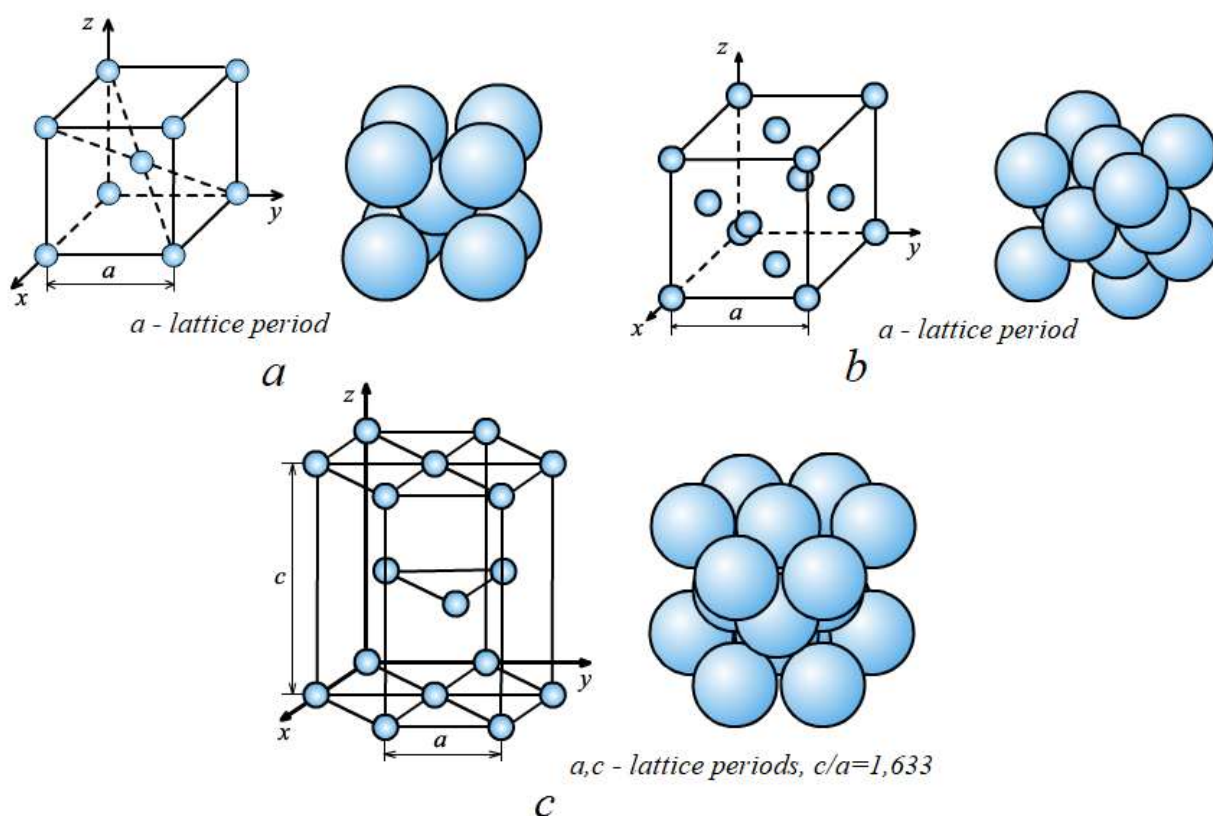


Figure 25. Elementary crystalline lattices: body-centered cube (a); face-centered cube (b); hexagonal close packing (c)

Examples of calculation of the crystallochemical radii

Example 1: there is compound CsCl. The value of radius of $\text{Cl}^- = 1,81 \text{ \AA}$. Determine the Cs^+ radius. The value of internuclear distance is $a = 7,132 \text{ \AA}$.

Solving: To calculate the radius Cs^+ we use the Pythagorean theorem (Figure 26):

$$(2 \cdot R_{\text{Cl}^-} + 2 \cdot R_{\text{Cs}^+})^2 = a^2 + a^2,$$

$$2 \cdot R_{\text{Cl}^-} + 2 \cdot R_{\text{Cs}^+} = \sqrt{2a^2},$$

$$R_{\text{Cl}^-} + R_{\text{Cs}^+} = \frac{\sqrt{2}a}{2},$$

$$R_{\text{Cs}^+} = \frac{\sqrt{2}a}{2} - R_{\text{Cl}^-} = \frac{\sqrt{2}}{2} \cdot 7,132 - 1,81 = 3,23 \text{ \AA}.$$

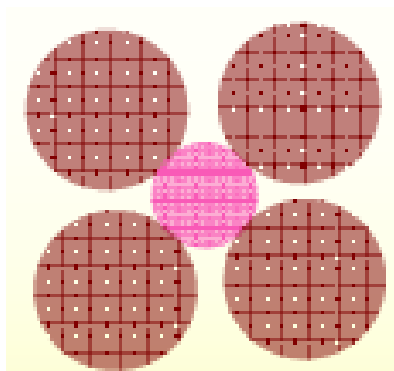


Figure 26. The structure of the CsCl compound

Task for the individual work

The values of internuclear distances are given in the Appendix 4.

1. Determine the crystallochemical radius of the potassium. Type of close packing – cubic body-centered.
2. Determine the crystallochemical radius of the α -Ca. Type of close packing – cubic face-centered.
3. There is substance NaCl. The value of radius of the $\text{Na}^+ = 0,98 \text{ \AA}$. Determine the radius of Cl^- , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

4. Determine the crystallochemical radius of the lithium. Type of close packing – cubic body-centered.
5. Determine the crystallochemical radius of the cerium. Type of close packing – cubic face-centered.
6. There is substance BaO, which has structure of NaCl. The value of radius of the $O^- = 1,36 \text{ \AA}$. Determine the radius of Ba^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.
7. Determine the crystallochemical radius of the β -Ti. Type of close packing – cubic body-centered.
8. Determine the crystallochemical radius of the α -Sr. Type of close packing – cubic face-centered.
9. There is substance CaO, which has structure of NaCl. The value of radius of $O^- = 1,36 \text{ \AA}$. Determine the radius of Ca^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.
10. Determine the crystallochemical radius of the β -Zr. Type of close packing – cubic body-centered.
11. Determine the crystallochemical radius of the plumbum. Type of close packing – cubic face-centered.
12. There is substance CsF, which has structure of NaCl. The value of radius of $F^- = 1,33 \text{ \AA}$. Determine the radius of Cs^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.
13. Determine the crystallochemical radius of the tantalum. Type of close packing – cubic body-centered.
14. Determine the crystallochemical radius of the nickel. Type of close packing – cubic face-centered.
15. There is substance LiF, which has structure of NaCl. The value of radius of $F^- = 1,33 \text{ \AA}$. Determine the radius of Li^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

16. Determine the crystallochemical radius of the tungsten. Type of close packing – cubic body-centered.

17. Determine the crystallochemical radius of the argentum. Type of close packing – cubic face-centered.

18. There is substance CsI, which has structure of CsCl. The value of radius of $I^- = 2,2 \text{ \AA}$. Determine the radius of Cs^+ .

19. Determine the crystallochemical radius of the vanadium. Type of close packing – cubic body-centered.

20. Determine the crystallochemical radius of the aurum. Type of close packing – cubic face-centered.

21. There is substance MgO, which has structure of NaCl. The value of radius of $O^- = 1,36 \text{ \AA}$. Determine the radius of Mg^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

22. Determine the crystallochemical radius of the α -Fe. Type of close packing – cubic body-centered.

23. Determine the crystallochemical radius of the palladium. Type of close packing – cubic face-centered.

24. There is substance NaI, which has structure of NaCl. The value of radius of $I^- = 2,2 \text{ \AA}$. Determine the radius of Na^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

25. Determine the crystallochemical radius of the chromium. Type of close packing – cubic body-centered.

26. Determine the crystallochemical radius of the platinum. Type of close packing – cubic face-centered.

27. There is substance RbBr, which has structure of NaCl. The value of radius of $Br^- = 1,96 \text{ \AA}$. Determine the radius of Rb^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

28. Determine the crystallochemical radius of the barium. Type of close packing – cubic body-centered.

29. Determine the crystallochemical radius of the rhodium. Type of close packing – cubic face-centered.

30. There is substance SrO, which has structure of NaCl. The value of radius of $O^- = 1,36 \text{ \AA}$. Determine the radius of Sr^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

31. Determine the crystallochemical radius of the niobium. Type of close packing – cubic body-centered.

32. Determine the crystallochemical radius of the γ -Fe. Type of close packing – cubic face-centered.

33. There is substance KBr, which has structure of NaCl. The value of radius of $Br^- = 1,96 \text{ \AA}$. Determine the radius of K^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

34. Determine the crystallochemical radius of the magnesium. Type of close packing – hexagonal.

35. Determine the crystallochemical radius of the α -Co. Type of close packing – cubic face-centered.

36. There is substance CsBr, which has structure of NaCl. The value of radius of $Br^- = 1,96 \text{ \AA}$. Determine the radius of Cs^+ .

37. Determine the crystallochemical radius of the α -Ti. Type of close packing – hexagonal.

38. There is substance KCl, which has structure of NaCl. The value of radius of $Cl^- = 1,81 \text{ \AA}$. Determine the radius of K^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

39. Determine the crystallochemical radius of the cadmium. Type of close packing – hexagonal.

40. There is substance KF, which has structure of NaCl. The value of radius of $F^- = 1,33 \text{ \AA}$. Determine the radius of K^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

41. Determine the crystallochemical radius of the rhenium. Type of close packing – hexagonal.

42. There is substance KI, which has structure of NaCl. The value of radius of $I^- = 2,2 \text{ \AA}$. Determine the radius of K^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

43. Determine the crystallochemical radius of the osmium. Type of close packing – hexagonal.

44. There is substance LiI, which has structure of NaCl. The value of radius of $I^- = 2,2 \text{ \AA}$. Determine the radius of Li^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

45. Determine the crystallochemical radius of the zinc. Type of close packing – hexagonal.

46. There is substance NaBr, which has structure of NaCl. The value of radius of $Br^- = 1,96 \text{ \AA}$. Determine the radius of Na^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

47. Determine the crystallochemical radius of the β -Co. Type of close packing – hexagonal.

48. Determine the crystallochemical radius of the beryllium. Type of close packing – hexagonal.

49. There is substance PbS, which has structure of NaCl. The value of radius of $S^- = 1,82 \text{ \AA}$. Determine the radius of Pb^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

50. Determine the crystallochemical radius of the β -Ca. Type of close packing – hexagonal.

51. There is substance RbCl, which has structure of NaCl. The value of radius of $Cl^- = 1,81 \text{ \AA}$. Determine the radius of Rb^+ , assuming that in the structure of the ionic crystal the connection occurs between the ions of different signs.

52. Determine the crystallochemical radius of the ruthenium. Type of close packing – hexagonal.

Practical work 5. Determination of the coordination numbers and coordination polyhedra

Purpose of work: the establishment of coordination numbers and coordination polyhedra of atoms (ions) in the structure of various compounds

Brief theoretical information

The number of identical neighboring atoms (ions of the opposite sign) from the nearest environment of this atom (ion) in the crystalline structure is called the *coordination number* (CN) of the atom (ion). The geometric figure obtained by connection the centers of these atoms (ions) with straight lines is called the *coordination polyhedron* (CP) [7,15].

The CN and CP history was as follows. L.K. Pauling proposed to provide images of cations in the form of coordinate polyhedra – octahedra and tetrahedra (Figure 27).

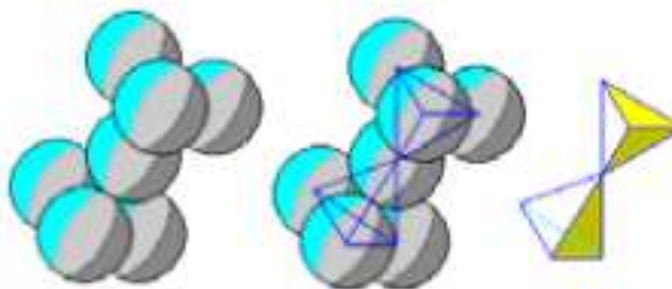


Figure 27. Cations and respective to them CPs

Then M.V. Belov proposed to use the method of the L.K. Pauling for any structures (Figure 28). At the same time, it became clear that different polyhedra can have the same coordination number (Figure 29).

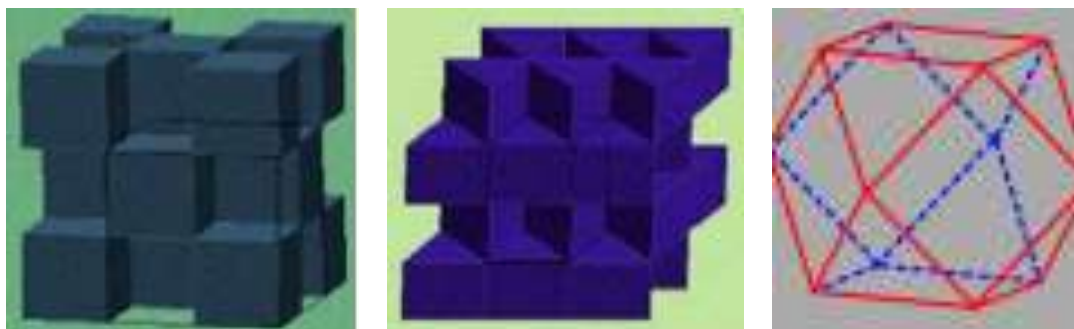


Figure 28. CP images for different structures

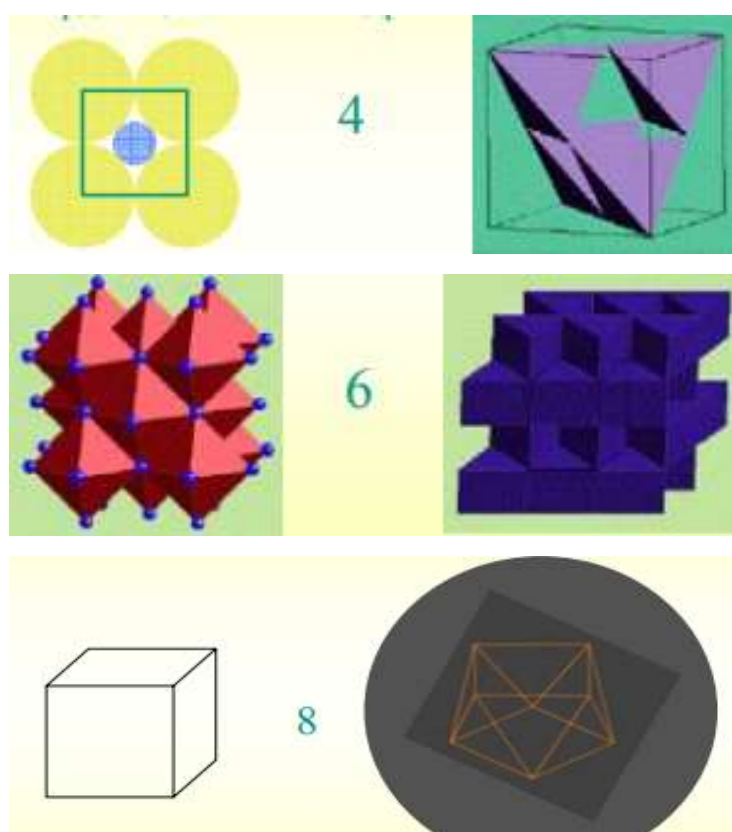


Figure 29. Different structures and identical KP

Typical coordination numbers and corresponding coordination polyhedra are given in Chapter 3, Table 3.2.

