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" C R Y S T A L L O C H E M I S T R Y "

from science

TRAINING AND METODOLOGY COMPLEX

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LECTURE 1

An introduction to crystallochemistry and the history of its development as a science.

Plan :
1. Introduction. Crystals and crystallography
2. The science of crystallochemistry and its tasks
3. Development of crystallochemistry as a science.

Crystallochemistry, crystal chemistry is a science that studies how the structure and properties of crystals depend on their chemical composition. The systematic study of crystal structure began in 1912 after the discovery of the phenomenon of X-ray diffraction in a crystal lattice. The basis for determining the structure of matter is the theory of the space group of symmetry developed by ESFyodorov.

Crystallochemistry is inextricably linked with crystallography. Crystallography is the science of crystals, which first of all arises as a structural, initial part of the science of mineralogy. Before he came to the field of science, mankind dreamed of using natural resources, and in order to achieve this dream, while searching for useful minerals or traveling around the country for other purposes, he found crystalline bodies, limited by flat sides, remarkable for both transparency and clear color. It certainly gets people interested: makes them think about what they are, how they came from, and where they came from. At first, it was difficult to find an answer to this question on a scientific basis. Some religious beliefs did not allow it. That's why some stones were given divine names such as "Devil's Miracle", "Power Stone". Firstly, such unnatural explanations could not satisfy people for a long time, and secondly, the number of natural crystals found has also increased. This led to the emergence of the science of crystallography.

The science of crystals begins with the study of geometric shapes and physical properties of crystals (minerals). Later, with the birth of chemical concepts, their chemical composition attracts people's attention.

A crystal is a chemical substance. Studying the chemical composition of crystals, their formation, growth, dissolution, the organic connection between the geometrical shape of crystals and their chemical composition, and obtaining artificial crystals are a number of issues that belong to the sciences of chemistry and physics. This branch of crystallography is called crystallochemistry, crystal chemistry, or chemical crystallography.

Thus, hundreds of names of artificial minerals used in various fields of science and technology, including precious stones that decorate jewelry with their shimmering color, are also crystals.

The tasks of the science of crystallography include the artificial extraction of mineral crystals, which are extremely necessary for industry and science, but are not found in sufficient quantities in nature, and the research of theoretical issues necessary to solve this problem. In this regard, "it is known that crystallography takes place in the center of the triangle formed by physico-chemical mineralogy. Until recently, for historical reasons, it stood closer to mineralogy than to kamma. In recent years, it has become closer to physics. However, it should be recognized that the more crystallography develops as an independent science and approaches physics and chemistry, the more the science of mineralogy is interested in the achievements of physics and chemistry. closeness will continue to develop." Life confirms how true this prediction of the famous Russian crystallographer VNBelov (1891-1984) is.

Besides these, metals and their alloys are also crystals. All their properties are related to the structure of the crystal lattice and obey the laws of crystallography. Therefore, metallurgists also use the achievements of crystallography in their practical work. Also, as crystals are widely used in radio engineering, electronic computing and other fields in various branches of technology, many technical sciences dealing with these issues are also interested in the achievements of crystallography. Therefore, the science of crystallography has been developing in the directions of fields with unprecedented big steps in recent years. Therefore, studying the science of crystallography is extremely necessary not only for geologists, prospectors and miners, but also for chemists, physicists, metallurgists, etc.

The emergence of the first theories about the formation and growth of crystals was the main reason for the further development of the science of crystallography, which brought it closer to the sciences of thermodynamics and physical chemistry. In turn, this will be a practical factor for improving the methods of obtaining artificial crystals. Artificial crystals continue to penetrate more and more into physical research and various branches of technology. Among them, today it is increasingly used in jewelry, and especially in optical and acoustic devices in the fields of radio electronics, semiconductors and quantum electronics. Now , scientific research is being carried out more intensively in the fields of achieving important physical and technical solutions, artificially obtaining crystals with the ability to remember in EHM and developing new methods for it, studying the structure of crystals .

In general, the main problem of great importance in the research of crystals is the in-depth study of the existing general law between their structure, formation and properties. These three properties of crystals are inseparable and a problem to be solved as a whole, and are of great importance in the study of natural crystals

(minerals). As a result of the study of such a law, it is possible to give accurate information about its chemical composition or appearance, depending on the crystal structure and shape of the mineral; as a result of accurate imitation of the geometrical shape of the crystal and the conditions of occurrence and conditions, and based on the mixture of chemical elements contained in this crystal, it is possible to predict what other deposits can be found in the nearby environment. We will give examples to support this point in later chapters of the book (after having some knowledge about crystals). Also, depending on the chemical composition and structure of the crystals, it is possible to predict their physical and mechanical properties or to estimate the possibilities of obtaining crystals with predetermined necessary properties.

The word crystallography in the sense of "definition of crystals" was first used in 1723 by the Swiss scientist MN Kapeller, and long before that, in 1698, this science was called "Crystalology" by I. Gottinger.

The birth of the science of crystallography and its development are directly related to the sciences of geology, first of all, to the science of mineralogy. Almost all minerals are crystals, and some of them are known for their geometric shapes, so that the history of the development of the science of mineralogy cannot be imagined in isolation from the science of crystallography. The science of crystallography determines not only the science of mineralogy, but also the future development of a number of sciences that have made a sharp turn in the process of technical development. Let's look at its history in order to explain its essence and reasons.

Before the science of crystals came into the world as a science, during the search for mineral deposits and their use, a number of laws specific to crystals were discovered, and they were applied to the study of minerals at that time. For example, in the 1000s of the Middle Ages, Abu Rayhan Beruni showed that it was possible to distinguish precious minerals and some rare rocks based on the method of determining their specific gravity. For this purpose, he used a device for measuring specific gravity that he invented. Alloma is the first and weighs 1 gr. not the weight of 1 cubic cm of water equal to 19.2 gr. he took the incoming gold as a unit and calculated the relative weight of the minerals known at that time on this basis. In this, the scientist also took into account the crystal structures of stones. Abu Ali ibn Sina also mentions the properties of these crystals in the description of medicinal minerals and stones known to him and recommended for use in medicine. As in the long past, in our country, the properties of crystals, such as transparent light transmission of crystals, durability of mineral fibers, the possibility of using rare stones in jewelry, the possibility of extracting pure metal from minerals and making articles from it were obvious. In addition, they became aware of the coincidences that sometimes occur during the formation and growth of mineral-rock bodies.

Beruni commented on the geometric shape of diamond crystals known in those times and recognized in primary sources. He emphasizes that they have a distinct geometric shape, i.e. an octahedral shape similar to a sharp-pointed dipyramid with triangular sides, but not to be fooled by fake "diamonds" made of other minerals, such as rock crystals. At the same time, the appearance, characteristics, and quality of crystals of precious stones suggest that their value is related to the past, "history", and environment of the mine where it appeared. Also, Abu Ali ibn Sina evaluates the quality and properties of mineral crystals used in medicine depending on the mine where they are found, which mine is good and which one is bad. Therefore, it indicates that the composition and properties of mineral crystals are related to the environment of the deposit-forming process.

In the Middle Ages, in Eastern countries, including Central Asia, the development of the science of minerals, rocks and inorganic substances reached somewhat higher levels on a global scale. In order for science to develop to such an extent, the rich culture in those countries was suitable for it. The scientists who were born in such an environment and raised science to the highest heights are the Iranian chemist al-Jabir (721-815); Arab philosopher, mathematician al-Kindi (800-879) and Iranian chemist-physician Ar-Razi (864-925); The masterpieces created by scholars such as the Azerbaijani Muhammad Nasritdin (1201-1274), the Arabian naturalist Zakhariya Qazvini shine like guiding stars in the development of world thought. Unfortunately, the scientific heritage left by these scientists has not been fully preserved, the preserved ones have not been studied, and are not known to the general public. In this regard, according to AS Povarennykh, a Ukrainian scientist who studied mining in Tashkent (1965), "the works collected in the Arab East, Central Asia, especially in the field of mineral description, were written at a higher level than the scientific heritage left by the authors of ancient China and the ancient world." This indicates the breadth of work that has been done in the field of historical studies as well.

From 1669, scientific theories about crystallography began to appear in the world of science. In the same year, the Danish doctor Nils Stensen (1638-1686) as a result of his work on the measurement of quartz crystals, concluded that the angle between the corresponding sides of the crystals is constant regardless of their size and appearance.

Hundreds of years later, the great Russian scientist MV Lomonosov rediscovered the law of constancy of angles thanks to his research on saltpeter crystals. From that moment on, the conclusions of Stensen-Lomonosov about the angular constancy were clearly formed as the first fundamental law of crystallography. At the same time, O. Bartholin discovered the birefringence property of iceland spar crystals, and the existing connection plane of this crystal was

determined. This innovation also serves as a basis for studying the optical properties of crystals. Later, the Dutch scientist H. Huygens studied the properties of birefringence of crystals in detail and assumed that these properties are related to the internal legal structure of crystals. Finally, he came to the idea that a single crystal is made up of different particles with a unique shape.

Russian chemist MV Lomonosov (1711-1765) created the corpuscular theory of the structure of matter, the particles that make up matter were imagined as spherical. Based on this theory, as we said above, the law of constancy of the angle between corresponding sides of crystals was scientifically justified. It is shown that during the growth of crystals, the corpuscles are stacked one on top of the other, forming the crystal sides, and the crystal sides grow parallel to the initial state. Lomonosov also studied the shape and physical properties of crystals. The scientist paid special attention to the influence of existing conditions and environment on the growth rate of crystals.

| **N. Steno** | **M. Lomonosov** | **R. Gayui** | **Rome de Lille** | **E. Fyodorov** |

Figure 1.1. Scientists who contributed to the development of crystallography

The French mineralogist Jean-Baptiste Louis Rome de Lille (1736-1790) also rediscovered the law of constancy of angles about 20 years after MV Lomonosov's discovery, that is, without knowing about the work of Stensen and Lomonosov, and published this law in 1772 under the name "Crystallography or crystals". "Description of the geometric shapes of various bodies characteristic of the world of minerals".

RJ Gayoui (1743-1822) discovered the second fundamental law of crystallography in 1784, the proportionality of crystal sizes, or the law of whole numbers. The reason for this discovery was the fact that calcite crystals fracture in certain directions, forming flat surfaces (according to the existing perfectly aligned planes). Gayui assumed that the molecules that make up crystals are always in the form of parallelepipeds. Because at that time, the theory of the internal legal structure of crystals (described by the spatial grid known to us today) had not yet been discovered.

The discovery of the third fundamental law of crystallography by the German mineralogist and crystallographer XS Weiss (1780-1856) also dates back to this period. According to this law, the relationship between the sides and edges of the crystal is given. In 1818, the expression of the relative sizes of each side and edge of crystals by three integers was first applied to kayot.

In the history of the subsequent great development of the science of crystallography, the services of mining geological engineers also deserve special attention. A large number of crystallographers and mineralogists, under the leadership of NIKoksharov and PV Yeremeyev, graduated from the St. Petersburg Mining Institute. One of their followers was the famous crystallographer E.S. Federov. After that, AKBoldirev, VVDolivo-Dobrovolsky, VIMikheyev and their students made discoveries that have not lost their significance even today. By the first half of the 19th century, the measurement of the angles between the sides of natural crystal-minerals became popular as one of the main methods of detailed examination of minerals.

In 1899, Miller applied analytical geometry in crystallography and created proportional numbers to represent crystal faces using special symbols (indices).

In 1830, the German professor mineralogist IFGessel (1796-1872) came to the conclusion that the forms of symmetry (classes) of crystal forms are limited and identified them as 32 forms. But the essence of this innovation was not noticed by contemporaries due to the complexity of the method of application. About 40 years later, in 1867, the Russian scientist, Academician AV Gadolin (1828-1892), who was not aware of this, repeated this discovery and came to an almost similar conclusion, and only then did this discovery take its proper place in the science of crystallography.

In the second half of the 19th century , the study of artificial crystals began, and the laws of crystal chemistry (phenomena of isomorphism, polymorphism) were discovered. Optical properties of crystals began to be investigated in detail. By the end of the 19th century, geometric theories of the internal structure of crystals were developed.

The great Russian crystallographer E.S. Fedorov became world-famous for his achievements in this field: the book "Symmetria pravilnix sistem figur", the "Fedorov table" of the microscope he created, the "double circle goniometer". Theories about the discovered crystal structure, the "Fedorov table", which is important for checking the optical (refraction, transmission) properties of crystals, and the double-circle goniometer, an instrument for measuring the angles between the sides of a crystal, are used in all laboratories working in this field, all over the world, including university departments. is also widely used.

Wolff (1863-1935) in the former USSR, father and son VGBregg and VLBregg in England developed an equation (formula) that can be used to determine the distance between the flat lattices of the crystal spatial lattice, as well as the size of the structural units (ion and atomic radius). Wolff was a crystallographer-physicist who started work in the field of X-ray crystal structure analysis in Russia and created a special grid for calculating crystals graphically.

Thus, the second great Russian scientist Wolf spread his name to the whole world. But the great theoretical discoveries of most Russian crystallographic scientists were very far from practical work and separated from the national economy at that time. On the other hand, scientists working in the field of crystallography were relatively few. Nevertheless, special attention was paid to the development of science and technology and, in particular, to the development of the national economy. Along with concrete sciences such as physics and mathematics, which are the basis of science and technology development, a wide path has been opened for the development of crystallography. However, in the early years, our science developed very slowly due to the lack of crystallographic specialists and the lack of fully equipped scientific institutions capable of working in this field. Another reason was that almost all of the crystallographic scientists working at that time were concentrated in Leningrad, now Saint-Petersburg, and partly in the Moscow region (in Leningrad, only in the Department of Mining and Crystallography under the university and in the single crystallographic laboratory of AVShubnikov, established in 1925 under the mineralogical museum of the former USSR Academy of Sciences).

During this period, under the leadership of AKBoldirev (1883-1946), VVDolivo-Dobrovolsky, II Shafranovsky and other crystallographers worked on the development of scientific ideas inherited by E.S. Fedorov at the St. Petersburg Mining Institute. The development of geometrical shapes of crystals and models of crystal structures was started at this university under the leadership of Boldirev, which became important in improving the study and teaching of the science of crystallography . At Leningrad University, Fedorov's student Ansheles (1885-1957) conducted scientific work together with Tatarsky and Frank Kamenesky.

The famous scientist Yu. Under the leadership of AV Shubnikov, a student and follower of V. Wolf, research was conducted on piezoquartz crystals and the first world-wide artificial piezoquartz production industry was founded in the former Soviet Union. This was the first connection between the science of crystallography and the development of technology. He was the first to create a special laboratory where single crystals could be grown, which are considered very necessary for technical and physical devices, and carefully studied the conditions of growth of these crystals and their physical properties obeying the law of relative equality (symmetry). He developed many scientific theories about the relative equilarity of

crystals. In particular, considering the crystals themselves as a crystallized medium, he conducted research in the field of relativity of the continuum limited geometric shapes, in which the discontinuity is opposed to the infinite geometric shape, and finally he published the book "Symmetry and Antisymmetry of Finite Shapes". These 1651 groups of relative equality (symmetry) and antisymmetry (antisymmetry) of Shubnikov also include 230 space groups of Fedorov.

AV Shubnikov actively participates in the work of the organization committee of the world society of crystallographers and the organ of this organization "Asta Crytallographica" magazine (according to Shubnikov's proposal, the magazine published internationally was given this name).

NVBelov applied AVShubnikov's theory of antisymmetry to the study of crystal structure and showed that it is possible to develop this theory by studying "multicolored" symmetry groups.

After AVShubnikov, NVBelov took an active part in the organization of the international society of crystallographers. Until the last moments of his life, he worked as the deputy chairman of this society.

Until the 1920s and 1930s, not a single special research center for conducting scientific research in the field of crystallography was established in Central Asia, including Uzbekistan. Therefore, specialists, especially mineralogists, conduct their scientific research at Tashkent State University (now the National University of Uzbekistan) and Tashkent State Technical University (former SAGRI Central Asian Institute of Geology and Exploration), SAII Central Asian Industrial Institute, SAPI Central Asian Polytechnic Institute (TashPI Tashkent Polytechnic Institute) were carried out in the departments of mineralogy and crystallography, mineralogy and geochemistry, crystallography and crystallochemistry under the management of the faculties of geology and mining. In addition, on some mineralogical and geochemical issues specific to crystallography, various scientific-research works were carried out at the Institute of Mineral Raw Materials of Central Asia (now Mineral Resources of the Republic of Uzbekistan) and in the laboratories of the Institute of Geology and Geophysics named after KMAAbdullayev of the Academy of Sciences of Uzbekistan. In most cases, the relevant organizations in Moscow and St. Petersburg were referred to the "center" to perform the necessary research.

It is known that the famous scientist and academician QMAbdullayev is the President of the Academy of Sciences of Uzbekistan, a great statesman, the Deputy Chairman of the Council of Ministers of Uzbekistan (1942), the Chairman of the State Planning Commission of Uzbekistan (1944), the founder and first director of the Institute of Geology and Geophysics, the director of the Central Asian Industrial Institute (1941), a professor of the Faculty of Geology, drew up plans for the development of other branches of science and industry in Uzbekistan, including the

study of the geology of mines, exploration and mining, and the development of the mining industry, and managed its implementation. In addition, he created ample opportunities for the development of mineralogy-geochemistry sciences, and most importantly, he paid special attention to the training of experts from the youth of Makalli nation.

The introduction of such sciences as crystallography, mineralogy and geochemistry to Central Asia, the development of scientific research, and the establishment of an educational institution in this field under the authority of Tashkent State University in 1920 is directly related to the name of Academician ASU Klonsky. Until the end of his life, the famous scientist managed the scientific research and practical work carried out in these directions throughout Central Asia, including in Uzbekistan. He supervised the training of advanced specialists in these fields.

At the scale of our republic, all scientific works related to mineralogy and geochemistry are carried out based on crystallography and crystallochemical concepts and theories.

The composition of minerals and rocks that make up the uppermost part of the crust of our planet, which is the most necessary mineral wealth for the development of our industry, consists of crystals, which are the main content of this guide.

Key words and phrases: crystal substance, mineral, crystallography, basic laws of crystallography, goniometer, law of constancy of angles, law of whole numbers, law of regions;

LECTURE 2

Crystalline and amorphous substance. Formation and growth laws of crystals.

Plan:
1. Crystal and its properties.
2. Crystal formation and growth.
3. Theories about the causes and growth of crystals.
4. Growth rate of crystal sides and appearance of crystals.
5. The geometric shape of crystals and the effect of the external environment on it.

What is a crystal? It is known that all chemical compounds and chemical elements, whether natural or artificial, consist of crystallized (crystal means ice in ancient Greek) or amorphous (amorphous means without form) substances.

Almost all of the minerals that make up the surface of the earth's rocks, including ore that is found and mined among the rocks (except for coal and oil), raw materials used in some factories, metal alloys of finished products, and tools prepared from them. equipment, even food products, medicines used in medicine, mineral fertilizers and chemicals used in agriculture are all made of crystals. It should also be said that chemical substances with clear geometric shapes, which can be called crystals based on their appearance, with visible smooth sides, are rare both in nature and among industrial products. In order for all these chemicals to be called crystals, apart from their geometric shape, they must be distinguished by other characteristics.

Crystals differ from amorphous substances by the following characteristics:

1. The crystallized state of any body is the thermodynamic equilibrium state of the substance that makes up that body. The solid state of a substance with a certain chemical composition has a specific geometric structure of its atoms corresponding to a certain pressure, temperature, and thermodynamic conditions, that is, a crystal shape.

So, a crystal is a solid body, a chemical compound or an element in nature, without the participation of people, limited by flat-smooth sides with straight edges.

A crystal fragment tends to take a specific crystal form for this substance based on certain laws in the solution of the substance contained in the crystal, and forms spontaneously in that crystal form when the necessary physico-chemical environment and process exist.

2. Properties of the crystal, such as chemical composition and specific gravity, are the same in all parts, so it is homogeneous. A piece of the crystal of the same size, taken in the same y direction from any place, has the same physical, physico-chemical properties, and the same chemical composition (Fig. 1.2). Such uniformity, that is, invariable properties, is maintained only under the influence of pressure, temperature and other factors in a certain environment. Due to this apparent homogeneity, crystals can be considered as an infinite medium that continues continuously in space. Homogeneity exists in amorphous bodies, liquids, and gases. But the homogeneity characteristic of crystals is distinguished by its anisotropy (uniformity of physical properties in certain directions). Anisotropy in crystals is also clearly visible from their geometric shape (Fig. 1.3).
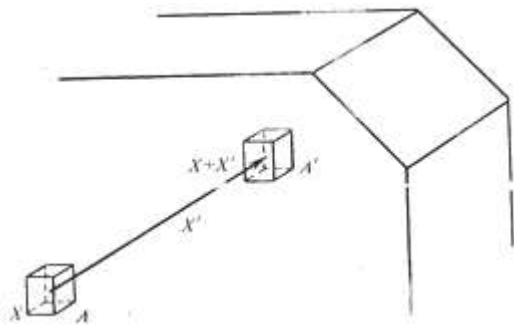
Figure 1.2
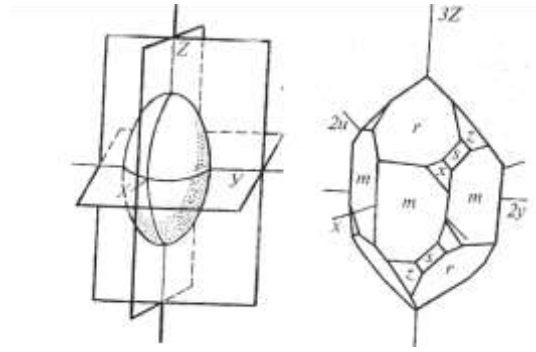
Figure 1.3

3. A number of physical properties of a crystal, such as its refractive index and hardness, have the same value in certain directions, that is, a crystal is an anisotropic physical body.

4. Crystallized substances melt at specific temperatures. For example, ice melts at 0° and k.

5. A crystal is an anisotropic medium with the same composition, similar - equal parts.

Crystals are symmetrical (relatively equal) bodies, consisting of similar equal parts determined by means of additional geometrical means that are repeated according to a certain procedure. For example, a crystal of table salt halite is in the form of a cube, and it is repeated three times around an axis through the middle of the sides of that cube and twice around the axes taken over the edges.

The concept of symmetry (relative equality) found its logical development thanks to the science of crystallography and became widely used. Also, the theory of crystallographic symmetry found its relevance in life, including the world of plants and animals.

6. The crystal has a periodic internal legal structure, and this law is reflected in the periodic, endless repetition of the molecules, atoms, ions that make up the chemical compound forming the crystal, in other words, the material points that make up this crystal structure. We can imagine and explain such a legal internal structure in the form of "spatial grids". The above-mentioned properties of crystals are the visible consequences of this internal legal structure in them.

Amorphous substances do not have an internal, continuous legal structure, and the properties listed above do not appear in them at all. For example, glass is an amorphous substance. Figure 1.4 shows the spatial lattice of a crystal, a flat lattice. In the spatial grid, the locations of the ions or the unit material points that make up these spatial grids in general are the nodes of the spatial grid (A^0, A, $A^{\prime}$ $A^{\prime\prime}$ ... points). The straight line connecting these nodes is called the row of the spatial lattice and the grid (cell) consisting of intersecting rows lying in the same plane is called the straight line of the spatial lattice. (Fig. 1.5).
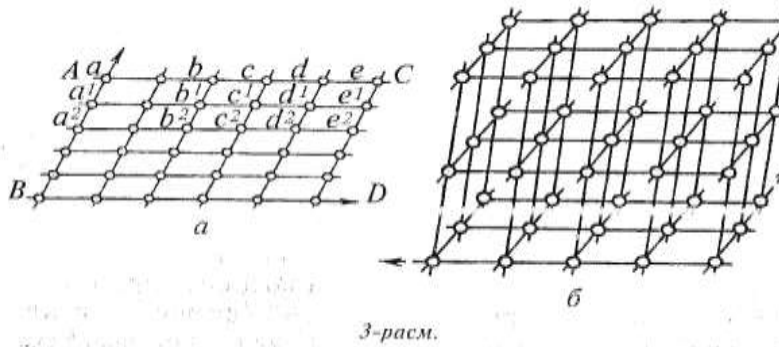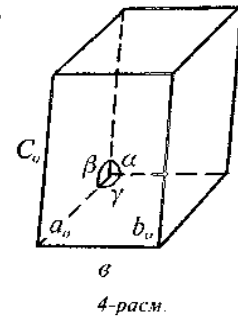
Figure 1.4   **Figure 1.5**

Hence, the imagined internal regular structure of a crystal is said to be a spatial lattice to the hypothetical form depicted. Each crystal is distinguished by the arrangement of the material points that make up the crystal, i.e., the shape of the elementary cell of the spatial grid, the shape of the endlessly repeating parallelepiped in the crystal structure. The length of the edges of elementary cells (a_o, b_o, c_o) and the angle between these edges - a, b, g are different from each other, characteristic of the crystal of each substance .

Crystal formation and growth. The issues of crystal formation and growth are of great scientific-theoretical as well as practical importance. The scientific and research work carried out in this field in recent times, in connection with the rapid development of science and technology, has been adapted to the demand of the national economy, including industry.

is developing accordingly. This demand is primarily due to the development of methods for artificial preparation of crystals with specific properties, in particular, various hard alloys, semiconductors, crystals with high-quality piezoelectric and optical properties.

consists of In addition, the quality of many metals and metal alloys depends on the conditions of their crystallization environment, the position of the atoms participating in the alloy in the spatial lattice. That is why this issue attracts the attention of metallurgists and metallurgists. Also geologists and mineralogists working in the field of crystallogenesis

they study the formation and growth of crystals and conduct research in this field. In the end, they will find out where the unseen and invisible rocks form minerals, what environmental conditions are necessary for their formation and what substances are involved. It should also be noted that crystal growth has many unique theoretical and practical problems that have not yet been solved.

Crystals occur as a result of phase changes that occur in nature or are created in the laboratory.

Crystals are formed as a result of precipitation from a solution (for example, various salts), solidification of a dissolved substance (metals and metal alloys), solidification of substances in a vapor state (for example, iodine, snow, etc.). In addition, some amorphous solids can crystallize over time or sometimes under the influence of temperature and pressure.

The solution of some practical and theoretical problems related to the formation and growth of crystals can be clearly seen and imagined in the example of crystals sinking in solution.

In order for crystals to start forming in a solution, the solution must be supersaturated in that environment (at a certain temperature and pressure). It is known that the amount of a substance that needs to be dissolved in order to saturate 100 cm^3 of a liquid (solvent) is called the solubility of that substance, and this amount changes mainly depending on the temperature (pressure has almost no effect). With increasing temperature, it often increases, and sometimes decreases (for example, Na$_2$CO$_3$, NaF, Ka$_2$SO$_4$, etc.).

When the solubility property of the crystal growing substance is unknown, it is determined experimentally. For this purpose, 100 ml of solvent water is taken, and the substance (measured by weight) is dissolved in it little by little. The amount of substance consumed until it finally reaches a state in which excess is insoluble is the degree of solubility of that substance. A few percent of the substance in the solution is further dissolved by heating to form a supersaturated solution.

Supersaturated solutions can be produced by cooling, i.e., lowering the temperature of a saturated solution, evaporating a saturated solution, as well as by chemical reactions.

Table 1.1

given in grams per 100 cm $^{3\ of\ water)}$

The name of the salts	Temperature				
	0°	10°	20°	30°	40°
Aluminium-Potassium Bitter Stone	3.90	9.52	15.13	22.01	30.92
Copper tube (tiger)	31.61	36.95	42.31	48.81	56.90
Magnesium sulfate	76.9	96.5	119.5	146.3	179.5
Sodium nitrate	73.0	80.6	88.5	96.6	104.9

For example, bitter stone dissolves in 100 cm^3 of water heated to 40°, and when the temperature of the solution is cooled to 20 30,92 g^0, it turns into a supersaturated solution. Because 15,13 gthe amount of bitter stone dissolves in water at such a temperature. So, in a solution with a reduced temperature 15,79 g. there is excess

solute. It can remain unprecipitated in solution for a certain period of time, and then, over time, it will precipitate after becoming somewhat larger, forming crystal "buds".

A saturated solution prepared at that temperature becomes a supersaturated solution over time as the solvent evaporates. In this case, the solvent itself evaporates and decreases, and the solute does not evaporate and almost does not decrease.

As a result of chemical reactions between well-soluble substances in a saturated solution, a poorly soluble substance is formed, this solution becomes a supersaturated solution for this poorly soluble substance. For example, when K_2SO_4 and $BaSO_4$ are mixed together, since KC1 and $BaSO_4$ are hardly soluble compounds, it precipitates as crystals in the solution. Crystals do not form in unsaturated solutions, on the contrary, the crystal itself dissolves when placed in such a solution. In a saturated solution, crystals do not begin to form, and the excess substance added to it does not dissolve.

Both in nature and in industry, many crystalline substances are formed from supersaturated solutions. For example, layers of table salt, potash salt, Glauber's salt, etc. are deposited in natural lakes of saline water.

Rock crystal, fluorite, and ice spar crystals are formed under the influence of high pressure and temperature in the hydrothermal process associated with residual magma. Also, in factories, crystalline substances are precipitated from the solution.

Hot melting substances also turn into crystallized substances as a result of cooling down the temperature. However, despite the fact that the crystals formed in this way are widespread in nature, they do not have the characteristic features of crystals. They form a body consisting of very small, even invisible to the naked eye, irregularly shaped crystal grains. Metals and metal alloys that are widely used in our daily life and igneous rocks formed by boiling magma are crystalline bodies formed as a result of the cooling of heated substances. The physical properties of many metals and metal alloys (including their hardness) depend, on the one hand, on the properties of the atoms participating in this crystal structure, and on the other hand, on how much the temperature of the melting substance decreases.

There are not so many crystalline substances in nature that are formed in the process of gas-vapor substances directly turning into a solid state without turning into a liquid. Crystals of substances such as sodium (NH_4Cl), table salt (NaCl), iodine (I_2), sulfur (S) and iron chloride ($FeCl_2$) are formed from the gas and steam released together with volcanic substances. Snow is also a crystal skeleton formed naturally from water vapor. Some factory products are also crystals formed from gas-vapor. For example, magnesium in the crystalline state, corborundum vac.

In addition, amorphous substances in a solid state can also change to a state with a crystalline structure. Because layers of limestone ($CaCO_3$) turn into marble over time under certain conditions, and silica (silicon oxide opal, chalcedony - SiO_2)

turns into quartz, and so on. Also, those crystal particles that make up very small crystal bodies can grow larger under the influence of temperature, pressure, and other factors. Such flaking of crystals occurs due to the reduction of the number of crystals per volume unit. Sometimes metal objects, as a result of a lot of exposure, lose their hardness, i.e. "get old", this is the only reason. This phenomenon also occurs in nature. Fine-grained limestone becomes coarse-grained marble.

Theories on the causes and growth of crystals. It is known that molecules are always in motion in a liquid state. As it goes into gas mode, this movement becomes faster. In amorphous solids, the movement of individual molecules proceeds slowly and with difficulty until those molecules reach their legally stable positions. In crystalline substances, molecules are in motion and do not move from one place to another. Perhaps the atoms and molecules of crystalline substances are in vibrational motion only in their place. In addition, some crystalline body is affected by thermal power (power), that is, when it is heated, it begins to melt under the influence of a certain temperature. No matter how much the temperature of this substance is heated, it will not rise until it is completely melted, that is, the temperature of the crystalline substance can rise only after it is completely melted. For example, the heat given to an ice crystal is used for the melting of this crystal, and the temperature does not rise until the ice completely melts and turns into water. From this example, it is known that the substance in the crystalline state has the smallest (minimum) internal energy compared to the other state. So, a substance in any state tends to transition to a crystalline state, and when the necessary conditions for this occur, it turns into a crystallized substance due to a change in the environment.

How does this crystal form and grow? This issue attracts the attention of many scientists at the international level, both theoretically and practically. But there are still aspects of this issue that have not been resolved.

As the temperature decreases, the motion of dissolved substance particles (molecules, atoms or ions) slows down, first one-dimensional, and then two-dimensional "buds" appear due to the attraction between negatively and positively charged particles. These crystal particles are the "basis" for future crystals from which crystallization centers will grow, thus the crystallization centers remain stable only in supersaturated solutions. Even if such "buds" sometimes form in saturated or unsaturated solutions, they dissolve very quickly. According to existing theories, it is understood that supersaturated, supercooled solutions can be kept for a very long time without crystallizing until centers of crystallization come from outside. However, in practice, even from such solutions, "buds" crystals appear by themselves.

The process of growth and development of the crystal center has been of interest to our scientists in many ways. As the crystal grows in the solution, the negatively and positively charged ions are attracted one after the other by the same

crystallization center according to the law of mutual attraction and settle on the crystal in a certain order. This is how the process of further growth of crystals can be imagined.

The process of crystal growth can be interpreted differently. Ions in the solution combine with each other to form larger units of one or two dimensions: "crystals" and "protocrystals". Large units consisting of a number of these ions gather around the centers of crystallization in a certain order and form a large crystal. These substances may have fallen into the solution or molten alloy as dust from the air, or they may have been deliberately added to the solution to accelerate crystallization.

In addition, frequent mixing of the solution, shaking or shaking of the container containing the solution accelerates the formation of crystal centers, in which the movement of the dissolved substance or particles in the solution accelerates, they approach each other in a faster direction and take place in the structure in a stable connected state.

Therefore, particles of a crystalline substance (ions, atomic molecules) are more stationary than other particles in a liquid, gas, or vapor state. In a crystallized substance, the stable place and position of the particles in this medium, which are trying to move to a state of equilibrium with a very small internal energy, are reflected . As the formation of the crystal is related to the natural force and the internal force, its final growth also takes place based on a certain law under the influence of a certain force.

According to the theory of crystal growth, the order in which those particles approach the growing crystal surface is also important. Ultimately, the appearance of the crystal depends on the order of growth of these crystal sides (Figure 1.6).
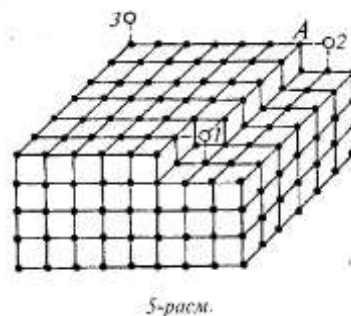
Figure 1.6

Near the growing crystal, the -1 ions located in the A position are attracted to this surface in three directions, the -2 ions in the B position are attracted in two directions, and the -3 ions in the C position are attracted to this surface in one direction. A freely moving ion in such a solution first occupies a position in which it is attracted in three directions, then in two directions, and finally in one direction. So,

next to the growing crystal, each ion fills the row where it started to grow, and after that row is filled, it fills a new row in that layer. After all the rows in this yoda are filled, a new layer of the crystal begins to grow. The thickness of rows and layers is measured by the size of the structural units of ions, atoms or molecules.

So, from a theoretical point of view, growth in a new layer does not occur until the layer from which the crystal started growing is filled. According to the order of these crystal growth processes, straight-grown crystals are bounded by flat-smooth sides, and the sides are intersected by straight edges. This law is called the law of restriction of crystals to flat sides and edges.

Crystal facet growth rate and crystal appearance.

We already mentioned in the introduction of our book that the wonderful shape of crystals, limited by flat, smooth sides and straight edges, has been attracting people's attention. The main reason or reason for this is explained in the theory of crystal growth. The side of the crystal consists of a flat surface on which the particles that make up the crystal are located, that is, a flat lattice of the spatial lattice. and the edges are straight lines intersected by straight smooth sides, i.e. rows of the spatial grid. Therefore, as mentioned above , the growing side of the crystal is pushed parallel to its previous position.

6-расм.

Figure 1.7

7-расм.
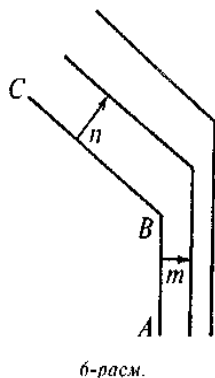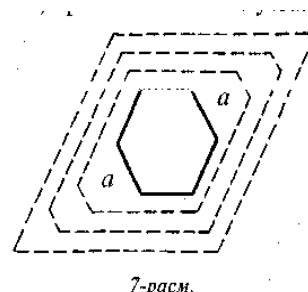
Figure 1.8

Crystal ion growth rate refers to the distance of this side's vertical movement (displacement) to this side within a unit of time. This rate is measured by the thickness of the layer grown on the side of the crystal per unit of time. The growth rate of the AB side is indicated by the letter t, and the speed of the BC side by the letter n (Fig. 1.7).

As can be seen from Figure 1.8. the fast-growing side of the crystal later disappears (a crystallization tip appears in its place), while the slow-growing side is constantly developing. From this, it can be concluded that the crystal growth rate is limited to the sides.

So, the shape of a freely growing crystal depends on the growth rate of these crystal sides. This is determined by the arrangement of ions, atoms or molecules in

specific directions specific to each crystallizing substance. It is known from experiments that crystal sides correspond to surfaces with high (excess) reticular density. The number of material points (ion, molecule, atom) located within the surface unit of a given crystal side is called the reticular density of this side. Crystals are covered with ions of high reticular density. (Law of Brave (1811 -1863)). From this it can be concluded that the appearance of the crystal depends on the growth rate of those crystal sides.

The geometric shape of crystals and the effect of the external environment on it . It is known that crystalline substances are very common in nature, but among them it is very difficult to find those with a specific geometric shape. There are many reasons for this, and the main reason is the time of formation and growth of those crystals. This can be seen in the following examples.

1. If the solution is very saturated and dark, the "buds" of crystallization centers are numerous and small, and none of them can form a correct geometric shape due to their density.

2. Even if the temperature of the solution drops sharply, as in the first example , a lot of crystal buds appear, because of this, those grains cannot grow and form a large crystal with a correct geometric shape.

3. In order for a passing crystal to have a correct geometrical shape both in natural conditions and in laboratories, it should be continuously provided with the same amount of matter from all sides, depending on the location of that crystal. But for certain reasons, such conditions do not occur. The crystal grain growing at the bottom of the crystallizer is supplied with the substance in the solution only from above and from the side and grows. The sides of the crystal grains touching the crystallizer do not grow. Only a suspended crystal grain suspended in a crystallizer can develop in all directions. Due to the fact that the crystal is suspended, the substance in the solution is supplied equally from all sides. Therefore, crystal grains touching the surface of any object cannot have a correct geometric shape. It is known that during the growth of the crystal, the amount of the substance in the solution touching it and at the same time its specific gravity decreases. The lightened solution rises to the top and is replaced by a more saturated solution. As a result, a flow of substances occurs in the solution, as shown in Figure 1.9.

a

8-расм.

б

9-расм.

21
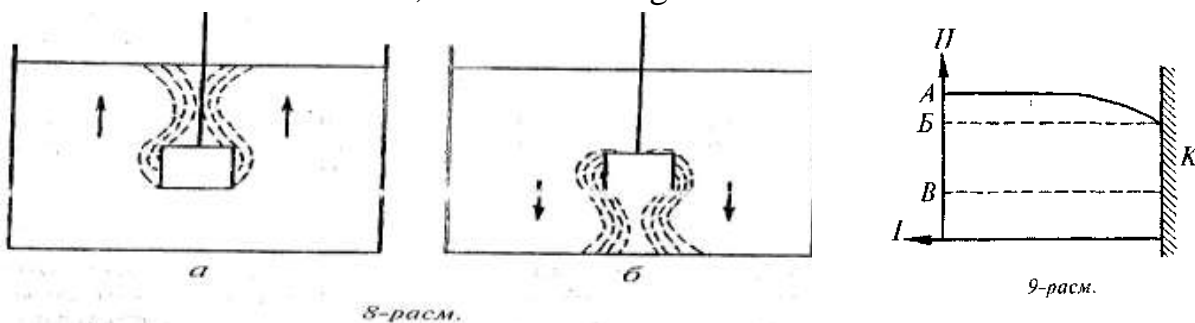
Figure 1.9   **Figure 1.10**

Figure 1.10 shows the change in the composition of the solution during the growth of the K crystal. A is supersaturated, and V is the amount of solute in a saturated solution. During crystal growth, the amount of dissolved substance in the solution decreases as it gets closer to the crystal. During the growth of crystals, the difference between the amount of the substance that is reduced in the solution shown in level B and the amount of dissolved substance in the supersaturated solution shown in level A creates a flow of substances in this solution.

4. Impurities in the composition of the solution, sometimes in the amount of one hundredth or one thousandth of a percent, lead to the speed of development of crystal sides and, finally, to a change in the external appearance of the crystal. For example, if the solution of bitter stone contains tanakor (bura) mixture, its octahedral crystals become cubic (Fig. 1.11).

a   *б*   *в*   *г*

10-расм.
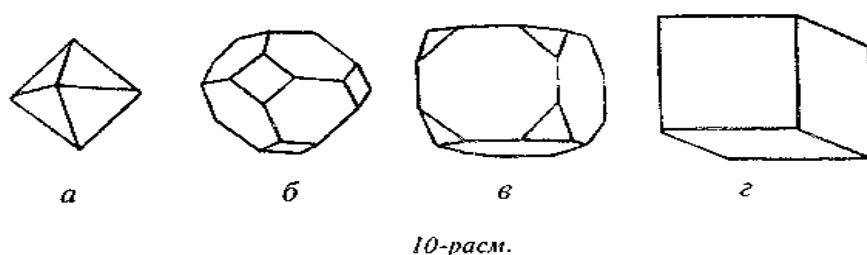
Figure 1.11

Also magnesium sulfate ($MgSO_4$ · The appearance of the crystal grown in the presence of a 0.01% tanacor mixture in a $7H_{2}O)$ solution is also different. Finally, as a result of the increase in the amount of tanacor in the solution to one percent, the long, prismatic sides of the crystals are short, and the isometric tetrahedral sides of the crystals are formed (Fig. 1.12). When a mixture of $CO(NH_4)_2$ is present in a similar halite solution, its crystals are not cubic, but octahedral.

a   *б* ·   *в*   *г*   *д*   *e*

11-расм.
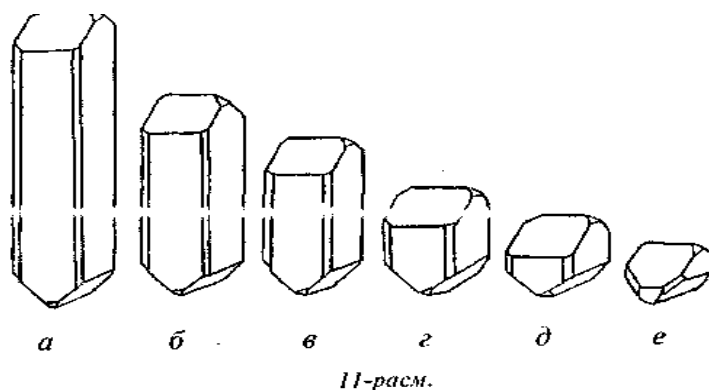
Figure 1.12

5. The shape of the crystal also changes as a result of the temperature change of the growing environment. For example, epsomite $MgSO_4 \cdot 7H_2O$ crystals grow in an elongated prismatic shape at a high temperature, and in a short isometric shape at a relatively low temperature (Fig. 1.13).

12-расм.
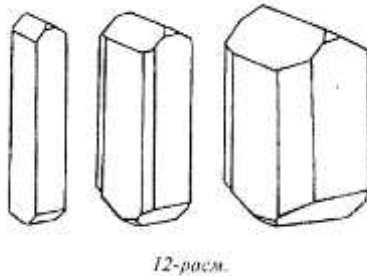
Figure 1.13

Many factors can be attributed to changes in the appearance of crystals. But each substance is tested in practice for the basis that affects its crystal form, which is specific to that substance.

LECTURE 3
Symmetry of crystals.

Plan :

1. Crystal symmetry and its study
2. Combining the means of symmetry in a geometric way
3. Consolidation of symmetry means of unidirectional crystal forms
4. View of symmetry - classes syngonia and classes

A crystal, as mentioned above, is a geometrical form of a body formed in a specific environment, consisting of atoms or ions, structural units arranged periodically in a regular order, limited by flat sides. Therefore, their shape does not appear random. On the contrary, it occurs in connection with the element that is part of the chemical compound that forms this crystal, and finally, the environment in which the crystal is formed. In the words of NV Belov, "a large macrocrystal is an open book for a mineralogist, in which the history of the mineral and the fate of the mine where it is found are written." In this chapter of the book, we begin to turn the "pages of an open book" that NV Belov said. Crystals are geometric shapes, but from the science of geometry

not all familiar forms are crystalline forms.

Since the crystal has a clear geometric shape, its study has long been based on the laws of mathematics and geometry. Therefore, in this topic, the geometric properties of crystals are studied.

When examining and studying the shape of crystals and distinguishing them from each other, one of the most noticeable signs is their symmetrical (symmetry means equal, similar in ancient Greek) structure. If one of the two shapes is similar, equal and compatible with the other, they are mutually symmetrical shapes. If one of them is a mirror image of the other, such forms are called *enantimorphic forms* (Fig. 1.14).
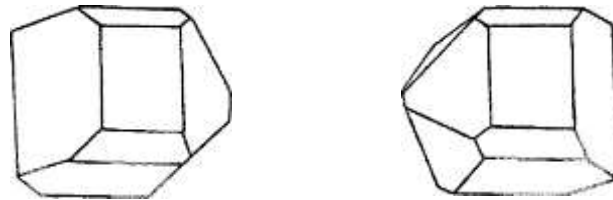
Figure 1.14

If a shape itself consists of similar, equal and congruent parts, then such a shape itself is a symmetrical shape. This equality and similarity between the parts of the figure can be imagined using geometric means. In this case, the geometric tools used to visualize the similarity and equality between the corresponding pieces (parts) of the shapes are called the tools of symmetry. Below is an overview of these symmetry tools.

Symmetry tools. Any crystal form has its own means of symmetry, and the degree to which the crystal form is symmetrical can be determined based on the type and number of symmetry means found in this crystal. Accordingly, they are divided into classes, syngonia and castes in a certain order.

At this point, we will only consider the macro-visible means of symmetry for limited geometric shapes, we will talk about the specific micro, i.e., invisible means of symmetry for infinite-continuous forms in the next chapters of the book, giving only general concepts.

Thus, a crystal is a form of similar and equal parts. This similarity and equality can be explained using certain geometric means. Such geometric means can be a plane, a straight line, or a point. If a crystal is determined to be composed of similar equal parts relative to a known plane, that plane is a plane of symmetry; when defined with respect to a straight line, that line is the axis of symmetry, and finally, when defined with respect to a point, this point is called the center of symmetry. Below, the means of symmetry are described starting from the center of symmetry.

a). Center of symmetry. A crystal form has a point at its center where its axes of symmetry (if any) intersect, and since this point is the center of symmetry, then every end, edge, and side of the crystal form is congruent, similar, and equal in opposite directions. three. it will have edges and sides, that is, its reflection. So, the center of symmetry repeats the image of each point of the crystal shape by moving it

back to its opposite side. For example, point A is given (in figure 1.15-a), the reflection of this point through the center C is taken as A; In order for point C to be the center of symmetry, AC and A, C sections should lie on one straight line, and secondly, these sections should be equal, that is, $AC = A_1C$.
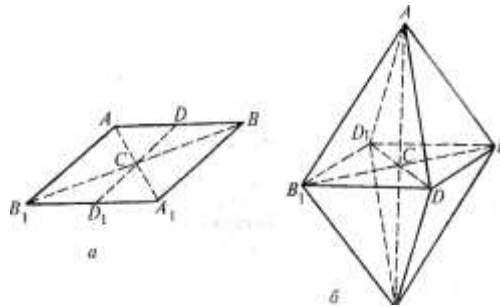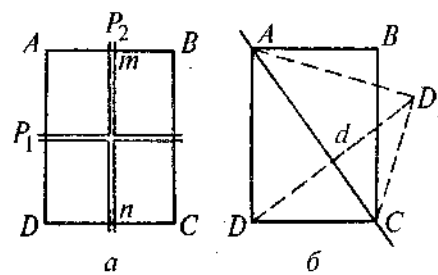

Figure 1.15

B and B $_{1 \text{ shown in the figure}}$, as well as the points A $_1$, meet the following condition, that is, the cross sections BC and B $_1$ C lie on the same straight line, and since BC q B(C), according to the laws of geometry, A $_1$ B with the cross section AB $_1$, the cross-sections are parallel to each other. From this, it can be concluded that the crystal edge with the center of symmetry must have an axis equal and parallel to itself on the opposite side. Therefore, the cross-sections AB, BD and AD bounding the side of the crystal shown in Fig. 1.15-b are edges also has cross-sections A $_1$ B $_1$, B $_1$, A $_1$ D $_1$ and A $_1$ D $_1$, equal to and parallel to itself through the center C. It is also known from geometry that as the cross-sections move in the opposite direction parallel to itself, the plane bounded by the sections also moves parallel to itself in the opposite direction.In the example shown, ABD and A $_1$ B $_1$ D $_1$,, that is, the side of the crystal, having the center of symmetry C, will have an axis parallel to itself on the opposite side.

