MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
NATIONAL TECHNICAL UNIVERSITY OF UKRAINE
“IGOR SIKORSKY KYIV POLYTECHNIC INSTITUTE”

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CRYSTAL CHEMISTRY OF REFRACTORY COMPOUNDS

Approved by the Scientific Council of National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute” as textbook for students of speciality 132 “Materials Science”

Kyiv
Igor Sikorsky Kyiv Polytechnic Institute
2021

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Approved by the Scientific Council of Igor Sikorsky Kyiv Polytechnic Institute (protocol № 10 from 13.12.2021)

Electronic online educational publication

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CRYSTAL CHEMISTRY OF REFRACTORY COMPOUNDS

Crystal Chemistry of refractory compounds [Electronic resource]: a textbook for students specialty 132 "*Materials Science*" / L. O. Biriukovych, Yu. I. Bogomol ; translator N. S. Nikitina ; Igor Sikorsky Kyiv Polytechnic Institute. – Electronic text data (1 file: 2.92 MB). – Kyiv : Igor Sikorsky Kyiv Polytechnic Institute, 2021. – 140 p.

The textbook contains seven chapters and covers sections of the discipline "Crystal Chemistry of refractory compounds" and is intended for Bachelor program students of specialty "*Materials Science*", specialization "*Nanotechnologies and Computer-aided Materials Design*".

Reviewed of the classification of refractory compounds, the basics model of the condensed state of matter, which are the basis for understanding the formation of properties of materials based on refractory compounds and the term "interstitial alloys", which include the majority of refractory compounds.

Considered the main types of crystal lattices formed in the structures of most common refractory transition metal compounds with light non-metals (carbon, nitrogen, boron and silicon) and mutual compounds of this non-metals. It analyzes of the electronic structure this compounds and its influence on the basic properties of refractory compounds in fundamentals of Configuration Model of a Solid.

The seventh section includes practical works. The purpose of practical works is teaching students to apply theoretical knowledge of the basics of structural crystallography and crystal chemistry for analytical description of crystalline structures of refractory compounds.

It is for students in material science, metallurgical and engineering specialties of higher-educational institutions on. It may be useful to graduate students, researchers and technical employees.

CONTENT

INTRODUCTION

The main directions of development of modern scientific and technological progress are determined by energy, automation and materials. But it should be noted that neither the development of energy nor the development of automation is possible without the development of materials with new properties, or improvement of existing ones. New materials are required by all modern industries – construction, machine and machine tools, ships and aircraft, nuclear power and rocketry, radio and electronics. Therefore, material science, which studies the structure, composition, properties of materials and the relationship between them, examines the dependence of the structure and properties on the methods of production and processing of materials, as well as their change under the influence of external factors: power, thermal, radiation, etc. are among the priority directions of modern science.

An indispensable essential component of many modern materials and coatings are refractory compounds that have a complex of unique physical, chemical, operational and technological properties.

Since modern science is not able to unambiguously answer the question of what properties the newly created material, which includes certain elements of the periodic table, will have, the research and knowledge of the electronic structure and crystalline structure play a significant role in predicting its possible properties. Therefore, teaching the discipline “Crystal Chemistry of Refractory Compounds” is a necessary component in the training program for students of material sciences.

There is now a great deal of basic research devoted to research and generalization of refractory compounds and materials results. The purpose of the “Crystal Chemistry of Refractory Compounds” manual is to familiarize students of material science with the results of these studies in a concise and understandable format for students.

The first section of the “Crystal Chemistry of Refractory Compounds” manual discusses general information concerning refractory compounds and without which it is impossible to further present the issues of electronic and crystalline structure and

properties of specific refractory compounds. This section discusses the classification of refractory compounds, the basic condensed-state models of matter, which are the theoretical basis for understanding the formation of properties of materials based on refractory compounds, and the concept of “interstitial phase” to which a large number of refractory compounds belong.

The sections from the second to the fifth introduce the students into the peculiarities of the electronic structure and crystalline phase structure, which are formed in the double systems of transition metal of IV–VI groups–non-metal (carbon, nitrogen, boron, silicon). Each section also presents the basic properties of refractory compounds from the point of view of the configuration model of the substance.

The sixth section is devoted to non-metallic, so-called covalent, refractory compounds: boron nitride, silicon, aluminum, silicon and boron carbides, boron silicide.

The seventh section is practicum. The purpose of practical works is teaching students to apply theoretical knowledge of the basics of crystallography and crystal chemistry for analytical description of crystalline structures of refractory compounds.

Each of the five practical works is accompanied by theoretical information on the basics of crystal chemistry or crystal chemistry of refractory compounds, the procedure of work and detailed examples of the task. There are questions for students’ self-control regarding the acquisition of theoretical knowledge.

The authors express their special gratitude to the distinguished reviewers for their comments and advices in the preparation of the textbook.

1. GENERAL INFORMATION ABOUT REFRACTORY COMPOUNDS

1.1. Classification of refractory compounds

It is difficult to define the concept of “refractory compounds” because any division into refractory and non-refractory compounds is conditional and involves setting some limit value for the melting point above which the chemical compounds are considered refractory. This value was set many times and gradually moved to a higher temperature range. In the second half of the XIX century this limit was determined by the temperature of 1000 °C, in the first half of XX century – 2000 °C, today – this value has reached 3000 °C.

However, over time, the concept of refractory compounds has lost its primary meaning. Today, it is no longer limited to the magnitude of the melting point of a compound, but contains a whole set of properties that include high hardness, brittleness, heat of formation, resistance to corrosive media, as well as specific electrical and magnetic properties determined by the electronic structure of the corresponding compounds and components arrangement in the periodic table of elements.

Essential in the term, traditionally referred to as “refractory compounds” is the nature of chemical bonding between the components of the compounds. Such bond is preferably metallic or covalent with a small ionic fraction. These types of bonding occur, as a rule, in compounds of metals (mainly, transitional or close in some respects) with non-metals, such as boron, carbon, silicon, nitrogen, sulfur, phosphorus and others, as well as in compounds of non-metals between themselves and some metals among themselves.

Nowadays, although the physical and chemical properties of refractory compounds have not been sufficiently studied, it is already possible to propose their scientific classification as a basis for further in-depth research and approximation to the creation of refractory compounds with predetermined properties.

Refractory compounds are formed by elements of unpaired subgroups of II–VII groups, VIII group, lanthanides, actinides, and light non-metals of II and III

periods (B, C, N, O, P, Si, S) and aluminium. These components are reciprocally combined to form the following three major classes of refractory compounds [1]:

1. Compounds of metals with non-metals, to which belong borides, carbides, nitrides, oxides, silicides, sulfides.

2. Compounds of non-metals, including carbides, sulfides, phosphides of boron and silicon, and boron-silicon alloys.

3. Metal-metal intermetallic compounds.

1.2. Condensed matter models

The creation of new materials which properties face the needs of the most modern industries is a priority area of scientific and technological progress.

To create new materials with a complicated complex of properties requires the development of theoretical foundations and apparatus for the formation of such materials.

The development of ideas about the substance and material of this substance, which are necessary for the creation of theoretical foundations, go through three main stages:

1. Establishment of comparative links between different properties of the same or different substances.

2. The connection between the properties of the substances and their crystalline structure, as well as the defects of this structure.

3. Identification of the properties with the crystalline structure of a substance, on the one hand, and its electronic structure, on the other.

The first way, the most elementary one, helped to establish a number of important dependences of a descriptive nature, allowed to predict and extrapolate dependencies between properties on similar series of not previously studied substances, to correct experimental data, choosing from them satisfactorily fit into the established dependencies. This path is successfully used nowadays [2].

The natural extension of the first stage is the second, which consists of establishing relationships between properties and structure. This stage is now being developed for real crystals using the formal apparatus of dislocation theory. It has gained immense popularity and is more or less easily come under the basis of interpretation for many authors.

Both described steps are essentially paraphrasing experimental data and make little or no clarity in answering the question why are there such characteristics, in general, other than the characteristics of a substance; what is the internal structure; “why” rather than “how”, that is usually assumed in the first two stages.

Obviously, all of these questions can be answered if to know and understand the functional dependencies between the electronic structure and the properties of a substance, that is, if the third stage of the doctrine of matter is mastered. An electronic structure is the basis that determines the crystalline structure, and the last, when formed, naturally affects the electronic structure like any superstructure, but this influence can never be decisive and overwhelming.

For the third stage, concepts of matter should be created that would be based on a given electron structure of the atom and indicate a functional relationship between the structure and the properties.

There are basically two approaches to solving this problem. The most direct of these assumes the solution of the Schrödinger equation for a multi-electronic system, taking into account as many interactions as possible and comparing the results obtained with experimental methods of studying the electronic structure: X-ray, neutron and electronography, magnetic resonance, the Messbauer effect, positron annihilation. The fundamental information obtained by these methods does not satisfy the requirements of the present day material science practice. Therefore, different models of condensed matter are being developed, which, if they do not allow solving the problem of creating materials with predetermined properties, in any case, facilitate the search for new materials, and provide a conscious and purposeful approach to solving material problems. These models, from a theoretical point of

view, are temporary “constructions” and should be replaced with the development of the theory of condensed matter.

The essence of the nuclear-electron interaction that leads to the formation of a chemical bond has only been clarified through a quantum-mechanical approach to address this. And from the point of view of quantum mechanics, the electron clouds of all the electrons of each of the atoms occupy together a certain area of space, that is, they overlap, during the chemical bonding between atoms. As a result of the overlapping of electron clouds in the nucleus, an increased electron density is generated compared to the electron density in isolated atoms at the same distance from each nucleus. The nuclei seem to be compressed by a condensed part of a shared electronic cloud into a single stable system.

If, due to the peculiarity of the electron states of colliding atoms, none of the electron clouds of any of the atoms were trapped in the nucleus, then the nucleus does not form an electric charge, but on the contrary, the electron density decreases to zero. In this case, the chemical bond is not formed – the system of individual atoms is more energy efficient.

The presence of electron density between nuclei is a necessary and sufficient sign of chemical bonding between them in any molecule. The individual properties of molecules: the bonding energy, the structure of the nuclear framework, the polarity, etc., and therefore the chemical properties, are determined by specific features in the distribution of electron densities within the molecule. The density distribution in a given molecule can be found only approximately, since the Schrödinger equation describing the molecule is solved only approximately.

In the early 20th century, two different approaches to the chemistry of chemically bound atoms were widely used in chemistry and physics. According to one of them, a molecule is considered a system of atoms, between which there electron pairs are generalized, each of which is formed by overlapping one electron cloud from the outer electron layer of two atoms and is localized between the nuclei of these atoms. A generalized pair of electrons is considered a unit of chemical bonding, a unit of valence of each of the two bonded atoms. The number of

generalized pairs of a given atom with other atoms determines the number of valence bonds in a molecule. The theory based on such ideas about the molecule is called the theory of valence bonds (TVB) – the method of Geitler – London – Heisenberg.

The main statements of the TVB are as follows:

1. The chemical bond between two atoms is due to the pairwise generalization of part of the electrons from their outer electron layers, whereby the electron clouds that partially overlap are distributed in the space between the nuclei of the bonding atoms.

2. The electron density of the combined electron pair is localized in the field of two related atoms and corresponds to the chemical bond unit. The number of electronic pairs that bind a given atom to another determines the number of units of its chemical bond – its valence.

3. Only electrons that occupy one quantum cell during the interaction of atoms, i.e. the so-called unpaired electrons inside the atom, can be generalized.

4. For single electrons of two atoms to form a common electron pair, the spins of these electrons must be distinguished by a sign – be antiparallel [3].

Another approach to chemically bound atoms is to consider them as a single system of nuclei and interacting electrons. The original atoms are not distinguished in the molecule, only the nuclei of atoms are distinguished. Each electron in a molecule is considered as being in the field of all nuclei and other electrons in a molecule, by analogy, as every electron in an atom is considered in the nucleus of an atom and other electrons of an atom. The state of the electrons in a molecule is described by the molecular orbitals that were found when solving the Schrodinger equation for an atom.

The theory based on the description of electron states by molecular orbitals is called the Bloch theory of molecular orbitals (TMO). This theory is a natural extension of quantum-mechanical ideas about an atom and molecule.

These two theories of the electronic structure of crystalline bodies – TVB and TMO – arbitrarily explained the majority of the laws characteristic of solids with a relatively simple electronic structure. But the application of these models to the

description of the properties of transition metals and the compounds based on them did not match the theoretically calculated and experimentally obtained content. The analysis of the complex of physical-chemical properties of transition metals, their alloys and compounds allowed to conclude that the most important factors determining the behavior of substances under different conditions are the degree of localization of electrons in them and the stability of the valence subshells of isolated atoms from which a solid is built [3].

Some properties of these substances can be explained only from the standpoint of the theory of collectivized electrons, while other properties can only be explained from the standpoint of the model of the Geitler-London localized states. It is obvious that the band theory and the Geitler - London theory are mutually exclusive. This contradiction between the methods of valence bonds and molecular orbitals, or between the individuality of the element that has been the focus of chemistry and the band nature of the energy spectrum, which was taken as the basis for most physical constructions, is eliminated by the use of a solid-state configuration model.

The configuration model of the structure of a solid body began to come into being rather intuitively, in chemistry and physics in 1933. G. V. Samsonov, I. F. Pryadko and L. F. Pryadko made a great contribution to its formation and development.