Examples of the determination of coordination numbers and coordination polyhedra

Example 1: to determine the coordination numbers and coordination polyhedra of sodium and chlorine ions in the structure of rock salt (Figure 30).

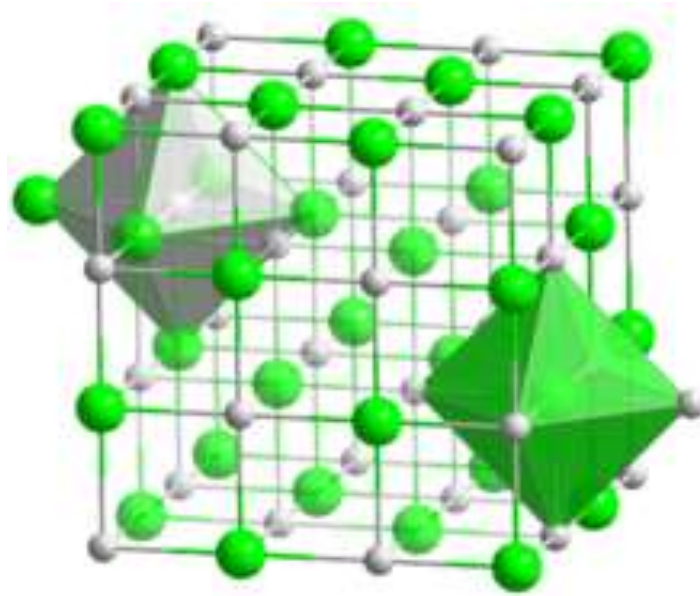


Figure 30. The structure of NaCl

Solving: in the structure of rock salt, each ion of sodium is surrounded by six chlorine ions, that is, $CN = 6$. Chlorine ions are located at the vertexes of the octahedron, therefore the coordination polyhedron is the octahedron. The same environment is characteristic for the chlorine ions in relation to sodium ions.

Example 2: to determine the coordinating number and coordination polyhedron of carbon ions in the diamond structure (Figure 31).

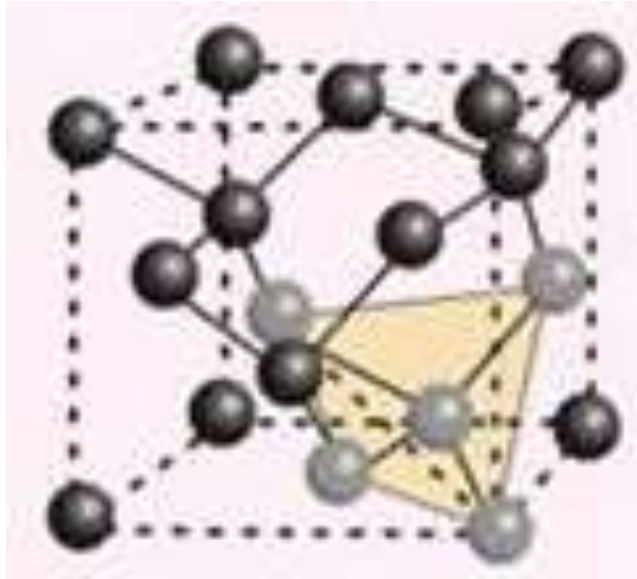


Figure 31. The diamond structure

Solving: in the diamond structure, the number of closest adjacent atoms, that is, the coordinating number, is 4, the coordination polyhedron is the tetrahedron.

Example 3: to determine the coordination numbers and coordinate polyhedra of calcium and fluoride ions in the structure of fluorite (Figure 32).

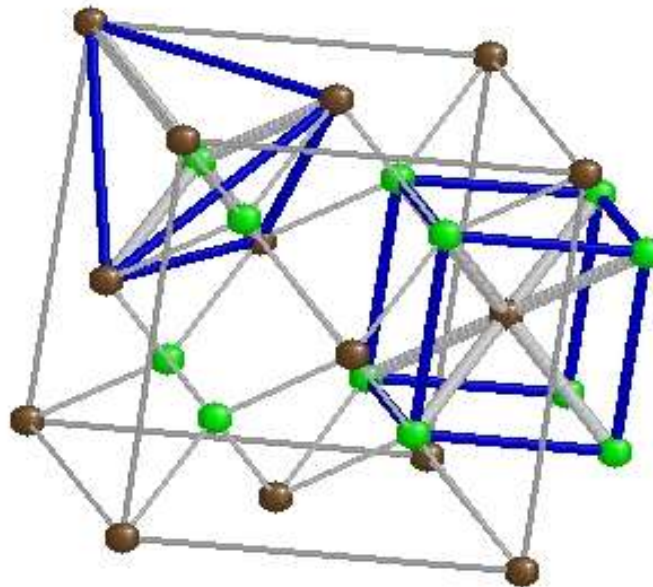


Figure 32. The structure of fluorite

Solving: in the structure of the fluorite CaF_2 the calcium ion is surrounded by 8 fluoride ions, and the fluoride ion – by 4 calcium ions; $\text{CN}_{\text{Ca}_\text{F}} = 8$; coordination polyhedron – cube; $\text{CN}_{\text{F}_{\text{Ca}}} = 4$; coordination polyhedron – tetrahedron.

Tasks for the individual work

Additional information for the tasks is provided in Appendix 5.

1. There is structure LiF . To determine the coordination numbers and coordination polyhedra of lithium and fluorine ions in the structure.
2. To determine the coordination number and coordination polyhedron of atom in the structure of germanium.
3. There is structure CaO . To determine the coordination numbers and coordination polyhedra of calcium and oxygen ions in the structure.
4. To determine the coordination numbers and coordination polyhedra of cesium and iodine ions in the structure CsI .
5. There is structure NaF . To determine the coordination numbers and coordination polyhedra of sodium and fluorine ions in the structure.
6. To determine the coordination numbers and coordination polyhedra of strontium and fluorine ions in the structure SrF_2 .
7. There is structure PbS . To determine the coordination numbers and coordination polyhedra of plumbum and sulfur in the structure.
8. To determine the coordination numbers and coordination polyhedra of cesium and bromine ions in the structure CsBr .
9. There is structure AgBr . To determine the coordination numbers and coordination polyhedra of argentum and bromine ions in the structure.
10. To determine the coordination numbers and coordination polyhedra of aurum and zinc ions in the structure AuZn .
11. There is structure RbF . To determine the coordination numbers and coordination polyhedra of rubidium and fluorine ions in the structure.

12. To determine the coordination numbers and coordination polyhedra of thallium and chlorine ions in the structure TlCl .

13. There is structure MgO . To determine the coordination numbers and coordination polyhedra of magnesium and oxygen ions in the structure.

14. To determine the coordination numbers and coordination polyhedra of cesium and fluorine ions in the structure CsF .

15. There is structure GeTe . To determine the coordination numbers and coordination polyhedra of germanium and tellurium ions in the structure.

16. To determine the coordination number and coordination polyhedron of atom in the structure of silicon.

17. There is structure LiCl . To determine the coordination numbers and coordination polyhedra of lithium and chlorine ions in the structure.

18 To determine the coordination numbers and coordination polyhedra of copper and fluoride ions in the structure CuF_2 .

19. To determine the coordination numbers and coordination polyhedra of rubidium and bromine ions in the structure RbBr .

20. There is structure AgCl . To determine the coordination numbers and coordination polyhedra of argentum and chlorine ions in the structure.

21. To determine the coordination numbers and coordination polyhedra of copper and zinc ions in the structure CuZn .

22. There is structure MnO . To determine the coordination numbers and coordination polyhedra of manganese and oxygen ions in the structure.

23. To determine the coordination numbers and coordination polyhedra of thallium and bromine ions in the structure TlBr .

24. There is structure RbCl . To determine the coordination numbers and coordination polyhedra of rubidium and chlorine ions in the structure.

25. To determine the coordination number and coordination polyhedron of atom in the structure of gray tin.

26. There is structure FeO. To determine the coordination numbers and coordination polyhedra of iron and oxygen ions in the structure.

27. To determine the coordination numbers and coordination polyhedra of rubidium and iodine ions in the structure RbI.

28. There is structure SnTe. To determine the coordination numbers and coordination polyhedra of tin and tellurium ions in the structure.

29. To determine the coordination numbers and coordination polyhedra of zirconium and fluoride ions in the structure ZrF_2 .

30. There is structure AgF. To determine the coordination numbers and coordination polyhedra of argentine and fluoride ions in the structure.

31. To determine the coordination numbers and coordination polyhedra of argentine and zinc ions in the structure of AgZn.

32. There is structure PbTe. To determine the coordination numbers and coordination polyhedra of plumbum and tellurium ions in the structure.

33. There is structure TiO. To determine the coordination numbers and coordination polyhedra of titanium and oxygen ions in the structure.

34. There is structure NiO. To determine the coordination numbers and coordination polyhedra of nickel and oxygen ions in the structure.

Practical work 6. Determination of the stoichiometric formula of the substance

Purpose of work: the determination of structural, formula units, and the calculation of the total number of atoms per elementary cell.

Brief theoretical information

The determination of the chemical (stoichiometric) formula of the substance is based on the calculation of the number of atoms of each class, belonging to one elementary cell.

The number of structural units (SO) shows how many atoms (molecules) of this chemical compound must be taken to build one elementary cell. The number of SO is always greater than one and acquires only integer values [7].

For *simple substances* that consist of atoms of one element (Cu, Fe, Se), the number of structural units corresponds to the number of atoms in the elementary cell. For *simple molecular substances* (I_2 , S_8) and molecular compounds (CO_2), the number of SO is equal to the number of molecules in the cell. In the vast majority of *inorganic compounds* (NaCl, CaF_2 , CuAu), instead of the term «number of molecules», the term number of “formula” units Z is used.

Examples of the determination of structural and formula units

Example 1: there is structure CsCl. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number (Figure 33).

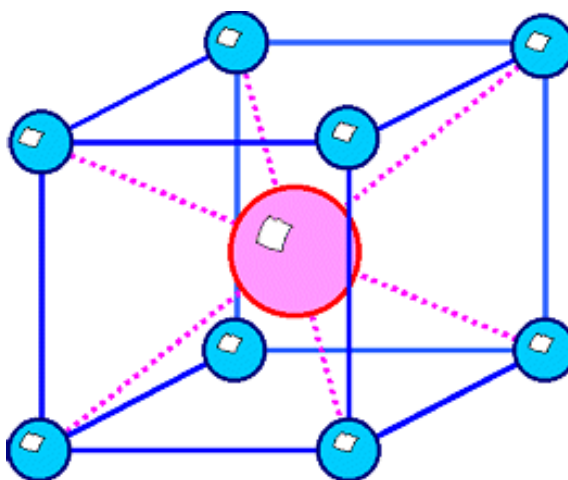


Figure 33. Structure of cesium chloride

Solving: in the CsCl structure, one Cl atom is in the center of the cell, the Cs atoms occupy 8 vertices, that is, 1 cell contains $8 \times 1/8 = 1$ Cs atom, hence $A : B = 1 : 1$, stoichiometric formula AB (CsCl), $Z = 2$.

The calculation of the total number of atoms per one elementary cell of CsCl is shown in Table. 2.

Table 2. Calculation of the total number of atoms of the elementary cell in the CsCl structure

Atom location	Volume that enters the cell	Number of atoms	Total number of atoms per cell
At the vertex	1/8	8	1 (cesium)
In the middle of rib	1/4	0	-
In the center of facet	1/2	0	-
In the center of cell	1	1	1 (chlorine)

Example 2: there is structure CaF_2 . Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number (Figure 34).

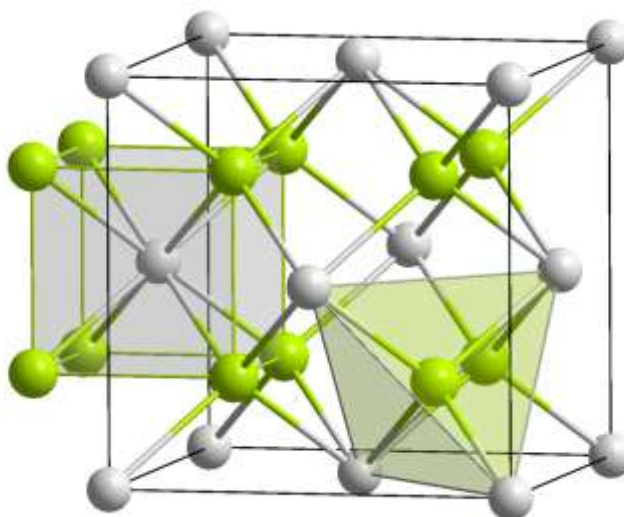


Figure 34. Structure of fluorite

Solving: in the structure of the fluorite CaF_2 , Ca atoms occupy the nodes of the face-centered cell, the number of structural units of A type (Ca) is equal to 4 (Table 3). In the fluorite structure, the coordination number Ca = 8 (Table 3), the coordination number F = 4, the ratio of coordinating numbers is $8 : 4 = 2 : 1$, the stoichiometric formula AB_2 (CaF_2). One elementary cell contains 4 atoms of Ca and 8 atoms of F. Number of structural units $Z = 4$.