Therefore, any crystal shape with a center of symmetry must be made up of corresponding, equal, and parallel sides on opposite sides. Accordingly, during practical work, a conclusion is made about the presence or absence of a center of symmetry in the given crystal shape, depending on the parallelism of the opposite sides (Fig. 1.16) .

Figure 1.16

16-расм.

Figure 1.17

25
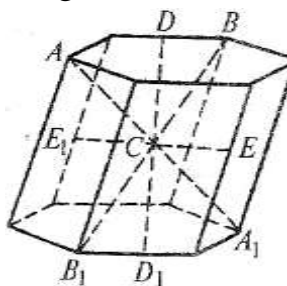
The center of symmetry is denoted by the letter C. When describing the symmetry of crystals, the center of symmetry - C is not written in special books on crystallography and mineralogy. But as an equal effector of other existing means of symmetry, it is imagined geometrically or written in the form, only if it is the center of symmetry itself, in the form of I.

b). **Plane of symmetry** . In order to determine the existence of a plane of symmetry in a crystal shape, it is imagined to pass a plane over this shape that divides it into two equal parts. For example, Figure 1.17 shows a crystal ABCD and shows the lines P_2 and P_1 that divide the crystal into two parts. The end A of the first half of this crystal, where the P plane has been transferred, and the end B of the second half, as well as the ends C and D, are compatible and similar ends. In order for the indicated planes P and P_1 to be the plane of symmetry, the following conditions must be met:

a) the corresponding ends of the crystal should lie in the same plane, that is, the shadow P and P_1 of the corresponding ends of A and B and C and B should be at the same point (as shown in the figure). Then the shadow of the ends of the crystal A and B falls on point *n* , and the shadow of ends E and D falls on point *m* , and k.

b) the distance between each corresponding end of the crystal and the shadows of these ends in the imaginary plane of symmetry is equal, that is, Am=Bm; As Cn = Dn, that is, both parts of the crystal separated by the plane P and P_1 must be equal to each other. So, a plane of symmetry is a plane that divides a given crystal shape into two equal and similar parts, the first half of which is a mirror image of the second half. The plane AC across the crystal ABCD shown in Fig. 1.17 cannot be a plane of symmetry. Because the corresponding ends A, C and B, D are not in the same plane, their shadow in the d plane does not fall on the same point, that is, although the crystal is divided into equal parts, one of these parts cannot be a mirror image of the other. The plane of symmetry is denoted by the letter "P" in special books in educational activities.

c). Axes of symmetry . In geometry in general, a straight line connecting two arbitrarily chosen points on some object or drawing is called an axis. In similar crystallography, two arbitrary points are selected on the crystal shape, one of them is connected to the other, and it is assumed that some bullet is passed through these points. However, these points chosen on the crystal form are not random, but formed as a result of their connection; an imaginary axis is chosen based on the idea that it can be an axis of symmetry, and it is proved that this imaginary axis is an axis of symmetry. This axis of symmetry must meet the following conditions:

a) when rotated around the axis of symmetry, similar points of the crystal shape (crystal edge, side and ends) are repeated around this axis an integer number of times after equal angles;

b) similar equidistant points of the crystal shape repeating around this axis lie in one plane (Fig. 1.18).
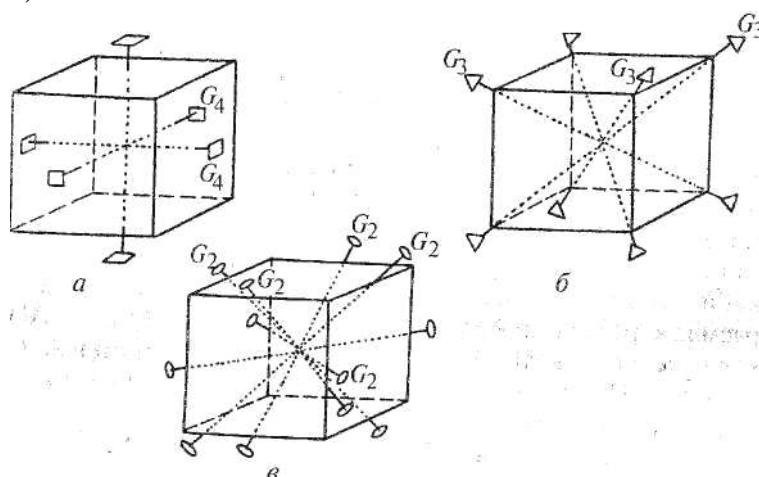
Figure 1.18

The smallest angle between similar points of the crystal form repeated around the axis of symmetry is 60 $^\circ$, 90 $^\circ$, 120 $^\circ$ or 180 $^\circ$, and they are called elementary angles. As the elementary angle is equal to 60 $^\circ$, the similar points of the crystal form are repeated six times around this imaginary axis of symmetry, that is, when the crystal form is rotated once by 360 $^{\circ\;,\;\text{the angles of}}$ 60 $^\circ$ are repeated six times. If the elementary angle is equal to 90 $^\circ$, the similar points of the crystal shape are repeated four times. Also, if the elementary angle is 120 $^\circ$, similar points of the crystal shape are repeated three times.

The degree of this axis of symmetry is called the number of repeating points when the crystal shape is rotated once -360 $^{0\;\text{around the axis of symmetry.}}$ So, the axis of symmetry in the first case will be of the sixth degree, in the second case of the fourth degree, and also of the third degree and the second degree. In crystallography, the axes of symmetry are designated by the letters , **L, G** or *g* during training, and their level is to the right of these letters, down L $_2$, L $_3$, L $_4$, L $_6$ or g $_2$, g $_3$, g $_4$, g $_6$ (G $_2$, G $_3$, G $_4$, G $_6$) or above L ^{2}; L ^{3}; L ^{4}; It is written as L ^{6} or g ^{2}, g ^{3}, g ^{4}, g ^{6} (G ^{2}, G ^{3}, G ^{4}, G ^{6}). However, in special books on crystallography and definition of minerals, the axis of symmetry is written only as level 1,2,3,4,6. Crystal forms cannot contain fifth, seventh or higher order axes. It was mentioned above that the unit cell of the crystal lattice is represented as a parallelepiped. The flat grid of such a Krlstall spatial lattice should be composed of parallelograms. Based on this, it is shown in Figure 1.19 that the fifth, sixth and higher order axes cannot exist in crystals. In this case, the plane of the drawing should coincide with the flat grid of the spatial grid, and the assumed axis of symmetry of the fifth degree should pass through the point in the direction perpendicular to this plane. Similar ends of the figure are A $_1$, A $_2$. A $_3$, A $_4$, A $_5$ are repeated every 72° around this axis. In order for such an axis to exist, the five

equilateral angles shown in the figure must be divided into parallelograms without leaving a gap, that is, they must be composed of parallelograms.

18-расм.
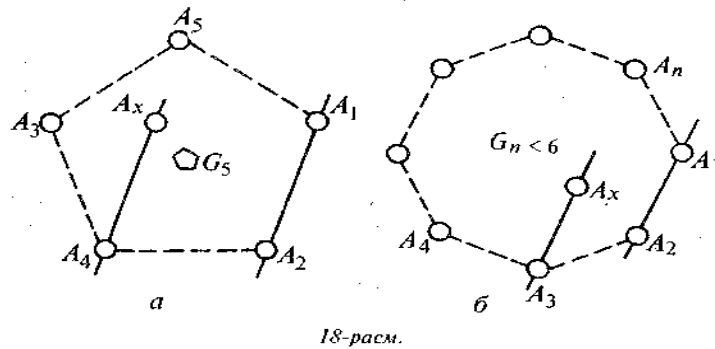
Figure 1.19

But it can be seen from the picture that this shape cannot be divided into parallelograms. Figure 1.19 shows a flat grid of a spatial grid and a rotating plane for its repetition. If there is an axis of symmetry, it itself passes through this plane in a vertical direction. The displacement distance of the points creates the chance of those matching points repeating. However, repeating points A_1 -A_5 cannot be combined to form a parallelogram. Therefore, they do not form elementary cells. The smallest distance between such points that can be repeated is a, and moves to N' and N» around the N axis. If there is L_2 and N = 3 (or 6), then there are 3 points based on N_1 or N_2 around this axis , and the distance between these points is equal to a. Thus, both L_3 and L_6 can exist. If N is $_4$, there will be 4 points in the plot. The interval between N' and N»-4 is $\sqrt{2}$ equal to a, that is, greater than a. So, L can also be $_4$. But if N is $_5$, the distance between the 5-5 points is smaller than the distance between N' and N» (from a), that is, L_5 cannot be in crystals; The same result is obtained even if N is $_2$. The absence of fifth-order axes in crystal forms can be explained in other ways, but we will limit ourselves to this in this book (Figure 1.20).
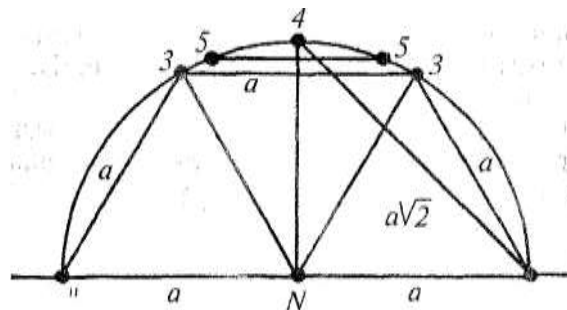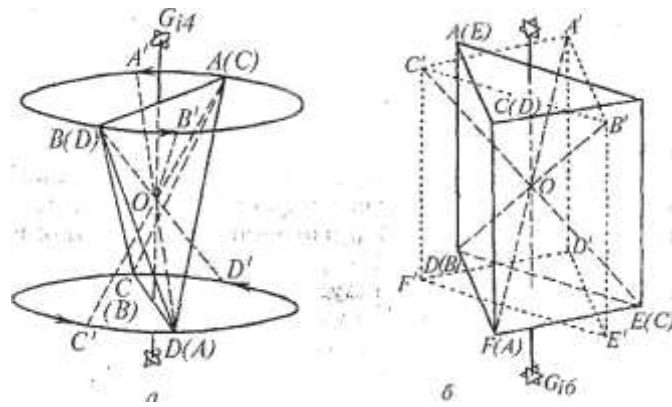

Figure 1.20

It should also be mentioned that some natural organic bodies, as well as very complex organic crystal structures, may have fifth-order symmetry axes. For example, marigold and other similar plant petals are made of five, and there is an

28

imagined fifth-order axis in the center. During the following years, there is a debate among crystallographers about the existence of the fifth-order axis in the crystal forms of the inorganic world as well. But how these discussions end has no effect on the practical work of mineralogist-geochemists.

In addition to the simple rotational symmetry axes described above, crystals also have translational or torsional axes, which will be discussed later. There are also more complex "centered" and "plane" axes of rotational (mirror-rotational) symmetry, which will be discussed below.

"Central" axes of symmetry . As the name suggests, in some crystal forms, both the axis of symmetry and the center of symmetry become equal influencers at the same time. The existence of the axis of symmetry G_{14} in the form shown in Fig. 1.21-a is unquestionable. However, let's assume that this figure also has a center of symmetry C. In that case, the reflection of the upper ends A and B is repeated at the points D_1 and $C_{1\,below}$, and the reflection of the lower ends B and C is repeated at the points A_1 and $B_{1\,above}$. After that, the axis of symmetry, which was assumed to be of the second degree above, becomes the axis of the fourth degree. Because the upper ABA_1B_1 and the lower DD_1C_1C ends of the crystal shape lie in the same plane, and the angle between these points is equal to 90^0. Therefore, considering that there is also a center of symmetry of the second order, there will also be an axis of symmetry of the fourth order. Such axes are called "Central" axes of symmetry. Similarly, Figure 1.21, b shows a crystal form with a third-order symmetry axis - G_3. Assuming that it also has a center of symmetry, then this axis of symmetry itself becomes a sixth degree axis of symmetry, that is, the third degree is real and the sixth degree remains the "centered" axis. It is recommended to write "central" axes of symmetry differently in different books, L^4_2, Gi_4 or L^6_3, G_{i6}. Crystal forms do not have "central" axes of symmetry with degrees other than those indicated. In addition, it should not be forgotten that the normal axes of symmetry and the plane of symmetry can be equal effects of such "centered" axes.

"Flat" axes of rotational symmetry . Such axes of symmetry are imagined by equalizing the plane of symmetry with an ordinary rotational axis of symmetry. On the crystal form ABDC in Fig. 1.21, the plane of symmetry P is depicted perpendicular to the axis of symmetry Gi_{4C}.

Figure 1.21

As the reflection of the ends of the crystal form is placed on this plane of symmetry P, then we will have points A $_1$ B $_1$ D $_1$ and C $_{1\ \text{lying on this plane, which form an}}$ $_{\text{elementary angle of 90}}$ ^{0} around the ordinary, secondary axis through which these points have been transferred, after an equal distance is repeated. Accordingly, the simple, second-order axis of rotational symmetry depicted in this figure is also a planar, fourth-order, rotational axis of symmetry, written in the form L ^{4} $_{2\ \text{as shown above}}$. So, together with the P-plane, the axis of symmetry of the second order Gi $_4$ is the co-effector of the axis of inversion of the fourth order.

In both cases described above, it was concluded that there is an imaginary "central" and "plane" axis of symmetry. For this, two additional methods were used: center of "symmetry" and "plane" of symmetry.

Summarizing means of symmetry in a geometric way. The number of means of symmetry in the imagined crystal forms can be one or several. Each of the axes of symmetry of several degrees and the plane of symmetry can be found in more than one such figure. Of course, the type and number of these means of symmetry, which can be in the form of a single crystal, appear in relation to each other according to certain geometric laws.

Before discussing the summation of symmetry means, we mention a number of mathematically proven rules related to this issue, which have been tested in natural crystal forms. But here, for brevity, we accept them without proof. In the meantime, we leave it up to the students to keep these rules in mind and check their accuracy when studying natural crystal forms as well as artificial forms. The following rules allow us to mathematically calculate the means of symmetry that we can imagine in every crystal form in the same way.

Rules for summarizing means of symmetry, showing the relationship between them.

a) Euler's rule . In a form with two secondary symmetry axes, there must be a third secondary symmetry axis passing through the point of intersection of these two symmetry axes (see Fig. 1.27, a).

b) The first rule. A straight line intersecting several planes of symmetry consists of an axis of symmetry that is equally affected by the planes of symmetry, and the elementary angle of this axis is twice as large as the angle formed by the planes of symmetry. In other words, the degree of the axis of symmetry is equal to the number of planes of symmetry intersecting on this axis.

c) The second rule . In forms with a center of symmetry and an axis of even-level symmetry, a plane of symmetry perpendicular to this axis of symmetry also passes (see Fig. 1.28).

Let's assume that point A_1 is the tip of the crystal (see Fig. 1.25), this point is moved to point A_2 through the secondary axis of symmetry - L_2, through the center of symmetry C to point A_3, and point A_1 to point A_4. Therefore, there is definitely a plane of symmetry P perpendicular to the axis of symmetry over the center of symmetry C. Since the points A_1 and A_2 and A_3 and A_4 are equidistant from this plane and lie on the same straight line, the image of these corresponding points on the plane P falls to one point. Otherwise, one of the means of symmetry mentioned in the second rule would not exist. It can be concluded that:

1) Crystal forms have a center of symmetry and a plane of symmetry passing over this center, then there is also an axis of even degree of symmetry directed perpendicular to this plane of symmetry.

2) Crystal forms have a pair of levels perpendicular to the plane of symmetry

if there is an axis of symmetry, then there is also a center of symmetry (see Fig. 1.25, b, v, g).

3) The number of two-level symmetry axes in crystal forms with a center of symmetry

symmetry is equal to the number of planes, and each of these planes of symmetry is perpendicular to the axis of even-degree symmetry.

d) The third rule . The number of secondary symmetry axes in crystal forms with high-degree and perpendicular secondary symmetry axes is equal to the number of degrees of the high-degree symmetry axis, for example, $L_3 3L_2$, $L_4 4L_2$, $L_6 6L_2$ (see Fig. 1.27).

Since there is a secondary axis of symmetry instead of the higher axis of symmetry, then $L_2 + 2L_2$ is $3L_2$ and they are perpendicular to each other.

Rows of symmetries in natural crystals . Crystal forms are divided into two groups according to their appearance. The first group is called unidirectional, and the second group is called unidirectional or multidirectional.

A unique direction in crystal forms that does not repeat itself is called a single direction. The direction of the axis of symmetry of the sixth degree (L_6 and L_3; L_4; L^4_2) is the only direction (Fig. 1.22), since such a direction is not repeated in the figure.
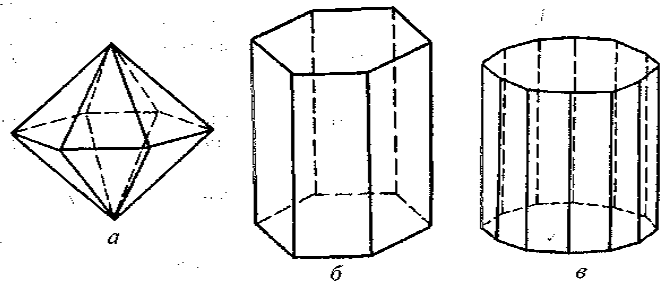
Figure 1.22

A unidirectional crystal can have a center of symmetry, a plane of symmetry, and axes of secondary symmetry. They run either perpendicular to or across a single direction. A single direction corresponds to the direction of a higher order axis, i.e. falls on that axis (shapes with more higher order axes are multidirectional shapes). Therefore, in unidirectional crystal forms, neither the axis of symmetry nor the plane of symmetry can have an angle other than 900 with respect to this direction. Otherwise, the so-called single direction around this axis or plane would be repeated two or more times and it would not remain a single direction (Fig. 1.23).
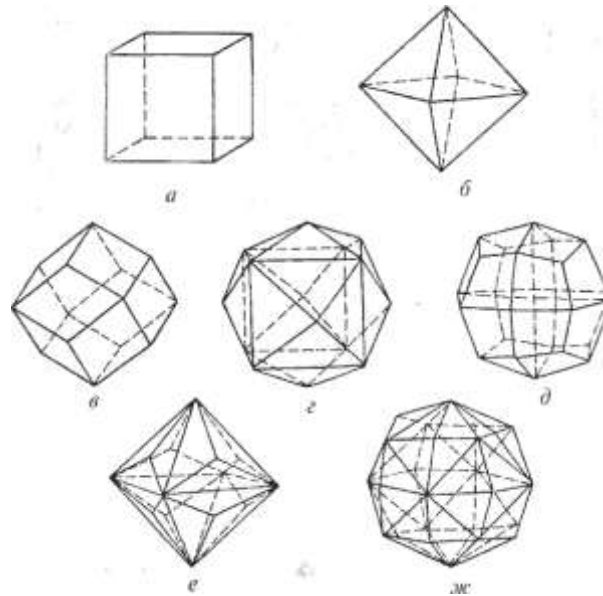
Figure 1.23

I. In triclinic syngonia crystals in low class crystals, there is no equivalent direction, that is, all directions in them are single directions. Monoclinic syngonia crystals have both a single orientation and repeating equidistant orientations. For example, L $_2$ is the only direction, and the directions passing through the surface of the plane perpendicular to it are also the only directions, but the directions that make a certain angle with it are not the only directions and are repeated twice around C. In rhombic syngonia crystals, the only direction is three

are three , over, or over C and a plane of symmetry perpendicular to it.

32

II. In the crystals of the middle layer, the only direction is one, and the axes of higher symmetry coincide with the directions L_3, L^4_2, L^6_3, L_6.

III. High class cubic syngonia crystals do not have a single direction. In these syngonia crystals, similar u-equal orientations are repeated at least 3 times and overlap with $3L_4$ or $3L_2$.

Unidirectional Crystal Forms Aggregation of Symmetry Means. The starting lines of symmetry tools for these unidirectional shapes can be:

1. Lines consisting of axes of symmetry passing in the same direction.

2. Rows with a center of symmetry.

3. Lines with a plane of symmetry perpendicular to the initial direction.

4. Lines with a plane of symmetry oriented in the same direction as the initial state.

5. Rows with second order symmetry axes perpendicular to the single direction in the initial state.

6. All imaginable means of symmetry are aggregated series.

According to the first order, there are five axes of symmetry aligned with the only direction, that is, L_1; L2; $\_L_3$; L_4; L_5; 1; 2; 3; 4; 6 forms a series of symmetry means. Of these, L_1

conditionally obtained, it can be repeated infinitely many times in the form of a crystal. In this form, there are many single directions. The series of symmetry means shown above consisting of a single axis are called "simple" "primitive" series of symmetry representations or classes (Fig. 23).
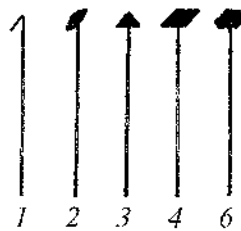
Figure 1.24.

We write the center of symmetry to each of the five lines formed in the second order. This will result in the following new lines.

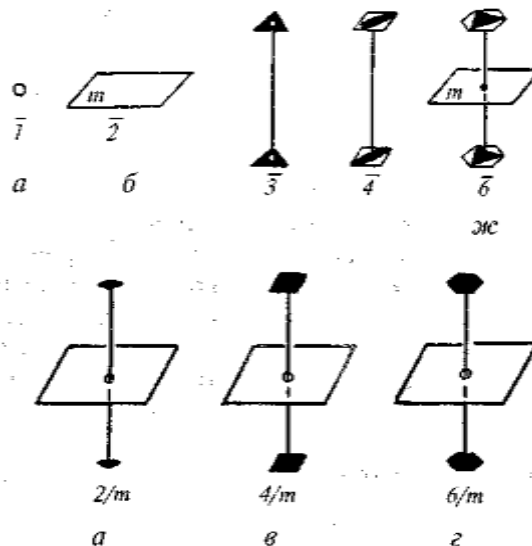The first row is written in C-form, excluding the first-order axis C (Fig. 1.25).

Figure 1.25.

According to the second rule, shapes with an even-level axis of symmetry and a center of symmetry must have a plane of symmetry perpendicular to the axis of symmetry. Accordingly, instead of $L_2 C$, the series $L_2 PC$, instead of $L_4 C$, $L_4 PC$, and instead of $L_6 C$, series $L_6 PC$. So, as a result of the second operation, the symmetry means C(l); $L_2 PC(2/m)$; $L_4 PC(4/m)$; A series such as $L_6 PC(6/m)$ is formed, and these series are called "centered series". The line $L_{3 C}$ in Figure 1.25 seems to violate Euler's rule. If we take into account the existence of an inversion axis L_3^6 corresponding to 3 in such a form , that is, this axis itself is an axis of symmetry of the inversion of the sixth degree, there is no room for such doubt.

In the third order, we add a plane of symmetry perpendicular to the unique direction to the initial state. But in the previous practice, according to the second rule, this was done before, and $L_2 PC(2/m)$; $L_4 PC(4/m)$; Lines $L_6 PC(6/m)$ were written above.

axes of odd degrees are $L_1 P = P(m)$; gives the series $L_3 P = L_3^6 (6)$, which we will discuss in detail below. According to the fourth order, the symmetry planes corresponding to it are added to the initial state over a single direction. For this, using the first rule, the number of symmetry planes is equal to the degree of the higher axis, and the following series follows: $L_1 P = P(m)$; $L_2 2P(mm2)$; $L_3 3P(3mm)$; $L_4 4P(4mm)$; $L_6 6P(6mm)$. These lines are called "planar" planes of symmetry (Fig. 1.26).
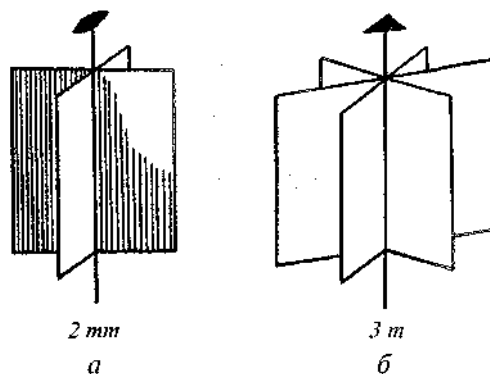
Figure 1.26

Secondary arrows perpendicular to a single direction are written in the following order. The number of these is equal to the level of the symmetry axis of higher degree (matched with its only direction) according to the third rule, that is, $L_1 L_2 = L_2 (2)$; $L_2 2L_2 = 3L_2 (222)$; $L_4 4L_2 (32)$; $L_4 4L(422)$; L_6 becomes $6L_{2 (622)}$ (Fig. 1.27).
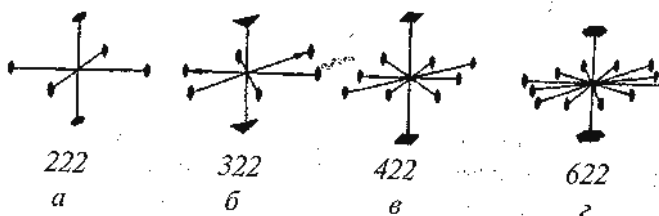

Figure 1.27

This series of means of symmetry is called the series of "axial" axis of symmetry.

Now add all the means of symmetry to the initial state, i.e. the center of symmetry (C), the plane of symmetry (P), and all the secondary axes of symmetry that are perpendicular to the single direction. According to the above rules, we create the following new symmetry views (Fig. 1.28):
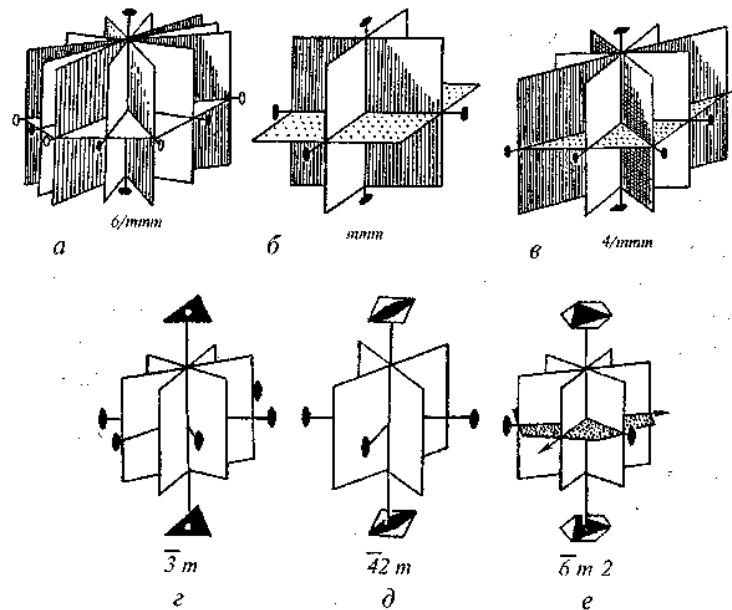
$L_1 C + P + L_2 = L_2 PC$ (2/m $_7$)

$L_2 + P + 2P + 2L_2 = 3L_2 3PC$ (mmm)

$L_3 C + 3P + 3L_2 = L_2 3L_2 3PC$ (3m)

$L_4 C + P + 4P 4L_2 = L_4 4L_2 3PC$ (4mmm)

$L_6 C + P + 6P + 6L_2 = L_6 6L_2 7PC$ (6mmm)

These are called "planaxial" symmetries. Finally, if the inversion axes are aligned with a single direction. the following "gyroidoprimitive" (inversion axis simple) symmetry means: $L_{i1} = C(I)$; $L_{i2} = P(m)$; $L_{i3} = L_3 C(3)$; $L_{i4} = L^4{}_2 (4)$; $L_{i6} = L_3 P(6)$.

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Figure 1.28

(Fig. 1.28) and if planes with corresponding directions are added over the axes of inversion symmetry aligned with this single direction, the following series of "gyroidoplanal" means of symmetry:

$$L_{i4} 2L_2 2P = L^4_2 2L2_2 P (42m);$$

$$L_{i6} 3L_2 3P = L^6_3 3L_2 4P (6m2);$$

$$L_{i6} 3L_2 3P = L^6_3 3L_2 3PC (3m)$$ is generated. These 27 lines of symmetry are typical for unidirectional crystal forms.

Shapes that do not have a single direction are series of means of symmetry.

Below is a series of characteristic symmetries for unidirectional crystal forms. It is known from elementary geometry that crystal forms that do not have a single direction consist of such forms as cubic tetrahedron, cube, octahedron. This was proved mathematically at the time. Without dwelling on these proofs in this book, adding other symmetries to the most "simple" (primitive) symmetries directly belonging to one of those forms, the tetrahedron, leads to a whole series of symmetries characteristic of non-unidirectional crystal forms:

1) The axes of symmetry imagined in the tetrahedron are $4L_3 3L_2 (23)$, and this line of symmetry means is considered a simple line.

2) By increasing the center of symmetry q to it, a series of "centered symmetry means" is formed, in which, according to the second rule, there should also be a plane of symmetry perpendicular to the secondary axes. The result is the line $4L_3 3L_2 3PC (m^3)$.

3) If we take into account the plane of symmetry passing through any tertiary axes, a series of "planar" means of symmetry is formed. Taking into account that the number of symmetry planes passing over any L_3 is three, and at the same time that

each symmetry plane passes through two L_3, then the following line of means of symmetry arises: $3L^4_2$ $4L_3 6P(43)$.

4) If three axes of symmetry of the second order perpendicular to these axes passing over each axis of the third order are added, a series of means of "axial" symmetry is formed. In this case, each L_2 passes over two L_3, and L_3 in the series of "ordinary" means of symmetry becomes L_4 here. As a result, this series of means of symmetry will have the following form: $3L_4 4L_3 6L_2 (432)$.

5) Finally, if the center of symmetry is added to this last line, the line of "planaxial" means of symmetry is obtained according to the second rule: $3L_4 4L_3 6L_2 9PC(m3m)$ (Fig. 1.29).
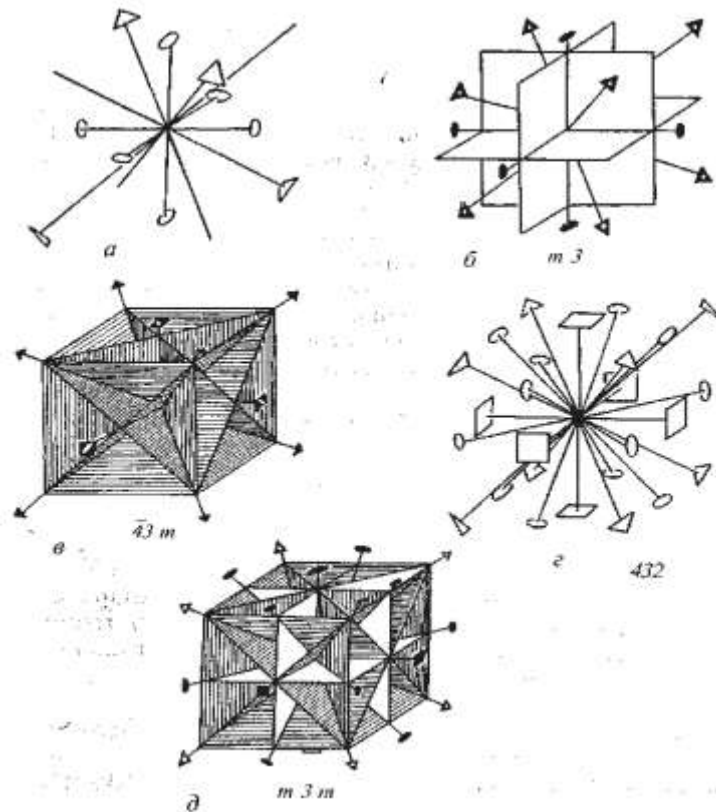
Figure 1.29.

Thus, the 32 possible rows of scmetry tools that can be imagined in natural crystals have been considered on a rigorous mathematical basis. Therefore, it is not possible to make any corrections to these reviewed rows. These 32 lines of symmetry were first worked out by Hessel in 1830 in a very complicated way , which was largely overlooked in his time.

Later, in 1869, these lines were rediscovered by AV Gadolin, and the Russian scientist became world famous. It should not be forgotten that the above-mentioned 32 rows of symmetry means are characteristic only for the limited class of geometric forms of crystal forms.

View of symmetry - classes syngonia and classes

The 32 lines of symmetry tools discussed above are called symmetry views or classes. In other words, a complete set of symmetry tools is a representation or class of symmetry. If we look closely at the series of means of symmetry, we will see that there is some similarity between them. For example, in a certain group of these lines of symmetry, there is only one L_2, in another group only L_3 or L_4, in another group L_6, so that all these axes move in the same direction. Another group of non-unidirectional crystal forms includes $3L_4$ or $3L_2$ with $4L_3$.

Groups of symmetry forms separated by similarity are called syngonia (meaning similar angles). At the same time, each syngonia crystal differs from other syngonia crystals by its unique geometric shapes and the shape of the spatial grid and elementary cells that make up those crystals. There are seven syngonias in total, and their name is based on the geometric properties of the elementary parallelepipeds of the elementary cell of the spatial lattice. Below is a brief description of these syngonias.

1. Triclinic syngonia . The name is made up of the Greek words tri three and klin - crooked, because in the parallelepipeds of the elementary cell of these syngonia crystals, all three of the angles between the edges are not right (not equal to 90^0).

2. Monoclinic syngonia (Greek mono means one). Two of the angles between the edges of the elementary cell are right (90^0 li) and the third is not equal to 90^0.

3. Rhombic syngonia. Most of these syngonia crystals have a rhombic cross-section perpendicular to the axis of secondary symmetry, so named.

4. Trigonal syngonia . This syngonia has one axis of third or inversion sixth degree symmetry.

5. Tegrogonal syngonia crystals must have at least one formal or hypereion fourth degree symmetry axis.

6. Heck sagonal syngonia crystals have an axis of formal or inversion symmetry of the sixth order. These last three syngonias are named after the specific degree of symmetry of these syngonia crystals,

7. Cubic syngonia . The unit cell of these syngonia crystals is cubic, with $4L_3$ and $3L_2$ or $3L_{4\ present}$. The syngonias listed above are divided into three classes based on their level of symmetry: I) a class with a low level of symmetry; II) a class with an average level of symmetry and III) a class with a high level of symmetry.

It can be concluded as follows: in crystals belonging to the class of low symmetry, each direction is repeated three or more times, which means that they do not have a single direction. Accordingly, the crystal forms of this class may not have symmetry means and may have them at the same time. The degree of existing symmetry axes does not exceed two; the degree of symmetry is unique in medium-class crystal forms

there is a direction which is in the same direction as the axis of higher order symmetry. Therefore, it is necessary to have one high-order symmetry axis in the characteristic crystal forms for this class. In crystal forms with a higher degree of symmetry, there is a single direction and the number of high-order axes is more than one.

The names and symbols of the 32 calculated symmetries are written in the form of internationally accepted German-Mogen symbols in books on crystallography and mineralogy. In addition, Groth, Schönflis and Shubnikov

There are also signs.

Above, the means of symmetry were defined and written in the symbols developed by Groth so that they would be easy to write. Below is a general understanding of the existing signs and methods of the class of crystals used at the international level. German Mogen signs are given. In this case, only the degrees of the axes of symmetry are written in AVShubnikov symbols. The number of secondary axes and the number of symmetry planes (m) passing over these higher-order symmetry axes are not written, because their number is equal to the number of levels of that higher-order axis; The sign 1, 2 is the center of symmetry, and the sign 6, 4, 3 indicates the presence of inversion axes.

If the plane of symmetry in the German-Mogen notation passes in the direction corresponding to the axes of symmetry, then no sign is placed next to the number, and if it is perpendicular to this axis, then it is written as 2/m after the decimal point, the symmetry representation of 2/m2/m2/m can be briefly expressed as mmm . It imagines the existing $3L_2$ and C in the form of symmetry. Similarly, the hexaoctahedral symmetry representation, which should be written as 4/m32/m, can be abbreviated as m3m. In general, in such a designation, first of all, it is written that the means of symmetry are aligned with the crystallographic axes depending on their position in space.

In AVShubnikov symbols, the plane of symmetry passing perpendicular to the axes of symmetry is written after a colon (:). A dot (.) is placed between the level of the axis and the plane passing in the corresponding direction with these axes. A decimal point (-) between the numbers indicates that these symmetry elements intersect at a wrong angle $(< \neq 90^{0})$.

$_1$, C_2 , C_3 , and C_6 (the German initial for Sirk Cyrk) in the Scheinflis symbols indicate that there are only one unpolarized symmetry axis of the degree shown in the symmetry representations. If there is a plane of symmetry perpendicular to these axes, it is written as C_{2h} , C_{3h} , C_{4h} , C_{6h} (h is the initial letter of the German word "horizontal") in addition to these symbols. As a result, the planes of symmetry oriented corresponding to that axis of symmetry are as follows additional **v** (vertical) and written as C_{2v} , C_{3v} , C_{4v} , and C_{6v} . The appearance of dihedral symmetry

without axis in monoclinic syngonia is expressed in the form C_s. s (spigelaxe is the initial letter of the German word for mirror) and the number of secondary axes perpendicular to it are written as follows: Д (Diodere is the initial letter of the German word meaning that it consists of two sides) $Д_2$; D_3 ; D_4 ; Like D_6, $_{D2}$ symmetry in rhombic syngonia is sometimes written as **v** . Adding the letter h to these symbols means that these classes have symmetry planes and secondary symmetry axes. D_{2h} in rhombic syngonia is sometimes shown as v_h .

Tetragonal scalenohedral and ditrigonal scalenohedral classes D_{2d} (or v_d) are also denoted by D_{3d} symbols. In this case, the position of the plane of symmetry relative to the axis of symmetry (d-diagonal) is taken into account, and the symmetry views with inversion symmetry axis of 2 and 3 degrees are expressed as s_4 and s_6.

Also, the rhombohedral symmetry view can be expressed in a different C_{3i} form, since it is written in the form of a pinacoidal symmetry view with a specific center of symmetry. The letters T (tetrahedron) and O (octahedron) are involved in symbols of cubic syngonia symmetry forms, and letters h and d are added to them as shown in the table in the necessary places.

Basic words and phrases : symmetry, center, plane, torsional reflection, projection, stereography, translation, triclinic, monoclinic, rhombic, trigonal, tetrogonal, hexanal, syngonia;

LECTURE 4

Simple and complex forms, open and closed forms, their class, syngonia and division into classes.

Plan:
1. Geometric shapes of crystals
2. Open simple forms
3. Closed simple forms
4. Geometric forms of crystals of a low level of symmetry
5. Geometric shapes of crystals of average symmetry level

Crystals differ from each other in the level of symmetry, the type and number of means of symmetry. But often, crystals of different shapes and appearances, for example, an octahedron and a cube, have the same means of symmetry. Therefore, in the geometrical examination of crystals, it is necessary to study their shape along with symmetry tools.

A free-growing crystal is eventually bounded by several facets of different or uniform appearance. Accordingly, crystal forms are called simple or complex. If the shape of a crystal consists of only the same type of faces, then its shape is called a simple shape. Cube, tetrahedron, dipyramid are examples of simple shapes. If the shape of the crystal consists of several different, different haze-like sides, it is called a complex shape. For example, pyramids and prisms, etc., because their bases are the same, but the sides that form a pyramid or a prism have a different appearance. In addition, simple forms themselves are divided into two types of open and closed forms.

If the crystal is bounded only by the same sides, or if the non-intersecting same sides of the crystal are continued until they intersect, then they completely surround the top of the crystal, then the shape formed by such sides is called a closed shape. For example, a cube has six equal, rectangular sides, and so on.

Open shapes are the opposite of closed shapes, where the sides of the same type of crystal do not wrap around the top of the crystal. Even if similar non-adjacent sides are continued until they intersect, the crystal surface will not be surrounded by the same sides. Therefore, a shape consisting of the same type of sides that does not completely surround the crystal surface under any conditions is an open shape. For example, prisms and pyramids. As the sides forming these prisms or pyramids cross each other, their bases remain open. Also, the basics are open in every way. One of the open, simple forms alone cannot form an entire crystal form. There must be two or more open, simple forms in order for a single crystal form to form .

In crystals, both open forms and closed forms, as well as open forms and closed forms, can form combinations and complex forms. Each of the crystal shapes depends on the appearance of the simple shapes in the crystal, the position of the sides that make up this shape relative to each other, and finally, they themselves depend on the existing means of symmetry in this shape. There can be general forms specific to each form of symmetry. All special forms can be calculated theoretically and mathematically. Simple forms consisting of sides that are perpendicular or congruent to the means of symmetry, or intersect the same means of symmetry to form equal sections, are called special forms. On the contrary, simple shapes consisting of sides that do not pass perpendicularly to the means of symmetry or do not form equal sections in these means of symmetry are called general shapes. The existing relationship between the means of symmetry and the simple forms of crystals is given in the detailed description of each syngonia and symmetry.

Below is a description of the simple shapes that crystals can have (starting with the open, simple shapes).

Open simple forms

A monohedron is a simple shape consisting of only one crystal face (mono-Greek, one, face of a crystal face) (Fig. 1.30-a).

A dihedral is a simple shape consisting of two (di-two) equal, similar, intersecting sides (Fig. 1.30-g, v).
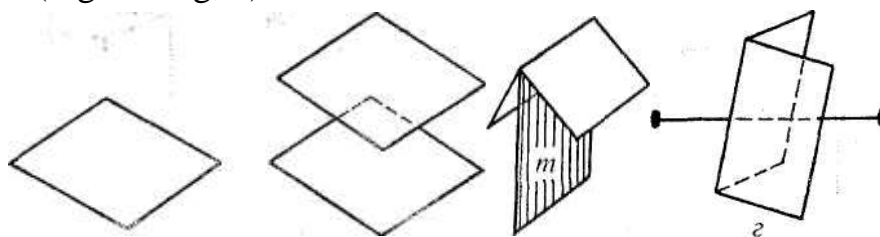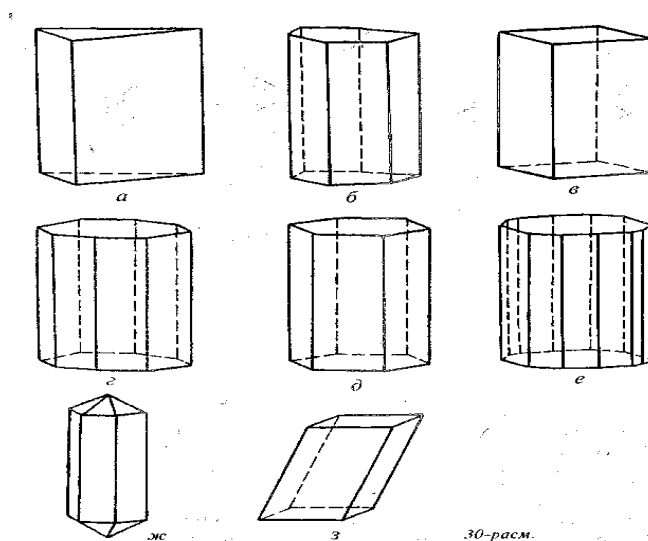

Figure 1.30.

A pinakiod is a simple shape consisting of two equal, similar, parallel sides (pinax is the Greek word for board) (Fig. 1.30-d).

Prisms are simple shapes made up of three or more similar and equal sides that intersect to form parallel edges. Prisms are three-sided, four-sided, six-sided. In this case, the first is a trigonal prism, the second is a rhombic prism if the angle between the sides is 90°, and the tetragonal prism is a rhombic prism if the angle between the sides is not 90° (Fig. 1.31 j), if the angle between the sides of this prism and the base is not equal to 90°, then it is a monoclinic prism (Fig. 1.31 z figure), the third with six sides is called a hexagonal prism (Figure 1.31-a, v, d).

Each side of a prism can be bisected by a small edge from the middle. When naming such prisms, the prefix "di" is added to the number indicating the sides. A three-sided prism with double sides is called a ditrigonal prism, a prism made of four double sides is called a ditetragonal prism, and a prism with six double sides is called a dighexagonal prism (Figures 1.31-g, b, c).

Figure 1.31.

Pyramids are simple shapes made up of three or more equal and similar sides whose edges intersect at a point. Similar to prisms, pyramids come in several varieties:

a) trigonal (three-sided) pyramid; b) tetragonal (four-sided) pyramid; c) hexagonal (six-sided) pyramid; g) ditrigonal pyramid, d) ditetragonal pyramid; j) di-hexagonal pyramid (Fig. 1.32-a, b, v, g, d, e, j), rhombic pyramid are open forms.
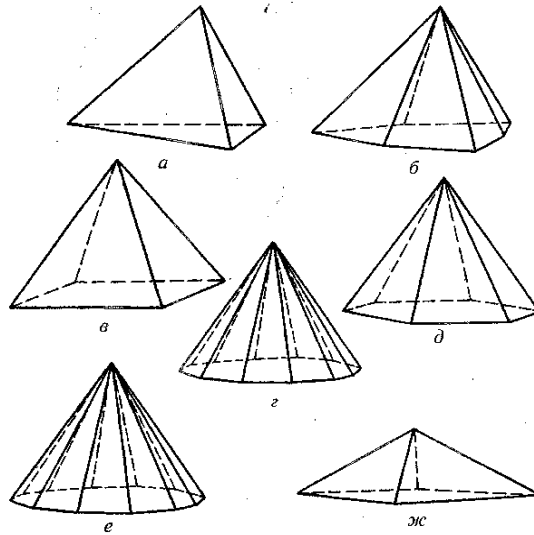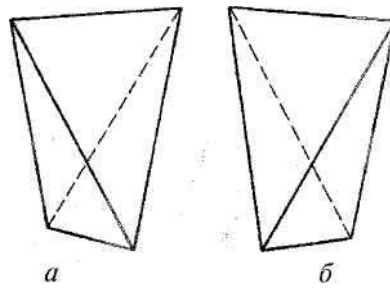

Figure 1.32.
Closed simple forms

Closed simplices are restricted to having only the same sides, and they are: Dipyramids are simplices consisting of two equal and similar pyramids joined by their bases. a) trigonal dipyramid; b) tetragopal dipyramid: c) hexagonal dipyramid; d) rhombic dipyramid, and if the sides are double, e) ditrigonal dipyramid; j) ditetragonal dipyramid; i) dihexagonal dipyramid (Fig. 1.33).
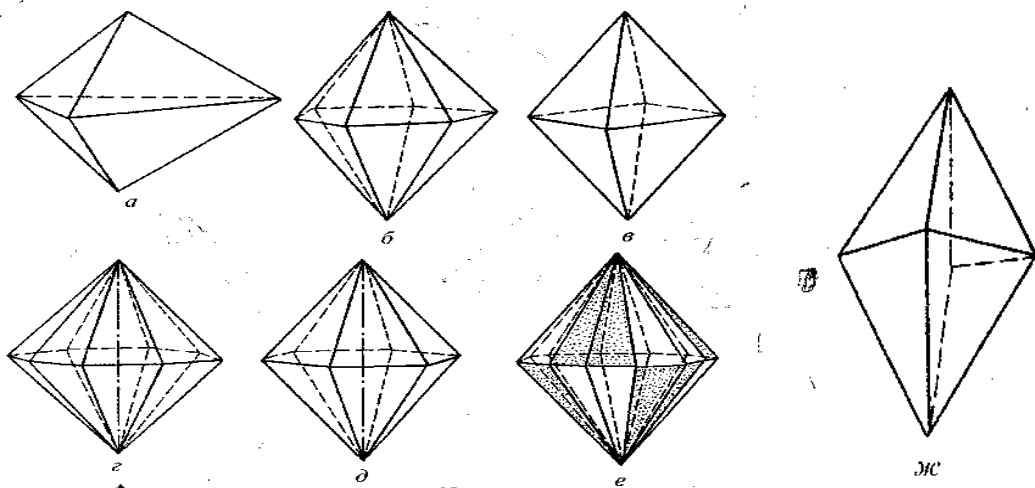
Figure 1.33

A tetrahedron is a simple shape made up of four equal triangular sides. If each side of the tetrahedron is in the form of an equilateral triangle, then the cubic

tetrahedron is in the form of an equilateral triangle, tetragonal tetrahedron, and if it consists of different sided triangles, it is called a rhombic tetrahedron.