The model of valence electron configurations is widely used to describe the structure of refractory compounds. This model makes it quite easy and from a single point of view to describe the peculiarities and varieties of properties of these compounds. The disadvantage of this model is its quality. But this drawback is offset by the ability of this theory to explain any properties from a single position.

A number of assumptions (postulates) are the basis of the model of valence electron configurations (MVEC) [2].

The essence of the first postulate of the MVEC model is that during the formation of a condensed state of a substance from isolated atoms, the valence electrons of these atoms are distributed into localized and collectivized groups.

Part of the electrons is localized in the atomic spheres of different types of atoms. Other electrons are considered to be collectivized, shifting between atomic spheres throughout the crystal and indistinguishable from atomic spheres.

The essence of the next postulate of the MVEC model is that, despite such separation, the difference in the atomic symmetry of the wave functions of electrons, that is, *s*-, *p*-, *d*-, and *f*-electrons, remains. The formation of the condensed phase preserves the genesis of the electron orbitals.

The atomic spheres occupying the lattice nodes equivalent to the point group are not quantum mechanically different. As a quantitative measure of the electrons that settle such spheres, it has been suggested to consider the statistical weight of instantaneous electronic agglomerations with the same symmetry of the wave function. It is assumed that if at some particular moment in time there are n electrons in the *i*-th atomic sphere and in the *j*-th atomic sphere at the same moment of time there are m electrons of this symmetry, and in the *k*-th atomic sphere – *q* electrons, where *m*, *n*, *q* – acquire values of integers from zero to the limit number of electrons with this symmetry of the wave function in an isolated atom (i. e. 2 for *s*-, 6 for *p*-, 10 for *d*-, 14 for *f*-electrons). So in the next, closest to the previous, moment of time the distribution of the number of electrons (electronic configurations) changes, but so that the total number of electrons of the given symmetry remains unchanged.

The relative number of electrons in the atomic spheres to the total number of electrons in the condensed phase is considered to be a hundred thousandth weight of MVEC, and the relative number of atomic spheres, each occupied by *m*-, *n*-, *q*-electrons, to the total number of atomic spheres is regarded as the statistical weight of this electronic configuration. Thus, the MVEC model, like any quantum mechanical model, considers the probable electron distribution in the condensed phase.

The next postulate of the MVEC model is the energy imbalance of electronic configurations localized in atomic spheres. The most stable, and therefore, with the maximum service life, are considered to be configurations characterized by the *m*, *n*, *q* numbers multiple of 1 (for *s*-electrons), 3 (for *p*-electrons), 5 (for *d*-electrons), 7

(for *f*-electrons), with zero being considered as an integer. Such “half” filled and “fully” filled electronic systems have spherical symmetry and the lowest energy, as established by the English physicist Henry back in the 1930s.

In the MVEC model, such electronic configurations are considered to be the most stable, forming a discrete set of configurations s^0, s^1, s^2, p^0, p^3, p^6, d^0, d^5, d^{10}, f^0, f^7, f^{14}, at the background of continuous-spectrum electronic configurations, which corresponds to all other possible numbers *m*, *n*, *q*. In the MVEC model, such stable electronic configurations are considered as valence bonds. The maximum chemical bonding potentials are half-filled configurations, since they have the largest number of half-space (per atom) cells in the phase space. In this case, valence *s*-configurations having only two cells of the phase space and the highest energy in the free atom can make a small contribution to the interatomic coupling. The *f*-symmetry state, on the contrary, has very low energy, strongly bound to the nucleus of this particular atom, and shielded by electrons of higher states. Except in some special cases, *f*-electrons do not participate directly in chemical bonding, but the $d \rightarrow f$ transitions may affect the distribution of *d*-electrons. Thus, p^3 and d^5 configurations make the greatest contribution to chemical bonding.

As opposed to the stable configurations discussed above, the intermediate spectrum configurations are considered unstable. They are in a state of continuous exchange with the collectivized electrons and, in fact, are slightly different from their energy. These configurations do not contribute to the interatomic coupling, but contribute to the electronic heat capacity, Paulian paramagnetism and other electronic processes associated with the free energy of the Fermi surface. The statistical weight of stable atomic configurations (SWSAC) is defined as the ratio of the number of electron configurations *m*, *n*, *q* = 0, 1, 2, 3, 5, 6, 7, 10, 14 (depending on the orbital quantum number, i. e. the type of symmetry wave function *s*, *p*, *d*, *f*) to the number of possible configurations in equivalent atomic spheres.

With the formation of solids from isolated atoms, external, far from stable, subshells are not stored, but undergo significant changes. Thus, the s^2p^2 state characteristic of an individual atom is easily transformed by the $s \rightarrow p$ excitation into

the condensed phase sp^3 configuration; the $s \rightarrow p$ transitions are easier to implement if the predicted spectra of sp, sp^2, sp^3, ..., s^2p^6 are dominated by more energetically stable configurations. Atoms with the outer subshells of s^2p, s^2p^2 seek to obtain the quasistable electronic configuration of sp^3 through $s \rightarrow p$ junctions and electron exchange.

Elements in which isolated atoms have a state of s^2p^3 (nitrogen, phosphorus) due to $s \rightarrow p$ transitions in the $s^2p^3 \rightarrow sp^4 \rightarrow sp^3 + p$ scheme, acquire configuration either sp^3 (with a weakly bound electron), or s^2p^6 extra electrons. If atoms have the s^2p^4, s^2p^5 configuration, then they are most likely to form the s^2p^6 configuration due to additional electrons. The consequence of the stability of the s^2p^6 configuration is the monoatomic of inert gases.

If the number of localized *d*-electrons per atom is greater than zero or equal to five, then there are stable configurations d^0 and d^5 in the transition metal, when the number of localized *d*-electrons is from 5 to 10, the transition metals are characterized by the formation of stable d^5 and d^{10} configurations.

Nowadays the solid-state configuration model postulate of the striving to create stable electronic configurations by atoms involved in chemical bonding, as a special physical-chemical factor that affects the stability of the phases, is soundly justified and is an integral part of the fundamental quantum-statistical substances. This postulate made it possible to explain the abnormally low melting points of Eu and Yb in a number of rare earth metals.

G. V. Samsonov showed, in a wide experimental material, a close relationship between the susceptibility of elements to electronic transformations and the peculiarities of the behavior of their physical properties in a series and group of a periodic system, in various polymorphic modifications, in various phases and alloys.

1.3. Interstitial phases

With the onset of the Iron Age, when our ancestors first succeeded in “mixing small carbon atoms with large iron atoms”, the interstitial phases began to play an important role in human history. However, the scope of application of the interstitial phases expanded significantly only in the mid-twentieth century, when these substances both in science and in production became necessary.

Moreover, at this time most of the transition metals, which are the basis of the interstitial phases, have become relatively accessible.

The following examples give an idea of the variety of materials, phenomena and processes in which the atoms introduced into the interstitials of the metal lattice play an important role [4]:

1. The formation of the interstitial phasesspace in the products of ferrous metallurgy provides an opportunity to harden the steel and obtain carbides. In addition, the interstitial phasesspace are present in steel in the form of harmful impurities, the amount of which must be minimized.

2. Refractory hard alloys used for tool manufacturing are mainly interstitial phasesspace.

3. The oxidation and diffusion processes in the solid state are related to the existence of atoms in the interstitials.

4. The emergence of the interstitial phasesspace usually occurs during the formation of solid surface coatings, for example during nitriding.

5. The occurrence of clusters of interstitial atoms in the form of micro segregations, such as dislocations, grain boundaries, and inclusions, often determine the mechanical strength or, conversely, the alloys brittleness used both at normal conditions and at low and high temperatures.

6. By nuclear irradiation of metals it is possible to create artificial interstitial phases, which can significantly expand the field of application of the interstitial phases.

7. The problem of heat-resistant materials, which are able to withstand increasingly higher temperatures, such as gas turbines, rocket engines and metallurgical furnaces, require exceptional heat-resistant properties that can only be obtained by using some of the compounds which are interstitial phasesspace.

It is difficult to clearly define the concept of " interstitial phase". Originally this term was used by Hägg G. in his classic work on the structure of carbides, nitrides, hydrides and transition metal borides. In this term, the characteristic features of the crystal lattice of the obtained material were reflected. In addition, this term implies the independent existence of a lattice of pure metal, which is the parental lattice – a matrix for various kinds of additional atoms (smaller size) that are introduced into its "interstitial cavities". This lattice can exist without them at the same time. However, in some important cases, such an interpretation of the concept of "interstitial phase" is unacceptable. In all carbides and other interstitial phases – transition metal compounds – non-metal atoms are an integral part of the material, and without them, the metal lattice has completely different properties.

The broad definition should reflect not only the geometric features of the lattice, but also the nature of the chemical bond in it. For example, the interstitial phases could be defined as substances in which chemical bonds between metal atoms play a dominant role, and non-metal atoms are so small that they are placed inside the metal lattice (in its interstitials) without causing its symmetry to be distorted or to cause slight distortion. This premonition, which implies some distortion of the lattice symmetry, is a very important "flexibility condition" of the above definition, which allows for the inclusion of more substances in the number of interstitial phases.

Hägg G. used the term "interstitial phase" in a very limited sense, applying it to substances in which "H, B, C and N atoms are located inside a simple metal lattice". Recently, the concept of "interstitial phase" has become more widely used: compounds of oxygen, silicon and some other elements have also begun to be referred to as interstitial phases.

A detailed picture of the distribution of structures between different types is shown in Fig. 1.1.

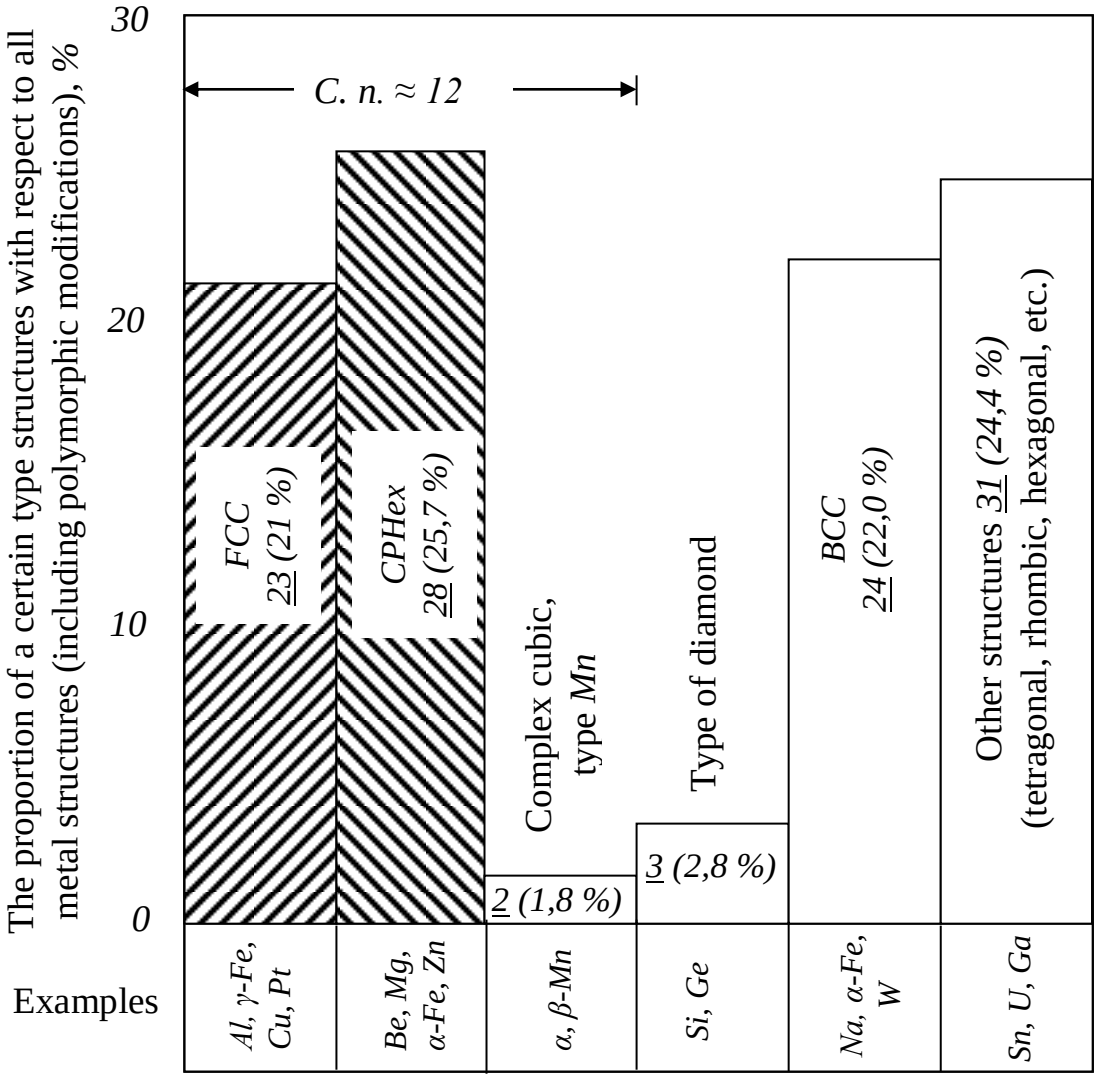


Fig. 1.1. Statistical picture of the crystalline structures of pure metals distribution (including all modifications) by types
FCC – face centered cubic structure; *BCC* – a body-centered-cubic structure; *CPHex* – aclose-packed hexagonal structure; *C. n.* – coordination number [4]

Among metals, which are the matrix of the interstitial phases, there is a strong tendency for the formation of dense packs of atoms having a coordination number of 12 or close to 12 (~ 50 %), others – a number of 8 and less. That is, 55 structures of 109 known structures of pure metals, corresponding to 75 metal elements and their polymorphic modifications. Most metals tend to form face-centered cubic (*FCC*) or close-packed hexagonal (*CPHex*) structures: the absolute majority of structures are from these 50 %, namely 23 to *FCC* (accounting for 21 %) and 28 to *CPHex* (26 %).