Table 3. Calculation of the total number of atoms of the elementary cell in the CaF₂ structure

Atom location	Volume that enters the cell	Number of atoms	Total number of atoms per cell
At the vertex	1/8	8	1 (calcium)
In the middle of rib	1/4	0	-
In the center of facet	1/2	6	3 (calcium)
In the center of cell	1	8	8 (fluorine)

Tasks for the individual work

Additional information for the tasks is provided in the Appendix 5.

1. There is structure LiF. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.
2. Specify the number of structural and formula units in the structure of germanium.
3. There is structure CaO. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.
4. Specify the number of structural and formula units in the structure CsI.
5. There is structure NaF. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.
6. Specify the position and number of atoms in the structure SrF₂. Determine the number of structural and formula units.
7. There is structure PbS. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.
8. Specify the number of structural and formula units in the structure CsBr.
9. There is structure AgBr. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.
10. Specify the number of structural and formula units in the structure AuZn.
11. There is structure RbF. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.
12. Specify the number of structural and formula units in the structure TiCl.

13. There is structure MgO. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

14. Specify the number of structural and formula units in the structure CsF.

15. There is structure GeTe. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

16. Specify the number of structural and formula units in the structure of silicon.

17. There is structure LiCl. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

18. Specify the position and number of atoms in the structure CuF_2 . Determine the number of structural and formula units.

19. Specify the number of structural and formula units in the structure RbBr.

20. There is structure AgCl. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

21. Specify the number of structural and formula units in the structure CuZn.

22. There is structure MnO. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

23. Specify the number of structural and formula units in the structure TlBr.

24. There is structure RbCl. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

25. Specify the number of structural and formula units in the structure of gray tin.

26. There is structure FeO. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

27. Specify the number of structural and formula units in the structure RbI.

28. There is structure SnTe. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

29. Specify the position and number of atoms in the structure ZrF_2 . Determine the number of structural and formula units.

30. There is structure AgF. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

31. Specify the number of structural and formula units in the structure AgZn.

32. There is structure PbTe. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

33. There is structure TiO. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

34. There is structure NiO. Determine the number of structural and formula units; indicate the position of the atoms in the structure and their number.

METHODOLOGICAL RECOMMENDATIONS FOR THE IMPLEMENTATION OF THE HOME TEST WORK (HTW)

Basis thesis

The home test work (HTW) should be presented in the form of the manuscript in Ukrainian (font Times New Roman, 14 pt, one and a half interval). Margins: left – 30 mm, right – 10 mm, top – 20 mm and bottom – 20 mm.

The title page must contain the full name of the institution and its departmental subordination, the name of the faculty and the department, the title of the work, data about the student and the scientific leader, the city and the year of work presentation for defence. Title page should not include the page number.

The content of the work should correspond to the task of the HTW. The only difference is the indication of page numbers.

The conclusions should include the results of the task. After the conclusions, the "List of references" shall be indicated, which shall contain the full bibliographic description of any documents, scientific works and reference literature used by the author in any form. The list of references should be made in accordance with the current requirements or one of the international style. List of references should be placed in the order of the appearance of references in the text.

Tasks

Home test work should contain:

1. Theoretical part.

Description of the given compound (*volume 2-3 pages*) by the following items:

- 1) chemical composition and origin;
- 2) physical (density, mechanical, thermal, electric, optical, magnetic, scalar characteristics) properties with the representation of the compound's appearance (crystal);
- 3) chemical bond and character of the structure;

4) deposits in Ukraine;

5) practical value and application.

2. Practical part.

1) Elementary cell (figure) and its projection, cell parameters, number of atoms in the cell, their coordinates (basis);

2) lattice type with justification, number of structural and formula units;

3) CN (calculation); the distance between the atoms;

4) CP (figure); simple forms: indexing faces;

5) elements of the Bravais symmetry (Flint formula), symmetry class, recording according to the international symbols (by Herman-Mogen), stereographic projection.

Example of the implementation of the HTW practical part

Substance: *tin (II) oxide*.

1. Figure 35 shows the SnO elementary cell and its projection onto the plane.

For the tin (II) oxide compound, the tetragonal syngony with cell parameters:

$a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$ is characteristic; $a = 0,3802$ nm; $c = 0,4837$ nm.

Coordinates of atoms in the cell (their basis):

1) O $[[0;0;0]]$;

2) Sn $[[0;1;0]]$.

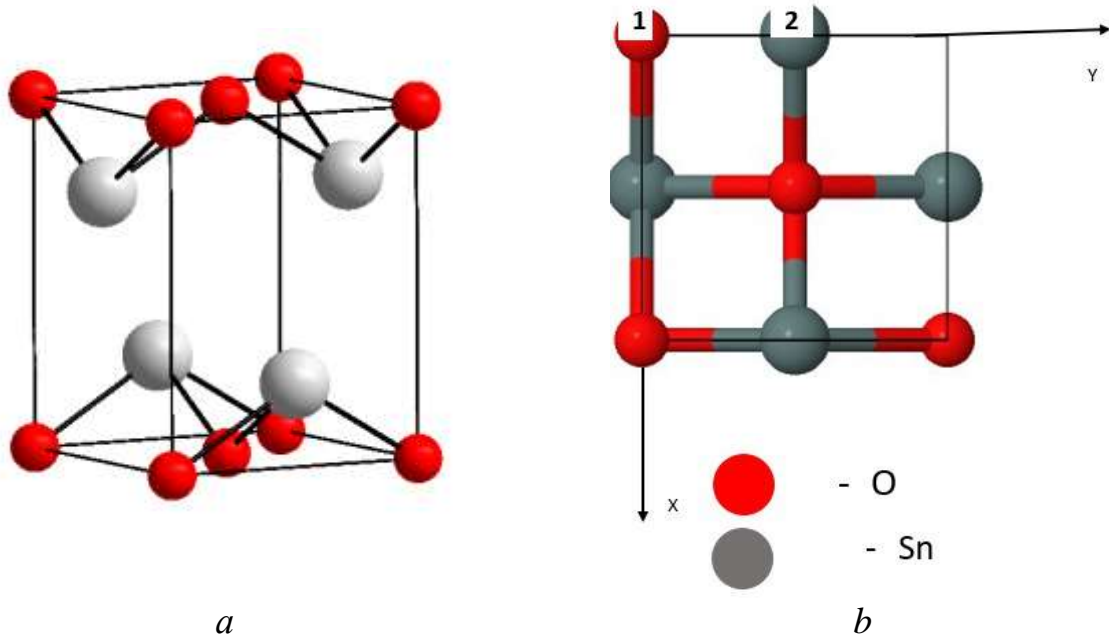


Figure 35. Elementary cell SnO (a) and its projection (b)

The number of atoms in the elementary cell is calculated, taking into account the location of the atoms. The calculation of the number of atoms per unit cell SnO is given in Table. 1.

Table 1. Calculation of the number of atoms in the cell

Atom location	Volume that enters the cell	Number of atoms	Total number of atoms per cell
At the vertex	1/8	8	1 (Oxygen)
In the middle of rib	1/4	-	-
In the center of facet	1/2	6	2 (Tin) 1 (Oxygen)
In the center of cell	1	-	-

Consequently, the cell contains 4 atoms.

2. The Bravais lattice type of SnO – primitive tetragonal. In the tetragonal syngony, two of the three basic vectors have the same length, and the third is different from them. In this case, all three vectors are perpendicular to each other (Figure 36).

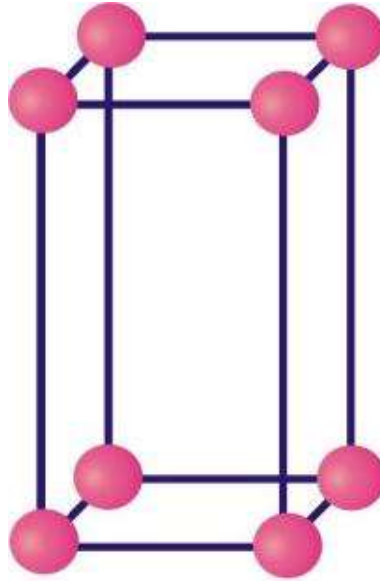


Figure 36. Type of the SnO Bravais lattice

The characteristic element of the symmetry of the SnO structure is the presence of the 4th order axis. Spatial group: $P4_2/nmm$.

Pearson Index: tP4 (t – tetragonal syngony; P – primitive lattice; the number indicates the number of atoms or structural units).

The number of structural units, that is, the number of atoms to form one elementary cell SnO, $CO = 1 (O) + 2 (Sn) + 1 (O) = 4$.

Number of formula units SnO are $Z = 4 / (1+1) = 2$.

3. In the SnO structure, each tin atom is surrounded by four oxygen atoms, and each oxygen atom has in its environment four atoms of the tin. That is, the coordination numbers of the tin and oxygen atoms are equal:

$$CN (Sn) = CN (O) = 4.$$

The atomic radii for tin and oxygen:

$$R (Sn^{2+}) = 0,99479 \text{ \AA};$$

$$R (O^{2-}) = 1,40 \text{ \AA}.$$

The value of interatomic distance is calculated by the formula:

$$a = 2 R (O^{2-}) + 2 R (Sn^{2+}) = 2 \cdot 1,40 + 2 \cdot 0,99479 = 4,78958.$$

4. Proceeding from the value of the coordination numbers, the coordination polyhedra of atoms in the tin (II) oxide are octahedra (Figure 37). The simple form, octahedron, contains 8 identical faces in the form of triangles ($\alpha = 45^\circ$).

The indexes of the bipyramid's faces – (1 0 1).

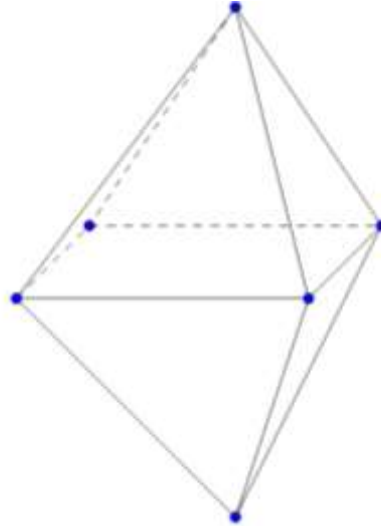


Figure 37. Coordination polyhedron SnO

5. The crystalline polyhedron of the tin (II) oxide structure contains one axis of the fourth order, four axes of the second order, five planes and the center of symmetry. Consequently, this substance belongs to the plane and axis class of symmetry.

Formula by Flint – $L_4L_2^4PC$.

The formula by the international symbols – $4/m\bar{3}m$.

Figure 38 shows the stereographic projection of SnO with symmetry elements.

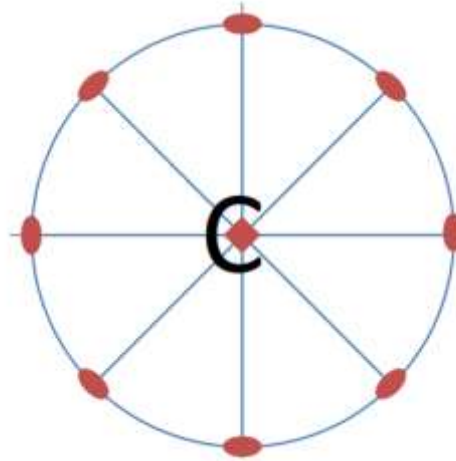


Figure 38. Stereographic projection SnO

Conclusions: should include information on the Bravais lattice type, spatial group, coordinate numbers and coordination polyhedra, the number of structural and formula units, elements, and the class of symmetry.

Task variants for the HTW

Variant	Substance
1	Au
2	CdS
3	δ -Fe
4	α -Ti
5	MnO
6	α -Fe ₂ O ₃
7	VO ₂
8	BaTiO ₃
9	NiCo ₂ O ₄
10	NiO
11	Ti ₂ O ₃
12	Ca ₁₀ (PO ₄) ₆ (OH) ₂
13	β -Ca
14	CdSe
15	Ag
16	γ -Fe ₂ O ₃
17	Ca(OH) ₂
18	CoS ₂
19	Sn (сіре олово)
20	ZnO
21	Fe ₃ O ₄
22	Fe(OH) ₂
23	CaCO ₃
24	ZrO ₂ (кубічна модифікація)
25	Al(OH) ₃
26	SnO ₂
27	CaSO ₄
28	C ₆₀ (фулерен)
29	FeO
30	WSe ₂
31	TiO ₂ (анатаз)
32	Ca ₃ (PO ₄) ₂
33	SiO ₂
34	C (алмаз)
35	TiO ₂ (рутил)

REFERENCE

1. Азимов А. Краткая история химии. Развитие идей и представлений в химии / А. Азимов. – М. : Мир, 1983. – 187 с.
2. Зефирова О. Н. Краткий курс истории и методологии химии / О. Н. Зефирова. – М. : Анабасис, 2007. – 140 с.
3. Левченков С. И. Краткий очерк истории химии / С. И. Левченков. – Ростов н/Д : Изд-во РГУ, 2006. – 112 с.
4. Миттова И. Я. История химии с древнейших времен до конца XX века : учеб. пособие в 2-х томах / И. Я. Миттова, А. М. Самойлов. – Долгопрудный : ИД «Интеллект», 2009. – 416 с.
5. Соловьев Ю. И. История химии. Развитие химии с древнейших времён до конца XIX века / Ю. И. Соловьев. – М. : Просвещение, 1983. – 368 с.
6. Пчелінцев В. О. Кристалографія, кристалохімія та мінералогія : навч. посіб. / В. О. Пчелінцев. – Суми : СумДУ, 2007. – 226 с.
7. Зиман З. З. Основи структурної кристалографії : навч. посіб. для студ. вищ. навч. закл. / З. З. Зиман. – Харків : ХНУ імені В. Н. Каразіна, 2008. – 212 с.
8. Вест А. М. Химия твердого тела. Теория и приложения, в 2-х ч. Ч. 1 / А. М. Вест под ред. Акад. Ю. Д. Третьякова, – М. : Мир, 1988. – 558 с.
9. Карапетьянц М. Х. Строение вещества / М. Х. Карапетьянц, С. И. Дракин. – М. : Высш. шк., 1978. – 304 с.
10. Партэ Э. Некоторые главы структурной неорганической химии / Э. Партэ. – М. : Мир: 1993. – 144 с.
11. Мюллер У. Структурная неорганическая химия / У. Мюллер. – Долгопрудный : Изд. дом «Интеллект», 2010. – 352 с.
12. Кузьмичева Г. М. Основные разделы кристаллографии : учеб. пособ. / Г. М. Кузьмичева. – М. : МИТХТ, 2002. – 80 с.
13. Попов Г. М. Кристаллография / Г. М. Попов, И. И. Шафрановский. – М. : Высш. шк., 1972. – 352 с.