*a*   *б*

Figure 1.34

Cubic tetrahedron belongs only to cubic syngonia crystal forms. Also, rhombic tetrahedron is characteristic of rhombic syngonia crystal forms, and tetragonal tetrahedron is characteristic of tetragonal syngonia crystals.

A rhombohedron is a shape bounded by six similar and equal rhombic sides, resembling a curved cube (Figure 1.35). The shape of a cube is formed by making the edges of the wire and extending it from the opposite ends.
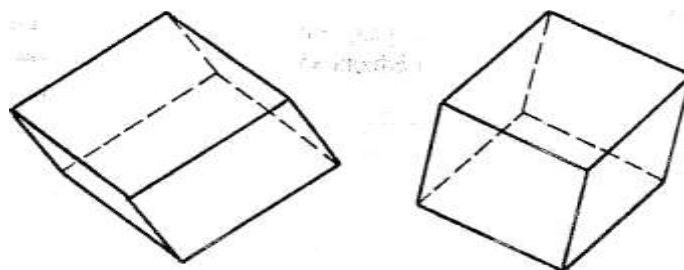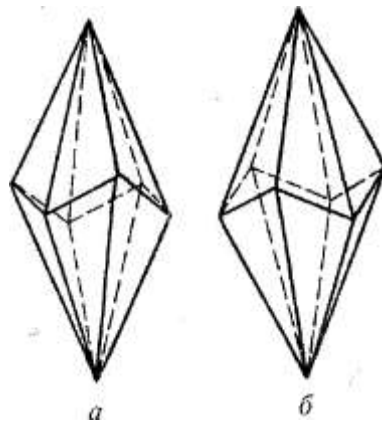

Figure 1.35.

Scalenohedra are tetragonal and ditrigonal. A tetragonal scalenohedron (Fig. 1.36).

*a*   *б*
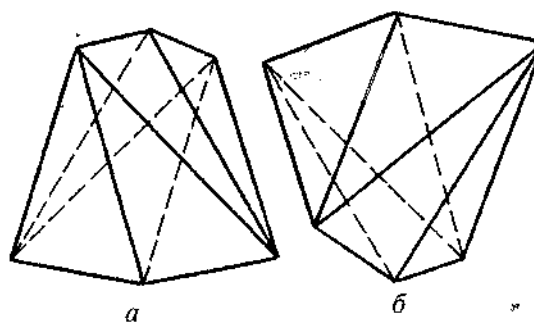
Figure 1.37

So, a tetragonal scalenohedron has eight sides, and a ditrigonal scalenohedron has twelve sides (Fig. 1.37).
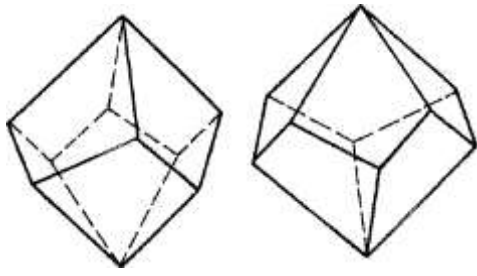
Figure 1.37

Trapezohedrons are shapes similar to dipyramids, but in which planes of symmetry cannot be imagined. They are also formed by joining the bases of two pyramids. However, in this case, the edge of the first pyramid does not coincide with the edge of the second pyramid, but is right next to it, that is, the first pyramid is slightly twisted relative to the second, the angle of rotation is less than half of the elementary angle (Fig. 1.38).
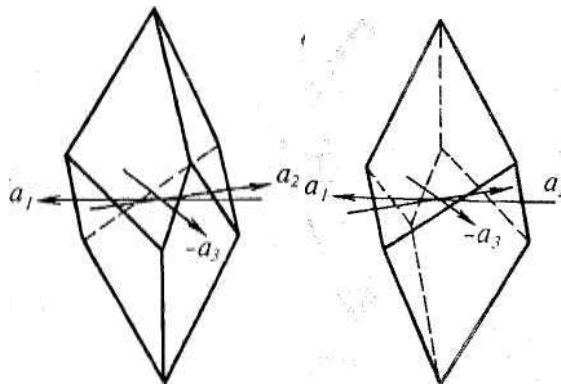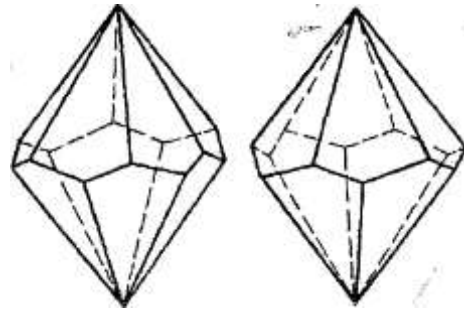

Figure 1.38.

Types of trapezohedrons are trigonal six-sided (Fig. 1.38), similar to a trigonal dipyramid, tetragonal eight-sided, similar to a tetragonal dipyramid (Fig. 1.39), hexagonal twelve-sided, similar to a hexagonal dipyramid (Fig. 1.40). Also, since they are enantiomorphic forms, they appear in both left and right forms.

The previously described five of the above simple forms, monohedron, dihedral, pinacoids, and rhombic prism, rhombic pyramid, and rhombic dipyramid (Figures 1.35, 1.36) are typical for low-symmetry layer crystals. These and all other shapes (except for the cubic tetrahedron) are typical for crystals of an average degree of symmetry.

Figure 1.39   **Figure 1.40.**

The appearance of the simple forms of cubic syngonia is determined by the existing axes of symmetry of a higher order. Each side of the crystal is repeated around several axes of symmetry present in this syngonia. Therefore, crystals belonging to cubic syngonia with a high degree of symmetry have unique shapes. They can be seen only in this syngonia. The following simple forms are seen in cubic syngonia:

Tetrahedron is a shape consisting of equilateral triangular sides of a similar grid (Fig. 1.41-a);

An octahedron is a shape made up of eight equal and similar equilateral triangles (Fig. 1.41 j). It differs from a tetragonal dipyramid in that its sides are in the form of an equilateral triangle. The tetragonal dipyramid was a shape with eight equilateral triangle sides.

Forms resulting from the complexation of a **cubic hexahedron (figures 1.41 n, o, p, r, s):**

Each of the rectangular sides of the **tetrahexahedron cube is quartered, that is, divided into four triangles by small edges (Fig. 1.41, o).**

A rhombododecahedron is a figure consisting of twelve rhombus with similar and equal sides (Fig. 1.41, ya).

A pentagon is a dodecahedron- like shape made up of twelve equal pentagonal sides (Fig. 1.41 r).

Didodecahedron pentagon is a figure formed by doubling any of the sides of a dodecahedron (Fig. 1.4-c).

a tetrahedron (a) and its complexation (Figures 1.41-a, b, v, g, e, d).

Trigon tritetrahedron (b) a shape formed by triangulation of each of the triangular sides of a tetrahedron, i.e. by dividing into three triangles with small edges.

Tetrahedron tritetrahedron (e) in which each of the sides of the tetrahedron is tripped, that is, it is divided into three quadrilaterals by small edges.

the pentagonal tritetrahedron (g, d), the sides of the tetrahedron are three, and each side is divided into three pentagons. It is also an enantiomorphic form, occurring in both left and right forms.
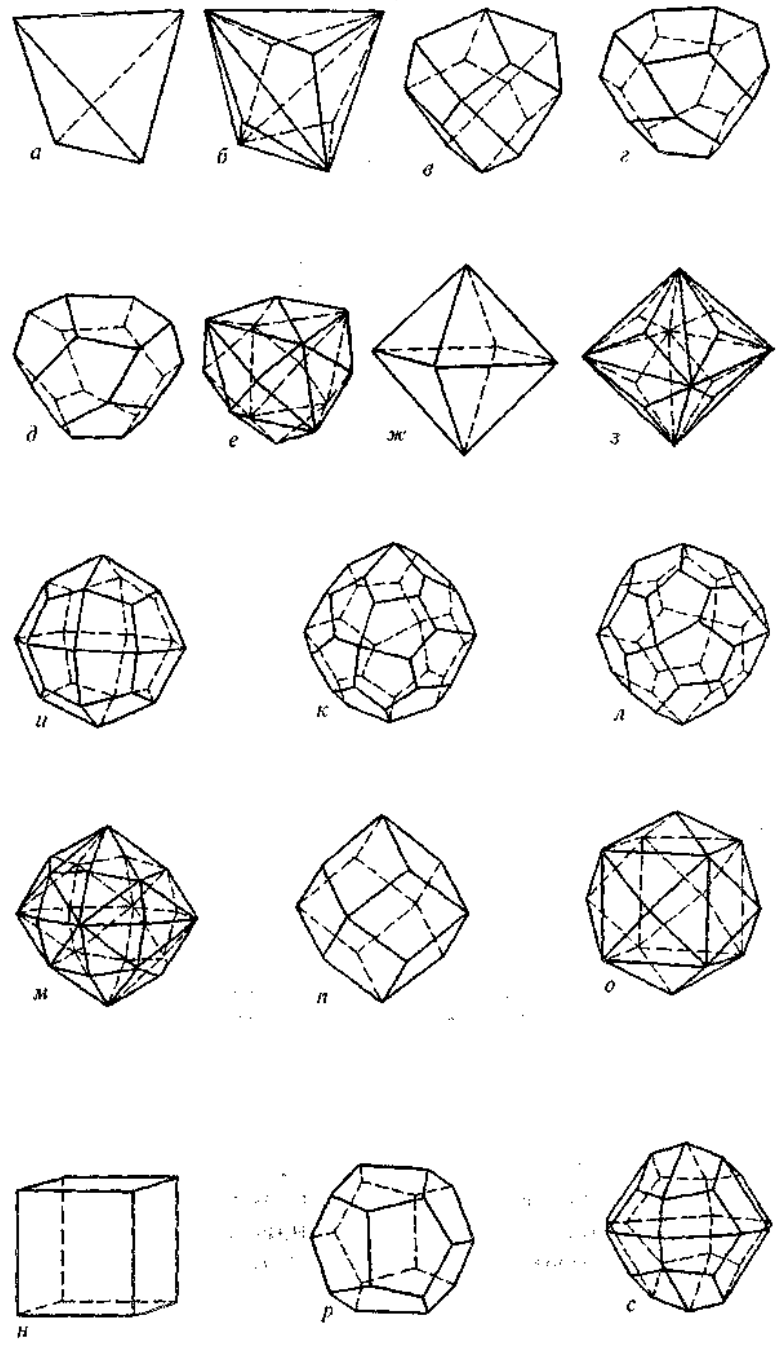
Figure 1.41

Figure 1.42

Hexatetrahedron (e) is a tetrahedron with six sides each, i.e. divided into six triangles (Fig. 1.41 e).

an octahedron (j) and its complexation (Fig. 1.41-z, i, k, l, l):

Trigontrioctahedron (z) Each side of the octahedron is divided into three triangles, that is, it is triangulated.

Tetragontrioctahedron (m) in which the sides of the octahedron are tripled, that is, divided into three quadrilaterals, which is also a twenty-four-sided shape.

A pentagontrioctahedron (k) is an enantiomorphic form in which the octahedron is divided into three pentagons with three sides. That's why there are left and right views.

Hexaoctahedron (m) is a figure formed by dividing the sides of an octahedron into six triangles with small edges.

Sometimes, the sides of the crystal are covered with lines, which should also be taken into account when determining the means of symmetry. The types of lines on the sides of cubic syngonia crystals are shown in Figure 1.42, which belong to different classes.

Geometric shapes of crystals with a low degree of symmetry

In crystals of this class, only symmetry means such as 2/m, 2, m, 1 can be imagined. Accordingly, the crystal forms of this class consist mainly of the complexation of simple open forms, and the closed forms are in the form of simple forms or are much less complex (see Fig. 1.30, 1.31).

1. Triclinic syngonia . The first monohedral symmetry view has no symmetry tools. Sometimes its degree of symmetry is written as 1, which means that each end, edge, and side of the crystal shape is repeated only once when the shape is rotated 360^0, meaning there are no means of symmetry. Hence, no facet of the crystal repeats itself around the means of symmetry. From this, it can be concluded that only monohedra can be simple forms in crystals of monohedral symmetry.

the second pinacoidal $\bar{1}$ symmetry transfers each side mirror of the crystal form "C" to the opposite side in an equal and suitable direction. So, even in this view of symmetry, only one of the simple forms can be pi-nakoids.

2. Monoclinic syngonia. 1) Axial dihedral symmetry can have only one secondary axis of symmetry 2. Accordingly, the forms of this class include a monohedron perpendicular to the axis of symmetry, as well as a dihedron with a pinacoid. 2) In the form of non-axis dihedral symmetry, there is only one plane of symmetry, and accordingly, the crystal forms of this form of symmetry include pinacoid and monohedron (dihedrals of a special general shape oriented perpendicular to the plane of symmetry also participate. 3) In the form of prismatic symmetry, 2m participates in the means of symmetry. Due to the repetition of the

sides of the crystal shape under the influence of these symmetry tools, pinacoids with a general shape of a monoclinic prism and a specific shape are formed.

3. Rhombic syngonia . 1) In the form of rhombotetrahedral symmetry, three axes of secondary symmetry 222 perpendicular to each other can be imagined. A rhombic tetrahedron is a closed shape, which is the general form of its appearance. In addition, rhombic prisms and pinacoids can also be involved in complex forms. 2) Rhombus pyramidal 2m symmetry is open, there are crystals consisting of a complex of simple forms: common forms are rhombic pyramids, special forms are rhombic prisms, pinacoids, dihedrals and monohedra. 3) Crystals of mmm symmetry with a rhombic dipyramid have simple forms consisting of only pairs of sides: the general form of a rhombic dipyramid, a rhombic prism (four-sided) and pinacoids, special forms with two corresponding sides. Thus, this class of crystals is distinguished among the forms of symmetry and is easily identified.

Geometrical forms of crystals of average symmetry level

must have a single higher symmetry axis, 3, 4, 6, or 6, that coincides with the so-called single direction . $\bar{3}:\bar{4}:$ Since there are other secondary symmetry axes, they intersect only with the higher symmetry axis forming an angle of 90°.

It is known that the crystals of this class are divided into tetragonal, trigonal and hexagonal syngonies.

Trigonal and hexagonal syngonia. In these syngonia crystals, the only direction $\bar{6}$ coincides with one of the higher order symmetry axes such as 3, 6, and . $\bar{3}$ That's why the appearance of the crystal has six or three sides of simple shapes according to the level of the main axis of symmetry. The typical forms of trigonal and hexagonal syngonias consist of rhombohedrons and ditrigonal scalenohedra. Below are simple forms that these syngonias may have for symmetry representations. These two syngonia crystals are so close to each other with their symmetry and simple shapes that many books treat them as one hexagonal syngonia and divide them into trigonal and hexagonal syngonia. The simple forms of these two syngonias are described below, starting with the trigonal syngonia.

1. The means of symmetry imagined in the trigonal pyramidal 3-symmetry view crystals consists only of the axis of symmetry of the third degree. According to this, the crystals of this symmetry feature include monohedron, trigonal prism, and trigonal pyramids.

2. Crystals of rhombohedral 3-symmetry appearance can include rhombohedrons (general form), hexagonal prisms and pinacoids from specific forms. Since this class of crystal forms has a center of symmetry C, monohedra and pyramids are not possible in this form of symmetry.

3. Ditrigonal pyramidal - 3m symmetry crystals have a lot of simple forms and because they are open forms, they participate only in the complex hand. These forms are monohedron, trigonal prism, ditrigonal prism, hexagonal prism, dihexagonal prism, trigonal pyramid, and the general form is ditrigonal pyramids.

32 symmetry view **with trigonal trapezoid .** The following simple forms can be involved in the forms of this symmetry appearance: pinacoid, trigonal prism, hexagonal prism, trigonal dipyramid, trapezohedron, rsjboedr. In addition to these, there are also crystals with the general shape of a trigonal trapezoid.

5. Ditrigonal scalenohedral - 3m symmetry crystals can have the following simple forms: pinacoid, hexagonal prism, dihexagonal prism, hexagonal dipyramid, rhombohedron and ditrigonal scalenohedron (general form).

Tetragonal syngonia. 1. In the form of tetragonal pyramid 4 symmetry, the general shape intersecting with the main axis of symmetry 4 can consist of a tetragonal pyramid and a set of sides of a tetragonal prism corresponding to this direction with a monohedron passing perpendicularly to a single direction from specific forms.

2. Tetragonal dipyramid - in the form of 4/m symmetry, the plane of symmetry intersecting the axis of symmetry of the fourth degree forming a right angle, or its equivalent, as a result of repeating the sides of the shape with the center of symmetry, the tetragonal pyramid turns into a dipyramid (general shape) into a monohedral pinacoid, and a prism into its own will remain the same. So, in the crystals of this symmetry view, the general form is a tetragonal dipyramid, and the specific forms are pinacoid and tetragonal prisms.

3. In the form of ditetragonal pyramidal 4mm symmetry, the straight line intersecting the plane of known symmetry corresponds to the direction of the main fourth degree symmetry axis. So, a tetragonal pyramid and a prism can be double in width, and the base can be in the form of a tetragon and a tetragon. Since the principal axis is not a plane of symmetry perpendicular to a single direction, or there are no secondary axes of symmetry, the two ends of the principal axis in crystals of this symmetry view are not identical. Hemimorphic forms are those whose two ends look different. A high-level arrow is directed vertically

the plane of symmetry m or the direction of any axis of symmetry other than the secondary axis of symmetry 2 is called a polar direction. So, the crystals of this symmetry view are hemimorphic first and polar orientation second. Therefore, simple forms can be in this class: general form of ditetragonal pyramid, special forms include monohedron, tetragonal prism, ditetragonal prism and tetragonal pyramid.

4. In the tetragonal trapezoidal 422 symmetry form, due to the presence of four secondary symmetry axes perpendicular to the main 4 symmetry axes, although not connected to the plane of symmetry, the two ends of the crystal have the same

appearance, resulting in simple shapes called trapezoids. Because trapezoids are enantimorphic shapes left and right (equal to each other and the first is a mirror image of the second). In addition to the general form of trapezoids, pinacoid, tetragonal prism, ditetragonal prism, and tetragonal dipyramids can also participate in this symmetry view.

, four secondary symmetry axes 2 and the center of symmetry C are formed by increasing q of symmetry planes perpendicular to the main symmetry axis and corresponding to the direction of this axis . Accordingly, in the crystals of this symmetry view, the forms with a higher degree of symmetry can be special simple forms such as ditetragonal dipyramid (general form), tetragonal dipyramid, ditetragonal prism, tetragonal prism, and pinacoid.

6. Crystals with tetragonal tetrahedron 4 symmetry, according to these existing symmetry tools, include special simple forms such as tetragonal tetrahedron (general form), tetragonal prism and pinacoids.

7. Crystals with tetragonal scalenehedron - 42m symmetry can include simple forms (general form) such as tetragonal scalenohedron, tetragonal tetrahedron, tetragonal dipyramid, tetragonal and ditetragonal prism, and pinacoids.

Hexagonal syngonia. These syngonia crystal forms differ from trigonal syngonia crystals with 6 or 6 symmetry axes. They consist of:

1. Crystals belonging to the form of 6-symmetry with a hexagonal pyramid include monohedra, hexagonal prisms and hexagonal pyramids (general form).

2. Hexagonal dipyramid - crystal forms of 6/m symmetry are pinacoid, hexagonal prism, and the general shape consists of hexagonal dipyramids.

3. Dihexagonal pyramidal - pinacoid, dighexagonal prism, hexagonal prism, dighexagonal pyramid (general form) and hexagonal pyramids in forms of 6/μg symmetry are simple forms that form crystals of this class.

4. In crystals of 622 symmetry appearance with hexagonal trapezohedron, simple shapes such as pinacoid, hexagonal prism, hexagonal dipyramid and hexagonal trapezohedron (general form) can be found.

5. Dihexagonal-dipyramidal - 6mm symmetry view forms complicated shapes consisting of pinacoid, hexagonal prism, dihexagonal prism, hexagonal dipyramid and dihexagonal dipyramid (general form).

6. Trigonal dipyramid 6-symmetry crystals have many simple forms, including pinacoid, trigonadrism, ditrigonal prism, hexagonal prism, and trigonal dipyramid (general form).

7. Simple forms with ditrigonal dipyramid 6t2 symmetry can be composed of pinacoid, trigonal prism, trigonal dipyramid, ditrigonal dipyramid (general form), ditrigonal prism.

# LECTURE 5

Crystal lattice concept. Transmission grids

Plan:

1. Concept of crystal lattice. Crystal polyhedron and crystal lattice.
2. Transmission . _
3. Symmetry groups of Fedorov.
4. Brave's 14 different grills.

The first fundamental law of crystallography shows that the material points that make up the crystals repeat infinitely periodically in space, which is visualized in the form of a spatial lattice. Spatial grid is a geometric device that describes the infinite periodic repetition of material points in space based on a certain regularity, that is, an image of a part separated from an infinite geometric shape. From this point of view, the spatial grid has its own geometric properties and differs from limited geometric shapes. Accordingly:

1. In the examination of crystal systems - in the description, only a part of the structure of a particular crystal - the elementary cell - is taken into account. Fig. 1.43 shows the unit cell of halite (NaCl), Fig. 1.44-a, copper (Cu), Fig. 1.44-b, diamond (C) crystals.

2. An elementary cell and a crystal structure in general are considered to be the smallest fragment of an image of an infinite geometric shape consisting of a complex of material points located in a certain direction in space. Their symmetry is a variation of the symmetry of material points that repeat in space based on a certain regularity.
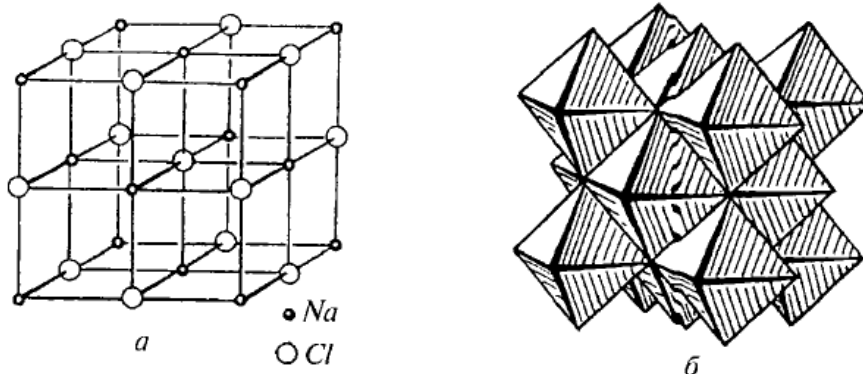
Figure 1.43

The concept of translation is used in the study of the internal structure and symmetry of crystals, which is explained on the basis of the spatial lattice. Translation - shows the movement of material points that make up a whole system or

that crystal structure in a certain direction. To accurately visualize the periodic repetition of material points in the crystal structure, it is necessary to determine the value of the translation period - the displacement distance (t)
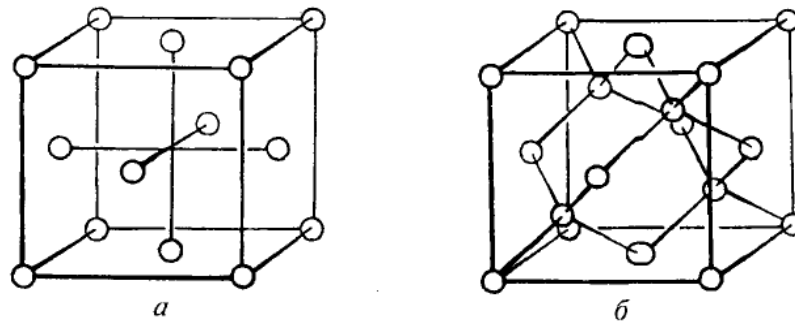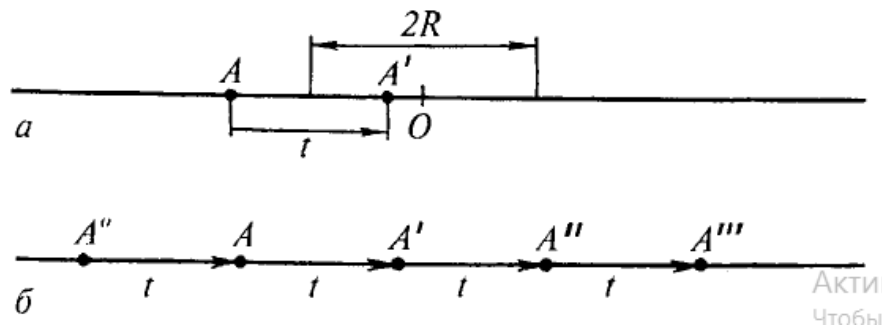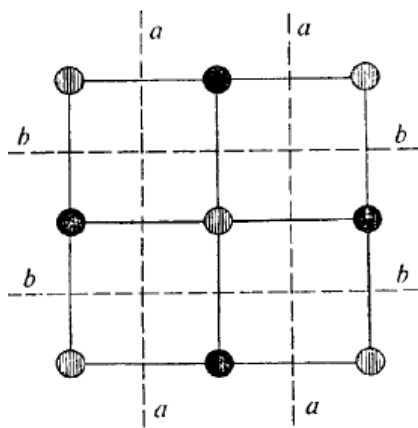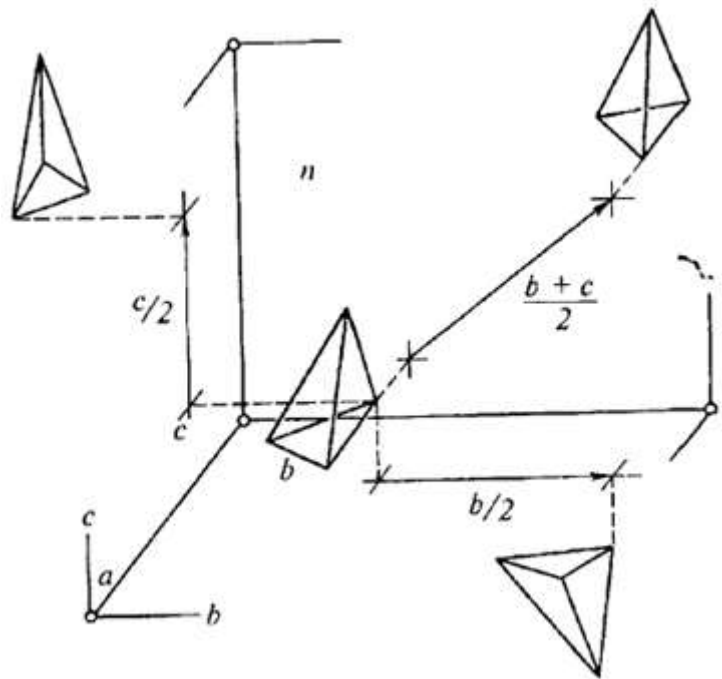

Figure 1.44

Figure 1.45

In connection with this, it is necessary to use somewhat complicated symmetry tools when describing the symmetry of the spatial lattice. They consist of axis of symmetry, plane of symmetry, and center of symmetry, as well as translational axes and planes of symmetry, as we have seen in limited geometric shapes.

Planes of translational symmetry . Infinite geometric shapes have translational planes of symmetry other than the formal plane of symmetry. Such planes of symmetry are repeated in 1/2 translation after the reflection of the surrounding material points has moved a certain distance along this plane (Fig. 1.46). The displacement distance of material points along these translational planes is always equal to 1/2t. If the translation of the material point in the imaginary plane occurs in the direction parallel to the first of the crystallographic axes, "a"; if it is directed along the second crystallographic axis, "b"; if it is a direction along the third crystallographic axis, it is called a "c" type plane and is denoted by such letters.

Figure 1.46   **Figure 1.47**

In addition, translational planes are oriented diagonally with respect to the crystallographic axes. These are determined in the form "n" and "d": for "n" the displacement distance of the material points along this plane is equal to l/2t. And for "d" it is equal to l/4t (Fig. 1.47). Thus, in infinite geometric forms, in addition to the formal symmetry plane "m", there are also the following translational planes: "a", "b", "c", "n", "d".

Axes of translational symmetry . The translational axis of the gray axis is a complex symmetry tool, which involves the repetition of material points around the axis of symmetry, as well as the displacement along this axis of symmetry - translation. Their degrees of symmetry are the same as the degrees of ordinary axes of symmetry. Below is their description and description.

Axis of translational symmetry of the second degree - this axis is written in the form of 2. Figure 1.48 depicts a formal axis of symmetry (2), in which the material points are repeated twice in the same plane around this axis. And in Figure 1.49: point 1 should have moved to point 2 when rotated 180° around the axis of symmetry. But the opposite of point 1, which should move to point 3, moves along the axis of symmetry and moves to point 2 in half the distance t. Also, when this material point is rotated by 180°, it will again have its reflection at 3 points after a distance of t. So, the point rotates around this axis and moves 1/2t when it turns 180°.
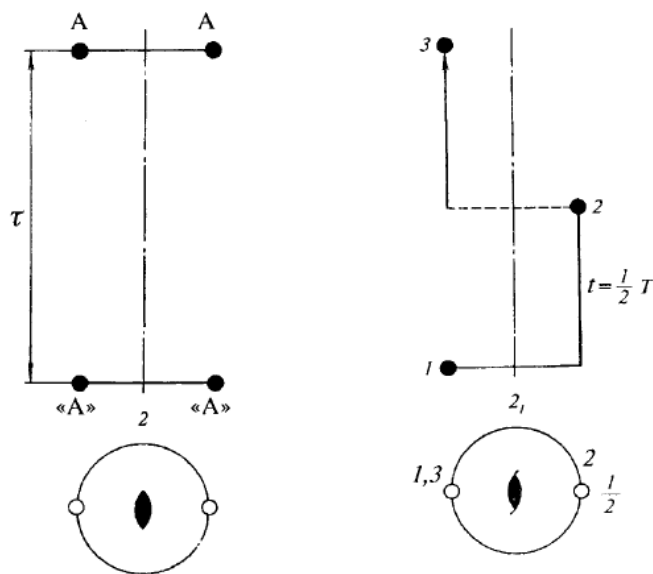
Figures 1.48 and 1.49

figure as "T" is called the translation (shift) distance. The position of point "1" in the picture is considered to be 0 (zero), the position of point 2 is 1/2 (half translation) and the position of point 3 is 1 (unit). The shadow of points 1 and 3 perpendicular to the plane of the drawing falls on one point, as shown in the figure. The opposite to point 2 is indicated by the sign 1/2. The image of this axis using the tetrahedron is shown in Fig. 1.52. As you know, arrows can advance when turning left or right. They do not differ from each other, as the result is the same when the translation axes of the second scale are turned left or right. In general, if the displacement (translation) of material points proceeds with the clockwise rotation of this axis, it is called the right translational axis, otherwise it is called the left translational axis.

Tertiary axes of translational symmetry. Since such an axis exists in the crystal structure, when the mode point is rotated by 120° around this symmetry axis, it is shifted by a third translation in the direction of the axis - 1/3t. After that, when turning 120°, the material point is moved to a distance of 2/3t. When this material point is rotated by 120° again, the entire translation (t) is moved by a distance of 2/3t right translation, equal value to 1/3t left translation, but with the opposite negative sign: $32 = 3_{-1}$

The official tertiary axes of rotational symmetry are denoted by the number 3, such that the translational axis of symmetry is of two types, 3_1 and 3_2 or 3_3. The first of them is the right, the second is the left screw axis. So, the material point moves from state 1 to state 2/3, then to state 1/3, and finally to state 0 under the influence of such a right screw axis. Around the left screw axis, on the contrary, the point in position 1 moves first to position 1/3, then to position 2/3, and finally to position 0. The representation of these axes using polyhedra is shown in Fig. 1.52. The left and right translational axis forms are enantimorphic, that is, the plane

55

reflection of such forms placed next to each other is equal and compatible with each other.
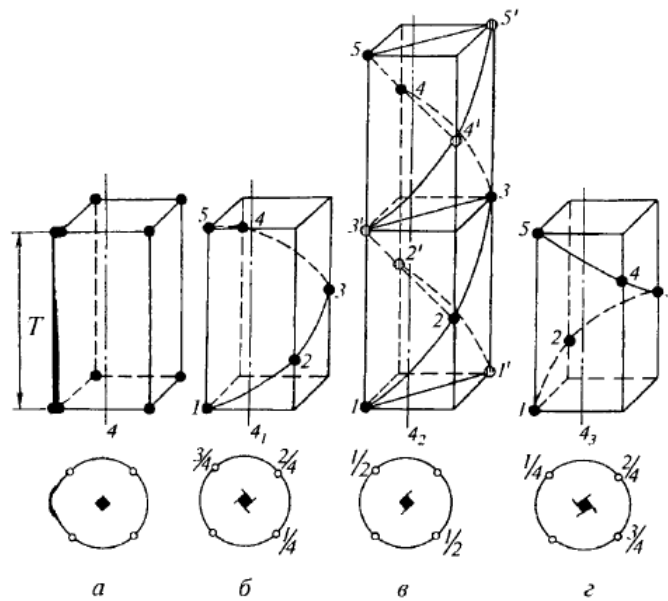
Figure 1.50

Axes of translational symmetry of the fourth degree. In crystal structure, the spatial lattice as a whole has formal quaternary (4) axes as well as translational axes around which material points move 1/4t for every 90° clockwise rotation. . Such axes are denoted as 4_1 and are called right axes.

Such translational axis can be left. Such an arrow is marked as 4_3 - 4_1. In addition to these, there are 4_2 types of translational axes, in which case the material points are repeated around the axis twice (the angle between the points is 90°) at 180° after 1/2 the distance (Fig. 1.50). Representation of these axes by polyhedra is shown in Fig. 1.52.
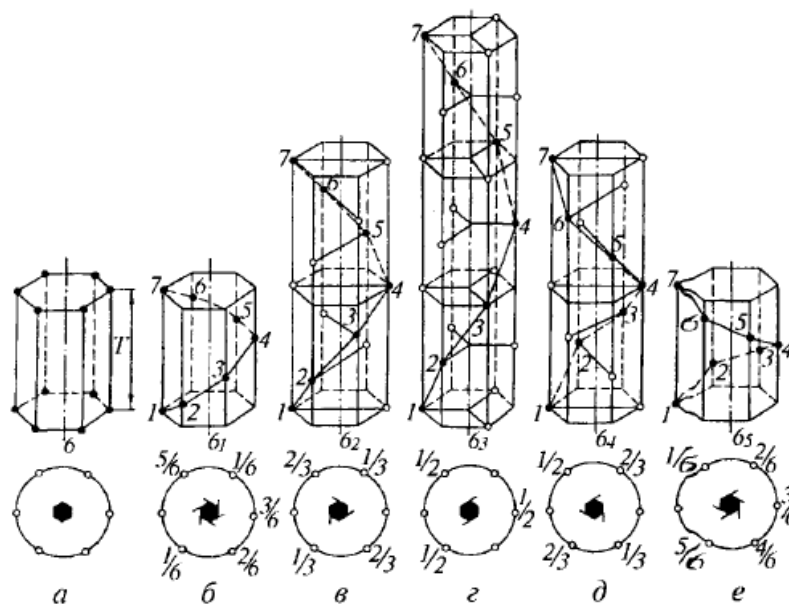
Figure 1.51

Axes of translational symmetry of the sixth degree. A material point repeats every 60° around such axes, as in the case of formal sixth-order symmetry axes. But the repeating material points are shifted by 1/6, 2/6, 3/6, 4/6 and 5/6 translational distances along this axis. In this case, since $2/6 = 1/3$, $3/6 = 1/2$ and $4/6 = 2/3$, such a conclusion can be reached; when the material points are rotated twice by 120° around this axis, they move by a distance of 1/3 t6 $_2$ when it is the right axis, t/2, 3 when it is the left axis, $6_4 = 6_{-2}$. In addition, the material points can be repeated in three (the angle between the three points lying in the same plane) shifted by 1/2 translation distance (Fig. 1.51). The representation of this axis with polyhedra is shown in Fig. 1.52.

The axis thus imagined is not 6_3 enantimorphic. Therefore, the axes of translational symmetry of the sixth degree 6_1, 6_2, $6_4 = 6_{-2}$ and $6_5 = 6_{-1}$ are mutually enantimorphic.

Fedorov space groups. The degree of symmetry of a particular crystal depends on the symmetry of the group of material points located at the ends of the unit cells that make up that crystal. For example, the spatial lattice of monoclinic syngonia crystal has a secondary symmetry axis -2 perpendicular to the plane of translational symmetry, which belongs to the prismatic 2/m class of monoclinic syngonia. Each material point belongs to class m or 2 if the group m has only one translation plane, or only 2. There are three classes of this monoclinic syngonia - 2/m, m or 2, depending on the type of elementary cell (simple, with bases centered) and what symmetry means (formal or translational) are available, the arrangement of material points can be several different.

Thus, each crystal form of the 32 classes has several different internal structures, that is, a specific arrangement of material points. Each of these orders - Fedorov groups to a specific type of elementary cell (P, I, F, C, R) and means of symmetry - axes of translational symmetry, for example, 4, 4_1, 4_2, 4_3 or translational and the normal plane of symmetry will have m, n, d, a, b, c, etc. Taking this into account, finally, the law of location of these material points in space reaches 230. The famous mineralogist-crystallographer ES Fedorov calculates this mathematically and describes it in the book "Symmetry of Regular Forms" in 1890. The manner in which Fedorov groups are presented internationally in scientific books is illustrated below by the example of a crystal of class Pmmm belonging to rhombic syngonia. But a detailed description of all these groups is beyond the scope of this book
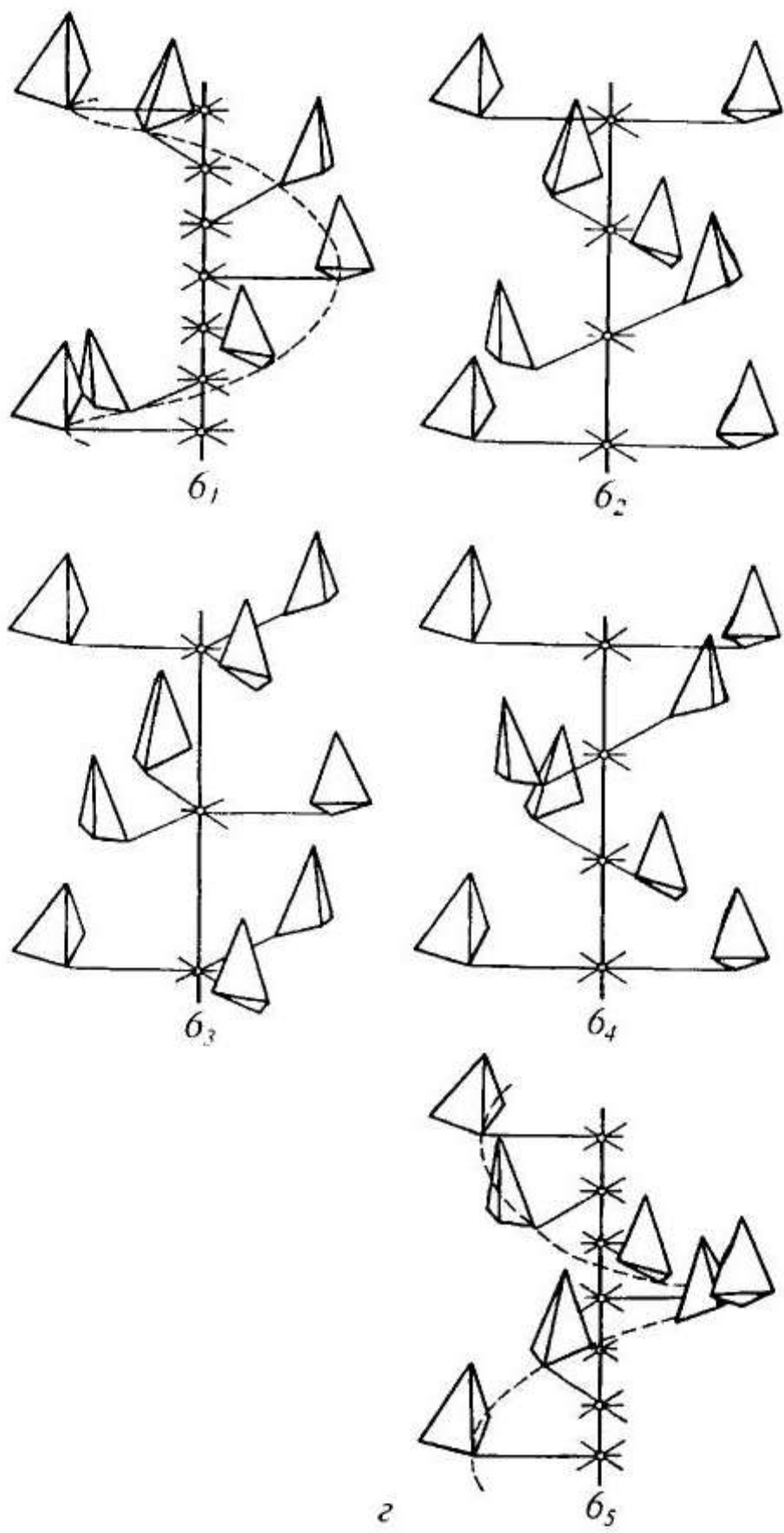
2_1

3_1

3_2

4_1

4_2

4_3

в

59

Figure 1.52.

60
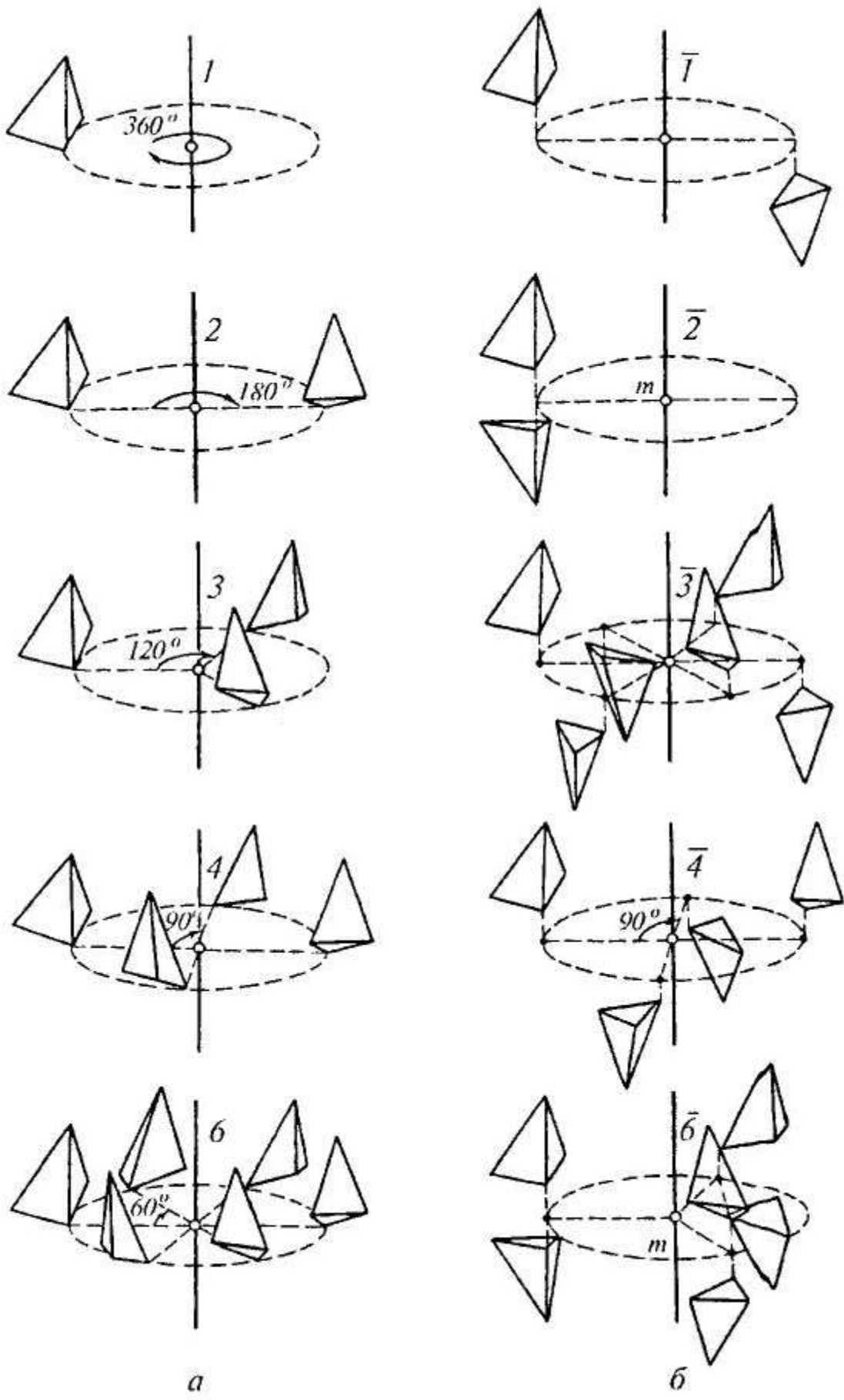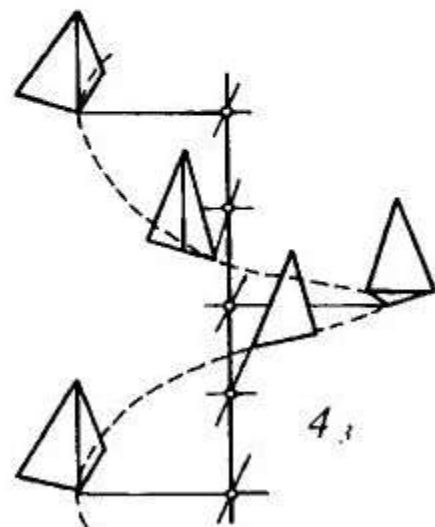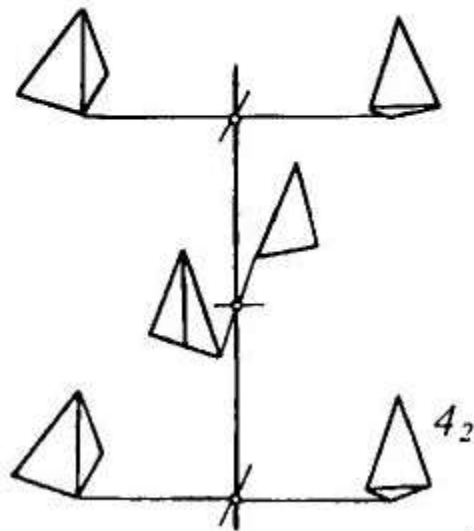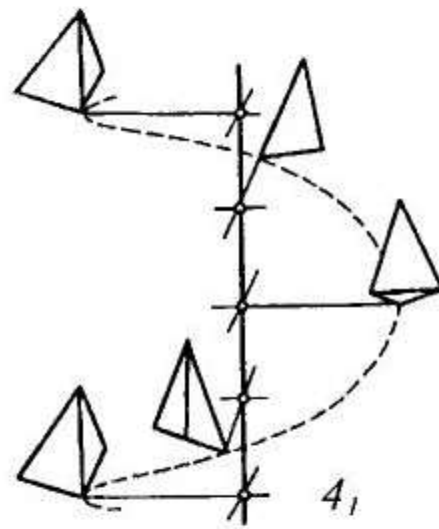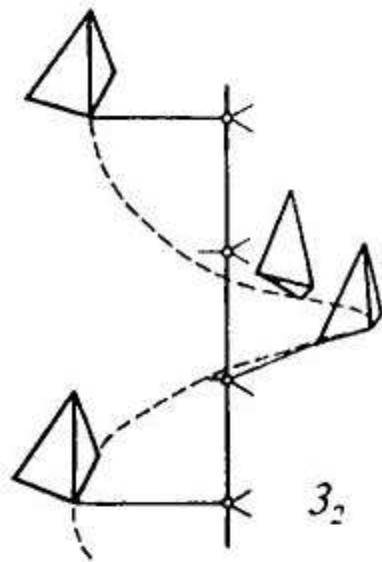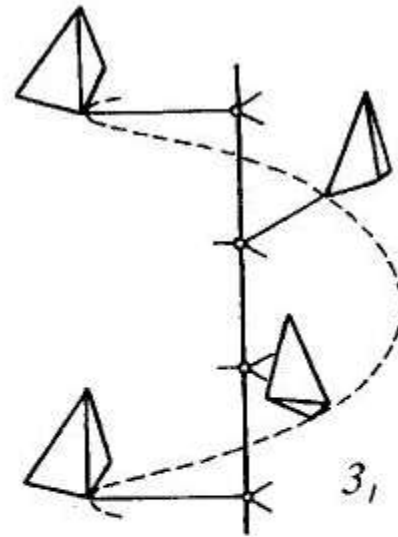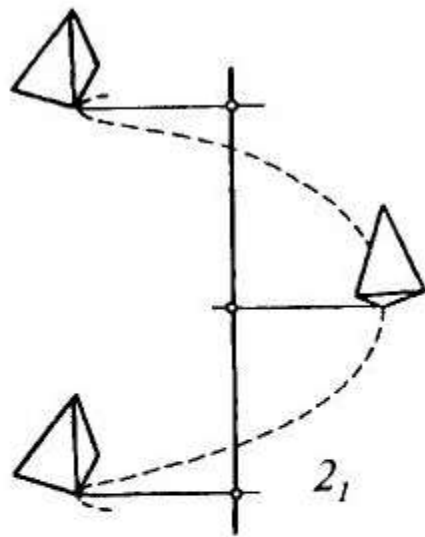
Brave's 14 bars. Crystal spatial lattices are composed of infinite repeating unit cells in space. Each syngonia or symmetry view - class has a unique unit cell - repeating parallelopipeds that repeat infinitely in space to form a whole crystal structure. Each elementary cell has its own dimensions: the ratio of the length of its edges and the value of the angle between its sides. Since all types of unit cells that can be in crystal structures were discovered by O. Brave in 1855, they are called Brave lattices. These 14 grids are divided into the following types: 1) primitive-simple type P - in which the material points are located only at the ends of the elementary cell, and their position is determined as (000). There are 7 types of cubic cells: they are triclinic, monoclinic, rhombic, tetragonal, hexagonal, cubic and rhombohedral. Taking into account that there are 5 types of plane planes of the spatial grid and that the material points can be located in the center of the base of the elementary cell, in the middle of any of its sides and in the center of its volume, then it is possible to imagine that these elementary cells have the following types and types (Fig. 1.53) ; 2) belongs to monoclinic, rhombic syngonia crystals with centered C − type; 3) type F with centered sides - typical for rhombic and cubic syngonia crystals; 4) size-centered type I - belongs only to rhombic, tetragonal and cubic syngonia crystals.