It should be noted that of the 18 modifications of transition metals of IV-VI groups of the periodic table of elements, only 4 (i. e. 22 %) are close-packed. Whereas all the richest metal of the 24 interstitial phasesspace – carbides and nitrides formed by these elements – have a close-packed metal lattice. I. e., the small atoms of non-metals implemented in the metal lattice cause the formation of more uniform structures of the interstitial phases. This effect of the interstitial atoms on the structure is explained mainly by the fact that they are electron donors for the metal lattice. The impact of these interstitial atoms is explained not so much by their own volume but by the filling of the orbitals of the atoms of the metal lattice.

The interstitial phases can be divided into the following classes [4]:

– interstitial solid solutions, such as carbon in austenite, oxygen in Ti, Zr;

– interstitial compounds, such as iron carbides in steels, WC, TiC, Fe_4N etc.; in general, hydrides, carbides, nitrides and borides of transition metals, some oxides and silicides;

– substances which are transitional between the two preceding classes, for example martensite in steels, rich in metal “semi–carbides”;

– interstitial temporary, or “interstitial atom flows”, which exist, for example, during the diffusion processes, the oxidation etc.;

– artificial interstitial phases that are created by irradiation.

Atoms that can be located in the interstitials of the metal lattice include:

– atoms of the non–metals H, C, N, O, B, Si, as well as (conventionally) P and S;

– atoms of the same metal from which the maternal lattice is constructed, or atoms of other metals;

– vacancies and electrons (as the atoms equivalent) can be added to 1 and 2 groups.

The inclusion of the latter in the list is a very important step, since the mathematical methods for describing their behavior in the lattice and the behavior of ordinary interstitial atoms in many respects are very similar, and phenomena such as

the formation of lattices defective in one component and deviations from stoichiometry in general are within the theory of interstitial phase.

In the above list, Si and B atoms are limiting in the sense that, in silicides and (to a lesser extent) in borides, direct Si–Si and B–B bonds become important and can be considered as transition substances from interstitial phases to true metal compounds.

There is an interesting fact: H, C, N and O – the main elements involved in the formation of the interstitial phases – at the same time are the main elements of organic chemistry (and living matter). These elements have not only small atoms sizes, but also a specific electronic structure, which on the one hand (in transition metals) causes the formation of strong bonds due to the transition of electrons to the unfinished inner shells of metal atoms and, on the other hand (in molecules of organic compounds), causes the formation and variety of complex bonds, but which are easily destroyed.

An important feature of the interstitial phases is that, like close-packed metals, they crystallize into lattices, which can be represented as packs of atomic layers alternating in a sequence …*ABABAB*… (for example in the case of Nb_2C, W_2C) or …*ABCABC*… (for example, in NbC, TiC). Non-metallic atoms are located between the metallic atomic layers, and the chemical bonds caused by them can be considered to interfere with easy slip due to the “adhesion” of the metal layers, which leads to increased hardness and brittleness.

In this regard, deviation from stoichiometry, such as the lack of carbon atoms or oxygen atoms excess, causes the formation of local deviations in the metal atoms and irregularly shaped “folds” that exert even more resistance to the sliding of the metal layers. Deviations from stoichiometry can cause an interesting side effect: they facilitate the flow of diffusion due to the appearance of larger holes and cavities; some interstitial atoms act under these conditions as a “screw shutter” that helps the movement of others. This may also be due to the formation of clusters of heterogeneous interstitial atoms, for example in the presence of C and O or B and C.

Of particular interest in this respect is WC tungsten mono-carbide and isomorphic to it MoC, MoN and others (Fig. 1.2) [4].

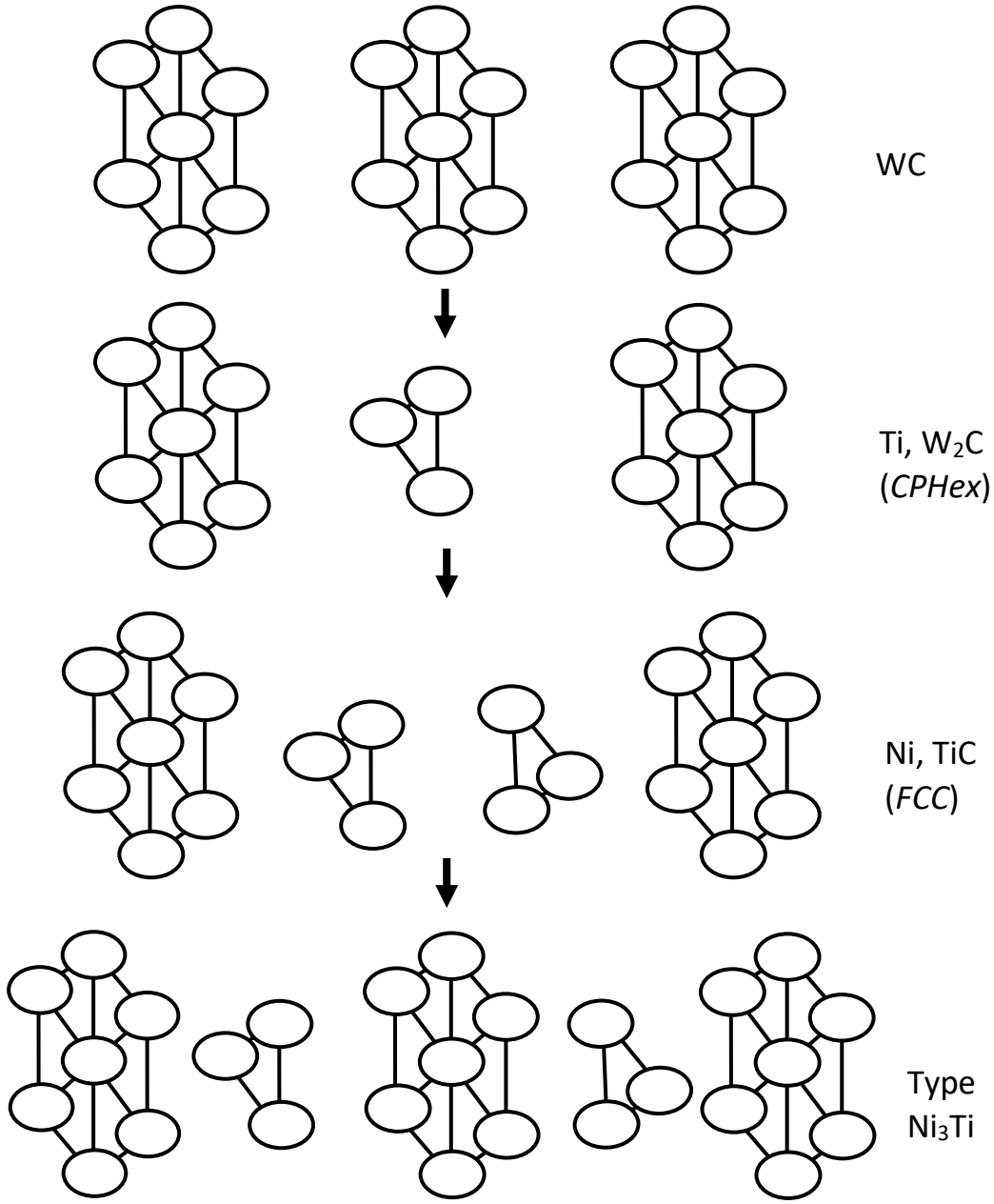


Fig. 1.2. The geometry of some structures of the interstitial phases

Their simple hexagonal structure corresponds to the packing of metal layers of type …*AAAA*…, which is not observed in pure metals; it becomes possible only because the layers of metal atoms alternate with the layers of carbon atoms. Such carbon layers in tungsten carbide can be regarded as similar to those in pure carbon,

namely in graphite, meaning that the WC structure is literally composed of hexagonal graphite and alternating carbon and tungsten layers. But tungsten carbide lacks C–C covalent bonds, and only W–C bonds exist.

In the case of borides in the lattice of the interstitial phase between the layers of metal atoms, there may be mains (one-, two- and three-dimensional) of covalently bonded boron atoms; in carbides, such carbon mains are not formed, but they are in free graphite.

Nitrides are also dominated by this interesting mixture of simple-type hexagonal packaging and close-packaging. So in the Ta–N system there are a number of compounds – $Ta_{2,5}N$, $Ta_{1,2}N$ and TaN, which (in the given order) have hexagonal packing of close-packaging type, simple type and new type, which is a mixture of close-packaging and simple packaging.

Control questions

1. How did the view of substances related to refractory change?
2. Definition and classification of refractory compounds.
3. Explain how ideas about the substance and materials of that substance have changed.
4. Explain the causes of various models of condensed matter. Give examples of such models.
5. Expand the main points of the configuration model of the substance.
6. What are the electronic configurations in the configuration model of a substance that are considered valence-forming? Explain why.
7. What characteristics of compounds refer to “interstitial phases”?
8. Explain the Hägg’s rule.
9. Explain the differences between the concepts of “interstitial phase” and “interstitial solid solution”. What compounds create transition metals with light non-metals?

10. What are the elements that make refractory compounds and what types of bond occur in them?

11. Why and how is the primary crystal lattice rearranged during the formation of refractory compounds?

2. CARBIDES

Refractory carbides of transition metals of IV-VI groups have the highest melting points and many other valuable physical and physical-chemical properties and are the most promising materials of modern high-temperature engineering.

2.1. Phase diagrams of transition metal-carbon systems

The phase diagrams of transition metals of group IV (Ti, Zr, Hf) systems with carbon are very similar to each other (Fig. 2.1). They are characterized by only one carbide phase – mono-carbide with a structure of NaCl type and a wide area of homogeneity.

All of these NaCl-phases melt congruently if they have an approximately stoichiometric composition or form eutectics with carbon at higher concentrations. And their melting points are much higher than the melting point of the corresponding transition metal.

Each of the metals in this group undergoes allotropic transformations, during which the low-temperature α-phase with a close-packed hexagonal (*CPHex*) structure is transformed into a high-temperature β-phase with a body-centered cubic (*BCC*) structure.

Phase diagrams of carbide systems of metals of group V (V, Nb, Ta) are more complex. They are characterized by the presence, in addition to mono-carbides, of sub-carbides of the M_2C type. The Nb–C and Ta–C systems are similar; they differ mainly in the width of the homogeneity region and the melting point of the mono-carbide from the V–C system. These diagrams have not been fully investigated. There are a number of questions that have not yet been fully resolved.

Even more complex are phase diagrams of VI group of metals (Cr, Mo, W) carbide systems. In addition, they are different. The Cr–C phase diagram is not at all similar to the diagrams of Mo–C and W–C systems or IV–V group carbide systems.

This is due to the fact that, in chromium carbides, metal atoms do not form close-packed structures.