14. Шевченко Л. Л. Кристаллохімія : підручник / Л. Л. Шевченко. – Київ : Вища шк., 1993. – 174 с.
15. Егоров-Тисменко Ю. К. Кристаллография и кристаллохимия / Ю. К. Егоров-Тисменко. – М. : КДУ, 2005. – 592 с.
16. Бокий Г. Б. Кристаллохимия / Г. Б. Бокий. – М. : Наука, 1971. – 400 с.
17. Кребс Г. Основы кристаллохимии неорганических соединений / Г. Кребс . – М. : Мир, 1971. – 304 с.
18. Урусов В. С. Теоретическая кристаллохимия / В. С. Урусов. – М. : Изд-во МГУ, 1987. – 275 с.
19. Уэллс А. Структурная неорганическая химия : В 3-х т. / А. Уэллс – М. : Мир, 1987.
20. Ахметов Н. С. Неорганическая химия / Н. С. Ахметов. – М. : Высш. шк. – 1978. – 716 с.
21. Хьюи Дж. Неорганическая химия. Строение вещества и реакционная способность / Дж. Хьюи. – М. : Химия, 1987. – 696 с.
22. Ормант Б. Ф. Введение в физическую химию и кристаллохимию проводников / Б. Ф. Ормант. – М. : Высш. шк., 1973. – 656 с.

APPENDICES

Appendix 1. Space groups

Crystal System	Laue Class	Crystal Class	Lattice Centring	230 3-Dimensional Space Groups
Triclinic	-1	1	<i>P</i>	<i>P</i> 1
		-1		<i>P</i> -1
Monoclinic	<i>2/m</i>	2	<i>P</i>	<i>P</i> 2, <i>P</i> 2 ₁
			<i>C</i>	<i>C</i> 2
		<i>m</i>	<i>P</i>	<i>P</i> <i>m</i> , <i>P</i> <i>c</i>
			<i>C</i>	<i>C</i> <i>m</i> , <i>C</i> <i>c</i>
		<i>2/m</i>	<i>P</i>	<i>P</i> 2/ <i>m</i> , <i>P</i> 2 ₁ / <i>m</i> , <i>P</i> 2/ <i>c</i> , <i>P</i> 2 ₁ / <i>c</i>
			<i>C</i>	<i>C</i> 2/ <i>m</i> , <i>C</i> 2/ <i>c</i>
Orthorhombic	<i>mmm</i>	222	<i>P</i>	<i>P</i> 222, <i>P</i> 222 ₁ , <i>P</i> 2 ₁ 2 ₁ 2, <i>P</i> 2 ₁ 2 ₁ 2 ₁
			<i>C</i>	<i>C</i> 222, <i>C</i> 222 ₁
			<i>F</i>	<i>F</i> 222
			<i>I</i>	<i>I</i> 222, <i>I</i> 2 ₁ 2 ₁ 2 ₁
		<i>mm</i> 2	<i>P</i>	<i>P</i> <i>m</i> <i>m</i> 2, <i>P</i> <i>m</i> <i>c</i> 2 ₁ , <i>P</i> <i>c</i> <i>c</i> 2, <i>P</i> <i>m</i> <i>a</i> 2, <i>P</i> <i>c</i> <i>a</i> 2 ₁ , <i>P</i> <i>n</i> <i>c</i> 2, <i>P</i> <i>m</i> <i>n</i> 2 ₁ , <i>P</i> <i>b</i> <i>a</i> 2, <i>P</i> <i>n</i> <i>a</i> 2 ₁ ,
			<i>C</i> or <i>A</i>	<i>C</i> <i>m</i> <i>m</i> 2, <i>C</i> <i>m</i> <i>c</i> 2 ₁ , <i>C</i> <i>c</i> <i>c</i> 2, <i>A</i> <i>m</i> <i>m</i> 2, <i>A</i> <i>b</i> <i>m</i> 2, <i>A</i> <i>m</i> <i>a</i> 2, <i>A</i> <i>b</i> <i>a</i> 2
			<i>F</i>	<i>F</i> <i>m</i> <i>m</i> 2, <i>F</i> <i>d</i> <i>d</i> 2
			<i>I</i>	<i>I</i> <i>m</i> <i>m</i> 2, <i>I</i> <i>b</i> <i>a</i> 2, <i>I</i> <i>m</i> <i>a</i> 2
		<i>mmm</i>	<i>P</i>	<i>P</i> <i>m</i> <i>m</i> <i>m</i> , <i>P</i> <i>n</i> <i>n</i> <i>n</i> , <i>P</i> <i>c</i> <i>c</i> <i>m</i> , <i>P</i> <i>b</i> <i>a</i> <i>n</i> , <i>P</i> <i>m</i> <i>m</i> <i>a</i> , <i>P</i> <i>n</i> <i>n</i> <i>a</i> , <i>P</i> <i>m</i> <i>n</i> <i>a</i> , <i>P</i> <i>c</i> <i>c</i> <i>a</i> , <i>P</i> <i>b</i> <i>a</i> <i>m</i> , <i>P</i> <i>c</i> <i>c</i> <i>n</i> , <i>P</i> <i>b</i> <i>c</i> <i>m</i> ,
			<i>C</i>	<i>C</i> <i>m</i> <i>m</i> <i>m</i> , <i>C</i> <i>m</i> <i>c</i> <i>m</i> , <i>C</i> <i>m</i> <i>c</i> <i>a</i> , <i>C</i> <i>c</i> <i>c</i> <i>m</i> , <i>C</i> <i>m</i> <i>m</i> <i>a</i> , <i>C</i> <i>c</i> <i>c</i> <i>a</i>
			<i>F</i>	<i>F</i> <i>m</i> <i>m</i> <i>m</i> , <i>F</i> <i>d</i> <i>d</i> <i>d</i>

			<i>I</i>	<i>Immm, Ibam, Ibcm, Imma</i>
Tetragonal	<i>4/m</i>	4	<i>P</i>	<i>P4, P4₁, P4₂, P4₃</i>
			<i>I</i>	<i>I4, I4₁</i>
		-4	<i>P</i>	<i>P-4</i>
			<i>I</i>	<i>I-4</i>
		<i>4/m</i>	<i>P</i>	<i>P4/m, P4₂/m, P4/n, P4₂/n</i>
			<i>I</i>	<i>I4/m, I4₁/a</i>
	<i>4/mmm</i>	422	<i>P</i>	<i>P422, P4₂12, P4₁22, P4₁212, P4₂22, P4₂212, P4₃22, P4₃212</i>
			<i>I</i>	<i>I422, I4212</i>
		4mm	<i>P</i>	<i>P4mm, P4bm, P4₂cm, P4₂nm, P4cc, P4nc, P4₂mc, P4₂bc</i>
			<i>I</i>	<i>I4mm, I4cm, I4₁md, I4₁cd</i>
		-42m	<i>P</i>	<i>P-42m, P-42c, P-42₁m, P-42₁c</i>
			<i>I</i>	<i>I-42m, I-42d</i>
		-4m2	<i>P</i>	<i>P-4m2, P-4c2, P-4b2, P-4n2</i>
			<i>I</i>	<i>I-4m2, I-4c2</i>
		4/mmm	<i>P</i>	<i>P4/mmm, P4/mcc, P4/nbm, P4/nnc, P4/mbm, P4/mnc, P4/nmm, P4/ncc, P4₂/nmc, P4₂/mcm, P4₂/nbc, P4₂/nnm, P4₂/mbc, P4₂/mcm, P4₂/nmc, P4₂/ncm</i>
			<i>I</i>	<i>I4/mmm, I4/mcm, I4₁/amd, I4₁/acd</i>
Trigonal	-3	3	<i>P</i>	<i>P3, P3₁, P3₂</i>
			<i>R</i>	<i>R3</i>
		-3	<i>P</i>	<i>P-3</i>
			<i>R</i>	<i>R-3</i>
	-3m	312	<i>P</i>	<i>P312, P3₁12, P3₂12</i>
		321		<i>P321, P3₁21, P3₂21</i>

			<i>R</i>	<i>R32</i>
		<i>31m</i>	<i>P</i>	<i>P31m, P31c</i>
		<i>3m1</i>		<i>P3m1, P3c1</i>
			<i>R</i>	<i>R3m, R3c</i>
		<i>-31m</i>	<i>P</i>	<i>P-31m, P-31c</i>
		<i>-3m1</i>		<i>P-3m1, P-3c1</i>
		<i>R</i>	<i>R-3m, R-3c</i>	
Hexagonal	<i>6/m</i>	<i>6</i>	<i>P</i>	<i>P6, P6₁, P6₂, P6₃, P6₄, P6₅</i>
		<i>-6</i>		<i>P-6</i>
		<i>6/m</i>		<i>P6/m, P6₃/m</i>
	<i>6/mmm</i>	<i>622</i>		<i>P622, P6₁22, P6₂22, P6₃22, P6₄22, P6₅22</i>
		<i>6mm</i>		<i>P6mm, P6cc, P6₃cm, P6₃mc</i>
		<i>-6m2</i>		<i>P-6m2, P-6c2</i>
		<i>-62m</i>		<i>P-62m, P62c</i>
<i>6/mmm</i>	<i>P6/mmm, P6/mcc, P6₃/mcm, P6₃/mmc</i>			
Cubic	<i>m-3</i>	<i>23</i>	<i>P</i>	<i>P23, P2₁3</i>
			<i>F</i>	<i>F23</i>
			<i>I</i>	<i>I23, I2₁3</i>
		<i>m-3</i>	<i>P</i>	<i>Pm-3, Pn-3, Pa-3</i>
			<i>F</i>	<i>Fm-3, Fd-3</i>
			<i>I</i>	<i>Im-3, Ia-3</i>
	<i>m-3m</i>	<i>432</i>	<i>P</i>	<i>P432, P4₂32, P4₃32, P4₁32</i>
			<i>F</i>	<i>F432, F4₁32</i>
			<i>I</i>	<i>I432, I4₁32</i>
		<i>-43m</i>	<i>P</i>	<i>P-43m, P-43n</i>
<i>F</i>			<i>F-43m, F-43c</i>	

			<i>I</i>	<i>I-43m, I-43d</i>
		<i>m-3m</i>	<i>P</i>	<i>Pm-3m, Pn-3n, Pm-3n, Pn-3m</i>
			<i>F</i>	<i>Fm-3m, Fm-3m, Fd-3m, Fd-3c</i>
			<i>I</i>	<i>Im-3m, Ia-3d</i>

Appendix 2. Atomic and ionic radii

H 0,046 1 ⁻ 0,136 1 ⁺ 0,000	He 0,122	Li 0 0,156 1 ⁺ 0,068	Be 0 0,113 2 ⁺ 0,034	B 0 0,091 3 ⁺ (0,020)	C 0 0,077 4 ⁺ 0,020 4 ⁺ 0,015 4 ⁻ (0,260)
N 0 0,071 3 ⁺ 5 ⁺ 0,015 3 ⁻ 0,148	O 2 ⁻ 0,136	F 1 ⁻ 0,133	Ne 0,160	Na 0 0,189 1 ⁺ 0,098	Mg 0 0,160 2 ⁺ 0,074
Al 0 0,160 2 ⁺ 0,074	Si 0 0,134 4 ⁺ 0,039	P 0 0,013 3 ⁺ 5 ⁺ 0,035 3 ⁻ 0,186	S 2 ⁻ 0,182 6 ⁺ (0,029)	Cl 1 ⁻ 0,181 7 ⁺ (0,026)	Ar 0,192
K 0 0,236 1 ⁺ 0,133	Ca 0 0,197 2 ⁺ 0,104	Sc 0 0,164 3 ⁺ 0,083	Ti 0 0,146 2 ⁺ 0,078 3 ⁺ 0,069 4 ⁺ 0,064	V 0 0,134 2 ⁺ 0,072 3 ⁺ 0,067 4 ⁺ 0,061 5 ⁺ 0,040	Cr 2 ⁺ 0,073 3 ⁺ 0,062 4 ⁺ 0,032
Mn 2 ⁺ 0,067 3 ⁺ 0,053 4 ⁺ 0,053 7 ⁺ (0,046)	Fe 2 ⁺ 0,061 3 ⁺ 0,055	Co 2 ⁺ 0,065 3 ⁺ 0,061	Ni 2 ⁺ 0,069	Cu 1 ⁺ 0,077 2 ⁺ 0,073	Zn 2 ⁺ 0,074
Ga 3 ⁺ 0,062	Ge 2 ⁺ 0,073 4 ⁺ 0,053	As 3 ⁺ 0,058 5 ⁺ 0,056 3 ⁻ 0,191	Se 2 ⁻ 0,198 4 ⁺ 0,050 6 ⁺ 0,042	Br 1 ⁻ 0,196 7 ⁺ (0,039)	Rb 1 ⁺ 0,152
Sr 2 ⁺ 0,118	Y 3 ⁺ 0,090	Zr 4 ⁺ 0,072	Se 4 ⁺ 0,068 5 ⁺ 0,064	Mo 3 ⁺ 0,069 5 ⁺ 0,061 6 ⁺ 0,059	Ru 3 ⁺ 0,068 4 ⁺ 0,062
Rh 3 ⁺ 0,067 4 ⁺ 0,060	Pd 2 ⁺ 0,082 4 ⁺ 0,062	Ag 1 ⁺ 0,115	Cd 2 ⁺ 0,095	In 3 ⁺ 0,080	Sn 4 ⁺ 0,069
Sb 3 ⁺ 0,076 5 ⁺ 0,060 3 ⁻ 0,208	Te 1 ⁻ 0,221 4 ⁺ 0,097 6 ⁺ (0,056)	I 1 ⁻ 0,220 7 ⁺ (0,053)	Bi 3 ⁺ 0,103 5 ⁺ (0,076)	Cs 1 ⁺ 0,167	Ba 2 ⁺ 0,135
La 3 ⁺ 0,103 4 ⁺ 0,090	Hf 4 ⁺ 0,071	Ta 5 ⁺ (0,064)	W 4 ⁺ 0,066 6 ⁺ 0,060	Re 5 ⁺ 0,058 6 ⁺ 0,053 7 ⁺ 0,053	Os 4 ⁺ 0,063 6 ⁺ 0,055
Ir 4 ⁺ 0,063	Pt 2 ⁺ 0,080 4 ⁺ 0,063	Au 1 ⁺ 0,137	Hg 1 ⁺ 0,119 2 ⁺ 0,102	Tl 1 ⁺ 0,150 3 ⁺ 0,089	Pb 2 ⁺ 0,100 4 ⁺ 0,077
* in nm (according to M. B. Belov and G. B. Bokiy)					