All these unit cells (except hexagonal) are in the form of parallelepipeds, so they are sometimes called unitary parallelepipeds or repeating unitary parallelepipeds. A hexagonal lattice can also be divided into parallelepipeds. From this, two types of cells are formed:

1. C-type orthohexagonite cell. For this, the ratio of the lengths of the sides will be b -a a-$\sqrt{b}$.

2. hexagonal primitive, where a = b, the base is in the form of a rhombus, the angles are equal to 60° and 120° (Fig. 1.53, *e).*

So, Brave grids are distributed by syngonia as follows:

1. triclinic syngonia (*a*) may have only one P-type cell:
2. For crystals of monoclinic syngonia (*b) two cells of type P and C;*
3. rhombic syngonia (*v)* crystals, there are four types - P, C, F and I;
4. For tetragonal syngonia (g) crystals, two types −P and I;
5. trigonal syngonia (*d*) crystals, one is of the R type;
6. hexagonal syngonia (*e)* crystals, one − P type;
7. cubic syngonia *(j)* crystals, the presence of cells of three types - P, F and I is characteristic for these syngonias.
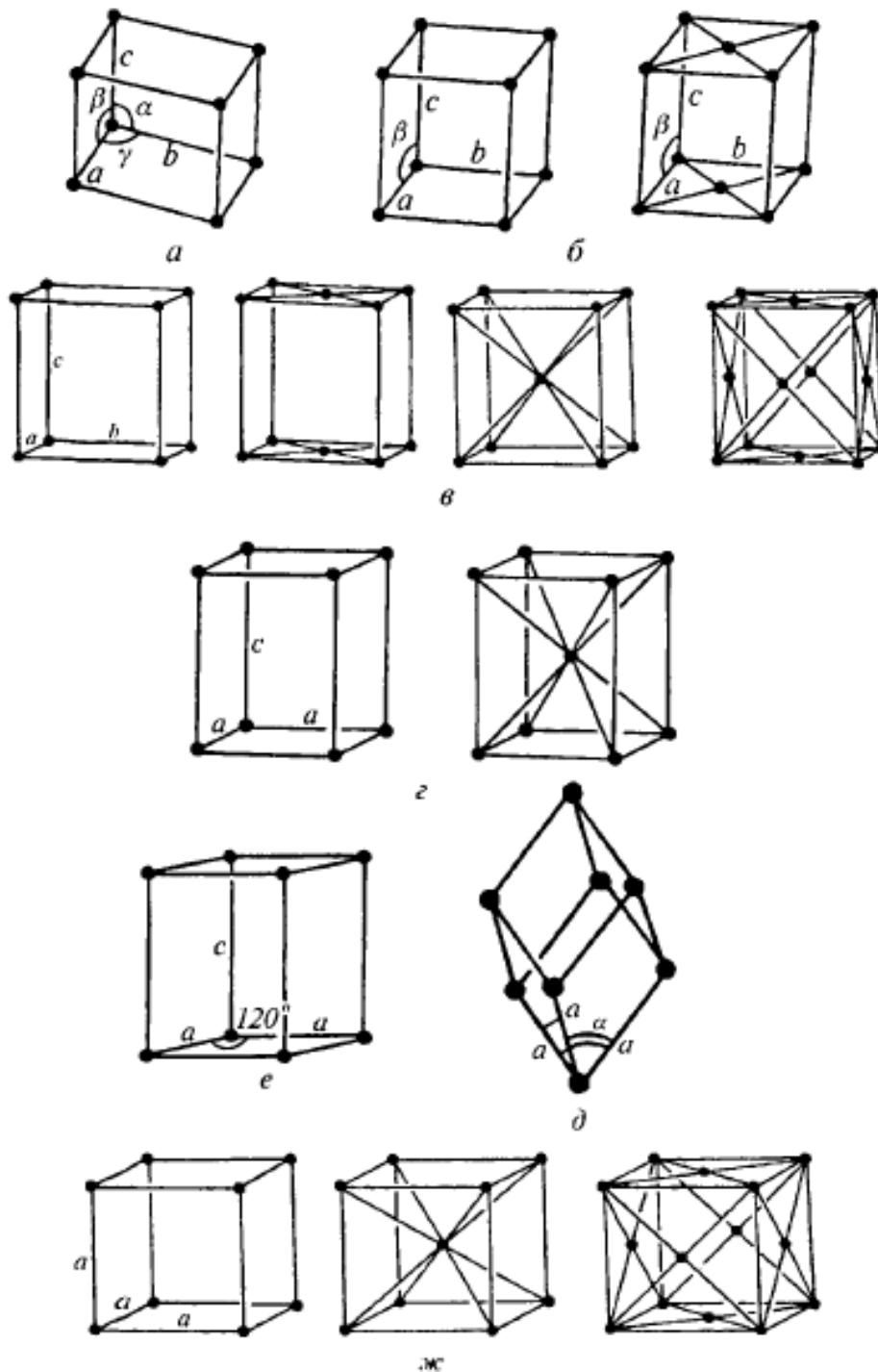
Figure 1.53

According to Fedorov's definition, the above-mentioned elementary cells can be formed from four primary types (changing them under the influence of force): 1) cubic primitive hexahedral cell according to Fedorov's definition; 2) volume-centered cubic (octahedral); 3) from a cubic (dodecahedral) and 4) hexagonal primitive (prismatic) cell with centered sides.

LECTURE 6

Factors determining the structure of crystals

Plan:

1. Determination of atomic and ionic radii.
2. Dependence of the sizes of atoms and ions on the coordination number.
3. Factors determining the structure of crystals.

The degree of symmetry of crystals is generally related to their chemical composition. The simpler the chemical composition of crystals, the higher the degree of symmetry, the more complex the composition, the lower the degree of symmetry. This law is called the Fedorov-Groth law. Fedorov comes to this conclusion in the process of preparing the tables he developed for his book "The World of Crystals". Later, the German crystallographer Groth (1843−1926) expressed the same opinion.

Artificial as well as many natural crystals confirm the idea stated in this law. For example, many pure elements crystallize in cubic syngonia (Li, Na, K, Cu, Ag, Au, etc.) or hexagonal syngonia (Be, Mg, Zn, Ca, Te, Re, etc.). Also, many oxides MgO, CaO, UO_2; Bi_2O_3, Cu_2O; sulfides: PbS, ZnS, FeS_2, Cu_2S and halogen compounds such as NaCl, KCl, CaF_2, CsCl all crystallize in cubic syngonia.

But despite this, there are such simple compounds, even pure elements, that their degree of symmetry is low. For example, S, Se, Cl, Br, I. There are sulfides and other simple compounds with such a low degree of symmetry. This is even more evident in the crystals of the chemical elements in Mendeleev's table.

In nature, compared to simple chemical compounds, crystals with a complex composition and low symmetry are more common than crystals with high symmetry. From the crystals known so far, the most common and tested 1308 crystals are divided according to the degree of symmetry: low-grade 760 mineral type - 57.5%; the middle layer 377 mineral types − 29.5% and finally, the upper layer 171 mineral types − 13% are crystallized.

All elements are listed in order of atomic number.

Rows in Mendeleev's table are separated by a dotted line, and periods are separated by two dashes.

The following symbols are used in the table:

A-1 Side-centered cubic dense arrangement: copper type

A-2 Size-centered cubic dense arrangement: Wolframite type

A-3 Hexagonal close arrangement: magnesium type

A-4 Cubic : diamond type

A-5 Tetragonal: white tin type

A-6 Tetragonal size centered: indium type

A-7 Rhombohedral gray marble: type

A-8 Hexagonal gray: Selenium type

A-9 Hexagonal: graphite type

A-10 Rhombohedral: type of mercury

A-ll Rhombic: type of mercury

A-12 Cubic: type of α-manganese

A-13 Cubic: β-manganese species

A-14 Rhombic: type of iodine

A-15 Cubic: tungsten type

A-16 Rhombic: A type of black phosphorus

A-17 Rhombic: Sulfur type

A-18 Tetragonal: A type of uranium

A-19 Simple cubic: polonium type

A-20 Rhombic: A type of uranium.

The degree of symmetry of crystals depends, firstly, on the atomic structure of the chemical element that is part of the crystal, secondly, on the position of the system units that make up this crystal - atoms or ions in space, and finally on the environment in which this crystal is formed. That is why some simple compounds have a low degree of symmetry, and on the contrary, complex compound crystals can have a high degree of symmetry.

Atomic and ionic radii . Crystals are composed of material points that are periodically repeated endlessly, and for the formation of a stable crystal system from those material points, the arrangement of the spheres, which are imagined as material points, in the crystal system, as well as the size and smallness of those material points, and the binding force between them are important. discovers importance.

Below we will talk about the size of the material points that make up the crystal system and how to determine them. Since the size of spheres is measured by radii, it is necessary to start the word with atomic and ion radii.

The effective radii of atoms and ions are equal to the radius of the orbit of the outer electron shell of this atom or ion. But this is not equal to the distance from the center of the expensive nucleus to the outer electron shell, but rather the distance from the outer boundary of the circle to which the neighboring atom or ions can approach to the nucleus of the atom, and it varies depending on the particular environment and conditions. . In general, the atomic or ionic radii of chemical elements depend on the filling of the outermost electron shell with electrons, instead of those specified in Mendeleev's table. are considered to be solids and their size is measured by X-ray interatomic distances or calculated theoretically. In this case, it is assumed that the distance between the centers of adjacent spheres in the crystal

structure is equal to the sum of the radii of these spheres. It is also important to determine the distance between positively and negatively charged atoms or ions in the crystal system. This value is also called the radius of any ion (atom), that is, the shortest distance that the ion atom center can approach the outer electron shell of the neighboring ion (atom) is the ion radius.

There are lanthanides (lanthanide contraction in the group of trivalent rare earth elements), according to which the ionic radii decrease as the order number increases from 57 (from lanthanide to 71(lutens)) For example, the ionic radius of La $^{+3}$ is 1.04A°, while Lu $^{2+}$ ionic radius − 0.80 A°.

Similar compression is seen in copper group (silver and gold) and other group elements (zirconium with hafnium and niobium with tantalum). This situation is also seen in the last elements of the table, starting with actinium, which, according to GBBokiy's proposal, is called "actinide compression."

Each element can have several different ionic radii depending on its valence: cations with high valence have a small radius, and on the contrary, cations with low valence have a large radius. For example, the Mn° radius of the neutral manganese atom is 1.29 A°, the Mn $^{+2}$ ion radius is 0.92 A°, the Mn $^{3+}$ ion radius is 0.70 A°, the Mn $^{+4}$ ion radius is 0.52 A. This situation is also seen in sulfur:

$$C^{2-} - 1.82\ A°;\ C^{4+} - 1.04\ A°;\ C^{6+} - 0.29\ A°.$$
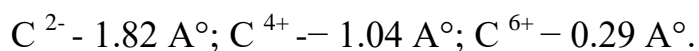
The system unit that makes up the crystal is imagined in the form of spheres that are close to each other and touch each other. But sometimes, under the influence of the electric field of neighboring ions, the spherical shape of these ions is broken. This phenomenon is called ion polarization. Accordingly, ions exhibit two different properties. Some ions easily break their range of motion under the influence of other strong ions, that is, they are polarized, while others change their range of motion very little under the influence of other ions, and other neighboring ions have a large effect on the range of motion. shows a secret, that is, it polarizes them. Therefore, each ion can be polarized by the influence of other neighboring ions, or this ion itself can affect another neighboring ion and polarize it.

This phenomenon mainly depends on the large or small ionic radii of chemical elements. Ions with a large ionic radius are more polarizable, and ions with a small ionic radius are strongly polarized. This can be clearly seen from Table 1.2 below:

(a - polarization property, b - polarization property, r $_1$ - ion radius).

Table 1.2

Polarization of ions

Elements	r_1	a	b
Lee	0.69	0.06	1.7
No	0.98	0.19	1.0
K	1.33	0.81	0.6
Rb	1.49	1.90	0.5
Cs	1.65	2.85	0.4

The polarizability of ions is directly proportional to the size of the ion radius, and the polarizability is inversely proportional.

Cations with small ionic radii, such as Cu, Ag, Zn, Cd, Hg, have strong polarizing properties and are not polarizable. Anions with a large ionic radius of small valence are strongly polarizable.

Such a change in the ionic radii can be measured by measuring the interionic distance in the crystalline saltation. For example, in the compound AgCl, the distance between the ions is 2.77 A°, which is much smaller than the sum of the ionic radii of both elements. In fact, Ag^{1+} ion radius was 1.13 A°, Cl^{1-} ion radius was − 1.81 A°, their sum should be − 2.94 A°.

Taking into account this property of atoms and ions, as well as the change of the radii of those ions depending on temperature and pressure, VM Goldschmidt discovered the following basic law of chemical crystallography. The structure of crystals depends on the quantitative ratio of system units - ions and atoms, the relative size of their radii, and polarization and depolarization properties.

In order to visualize the quantitative ratio of the units of that system, the concepts of coordination number and coordination polyhedra are used.

Coordination number and polyhedra . The crystal system is made up of spheres of material points that repeat endlessly and in three directions based on a certain rule, order, and each of them is surrounded by other neighboring spheres participating in this system. The appearance and many properties of crystals, including crystal systems, depend on the number and position of neighboring spheres surrounding a given sphere. Thus, it is about the relative position of the atoms or ions that make up the crystal system.

Table 1.3

Variation of interatomic distance depending on element coordination number

In ionic covalent		In covalent-metallic	
Coordination number	Interatomic distance	Coordinate number	Interatomic distance
12	100	12	100
9	94-96	8	96-98
8	92-94	6	93-95
6	86-90	4	86-87
4	78-75	3	79-82
3	72-75	2	74-78
2	63-68	1	(68-72)
1	57-63		

Coordination number is the number of nearest neighboring atoms or ions around a specific atom or ion in the crystal structure. If such neighboring atom or ion centers are assumed to be interconnected, a geometric shape is formed, which is called a coordination polyhedron. The atom or ion whose coordination number is being determined is located in the center of this coordination pattern. The shape of the coordination polyhedra can have a completely different appearance, which has nothing to do with the appearance of the crystal. The number of adjacent carbon atoms close to the carbon atom whose coordination number is determined in the crystal system diamond - C is equal to 4: in the structure of halite - NaCl, the sodium ion is surrounded by six chlorine ions, and the chlorine ion is surrounded by as many sodium ions, or The coordination number of sodium and chlorine ions is six, and the coordination number of each of zinc and sulfur ions in the sphalerite ZnS structure is four.

In the CsCl structure, the chlorine ion close to the cesium ion and the cesium ion close to the chlorine ion are 8, and the coordination number is 8 for each of these two different ions.

Copper, which has a side-centered cubic structure, has a coordination number of 12. Also, the coordination number of magnesium crystallized in hexagonal syngonia is 12.

The coordination number in the NiS structure is 6 for both the nickel ion and the sulfur ion, but the arrangement of neighboring ions is different for each element.

the fluorite - CaF $_2$ crystal system, the calcium ion is surrounded by 8 fluorine ions, and the fluorine ion is surrounded by 4 cadmium ions, so the coordination number is 8 for Sa and 4 for fluorine.

of metals , the coordination number of ions is always 12, and in the crystal system of semiconducting substances, the coordination number is 4 or 6.

Each of the system units - ions or atoms - that make up the crystalline substance can be in the same or several different coordination. At the same time, any equal coordination number can form different coordination polyhedra in space (Figures 1.54-1.55).

The relationship between the atomic or ionic radii and the coordination number . The relationship between atomic ionic radii and coordination can be theoretically calculated by considering crystals as composed of atoms or ions that form incompressible solid spheres.

1. For example, the coordination number of a known ion is 6, the coordination polyhedron is in the form of an octahedron, in which the length of the diagonal of the square in the section perpendicular to the axis of symmetry of the fourth degree is the sum of the two radii of the cation (r_a) and the anion (r_x) consists of the index, i.e. A $= 2r_a + 2_x$; from this equality, it can be concluded that $2_a + 2r_x = 2r_x \sqrt{2}$ or $r_a : r_x + 1 = 2$, therefore, $r_a : r_x = \sqrt{2} - 1 = 0.41$. This value is the lowest limit for the stability of a polyhedron with a coordination number of 6 in the form of an octahedron.

But between 0.41 and 2.41 there is a stable hexahedral polyhedron with coordination number 6.

In a hexahedral polyhedron with coordination number 8, those eight neighboring anions are at the ends of the cube, and the cation is in the center. The cross section over the cation coincides with the cross section along the volume diagonal. So, $2r_a + 2r_x = 2r_x \sqrt{3}$, or $r_a : r_x + 1 = \sqrt{3}$; from which the equality $r_a : r_x = \sqrt{3} - 1 = 0.73$ is derived. This is the lower limit of stability of hexahedral polyhedra with coordination number 8.

Below are examples of the stability limit of these coordination number − polyhedra:

Table 1.4

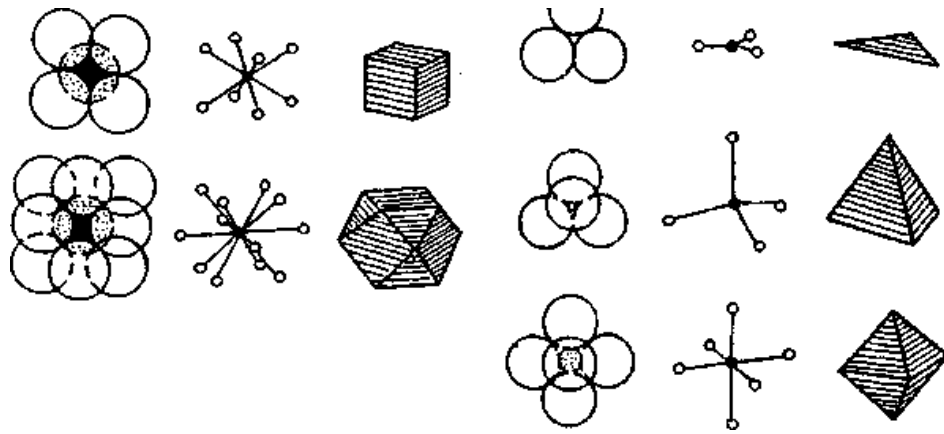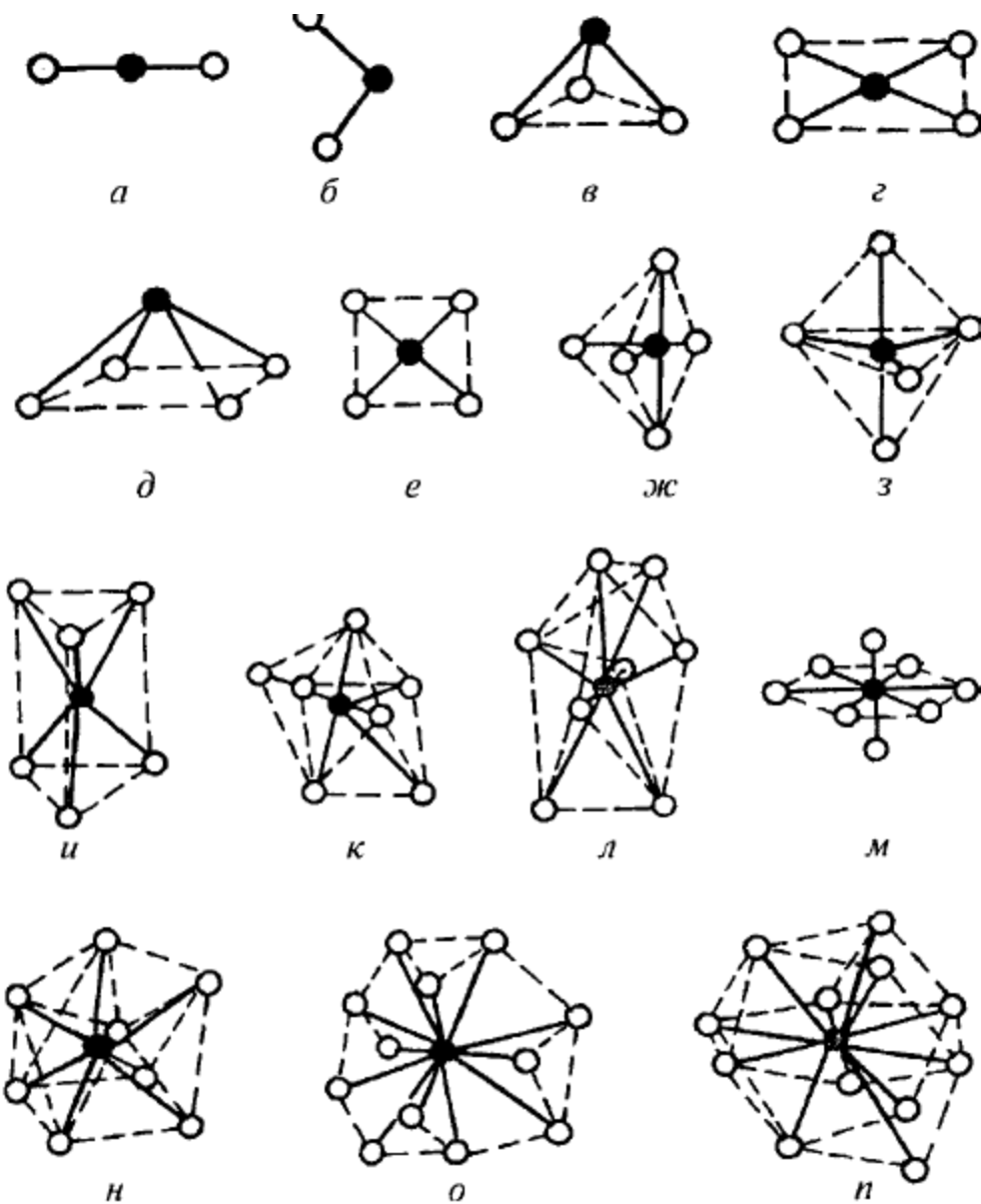| Coordination	Coordination polyhedron	g,: r,-
2	dumbbell	0 to 0.115
3	triangular	0.115 to 0.225
4	tetrahedron	0.225 to 0.414
6	octahedron	0.414 to 0.732
8	hexahedron	0.732 to 1.000
12	cuboctahedron	1.00

Figure 1.54

Figure 1.55

The mutual role of atoms in covalently bonded crystals is related to the shape of

69

the electron layers of the atoms involved in this bond.

The distance and coordination number between different electronic groups with covalent bonds are shown in the table above.

Covalent bonding can be seen in the diamond crystal system. In this case , a tetrahedron-shaped polyhedron with a coordination number of four is created as a result of the connection of carbon with electrons of the $sp^{3\ group}$ in four directions .

It is important to know the arrangement of atoms in the crystal structure, the stability of chemical compounds, and the coordination numbers of atoms and their shape in the analysis of chemical bonding problems. Sometimes chemical compounds are divided into groups depending on the number of coordination and polyhedra in the system and are described accordingly (Figures 1.54-1.55).

LECTURE 7

The nature of the chemical bond in crystallized substances .
Plan:
1. Types of chemical bonds in chemical substances.
2. The structure of the atom and the periodic table of chemical elements.
3. Electronic structure of atoms.
4. The rule of ratio of numbers to numbers in chemistry.

Ionic bonding is explained by electrostatic theory. According to this theory, oppositely charged ions formed as a result of electron transfer or electron attachment of an atom attract each other by means of electrostatic forces and form a stable system with 8 (octet) or 2 (doublet) electrons in their outer layer. Ionic substances are found in the crystalline state, and in aqueous solutions, instead of ionic molecules, they form mons. The ion binding energy is calculated by comparing the result with the value found in the experiment.

ionic bonds in the example of the formation of sodium chloride NaCI. The sodium and chlorine atoms forming this compound differ sharply in terms of electronegativity: this value is equal to 1.01 for the sodium atom and 2.83 for the chlorine atom. Electronic formulas Na $1s^2 2s^2 2p^6 3s^1$ and CI $1s^2 2s^2 2p^6 3s^2 3p^5$ show that these atoms have incomplete outer electron shells. To complete the outer step, a sodium atom is easier to give up 1 electron than to gain 7 electrons, and a chlorine atom is easier to gain 1 electron than to gain 7 electrons. The experiment shows that in chemical reactions sodium atom gives 1 electron, and chlorine atom attaches it. This can be written schematically as:

$$Na - e^- = Na^+ ; CI + e^- = CI^-$$
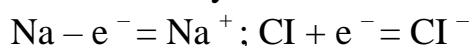
that is, the electron shell of the Na atom turns into the stable electron shell of the rare gas Ne - $1s^2 2s^2 2p^6$ (this is sodium ion Na^+), and the shell of the CI atom turns into the shell of the rare gas Ar atom - $1s^2 2s^2 2p^6 3s^2 3p^6$ (this is the chloride – ion CI^-). Electrostatic forces of attraction arise between Na^+ and CI^- ions, as a result of which NaCI compound is formed.

A chemical bond formed due to electrostatic attraction between ions is called an electrovalent or ionic bond. Compounds formed by the attraction of ions to each other are called ionic compounds.

Ionic compounds are formed by atoms that differ sharply from each other in terms of electronegativity, for example, atoms of elements of main groups I and II and atoms of elements of main groups VI and VII. There are relatively few ionic compounds.

Sodium chloride NaCI molecules exist only in vapor form. Ionic compounds consist of positive and negative ions arranged in a solid (crystalline) state. In this case, there are no molecules.

A covalent bond is a more general type of chemical bond. The bonding theory explains the formation of an ionic bond from a covalent bond by the extreme one-way polarization of the shared electron pair, in which the shared electron pair is transferred to one of the bonding atoms. For example:

$$Na + .Cl := Na : Cl : \text{ then } Na : CI := [Na^+] [: Cl : ^-]$$

In the given example, the chlorine atom, which exhibits nonmetallic properties (electronegativity $X_{CI} = 2.83$), is extremely one-sidedly polarized. The molecular electron cloud (electron pair) is completely shifted to the chlorine atom. This situation is equivalent to the transfer of an electron from a sodium atom to a chlorine atom.

Clearly, a polar covalent bond can be viewed as a partially unipolar network of covalent bonds (the bonding electron cloud is shifted toward the atom with greater relative electronegativity). It occupies an intermediate state between ionic and nonpolar covalent bonds.

Thus, there is no significant difference in the mechanism of formation of non-polar covalent, polar covalent and ionic bonds. They differ from each other only in the degree of polarization (displacement) of common electron pairs. The nature of a chemical bond is unique.

In reality, bonds are not 100% ionic. Therefore, the degree or contribution of ionicity of the bond is referred to. It is determined by experience. It is known that even in the CsF compound, the ionic bonding is only 89%.

Ionic bonding is formed as a result of interionic interaction. Any ion can be considered as a charged sphere: therefore, the field of force of the ion spreads evenly in all directions in space, that is, the ion can attract another ion with the opposite

charge equally in any direction. Therefore, the ionic bond does not show the directional property. In addition, even if the negative and positive ions are bonded together, the negative ion does not lose its ability to attract other positive ions. For example, a positive ion with a +1 charge attracts other negative ions even though it has one negative ion next to it. So, the ionic bond does not have elasticity.

the ionic bond does not have the properties of directionality and elasticity, each ion has a maximum number of oppositely charged ions around it. The maximum amount of ions depends on the larger or smaller radii of cations and anions. For example, a maximum of 6 chlorine ions can be placed around Na+, and 8 CI ions around Ss+.

ionic bonding does not show the properties of directivity and saturation, ionic bonding molecules consisting of one positive and one negative ion cannot exist individually under normal conditions, they combine to form a giant molecule consisting of many ions - a crystal.

Covalent connection Ionic bonding cannot explain the formation and existence of chemical bonds from nonpolar molecules composed of only the same atoms, such as N_2, N_2, O_2, F_2, CI_2, in organic and most inorganic compounds. These compounds differ from ionic compounds by a number of properties: they do not conduct electricity, they have low liquefaction and boiling points. Most of these are gases and volatile liquids. In such compounds, atoms are connected by covalent bonds.

In 1916, the theory of covalent bonds created by the American chemist GNL Lewis is based on the concept that "an atom with an outer layer of eight (or two) electrons is stable." In this bond, the stable configuration does not result from the transfer of electrons from one atom to another, but from the formation of one or more shared electron pairs between the two atoms. Both atoms participate in the formation of electron pairs. Therefore, each atom must give an electron from itself for a common pair. Covalent bond formation can be observed in several substances. When two hydrogen atoms, each with one electron, come close to each other, they form a hydrogen molecule (N_2). This process is expressed as follows:

$$N \bullet + \bullet N \to N : N$$

The electron that each atom gives for a common pair is represented by a dot in the diagram. A pair of electrons in a hydrogen molecule is located between two nuclei, resulting in the formation of a stable configuration b .

lacks one electron to form an octet, that is, an eight-electron shell . When one atom of fluorine joins another atom of fluorine, a covalent bond is formed as follows:

$$: F \bullet + \bullet F : \longrightarrow : F : F :$$
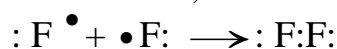
The nitrogen atom lacks three electrons to form an octet. The formation of a diatomic nitrogen molecule can be written as follows:

$$: N : + : N : \to : N : : N :$$
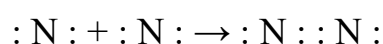
Langmuir assumed that the number of electron pairs formed between connecting atoms is equal to the valence of this element. For example, in the ammonia molecule, nitrogen is trivalent, hydrogen is monovalent, that is, in the formation of NH_3 , three electrons of nitrogen are involved, but one pair is not involved. A pair of electrons that does not participate in such a bond is called an unshared pair of electrons between nuclei. Such electron pairs are often called lone pairs.

Lewis and Langmuir's electron theory of covalent bonding explained chemical bonding in non-complex substances; but could not explain the nature of chemical bonds in complex substances (especially complex compounds). He could not fully answer the questions of why electrons are formed at the expense of pairs; moreover, the theory of Lewis and Langmuir was a static theory that did not take into account the state of motion of electrons and nuclei.

Only on the basis of quantum mechanics, coherent theories of chemical bonding have been created. Two methods are currently used to explain chemical bonding in quantum mechanics. One of them is the valence bond (VB) method, and the second is the molecular orbital (MO) method.

The more the electron cloud of interacting atoms covers each other, the stronger the chemical bond, and the more energy is required to break such a bond, in other words, the greater the "binding energy".

the same bond in a molecule and bring the resulting components to a state where they do not interact with each other is called bond energy.

chemical bond energy is eV or kJ. is represented by mol-1. the numerical value of the bond energy depends on the shape of the electron cloud of interacting atoms, the internuclear distance in the molecule, and other factors . For example, the binding energy of N_2 molecule is 434.8 kJ. mol-1, 498 kJ · mol-1 in O_2 molecule.

Non-polar and polar bonding. Two types of covalent bonds are known: nonpolar and polar.

a) Non-polar bonding. A non-polar covalent bond is formed when the electronegativity of the elements is equal to each other. N_2 , O_2 , The bond in N_2 and other molecules is a nonpolar covalent bond. When atoms interact, the connecting atoms give some (or all) of the electrons in their surface layers to form a bond, resulting in a pair of electrons. A pair of electrons belongs to two atoms and revolves around them. Electron pairs are between the two atomic nuclei and are attracted to both nuclei and bind the atoms together. The following examples show the formation of a nonpolar covalent bond. GN Lewis proposed to write the atoms involved in covalent bonds in the following form.

Here, the symbol for the element is the nucleus, and the dots represent the electrons in the outer shell. For example, a hydrogen molecule is formed from two hydrogen atoms as follows:

$$N\,{}^{\bullet} + {}_{\bullet}N \rightarrow N : N\,(N_2)$$
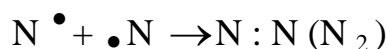
In this case, each hydrogen atom donates its electron to form a bond, resulting in a pair of shared electrons for both atoms. in such a bond, the pair of electrons is equally distributed between both connecting atoms (they are located at the same distance from them), so such molecules are called nonpolar molecules. A chlorine molecule is formed from two chlorine atoms:

electron pairs are formed only by electrons with antiparallel spin, because such electrons attract each other. If the spins of the electrons are antiparallel, the electric field charge density between the two atoms is greater than that of the surroundings, the electron clouds around the nucleus repel each other and, as a result, the atoms attract each other.

b) Polar bonding. When atoms of elements with slightly different electronegativity join together, a polar bond is formed. A polar bond does not differ from a non-polar covalent bond in terms of its nature, the pair of electrons, as in a covalent bond, is not located between two nuclei, but is slightly shifted towards the atom of an electronegative (non-metallic) element. This bond is usually expressed as follows: for example, the formation of HCI and $N_{2\,O\,molecules:}$

During the formation of a molecule, one side of the molecule becomes more positively charged, and the other side is more negatively charged, as a result of the electron pair moving to one side. The centers of gravity of these charges are at a certain distance from each other. Two poles are formed in one molecule, resulting in a dipole. A system consisting of opposite electric charges that are quantitatively equal and at a certain distance from each other is called a dipole system.

The dipole length - h multiplied by the electronic charge e k is called the dipole moment and μ is denoted by the letter:

$$\mu = eat \bullet h$$

For example, the dipole moment of a water molecule is 1.84 D. The dipole moment is measured in the unit debay. 1 Debye is denoted by the letter D and is equal to 10-18 electrostatic units.

The value of the dipole moment indicates the degree to which the polar bond is polarized. Therefore, the water molecule is a polar molecule.

with a dipole moment greater than zero are called polar molecules, and molecules with a dipole moment equal to zero are called nonpolar molecules.

In addition to the water molecule, polar molecules include alcohol and hydrogen halide molecules, and non-polar molecules include benzene and hydrocarbon molecules.

Metal connection. The most important physical properties of metals are properties such as high melting and boiling temperatures of metals, reflection of light and sound from the metal surface, good heat and electric current passing through them, and flattening under impact. These properties are explained by the presence of metallic bonding, which is characteristic of examples only.

A metal atom does not have many valence electrons, but a metal atom has many unfilled orbitals. Valence electrons are weakly bound to the nucleus of a metal atom. Therefore, they move freely between the metal ions in the crystal lattice of the metal. The structure of a metal should be imagined as follows: positively charged metal ions (cations) are densely located in the nodes of the metal crystal lattice, and valence electrons of atoms move freely within the lattice. Because the movement of these electrons resembles the movement of gas molecules, they are called electron gases . Therefore, each atom gives up its valence electron, and they bind together a large number of metal ions. At the same time, these electrons can move freely. Consequently, it appears that metals have a mobile type of chemical bond.

Metallic bonding is characteristic of metals in both solid and liquid states. These are properties of aggregates of atoms that are directly adjacent to each other. But atoms of metals, like atoms of all substances, are connected to each other by covalent bonds in the vapor state. Vapors of metals are composed of separate molecules (monoatomic and diatomic). Bonding in a crystal is stronger than in a metal molecule, so the process of forming a metal crystal is accompanied by the release of energy.

Metallic bonding is somewhat similar to covalent bonding in that it is also based on the sharing of valence electrons. But the electrons that form a covalent bond are close to the attached atoms and tightly bound to them. Electrons forming a metallic bond move freely throughout the crystal and belong to all its atoms. For the same reason, crystals with covalent bonds are fragile, and those with metal bonds are plastic, that is, they change their shape under impact, spread into thin sheets, and bend into wires.

Hydrogen bonding. The ionic, covalent, metal, donor-acceptor bonds considered above are the main types of chemical bonds. In addition to these types of bonds between atoms and molecules, there are also secondary bonds - hydrogen bonds and intermolecular forces of attraction (Vander-Waals forces). These include orientational, dispersion and induction forces. As a result of studying the boiling temperature of hydrogen compounds (hydrides) of V, VI and VII nonmetals in the DIMendeleev periodic system, it was found that there is a discrepancy between theory and experiment. For example, NF, N2O, and NH3 have higher boiling points than expected. The boiling point of N_2O should be lower than that of N_2S, because the boiling point of substances is often proportional to their molecular mass. Also, the

boiling point of HF should be lower than that of HCI, and that of NH $_{3\text{ should be lower than}}$ $_{\text{that of}}$ RN $_3$. But experience has shown the opposite. The reason for this can be explained by the theory of hydrogen bonding. Due to the presence of hydrogen bonds, the molecules of NF, H $_2$ O, NH $_3$ are attracted to each other and are in the state of (HF) $_n$, (H $_2$ O) $_n$, (NH $_3$) $_n$. Accordingly, the boiling point of hydrogen fluoride, water and ammonia is high.

of hydrogen bonding is that a monovalent hydrogen atom connected with atoms of electronegative elements such as fluorine, oxygen, and nitrogen in a molecule of a substance has the property of weak bonding with other fluorine, oxygen, and nitrogen atoms. This can be easily understood from the following examples. For example, in NF, due to the transfer of the electron of the N atom towards the fluorine atom, it becomes conditionally positively charged, that is, it can be said that a hydrogen ion is formed.

A pair of electrons from another fluorine or oxygen atom attracts a hydrogen ion, resulting in a double-bonded hydrogen atom:

$$N - F \ldots H - F ,$$

in general (HF) $_n$, where n = 2, 3, 4, 5, 6 can be.

So, the secondary chemical bond formed between an atom of an element with high electronegativity and a hydrogen atom in another molecule is called a hydrogen bond. But the energy of this connection is not so great. It is $8 - 42$ kJ $\cdot$ mol–1. The strength of intermolecular attraction forces is 0.1 - 8.4 kJ. b dies around mol –1 .

Key words and phrases: Coval ent, Energy. Lewis theory. Sigma bond. Pi bonding orbital. Orbital. Spin valence. Donor. Acceptor. Polar. Without a pole. Dipole. Tetrahedral crystallochemistry Electron cloud. Symmetrical uki. Dipole moment. Valent angle. Homodesmy crystallochemistry Heterodesmy crystallochemistry Orientation. Homodesmi crystallochemistry

LECTURE 8

Isomorphism and polymorphism

Plan:
1. The history of isomorphism and polymorphism .
2. Conditions necessary for the manifestation of isomorphism.
3. Classification of polymorphism types by structure.

Was introduced to science by E. Mitscherlich in 1819 , according to which KH $_2$ PO $_4$ and KH $_2$ AsO $_4$ it is noted that it is a complex form consisting of tetragonal prism and dighramide belonging to tetragonal syngonia to the same shape of crystals.

The angle between the (101) and (011) sides of this crystal is 58°, and as a result of further measurements, it is determined that this angle is 57°58 for potassium phosphate and 57°52 for potassium arsenate. At the same time, the ratio of crystallographic axes turned out to be 1:0.939 and 1:0.938, which indicates that the crystals of these substances are very similar to each other, but one is not the same as the other.

E.Mitcherlich called substances with the same or almost the same shape of different crystals chemically, and physically similar substances called isomorphous substances.

Initially, it was considered that isomorphous substances differed from one another in terms of their chemical composition when the same atoms were replaced by other atoms in a ratio of 1:1. This theory helped to determine the atomic weights of a number of elements in its time, in the first half of the 19th century. In particular, the isomorphism of $KMnO_4$ with $KClO_4$ made it possible to determine the atomic weight of Mn (relative to chlorine). Later, after the development of methods for examining the internal structure of crystals using X-ray rays, the phenomenon of isomorphism and its nature were determined in some detail.

The property of forming a mixed crystal of substances with different chemical composition is called isomorphism. In this case, atoms and ions of a substance forming an isomorphous mixture can exchange places with atoms and ions of another substance in different proportions. As a result of this exchange, mixed crystals are formed, such crystals are sometimes called solid solutions.

Substances with different crystal structures can form isomorphous compounds in two different ways. They are called isovalent and heterovalent isomorphisms. In isovalent isomorphism, ions in the crystal structure can exchange places only with ions of equal valence. In this case, the difference between the radii of these alternating covalent ions must not exceed 15%, otherwise the stability of the crystal structure will be lost. For example, from divalent cations Mg^{2+} (ionic radius 0.74 A°); Fe^{2+} (0.80A°); Na^{2+} (0.74 A°); Zn^{2+} (0.83 A°) and Mn^{2+} (0.91 A) trivalent cations Fe^{3+} (0.64A°), Cr^{3+} (0.64 A°); Among the anions Al^{3+} (0.57 A°), elements such as $- S^{2-}$ (1.82 A°) and Se^{2-} (1.93 A°) are isomorphous with each other in chemical compounds with different crystals. can exchange.

In isovalent isomorphism, the number of exchangeable system units in an isomorphic mixture remains unchanged. For example, Fe with Mg in the isomorphic series $MgCO3 • FeCO_3$; In the CuS - CuSe isomorph series, S and Se can exchange places with an equal number of ions.

Heterovalent isomorphism. In this type of isomorphism, atoms or ions of different valence chemical elements with equal or close ionic radii exchange places with each other. Even as a result of such an exchange, as is certainly known from

general chemistry, the electrostatic balance between anions and cations in the compound must be maintained. Since the excess valence caused by the exchange of a small valence ion with a large valence ion is in the cation part of the compound, it is necessary for ions to exchange places with other ions in the anion part of this compound. As a result, the balance between anions and cations is maintained, and vice versa, as anions of unequal valency are isomorphically exchanged, the cation part of this compound must be replaced to the extent that electrostatic balance is maintained. For example, when $Mg^{2+ \text{ is replaced}}$ by $Al^{3+ \text{ in micas}}$, three of the divalent Mg cations are exchanged with two of the A1 cations, that is, the electrostatic balance in the compound is maintained only when $Mg_3 \rightarrow Al_2$.

Also, isomorphous substitution is very common among complex anions with similar or equal radii, such as $[SiO_4]^{4-}$, $[AlO_4]^{5-}$, $[PO_4]^{3-}$ and $[SO_4]^{2-}$. In particular, infinite mixtures of plagioclase group minerals albite $Na[AlSiO_3O_8]$ with $[Al^{III}O_4]^{5-}$ anorthite $Ca[Al_2Si_2O_8]$ are widespread in magmatic rocks. In this case, as a result of the isomorphous exchange of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ complex anions, due to the fact that Al is trivalent and Si is quadrivalent, the excess negative valence in the anion part of the compound is due to the replacement of the Na cation with the divalent Ca cation. comes to equilibrium. Therefore, the valence of isomorphous exchangeable ions in the anion part and the cation part of the compound must always be equal.

In the examples given above, isomorphous substances can be interchanged with each other in infinite proportions. Such isomorphs are perfect isomorphs; and isomorphism is called perfect isomorphism. In addition, there are limited isomorphs. For example, $BaSO_4$ and $KMnO_4$ can be isomorphically exchanged only in certain proportions, that is, it can form a mixed crystal. Such an isomorphism is called a restricted - imperfect isomorphism. Calcite $Ca[CO_3]$ and magnesite $Mg[CO_3]$ are also finite isomorphous substances, only in a certain ratio they form a mixed crystal (dolomite $- CaMg[CO_3]_2$. Each of these substances is the unit cell in the crystal system. due to the much larger difference between the size (6.412A° and 6.064 A°) and the radius of the cations (1.06A° and 0.78 A°), it cannot form an infinite mixture. In the case of isomorphous mixtures, the difference between the radii of the units of the exchange system is much greater, that is, 20-25%. In addition, a complex situation, isovalent and heterovalent isomorphisms can appear simultaneously in one mineral.