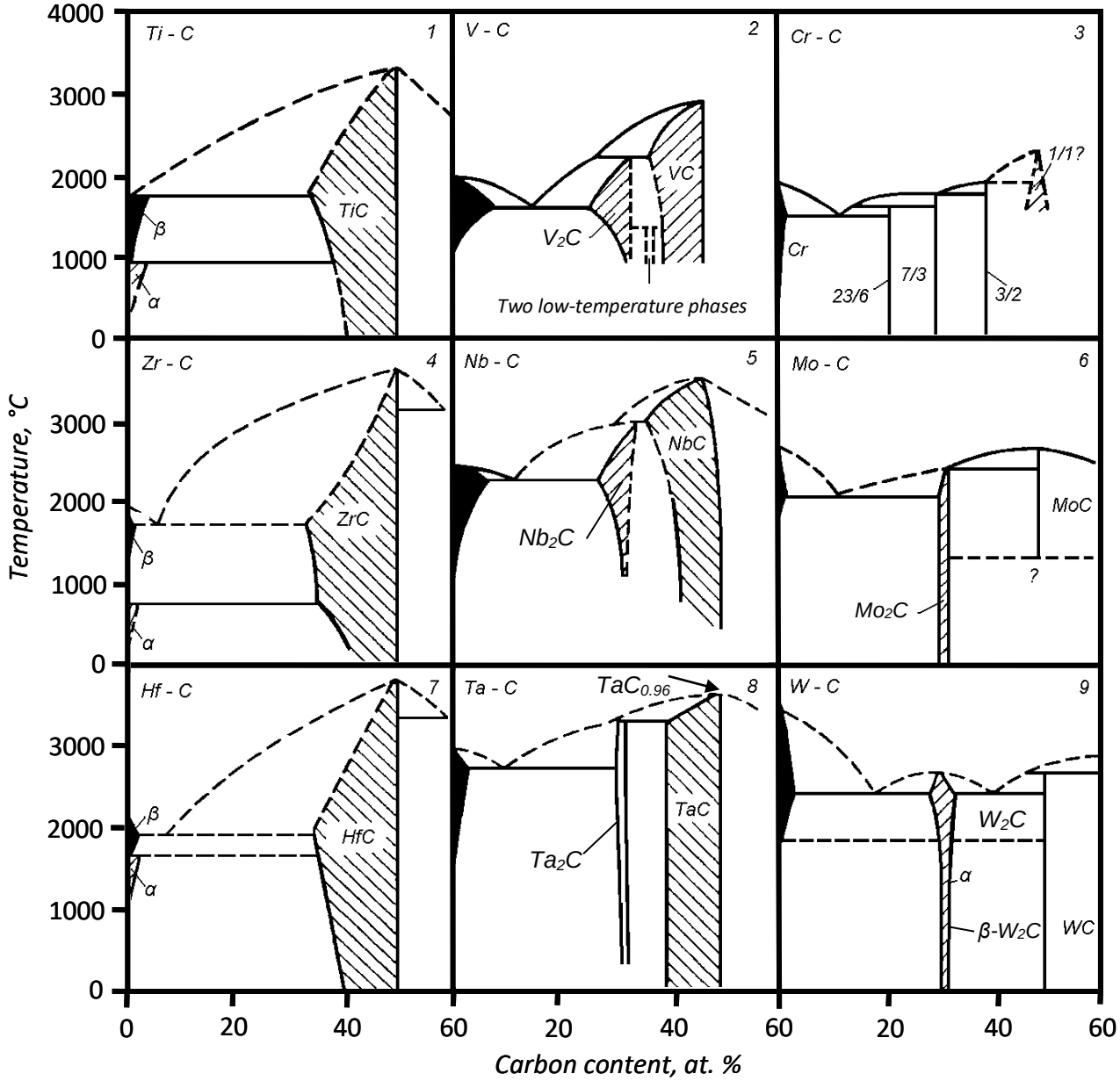


Fig. 2.1. Phase diagrams of binary metal-carbon systems [4]

It is extremely difficult to obtain phase diagrams of Mo–C and W–C systems, because some phases are only stable at very high temperatures.

The Mo–C system is very controversial. Precisely established existence of hexagonal carbide Mo_2C with packing type …*ABABAB*… with respect to MoC is now known about the existence of at least five structures [4]:

1. γ-MoC; simple hexagonal lattice, similar to WC (a = 2,898; c = 2,809 Å).

2. *CPHex* with complex unexplored substructure.

3. Hexagonal modification with a = 3,00 and c = 14,58 Å, which, however, may be a different interpretation of structure 2.

4. γ´-MoC (metastable): hexagonal lattice a = 2,932; c = 10,97 Å.

5. Another high-pressure modification of η-MoC, with a complex hexagonal close-packed structure. The occurrence of one or another modification depends largely on the method of producing the carbide and on the heat treatment, although the nature of this dependence has not yet been established.

6. MoC with a face-centered cubic lattice (α-MoC). This modification was obtained at temperatures of 1800–2500 °C and pressures of 4–7 *GPa* and it was possible to keep it at atmospheric pressure; the lattice constant was a = 4,27 Å.

The metal atoms in these carbides have the following sequences of packing:

– Mo_2C: …*ABABAB*…;

– γ-MoC: …*AAAAA*… (similar to WC) or …*ABCACBABCACB*… (packaging is close to NaCl structure …*ABCABC*…);

– γ´-MoC: …*AABBAABB*…;

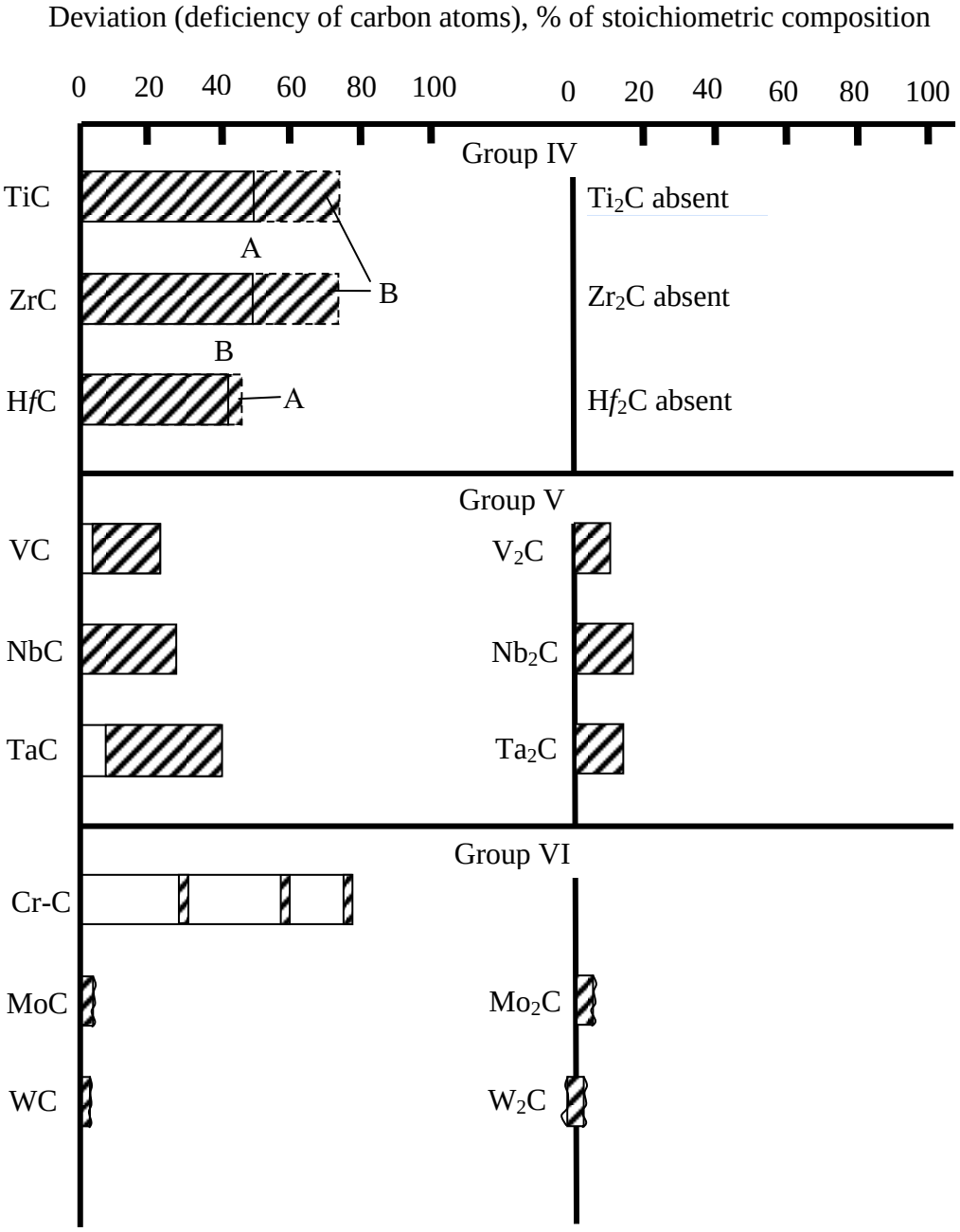
– η-MoC: …*ABABAB*…;

– α- MoC: …*ABCABCABC*….

Thus, in terms of the structure of carbides and their stability, molybdenum occupies in the second long period an interstitial position between simple stable carbides and more complex metastable carbides.

Many carbides, as well as other interstitial phases, have a tendency to deviate from stoichiometry. First of all, this concerns carbides with cubic (NaCl type) structure. Fig. 2.2 [4] represents information on the maximum deviation of the compositions of different carbides from stoichiometric. As can be seen, for cubic mono-carbides, the tendency for the deficiency of carbon atoms is mostly expected in IV group and decreases in V (but, there is a slight marked tendency to exclude a strictly stoichiometric composition 50/50 from the possible homogeneity interval). In each column, the interval of change in composition expands with increasing atomic

mass of the metal. For chromium – VI group element – the hypothetical region of solubility of carbon is suppressed and replaced by three different carbides with complex structure; this is caused by the smaller size of the metal atom.



A – according to Berezovsky; B – According to Samsonov

Fig. 2.2. Deviation from stoichiometry in carbides

For M_2C hexagonal carbides the deviation from stoichiometry is much smaller than for cubic carbides: the transition to hexagonal packing can essentially be

considered as the end result of an extraordinary increase in the ratio of vacancies to the number of carbon atoms in the mono-carbide lattice. It should be noted that in IV group, together with the absence of M_2C carbides (e. g. Ti_2C), *M*C carbides with the most defective lattice are observed; in V group, the top deviations from stoichiometry in MC carbides are much smaller, but M_2C carbides are formed. In addition, as can be seen from the phase diagram of the Ti–C (Fig. 2.2), in this system at low concentrations of carbon there is a β-Ti + TiC → α-Ti peritectoid reaction, which corresponds to the transformation into a hexagonal phase, which is a solid solution of carbon in titanium, but not carbide.

2.2. Crystal chemistry of refractory carbides

In 1931, Hägg G. formulated a number of interesting empirical rules for the construction of carbides, nitrides, borides, and hydrides crystalline structures. Although some exceptions to these rules are now known, their basic provisions have been hold true.

According to the Hägg's rule, the types of carbides, nitrides, borides, and hydrides structures of transition metals are determined by the ratio of the radii

$$r = r_x/r_{Me,}$$

where $r_x/r_{Me,}$ are the radii of the atoms of the implemented element and the transition metal, respectively.

If this ratio is less than 0,59, the metal atoms form simple structures: face-centered cubic (*FCC*), body-centered cubic (*BCC*), hexagonal close-packed (*CPHex*), and simple hexagonal (*SH*). In turn, atoms of light elements are placed in the largest interstitials of fairly simple metal structures. The intergrowth must necessarily be smaller than the atom introduced into it, otherwise the bond between the metal and non-metal atoms will not be strong enough and the structure will be unstable. However, the intergrowth cannot be much smaller than a non-metal atom, since its

implementation will cause such expansion of the original metal lattice that the metal-metal interaction will become weak and the structure will also lose its stability.

If *r* is bigger than 0,59, the transition metal compounds form complex and layered structures. Complex structures are formed to prevent the metal structure from expanding excessively with the larger non-metal atoms being introduced.

The crystalline structures of metals compounds with non-metals are fundamentally different from the structures of solid solutions of interstitial non-metals into the corresponding transition metal. The crystalline structure of metal are changed with the formation of carbide compounds, with the exception of cobalt. If the element has a *CPHex* structure, it does not form carbides with a hexagonal metallic sub-lattice (Table 1.1).

Table 1.1. Structures of metals and interstitial phases [5]

Group	Element	Metal structure		Cubic sub-lattice for metal atoms in carbides and nitrides	Hexagonal sub-lattice for metal atoms in carbides and nitrides
		BCC	*CPHex*		
IV	Ti	+	+	+	–
	Zr	+	+	+	–
	Hf	+	+	+	–
V	V	+	–	+	+
	Nb	+	–	+	+
	Ta	+	–	+	+
VI	Cr	+	–	+	+
	Mo	+	–	+	+
	W	+	–	+	+

If the element has an *CPHex* structure, it does not form a carbide with a cubic metal sub-lattice. If the element has a *BCC* structure and does not have allotropic modifications with the closest packing, then it forms compounds with hexagonal and cubic lattices of metal.

The crystalline structures of carbides can be characterized both by metal atoms and by carbon atoms. The crystalline structures can be distinguished by the arrangement of the metal atoms [5]:

1. Simple structures – *FCC*, *CPHex*, *SH* and combined, consisting of a combination of the above;

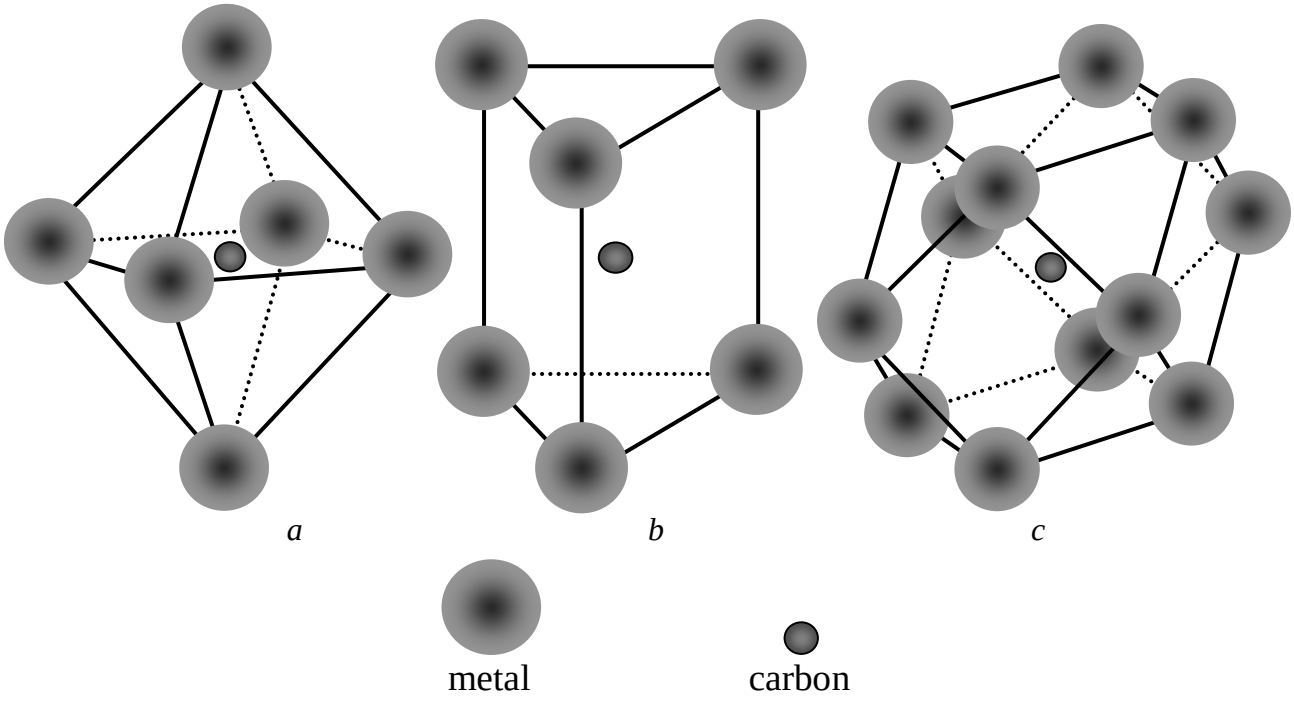
2. Complex structures – M_3C_2, M_7C_3, $M_{23}C_6$.