Appendix 3. Important inorganic structures

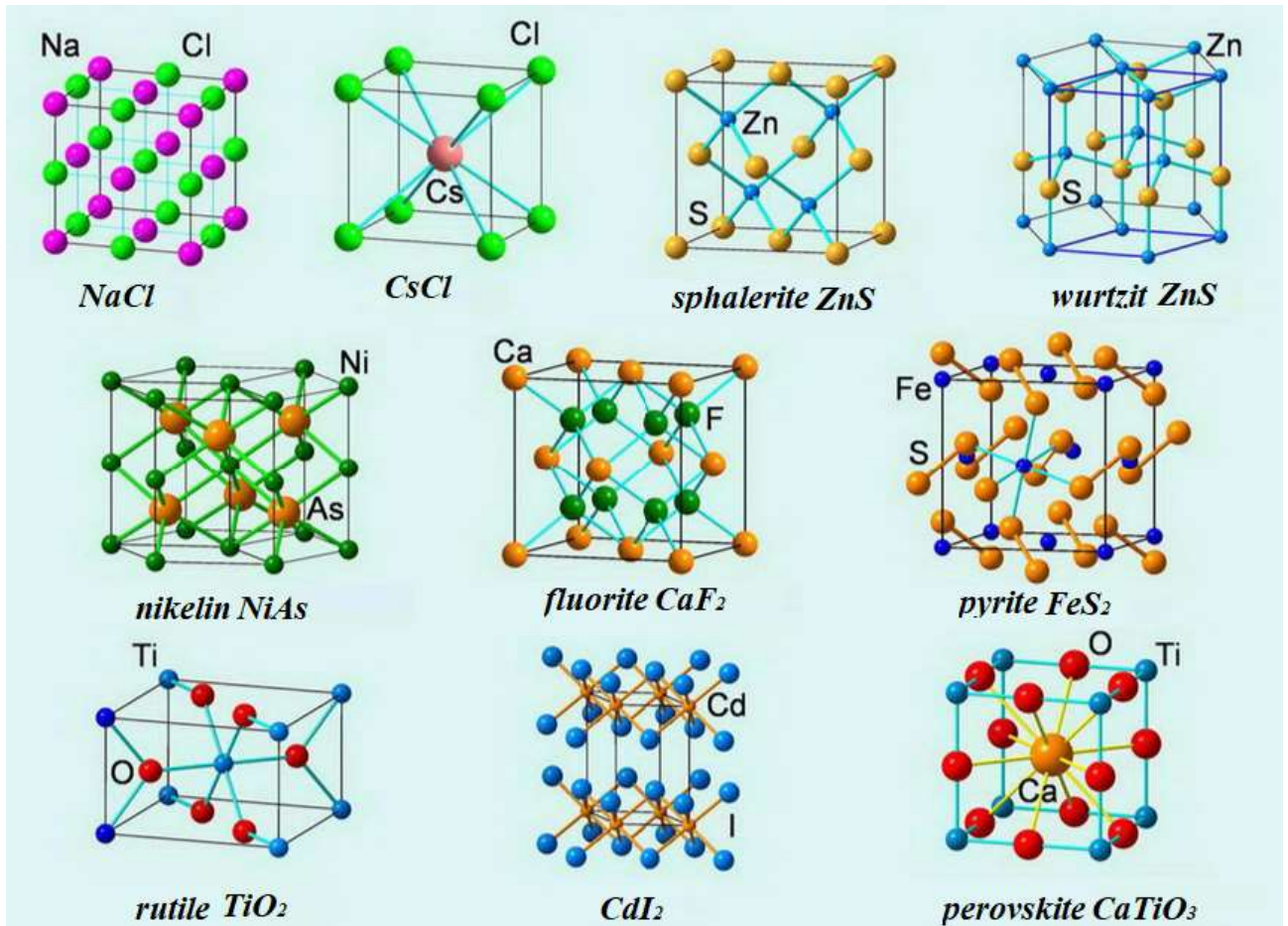
Structures of metals. 74 structures of metals are known. In the three structural types of Cu, Mg and α -Fe under normal conditions, respectively 16, 16 and 23 elements are crystallized, that is, more than 3/4 of all known metal structures.



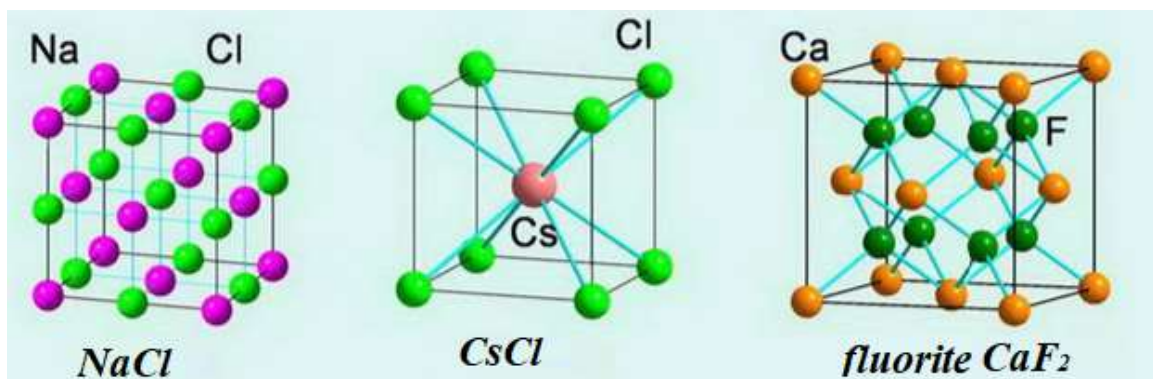
Structure	Metals
CCP	Al, Ca, Ni, Cu, Sr, Rh, Pd, Ag, Ce, Yb, Ir, Pt, Au, Pb, Ac, Th
HCP	Be, Mg, Sc, Ti, Co, Zn, Y, Zr, Tc, Ru, Cd, Pr, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Re, Os, Tl
BCC	Li, Na, K, V, Cr, Fe, Rb, Nb, Mo, Cs, Ba, Eu, Ta, W, Fr, Ra
Others	Mn, Ga, In, Sn, La, Nd, Pm, Sm, Hg, Bi, Po, Pa, U, Np, Pu, Am, Cm, Bk, Cf

The number of metal structures listed below are derived from three main types. Thus, the structure of In and α -Hg can be obtained by deforming the CCP along the axes of the fourth and third order, respectively. White tin and α -Ga have inorganic structures and low coordination numbers: CN = 6 for white tin and CN = 7 for α -Ga. And α -Mn, β -Mn and β -W have close structures with high CN = 12-16.

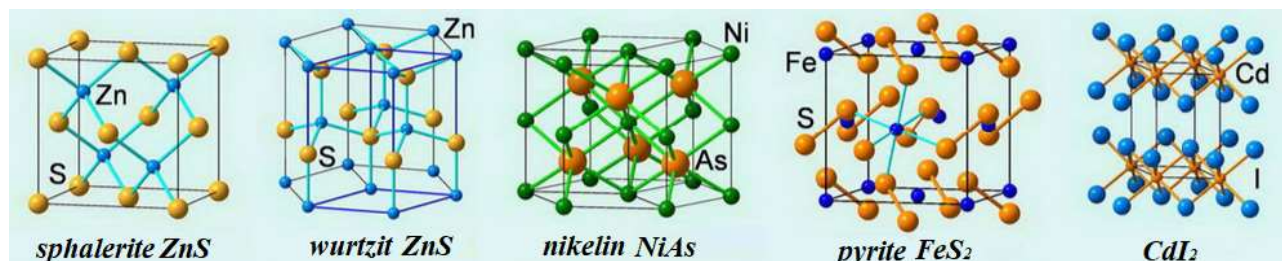
The most important structures of compounds



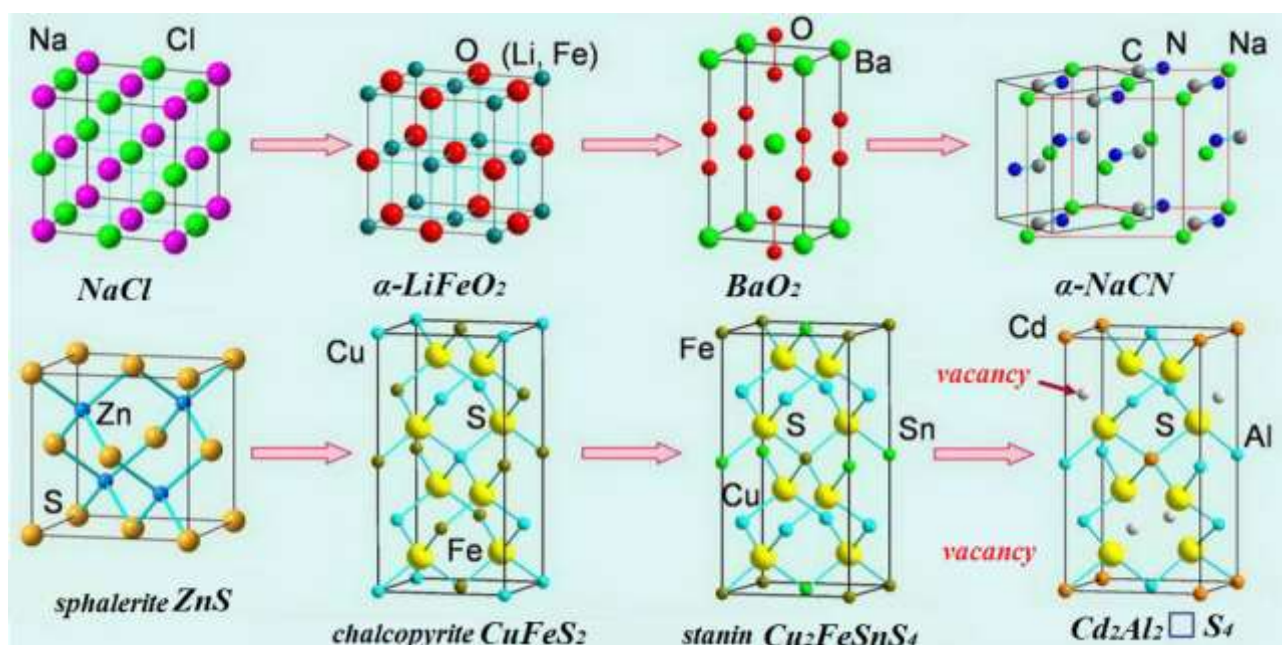
Classes of compounds and structures. Types of NaCl, CsCl and CaF₂, usually found in ionic compounds – halides and oxides of large enough and low-exchange capacity cations. The same structures are typical for some intermetallic compounds.



For covalent compounds (halides, chalcogenides, pnictides, etc.), structures of sphalerite, wurtzite, NiAs, FeS₂, and CdI₂ are characteristic. Among the oxides, the last three structures do not occur at all.

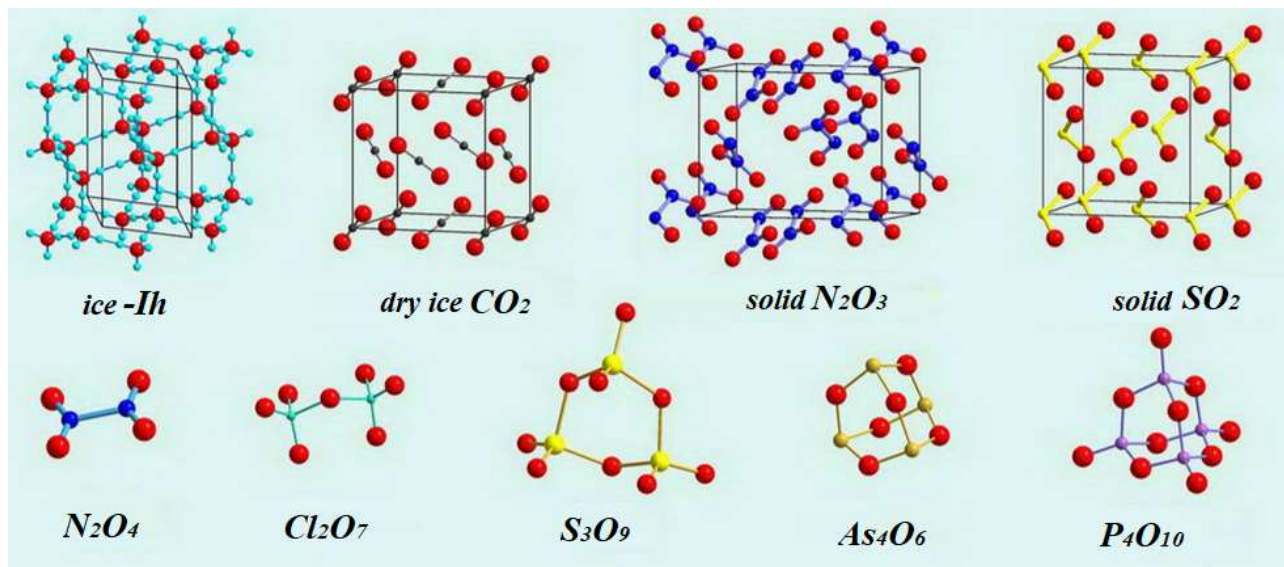


Derivative structures. The same patterns are kept in the transition to the derivative basic structures that arise as a result of isomorphous substitutions with the complication of the composition. Among the derivative structures, the record holders are structural types of NaCl, ZnS, CaF₂, CdI₂, CaTiO₃, whose motives can be found in hundreds and even thousands of structures.