Elements that form an infinite isomorphism (mixture) in the composition of minerals

Table 1.5

El. positive	El. positive elements	El. no. elements	El. positive elements
KH_3	La Ce(2)	Cl-Br(I)	Na-Ca(5)
Ag-Au(I)	Ce-Y(3)	OH-F(6)	Ca-Ce(l)
Sr-Ca(l)	Al-Fe^{3+}(5)	S-Se(2)	Mg-Al(2)
Ba-Sr(I)	Fe^{3+}-Mn^{3+}(1)	Te-S(l)**	Fe^{2+}-A1(2)
Ca-Mn(2)	Sb'''-As'''(1)	CO_3-SO_4(l)	Fe^{2+}-F^{3+}(3)
Mn-Mg(1)	Sn-Ge(l)	AsO_4-PO_4(2)	Mn^{2+}-Fe^{3+}(2)
Mn-Fe(20)	V^v-As^v(l)	Na$_3$[PO$_4$]-H$_2$O(1)	Si-Al(6)
Mg-	Ta-Nb(5)		Ti-Nb(l)
Zn-Cu(I)	Os-Ir(l)		
Co-Ni(4)			

*In parentheses are the number of pairs of elements identified in the mineral world

**Atoms are replaced layer by layer, not atom by atom.

Physical properties of those minerals as a result of complex isomorphous exchange of such elements. specific gravity; hardness and other properties and system dimensions will vary.

In addition to the formal mixed crystals described above, there are also complementary mixed crystals, in which the mixing substance is not located in the place of the system units, but in the spaces between them . In this respect, the parent crystal system is similar to the solvent, and the intervening substance is similar to the solute.

Metals mixed with some metal alloys occupy such voids in crystal systems. Blue table salt (halite − NaCl), which contains sodium metal compounds, is an example of these complementary mixed crystals.

Polymorphism . Depending on the conditions of crystallization (pressure, temperature, composition of the solution or alloy), a certain chemical element or chemical compound can form different crystals that are completely different in terms of shape, structure and physical properties. Substances with the same chemical composition and different crystal systems are called polymorphic modifications. Polymorphic modifications are distinguished from each other, first of all, by the difference in the crystal system. This is manifested in the ability of different system units to form different crystal systems according to certain conditions, that is, in different locations in the system. Some chemical elements or compounds can have several - two, three or even more polymorphic modifications. Sometimes in different crystal systems, atoms and ions differ from each other according to their position and

arrangement. For example, it crystallizes in two or more forms, such a property is called polymorphism.

Existing crystal systems can be transformed into various polymorphic modifications by changing the conditions of their formation. In general, modifications of chemicals that occur under the influence of high pressure and high temperature have a higher degree of symmetry than other modifications that occur in low temperature and pressure environments. For example, quartz (SiO_2) crystallizes in hexagonal syngonia in a high-temperature environment, and in a trigonal syngonia in a low-temperature environment; C - carbon is also diamond - cubic, graphite is hexagonal, calcium carbonate $CaCO_3$ is also calcite-trigonal, aragonite-rhombic crystallized in such different environments. But if a certain substance, for example, diamond and graphite, needs a very high temperature and pressure to change from one modification to another, a very small pressure and temperature is enough for another substance to change. For example, all five existing modifications of ammonium nitrate salt occur in the temperature range of 17-80°. There are also substances for which the external environment becomes more important than temperature and pressure for the formation of any of their modifications. For example, under the same thermodynamic conditions, Fe^{2+} crystallizes in the form of pyrite in cubic syngonia in an acidic environment, and in the form of marcasite in rhombic syngonia in an alkaline environment. All such polymorphic modifications are stable under certain temperature and pressure conditions and can meet together. TiO_2, which crystallizes in the form of rutile, anatase, and brookite, and ZnS, which is found in the form of sphalerite and wurtzite, are also included.

In the process of polymorphic changes shown above, not only the crystal system of the substance changes, but also the type of chemical bond between the system units in some cases. Polymorphic substitutions are so numerous and varied that polymorphism can be divided into three types as follows.

In the process of polymorphic substitutions within the framework of a different system, as a result of such substitutions, the crystal structure is preserved. Examples of this are various ammonium salts (NH_4NO_3, NH_4Br, NH_{4Cl}).

There are also polymorphic substitutions in which the system of the crystal is different, while the coordination number and the type of chemical bond are preserved. For this, the example of ZnS can be shown, where the Zn cation occupies half of the number of tetrahedral spaces with the ends facing the same direction in all five types of systems. As a second example, polymorphic modifications of silica - $SiO_{2\ can\ be\ shown.}$ In particular, quartz, cristobalite, tridymite and their forms formed at high and low temperatures differ from each other only in the order of interconnection of (SiO_{4})$_{tetrahedra.}$ From all this, the coordination number of atoms remains unchanged at four.

There are also polymorphic substitutions that differ in the type of crystal system, coordination number, and type of chemical bond. An example of this is polymorphic modifications of iron. These modifications are crystallized in the volume-centered cubic and side-centered cubic system, and they differ from each other by the coordination number of iron and the type of dense arrangement of atoms. Carbon modifications of graphite with diamond are also distinguished by their crystal system and type of chemical bonding, which are very different from each other.

LECTURE 9

Dependence of physical and chemical properties of solids on the structure of crystals

Plan:
1. Hardness of crystalline substances
2. Electrical properties of crystals
3. Magnetization properties of crystals

A crystal is a solid, homogeneous, anisotropic substance that can be limited to flat-smooth sides under certain conditions, that is, can have a certain geometric shape. Theoretically, only crystals can be true solids. The crystallized state of substances is the consequence of the periodic repetition of the material points that make up these substances in three directions, and this in turn is the main sign confirming the crystallized state of those substances .

In fact, only liquids are amorphous substances. But we must not forget the presence of liquid crystals. Amorphous solids can be thought of as supercooled liquids with extremely high viscosity. The physical properties of a solid amorphous body and a crystallized body, which appear to be the same in appearance, are very different from each other. The melting curves of these crystallized and amorphous substances are depicted in Fig. 1.56. It can be seen that the temperature does not rise as the substance is heated in the section BC of the curve ABD.
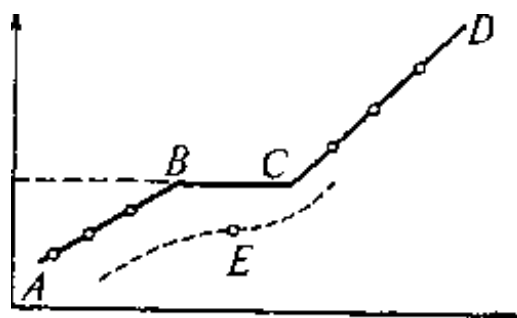

Figure 1.56

The given thermal energy is used to melt this substance. The energy released during crystal growth is absorbed during melting. Finally, its temperature does not rise until the crystal melts. Curve E shows the melting of the amorphous material from one end under the influence of the applied heat. The physical properties of amorphous and crystalline bodies are very different, as shown in the example above. Therefore, the physical properties described below are characteristic only of crystals, which differ from amorphous substances (although they are all solids) by these properties. The reason for this is that the material points are arranged in a certain order and based on certain geometric laws in the crystal system, the material points are infinitely repeated after a certain distance in a certain direction of movement, and the strength of the connection between these material points is varied. explained. As a result, all crystals have some degree of anisotropy. This feature is manifested differently depending on the chemical composition of those crystals, the conditions of their formation - the environment. Below are many examples of this in the description of specific physical properties of crystals.

The hardness of the crystals. The hardness of the crystals is the resistance of the surface to scratches. When the smooth surface of a crystal is scratched by a sharp point of something harder than itself, a mark is left on that scratched surface along with the powder. The hardness of the crystal is measured by the force exerted on the separation of the powder, that is, leaving a mark on the surface. Therefore, the hardness of the crystals indicates the strength of the connection between the units of the crystal system that make up this surface, and these values are characteristic for a crystal of a substance, which becomes a variable property in directions due to its symmetry. At the same time, as mentioned above, taking into account the anisotropy property of crystals, this determined value can be different depending on the direction of the line drawn in the crystal of the same substance. But the difference between these values will not be so great and in most practice it will not be taken into account. Only in some cases such anisotropic feature is clearly visible. For example, the hardness of the distene crystal has the smallest value (4-5) along the axis, and the largest (6-7) along the X and Y axis. The hardness of crystals is determined by mineralogists-geologists during practical work by comparing one with the other. For this, there is a series of hardness, which consists of the ten most common minerals in nature, and was introduced to science by the Austrian scientist Moos (1773 1839). Each of the minerals written in this order draws the one before it, and the one after it is not drawn with it. The ordinal number of each mineral indicates the relative hardness of that mineral.

Sometimes the crystal, whose hardness is determined, can be small or in powder form. In this case, the mineral powder is glued to the thumb and rubbed on another mineral surface with this finger.

Table 1.6

The order of hardness of minerals (according to Mohs)

Hardness	The name of the mineral	Hardness is determined surface mark
1	talc	(001)
2	gypsum	(010)
3	calcite	(011)
4	Fluorite	(111)
5	Apatite	(0001)
6	Orthoclase	(001)
7	quartz	(1011)
8	Topaz	(001)
9	Corundum	(1120)
10	Diamond	-

If the mineral powder is harder than a crystal rubbed with a finger, the surface of that crystal will be scratched and dull. Otherwise, if the hardness of the powder is small, the rubbed mineral surface will not be scratched - it will remain shiny. A special microtverdometer-sclerometer adapted for this is used to solve practical-scientific issues related to the actual hardness of crystals . Sclerometer is a special instrument with a pyramid or cone-shaped diamond needle.

Electrical properties of crystals . In general, properties of electrification of bodies such as "conductivity, dielectric and semi-conductivity" are known from the course of physics. Among such physical bodies, only some of the crystal's electrification properties, which are manifested under the influence of external energy in connection with the specific crystal system, are described below.

Piezoelectric property. Crystals have a piezoelectric property, where electricity is induced under the influence of mechanical force. When the crystal is pressed or stretched under the influence of mechanical force, it is electrified in a direction perpendicular to this force: a positive charge is formed at one end, and a negative charge is formed at the opposite end. Crystals can be electrified in a direction perpendicular to the applied force.
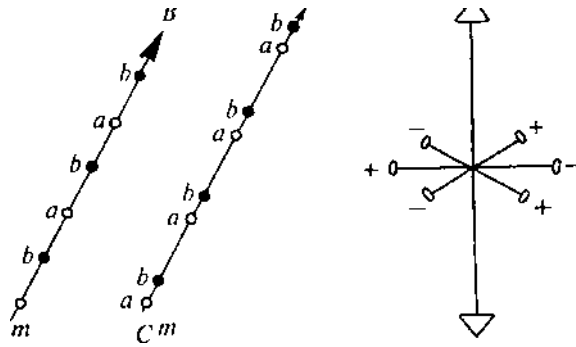
Figure 1.57

The existing polarization direction in a crystal system is related to the means of symmetry of that crystal. Including: 1) Crystals with a center of symmetry cannot have a polarized direction, that is, a piezoelectric property. Because every material point has its reflection in this direction through the center, then the distance between those material points must be equal. As you know, this direction is not polarized. 2) The direction towards the plane of symmetry is also not polarized, because the first half of the body with the plane of symmetry is the opposite of the second half. Since the two sides of a direction are the opposite of each other, it cannot be a polarized direction. 3) A direction perpendicular to the symmetry axes of even degrees is also not a polarized direction. The proof is the same as in the previous case. Therefore, the geometric shapes that can have a polarized direction can be predicted. Piezoelectric properties can be manifested in crystals with the following symmetry:

I; 2; 3; 4; 5; 6; m, 2mm, 3m, 4mm, 6mm, 222, 32, 422, 622, 42m, 6m, 2.23, 43m.

One of the forms of symmetry in this list is the 32 quartz crystal. The direction of the acting force must be aligned with the direction of 3. In this case, the charge is aligned with the direction of secondary symmetry axes perpendicular to that principal axis, which means that these secondary symmetry axes are the electrification axis of the quartz. Because the direction of these axes is polarized, the two ends of the axis are not connected to each other by the axis of tertiary symmetry.

Under the influence of the force directed by the tertiary symmetry axis of the quartz crystal, one end of the secondary axis is positively charged, and the other end is negatively charged. When the same crystal is stretched along the tertiary axis, the tip of the previously positively charged axis becomes negative, and the previously negatively charged end becomes positive. When an alternating electric current is applied in this direction, the crystal sometimes expands and sometimes narrows in the direction of the third-order symmetry axis - the crystal oscillates.

This property of crystals discovered by Pierre and Jacques Curie in 1880 is widely used in science and technology. For this purpose, a transparent quartz crystal with a thickness of one hundredth of a centimeter and a surface area of 3-4 sq. cm. an

incision is made. In an alternating current electric field, such cross-sections oscillate uniformly, without fading, from a thousand to a million times per second. This feature makes it possible to use it as a stabilizer of radio waves in radio engineering. Without it, it is impossible to imagine radio stations broadcasting on certain radio waves.

The quartz crystal also "feels" the change in pressure applied to it. Such a crystal quickly and accurately takes into account the effect of gravity from milligrams to tens of tons falling on each square centimeter of the surface. Because the current charge generated along the axis of electrification is proportional to the force of gravity acting on that crystal surface. If the resulting electric charge is measured using special electrical devices, it is possible to know exactly the force of gravity falling on the surface of the crystal. In this way, any compressive force can be measured through a piezoelectric quartz cross section.

Piezo quartz cut also very well "feels" sound, "hears" sound waves, writes and "speaks" with the help of special devices. Also, ultrasound is "sensed" by pezocrystals. In communication with submarines, in measuring the depth of the sea (echolot), in general, in modern science and technology, this property of crystals is especially important.

Pyroelectricity of crystals. Electrification of crystals due to temperature changes is called pyroelectric property (pyros means fire in Greek). Such a feature can occur in crystals only along certain directions corresponding to the single direction of polarization. This property is only in crystals belonging to the following symmetry form 1; 2; 3; 4; 6; m; 2mm; 3m; 4mm; It can appear in classes like 6mm. It can be seen from this list that in crystals with this property, the center of symmetry is oriented perpendicular to this single direction of polarization or the plane of symmetry passing through it at a certain angle and oriented perpendicular to the higher order axes. should not have a secondary axis of symmetry .

The most important example of crystals with such properties is tourmaline. It has an axis of symmetry of the third degree, three planes of symmetry passing along this axis, and its symmetry representation has the form 3m. The axis of tertiary symmetry in this 3 is polarized, coincident with the single direction. When such a crystal is heated, one end is negatively charged, and the other end is positively charged; when the crystal is cooled and discharged, its ends are opposite: the positive end is negative, the negative end remains positively charged. This can be done by sprinkling a mixture of lead oxide [Pb_3O_4] and sulfur (S). The positively charged part of the crystal attracts the negatively charged sulfur particles and turns yellow. The negatively charged part attracts positively charged oxide particles and becomes red. Pyroelectricity is very important in the development of science and technology, especially it is widely used in physics.

Magnetism of crystals . In nature, all substances have some degree of magnetic properties, and according to these properties, they are divided into five groups; diamagnetic, paramagnetic, ferromagnetic, activeferromagnetic and ferromagnetic - ferrites.

Since all substances have the property of magnetism, it can be considered that this property in them depends on the particles of elements that are part of atoms. All atoms are composed of the same electrons, protons, and neurons. It is known from the conducted studies that the magnetic moment of neutrons and neutrons is several tens of times smaller than the magnetic moment of electrons. Therefore, it is necessary to think that the property of magnetism is related only to electrons.

Any atom is an equilibrium system consisting of a "cloud" of nuclei and electrons. Each electron has its own magnetic spin number. In addition, the movement of electrons inside the atom along a certain orbit creates an orbital magnetic field. Therefore, the complete magnetic moment of an atom consists of the geometric sum of the orbital and magnetic spin numbers of these electrons.

Diamagics. The property of diamagnetism occurs as a result of the influence of the magnetic field on the movement of the electronic layers of atoms or molecules. Hence, this property is characteristic of atoms or molecules. This property is manifested in substances whose atoms or ions have a magnetic moment equal to zero. For this, the magnetic moment of all orbits and spins in those substances must be in balance. This is the case in inert gases and in substances whose outer electronic layer of ions is structured like that of inert gases, for example, in elements such as Na, Cl. In all of them, the magnetic moment of the spins is equal to zero, that is, the number of electrons is even. Thus, Pb, Zn, S, Hg, Si, Ge, S, CO_2 , H_2O, glass, marble and many organic substances are diamagnetic. Among them is Si, which has a different electron shell structure. Because it has only one 4s electron, which gives it the paramagnetic property. The number of electrons in the 3d shell, which gives it diamagnetism, is ten. Accordingly, it remains a weak diamagnet.

Paramagnetism. Paramagnetic substances do not magnetize as quickly as ferromagnetic substances under the influence of an external magnetic field, but even when magnetized, they are magnetized in accordance with the direction of the external magnetic field. It is known that the magnetic field of some atoms is irregularly oriented in places where there is no external magnetic field. Therefore, only substances with a value other than 0 of the magnetic moment of atoms or molecules can have paramagnetic properties. Such substances include elements with an odd number of electrons in atoms or molecules. The total magnetic moment of such elements is not zero. For example, in alkali metals (Na, K, etc.), Al, nitrogen oxide (NO), etc. Cu, Ag are exceptions to this rule. Elements of the transition group in the Mendeleev table, such as Cr, Mn, Pt, whose internal electronic layers are not

filled, and alkaline earth elements also have paramagnetic properties.

Paramagnetics are attracted by their magnetization along the direction of the magnetic field, while diamagnetics are attracted away from the magnetic field by their opposite magnetization.

Ferromagnetism. Ferromagnetic materials have strong magnetism. They are quickly magnetized and their magnetism is easily recognized. Ferromagnetism is derived from the Latin word ferrum - iron, because this property was first discovered in iron - iron ores. At present, it has been found that such a feature exists in elements such as nickel cobalt gadolinium, erbium, dysprosium, thulium, holmium and terbium, in addition to iron.

Table 1.7

Temperature of loss of ferromagnetic property

Substances	Temperature C°
iron	770
cobalt	1127
nickel	357
gadolinium	16
dysprosium	168
polite	-43
full	-222
Erbian	-253
50% alloy of bismuth with manganese	-340

The last rare elements are magnetized at very low temperatures. Although the number of chemical elements with ferromagnetic properties is 9, the number of such substances is actually very large. Because these metals can be alloyed with each other and with other metals, even non-magnetic metals.

Sometimes, some paramagnetic substances also exhibit ferromagnetic properties as the temperature decreases. The main characteristics of ferromagnets are as follows:

1. It is magnetized under the influence of an external magnetic field.

2. It remains magnetized even after the magnetic field is removed.

3. It loses its ferromagnetic property under the influence of a certain temperature. As the temperature increases, it exhibits paramagnetic properties.

In addition, the magnetic moment of ferromagnets is related to the ordered orientation of the magnetic moment spins of electrons.

Despite the fact that the magnetic moments of atoms of ferromagnetic elements are almost the same as those of paramagnetic elements, even in strong magnetic fields, paramagnets are weakly magnetized, and ferromagnetic ones are strongly magnetized.

It is known that ferromagnetism is related to spins. In the atoms of ferromagnets, the spin magnetic moments of electrons are not balanced. All ferromagnetic elements have unbalanced spins of electrons in the unfilled electron shells. For example, iron has 4 non-equilibrium spins, cobalt - 3, and nickel - 2.

This alone is not enough for the occurrence of ferromagnetism. Manganese has 5 unbalanced spins and chromium has 4, but neither is ferromagnetic. Therefore, this property is also related to the crystal system of the substance, that is, the dimensions of the crystal lattice depend on the ratio of the electron arrangement with unbalanced spin to the layer diameter. This value should be in the ratio $d : 2R > 1.5$. In this case, d is the lattice size, R is the radius of the electron shell with unbalanced spins. As shown above, this condition is not met for chromium and manganese - therefore, they cannot be ferromagnetic. Thus, the ferromagnetic property of substances is directly related to the crystal system.

Ferromagnets are self-magnetized in the crystal system, very small, the magnetic moment is directed in different directions, and under the influence of an external magnetic field, they have a common magnetic field, that is, they are magnetized.

Antiferromagnetism. Compounds such as MnO, MnS, NiCr, Cr_2O_3, VO_2 have this property. Antiferromagnets and ferromagnets, when heated up to a certain level, lose their antiferromagnetic properties with increasing temperature, and when heated a little more, they become normal paramagnetic properties. So far, such properties of substances are not used in technology - they have not been put into practice.

Ferrites consist of solid solutions - iron oxide (Fe_2O_3) and some other metal oxide alloy. Such compounds may consist of lithium, zinc, nickel, cadmium, lead, copper, magnesium, manganese and other metal oxides. Ferrites are semiconductors and are used in the logic and memory devices of electronic computers. Such crystal systems consist of two types of cells, each of which has a different antiferromagnetic coupling and a different magnetic moment. Accordingly, some areas of such crystals are magnetized due to the difference between the magnetic moments of the two cells.

Key words and phrases: Mohs scale, pyroelectric property, peso crystals, liquid crystal, diamagnetic, paramagnetic, ferromagnetic, actiferromagnetic, ferromagnetic;

LECTURE 10

Crystallography of simple substances and chemical compounds

Plan:

1. Crystal chemistry of simple substances
2. Crystal structures of metal alloys.
3. Polymorphism and solid solutions.

Crystal systems of chemical elements and their compounds are directly related to the position of these elements in Mendeleev's table. On the right side of that table are the mirrors, and on the left are the elements with distinct metallic properties. Therefore, the structure of the crystal varies depending on the number and quality of the elements included in the mineral composition of the crystal, as well as the chemical properties.

Table 1.8

Polymorphic minerals

The type of change	Minerals and composition	Crystal system	Syngonia	Change temperature	Environment
Ks system type will change	Diamond C	Coordination	Cube	1300	Upper r
	Graphite C	Leafy	Hex. g		Low r
	Dysten	Insular	Trick		Upper r
	Sillimanite Al AlSiO $_5$	Chainlike	Rhombus	1400	High t
Atoms change	Aragonite CaCO3 $_-$	Insular	Rhombus	400	Low t
	Calcite CaCO3 $_-$	Insular	Trig	400	
The system type	Valentinite SboOi	Chainlike	Rhombus	557	Low t
	Senarmontit Sb $_2$ O $_3$	Insular	Cube		Low t
	Anatase TiO2 $_-$	Textured	Tetr		Low t

	Rutile TiO2	Chainlike	Tetr	915	Medium and low t
The system type changes	Sphalerite ZnS	Coordination	Cube	1020	Alkaline
	Vursit ZnS	Coordination	Hexg		Sour
	Marcasite FeS $_2$	Insular	Rhombus	415	Sour
	Pyrite FeS $_2$	Insular	Rhombus		Alkaline
	Quartz SiO $_2$	Textured	Trig	573	Average
	Hexaquartz SiO2 _	Textured	Hexg		High t
	Hexachristo-balit SiO2 _	Textured	Hexg		High t
	Hexatridymite SiO2 _	Textured	Hexg	870	Very good
The orientation of the polyhedra changes in the layers	Wursite-2H ZnS	Coordination	Hexg		Average t
	Vursite-4H ZnS	Coordination	Hexg		Average 1
	Hegbomit-15R Mg $_2$ Al $_4$ O $_8$	Coordination	Trig		High
	Hegbomite-21R Mg $_2$ Al $_4$ O $_8$	Coordination	Trig		High

The most common crystal structures of metals are hexagonal close-packed, cubic close-packed, and cubic volume-centered structures. As calculated above, the volume occupied by metal atoms in such structures is 74.05% in the first and second cases, and 68.01% in the third case. At the same time, the coordination number is equal to Z = 12 in the cubic and hexagonal close-packed structures, and Z = 8 in the volume-centered cubic structure. In metals, the binding force does not have a specific direction, so each atom tends to attract more electrons to itself. Only a and b - U, Pa, and all other modifications of Mn, other metals crystallize in the three different systems listed above. This can be seen in the case of α-Mn. The actual 58 Mn atoms

per unit cell are divided into four groups of 2, 8, 24, and 24 more. None of these can be reconciled by means of symmetry. The electronic states of these atoms are also different. Although the α-Mn structure is unique, it resembles general formal metal structures, that is, it has a high degree of symmetry - cubic, and a large coordination number. x − Although it crystallizes in rhombic syngonia, the system closely resembles the hexagonal close-packed structure.

B-Mn − crystallizes in cubic syngonia, which is very close to the type of cubic dense arrangement, and the coordination number is Z = 12, despite the fact that its atoms are arranged in two different ways. But the distance between them varies from 2.36 A° to 2.67 A. The g-Mn crystal structure is similar, but deformed along the 4th degree symmetry axis; accordingly, the crystals belong to the tetragonal syngonia . To sum up , in general, the structure of the elements of this group is mainly of three types, as mentioned above.

The crystal structure of elements such as Hg, Zn, and γ-Mn is completely different, although Mn atoms appear to be cubic densely arranged in the α-Mn crystal structure. If the elementary cell of the cube is slightly stretched or shortened along the 4 axes, the degree of symmetry decreases sharply; two 4, four 3 symmetry axes disappear; the spatial lattice belongs to the tetragonal syngonia. Tetragonal syngonia has a volume-centered unit cell, not sides, according to Brave's rule. At the same time, the volume of this cell remains two times smaller than the centered cube.

The wire crystal structure also resembles the γ-Mn structure. But the size of the cubic unit cell changes in the other direction. From this point of view, the Hg crystal structure also has its own characteristics. It crystallizes in the form of a rhombohedron, but its general appearance closely resembles a concentric, cubic cell. As that cube is transformed into a unit cell with side angles of 60°, a number of its means of symmetry are reduced, that is, the four 3 axes of symmetry remain single, and the three 4s disappear altogether. As a result, instead of a cubic elementary cell, a simple rhombohedron-shaped elementary cell with a volume 4 times smaller than a cube appears. Thus, a transition from a cubic close-packed structure to a hexagonal close-packed structure can occur, as seen in the case of mercury.

In the crystal structure of non-ferrous chemical elements, the coordination number is equal to K = 8 - N, where N is equal to the order number of the group in the periodic table of elements. This is a consequence of the tendency for each chemical element to be surrounded by 8 mt electrons. Therefore, it forms a shared pair of electrons with neighboring atoms. Electrons located between these atoms, belonging to both atoms, create a covalent bond between these atoms. As a result, the coordination number of halogen elements and hydrogen is equal to one. Because each atom has only one nearest neighbor atom, such as Cl-Cl.

The coordination number of VI-b group elements is equal to 2. Berk can be like this in loops or infinite chains. This is true: with sulfur, which crystallizes in rhombic and monoclinic syngonia, a ring of eight atoms is located at the ends of the selenium unit cell.

The coordination number of the elements of the V-6 group should be equal to 3. In fact, P (black) is like this in the crystal structure of As, Sb and Bi. All these elements are located in layers with an uneven surface, and the distance between atoms located in this layer is smaller than the distance between atoms located in other layers.

Similarly , elements of the V-6 group form a molecule in the form of a tetrahedron consisting of four atoms. This can also be seen in phosphorus, which is made up of cubic, densely packed molecules formed at low temperatures.

One of the elements belonging to the IV-6 group, diamond-carbon with a coordination number equal to 4, also crystallizes in such a structure as Si, Ge, Sn. The crystal structure of graphite and white tin is different in terms of the $K = 8 - N$ rule - it is very complex. According to the known rule $K = 8 - N$, the coordination number of Sh-b group elements should be equal to 5. However, the absence of a 5-degree symmetry axis in natural crystals is a consequence of the absence of a structure with a coordination number equal to five. Because the elements of this group are far from the group of non-metallic elements and their metallic properties are more obvious. Therefore, in addition to covalent bonding, they also exhibit the type of bonding specific to metals.

II -b group elements is equal to K=6, which is completely consistent with the known rule. These elements lack electrons to form covalent bonds, and the metallicity is more pronounced. Therefore, their crystal structure is very similar to that of metals with a coordination number equal to 12, but it is still close to the dense arrangement of spheres characteristic of metals. The coordination number is six, but there are also other sixes that are slightly further apart than the previous ones. For example, the distance between neighboring atoms around zinc is 2.66, and the distance between the remaining 6 atoms is - 2.91 A°; 2.97 and 3.29 in similar cadmium; in mercury - 3.00 and 3.47 A°.

Therefore, the main part of the elements of group "b" in the Mendeleev table crystallizes in systems that follow the molecular structure or the rule $K = 8 - N$. Sometimes there are some complex structures where this general order is violated.

Crystal structures of metal alloys. The radius of metal atoms is determined by dividing the distance between atoms in pure metal structures with a coordination number equal to 12. If their coordination number is different from 12, it is corrected according to special tables.

Atoms of different metals can be bonded to each other in different ways. Some of them do not chemically react with each other either in the liquid or solid state and form separate (one does not mix with the other) layers. Finally, these two metals enter into a chemical reaction, a compound with a specific composition is formed. Here are a few different cases in between:

a) metal atoms, as mentioned above, do not chemically react either in the liquid state or in the solid state;

b) metals mix in a liquid state and then form a solid mixture;

c) metals form an infinite solid solution with each other;

d) metals form one or more alloys with each other. There are no clear boundaries between these states, one can pass from one to another through certain intermediate states. At the same time, the stability of these compounds is also different.

Mixed metals in the liquid state. These form neither a solid solution nor a solid mixture when solidified. The radii of metal atoms are very different from each other. If their atomic radii are closer together, a solid solution occurs. For example, K and Li liquid layers, and K and Rb also form an infinite series of Cs solid solutions. Li forms an infinite series of solid solutions with magnesium. But Na also separates into different liquid layers with K.

Neither the sharp difference in the electronic layers of atoms nor the large difference between the melting temperatures of similar metals does not allow the formation of solid solutions.

Solid solution and metal alloys. In crystal structures, alloying metal atoms are arranged in a certain order. But the arrangement of those mixed atoms is rarely 100%. Thus, there is no sharp difference between a chemical compound and a solid solution. Atoms are arranged in a certain order in both of them.

An alloy of two and infinitely miscible metals. Metals and nonmetals form an infinite series of solid solutions that replace each other. Metals form solid solutions filled with non-ferrous elements with very small atomic radii (N, B, S, N).

Solid solutions with excess atoms in the crystal system can be seen in the combination of metals with some non-metallic elements - sulfur, selenium. The ionic radii of the mirrorless elements formed in such a system are very small. It also occurs in the solid solution where atoms are left vacant in the crystal system of these mirror elements. Among these different solid solutions, the most common are solid solutions with alternating atoms. In order to create an infinite series of solid solutions, the crystal structure of the chemical elements included in that solution should be the same or very similar to each other, and the difference between the ionic radii of these atoms should not exceed 10-12%. The chemical properties of the elements contained in this solid solution are also the same, that is, they should be located in one subgroup

or one period in the Mendeleev table. In some cases, even though the difference between the ionic radii of the chemical elements is large, this chemical affinity between the elements results in a series of stable solid solutions. The stability of the solid solution of In and Tl is related to the chemical similarity of these elements. It is known that In tetragonal has a cubic structure, and while forming a solid solution, it passes from one system to another depending on the amount of the element in it.

Polymorphism and solid solutions. The elements forming a continuous series of solid solutions must, as you know, have the same structure, but one of the elements forming the solution can crystallize in several systems in relation to the external environment. In this case: a) the types of element systems in the solid solution that occur at high temperature should be the same; b) one of the systems of elements in the solution must be compatible with the structure of the second element, that is, the type of systems of elements must not be associated with high temperature; c) none of the elements in the solution may have similar types of systems. For example, Pt with Ru, CO with V can form solutions. But they cannot create an infinite series of solid solutions.

These considerations can be seen in the example of a solid solution containing iron. Iron is known to crystallize in 3 different structures. a, b and d iron have the same structure, and g - iron belongs to a different structure. Iron pairs with other elements are in 4 categories.

1. A series of continuous hardening alloys formed on the basis of structural types a, b, d: V-Fe, Cr-Fe and k. a series of .

2. g - continuous solid solutions formed on the basis of the iron system. For example, Fe-pd, Fe-Pt, etc.

a, b and d - iron form a limited series of solid solutions under the same conditions. For example, Ti-Fe, Mo-Fe, etc.

The α − type and the d type of iron separate separately and form a limited series of solid solutions. For example, Zr-Fe, etc.

There is a certain relationship between the composition of the solid solution and the size of the unit cell. Since the solid solution consists of two metals, the size of the unit cell of that substance is related to the atomic radius of the metals. This value changes in a straight line according to the amount of metals participating in the composition of this solid solution, so that depending on the amount of these metal atoms, the change in the volume of the unit cell is expressed as follows - according to Vegard's rule:

$$a = \frac{a_1 c_1 + a_2 c_2}{100}$$

where a_1 and a_2 − spatial lattice size of each metal; c_1 and c_2 - molecular amount of each metal in the solid solution (in percent).

Most of them, including Pt-Au, Pd-Au alloy, obey Vegard's rule. But there are also cases that do not correspond to this rule. For example, this happens in solid solutions of Cu-Pd, Cu-Au, Ag-Au. For the formation of finite solid solutions, the above conditions for creating an infinite solution must not be fulfilled. In particular, metals in solid solution crystallize in other systems; the difference between the atomic radii is more than 12%, each of those metals is not chemically close to each other.

When any of these defects are present in the formation of a solid solution of metals, an alloy of limited composition is formed. For example, although metals crystallize in different systems, metals close to each other in terms of size are Li and Mg; Pd with Os; Hg with Cd; Hg with Ag; Zn with Cu; Cd with Ag and finally Al with Zn form a solid solution. If the difference between the size of the atoms is more than 10-15%, their solubility decreases sharply.

Solid solutions are formed even in cases where the chemical properties of metals are close to each other. In particular, metals of subgroup b form a solid solution more with each other and less with alkali metals.

The valency of the intervening elements is also important. Metals with a large valence can easily "fit" with low-valence elements, and conversely, low-valence elements cannot easily fit between multivalent metals.

The limit of formation of finite solid solutions is determined by the concentration of electrons. The ratio of the number of free electrons in a compound to the number of atoms is called electron concentration. The amount of crystal free energy is determined by the concentration of these electrons.

Solid solutions in which atoms are vacant in the crystal structure can be seen in the example of Ni-Al. As CsCl to the Al crystal system. An amount of up to 50% of alunite forms a formal exchange hardening solution. More than 50% of nickel is placed in place of Al. As the composition of the alloy changes, the volume and density of the unit cells also change. Because Al; - atomic radius - 1.43 atomic weight - 26.97; Ni - atomic radius - 1.23, atomic weight 58.69.

Therefore, as the light metal Al in the alloy replaces the heavy metal Ni, its density should also increase, but in reality, when the alloying amount approaches 50%, its density drops sharply. The reason for this is that when the amount of impurities reaches a certain ratio, in our case 50% of copper, the density of the alloy legally increases. part remains empty, and finally, as a result, the volume of the spatial lattice increases, the density of the solid solution decreases. When the amount of A1 in the Ni-Al solid solution approaches 60%, a compound containing Ni_2Al_3 is formed, and 1/3 of nickel remains empty in its crystal structure. All the free space corresponds to the (III) plane of the crystal system. The NiAl cubic form of the crystal remains trigonal (Ni_2Al_3).

Among the natural chemical compounds, there are more and more complex solid solutions metal alloys - intermetallic compounds than described above, the description of which is read as a special science.

Key words and phrases: disten, sillimanite, aragonite, calcite, valentinite, senarmontite, anatase, rutile, sphalerite, wursite, marcasite, hexaquartz , egbomite , hexatridimite;
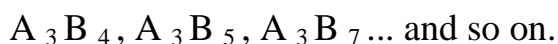
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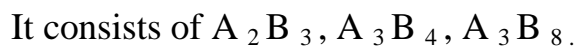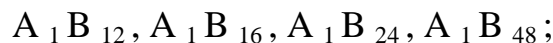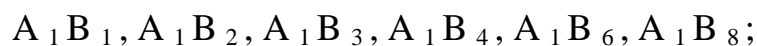
Crystal chemistry of inorganic compounds

Plan:
1. Binary compounds.
2. Crystal system of compounds of three or more elements
2. Crystal system of silicates.

From compounds consisting of two elements, it is possible to calculate the possible proportions of these elements. It is known from chemistry that the elements that make up the chemical compound are always in the ratio of whole numbers based on their valency. For example, AB, AB_2, AB_3, AB_6, AB_7, etc.

$$A_2B_3, A_2B_5, A_2B_7 \text{ ... and so on.}$$
$$A_3B_4, A_3B_5, A_3B_7 \text{ ... and so on.}$$
$$A_4B_5, A_4B_7, A_4B_9 \text{ ... and so on.}$$

But not all combinations in this series will be available. Valence theory and theories of the internal structure of crystals make their corrections to these lines.

According to the theory of the 230 group of symmetry of material points, taking into account the degree of repetition of material points, the possible rows of compounds in the crystal system are:

$$A_1B_1, A_1B_2, A_1B_3, A_1B_4, A_1B_6, A_1B_8;$$
$$A_1B_{12}, A_1B_{16}, A_1B_{24}, A_1B_{48};$$
$$\text{It consists of } A_2B_3, A_3B_4, A_3B_8.$$

Also, if valence theory is taken into account, the middle row of the listed possible compound types should be deleted. According to this theory, such chemical compounds cannot exist.

As a result of the fact that the positive valence of electricity does not exceed 8, and the negative valence of electricity does not exceed 4, these lines are shortened again,

AB_1, AB_2, AB_3, AB_4, AB_6, AB_8;
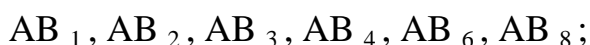
A_2B_3, A_3B_4, A_3B_8 will have the form.

But there may be such series as AB_5, AB_7, A_2B_5, A_2B_7, A_3B_5, A_3B_7, one of the elements participating in the composition of the phase occupies 2 or more types of positions in the crystal structure. and the result is a complex crystal structure similar to a compound system involving 3 or more chemical elements.

The crystal system of compounds of three or more elements is of two types. The first is conventionally labeled as ABX. In this case, A and B - metals form a compound with non-metallic element - X. The second different compound is designated as AuXy. A - metal, x and y - non-metal elements form a compound.

These two compounds are structurally very different. An example of the first type of compound is perovsknit $-$ $CaTiO_3$. In this case, the coordination number of calcium is 12, that of titanium is 6, and since there are 3 oxygen atoms corresponding to each metal atom, the atoms are not divided into separate groups.

In the second type of compounds, two elements form a complex anion group. For example, $[CO_3]^{2-}$, $[SO_4]^{2-}$ forms carbonates and sulfate compounds with metals. $[CO_3]$ group ^{2} has a planar triangle in the center with oxygen at the carbon ends, $[SO_4]$ is in the form of a tetrahedron with sulfur occupying the center ^{2} and oxygen at the ends (Figures 1.59, 1.60)
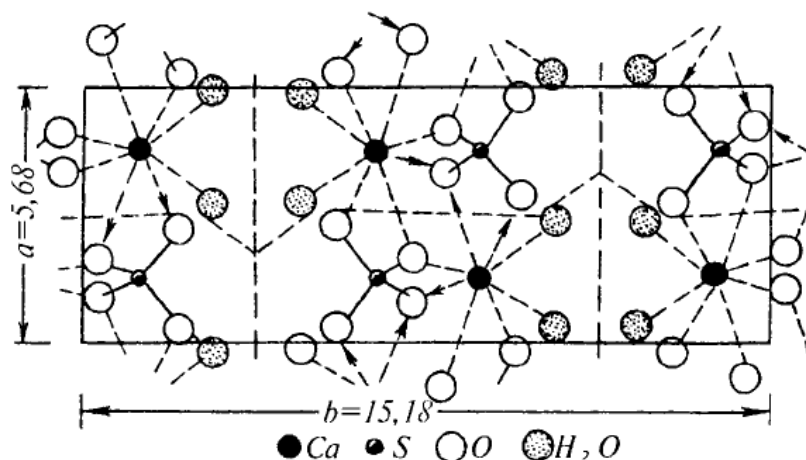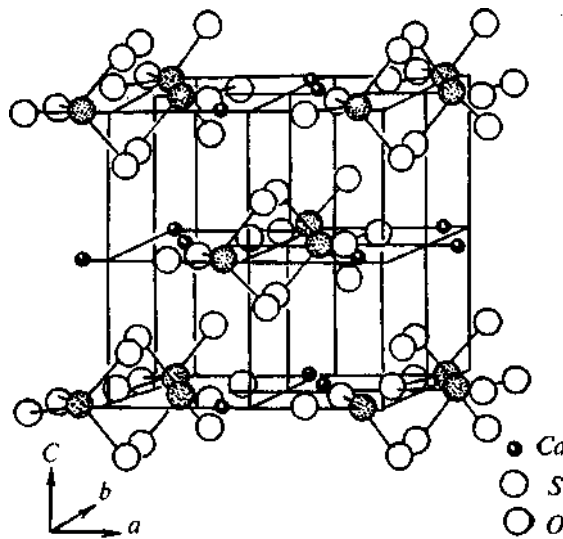

Figure 1.58

In compounds with a more complex composition, for example, ABXY type, the position of A metal is occupied by a part of B metals, as a result, the previous state of the crystal structure is almost preserved. In particular, in the crystal structure of dolomite ($CaMg[CO_3]_2$), part of the calcium in calcite is replaced by magnesium, layers perpendicular to the Z axis are occupied by Ca or Mg, respectively.
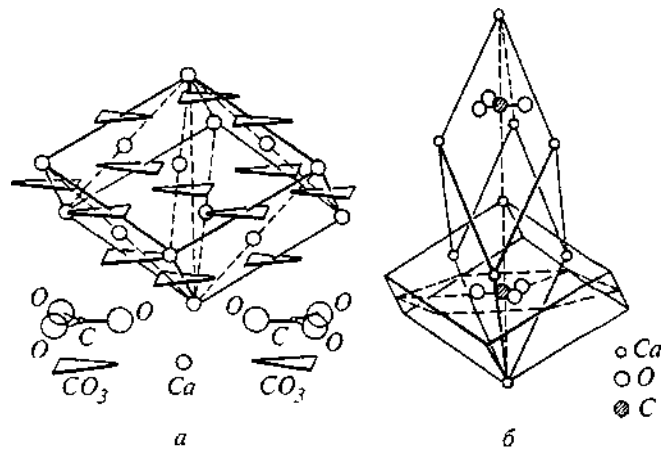
Figure 1.59

Figure 1.60

A similar situation can be seen in other complex compounds. In sphalerite - ZnS, chalcopyrite - $CuFeS_2$ and stannine - Cu_2FeSnS_4. In crystal systems, metals such as Cu, Fe, Sn occupy the place of Zn in that sphalerite according to a certain rule. In this case, the previous cube-shaped elementary cell turns into a tetragonal prism.

In sulfate crystal systems, which are one of the complex compounds, $[SO_4]^{2-}$ anion group always takes part separately. From this point of view, sulfates can be considered as having an island structure. However, depending on the strength of the connection between the tetrahedra of $[SO_4]^2$ and other polyhedra and the octahedra formed by two or more valence cations, they can be divided into island-like, chain-like, sheet-like, tissue systems. For example, in the crystal structure of gypsum $Ca[SO_4] \cdot 2H_2O$, $[SO_4]^{2-}$ tetrahedra combine with the Sa cation to form eight-pointed forms that form separate layers. Also, leongardite − $Mg[SO_4] \cdot 4H_2O$ has a complex island structure. Chain systems are formed as a result of successive exchange of $[SO_4]^{2-}$ tetrahedra with metal polyhedra or from $[SO_4]^{2-}$ tetrahedra adjacent to metal polyhedra.

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Crystal system of silicates . Silicates are inorganic compounds that are very common in the earth's crust with a very complex crystal system. Currently, many different silicate compounds are obtained artificially in laboratories and on an industrial scale. In order to explain the relationship between their very complex crystal structure and their chemical composition, a number of silicic acids were assumed to exist, and silicates were considered to be salts of these assumed acids.

Thanks to the development of science and technology, including the science of crystallography, as well as the discovery of X-rays and their use in the study of crystals, the whole inner "secret" of silicates has been revealed.

Thus, silicates are composed of system compounds consisting of $[SiO_4]^{4-\text{ anion}}$ group. Their diversity and complexity of composition is related to the spatial position of that silicin and tetrahedrons consisting of four oxygen atoms surrounding it and the order of their connection with each other. In addition, the size and chemical properties of the cations located between silicon-oxygen tetrahedra are also important in the structure of silicates. These will be discussed in more detail below.

Alternatively, in the composition of silicates, Si can be isomorphically substituted with a number of chemical elements. Such exchanges are especially pronounced with aluminum. Therefore, in a certain part of the tetrahedra formed from silicon and oxygen atoms, the place of Si_4^{4+} is occupied by $Al^{3+,\text{ that is, in the chrysgal}}$ structure, together with the $^{4-\text{ tetrahedra of }[SiO}_4]$, $[AlO_4]^{5-}$ tetrahedra are also involved, and such silicates are called aluminosilicates. Aluminum silicates also participate as cations, so they are called aluminum silicates.

From feldspars - orthoclase, microcline, albite, anorthite; minerals such as mica - muscovite, flagopite belong to aluminosilicates. Some silicates sometimes contain aluminum as both cation and anion. In this case, the mineral will be both an achymosilicate and an aluminum silicate at the same time. It also forms iron-ferrosilicate, boron-borosilicates, Be - beryllosilicates, etc.

When expressing the chemical composition of minerals, the element forming an isomorphous mixture with Si is written as a complex anion together with Si in a big parenthesis, and after the parenthesis, a sign indicating the crystal structure is placed. For example, $\infty -$ indicates that tetrahedra continue continuously in one direction, and k.

Silicon - oxygen tetrahedrons in the $[SiO_4]^4$ crystal system are separate or several of them are united through their mutual ends to form an "island". For example, in the crystal structure of minerals of the olivine group, $[SiO_4]^{4-}$ tetrahedra participate individually, in addition, "islands" consist of two tetrahedra $[Si_2O_7]^{6-}$, three tetrahedra $[Si_3O_9]^{6-}$, It can be composed of four tetrahedra $[Si_4O_{12}]^{6-}$, six tetrahedra $[Si_6O_{18}]^{12-}$ and double six tetrahedra $[Si_{12}O_{30}]^{12-}$. If the tetrahedrons

forming an "island" are located in one plane, they are called "ring-shaped" structured silicates (Fig. 1.61).

In the crystal structure, silicon-oxygen tetrahedrons connect with each other through an oxygen atom, continue continuously in one direction, and form a chain. In this case, a series of tetrahedra forming a chain is directed in the same direction as the ends of the tetrahedrons, in others, one of the ends of the tetrahedra is directed in the same direction, and the other is directed in the other direction, and it can be more complicated than this (Fig. 1.62). In the crystal structure of some minerals, those chains form a ribbon, that is, a ribbon-like or two-row chain. Many types of such bands can be seen in the structure of natural crystals (Fig. 1.63).