The arrangement of the carbon atoms of the structure can be divided into the following groups (Fig. 2.3):

1. Octahedron type – the carbon atom is located in the center of the octahedron formed by six metal atoms (for example, *FCC* carbides and *CPHex* structures).

2. Prism type – the carbon atom is at the center of a trigonal prism formed by six metal atoms (for example, carbides of a simple hexagonal group, M_3C_2, M_7C_3).

3. Dodecahedron type – the carbon atom is at the center of the dodecahedron formed by metal atoms (for example, carbides of type $M_{23}C_6$).



a – octahedron type; *b* – prism type; *c* – dodecahedron type
Fig. 2.3. The location of the carbon atom in the carbide

Carbides of many transition metals in structure and physic-chemical properties are typical interstitial phases or close to them. A distinctive feature of the structures of such phases is that non-metal atoms are placed in octahedron, trigonal-prismatic,

or tetrahedral interstices of the closest (cubic or hexagonal) packings of metal atoms. The octahedron environment is dominant.

For a general investigation of the crystalline structures of such phases, atoms can be considered as spheres. Each carbon atom is surrounded by six straight-distant metal atoms which centers form a regular octahedron around the carbon atom. For carbides, the principle of crystalline stability of the coordination lattice is formulated as a whole by Polling, which is to reduce the stability of the transition from the packing of coordination polyhedron connected by common vertices to polyhedron having common edges and common boundaries.

The packing of octahedron joined by common edges forms a NaCl-type lattice. This type of lattice is typical for most stable carbides. This element of structure, packaged in various ways, occurs in most structural types of binary and poly-component carbides. In a complete NaCl-type lattice, a metal atom is also surrounded by six carbon atoms forming an octahedron [MC$_6$]. However, the octahedrons [CM_6] and [MC$_6$] are not equivalent in structural and chemical nature. Carbides of NaCl type structure have rather wide homogeneity regions with varying degrees of filling of octahedron interstices by carbon atoms (i. e., with different number of vacancies of carbon or “empty” octahedron [$\boxed{\text{C}}M_6$]). At the same time, the metal sub-lattice (packing) within the homogeneity region of the carbide is remained complete – there are no structural vacancies of metal atoms in such packing. Thus, the octahedron [CM_6] is essentially constant, and the octahedron [MC$_6$] has a variable composition and its structural formula can be written as [MC$_{6-x}$]. The vacancies promote the formation of direct exchange M–M bonds and, as a result, the appearance of non-uniform compression stresses in the "empty" octahedra [$\boxed{\text{C}}M_6$]. Therefore, the stability of a NaCl-type structure with an increase in the number of carbon vacancies is determined by the ability of structurally constant [CM_6] octahedrons to resist these stresses.

Such stresses naturally increase with the formation of adjacent hollow octahedrons and, with the appropriate concentration of vacancies, can lead to a restructuring of the packaging system by super-structural ordering “empty” octahedron (carbon vacancies) (Fig. 2.4) or to the emergence of a new phase with a lower symmetry and other packing octahedron purposes. The limiting concentration of carbon vacancies that the packaging “holds” depends, of course, on the relationship between the strength of the *M*–C bond (in complete octahedron seeking to preserve the pack) and the *M*–*M* bond in the empty octahedron seeking to change it to obtain a closer pack of metal atoms [5].

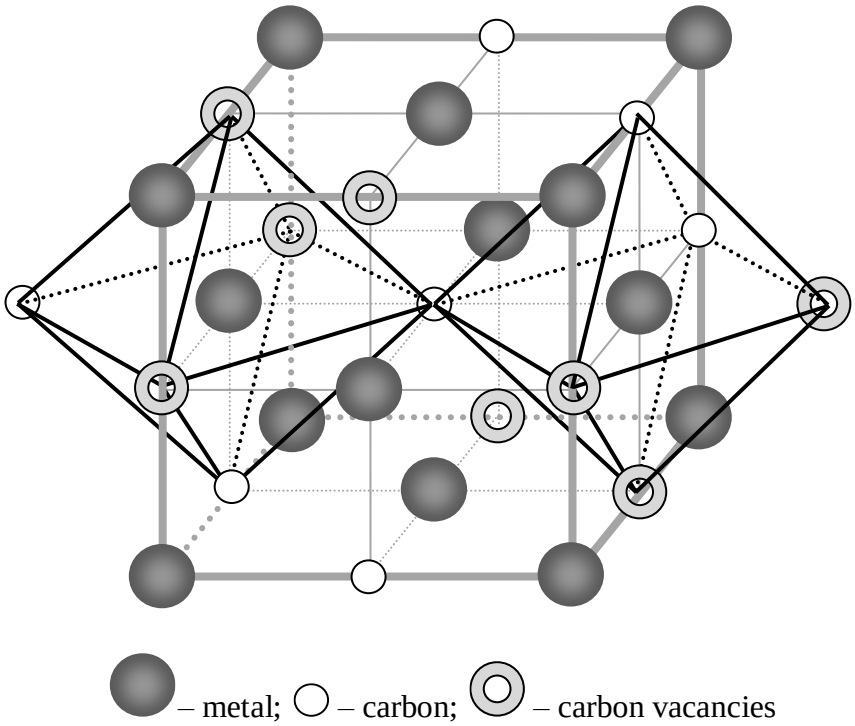


Fig. 2.4. Possible placement of three carbon vacancies in mono carbides with NaCl structure

The interaction between the metal atoms in the carbide lattice is determined by [5]:

1. The number of valence electrons is’n occupied by carbon.

2. The degree of mutual overlap of the valence orbitals in the *M*–*M* bond directions (the relative distance of the metal atoms from each other, which depends on the ratio of the radii of the metal and the carbon).

3. Stability of electronic configurations in *M*–*M* bond.

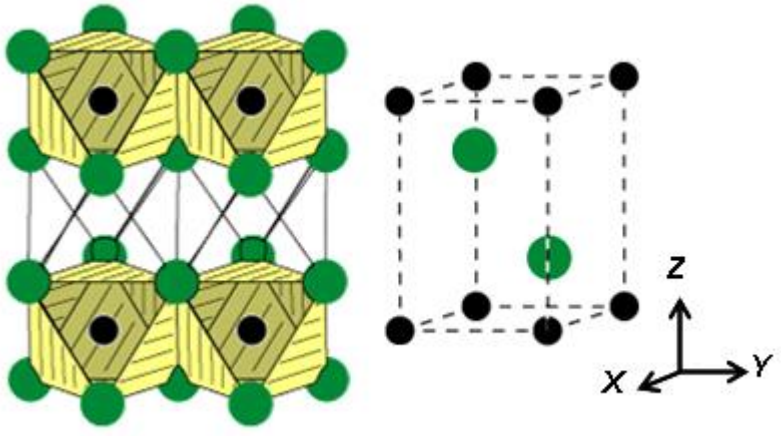
4. The degree of shielding of these bonds by carbon electrons.

For IV group metal carbides (Ti, Zr, Hf), the thermodynamic equilibrium of the number of adjacent “hollow” octahedron pairs can be large enough (more than 50 %) without lattice rearrangement.

The structure and properties of transition metal carbides are systematically and constantly changing with the change of metal position in the periodic system.

IV and V group metals form the most refractory carbides with cubic or hexagonal close-packed lattices of metal atoms. These carbides are followed by less stable VI group metal carbides, of which molybdenum and tungsten carbides still retain simple structures, but chromium carbides have more complex structures with large elementary cells.

Another important difference is that IV group carbides form only *M*C mono-carbidys (TiC, ZrC, HfC), which composition can deviate significantly from stoichiometric, while V group metals together with *M*C carbides (VC, NbC, TaC) form M_2C carbides with a hexagonal close-packed structure (Fig. 2.5). The homogeneity regions for the metals of this group are narrowed, although they are remained broad enough.



● – metal (V, Mo, Ta, W, Co); ● – carbon

Fig. 2.5. M_2C structural type [6]

The tendency for variety of forms and narrowing of the homogeneity regions is remained also for carbides of VI group metals. In this case, the sizes of the metal atoms become so small that during the formation of the carbides, either a strong curvature of the metal crystal lattice (Cr) or a change in the sequence of packing (Mo, W) occurs. However, it applies only to mono-carbides and does not extend to lower M_2C carbides. In the case of the richest carbonic chromium carbide (Cr_3C_2), the formation of direct C–C bonds and chains of carbon atoms is similar to those of non-metal atoms in borides and silicides, but much stronger. C–C bonding is also observed in the MoC compound and in the WC simple hexagonal lattice.

2.3. An overview of the basic properties of carbides

Transition metal carbides have rather peculiar properties.

The implementation of a non-metal atom into the lattice of a transition metal atom is not a simple placement of a non-metal atom in the pores of a metal lattice, but a process that co-occurs with the formation of strong chemical bonds between metal atoms and non-metal, fundamentally altering their chemical individuality and physical identity.

During the formation of transition metal carbides, there is a kind of competition between the two main processes: the *M–M* bond tends to stabilize the d^5 configuration of the metal atoms, and the *M*–C bond – to the formation of stable sp^3 configurations of the carbon atoms.

An important property of carbides is the very high hardness, which is responsible for the sp^3 configurations of the carbon atom. These compounds are one of the strongest. The micro-hardness of many binary carbides ranges from 20 *GPa* to 60 *GPa*, which corresponds to the micro-hardness of Al_2O_3 and diamond, that is why carbides are used as a cutting tool and to obtain wear-resistant surfaces of parts. Carbides of transition metals of IV*A* subgroup have the highest hardness as a

consequence of maximal stabilization of sp^3 configurations by non-localized metal electrons. The hardness of the VI*A* subgroup carbides is the lowest due to the smallest stabilization and possibly destabilization of the sp^3 configuration of the carbon atoms.

Another outstanding feature of transition metal carbides is the very high melting points. Some carbides melt or decompose at temperatures above 3000 °C. Carbide melting temperatures are generally higher than in the corresponding transition metals.

The melting point of refractory carbides mainly determines the presence of non-localized loosening electrons. With the transition from TiC to ZrC and HfC, the melting point increases (3150, 3530, 3890 ºC, respectively) with increasing localization of valence electrons of metal atoms. During the formation of carbides of V group metals, the atoms of which are less powerful donors than the IV group metal atoms, due to some predominance of the delocalization of the sp^3 configurations of the carbon atoms over the localization of the valence electrons of the metal atoms, the melting point are decreased (2810, 3480, 3880 ºC for VC, NbC, TaC respectively). In VI group metal carbides, the reduction of SWSAC d^5 becomes even more significant, which leads to a decrease in melting point (chromium carbides – 1550–1900 ºC; Mo_2C – 2418 ºC; W_2C – 2700 ºC). The decrease in the proportion of *M*–C in the carbides of V group metals compared to IV group metal carbides is evidenced by the fact that the increase in the melting point of these carbides compared to the melting temperature of the corresponding metal is only about 1000 °C instead of 1500 °C. Further reduction of the *M*–C bond fraction in the carbides of the VIA subgroup metals causes that the melting temperatures of these carbides are even lower than the melting temperatures of the corresponding metals.

Probably the most important property of this group of carbides is the deficiency of their structure. Ideal stoichiometry in these phases is usually not observed, they are more characteristic deviation from stoichiometry. These phases exist in a wide range of structures, with significant concentrations of vacancies (up to 50 at. particles, %) possible in the non-metallic sub-lattices, while the vacancy

concentration in the metallic sub-lattices is much lower. In some cases, even with stoichiometric composition, there may be noticeable vacancies concentrations (some at. particles, %) in both sub-lattices. It was possible to establish that if a considerable part of non-metallic positions is vacant, then their tendency to form a long-range order is observed. This dependence is observed in almost all sub-carbides and some mono-carbides. The presence of large concentrations of vacancies, whether or not ordered, significantly influences the properties of materials such as thermodynamic, mechanical, electrical and magnetic. Differences in production technologies can be the cause of different defects and, as a consequence, different properties of carbides.