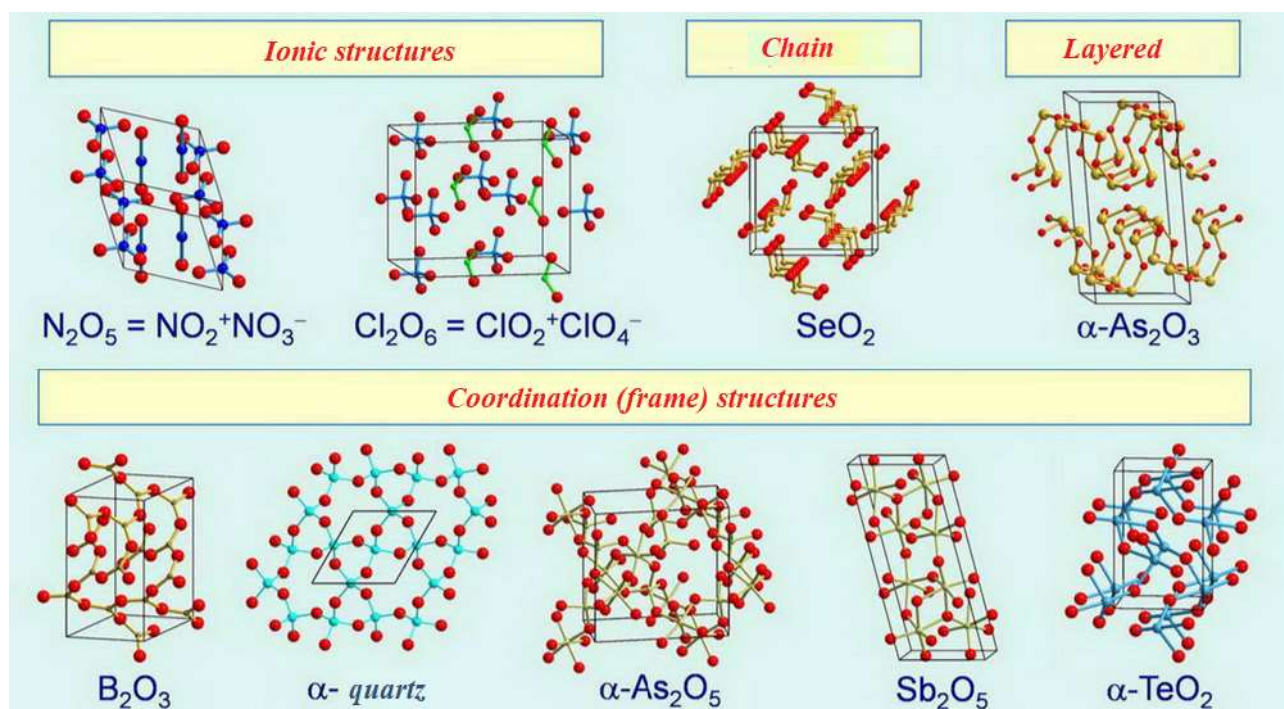


Molecular oxides of nonmetals. The structures of oxides are the most important for inorganic crystallochemistry. The structures of simple oxides of typical nonmetals are molecular. The special place takes ice with hydrogen bonds between H₂O

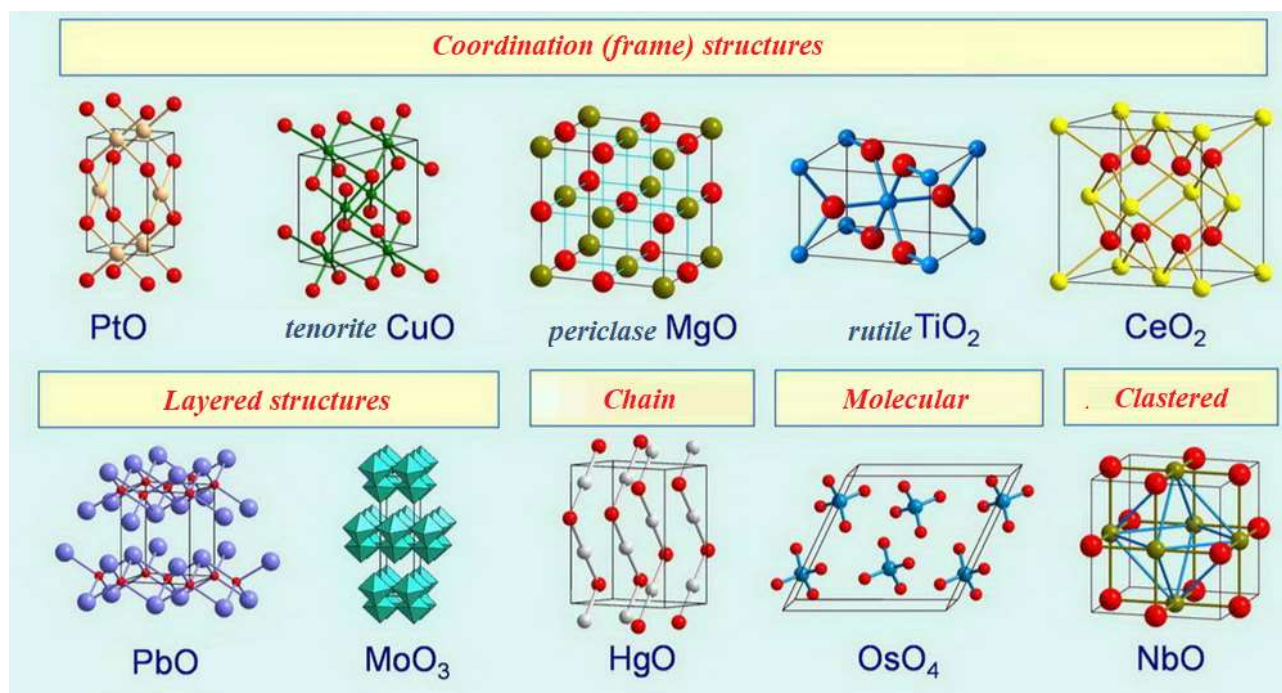
molecules. The connections of nonmetal-oxygen in molecules are covalent, and the CN does not exceed 4.



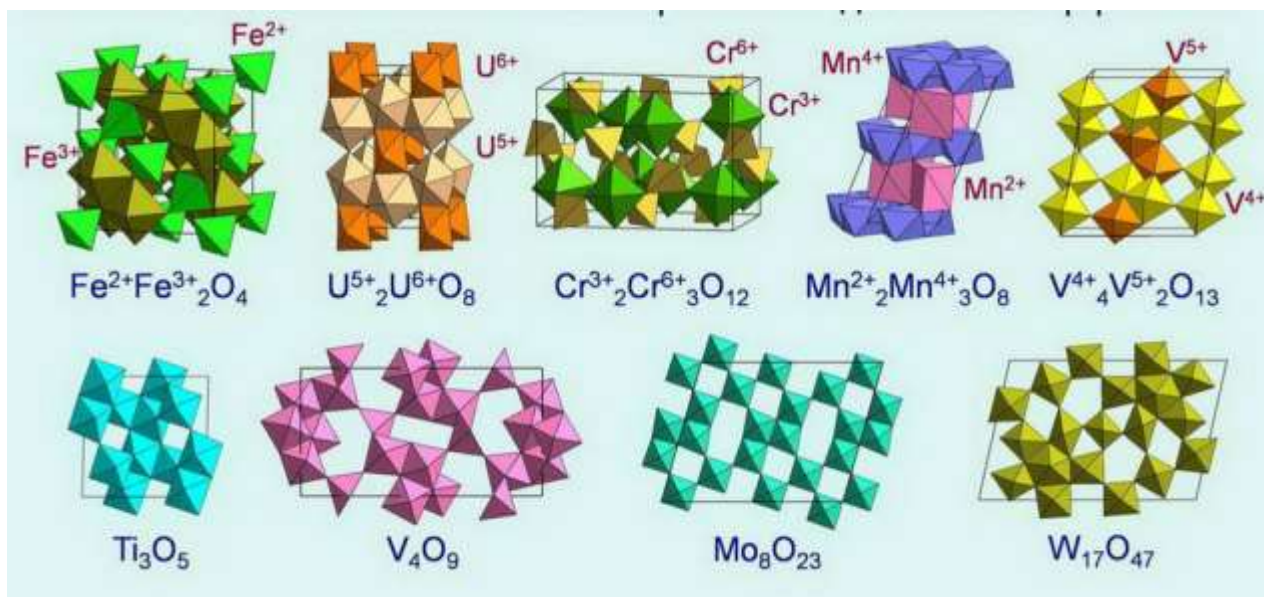
Non-molecular oxides of nonmetals. Unusual ionic structures found in N_2O_5 and Cl_2O_6 . Oxides B, Si, Ge, As, Sb, Se and Te have polimartic nature. In non-molecular simple oxides of nonmetals, CN = 3-6 (most often no more than 4).



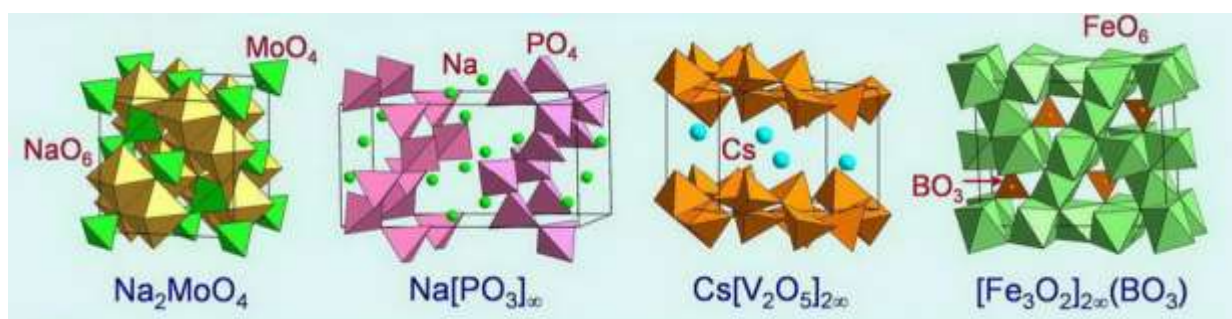
Structures of simple metal oxides. There are coordinative (skeleton), layered, chain, molecular and cluster structures of simple metal oxides, metal cations usually have the CN = 4–8.



Mixed valence oxides of metals. Among the binary metal oxides there are mixed valence phases: F₃O₄, U₃O₈, U₄O₉, Cr₅O₁₂, Mn₅O₈, V₆O₁₃, Pr₆O₁₁, Tb₇O₁₂. Various charge cations can be ordered or located in some crystallographic positions, as in the crystallographic shift phases and other Ti, V, Mo, and W oxides. Many of the oxide of transition metals are diverted from stoichiometry and have polymorphism.

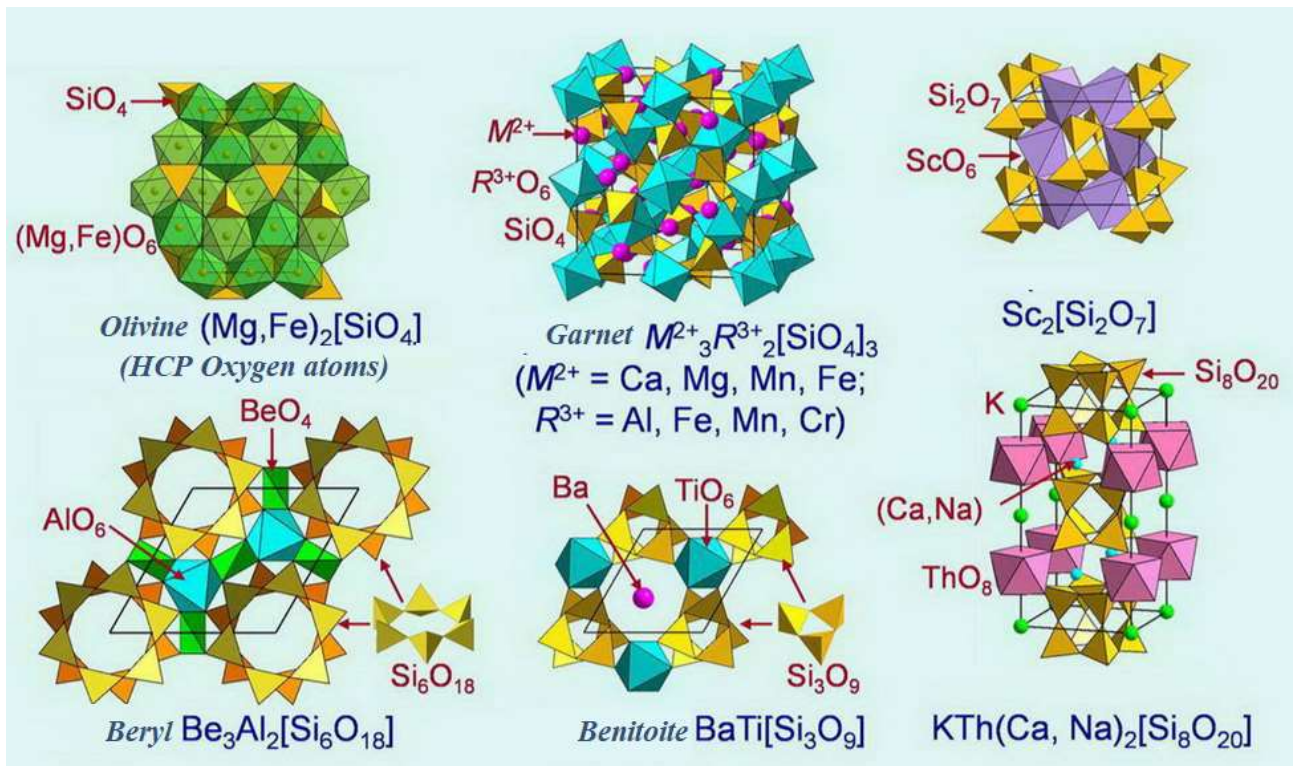


Multicomponent oxides. The concept of "oxo-acid salts" and "complex oxides" are also generalized to oxides with the large number of components (that is, they contain atoms of three or more elements in addition to oxygen).