Tetrahedrons made of silicon-oxygen connect with each other with their ends and form a "layer"-"sheet" - a flat network that continues continuously in two directions in the crystal structure.
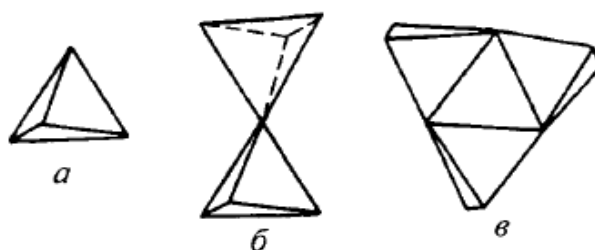
Figure 1.61
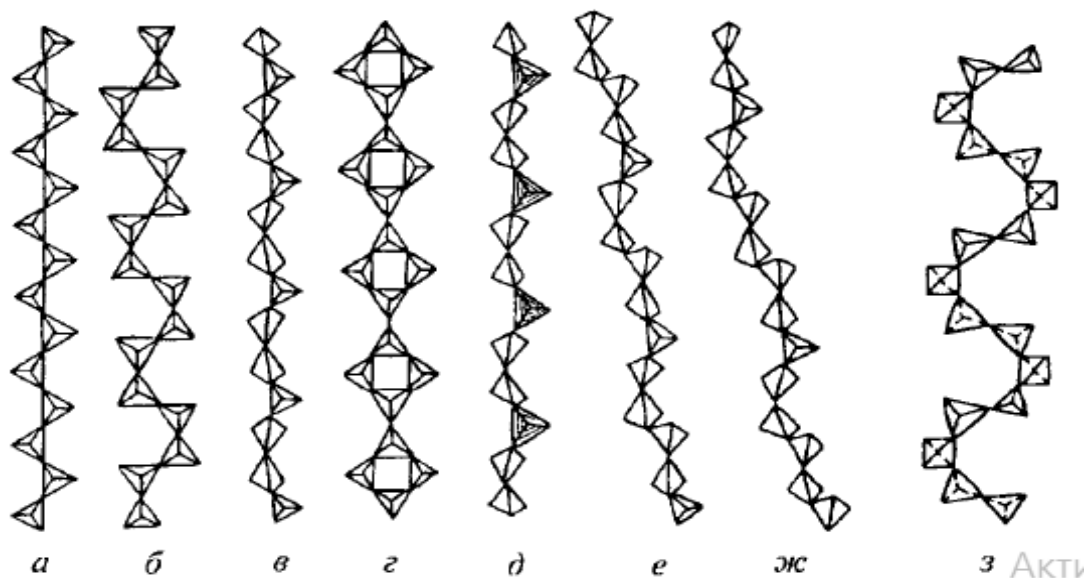
Figure 1.62

several types of such flat meshes, which are illustrated in Fig. 97. In particular, such types as talc (mica), b-apophyllite, v-okenite, g-melilite, d-datolite, e-epirosmalite are known. The difference between silicon-oxygen "sheets" in silicate and aluminosilicate minerals with such a structure can also be known by looking at their cross section.
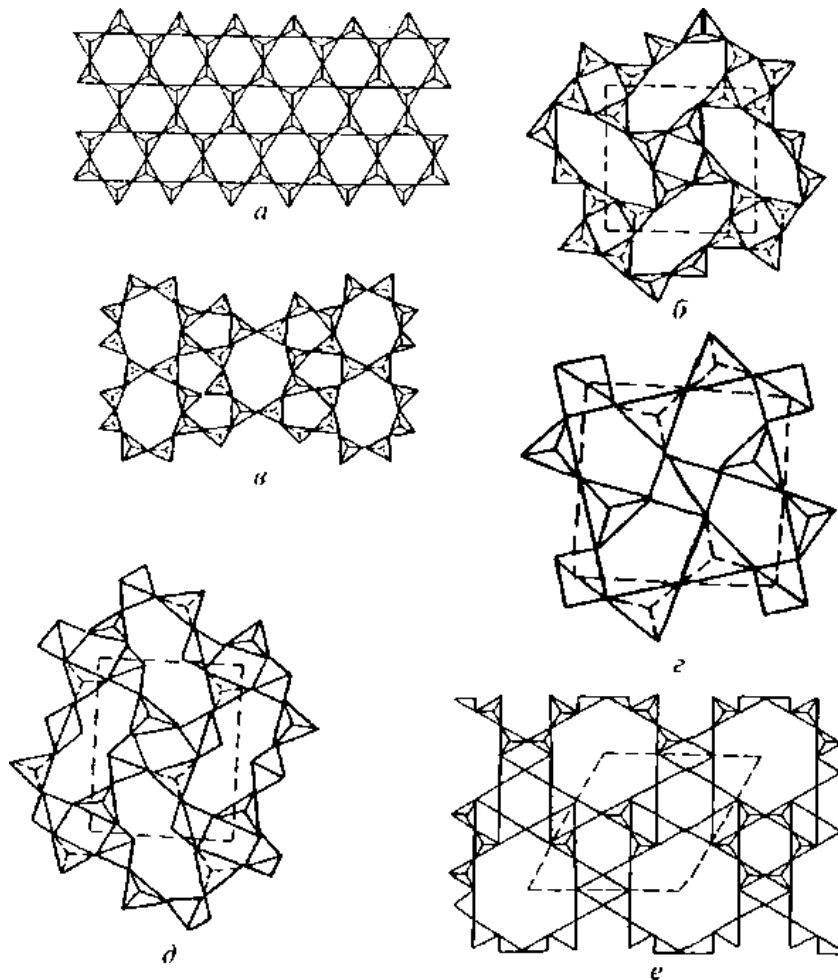
Figure 1.63.

Silica-oxygen tetrahedrons connect with their ends in three directions and form a "texture" as a result of continuous continuation of these tetrahedra. For example, SiO_2 compounds - crystals of minerals belonging to the group of quartz, tridymite, cristobalite and feldspars have such a structure. The internal structure of cristobalite, consisting of a three-dimensional structure of silicon-oxygen tetrahedra, is described; it crystallizes in cubic syngonia. In this case, the polyhedron is in the form of a tetrahedron, the number is 4, oxygen is located between each pair of silicon atoms - the coordination number is equal to 2

Key words and phrases: mica, apophyllite, okenite, melilit, datolite, epirosmalite, "sheets", perovsknit, coordination number

LECTURE 12

Classification of crystal chemical structure

Plan:

1. Crystal system of pure metals.

2. Structure of diamond, graphite.

Crystal system of simple substances such as AX, A_2X and AX_2.

The degree of symmetry of crystals is generally related to their chemical composition. The simpler the chemical composition of crystals, the higher the degree of symmetry, the more complex the composition, the lower the degree of symmetry. This law is called the Fedorov-Groth law. Fedorov comes to this conclusion in the process of preparing the tables he developed for his book "The World of Crystals". Later, the German crystallographer Groth (1843−1926) expressed the same opinion.

Artificial as well as many natural crystals confirm the idea stated in this law. For example, many pure elements crystallize in cubic syngonia (Li, Na, K, Cu, Ag, Au, etc.) or hexagonal syngonia (Be, Mg, Zn, Ca, Te, Re, etc.). Also, many oxides MgO, CaO, UO_2; Bi_2O_3, Cu_2O; sulfides: PbS, ZnS, FeS_2, Cu_2S and halogen compounds such as NaCl, KCl, CaF_2, CsCl all crystallize in cubic syngonia.

But despite this, there are such simple compounds, even pure elements, that their degree of symmetry is low. For example, S, Se, Cl, Br, I. There are sulfides and other simple compounds with such a low degree of symmetry. This is even more evident in the crystals of the chemical elements in Mendeleev's table.

In nature, compared to simple chemical compounds, crystals with a complex composition and low symmetry are more common than crystals with high symmetry. From the crystals known so far, the most common and tested 1308 crystals are divided according to the degree of symmetry as follows: low grade 760 mineral type - 57.5%; the middle layer 377 mineral types − 29.5% and finally, the upper layer 171 mineral types − 13% are crystallized.

All elements are listed in order of atomic number.

Rows in Mendeleev's table are separated by a dotted line, and periods are separated by two dashes.

The following symbols are used in the table:

A-1 Side-centered cubic dense arrangement: copper type

A-2 Size-centered cubic dense arrangement: Wolframite type

A-3 Hexagonal close arrangement: magnesium type

A-4 Cubic: Diamond type

A-5 Tetragonal: white tin type

A-6 Tetragonal size centered: indium type

A-7 Rhombohedral gray marble: type

A-8 Hexagonal gray: Selenium type

A-9 Hexagonal: graphite type

A-10 Rhombohedral: type of mercury

A-ll Rhombic: type of mercury

A-12 Cubic: type of α-manganese

A-13 Cubic: β-manganese species

A-14 Rhombic: type of iodine

A-15 Cubic: tungsten type

A-16 Rhombic: A type of black phosphorus

A-17 Rhombic: Sulfur type

A-18 Tetragonal: A type of uranium

A-19 Simple cubic: polonium type

A-20 Rhombic: A type of uranium.

The degree of symmetry of crystals depends, firstly, on the atomic structure of the chemical element that is part of the crystal, secondly, on the position of the system units that make up this crystal - atoms or ions in space, and finally on the environment in which this crystal is formed. That is why some simple compounds have a low degree of symmetry, and on the contrary, complex compound crystals can have a high degree of symmetry.

Structures of ordinary metals. We know the spatial arrangement of atoms in a substance as the structure of substances.
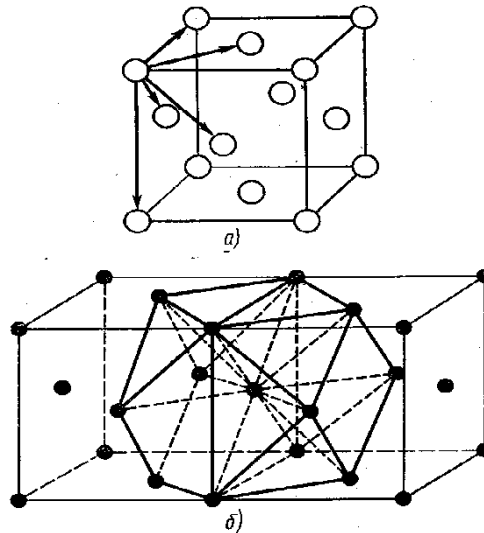
Figure 1.64

1. Structure of copper (syngonia cubic)

Parameters: a= b=c=3.61 A°

Au (α=4.07 A°), Ag(α=4.08 A°)

Al (α=4.04 A°)

Number of atoms in elementary cells

$$n = \frac{1}{8} \cdot 8 + \frac{1}{2} \cdot 6 = 1 + 3 = 4$$
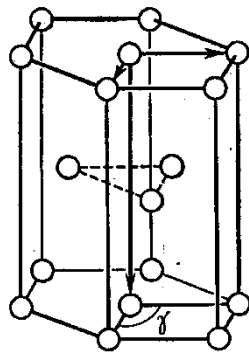$$R \ (\alpha = 4.07 \ A°)$$

The law of arrangement of atoms in these metals is the same, so the structure type is similar to copper.

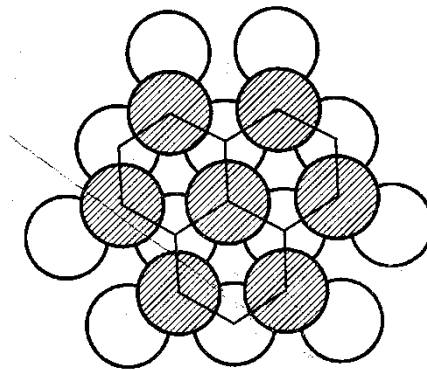2. αFe structure, the number of atoms in the element cell is n= 2

α-Fe(α= 2.86 A°) n=8*1/8+ 1=1+1=2 K(α=5.33 A°), Na(α=4.28 A°), Ba (α=5.01 A°)

3. Mg structure (syngony hexagonal) a=3.20 A0

Atomic number $n = 12\frac{1}{6} + 2\frac{1}{2} + 3 = 6$C=5.2 A°

Figure 1.64   **Figure 1.65**

α-Be (a=2.86 A° c=3.58 A°)
α-Co (a=2.65 A° c=4.07 A°)
Diamond structure.
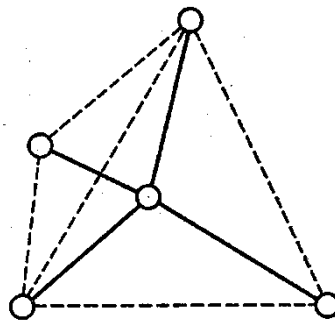
Figure 1.66

To describe the structure of a diamond, if we cut a cubic primitive cell with planes perpendicular to each other, the result is 8 octants. C atoms CC=1.54 A°

primitive cell is 8 deep, 6 facet centers and 4 octant centers out of 8 alternately present in one and absent in one.

The number of atoms $n = 8\frac{1}{8} \cdot 6\frac{1}{2} + 4 = 8$ is a coordination polyhedral tetrahedron.

Graphite structure

Figure 1.67
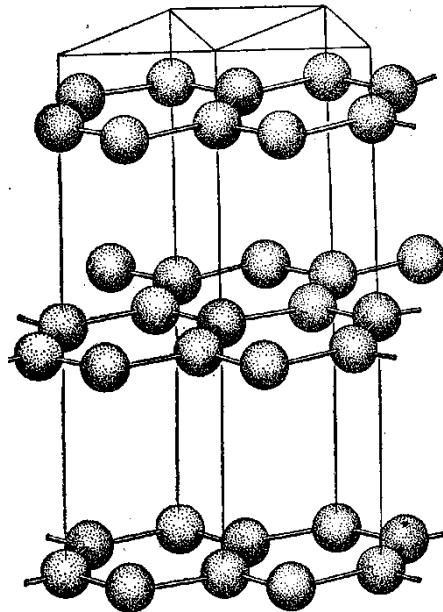
CC= 1.54 A° These structures are called layered structures.

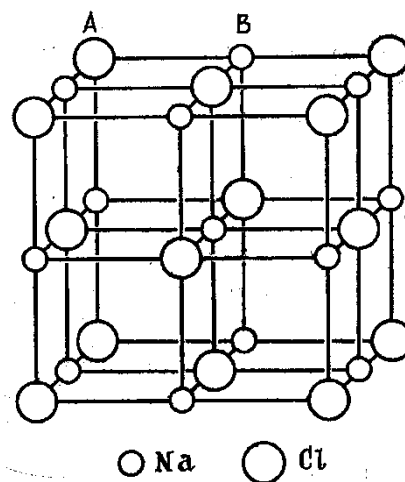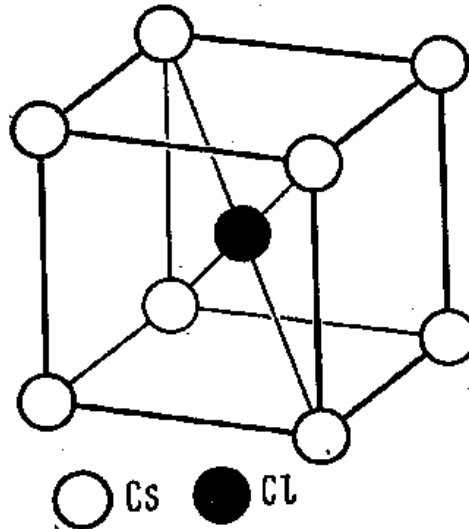**Simple structures of type AX.** The coordination number of an atom is the number of nearby atoms.

○ Na ○ Cl

Figure 1.68

Number of atoms nCl = 4 nNa = 4

105

Cl number of coords = 6
Na coord number is 6
Cl is a coordination polyhedral octahedron
No coordination polyhedral octahedron

Figure 1.69. The unit cell of the CsCl crystal

The number of Cl O atoms is nCl
The number of Cs o atoms is nCs
Cl number of coords = 8
Cs number of coords = 8
Cs coord. Polyhedral hexahedron
Cl coord. cube

LECTURE 14
X-ray structure analysis devices and their working mechanisms

I. ZnS sphalerite mineral (singonia cube). Its structure is similar to that of a diamond. Zn atoms are arranged according to the law of the F cell, but in the case of C atoms, 4 out of 8 octanes are arranged in one of the octane centers. The coordination number of ZnS structure is equal to 4.

II. ZnS wurtzite mineral structure type is hexagonal syngonia, wurtzite structure is similar to Mg structure, but Zn atoms are in the centers of two bases and 3 trigonal prisms in the hollows of the hexonal prism, and "S" atoms are in the centers of 3 trigonal prisms and in the middle of all vertical edges.
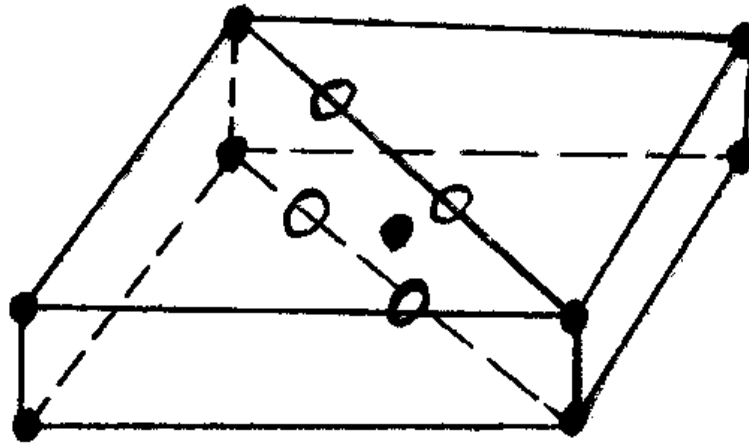
Rutile (TiO$_2$) structural type.

Figure 1.70

Ti coord. number = 6, multifaceted

O will be an octahedron, coord. number = 3 triangles

Ti atoms are located at the vertices of the cell and at the center of the volume, but oxygen is located in parallel diagonals located at the two bases and also perpendicular to them in such a diagonal that passes through the center of the cell and is located parallel to them.

AX$_2$. Li$_2$O, Na$_2$O, Na$_2$S, anion takes place of cation in this structure.

CaF$_2$ roofs:

$$nCa = 1\frac{1}{8} + 3\frac{1}{2} = 4nF=8$$

Ca coord. number 8 "Ca" polygonal cube,

"F" coord. number is 4, polyhedral tetrahedron.

The structures of most metals are arranged by the law of compaction. There are two variants of the laws of breaking the spheres: cubic and hexagonal. The second layer can be poured into the depth between the spheres. In options I and II, if we fill the volume of space with balls of one size, it will be 74.05%, but 25.95% space will remain.

α-Fe structure.. Coord. number 8, the CsCl structure has a "Cs" ion in the volume of the cubic cell, that is, two different ions are located in the cell.

Sodium ions are located at the peaks, in the centers of the edges, coord. the number is 6 and the shape is an octahedron. Type CsCl$_4$, CsBr. But simple substances (Si, Ge, Pb) have a diamond-like structure. ZnS sphalerite similar to diamond crystal lattice, Zns-type structures: SiC, BN, AlP, ZnAs, ZnSb, GaAs, CuCl
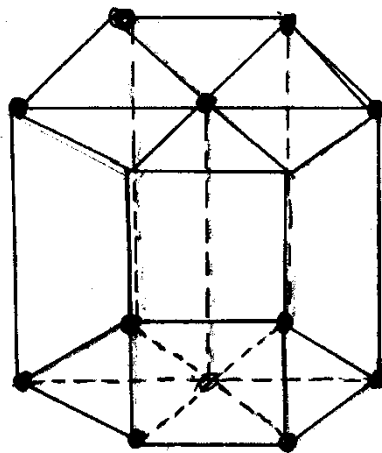
Figure 1.71

ZnS wurtzite structures. Zn has 6-sided prisms at the vertices and base centers, and 6 three-sided prisms with 3 S atoms in the center, all 3-sided prisms on the sides and Zn atoms, in 3-sided prisms, each Zn atom is located between 4 "S" atoms.

The structure of ice is similar to the structure of wurtzite, but instead of Zn and S atoms there are only water molecules. Each water molecule is connected to each other by hydrogen bonds with 4 neighbors, that is, hydrogen bonds surround the molecule like a tetrahedron. The oxygen atomic orbitals are bonded to the hydrogen atoms by sp hybridized bonds, but the two occupied by q are bonded by lone electron pairs. They attract a hydrogen ion to a neighboring water molecule.

AX $_2$. In the structure of CaF_2 fluorite, 8 "F" are located at the vertices of the cube. Around the cube there are 8 grains on the vertices of the big cube.

Energetics of ionic crystals. The amount of energy in the crystal lattice is shown in such a way that it is used to spread the ions of substances over a long distance from each other. The size of the energy of the crystal lattice indicates the strength of the crystal, its solubility, etc. properties. If the energy of the crystalline substance is known, the solute interactions between ions and the solvent interactions with molecules can be determined.

Table 1.9

Structure type	Formula	Coord. the number	
Sodium chloride	NaCl	Na= 6 Cl= 6	1.7475
Cesium chloride	CsCl	Cs=8 Cl=8	1.763
Sphalerite	ZnS	Zp =4 C= 4	1.638
Wurtitz	ZnS	Zp =4 C= 4	1.641
Calcium phtoide	SaF	Ca= 8 F=4	2.520
Rutile	TiO2 _	Ti= 6 O= 3	2.408

A large amount of energy must be released in order for a crystal to form from an ion mole ash. Therefore, a lot of energy is spent for the ionic crystal substance to pass through the gas state. Therefore, the melting temperature of ionic crystals is high and the heat of sublimation is also high.

Key words: atomic number, diamond, graphite, copper, iron, magnesium, structure, hexagon, wurtz, sphalerite, octahedron, tetrahedron, coordination, prism, fluorite, energy, solvation;

LECTURE 15

Diffraction of X-rays in a crystal

Plan:
1. Entgenostructural analysis of crystals
2. Determination of spatial grid types and sizes **.**
3. Defects of crystal systems.

The crystal system is made up of periodically repeating material points, a row of these points, a flat grid formed by those rows, a spatial grid formed by the periodic repetition of these flat grids, i.e. parallelepipeds. These material points - ions and atoms - have a definite size, as well as a definite distance between the rows and lattices of the spatial lattice. The common unit of measurement for these is A° - one millionth of a centimeter. It should also not be forgotten that at the time ESFedorov discovered the regularity of spatial location of material points, there was no information about the exact size of the units of the crystal system. After the discovery of X-rays, in 1912, Laue proved that this light is similar in nature to light, except that it has very short wavelengths. Its wavelength is about 10,000 times smaller than that of light. In the same year, VLBregg, and later GWWulf, used this short-wavelength light as a unit of measurement to determine the size of ions and the distance between the plane lattices of spatial lattices, and finally the size of the unit cell. For this, the following equation was developed, which determines the relationship between the distance (d) between the flat grids of the spatial grid, the X-ray wavelength (l) and the angle of return of the beam (α): nl = 2dsin $_a$. VGBregg and VLBregg experimentally determined the value of d for various crystals.
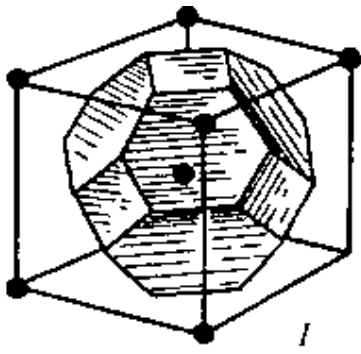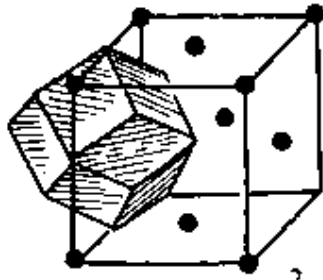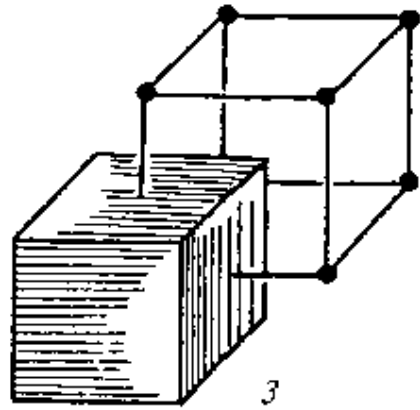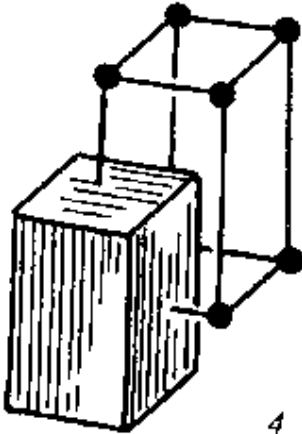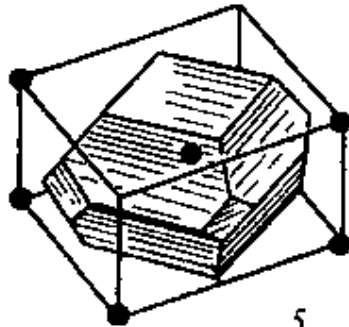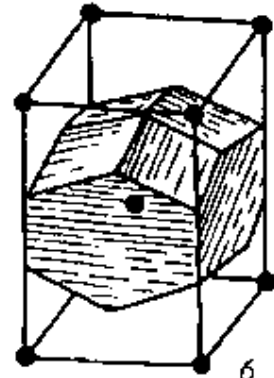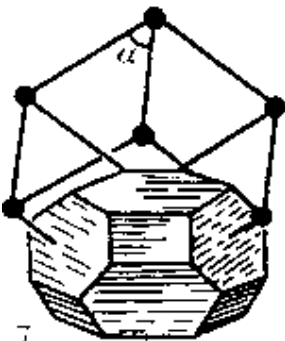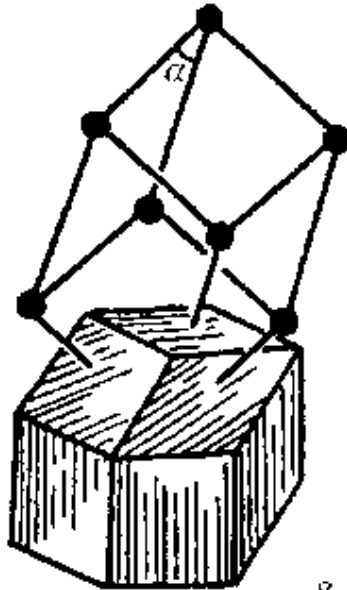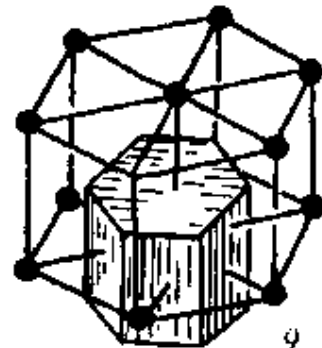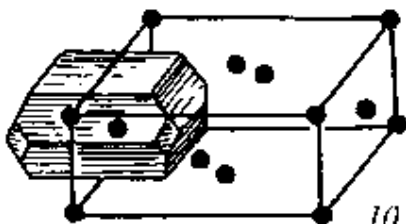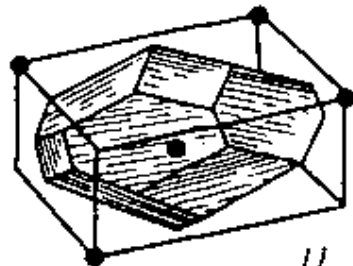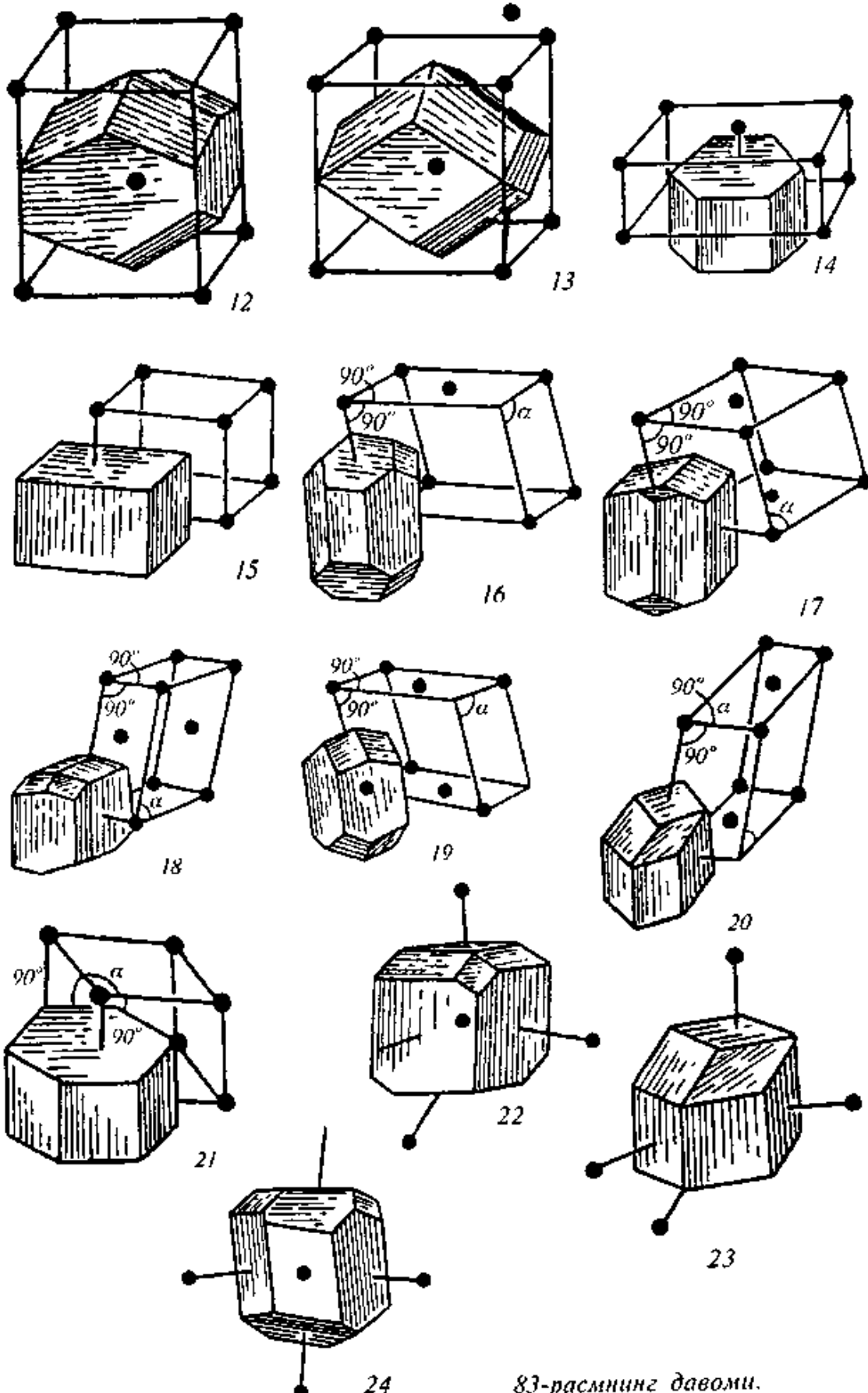
Figure 1.72

1.73 shows the operation of the device that examines the crystals discovered by Bregg using X-ray light. In this case, S is the X-ray source, K is the crystal to be tested, F is the ionization chamber, n 1,2, 3... in the equation is the return rate. The K - crystal is mounted on a vertical axis, and by rotating it around this axis, the angle of incidence of the X-ray beam can be changed, while the F - ionization chamber also rotates around this axis and returns from the side of the crystal. receives light.

It is known from the conducted experiment that the crystal consists of flat bars arranged in parallel - in a row.
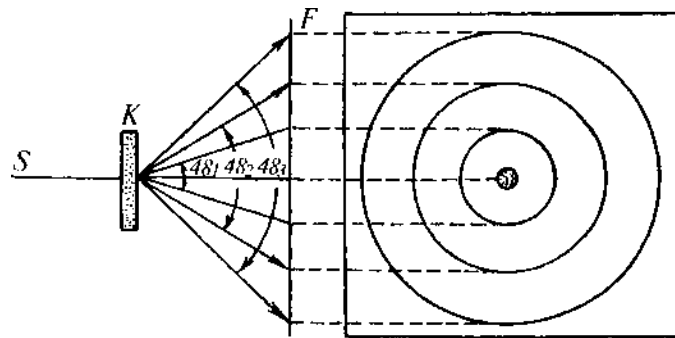
Figure 1.73
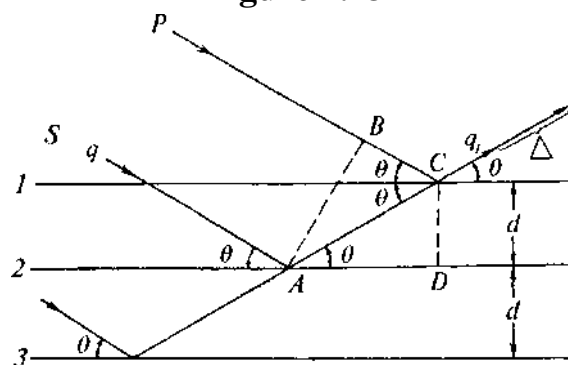
Figure 1.74

As shown in Figure 1.74, one of them lies at a distance d from the other. Therefore, the x-rays return at certain angles relative to the plane gratings in connection with this d value. The X-ray beam returns from different materials, as well as from different sides of crystals of the same material, at different angles. If the wavelength of the light is known according to the equation given above, it is possible to calculate the spacing of the flat meshes of the lattice d. Then: d = l/2sin $_a$. After Laue's discovery, after VG and VL Breggs and Wolf developed the basic equation for X-ray analysis, X-ray analysis was greatly developed, and the determination of the distance between atoms began. In particular, the crystal structure of copper was investigated among the first.

Determination of spatial grid types and sizes . With the discovery of X-ray light, it became possible to determine the internal structure of crystals, that is, the

position of the system units that make up that crystal in relation to each other in space. Certain methods are used for this. Among them, the "rolling method" - the Debye-Scherrer method is used a lot. With this method, it is possible to study the internal structure of crystal fine powder as well as properly structured crystals. For this, the crystal to be analyzed or its powder is placed on the tip of the arrow K, the light from the anticathode d passes through the diaphragm F, falls on the crystal K - and returns through its system units to the X-ray strip installed in the form of a circle. falls and forms a striped black spot in this band in a certain order characteristic of that crystal structure. Then, based on the spots in this band (Fig. 1.75), the crystal system is calculated. Such calculations are carried out on a very large scale for compounds with complex composition. The possible error in determining the crystal structure with this method does not exceed 0.001 A°. Now this task is performed on computing machines.

Using such methods of examination of crystals, many properties that are not obvious to the naked eye, and at the same time unique to each crystal, are revealed.
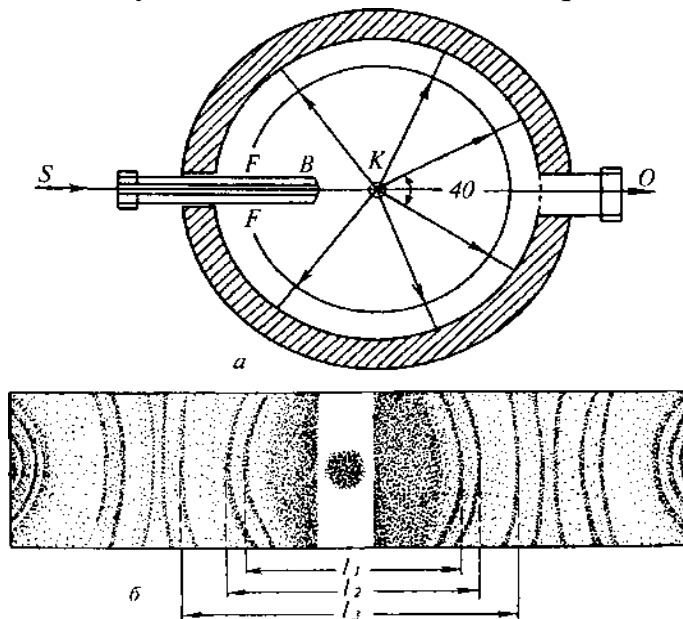
Figure 1.75

It turns out that atoms, ions and molecules, which we think must be arranged in a clear, legal order in the crystal system, to some extent violate that naturally determined arrangement, and as a result, various defects appear in the crystal system.

Defects of crystal systems . Disruption of the arrangement of the material point is due to the fact that material points that are repeated infinitely periodically are sometimes left empty . Such a structural defect is called a vacancy. As shown in Fig. 1.76-a, when such a defect occurs in the official - legal flat grid, then a change occurs in the location of the material points surrounding the place of the vacant point. As a

result of the displacement of a material point next to a vacancy to this vacancy, a shift in a certain direction in the system can occur. Such displacement or displacement accelerates with increasing temperature.

The location of a material point can also have a second case, that is, among those material points located in a certain order, there can be additional material points that do not have a "separate place" for themselves (Fig. 1.76 , b). Even in this case, the general order in the crystal lattice is disturbed around this excess point.

Defects of crystal systems are caused by the growth medium of that crystal and the replacement of material points in the crystal structures with other material points with a larger or smaller radius (Fig. 1.76-e).

^{12} -10 $^{14\ units}$ per cubic cm of the crystal . Over time, these defects may decrease and disappear on their own. Modern techniques require obtaining crystals without defects. But crystals without defects cannot be obtained artificially, they are not found in nature. Such defects are not less than 10-6% ^{even} in crystals of the substance with the highest purity .
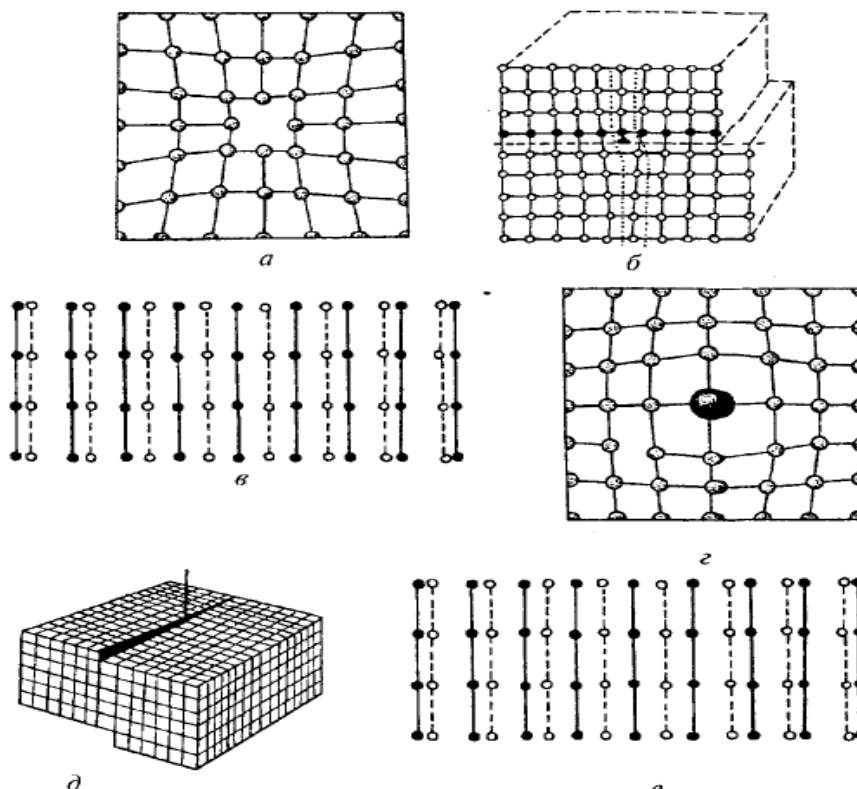
Figure 1.76

In the structure of crystals, displacements caused by sliding are also defects called dislocations. When a force is applied to a crystal in a certain direction, a certain part of it moves in a certain direction. In the structure of that crystal, a dislocation occurs. If the dislocation is oriented in a straight line, as shown in Fig. 1.76-e, it is called a linear defect. Such a defect can also occur due to the

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displacement of one part of the crystal relative to another part of the interatomic distance. In this case, such a distortion in the crystal structure is called a twist defect (Fig. 1.76-d).

Key words and phrases: distance between spatial grids, X-ray beam, wavelength, beam return angle, return rate, ionization chamber, "rotation method", torsional defect, linear defect;

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LABORATORY EXERCISES

LABORATORY EXERCISE-1

Crystal, the main properties of crystalline substances

The works of great medieval scientists - Abu Raykhan Beruni and Abu Ali Ibn Sina played a major role in the creation and development of crystallography, mineralogy and crystallochemistry. Abu Raykhan Beruni (973-1048) in a number of his works written in Arabic, mentions very wonderful ideas about mineral ores and geological processes. He believed in the roundness of the Earth and was one of the first to measure its size. In Beruni's work entitled "Determining the final limit of the distances between inhabited lands", stones and gravels and small particles are separated from the mountain under the influence of various forces; then, due to the force of water and wind for a long time, the edges are broken, smoothed and rounded. From them, in turn, small grains - sand and dust - appear. If these gravels are collected in the riverbed, clay and sand will enter between them and turn into a whole dough. Over time, the mixed material is buried under the water.

A contemporary of Beruni, the great scientist, naturalist and philosopher Abu Ali Ibn Sina (980-1037) also contributed to the development of geological science. Ibn Sina's views of the geological world are covered in the "Nature" section of his scientific book "Ashshifa" (Healing of the Heart). 5 parts of this book are devoted to meteorological phenomena. In this book, the causes of the formation of rocks and minerals and the origin of meteorological phenomena are studied.

Ibn Sina investigated the physical properties of rocks and minerals, the conditions of formation of mountains and valleys, and developed a hypothesis about them. The famous scientist Ulugbek spent a lot of effort and energy in the development of mathematics "Al-jabr" and astronomy in Central Asia. He was one of the first to correctly interpret the law of distribution, movement, and number of celestial bodies, including the solar system.

KhM Abdullaev, IXHamrabaev, IM Mirkhojiev, XN Boymuhamedov and IM Isamuhamedov did a great job in the development of Central Asian mineralogy and petrography. AP Vinogradov, DISherbakov, AA Saukov and others played a big role in the further development of this field of geological science, founded by Russian scientists VI Vernadsky and AE Ferdsman. Geologists of the 20th century developed theories about the movement and division of underground water into zones, mineral waters. In Central Asia, OM Akramhojaev contributed a lot to this issue.

bounded by several faces of different or identical k- shapes. Accordingly, crystal forms are called simple or complex. If the shape of a crystal consists of only the same type of faces, then its shape is called simple shape. Cube, tetrahedron,

dipyramid are examples of simple shapes. If the shape of the crystal consists of several different, different haze-like sides, it is called a complex shape. For example, pyramids and prisms, etc. Because their bases are the same, and the sides that form a pyramid or prism have a different appearance. In addition, simple shapes themselves are divided into two types of open and closed shapes.

From 1669, scientific theories about crystallography began to appear in the world of science. In the same year, the Danish physician Nils Stensen (1638-1686) as a result of his work on the measurement of quartz crystals, concluded that the angle between the corresponding sides of the crystals, regardless of their size and appearance, is constant.

Hundreds of years later, the great Russian scientist MV Lomonosov rediscovered the law of constancy of angles thanks to his research on saltpeter crystals. From that moment on, the conclusions of Stensen-Lomonosov about the angular constancy were clearly formed as the first fundamental law of crystallography. At the same time, O. Bartolin discovered the feature of double refraction of iceland spar crystals, and the existing connection plane of this crystal was determined. This innovation also serves as a basis for studying the optical properties of crystals. Later, the Dutch scientist H. Huygens studied the properties of birefringence of crystals in detail and assumed that these properties are related to the internal legal structure of crystals. Finally, he came to the idea that each crystal is made up of different particles with a unique shape.

Russian chemist MV Lomonosov (1711-1765) created the corpuscular theory of the structure of matter, the particles that make up matter - corpuscles - were imagined in a spherical shape. Based on this theory, as we said above, the law of constancy of the angle between corresponding sides of crystals was scientifically justified. It is shown that during the growth of crystals, the corpuscles are stacked one on top of the other, forming the crystal sides, and the crystal sides grow parallel to the initial state. Lomonosov was also involved in researching the shape and physical properties of crystals. The scientist paid special attention to the issues of the influence of existing conditions and environment on the growth rate of crystals.

Figure 2.1. Caranjo goniometer and single circle goniometer

The French mineralogist Jean-Baptiste Louis Rome de Lille (1736-1790) also rediscovered the law of constancy of angles about 20 years after MV Lomonosov's discovery, that is, without knowing about the work of Stensen and Lomonosov, and in 1772 he published this law under the name "Crystallography or Crystals". describes in his book "the description of the geometric shapes of various bodies characteristic of the world of minerals".

RJ Gayui (1743-1822) discovered the second fundamental law of crystallography in 1784, the proportionality of crystal sizes, or the law of whole numbers. The property of calcite crystals to form flat surfaces in certain directions and fracture (according to the existing perfectly aligned planes) was the basis for this discovery. Gayui - assumes that the molecules that make up crystals are always in the form of parallelepipeds. Because at that time, the theory of the internal regular structure of crystals (described by the spatial grid as we know it today) had not yet been discovered.

The discovery of the third fundamental law of crystallography by the German mineralogist and crystallographer XS Weiss (1780-1856) also dates back to this period. According to this law, the relationship between the sides and edges of the crystal is given. In 1818, the expression of the relative sizes of each side and facet of a crystal by three integers was implemented for the first time.

Control questions:
1. How is the law of constancy of angles defined?
2. How is the angle of crystals determined?
3. What is the essence of the law of whole numbers?

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LABORATORY EXERCISE-2
Crystal growth laws and crystal growth.

It is known that molecules in liquid state are always in motion. As it passes into the gas state, this movement becomes more rapid . In amorphous solids, the movement of some molecules continues slowly and with difficulty until those molecules reach their legally stable positions . In crystalline substances, molecules are in motion and do

not move from one place to another. Maybe the atoms and moles of crystalline substances move only in their place . In addition, some crystalline body is affected by thermal power (power), that is, when it is heated, it begins to melt under the influence of a certain temperature. No matter how much the temperature of this substance is heated, it will not rise until it is completely melted, that is, the temperature of the crystalline substance can rise only after it is completely melted. For example, the heat applied to an ice crystal is used to melt the crystal, and the temperature does not rise until the ice completely melts and turns into water. From this example, it is known that the substance in the crystalline state has the smallest (minimum) internal energy compared to the other state. So , a substance in any state tends to transition to a crystalline state, and when the necessary conditions for this occur, it turns into a crystallized substance due to a change in the environment.

How does this crystal form and grow? This issue attracts the attention of many scientists at the international level, both theoretically and practically . But there are still aspects of this issue that have not been finally resolved .

As the temperature decreases, the movement of dissolved substance particles (molecules , atoms or ions) slows down, first one-dimensional, and then two - dimensional "buds" appear due to the attraction between negatively and positively charged particles . These crystal particles are the "base" for future crystals from which crystallization centers will grow , thus the crystallization centers remain stable only in supersaturated solutions. Although such "buds" sometimes form in saturated or unsaturated solutions, they are very small . z erib k e tadi. According to existing theories, supersaturated, supercooled solutions in containers closed on all sides are stored for a very long time without crystallization until the centers of crystallization fall out . However , in practice, regardless of such solutions, the "buds" of crystals appear spontaneously .

The process of growth and development of the crystal center also interests our scientists in many ways . As the crystal grows in the solution, negatively and positively charged ions are attracted to the center of crystallization according to the law of mutual attraction and settle on the crystal in a certain order . This is how the process of new growth of crystals can be imagined .

The process of crystal growth can be interpreted differently. Ions in the solution combine with each other to form larger units of one or two dimensions: "crystals" and "protocrystals". Large units consisting of a number of these ions gather around the centers of crystallization in a certain order and form a large crystal. These substances may have fallen into the solution or molten alloy as dust from the air, or they may have been deliberately incorporated into the solution to promote crystallization .

In addition, rapid mixing of the solution , shaking , shaking or shaking of the container with the solution also accelerates the formation of crystal centers , in which

the movement of the solute or particles in the solution accelerates and they are faster relative to each other . approaches and takes place in a stable bound state in the structure.

Therefore , particles of matter in crystalline form (ions, atomic moles) are more stationary than other particles in liquid, gas and vapor state . In a crystallized substance, the stable position of particles in this environment, which strives to move to an equilibrium state with a very small internal energy, is reflected in the position . As the formation of the crystal is related to the natural force and the internal force, its final growth also takes place based on a certain law under the influence of a certain force .