The crystalline structures of carbides can be regarded as the geometric arrangement of implemented atoms and vacancies in a relatively simple lattice of metal atoms, or as the geometric arrangement of coordination polyhedron based on the octahedral environment of carbon atoms by metal atoms.

Carbide structures are complicated by the increasing in the statistical weight of stable *d*-configurations of metal atoms and decreasing of their atomic radius, and their crystal-chemical stabilityare decreased. This can be observed in the reduction of the heat formation and melting temperatures of the carbide phases and the predominantly incoherent melting nature. At the sufficiently high statistical weight of stable configurations of localized *d*-electrons in transition metals, the formation of coordination lattices of carbide phases becomes impossible at all.

Transition metals with more than five *d* electrons are characterized by the presence of stable electronic configurations of the d^5 and d^{10} types. As the number of d^5 electrons of the SWSAC of the d^5-type configurations localized on the *M–M* bonds are increased and the SWSAC of the sp^3 configurations are decreased, the statistical weight of the d^{10}-type configurations localized on the ionic frames of the metal atoms are increased.

Transition metal carbides are chemically stable at room temperature and weakly corrode only in high concentrated acids. The exception to this general rule is VC, which is slowly oxidized in air at room temperature. At high temperatures, carbides are easily oxidized to oxides. The chemical activity and thermodynamic

properties of these compounds depend on the relative content of non-metal and metal.

Carbides of this class have remarkable plastic properties at elevated temperatures. They are characterized by high rates of the Young's modulus, $28 \cdot 10^{10}$–$65 \cdot 10^{10}$ *Pa,* while for most transition metals, the Young's modulus is $14 \cdot 10^{10}$–$30 \cdot 10^{10}$ *Pa*. At room temperature, carbides are brittle materials, but at high temperatures (about 1000 °C) they come into a plastic state, and at temperatures above 1000 °C they deform plastically like *CPHex* metals. At temperatures above the transition temperature, carbides are known as the strongest materials.

Refractory carbides have electrical, magnetic and optical properties typical to transition metals. Most of these parameters are not very different from the corresponding characteristics of the transition metals. The electrical and magnetic properties of carbides are extremely sensitive to structural defects, especially to the presence of vacancies in metallic and non-metallic sub-lattice. Probably, due to the large concentrations of vacancies, the temperature dependences of the electrical and thermal conductivity of the carbides differ significantly from the corresponding characteristics of the transition metals. The resistance of the carbides is poorly dependent or does not depend on temperature at all, and this property is widely used.

These compounds are characterized by a complex combination of covalent and metal bonds that are realized in localized metal-metal and metal-non-metal interactions. In addition to these two types of bonding, the carbides also bond with the ionic type, but to a very small extent. For metal-non-metal bonds, the octahedron arrangement of the carbon atom is preferred by the metal atoms. The presence of a non-metal atom in this octahedron helps to strengthen the metal-to-metal bond.

Control questions

1. What are the compounds of transition metals of IV–VI groups with carbon?
2. What is the structural type of crystalline lattices of IV–VI transition metal mono-carbides?

3. What coordination polyhedrons are formed in IV–VI transition metal monocarbides?

4. Which structural polyhedrons are structurally variable and which are structurally stable?

5. In the cavities of what shape are non-metal atoms in the interstitial phases?

6. What are the requirements for the size of cavities to which a non-metal atom is implemented?

7. What structural type of crystalline lattice is formed when non-metal atoms fill all octahedron cavities of a face-centered cubic lattice?

8. What are the areas of homogeneity?

9. What factors influence the preservation of the crystalline structure of the interstitial phase in the homogeneity range?

10. Give a classification of crystalline structures of transition metal carbides of IV–VI groups by the arrangement of carbon atoms and metal.

3. NITRIDES

The nitrides of the transition metals of IV–VI groups are characterized by high hardness, but now the specific electrical properties of these materials are of great interest and are increasingly used in integrated circuits. Nitrides are also superconductors, which determine the potential scope of their application.

The transition metal nitrides in many respects are very close to carbides in structure and properties (in the parent group metals, for example, both carbides and nitrides have a metallic nature, high melting points, high hardness) and in practice. The formation patterns of nitrides and carbides within the periodic table of elements and their stability are quite similar. However, there are important differences that are significantly dependent on the difference between the valence of nitrogen and carbon. Since the nitrogen atom is trivalent and the carbon atom is tetravalent, the bond strength between the metal atom and the non-metal atom in the nitrides is lower. The difference in atomic size in nitrogen and carbon is relatively small.

The fact that the nitrogen atom located in the interstitial is relatively small is also indicated by the close structural bond of the nitrides with the original solid solution. The Hägg's rule for nitrides is well-executed.

In terms of thermodynamics, another distinction between nitrides and carbides is inextricably linked to the elasticity of the nitrogen vapor itself, which in the case of nitrides with high nitrogen content tends to stand out in the free state (just as stable graphite is formed in carbides). This results in the formation near the dislocations, grain boundaries and in the cavities of isolated volumes of gaseous nitrogen, which is under high pressure first in the atomic and then in the molecular state. When free nitrogen is released to the free surface, an adsorbed layer is formed.

3.1. Phase diagrams of the transition metal-nitrogen systems

The information about phase diagrams of transition metal nitrides is very scanty, often unreliable and controversial (Fig. 3.1). The main difficulties in their study are due to

the fact that the stability of the intermediate phases, phase boundaries and lattice parameters depend on the methods of preparation. Depending on the preparation of TiN and ZrN mono-nitrides, these nitrides may have a defective sublattice or titanium and zirconium (Ti_xN, Zr_xN), or nitrogen sublattice (TiN_x, ZrN_x).

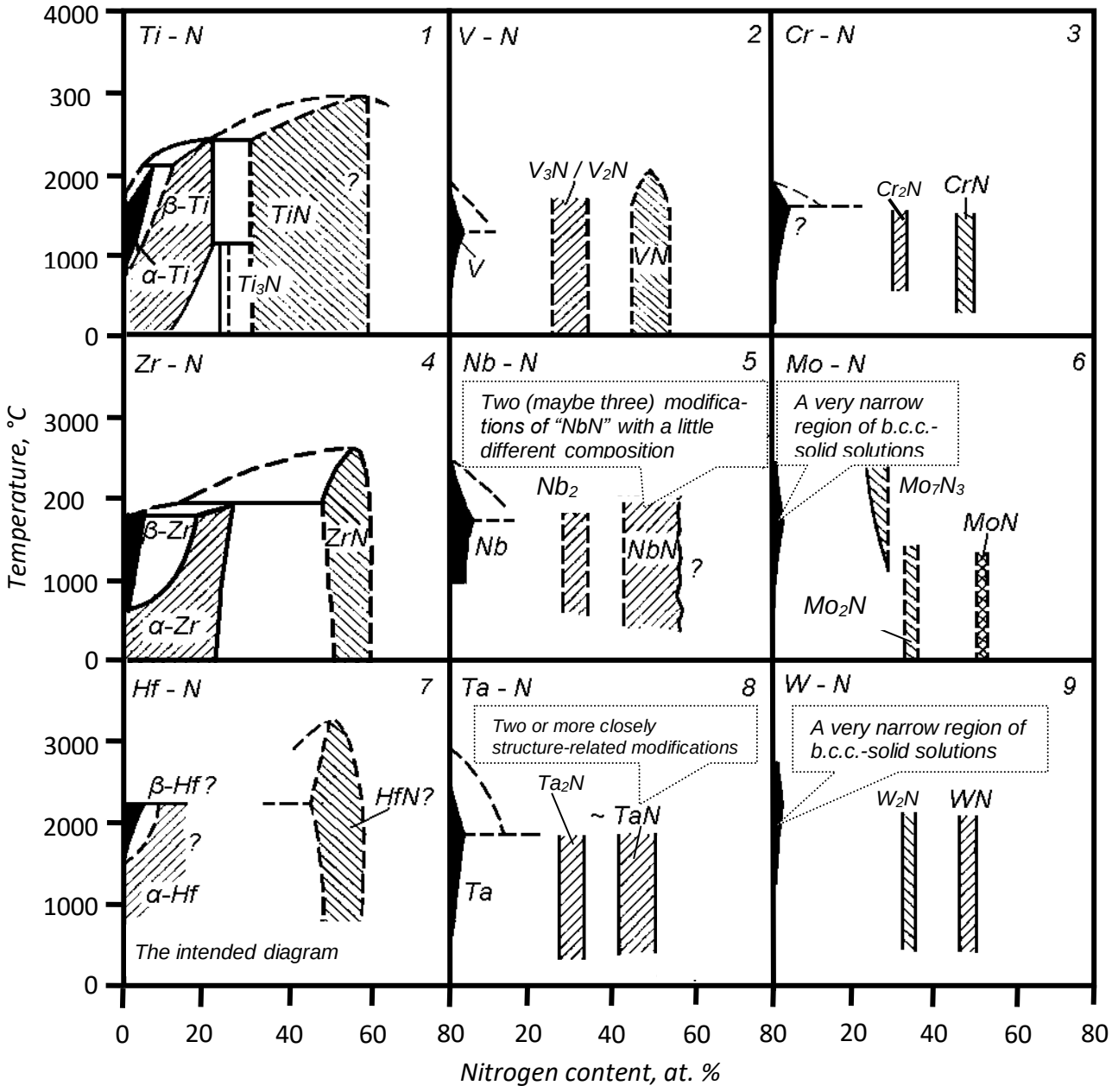


Fig. 3.1. Phase diagrams of the binary systems metal–nitrogen [4]

The crystal structures of thin nitride films also often differ from the structures of massive specimens.

Another problem arising from the study of nitride phase diagrams is the high rates of nitrogen extraction from nitrides and the difficulty of precise chemical determination of nitrogen and impurities. The influence of impurities such as oxygen is difficult to establish. Oxygen forms solid solutions with nitrides and, in addition, oxides. It is therefore very difficult to determine how much oxygen is dissolved in the nitride.

Nitrides of IV group metals. IV group metals have the ability to dissolve a large amount of nitrogen with the formation of an α-solid solution having a hexagonal lattice; due to the stabilizing action of nitrogen, α-modification is resistant to very high temperatures.

The composition of the metal nitrides of this group Ti, Zr, Hf is in the range of 30–50 *at.* % of nitrogen. The chart data has not been sufficiently studied. All nitrides have wide homogeneity ranges: TiN at a temperature of 1400 ºC has a composition from $TiN_{0,6}$ to almost $TiN_{1.0}$, and obtained at low temperatures captures the compositions of $TiN_{1,16}$ (Fig. 3.2).

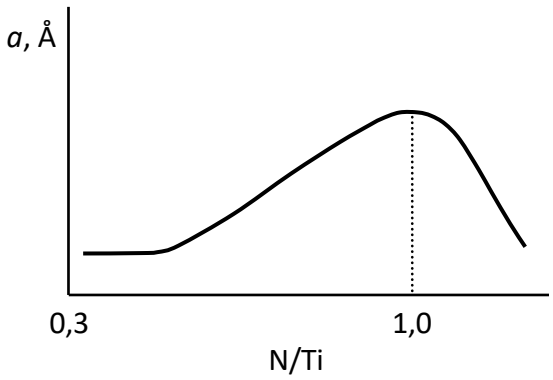


Fig. 3.2. The dependence of the lattice parameter *a*
on the TiN composition [7]

In the case of non-stoichiometric compositions, the nitrogen sublattice is defective, except stoichiometric compositions is titanium niteide. However, even stoichiometric TiN is characterized by a high concentration of vacancy positions in both (metal and non-metal) sublattices.

The existence of two phases – TiN and ε-Ti_2N – has been reliably established in the Ti–N system.

The Zr–N system has been reliably established for the existence of only one intermediate phase – ZrN_x. The ZrN_x lattice parameter irregularly changes with a change in composition. Due to the sub-stoichiometric composition, the lattice expands slightly when nitrogen is extracted from it. The reason for this is not clear.

In the Hf – N system, there is only one intermediate phase – HfN_x, which has a homogeneity range from $HfN_{0,74}$ to $HfN_{1,13}$. The upper boundary of the homogeneity range depends on the nitriding pressure and temperature. Changing the lattice parameter from composition (Fig. 3.3) shows that the Hafnium's sublattice is defective when the N/Hf ratio is higher than one. Thus, the non-stoichiometric composition revealed the same anomaly as in the case of ZrN.

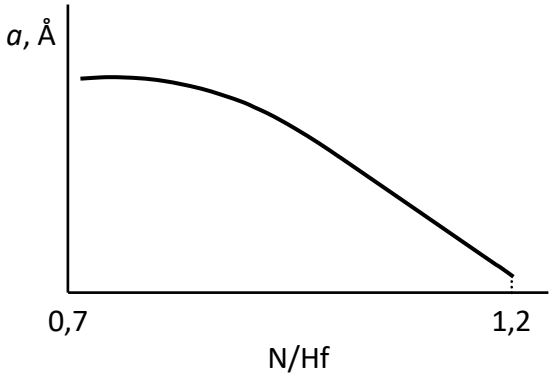


Fig. 3.3. The dependence of the lattice parameter *a* on the HfN composition [7]

The temperatures of peritectic reactions in all systems are much lower than the melting point of pure metal. As the nitrogen concentration increases, the hexagonal structure is transformed into a close-packed *BCC* according to the scheme α-(Ti, N) → TiN, α-(Zr, N) → ZrN, α-(Hf, N) → HfN.