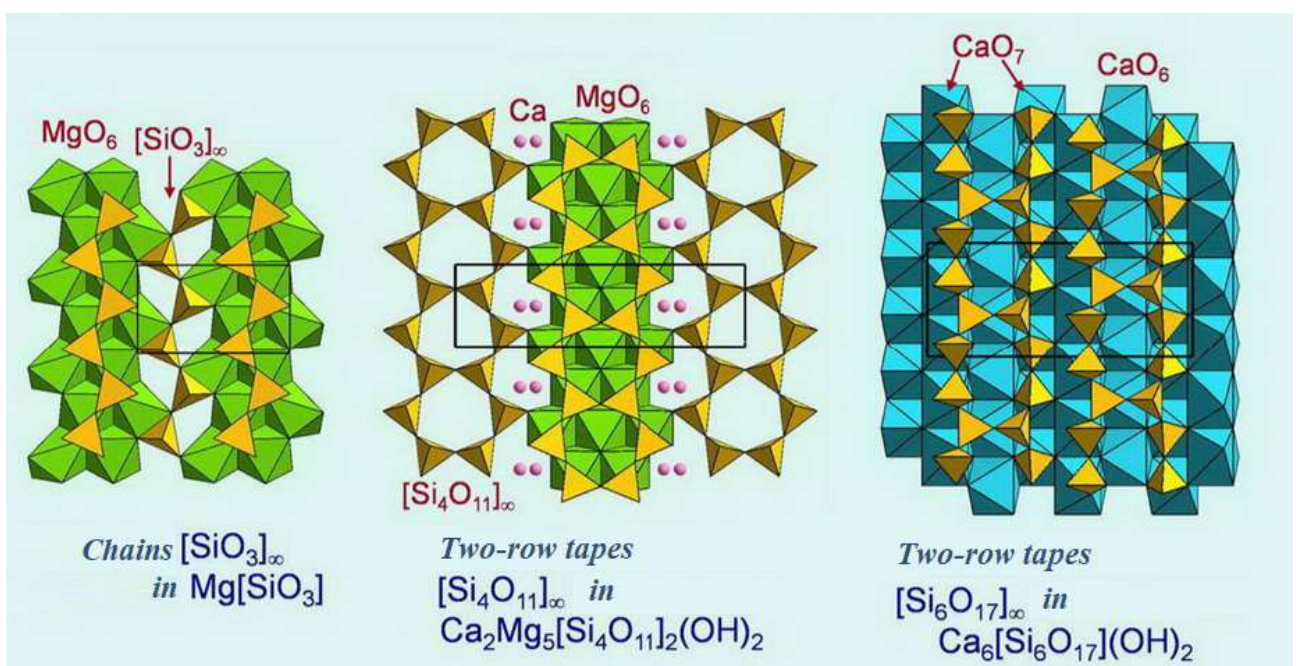
Between salts of oxo-acids and complex oxides there are no strict limits: a number of oxo-salts has the polymer structure, as well as complex oxides, and some of the structures of complex oxides are similar to oxo-salts (for example, the typical Na_2MoO_4 salt has the spinel structure MgAl_2O_4). For many complex oxides, old chemical names traditionally used, similar to salts: titanates, niobates, ruthenates and even "cuprates", what is not justified crystallochemically.

Island silicates. Island silicates contain separate tetrahedra SiO_4^{4-} (orthosilicates), double tetrahedra $\text{Si}_2\text{O}_7^{6-}$ (diorthosilicates), cyclic tetrahedral groups (ring silicates) and more complex groups.

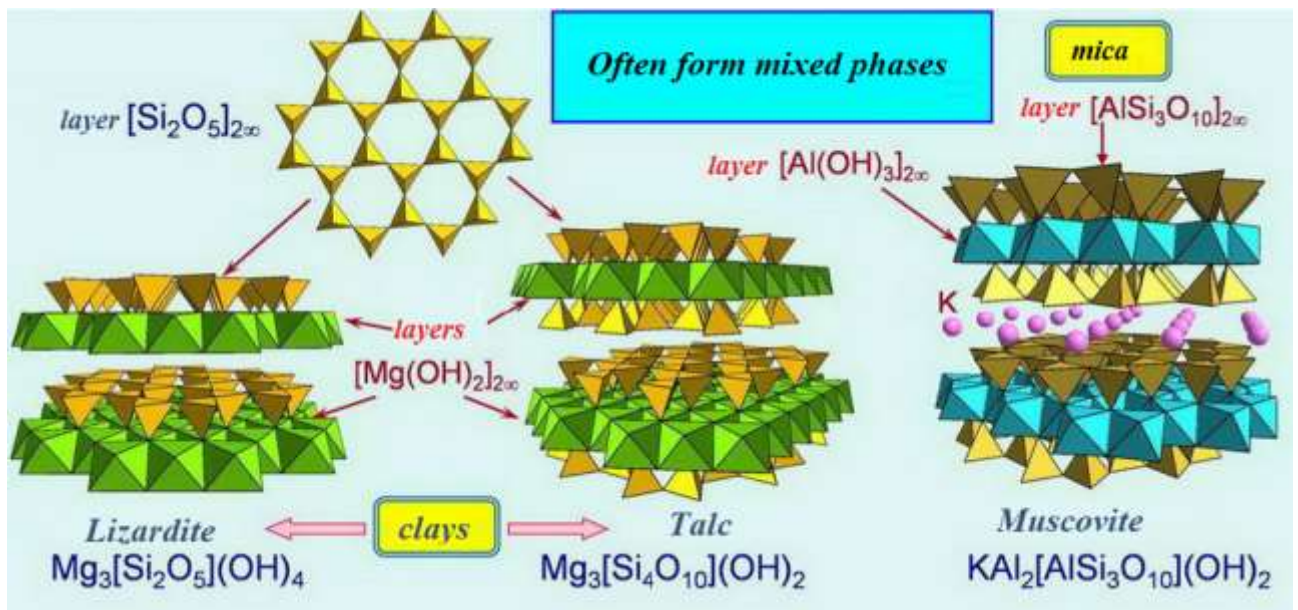


Chain silicates. Chain silicates contain single chains $[\text{SiO}_3]_\infty$ or strips of such chains, which consist of two, three and more rows.

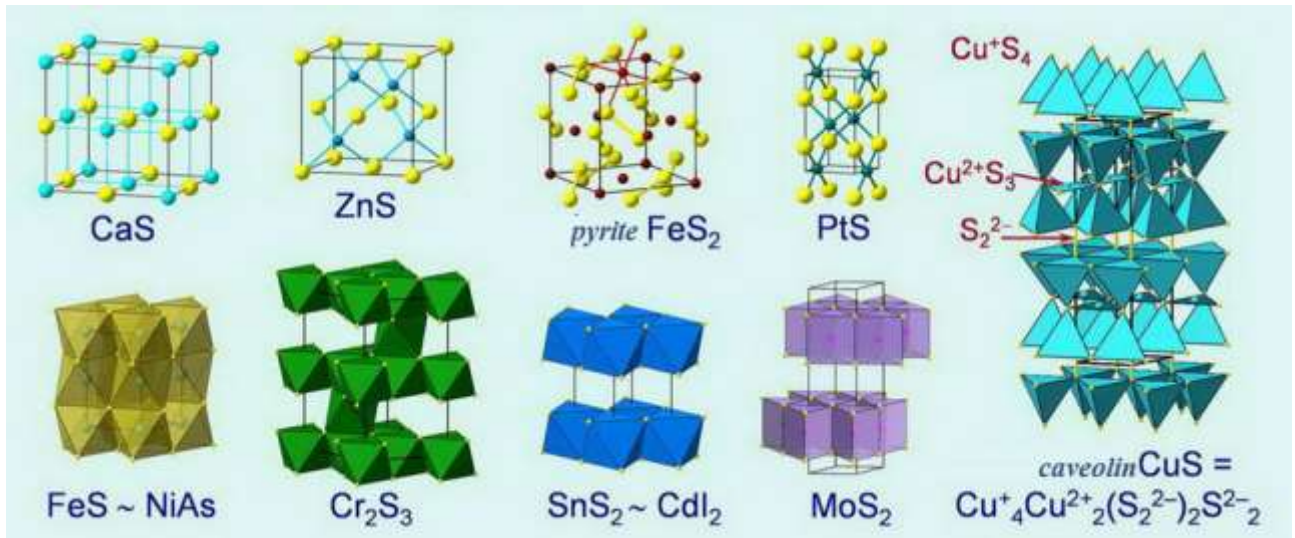
The most common are silicates with single chains – pyroxenes $(\text{Mg,Ca,Fe,Mn,Al,Na,Li})[\text{SiO}_3]$ and double-row tapes – amphiboles $(\text{Ca,Mg,Fe})_7[\text{Si}_4\text{O}_{12}]_2(\text{OH})_2$.



Layered silicates. Layered silicates and aluminosilicates contain salts $[\text{Si}_2\text{O}_5]_{2\infty}$ and $[(\text{Si},\text{Al})_2\text{O}_5]_{2\infty}$, which bind to layers of polyhedrons Mg^{2+} , Al^{3+} , Fe^{3+} , etc. in two- and three-level packages. In nature, usually, there are hexagonal layers that are neutral and connected by Van der Waals forces in rotten minerals, and in mica, the negative charge of the layers is compensated by interlayer cations.



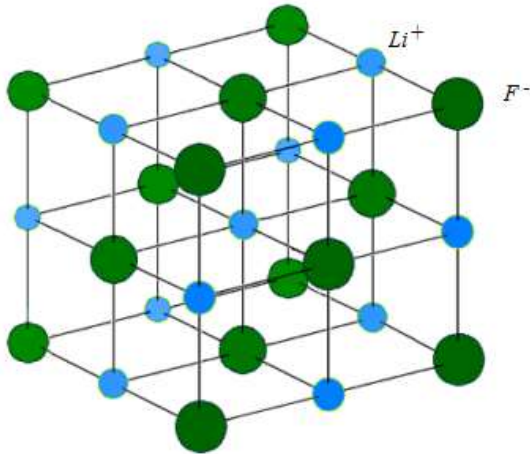
Simple sulfides of metals. Only the alkali, alkaline earth metal, rare earth elements and actinide sulphides have ionic nature of the bonds, which, as a rule, repeat the structure of oxides.



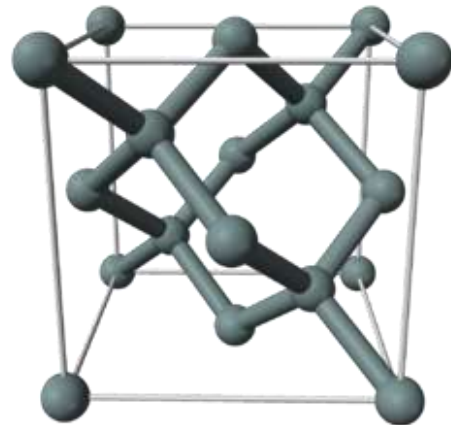
In the sulfides of d- and p-metals, the covalent bond of metal–sulfur is more pronounced. The structure of the sulfides of these metals usually differs from the structures of oxides, and types of NiAs, CdI_2 , MoS_2 among oxides, almost, do not occur. S–S bonds are characteristic of FeS_2 (pyrite and marcasite) and CuS.

Appendix 4. The values of the internuclear distances in metals

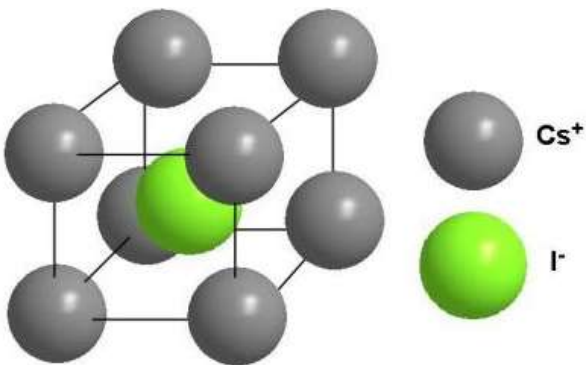
Metal	Formula	Internuclear distance, Å
Silver	Ag	2,889
Gold	Au	2,884
Barium	Ba	4,347
Beryllium	Be	2,226
Calcium	Ca	3,947
Cadmium	Cd	2,979
Cerium	Ce	3,650
Cobalt	Co	2,506
Chromium	Cr	2,498
Copper	Cu	2,556
Iron	Fe	2,482
Potassium	K	4,544
Lithium	Li	3,039
Magnesium	Mg	3,197
Sodium	Na	3,716
Niobium	Nb	2,858
Nickel	Ni	2,492
Osmium	Os	2,675
Lead	Pb	3,500
Palladium	Pd	2,751
Platinum	Pt	2,775
Rhenium	Re	2,741
Rhodium	Rh	2,690
Ruthenium	Ru	2,650
Strontium	Sr	4,303
Tantalum	Ta	2,860
Titanium	Ti	2,896
Vanadium	V	2,622
Tungsten	W	2,741
Zinc	Zn	2,665
Zirconium	Zr	3,179

Appendix 5. Elementary cells of crystalline structures

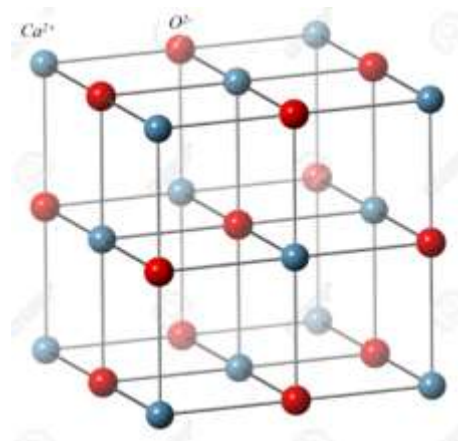
Structure LiF (LiCl)