According to the theory of crystal growth, the order in which those particles approach the growing crystal surface is also important. Ultimately, the appearance of the crystal depends on the order of growth of these crystal sides (Figure 1.6).
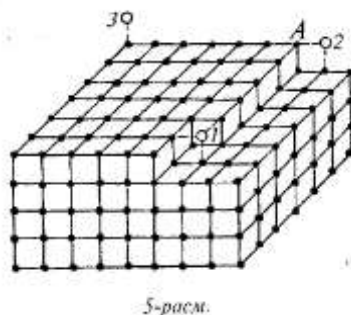
Figure 2.1

The -1 ions in position A near the growing crystal are attracted to this surface in three directions, the -2 ions in position B are attracted in two directions, and the -3 ions in position C are attracted to this surface in one direction . A freely moving ion in such a solution first occupies a position in which it is attracted in three directions, then in two directions, and finally in one direction. So, next to the growing crystal, each ion fills the row where it started to grow, and after that row is filled, it fills a new row in that layer. After all the rows in this yoda are filled, a new layer of the crystal begins to grow. The thickness of rows and layers is measured by the size of ionic, atomic or molecular structural units.

So , from a theoretical point of view, the growth of a new layer does not take place until the layer from which the crystal started growing is filled . According to the order of the growth process of these crystals, straight-grown crystals are bordered with small -smooth sides , and the sides are jagged with small edges . This law is called the law of limiting crystals with all sides and edges .

rate of crystal sides and appearance of crystals.

We already mentioned in the introduction of our book that the wonderful shape of crystals , limited by small , smooth sides and straight edges, attracts people's attention . The main reason for this, or the fact that it is so , is explained in the theory

of crystal growth . The edge of the crystal consists of t e kis surface, i.e. t e kis mesh of the spatial lattice, where the particles that make up the crystal are located. and the edges are a straight line, that is, a row of a spatial grid, with small smooth sides . Therefore, as mentioned above , the growing side of the crystal is pushed parallel to its previous position .

Figure 2.3

Crystal ion growth rate refers to the distance of this side's vertical movement (displacement) to this side within a unit of time. This rate is measured by the thickness of the layer grown on the side of the crystal per unit of time. The growth rate of the side AB is indicated by the letter t, and the speed of the side BC is indicated by the letter n.

fast -growing side of the crystal gradually disappears (a crystallization tip appears in its place), while the slow-growing side is constantly developing . From this, it can be concluded that the crystal growth is limited to the sides with a small speed .

That is , the shape of a freely growing crystal depends on the growth rate of the sides of this crystal . This, in turn, is determined by the arrangement of ions, atoms or molecules in specific directions specific to each crystallizing substance . It is known from the experiments that the sides of the crystal correspond to the surfaces with a large (excess) lattice density . The number of material points (ion, molecule , atom) located within the surface unit of a given crystal side is called the lattice density of this side . Crystals are covered with ions of high reticular density. (Law of Brave (1811 - 1863)). From this, it can be concluded that the appearance of the crystal depends on the growth rate of those crystal sides .

Control questions:
1. Explain crystal formation.
2. What are the theories of crystal growth?
3. How does the growth rate of crystal sides affect its shape?

List of used literature:
1. Zohidov K.S. Kristallografiya. Oʻzbekiston, 202. -256 b.

2. Попов Р.М., Шафрановский И.И. Кристаллография. М., "Высшая школа", 1972. – 352 с.

3. Егоров-Тисменко Ю.К. Кристаллография и кристаллохимия: Учебник для вузов. – М.: КДУ, 2005. – 592 с.

LABORATORY EXERCISE-3

Determination of symmetry, syngonia and classes of crystals.

symmetric tools are called a symmetric view or class, d e b . In other words, a complete array of symmetric tools is a view or class of symmetric. When we look closely at the array of symmetry tools, we can see that there are some similarities between them. For example, in a certain group of these lines of symmetry , there is only one L_2 , another group has only L_3 , or another group $L_{4\ has\ L\ 6}$, so that all these axes pass in the same direction. Another group of non-unidirectional crystal forms includes $3L_4$ or $3L_2$ with $4L_3$.

symmetric forms separated by similarity are called syngonia (similar angular d e mak), d e b. At the same time, each syngonia crystal differs from other syngonia crystals by its unique geometric shapes and the shape of the spatial grid and elemental cells that make up those crystals . There are seven syngonias in total , and their name is based on the geometric properties of the electric parallel tubes of the space grid electric cell . Below is a brief description of these syngonies .

1. Triclinic syngonia. The name is composed of the Greek words tri three and klin - crooked d e , because all three of the angles between the edges are not right (not equal to 900) in the parallel e lopip e d of the el e m e ntar cell of these syngonia crystals .

2. Monoclinic syngonia (Greek mono means one d e mak). Two of the angles between the edges of the element box are right (900) and the third is not equal to 900.

3. Rhombic syngonia. It is so named because in most syngonia crystals , the cross section perpendicular to the axis of secondary symmetry is rhombic .

4. Trigonal syngonia. This syngonia has one third or inverse sixth degree axis of symmetry .

5. Tetragonal syngonia crystals must have one formal or inv e rsion fourth degree symmetry axis .

6. Hexagonal syngonia crystals have a formal or inversion symmetry axis of the sixth order . These last three syngonias are named after the particular degree of symmetry of these syngonia crystals ,

7. Cubic syngonia. $_{The}$ unit cell of these syngonia crystals is cubic, with $4L_3$ and $3L\ 2$ or $3L_{4\ present}$. The syngonias listed above are divided into three classes according

to the level of symmetry: I) class with a low level of symmetry ; II) average degree of symmetry and III) high degree of symmetry.

drawn from this : in crystals belonging to the class with a low level of symmetry, each direction is repeated three or more times, so there is no single direction in them. Accordingly, in the crystal forms of this class, symmetry means may not be present, and at the same time it may be present. The degree of existing axes of symmetry does not exceed two; In crystal forms of moderate degree of symmetry, there is a single direction, which passes in the same direction as the axis of symmetry of the higher degree . Therefore , the crystal forms characteristic of this class must have one high-order symmetry axis . Crystal forms with a higher degree of symmetry have a single direction and a higher number of axes, which means more than one.

The names and symbols of the 32 calculated symmetries are written in the form of German - Mogian symbols accepted at the international level in books on special crystallography and mineralogy . In addition, there are also Groth, Sh e nflis and Shubnikov signs .

Above, the means of symmetry were defined, and they were written so that it would be easy to write them with the symbols developed by Groth . Below is a general understanding of the existing signs and methods of crystal class used internationally . German Mog e nb e lgies are raised . In this case , only the degrees of symmetry axes are written in AVShubnikov symbols . The number of second-order axes and the number of symmetries (m) passing over these higher-order axes of symmetry (m) are not written, because their number is equal to the number of levels of that higher-order axis ; The sign 1, 2 indicates the center of symmetry, and the sign 6, 4, 3 indicates the presence of inversion axes.

the degree of symmetry in the German-Mogue numbers is in the direction corresponding to the axis of symmetry , no sign is placed next to the number, and if it is perpendicular to this axis, it is written as 2/m after the decimal point. , 2/m2/m2/m symmetric representation can be briefly expressed as mmm. It is imagined that 3L2 and C are present in sym e tria form. Similarly, the representation of hexaoctahedral symmetry, which should be written in the form 4/m32/m, can be written briefly as m3m. In general, in such marking , first of all, it is written that the means of symmetry are aligned with the crystallographic axes depending on their position in space.

AVShubnikov's symbols , the symmetry axis perpendicular to the axis of symmetry is written after a colon (:) . A dot (.) is placed between the level of the axis and the t eth passed in the corresponding direction with these axes . The decimal point (-) between the numbers indicates that these symmetry elements form a wrong angle ($<$ $\neq$ 900) with each other .

C_1 , C_2 , C_3 , and C_6 (the initial letter of the Greek word Sirk Cyrk) in the schematic symbols indicate that there is one unpolarized axis of symmetry of the

degree shown in the symmetry representation . If there is a symmetry perpendicular to these axes, it is written as C 2_h , C $_3$ h, C $_4$ h, C $_6$ h (h is the initial letter of the German word "horizontal") in addition to these signs . As a result, the lines of symmetry corresponding to the axis of symmetry are denoted by the additional letter v (vertical) and written as C $_2$ v, C $_3$ v, C $_4$ v and C $_6$ v. The appearance of dihedral symmetry without an axis in monoclinic syngonia is expressed in the form of Cs. The number of s (spigelaxe - the initial letter of the German word mirror) axes of symmetry and secondary axes perpendicular to it is written as follows: Д (Di yo der - the initial letter of the German word consisting of two sides, d e gan meaning) D $_2$; D $_3$; D $_4$; Like D $_6$, $_{D 2}$ in rhombic syngonia is a symmetric triad , sometimes written as v. The addition of the letter h to these symbols means that these classes also have symmetry axes of the second degree . D $_2$ h in rhombic syngonia is sometimes shown as vh.

T e tragonal scal e nohedral and ditrigonal scal e nohedral classes D $_2$ d (or vd) are also denoted by D $_3$ d symbols. In this case, the 2nd and 3rd degree inversion symmetric axis , taking into account the position of the symmetric axis relative to the symmetric axis (d-diagonal), is expressed in the form of S $_4$ and S $_6$.

Also , the rhombohedral symmetry can be expressed in a different C3i form, since it is written as a pinacoidal symmetry with a specific symmetry center . The letters T (tetrahedron) and O (octahedron) participate in the signs of cubic syngonia symmetry, and the letters h and d are added to them in the necessary places .

Control questions:

1. Explain the symmetry elements and operations of crystals using crystal models.

2. What class of crystal syngonia is there?

3. What symbols represent the elements of symmetry?

List of used literature:

1. Zohidov K.S. Kristallografiya. Oʻzbekiston, 202. -256 b.

2. Попов Р.М., Шафрановский И.И. Кристаллография. М., "Высшая школа", 1972. – 352 с.

3. Егоров-Тисменко Ю.К. Кристаллография и кристаллохимия: Учебник для вузов. – М.: КДУ, 2005. – 592 с.

LABORATORY EXERCISE-4

Geometric shapes of crystals.

In crystals, both open forms and closed forms, as well as open forms and closed

forms, can form combinations and complex forms. Each of the crystal shapes depends on the appearance of the simple shapes in the crystal, the position of the sides that make up this shape relative to each other, and finally, they themselves depend on the existing means of symmetry in this shape. There can be general forms specific to each form of symmetry. All special forms can be calculated theoretically and mathematically. Simple forms consisting of sides that are perpendicular or congruent to the means of symmetry, or intersect the same means of symmetry to form equal sections, are called special forms. On the contrary, simple shapes consisting of sides that do not pass perpendicularly to the means of symmetry or do not form equal sections in these means of symmetry are called general shapes. The existing connection between the means of symmetry and the simple forms of crystals is given in the detailed description of each syngonia and symmetry.

1. Open simple forms

A monohedron is a simple shape consisting of only one crystal side (mono-Greek one, edr - crystal side) (Fig. 2.4 a, b, c).

A dihedral is a simple shape consisting of two (di-two) equal, similar, intersecting sides (Fig. 2.4-g, v).
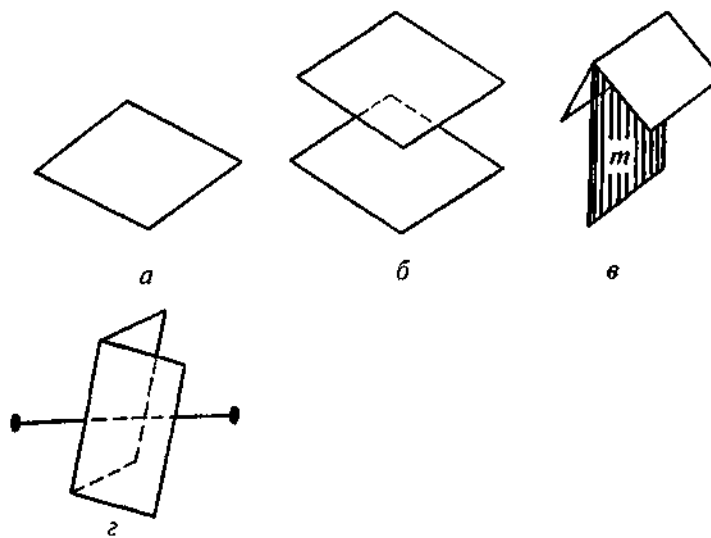
Figure 2.4 . It's open simple forms .

Pinacoid - two to each other equal , similar , parallel _ _ from the sides organize found (pinax - Greek so _ _ bo ' lib , board means) is simple form (2.4- b , picture).
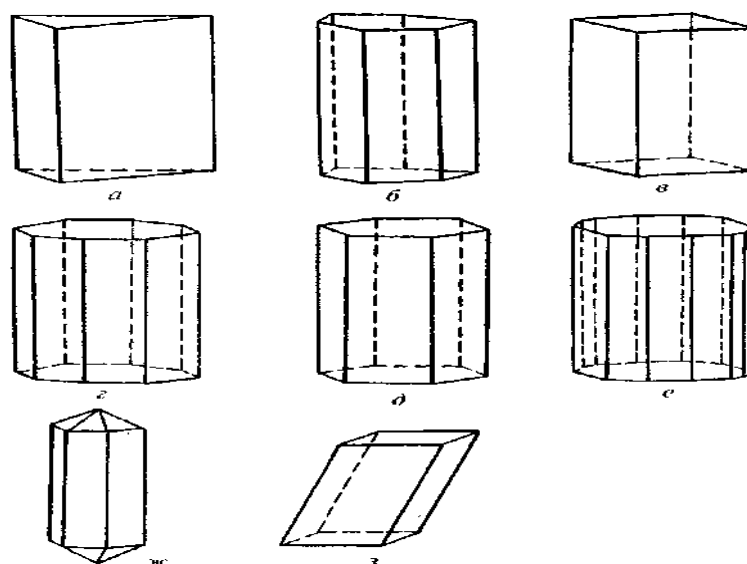
Figure 2.5. Prisms.

Prisms are simple shapes made up of three or more similar and equal sides that intersect to form parallel edges. Prisms are three-sided, four -sided, six-sided . In this case, the first is a trigonal prism, the second is a rhombic prism if the angle between the sides is 90°, a tetragonal prism and the angle between the sides is not 90° - a rhombic prism (Fig. 2.5, j), if the angle between the sides of this prism and the base is not equal to 90°, then it is a monoclinic prism (Fig. 2.5-z), the third with six sides is called a hexagonal prism (Fig. 2.5-a, v, d).

Each side of the prisms can be bifurcated by a small edge from the middle. When naming such prisms, the prefix "di" is added to the number indicating the sides. A three-sided prism with double sides is called a ditrigonal prism, a prism made of four double sides is called a ditetragonal prism, and a prism with six double sides is called a dighexagonal prism (Fig. 2.5 e).
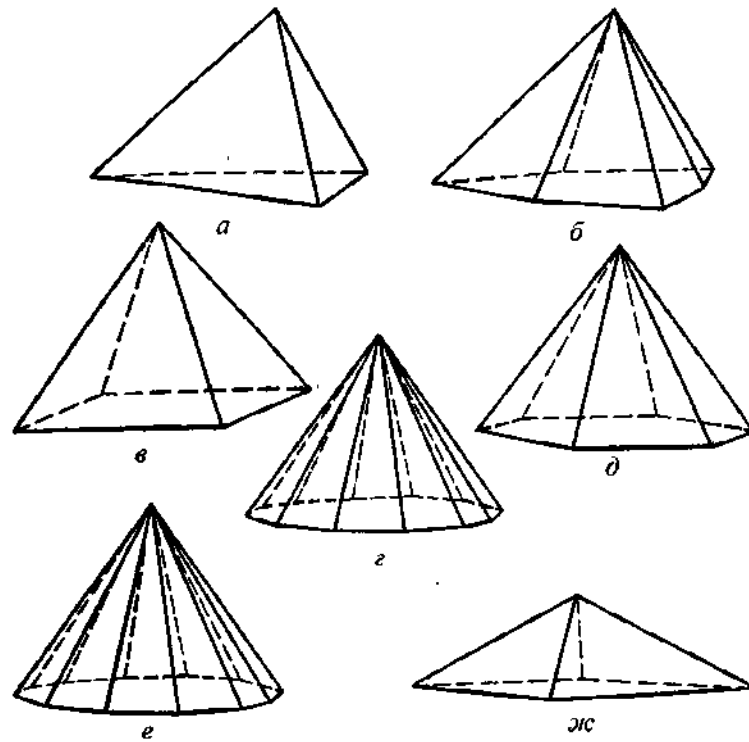
Figure 2.6. Pyramids .

Pyramids are simple shapes consisting of three or more equal and similar sides whose edges intersect at a point. Similar to prisms, there are several types of pyramids: a) trigonal (three-sided) pyramid; b) tetragonal (four-sided) pyramid; c) hexagonal (six-sided) pyramid; g) ditrigonal pyramid, d) ditetragonal pyramid; j) dighexagonal pyramid 2.6- a , 6, v, g, d, e , j-pictures), rhombic pyramid are open forms.

2. Closed simple forms

Epic simple shapes are limited only by the same sides, they are: dipyramids - simple shapes consisting of two equal and similar pyramids with their bases q multiplied. a) trigonal dipyramid; b) tetragonal dipyramid: c) hexagonal dipyramid; d) rhombic dipyramid, and if the sides are double, e) ditrigonal dipyramid; j) ditetragonal dipyramid; i) dihexagonal
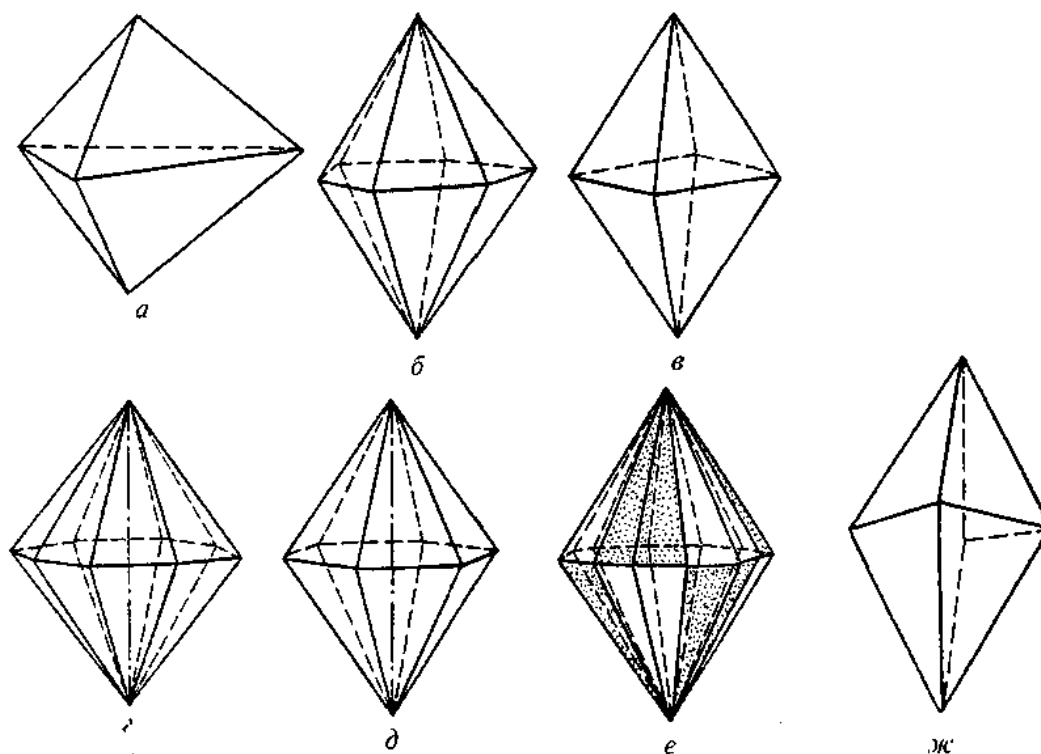
Figure 2.7

Control questions.

1. Understanding of simple forms.
2. What are open simple forms?
3. What are closed simple forms?
4. What is the difference between open and closed simple forms?

List of used literature:

1. Zohidov KS Crystallography. Uzbekistan, 202. -256 p.

2. Popov R. _ M. , Shafranovsky I. _ I. _ Crystallography . M. , "Vysshaya school , 1972. – 352 s .

3. Egorov - Tismenko Yu . K. _ Crystallography i crystallochemistry : Textbook for Vuzov . – M .: KDU , 2005. – 592 s .

LABORATORY EXERCISE-5
Study of crystal systems of substances. Defects of crystals.

Disruption of the arrangement of the material point is due to the fact that material points that are repeated infinitely periodically are sometimes left empty. Such a structural defect is called a vacancy. As shown in Figure 2.8a, when such a defect occurs in the official - legal flat grid, then a change occurs in the location of the material points surrounding the place of the vacant point. As a result of the displacement of a material point next to a vacancy to this vacancy, a shift in a certain

direction in the system can occur. Such displacement or displacement accelerates with increasing temperature.

There may be a second situation in the location of the material point, that is, among those material points located in a certain order, there may be additional material points that do not have a "separate place" for themselves (Fig. 2.8 , b). Even in this case, the general order in the crystal lattice is disturbed around this excess point.
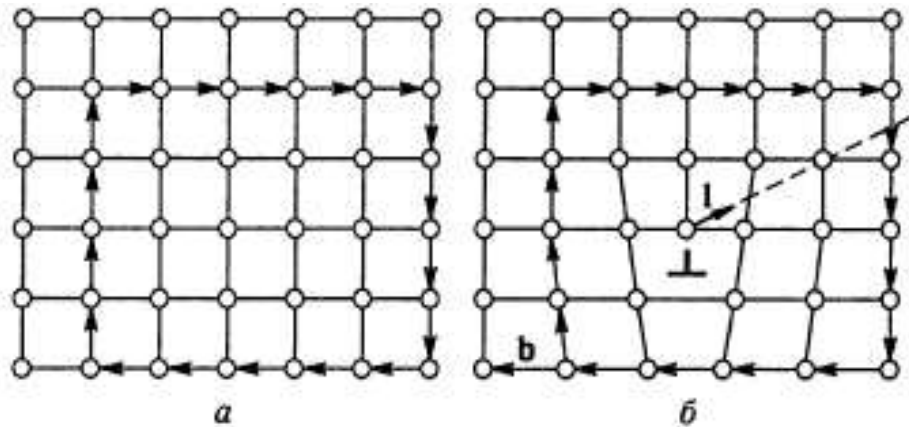
Figure 2.8

The formation of defects in crystal systems depends on the growth medium of that crystal and the exchange of material points in the crystal structure with other material points of larger or smaller radii.

Such defects reach up to 1012-1014 particles per cubic cm of the crystal. Over time, these defects may decrease and disappear on their own. Modern techniques require obtaining crystals without defects. But crystals without defects cannot be obtained artificially, they are not found in nature. Such defects are not less than 10-6% even in crystals of the substance with the highest purity.
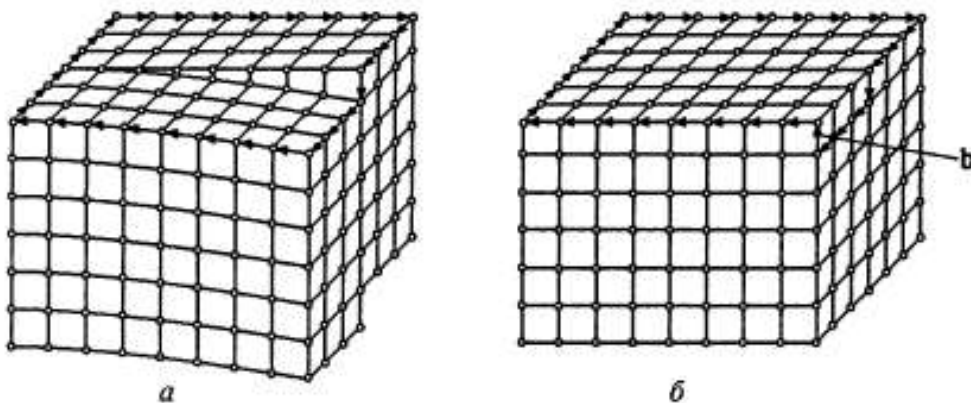
Figure 2.9

In the structure of crystals, displacements caused by sliding are also defects called dislocations. When a force is applied to a crystal in a certain direction, a certain part of it moves in a certain direction. In the structure of that crystal, a dislocation occurs. If the dislocation is oriented in a straight line, it is called a linear defect. Such a defect can also occur due to the displacement of one part of the crystal relative to another part of the interatomic distance. Then such a distortion in the crystal structure is called a twist defect.

Control questions:

1. Explain the reasons for the formation of crystal defects.

2. What are the types of crystal defects?

3. What methods are used in the research of crystal systems of substances?

List of used literature:

1. Zohidov K.S. Kristallografiya. Oʻzbekiston, 202. -256 b.

2. Попов Р.М., Шафрановский И.И. Кристаллография. М., "Высшая школа", 1972. – 352 с.

3. Егоров-Тисменко Ю.К. Кристаллография и кристаллохимия: Учебник для вузов. – М.: КДУ, 2005. – 592 с.

LABORATORY EXERCISE-6
The structure of solids (glass) in an amorphous state .

Pure crystal solution, Exact Freezing Point When a solution of a pure crystalline substance is cooled , it appears that they have an exact freezing point, at which point solidification occurs due to the formation of crystals. But sometimes a liquid can be cooled below freezing without forming crystals . In this case, the liquid is supercooled . Supercooling is a common condition. If dust is prevented from entering the liquid, the super-fast cooling process is perfect. If foreign particles appear in the liquid (extraneous matter, dust, hair fiber, etc.), there is a possibility of formation of crystallization centers. A supercooled liquid is in a metastable state because its free energy is greater than the free energy of the corresponding crystal. But a supercooled liquid structure has more free energy than any structure close to it. The connection between the glass state and the normal solid or liquid state can be explained by the processes that occur during liquid cooling.

There is a certain temperature for the substance that is being crystallized, at which temperature solidification occurs with a rapid reduction in volume. At the same time, heat is released during the solidification process. The cooling diagram of a crystalline substance (Fig. 2.10) can be viewed in the temperature-time coordinate.
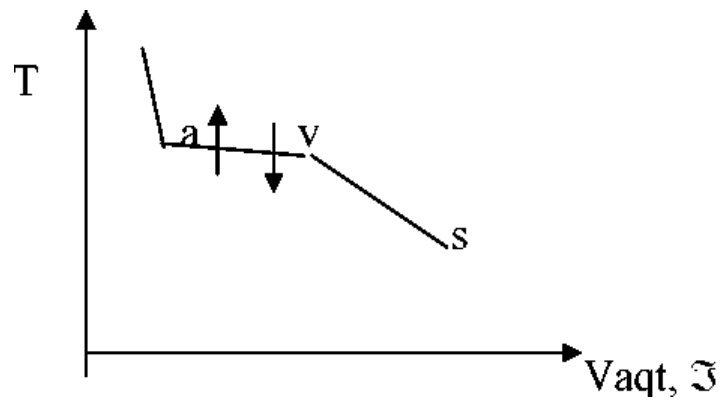
Figure 2.10

When the temperature of the substance cools in the direction indicated by the arrow, the sections a and v are in the liquid phase region. At point V, initial crystals of substance v appear. At point C, the substance is completely crystallized. A drop in temperature is observed at point B. This happens due to the heat of crystallization that is released in the section v_s corresponding to the temperature t_s, which is called the crystallization point or the melting point. This score depends on how the regime is doing. If it is caused by a high temperature characteristic of a given system, substance v will crystallize in the direction of temperature decrease, if it goes in the opposite direction, liquefaction will occur at point s. At this point, there is a transition from the liquid phase to the solid phase (crystallization). T_s point characterizes the equilibrium state of the dynamic phase.
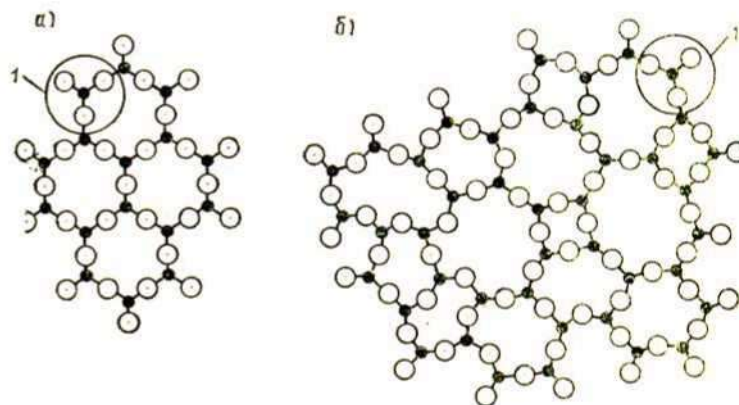
Figure 2.11. a) crystal lattice of quartz; b) quartz glass with an irregular structure.

Another difference between amorphous solids and crystals is that amorphous solids do not give clear X-ray diffraction spectra, so glass types cannot be continuous. The specific energy of the substance should not be significantly different from the energy of the corresponding crystal type in the glassy state. It can be seen from this

that for glass-forming oxides, the coordination number of cations in the glass should be the same as in the crystal. This indicates that the structural elements of glass and crystal must be the same. In a crystal, these structural elements create a regular crystal structure, but in a glass, the angular bonds are strongly disturbed, the structural elements are not arranged continuously and form a chaotic network.

Thus, amorphous bodies have short-range order, because regular polyhedra are placed at their ends, but no long-range order.

Control questions
1. What is an amorphous solid?
2. What kind of body is a crystalline body?
3. Concept of very rapid cooling.
4. Difference between amorphous and crystalline bodies.
5. Explain the cooling diagram of a crystalline substance.

List of used literature:
1. Zohidov K.S. Kristallografiya. Oʻzbekiston, 202. -256 b.
2. Попов Р.М., Шафрановский И.И. Кристаллография. М., "Высшая школа", 1972. – 352 с.
3. Егоров-Тисменко Ю.К. Кристаллография и кристаллохимия: Учебник для вузов. – М.: КДУ, 2005. – 592 с.

LABORATORY EXERCISE-7

Polymorphism and isomorphism.

In the world of minerals and crystals, the phenomenon of olimorphism and isomorphism is widespread.

Polymorphism is the phenomenon of formation of modifications with different structures and properties as a result of different physico-chemical processes. All polymorphic modifications have the same composition, but different structures. Polymorphic transitions are of two types:
1. Monotropic transition;
2. Enantiotropic transition.

In a monotropic transition, a substance easily changes from one modification to another. For example, gamma form Al_2O_3 changes to alpha form Al_2O_3 at high temperature. However, no matter how much the alpha-form Al_2O_3 is heated or cooled, the gamma-form does not change to Al_2O_3. The second example is that diamond is

easily transformed into graphite, but turning graphite into diamond is a laborious process. Only later did it transition from graphite to diamond at extremely high pressure and temperature.

Enantiotropic transitions are bidirectional. The substance changes from the first form to the second form under certain conditions. The second form changes back to the first form when the conditions change. As an example, we can mention the transition of sulfur from the rhombic form to the monoclinic form, and these transitions are reversed when the conditions change.

Enantiotropic transitions do not always occur easily, as a result, the phase cannot change to the desired form and is kept in a thermodynamically metastable state for a long time. Metastable forms can be very durable. We can clearly see this situation in the example of a window. An example is tempered glass. Their durability and metastability are preserved for hundreds of years.

Modifications prone to polymorphism have a robustness limit. For example, ammonium nitrate has four modifications: - from 18 to +32 ^{0} C beta-rhombic modification is stable, from +32 to 84 degrees alpha-rhombic, from 82 ^{0} to 125 ^{0} C trigonal, and above 125 ^{0} C there is a cubic chain.

Here are two more examples of monotropic and enantiotropic transformations. Beta-quartz transforms into alpha-quartz at 573 $^{0 \ C.}$ It, in turn, changes to alpha-tridymite around 840 $^{0 \ C.}$ Specific gravity decreases during these transitions. As a result, the material swells up to 25%. At high temperature in ceramic masses, water and carbon dioxide evaporate from the composition of the mass and the material undergoes deformation. But due to the presence of $SiO_{2 \ in \ the \ composition}$, the voids are filled and the shape of the material is preserved .

In titanium oxide, there is also communication between three minerals. The names of these forms are rutile, brookite and anatase. Brookite and anatase convert to rutile when heated, but rutile does not convert to the brookite and anatase forms.

The presence or absence of polymorphism in chemical substances is determined by X-ray and microscopic studies.

Calcium carbonate corresponds to the minerals calcite, which has a hexagonal structure, and aragonite, which has a rhombic structure.

The creation of the thermodynamic theory of phase equilibrium by DjVGibss , the practical study of many systems by scientists described the phenomenon of polymorphism from the theoretical side and showed that this phenomenon is widespread in nature.

The phenomenon of isomorphism was also discovered in 1819 by E. Mitscherlich. He determined that KH_2PO_4, KH_2AsO_4 and $NH_4H_2PO_4$ minerals crystallize in a homogeneous form, regardless of the fact that their composition is different, and he called this phenomenon the phenomenon of isomorphism. The term

"isomorphism" means "equal formality".

The Russian scientist DI Mendeleev also worked on the phenomenon of isomorphism. His candidate's thesis in 1856 was also devoted to isomorphism. Isomorphism was studied by Grimm and Goldschmidt. as a result, the rules for the implementation of isomorphism were determined:

- the difference between the radii of isomorphous atoms, ions and radicals should not exceed 15%;

- the electronic structures of cations and anions must be similar or close to each other;

- the chemical bond between cation-oxygen and anion-oxygen must be the same or close to each other.

If the difference between exchangeable ions or radicals is not more than 15%, two substances form hard alloys with each other.

Isomorphism divides into two ;

1. Isovalent isomorphism. For example, isomorphic exchanges between Ca 2 Al $_2$ SiO 7 and Sr $_2$ Al 2 SiO $_7$. Here, calcium ions can replace strontium ions. Therefore, calcium gelenite gives continuous hard alloys with strontium gelenite;

2. Heterovalent isomorphism. At this time, ions with different valences are exchanged. But the sum of the valences of these ions must match. An example is the isomorphism between ochermanite Ca $_2$ MgSi $_2$ O $_7$ and gelenite Ca $_2$ Al $_2$ SiO $_7$. Here Mg +Si = 2Al exchange takes place.

Heterovalent isomorphism, in turn, is of two types:

1. Cation and anion isomorphism:

a) $Ca^{2+} + Si^{4+} = TR^{3+} + Al^{3+}$ (happens in melilites);

b) $Ca^{2+} + R^{5+} = TR^{3+} + Si^{4+}$ (happens in apatites).

2. Isomorphism with cation or anion only.

$2Ca^{2+} = Na^{+} TR^{3+}$.

Heterovalent isomorphism A . E. _ It is derived from the diagonal row rules of Fersman and AF Kapo'stinsky. Usually the following diagonal rows occur:

1. $Li^{+} - Mg^{2+} - Sc^{3+} - Zr^{4+}$;

2. $Na^{+} - Ca^{2+} - Y^{3+} - Ce^{4+}$;

3. $K^{+} - Sr^{2+} - La^{3+}$;

4. $Rb^{+} - Ba^{2+}$;

5. $Cs^{+} - Ra^{2+}$;

7. $B^{3+} - Si^{4+}$.

6. $Be^{2+} - Al^{3+} - Ti^{4+}$;

Magnesium inclusions are found in lithium minerals due to the presence of diagonal rows. In magnesium minerals, you can find yttrium elements in scandium and calcium minerals. Lanthanum, cerium, prosaidium, neodymium and samarium

elements occur together with calcium-strontium minerals. Erbium, thulium, ytterbium and lutetium occur together with zircon minerals.

Diagonal isomorphism corresponds to the heterovalent type of isomorphism, so it is necessary to strictly observe the balance of valences.

Polymorphism - a substance with the same chemical composition and formula has two or more modifications that differ in symmetry and crystal form under different conditions.

Polymorphic transitions are of two types: 1-monotropic transition, 2-enotropic transition.

The phenomenon of isomorphism was discovered by E. Mitscherlich in 1819. He determined that KH_2PO_4, KH_2AsO_4 and $NH_4H_2PO_4$ minerals, despite their different composition, crystallize in a homogeneous form and called this phenomenon the phenomenon of isomorphism. The term "isomorphism" means "equal formality".

Isovalent isomorphism - isomorphisms between Ca $_2Al_2SiO_7$ and $Sr_2Al_2SiO_7$. In the buyer, calcium ions can exchange places with strontium ions. Therefore, calcium gelenite gives continuous hard alloys with strontium gelenite.

Heterovalent isomorphism - ions of opposite valence exchange. But the sum of the valences of these ions must match . An example is the isomorphism between ochermanite $Ca_2MgSi_2O_7$ and gelenite $Ca_2Al_2SiO_7$. Here $Mg^2{}^++Si^4{}^+ = 2Al$ exchange occurs.

Control questions :
1. Types of polymorphism.
2. Polymorphism of silica and alumina.
3. Conditions for formation of isomorphism.
4. Isovalent and heterovalent isomorphism.

List of used literature:

1. Zohidov K.S. Kristallografiya. Oʻzbekiston, 202. -256 b.

2. Попов Р.М., Шафрановский И.И. Кристаллография. М., "Высшая школа", 1972. – 352 с.

3. Егоров-Тисменко Ю.К. Кристаллография и кристаллохимия: Учебник для вузов. – М.: КДУ, 2005. – 592 с.

LABORATORY EXERCISE-8
Physico-chemical properties of crystals

Determination of hardness of crystals. The hardness of crystals refers to the surface's resistance to scratching. When the smooth flat surface of a crystal is scratched by a sharp object harder than itself, a mark is left on that scratched surface along with the powder. The hardness of the crystal is measured by the force used to

separate the powder, that is, to leave a mark on its surface. Therefore, the hardness of the crystals indicates the strength of the bond between the units of the crystal system that make up this surface, and this value is characteristic for each crystal of a substance, and it becomes a variable property in directions depending on its symmetry. At the same time, as mentioned above, taking into account the anisotropy of crystals, this determined value   can be different depending on the direction of the line drawn in the crystal of the same substance . But the difference between these values will not be so great and in most practice it will not be taken into account. Such anisotropy is evident only in some cases. For example, the hardness of the disten crystal has the smallest value (4-5) along the axis, and the largest value (6-7) along the X and U axes. The hardness of crystals is determined by mineralogists-geologists during practical work by comparing one with the other. For this purpose, there is a series of hardness, consisting of the ten most common minerals in nature, which was introduced to science by the Austrian scientist Moos (1773-1839). Each of the minerals written in this order draws the one before it, and the one after it is not drawn with it. The ordinal number of each mineral indicates the relative hardness of that mineral.

Sometimes the crystal that determines the hardness can be small or powdery . In this case, the mineral powder is glued to the thumb and   rubbed   on   another mineral surface with this finger. If mineral powder becomes hard from a crystal rubbed with a finger, the surface of that crystal will be scratched and dull. Otherwise, if the hardness of the powder is small, the rubbed mineral surface will not be scratched - it will remain shiny. A special micro-hardometer-sclerometer adapted for this purpose is used to solve practical-scientific problems related to the actual hardness of crystals. A sclerometer is a special instrument with a pyramid or cone-shaped diamond needle.

Control questions:
1. How to determine the structure of crystals?
2. What is intensity?
3. What is the distance between atoms and ions?
4. How is spatial content determined?
5. The importance of X-ray method.

List of used literature:
1. Zohidov K.S. Kristallografiya. O'zbekiston, 202. -256 b.
2. Попов Р.М., Шафрановский И.И. Кристаллография. М., "Высшая школа", 1972. – 352 с.
3. Егоров-Тисменко Ю.К. Кристаллография и кристаллохимия: Учебник для вузов. – М.: КДУ, 2005. – 592 с.

LABORATORY EXERCISE-9
Determining the structure of crystals using radiographic methods .

Substances in the crystalline state usually form rings of different intensities in the debaegrams.

A substance in a crystalline state has interplanar distances and intensities depending on its structure. By comparing the distances between the planes and the intensity with the card data, the spatial composition of the crystal can be determined using radiographic methods. The degree of accuracy of the X-ray method depends on many factors on the property of the atoms in the substance to reflect the rays. It depends on the X-ray absorption coefficient of the whole mixture and the examined substance, the perfection of the crystal lattice, and the size of the crystals.

The discovery of X-rays, the use of various methods and devices created in physics, chemistry, medicine, and especially technical sciences (metals

technology, metallurgy, mechanical engineering) opened opportunities.

have a wavelength of 0.01-0.00001 µm or 10 -10 A and are electromagnetic in nature like light rays. X-rays were first produced by Roentgen by sucking air in a glass tube with two electrodes welded together at a pressure of 10^{-5} mm Hg and passing an electric current through it. Specific, invisible rays were recorded from the installed electrodes.

X-rays belong to the group of quantum rays, the effect is similar to gamma rays. These rays have no smell. They are colorless and have properties such as penetration into objects, absorption, scattering, illumination, photochemical ion generation, and biological effects.

The penetration of X-rays into various substances and bodies depends on the length of the light waves. If the beam contains a lot of "hard" rays, i.e., shorter wavelength rays, penetration will be greater than "softer" (longer wavelength) rays.

1. How to determine the structure of crystals?
2. What is intensity?
3. The distance between atoms and ions.
4. How is spatial content determined?
5. The importance of the X-ray method.

List of used literature:
1. Zohidov K.S. Kristallografiya. Oʻzbekiston, 202. -256 b.
2. Попов Р.М., Шафрановский И.И. Кристаллография. М., "Высшая школа", 1972. – 352 с.
3. Егоров-Тисменко Ю.К. Кристаллография и кристаллохимия: Учебник для вузов. – М.: КДУ, 2005. – 592 с.

LABORATORY EXERCISE-10
X-ray structure analysis devices and their working mechanisms

The intensity of X-rays changes when passing through different substances and objects. It depends on their thickness, hardness, specific gravity and chemical composition. Gases and air pass all X-rays without absorbing them. But barium sulfate or lead do not transmit much light. Therefore, they are used as a barrier to avoid X-rays.

When X-rays are absorbed by a substance or object, they become a secondary source of X-rays.

X-rays are captured in modern devices of different structures, but their appearance is based on the same principle - when high voltage is applied to the cathode in the X-ray tube, electrons - gamma rays are emitted from themselves, and particles are ejected at high speed as a result of their strong impact on the polarized anticathode.

Roentgenography is the science of X-rays and their research of metals, metal alloys, chemical compounds, minerals and various raw materials. It serves to accurately know the atomic, sub-, micro- and macrostructures, as well as the chemical composition of the above-mentioned substances. When examining the structure of a chemical substance or mineral at the atomic level, it allows to determine the type and parameters of crystal lattices. His main achievements are based on terms such as crystals, crystal syngonias, crystal lattices.

The scattering of X-rays by hitting atoms of crystalline substances was studied for the first time by Moscow University professor GV Woolf and English physicists father and son G. and L. Bregg. According to scientists, the reflected rays can be considered as reflected from the plane of the atoms in the crystal.

Father and son G. and L. Bragg found a convenient way to describe X-ray diffraction in crystals. Their formula

nl=2dsin0

The Wolff-Bragg equation

is here

n is an integer, which gives the order of return of rays 1,2,3_;

X-ray wavelength, A;

d-the distance between the surfaces of atoms in the crystal lattice;

0 is the angle of incidence of x-rays falling on the atomic surface.

The presence or absence of any phase is first determined by the three most intense lines on the x-ray, then the remaining lines are compared for confirmation. If the phase under investigation is present in a small amount in the mixture, the intensity of the corresponding lines will be low, and some may not be visible at all. One of the complex aspects of phase analysis of compounds using X-ray method is that some

lines of low intensity of one phase overlap with more intense lines of another phase. As a result, the relative intensity of the first phase lines does not correspond to the information in the literature.

Below is the roentgenogram of the ceramic mass poured at 1400 $^{\circ}$C (Fig. 2.12) and the roentgenographic data of the phases (minerals) identified in it.
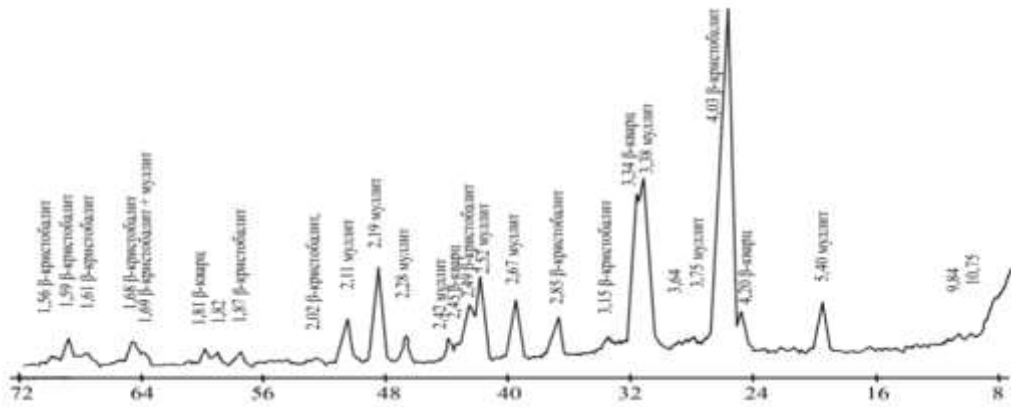
Figure 2.12. Roentgenogram of ceramic mass cast at 1400 $^{\circ}$ C.

Mullite mineral is part of almost all ceramic products. It crystallizes in rhombic syngonia with the following constants: a =7.52 A: b=7.65 A; s=2.89A.

Table 2.1

I	d/n, A	I	d/n
7	5.40	3	2.28
3	3.76	7	2.20
10	3.39	5	2.11
6	2.70	4	1.88
7	2.54	5	1,699
4	2.42	5	1.60

Mullite $3Al_2O_3 2SiO_2$ is related to rhombic syngonia.

Table 2.2

I	d/n, A	I	d/n
10	4.03	5	2.01
6	3.13	6	1.92
7	2.83	6	1,867
8	2.48	4	1,687
4	2.46	6	1,699
4	2.11	2	1.63

α -cristobalite α **-** SiO $_2$ belongs to the tetragonal syngonia.

Control questions

6. How to determine the structure of crystals?
7. What is intensity?
8. The distance between atoms and ions.
9. How is spatial content defined?

10. The importance of the X-ray method.

List of used literature:

1. Zohidov KS Crystallography. Uzbekistan, 202. -256 p.

INDEPENDENT STUDY WORKSHOPS

Form of organization of independent education

In addition to classroom training, students can expand on some topics for the purpose of learning, they read additional literature and prepare independent works in the prescribed manner . The results of independent education are evaluated based on the rating system.

Completing homework, independently learning new knowledge from additional textbooks, searching for the necessary information and determining ways to find it, collecting information from the Internet, conducting scientific research, within a scientific group or independently deepens scientific knowledge using scientific sources, develops their independent thinking and creative abilities. That is why educational activity cannot be effective without independent education.