Nitrides of V group metals. Phase ratios in V group nitride systems of metals are better studied than in the case of IV group nitrides.

There are two intermediate phases in the V–N system: a hexagonal β-phase of approximately V_2N composition and a VN mono-nitride, or δ-phase. Mono-nitride, which is highly saturated with nitrogen, has a composition $VN_{1,0}$; a compositions of

mono-nitride, which is extremely saturated with vanadium are from $VN_{0,74}$ to $VN_{0,71}$. The boundaries of the domain of β-phase homogeneity are less defined. β-V_2N has a hexagonal structure of Fe_2N type with lattice parameters *a* = 4,910 Å and *c* = 4,54 Å for the composition rich in nitrogen.

The phase diagram of the Nb–N system is very complex, and it is difficult to set it experimentally. The phase relations in this system are also interesting because there are a large number of related types of structures in this system: β-Nb_2N (hexagonal), γ-NbN_x (tetragonal), δ -NbN_x (cubic), δ′-NbN_x (hexagonal), ε-NbN.

The lattice parameters of the hexagonal β-phase change abnormally in the case of changing the content of nitrogen in the $NbN_{0.40}$–$NbN_{0.50}$ composition. The a lattice parameter is independent of composition, and the parameter c increases rapidly with the transition from $NbN_{0,48}$ to $NbN_{0,50}$, but remains almost unchanged in the composition of $NbN_{0,40}$–$NbN_{0,48}$.

γ-NbN has a curved structure of NaCl. With increassng in temperature and nitrogen concentration, the *c*/*a* ratio of the tetragonal cell approaches one, so it is likely that at temperatures higher than 1400 ºC γ- and δ-NbN represent a single phase.

Kinetics analysis of the interaction of Ta and N in the temperature range from 800 °C to 1300 °C revealed that depending on the pressure, temperature and time of interaction formed a complex series of phases from the original solid solution of nitrogen in tantalum to true nitrides. These series includes such phases as $Ta_{20}N$, Ta_2N, $Ta_{1,25\text{-}1,11}N$ and TaN. The $Ta_{20}N$ phase is essentially a slightly curved solid solution having a *BCC* superstructure and arising in the regions of the inter-granular boundaries. The occurrence of such phases at grain boundaries, which are, probably, metastable, are characterized by a high content of the metal component and differ in structure from the matrix – an important effect typical for the process of nitrogenization of refractory metals in general.

Niobium and tantalum have atoms larger than IV group metals and the transformation of the hexagonal packing into cubic packs is not practically realized; the lattice remains hexagonal: NbN and TaN compounds (nitrogen defective)

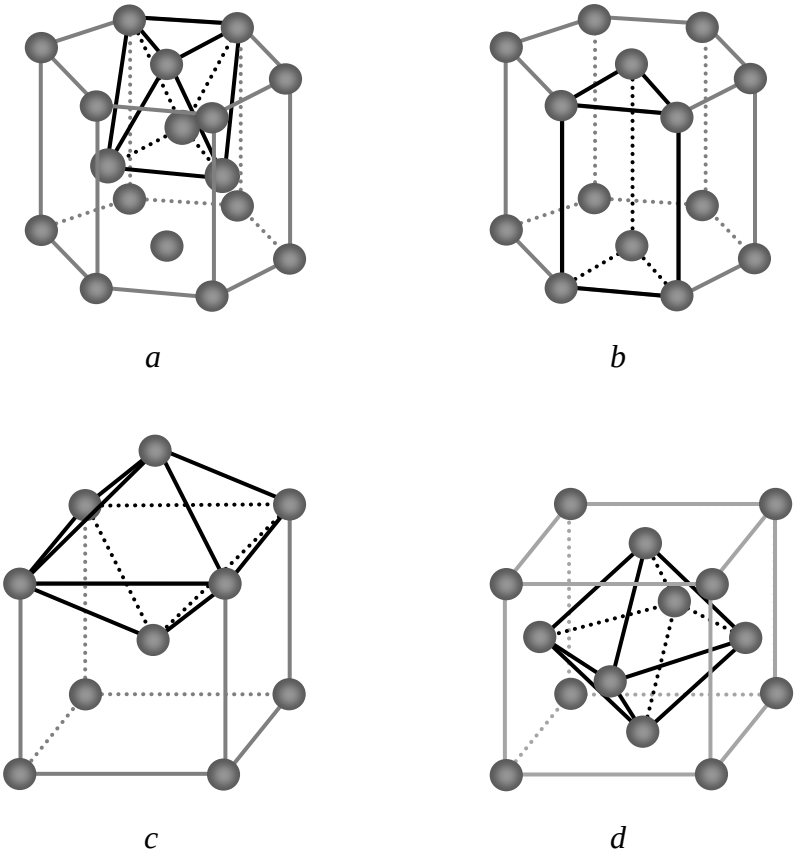
crystallize into a simple hexagonal WC-type structure. Thus, this type of structure moves from VI group carbides to V group nitrides.

Nitrides of VI group metals. There is a lack of information about the nitrides of metals in this group. This is due, firstly, to the fact that VI group metal nitrides are not chemically stable, and secondly, these compounds cannot be considered refractory since they are rapidly dissociated at high temperatures into N_2 and pure metal. Their chemical instability seems to be related to the filling of the anti-bonding electronic states. The stability of VI group nitrides decreases from Cr to Mo and further to W. Thus, tungsten does not form stable nitride in nitrogen at any temperature and only reacts poorly enough with ammonia at 600–800 ºC.

Chromium is characterized by the conversion of hexagonal nitride into a cubic $Cr_2N \rightarrow CrN$ scheme. In molybdenum and tungsten, on the contrary, that is, Mo_2N and W_2N have a close-packed cubic structure, and MoN and WN are hexagonal but simple and not close-packed.

3.2. Crystal chemistry of refractory nitrides

The crystalline structures of transition metal compounds with nitrogen can be characterized as the most dense (or close to them) packing of metal atoms, with small non-metal atoms implemented into the interstices. Most structures do not exhibit noticeable localized nitrogen-nitrogen interactions that are characteristic of organic compounds. Important characteristics of nitrides are the metal-to-metal interaction and the interstitial geometry. The nitrogen atom is usually located in the octahedral interstices or in the centers of trigonal prisms (Fig. 3.4). The implemented non-metal atom and the nearest metal atoms form a structural unit – the coordination polyhedron. If the entire structure of a compound is constructed from such units, it can be considered either as a structure of metal with occupied interstices, or as a structure constructed mainly of coordination polyhedron.



a – CPHex; b – simple hexagonal; *c – BCC; d – FCC*

Fig. 3.4. Types of interstices in structures of nitrides

Each of the offered types of description has its advantages. The structure of metal with occupied interstices is often easier to imagine, moreover, it is more familiar. The metal atoms in the nitrides often form *FCC*, *CPHex* or a simple hexagonal structure.

The filling of all octahedral interstices in the *FCC* lattice leads to the formation of a NaCl type structure (Fig. 3.5). The metal substructure can also be described as a sequential arrangement of close-packed layers of metal atoms. The alternation of layers in the usual designation is marked: …*ABCABC*… for *FCC*; …*ABABAB*… for the *CPHex*; …*AAA*… for simple hexagonal.

The main advantage of the coordination polyhedron model is that it describes complex crystalline structures in which the transition element atoms no more occupy close-packed (or close to them) positions, but in which there are still well-defined coordination polyhedron.

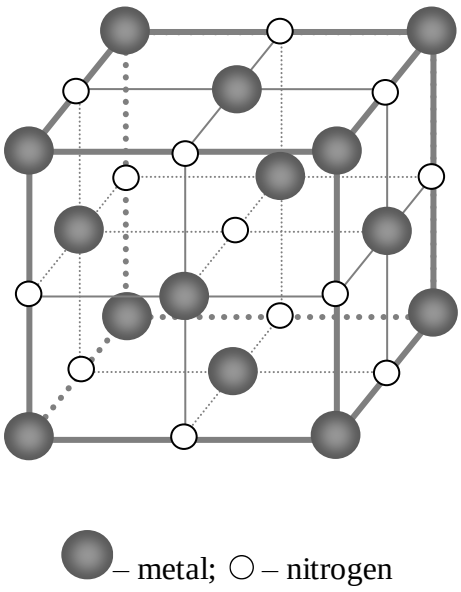


Fig. 3.5. Structure of type-NaCl

For nitrides of metals of the first large period (Ti, V, Cr) is characterized by octahedral coordination of metal atoms, for nitrides of metals of the second and third large periods (Nb, Mo, Ta, W) is characterized by prismatic coordination. In this case, there are structures with a complex sequence of stacking atomic layers, in which metal atoms can occupy the positions of three crystallographic non-equivalent types. The crystalline structures of nitrides, as well as carbides in the root, differ from the structures of interstitial solid solutions of nitrogen (carbon) into the corresponding structure of the transition metal. The crystalline structure of the metal changes during to formation of nitride compounds. If the element has a *CPHex* structure, it does not form a nitride with a hexagonal metal sublattice. If the element has a *BCC* structure, it does not form nitrides with a cubic metal lining. If the element has a *BCC* structure and does not have allotropic transformations with the densest packing, it forms nitrides with hexagonal and cubic metal sublattice. The crystalline structures of nitrides are not only determined by the component size ratio,

but also depend on the stabilization effect of a given coordination polyhedron by the implemented component and the metal-to-metal interaction. There are two types of interstices in the *BCC* structure: larger tetrahedral and smaller curved octahedral. Due to the implemented nitrogen atom is difficult to place in these positions and due to the octahedral positions are nonmetal atoms, it is obviously preferred that the metal atoms be rearranged into the *CPHex* and *FCC* structure to provide large octahedral interstitials. The limited solubility of nitrogen in many metals of IV–VI groups is related to the small size of the curved octahedron in the *BCC* structure.

Mononitrides of a number of transition metals often crystallize into a NaCl-like structure. The statistical filling of the interstices in the *CPHex* lattice is characteristic of sub-nitrides (M_2N). Filling of the trigonal prisms in a simple hexagonal structure leads to the appearance of a WC type structure (Fig. 3.6).

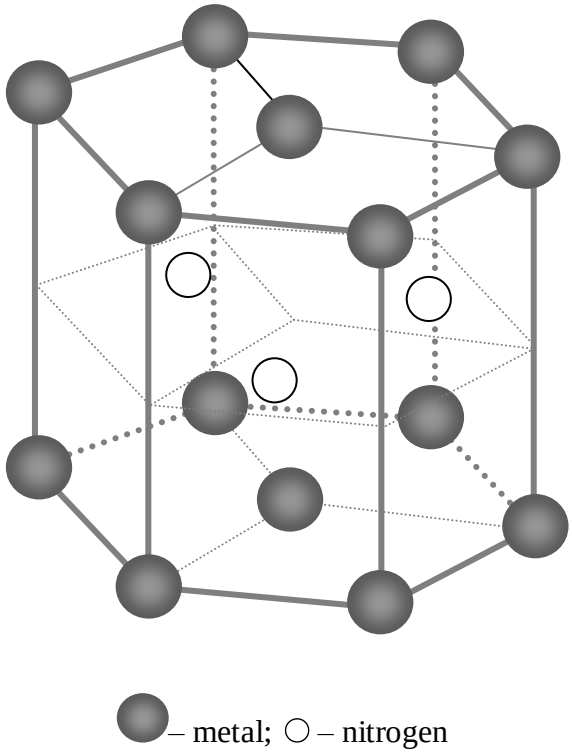


Fig. 3.6. WC type structure

While in M_2N nitrides the homogeneity range corresponds, as a rule, to a lattice defective in nitrogen, in mono-nitrides an excess of both metal atoms and nitrogen atoms can be observed.

A new phenomenon in the evolution of nitrides during the transition from IV group to V and VI groups of the periodic system is the appearance of tungsten dinitride. This compound has the highest nitrogen content. The WN_2 nitride has a rhombohedral structure with a three-layer packing of hexagonal layers spaced at a fairly large distance (5,47 Å). Nitrogen atoms are located in the centers of the tetrahedrons that form tungsten atoms and cause significant lattice distortion.

Some of these structures can already be compared with those of transition metal borides.

As mentioned above, transition metal nitrides having a cubic and hexagonal close-packed structure are very inclined to defective lattices (Fig. 3.7). The significant defect in the *FCC* structure characterized for IV group metal nitrides in V group metals is decreased. For the latter, this defect is partially transferred to lower nitrides (M_2N type), apart from mono-nitrides of IV group, in which the deviation from the equiatomic state in the direction of nitrogen deficiency begins, and at the same time their structure is complicated. It has been observed that, unlike carbides, mono-nitrides of metals of the IV and V groups can dissolve some amount of excess nitrogen, although the solubility ranges are poorly studied.