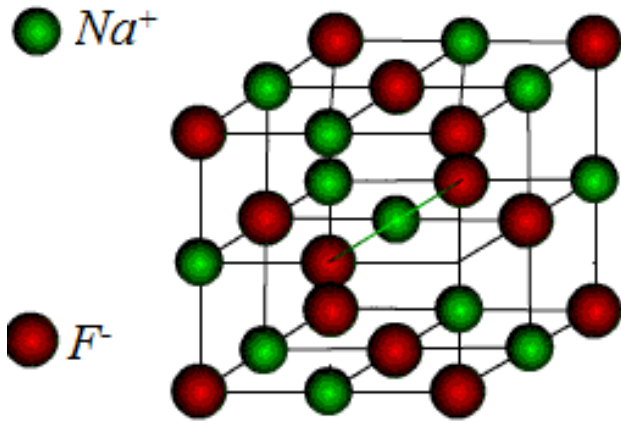
Structure of germanium



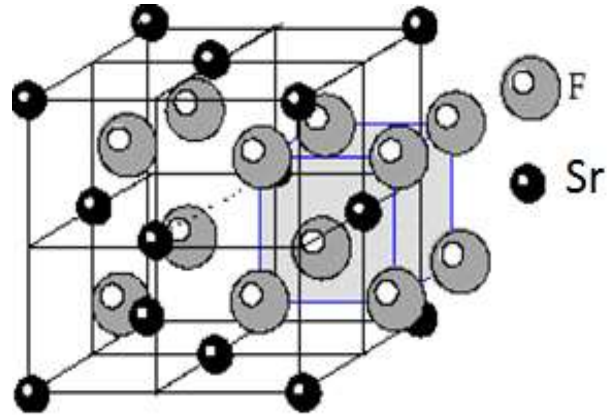
Structure CsI (CsBr, CsF)



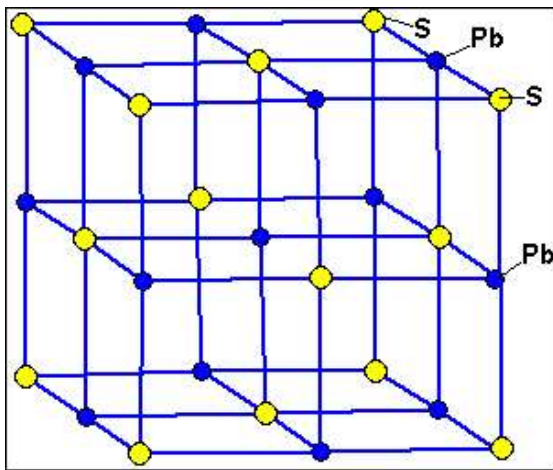
Structure CaO (MgO)



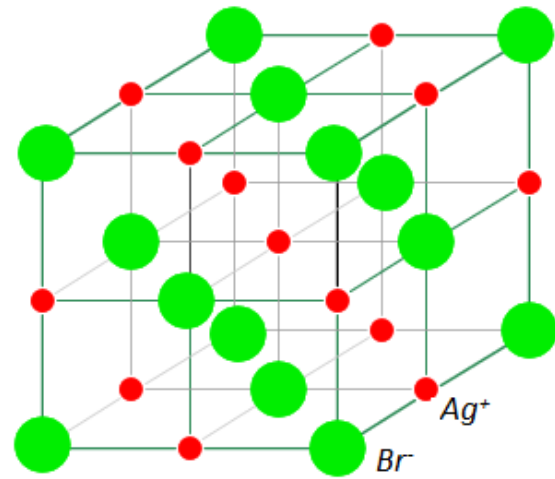
Structure NaF



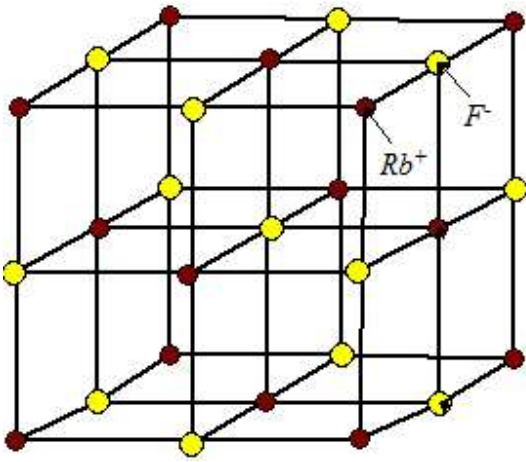
Structure SrF_2



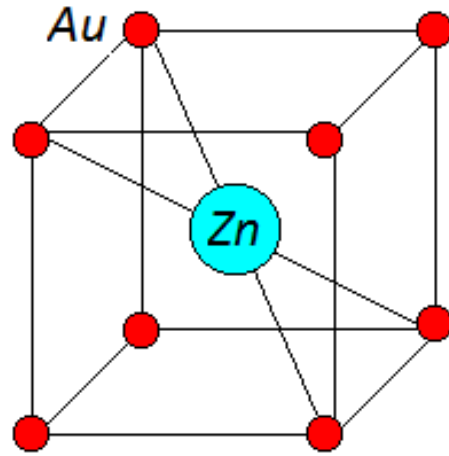
Structure PbS ($PbSe$, $PbTe$)



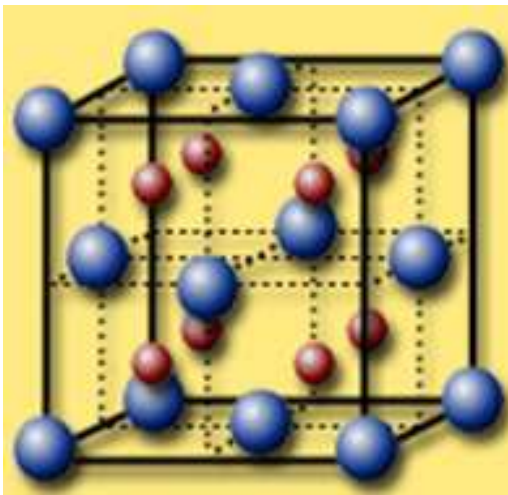
Structure $AgBr$ (AgF , $AgCl$)



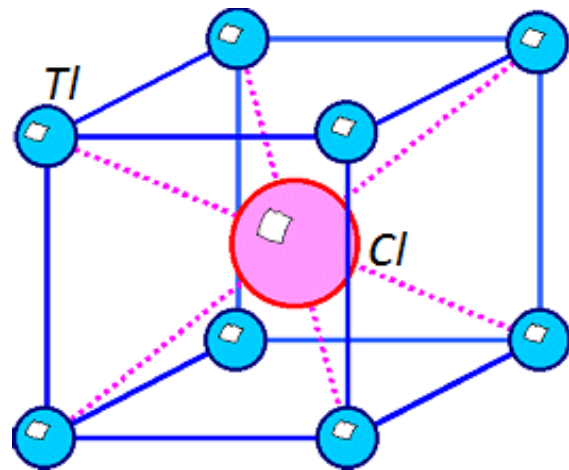
Structure RbF (RbCl)



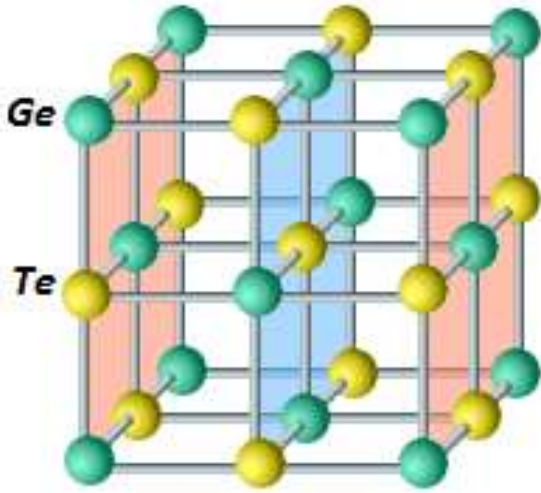
Structure AuZn (CuZn, AgZn)



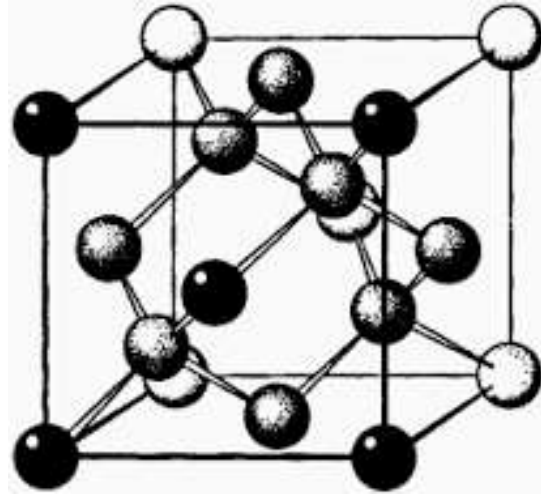
Structure CuF₂ (ZrF₂)



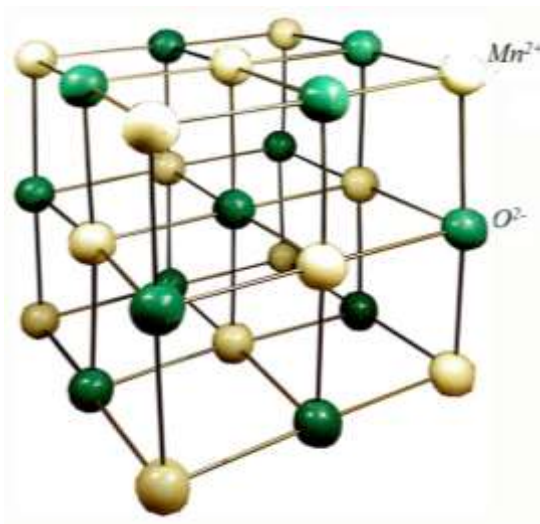
Structure TlCl (TlBr)



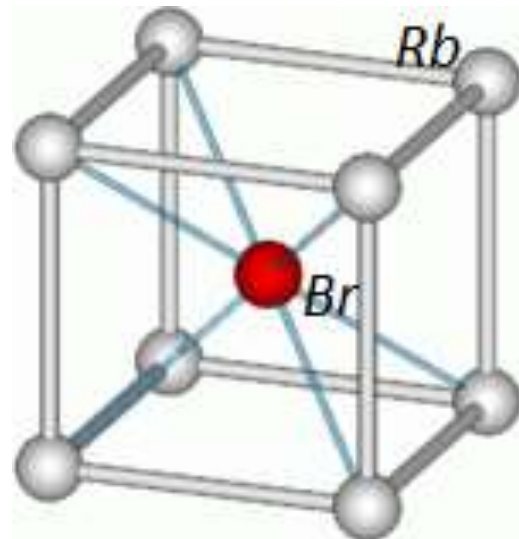
Structure GeTe (SnTe)



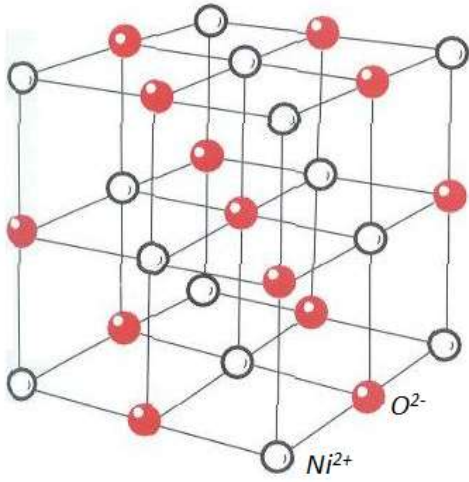
Structure of silicon



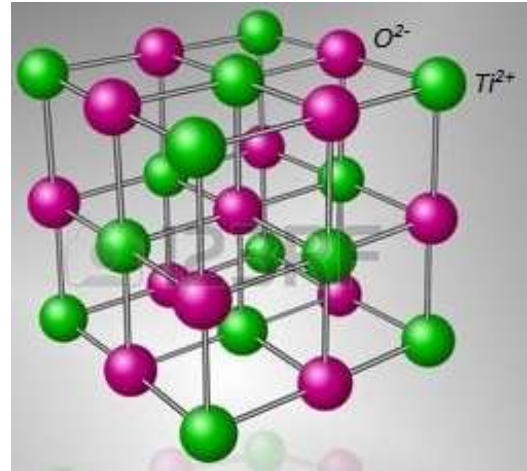
Structure MnO



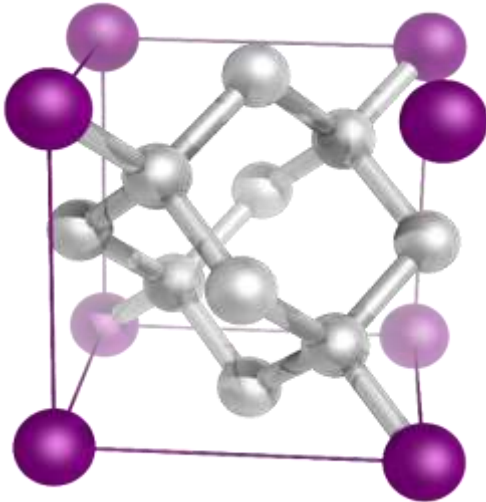
Structure RbBr (RbI)



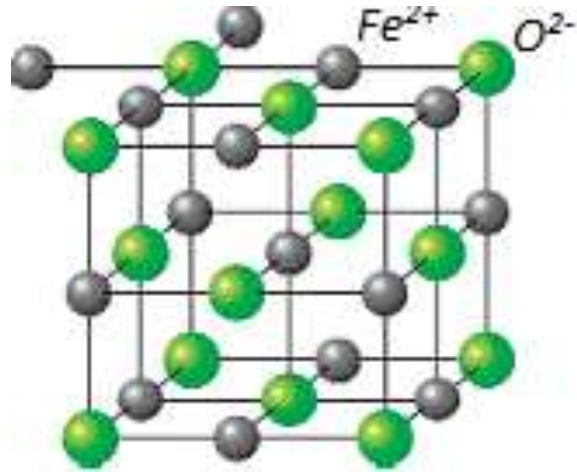
Structure NiO



Structure TiO



Structure of grey tin



Structure FeO