Suggested topics for independent work

No	Subject Name	TMI form
1	States of matter	Preparation of visual aids in cases of substances
2	The main properties of crystals	Repeating practical training, summarizing, familiarization with literature
3	Geometric shapes of crystals	Preparation of forms of crystals
4	Physical properties of crystals	Repeating practical training, summarizing, familiarization with literature
5	Formation and growth of crystals.	Crystal growth from a sugar solution
6	Stenon's law.	Preparation of an abstract on Stenon's law
7	Isomorphism and polymorphism	Preparation of visual aids on isomorphism and polymorphism
8	Types of chemical bonds in crystalline substances	Preparation of artificial forms of crystals
9	The concept of symmetry. Elements of symmetry	Making a video about crystal symmetry and symmetry elements
10	Symmetry operations.	Preparation of a video clip on symmetry operations
11	Signs of symmetry elements.	Preparation of abstract on signs of symmetry elements

12	X-ray structural analysis of crystals	Preparation of an abstract on X-ray structural analysis of crystals	4
13	Defects of crystals	Preparation of a presentation slide on crystal defects	4
14	Types of categories and syngonias of crystals.	Preparation of a presentation slide on the types of categories and syngonias of crystals	4
15	32 classes of symmetry elements.	Preparation of abstract on 32 classes of elements of symmetry	4

GLOSSARY

Amorphous state - a solid non-crystalline state of matter; characterized by the isotropy of properties and the absence of a melting point

Amorphous body - Greek. "amorphous" - "without form" - a body whose self-organized microparticles do not have the correct periodic arrangement

An amorphous substance is a solid substance that does not have an ordered structure

Angstrom (A°) is a nonsystematic unit of length used in atomic physics, molecular optics, and nanoelectronics, equal to 10-10 m

Accuracy - the degree of closeness of the measurement values or the readings of the measuring instrument to the standard value of the quantity or to the true value found with the help of an accurate measuring instrument

Anisotropic body is a substance whose physical properties depend on the direction chosen in it

Anisotropic medium is a medium whose physical properties depend on the direction chosen in it

Anisotropy is non-uniformity of the physical properties of the medium in different directions

An atomic crystal is a crystal in which electrically neutral atoms are located at the lattice nodes

An atom is the smallest part of a chemical element that retains its properties

A homogeneous medium is a medium whose specific physical properties do not depend on coordinates

A homogeneous system is a system that has the same properties in all its parts

A uniaxial crystal is a crystal that has only one optical axis

The Brave lattice is one of the three-dimensional geometric lattices that describe the possible types of crystal lattice symmetry

Brillouin zone - spatial domain of wave vectors; inside it, the electron energy in the crystal changes continuously, and it is interrupted at its boundaries

A unit cell is a part of a crystal lattice that can be made by parallel displacement of the crystal atomic structure in three dimensions.

An ideal crystal is a crystal without structural defects

Isomorphism is Greek. "isos" - "same", "equal" and "morphe" - "form", "appearance" - substances with a similar chemical formula and the same chemical bonds with the atomic crystal structure of its crystals similarity to

An isotropic body is a body whose properties are the same in all directions

An isotropic medium is a substance that has the same physical properties in all selected directions

Isotropy is the uniformity of the physical properties of the environment in all directions

Covalent crystals are crystals with covalent chemical interatomic bonds

A crystal lattice is an arrangement of atoms, ions, and molecules characterized by periodic repetition in space and characteristic of solids.

A crystal lattice is a characteristic structure of a substance characterized by periodic periodic arrangement of its microparticles in space

Monocrystals are single crystals with a single crystal lattice

A single crystal is a crystal that has a single crystal lattice over its entire volume

An inhomogeneous medium is a medium whose specific physical properties depend on coordinates

Optical anisotropy - different optical properties of the medium depending on the direction and polarization of optical radiation (light) in the medium

A ray of light is a line along which light energy travels

REPUBLIC OF UZBEKISTAN
MINISTRY OF HIGHER EDUCATION, SCIENCE AND INNOVATION
NAMANGAN STATE UNIVERSITY

"APPROVED"
Vice Rector for Akademic Affairs
_____ D.S.Xolmatov
" " _____ 2023 years

WORKING TRAINING PROGRAM BY SUBJECT

CRYSTALLOCHEMISTRY

For 3rd year for full-time education

Field of knowledge: 500000 - Natural sciences, mathematics and statistics

Field of study: 530000 - Physics and natural sciences
Education direction :   60530100-Chemistry (by type)

Namangan - 2023

Subject/Module Code KOKB204	Academic year 2023-2024	Semester 5-6	ECST-Credits 4	
Subject/Module Type Mandatory	**Language of education** English		**Class hours per week** 8 / 8 -6/8	

1	**The name of the subject**	**Auditorium training sessions (hour)**	**Independent education (hour)**	**Total download (hour)**
	Crystallochemistry	120	60	180

2 | **I. The content of science**

The content of science. This science covers issues such as forming general views on the structure (structure) of matter and determining the important classes of substances in the crystal structure, the forms of crystals, what physical and chemical properties they exhibit. The knowledge acquired by the master's student through mastering the science strengthens his conclusions that the structure of matter plays a key role in understanding the modern physical appearance of the world, the world around us and natural phenomena.

"Crystallochemistry" is a course included in the block of specialty subjects. The subject "Crystallochemistry" belongs to the group of natural sciences and is taught in the bachelor's courses of study in the specialty of Chemistry. This science, as a result of the development of the science of mineralogy, serves as a basis for studying the crystal structure and properties of compounds in its development.

II. The main theoretical part (lectures)

II.I. The subject includes the following topics:

Topic 1. An introduction to crystallochemistry and its science development history.

A crystalline substance. Crystallography. Relationship of crystallochemistry with other sciences. The development of crystallochemistry as a science. Teaching the basic laws of crystallography.

Topic 2. Crystalline and amorphous substance. Formation and growth laws of crystals.

The main properties of the crystal. Crystal structure and type of structure. Amorphous substance. Theories of crystal growth.

Topic 3. Symmetry of crystals.

Concept of symmetry. Elements of symmetry. Types of symmetry. A scheme for generating 32 types of symmetry. Forms of crystal polyhedra. Crystallographic characters.

Topic 4. Simple and complex forms, open and closed forms, their class, syngonia and division into classes.

Geometric shapes of crystals. Open simple forms. Closed simple forms. Geometric shapes of crystals with a low degree of symmetry. The geometrical forms of crystals of medium class of symmetry. Syngonia

Topic 5. Crystal lattice concept. Broadcasting.

Crystal lattice concept. Crystal polyhedron and crystal lattice. Translyas t iya. A flat grill grate. Brave's 14 different grills. Transmission grid. An understanding of crystal chemical analysis. Symmetry groups of Fedorov.

Topic 6. Factors determining the structure of crystals.

Heterodesmic and homodesmic structures. Effective radii of ions. Determination of atomic and ionic radii. Dependence of the sizes of atoms and ions on the coordination number. The number of atoms that fit into one unit cell of the structure. Coordination number and coordination multiplicity. Classification of structures according to coordination number.

Topic 7. The nature of the chemical bond in crystals.

Ionic bonding. Metal connection. Residual binding. Covalent bond. Hydrogen bonding. Intermolecular Van der Waals forces. Classification of compounds according to the type of chemical bond.

Topic 8. Isomorphism and polymorphism.

Opening history. Conditions necessary for the manifestation of isomorphism. Classification of polymorphism types by structure.

Topic 9. Dependence of physical and chemical properties of solids on the structure of crystals.

Physical and chemical properties of solids depend on the type of chemical bonds in crystals. Electrical properties. Optical properties. Malleability of metals. Melting point and hardness. The effect of hydrogen bonding on the physical and chemical properties of substances. Solubility.

Topic 10. Crystallography of simple substances and chemical compounds.

Crystal-chemical laws in DIMendeleev's periodic table of elements. Crystal structure of pure metals. Structure of graphite and diamond. Distribution of elements by groups of the periodic table based on crystal chemical results.

Topic 11. Crystallography of inorganic compounds.

On the classification of binary compounds. Tertiary and more complex inorganic compounds. Pauling's rule for the structure of ionic crystals. Tetrahedral covalent radii. Structure of crystal hydrates. The structure of complex compounds. The structure of clathrates and other complex chemical compounds .

Topic 12. Classification of crystal chemical structure.

Crystal structure and types of structure. Copper α-iron (α-Fe), magnesium

(Mg), diamond and graphite structures and their types. Concept of coordination number and "coordination polygon". Some cases of coordination polyhedra (cubic, octahedron, tetrahedron, etc.). Classification of structures by coordination numbers atomic and molecular structure. Structural types of chemical bonds. Determination of ionic radii, atomic and ionic radii.

Topic 13. X-ray structure analysis devices and their working mechanisms.
RTT device, powder diffractometer, goniometer, software packages .

Topic 14. Diffraction of X-rays in a crystal.

Physical basis of X-ray structural analysis (RTT). Parameters of X-ray waves and X-ray scattering . Issues that need to be addressed when RTTing crystals . Laue conditions. Methods of obtaining the diffraction effect . Breguet 's special interpretation of X - ray diffraction in crystals . Identification of radiographs . Devices for automation and acceleration of x-ray structural experiments .

Topic 15. Application of physical methods in studying the structure of solids.

Application of physical methods in studying the structure of solid substances .

Content of lectures and hours allocated to it

№	Topics	Hour
1	An introduction to crystallochemistry and the history of its development as a science	2
2	Crystalline and amorphous substance. Formation and growth laws of crystals	2
3	Symmetry of crystals.	2
4	Simple and complex forms, open and closed forms, their class, syngonia and division into classes.	2
5	Crystal lattice concept. Broadcasting	2
6	Factors determining the structure of crystals	2
7	The nature of the chemical bond in crystals	2
8	Isomorphism and polymorphism	2
9	Physical and chemical properties of solids depending on the structure of the crystals	2
10	Crystallography of simple substances and chemical compounds	2
11	Crystallography of inorganic compounds	2
12	Classification of crystal chemical structure	2
13	X-ray structure analysis devices and their working mechanisms	2
14	Diffraction of X-rays in a crystal	2
15	Application of physical methods in studying the structure of solids	2
	total	**30**

III. distribution of laboratory activities

№	Topics	Hour
1	Crystal, the main properties of crystalline substances.	2
2	Crystal growth laws and crystal growth.	4
3	Determination of symmetry, syngonia and classes of crystals.	4
4	Geometric shapes of crystals.	2
5	Study of crystal systems of substances. Defects of crystals.	2
6	The structure of solids (glass) in an amorphous state .	2
7	Polymorphism and isomorphism.	4
8	Physico-chemical properties of crystals	2
9	The structure of crystals detection using radiographic methods .	4
10	X-ray structure analysis devices and their working mechanisms	4
	Total	**30**

IV . Independent work topics

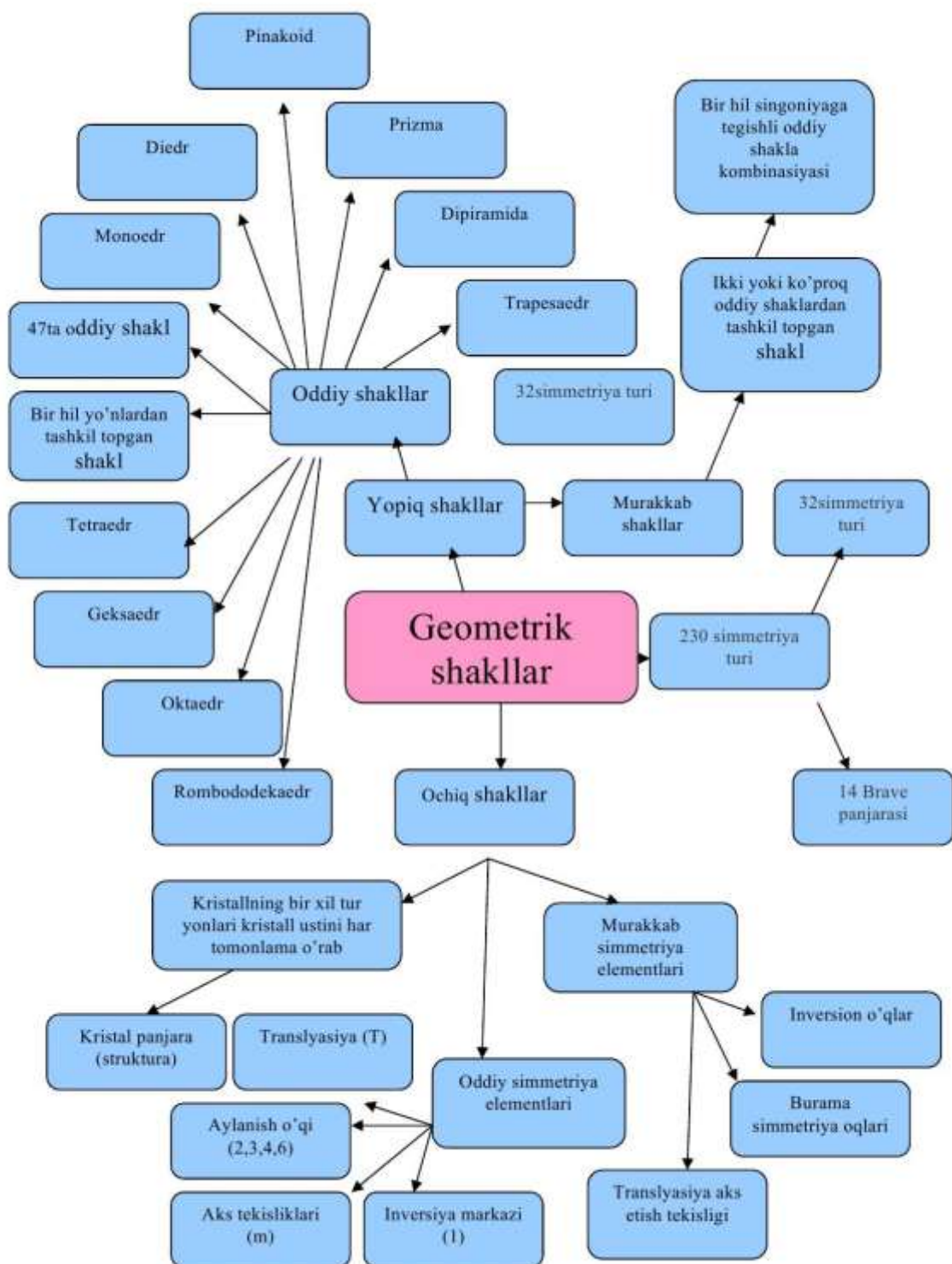| №	Subject Name	Hour
1	States of matter	4
2	The main properties of crystals	4
3	Geometric shapes of crystals	4
4	Physical properties of crystals	4
5	Formation and growth of crystals.	4
6	Stenon's law.	4
7	Isomorphism and polymorphism	4
8	Types of chemical bonds in crystalline substances	4
9	The concept of symmetry. Elements of symmetry	4
10	Symmetry operations.	4
11	Signs of symmetry elements.	4
12	X-ray structural analysis of crystals	4
12	Defects of crystals	4
14	Types of categories and syngonias of crystals.	4
15	32 classes of symmetry elements.	4
	Total	**60**

3

V. Results of science education (developing competences)

As a result of mastering the subject, the student:

To have an idea about the subject and tasks of crystal chemistry, the conditions and methods of reaction, taking a sample and preparing it for analysis, analysis methods;

| 4	**VI. Educational technologies and methods:**
	✓ lectures;
	✓ interactive case studies;
	✓ logical thinking, quick questions and answers;
	✓ work in groups;
	✓ preparation of presentations;
	✓ individual projects;
	✓ projects for teamwork and protection
5	**VII. Students to receive credits:**
	Full mastery of theoretical and methodological concepts related to science, ability to correctly reflect the results of analysis, independent observation of the studied processes and completion of tasks and assignments given in the current interim control forms, written work for final control submit
6	*Basic literature*
	1. Zohidov KS Crystallography. Uzbekistan. 2002. 255 p .
	2. Urusova V.S. Theoretical crystallochemistry. Izd-vo M GU, M ., 1987.
	3. The late G.B. "Crystallochemistry". M .: "Nauka". 1971.
	4. Popov G. M. Shafranovsky I.I. Crystallography. M. 1987.
	5. Aripova M. Kh ., Babakhanova Z. A. Mineralogy , crystallography and crystal chemistry basics from science laboratory and practical training perform according to methodical manual , Tashkent , 2013. - 64 p .
	Additional literature
	1. G.M. Kuzmicheva. Basic crystallography. M.: MITXT, 2002.-95p.
	2. E.V. Chuprunov, A.F. Khokhlov, MA Fadeev. Basic crystallography. Fizmatlit., 2004.-500 p.
	3. Kostov I. Crystallography. Izd-vo "Mir", M., 1965.
	Websites:
	www.chem.msu.su
	www.ziyonet.uz
	chembaby.com
	chemexpress.fatal.ru
	www.khumuk.ru
7	The provisional program of science is approved by the statement of the Council of Namangan State University dated "_____" 2023 No. "_____"
8	**Responsible for the subject/module: ZRMamadaliyeva** – teacher of the Department of Inorganic Chemistry, NamSU
9	**Reviewer: Y.Toshmatov**, NamSU, chemical sciences candidate, associate professor.

Pinakoid

Diedr

Prizma

Monoedr

Dipiramida

Bir hil singoniyaga tegishli oddiy shakla kombinasiyasi

47ta oddiy shakl

Trapesaedr

Ikki yoki ko'proq oddiy shaklardan tashkil topgan shakl

Oddiy shakllar

Bir hil yo'nlardan tashkil topgan shakl

32simmetriya turi

Tetraedr

Yopiq shakllar

Murakkab shakllar

32simmetriya turi

Geksaedr

Geometrik shakllar

230 simmetriya turi

Oktaedr

Rombododekaedr

Ochiq shakllar

14 Brave panjarasi

Kristallning bir xil tur yonlari kristall ustini har tomonlama o'rab

Murakkab simmetriya elementlari

Inversion o'qlar

Kristal panjara (struktura)

Translyasiya (T)

Oddiy simmetriya elementlari

Burama simmetriya oqlari

Aylanish o'qi (2,3,4,6)

Aks tekisliklari (m)

Inversiya markazi (1)

Translyasiya aks etish tekisligi

"Kristallarning geometrik shakllari" mavzusiga "Klaster" diagrammasi.

1-vazifa. **"Ochiq shakl" va "Yopiq shakl" tushunchalarini "Venna diagrammasi" yordamida solishtiring.**

"Ochiq shakl" va "Yopiq shakl" tushunchalari

Umumiy jixatlari

1.
2.
3.

Ochiq shakl   Yo'piq shakl
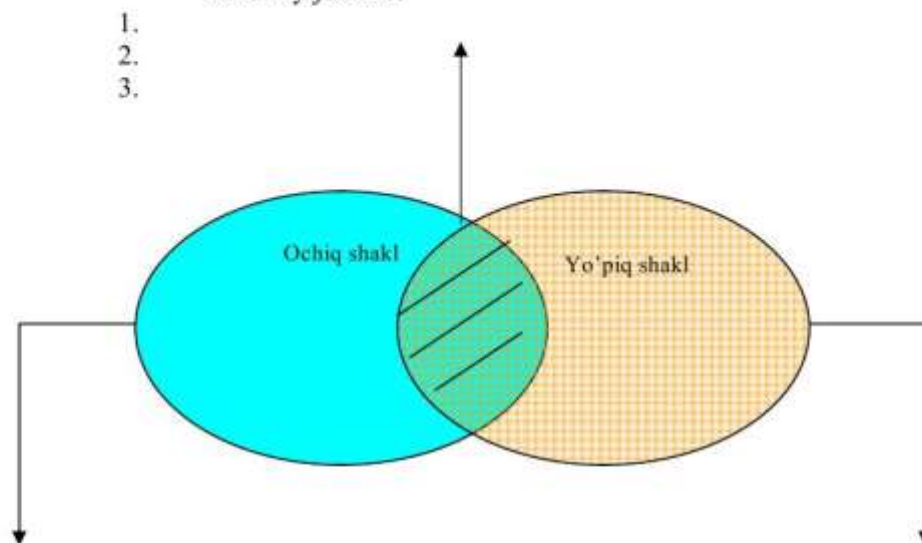
1.   1.
2.   2.
3.   3.
4.   4.

2-vazifa. **"Ochiq shakl" va "Yopiq shakl" tushunchasi** mavzusiga oid "Charxpalak" jadvalini to'ldiring (to'g'ri yoki notug'ri kelishiga qarab **+** **yoki** **–** belgisini qo'ying).

Tushuncha	Kub	Piramida	Tetraedr	Dipiramida	Prizma	Shar	Monoedr
Ochiq shakl							
Yo'piq shakl							
Oddiy shakl							
Murakkab shakl							
Kristal shakli faqat bir turdagi yo'nlardan tashkil topgan							
Kristal shakli bir necha hil turdagi yo'lardan tashkil topgan							

152

"Minerallarning qattiqligi " mavzusi bo'yicha "Klaster" diagrammasini tuzing:
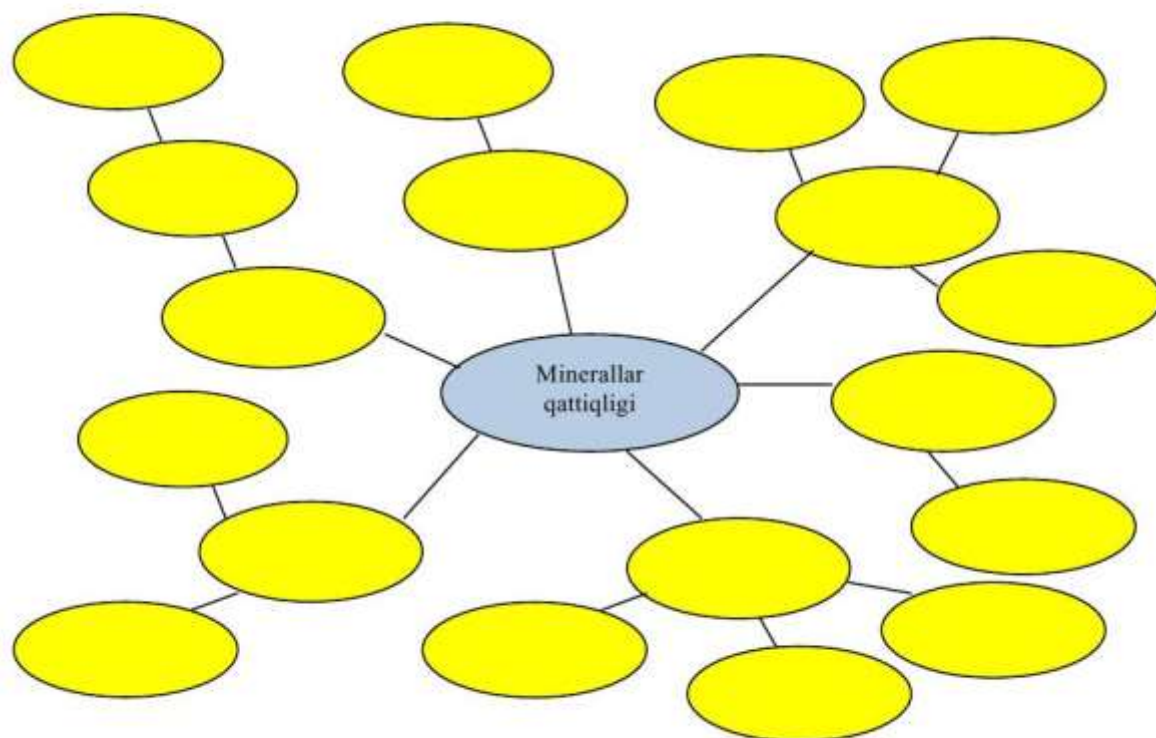
"BBB" usuliga asoslanib, jadvalni to'ldiring.

Bilaman	Bilishni hohlayman	Bilib oldim
Amorf holat-		
Amorf jismlarning asosiy hossalari		
Amorf holatning hosil bo'lish shartlari		

## "Kristall" va "Amorf" tushunchalari

Umumiy jixatlari

1.
  2.
  3.

Kristall   Amorf

1.
2.
3.
4.

1.
2.
3.
4.
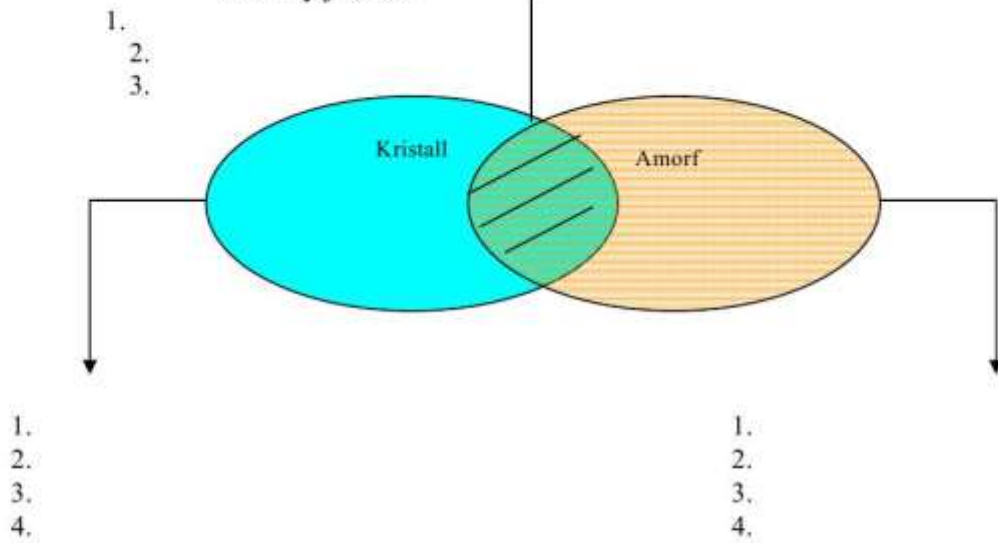
2 vazifa. Singoniyalarni bo'yicha "Charxpalak" usulida jadvalni toldiring:

№	Panjara parametrlari	Singoniyalar						
		Kubik	Geksagonal	Tetragonal	Rombik	Romboedrik	Monoklin	Triklin
1	$a=b\neq c, \alpha=\beta=\gamma=90^o$							
2	$a\neq b\neq c, \alpha\neq\beta\neq\gamma\neq90^o$							
3	$a\neq b\neq c, \alpha=\gamma=90^o, \beta\neq90^o$							
4	$a=b=c, \alpha=\beta=\gamma\neq90^o$							
5	$a=b=c, \alpha=\beta=\gamma=90^o$							
6	$a=b\neq c, \alpha=\beta=90^o, \gamma=120^o$							
7	$a\neq b\neq c, \alpha=\beta=\gamma=90^o$							

"Kristall", "Amorf", "Diagramma", "Panjara" so'zlariga Sinveyn tuzish kerak.

1. Kristall
2. Anizotrop jism
3. Ma'lum erish haroratoga ega
4. Moddaning strukturasida panjara mavjud
5. Korund

1. Panjara
2. ...
3. ...
4. ...
5. ....

1. Amorf
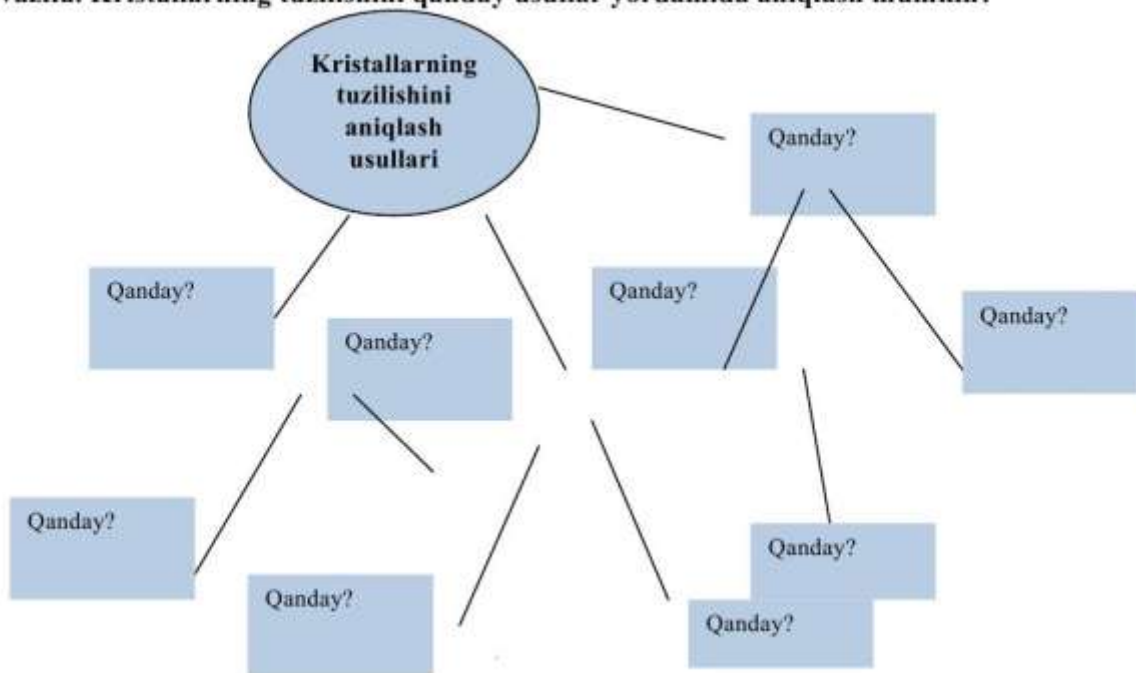2. ....
3. ....
4. ....
5. .....
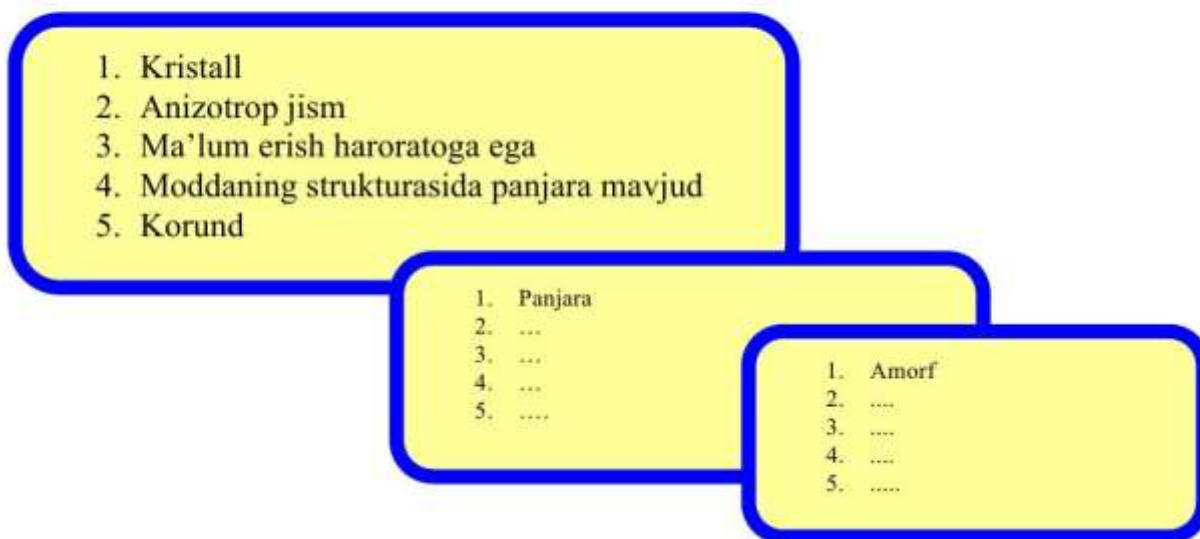
"Tabiatda metallar va metal qotishmalar" mavzusi bo'yicha "Klaster" diagrammasini tuzing:
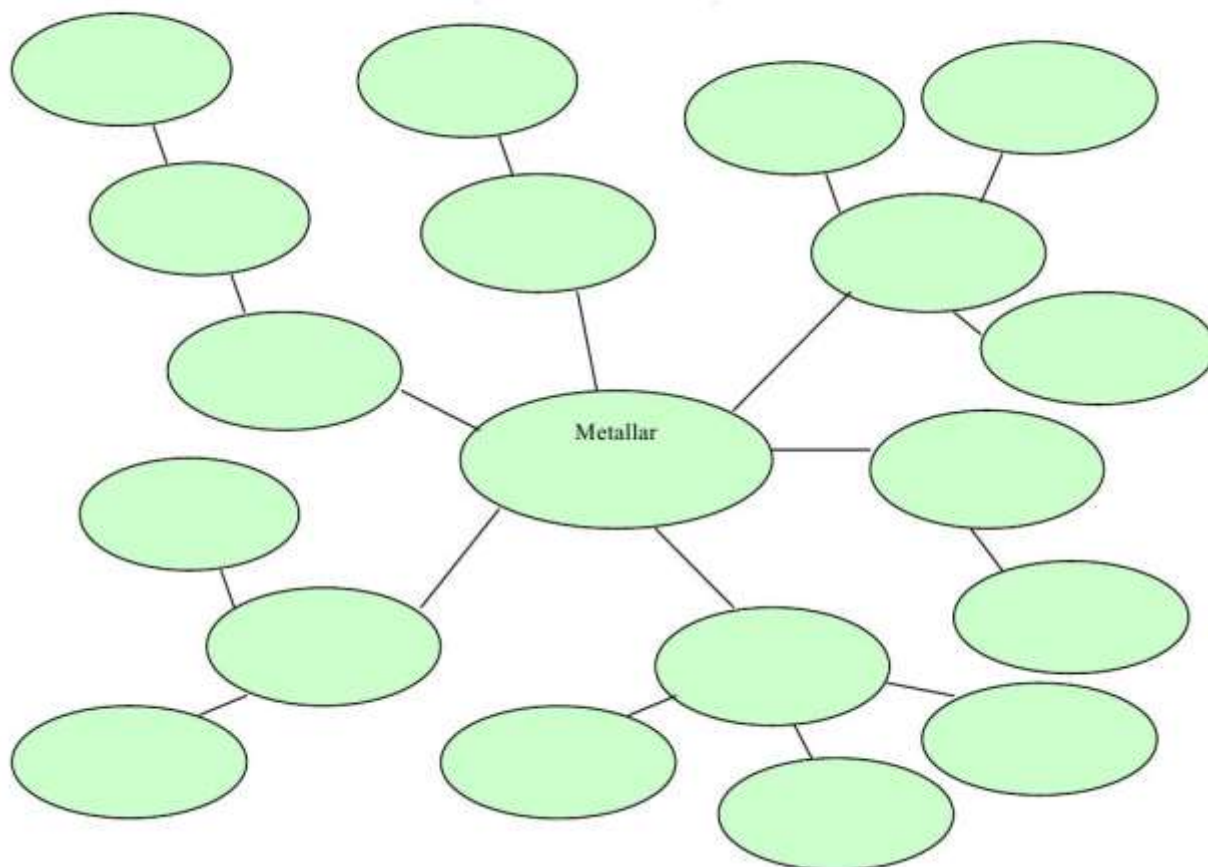
Metallar

1 vazifa. Singoniya turlari va ularning belgilari mavzusi bo'yicha "Qanday?" metodi yordamida diagrammani to'ldiring

Singoniya turlari

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?
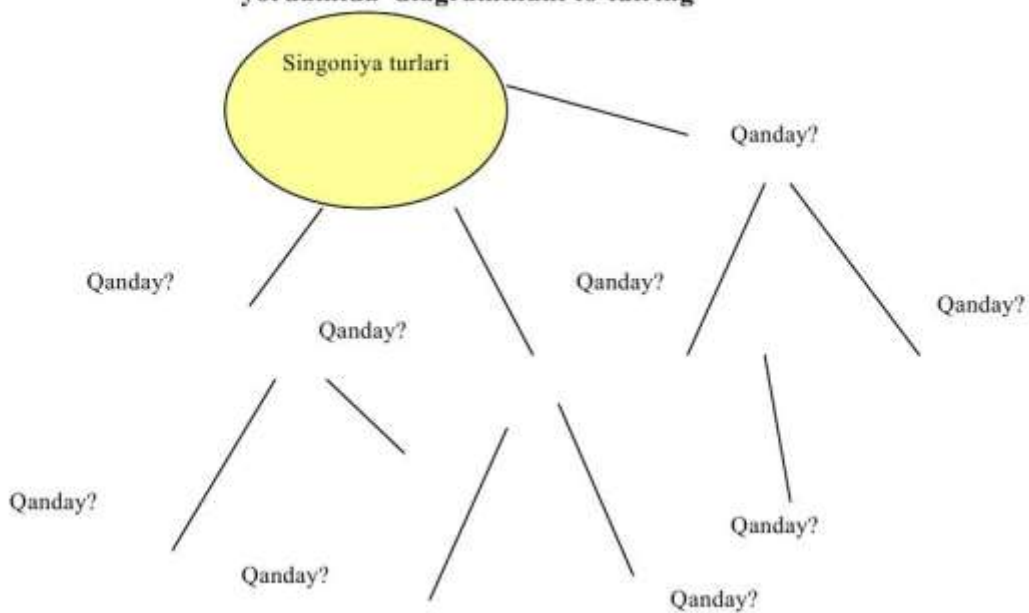
Qanday?

Qanday?

2 vazifa. Kristallarning tuzilishini qanday usullar yordamida aniqlash mumkin?

Kristallarning tuzilishini aniqlash usullari

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

Qanday?

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Izomorfizm mavzusiga klaster diagrammasi.

"Polimorfizm hodisasi " mavzusi bo'yicha "Klaster" diagrammasini tuzing:
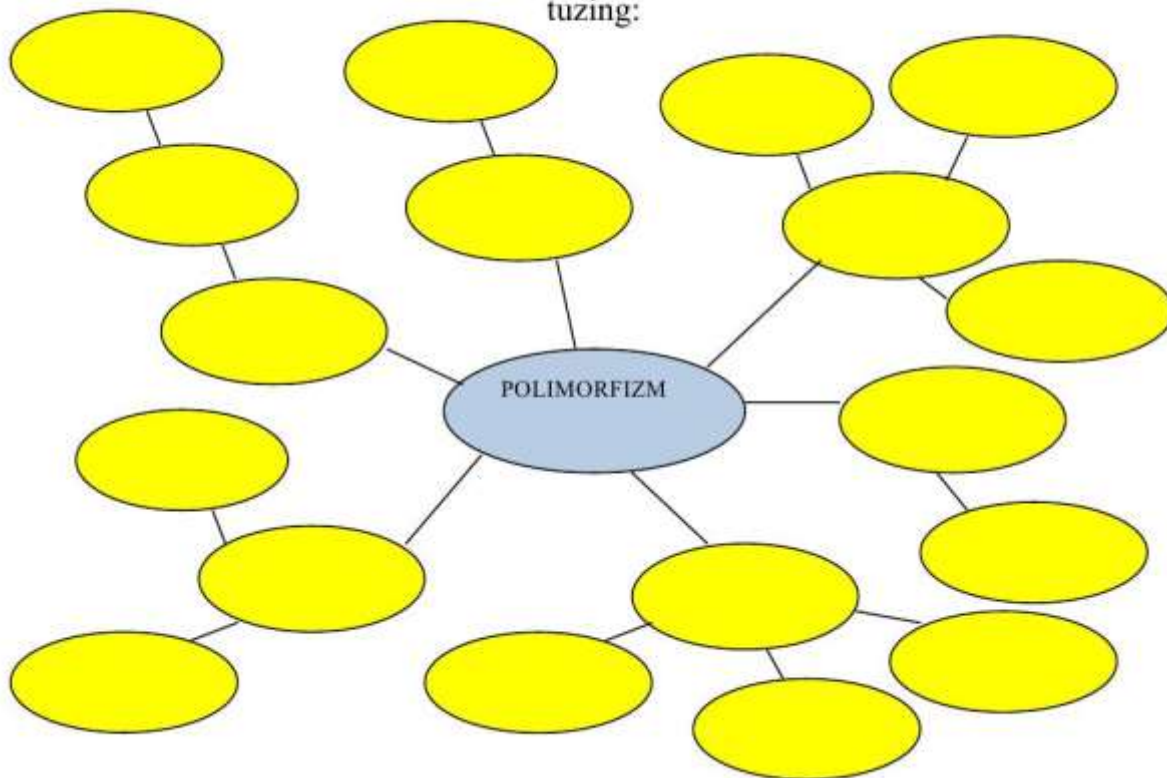
T EST QUESTIONS

1. What is a crystal structure?
* This is the exact arrangement of atoms at a certain distance

This is a three-layer arrangement in space

It is a cubic volume centered structure

This is the elementary cell

2. How is the structural type of crystals determined?
* Depending on the arrangement of atoms at the point of intersection edges of the elementary cell

Depending on the height of the intersection of the polygons corresponding to the center of the anions

Depending on the projection of the edges

Looking at the stereographic projection

3. What substances crystallize in the copper structure type?
* Au, Ag, Ni, Al, Ca, Th, Pb, α-Co

Mn, Cl_2O, α-Fe, Cr_3I_2, Se, HBr, S

TiO_2, V_2O_5, W, Ni, Pd, Mo, Mg, K

Ag, Zn, Ga, Ge, Bi, Ru, g-Fe

4. State the multifaceted coordination shape and coordination number of a copper crystal.
* KS =12, KSH- cubobooktahedron

KS = 9, KSH- hexaoctahedron

KS =12, KSH- tetrahedron

KS = 8, KSH- rhombictaedr

5. What is the dense structure of the copper structure?
*Cubic three-layer dense arrangement …ABCABC…, with all spaces between spheres filled

Hexagonal four-layer dense arrangement …ABCBABCB… , with all spaces between spheres filled

A cubic bilayer dense arrangement …ABCBAC…, all spaces between the spheres are filled

Trigonal four-layer dense arrangement …ABCAACBB…, with all spaces between spheres filled

6. How are the atoms in the copper unit cell?

*Atoms are located at the center and ends of the cubic cell edges

Atoms are located between the edges of the I cell

Atoms are arranged according to the rhombic syngonia F-cell law

Atoms are arranged according to the law of tetragonal syngonia I-cell

7. What intermetallic compounds have the copper structure type?

* $AuSb$, Au_2Bi, Au_2Pb, Cu_2Mg, Bi_2K, ZrH, TiH

FeS_2, $MgNa$, $AuCu$, $ZnMg$, Cu_2S, Mg_2S

MnS, $AuSb$, Au_2Bi, ZnS, Ag_2S, Cu_2Mg

$TiPb$, Ag_2O, Cu_2O, Au_3Cu_2, $CuAg$, CuS

8. What is the shape of the magnesium unit cell?

*Hexagonal primitive

The edges of the cube are centered

The tetragonal volume is centered

Monoclinic primitive

9. What substances crystallize in the magnesium structure type?

*Hexagonal metals – Cd, Be, Tl, Ti, Ni, Cr

Cubic metals - Li, Na, K, Hg, Tl, In, Se

Tetragonal metals – Cd, Ca, Al, Mn, Ti, Ge

Trigonal metals - Se, Te, Bi, Lr, Mo, Ba

10. What is the close-packed structure of magnesium?

*Double layer, hexagonal arrangement, not all spaces occupied

Double layered, rhombic arrangement, all spaces are unoccupied

Four layers, hexagonal arrangement, all spaces occupied

Single layer, tetragonal arrangement, all spaces are occupied

11. What intermetallic compounds have a magnesium structure?

*$AgCd_3$, $AuCd$, $AuCd_3$, $CuCd_3$, $AgZn_3$, $AuZn_3$, $CuZn_3$, $NiMo$, Ag_5Al_3

$NiAs$, Cu_2Mg, $AuSb$, Au_2Bi, $AgCd$, $NiCd_2$, $CuZn_3$

for Cu_2Mg and $AuZn_3$

Au_2Pb, Cu_3Al, Cu_5Sn, $LiAg$

12. Determine the coordination shape and coordination number of magnesium structure.

* KS= 12, KSH – cubetahedron

KS= 8, KSH – tetrahedron
KS= 6, KSH – octahedron
KS= 3, KSH – rhombictahedron

13. What class and syngonia does the diamond crystal belong to?
*m3m cubic syngonia
6mm hexagonal syngonia
4/m tetragonal syngonia
3m trigonal syngonia

14. What is the type of diamond cell?
*Cube sides are centered in a checkerboard pattern of centered octanes
Hexagonal primitive
The cubic volume is centered
Molnoklin primitiv

15. Determine the coordination number and coordination shape of the diamond structure?
* KS = 4, KSH – tetrahedron
KS = 12, KSH is a cubic tetrahedron
KS = 8, KSH – tetrahexahedron
KS = 6, KSH – hexaoctahedron

16. Graphite structure belongs to which class and syngonia?
* 6/mm hexagonal
4/mm tetragonal
m3m – cubic
2/m monocline

17. What is the structure of graphite?
*Layered structure
Checkered - layered structure
Poperechnaya structure
Sliding structure

18.Graphite layers are composed of which cells?
*Hexagonal cells
Cubic cells
Rhombic cells

Monoclinic cells

19. What are the bonds within the layers of graphite?
* Covalent bonds
Van der Waals bonds
Ionic bonds
Metal connections

20. Why are graphite crystals easily deformed?
*Due to layered structure
Due to its polarized structure
Due to weak van der Waals bonding
Due to the presence of anisotropic properties

21. Identify the type of NaCl unit cell?
* F - cell with diseased edges
Primitive P-cell
Size centered I – cell
Base-centered S-cell

22. What spaces do Na cations fill in the structure of NaCl?
*All octahedral spaces
Only ½ of the tetrahedral cube
All of the cubic tetrahedral space
All of the tetrahedral space

23. What substances have the NaCl structure type?
* AgCl, AgBr, AgF, PbS, NH_4Cl, TiO , MnO, NiO
CsCl, MnCl, NH_4Br, PbSe, AgI, LiCl
only CaF_2 and CsCl
FeO, FeS_2 , NiS, PbSe, NH_4I, KCl, CsCl

24. What arrangement (packing) does NaCl have?
* Three layered location , cube
Two layered location , hexagonal
Four-layer arrangement, tetragonal
Five-story layout, rhombic

25. What chemical bond is present in the NaCl crystal?
*Ionic bonding
Hydrogen bonding
Metal connection
Covalent bond

26. What type of arrangement (packing) is present in the wurtzite structure?
*Dense hexagonal arrangement
A loose cubic arrangement
Dense tetragonal arrangement
Location not available

27. What type of location is typical for sphalerite structure?
*Dense cubic arrangement
Dense tetragonal arrangement
Four-layer layout
A dense hexagonal arrangement

28. How is the dense arrangement of the wurtzite structure formed?
* With parallel layers of anions
With the sequential arrangement of anions and cations
Only with cations
By electrostatic interaction

29. For what structures is polytism characteristic?
* SiC, ZnS, MoS_2, CdI_2, SnS_2
$NaCl_3$, CsCl, CaF_2, α-Fe
for   PbS and MoS_2
Only for γ -Fe and α -Fe

30. Perovskite structure type is characteristic for which compounds?
* $BaTiO_3$, $CaZrO_3$, $PbTiO_3$
 Na_3SbS_3, Na_3AsO_4, $CaHAsO_3$
$KTiO_4$, NiAsS, K_2WO_4
$MgAl_2O_4$, $Fe(CrO_2)_2$, $CaIrO_3$

31. How are Ti, O, Ca ions located in the perovskite unit cell?
*Titanium ions are located at the nodes, oxygen ions are located between the edges, and calcium ions are located in the center of the cell;

Titanium ions are located at the nodes, oxygen ions are located inside the cell, calcium ions are located between the edges, and titanium ions are located in the center of the cell;

Calcium ions are located in the nodes, oxygen ions are located between the edges, and titanium ions are located inside the cell;

Barium ions are between the edges, oxygen ions are at the nodes, and titanium ions are inside the cell;

32. What symmetry class does the perovskite structure belong to?
*m3m
4mm
4/m
2/m

33. How many correct system points are there in the perovskite structure?
*Ti order 1, Ca order 1, O order 3;
Ti order 1, Ca order 2, O order 4;
Ti order 3, Ca order 6, O order 2;
Ti order 8, Ca order 7, O order 3;

34. Which compounds belong to magneto- and anti-magnetoelectrics, pyro- and piezoelectrics, semiconductor-magnetoelectrics and are widely used in technology?
*$CaTiO_3$, $BaTiO_3$, $PbTiO_3$
NaCl, CaF_2, $CaWO_3$
$CaVO_3$, K_3NiO_4, $Fe(TaO_3)_2$
$IrSiO_4$, $BaTiO_3$, ZnS

35. What symmetry class does the spinel structure belong to?
*m3m
hmm
6mm
222

36. What bonds form the spinel structure?
*Ionic - covalent bonds
Ionic and hydrogen bonds
Metal links only
Covalent - polar bonds