In the wide homogeneity range of TiN, which reach 30–50 *at.* % N, the nature of the chemical bond changes from metallic to ionic. This is evidenced by the nonlinearity of the curves of the dependence of the electrical resistance on the Ti/N ratio in the case of TiN_{1-x}; whereas for TiC_{1-x} these dependences are linear. In the case of a stoichiometric composition, the temperature dependence of the resistance is linear, but with an increase in the concentration of vacancies there is an anomaly: the curves show a maximum, the position of which depends on the content of nitrogen. This effect is attributed to the change in the ratio of the contributions of the metallic and ionic bonds to the nature of the chemical bond as the degree of defect of the lattice changes. If the chemical bond in TiC is still substantially metallic, TiN is already of a more ionic type.

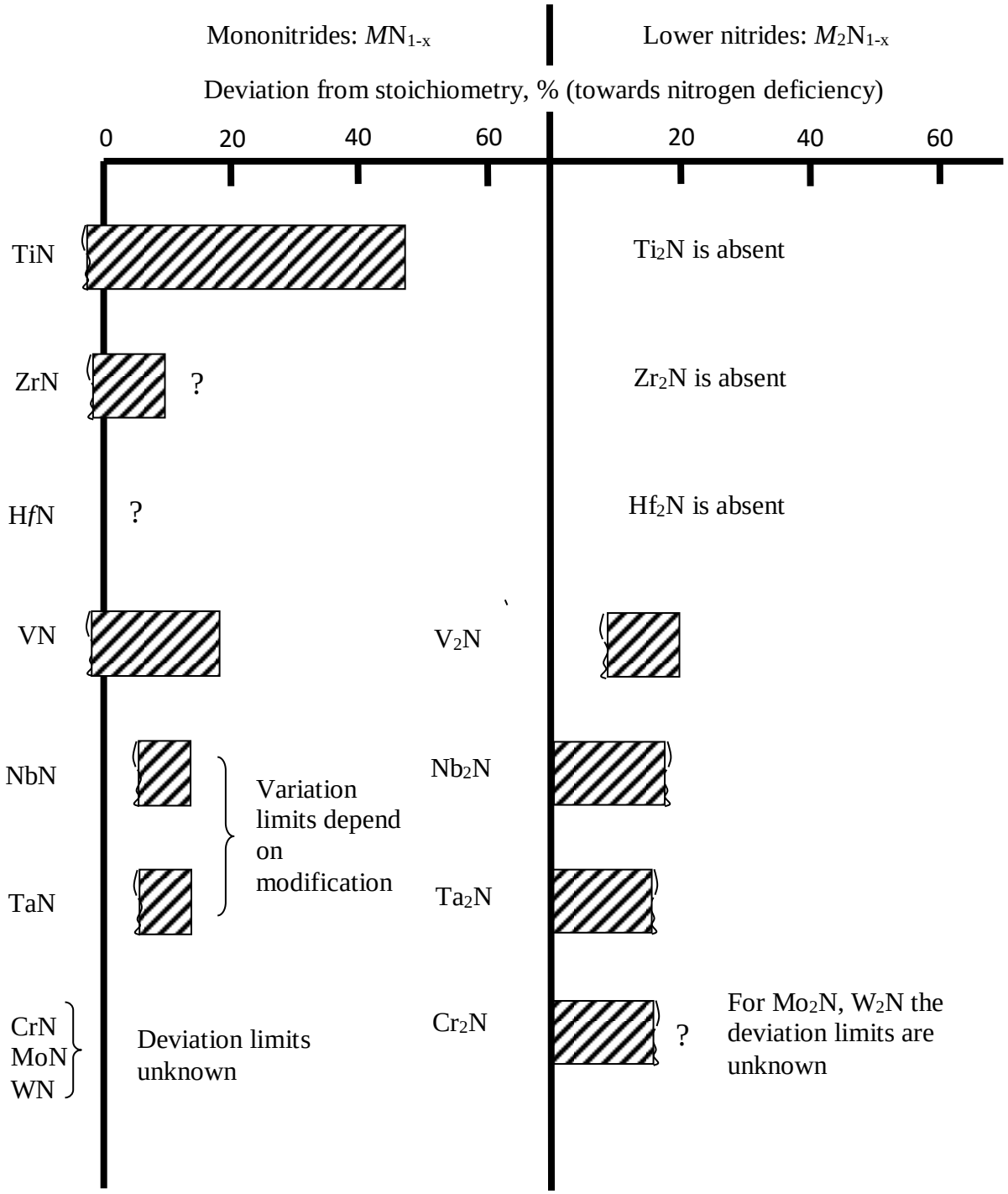


Fig. 3.7. Homogeneity range of transition metal nitrides [4]

3.3. An overview of the nitrides basic properties

The main difference between carbon and nitrogen atoms (one additional electron) is also evident in their transition metal compounds. Due to the presence of an additional electron in the nitrogen atom, the basic properties of the fifth group metal nitrides are closer in properties to the carbides of the sixth group metals than to the carbides of the fifth group metals.

The transition metal nitrides in many respects are very close to carbides. They are close to carbides in structure and properties (in the metals of the initial groups, for example, both are metallic in nature, high melting points, high hardness) and in practice. However, there are also important differences that are more related to the difference between the valence of nitrogen and carbon. Because the nitrogen atom is trivalent and the carbon atom is tetravalent, the bond strength between metal and non-metal atoms in the nitrides is much lower.

In terms of thermodynamics, another difference between nitrides and carbides is due to the elasticity of the nitrogen pair itself. In the case of nitrides with a high content of nitrogen, it tends to stand out in the free state. This leads to the formation of isolated volumes of gaseous nitrogen near dislocations, grain boundaries, and in the cavities, which are initially under high atomic pressure and then in a molecular state.

Nitrides have low resistance to oxidation, which can be partly explained by the defective nature of their structure and deviation from stoichiometry, which facilitates the dissolution of oxygen in vacancies in the lattice.

The scope of nitrides application is more limited than that of carbides.

Control questions

1. What are the compounds of the transition metals of IV–VI groups with nitrogen?

2. What structural types of crystalline lattices have IV–VI transition metal mono-nitrides?

3. What structural type of crystalline lattice are sub-nitrides of IV–VI transition metals?

4. In the cavities of which form are the nitrogen atoms in the transition metal nitrides of IV–VI groups?

5. What are the requirements for the size of cavities in which the nitrogen atoms in the nitrides of transition metals of IV–VI groups are located?

6. What do carbides and nitrides of transition metals of IV–VI groups have in common and how do they differ?

7. What determines the high hardness of IV–VI transition carbides and nitrides of transition metals?

8. What determines the high melting point of carbides and nitrides of transition metals of IV–VI groups?

9. What determines the specific electrical properties of carbides and nitrides of transition metals of IV–VI groups?

4. BORIDES

Already in ancient works of chemistry and metallurgy dating back to 800 AD, the borax is mentioned in connection with its use as a flux.

But despite its long history of exploration and use, boron and its compounds are still poorly understood. This is due to the relatively low content of boron in the earth's crust (the boron Clarke is $1 \cdot 10^{-3}$), the specificity of its raw materials sources and the difficulty of conducting relevant studies, which is caused by the specific nature of boron occupying a transitional position between metals and non-metals.

The high affinity of boron for most elements, especially oxygen, for a long time made it impossible to obtain boron and its compounds in pure form.

Nowadays, boron compounds and alloys have widely used in new technology as high-temperature materials having a unique complex of physical, physical-technical and chemical properties.

Metal compounds with boron – borides – an important and numerous class of inorganic compounds, characterized by refractory properties, high chemical resistance in various corrosive environments, as well as metallicity, which is revealed in their high electrical and thermal conductivity, magnetic properties, and electron specificity.

4.1. Phase diagrams of the transition metal boron systems

From the 70 binary systems studied, boron compounds are formed in only 55 systems. These are the compounds between the elements I*A*–VIII*A* subgroups and zinc with boron. I*B*–IV*B* subgroups do not form subgroups of boron compounds.

Binary boron systems differ in the intervals and formulations in which compounds are formed. For most systems, the compounds contain 25–66,7 % boron, which corresponds to the M_4B–MB_2 formula composition [7], [8].

The maximum number of boride phases with different boron content in them (the atomic ratio of B/*M* varies from 1/4 in M_4B to 12/1 compounds in MB_{12} compounds) is formed by rare earth and refractory transition metals of III–VIII groups, for which different valence states are possible, are associated with the overlapping of the *d*-, *f*-, and *p*-orbitals.

The phase diagrams of the transition metals of IV group (Ti, Zr, Hf) differ from each other in appearance and in the number of detected compounds (Fig. 4.1).

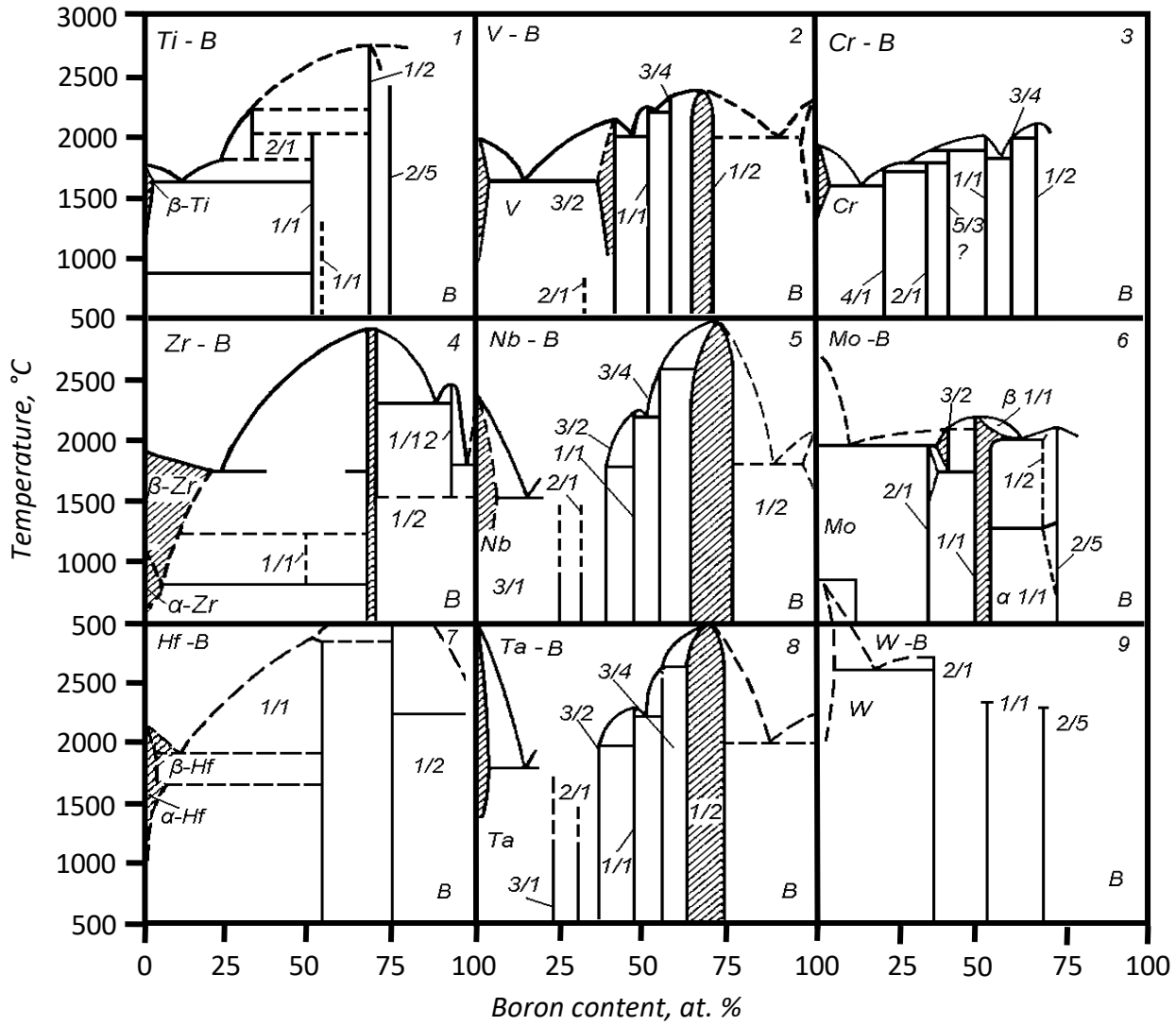


Fig. 4.1. Phase diagrams of binary metal-boron systems [4]

So in the Ti–B diagram such phases as Ti_2B, TiB, Ti_3B_4, TiB_2 are detected. But the existence of the Ti_2B phase is open to question. The existence of the Ti_2B_5 and TiB_{12} phases is also uncertain.

Only two phases of ZrB_2 and ZrB_{12} have been detected in the phase diagram of the Zr–B system.

The phase diagram of the Hf–B system has only one HfB_2 compound, which crystallizes into a hexagonal structure of AlB_2 type.

Phase diagrams of metals of V group (V, Nb, Ta). The phase diagram of V–B system is an estimate, with no V_5B_6 and V_2B_3 copmpounds. The structures of these compounds are defined, but the conditions of formation and the temperature stability interval are unknown (the compounds were not obtained in pure form). In addition to these compounds, such compounds as V_3B_2, VB, V_3B_4, VB_2 are defined.

The phase diagram of the Nb–B system determines the presence of four phases Nb_3B_2, NbB, Nb_3B_4, NbB_2.

There are five phases in the phase diagram of the Ta–B system, including Ta_2B, Ta_3B_2, TaB, Ta_2B_3, TaB_2. Almost all phases have narrow ranges of homogeneity.

Phase diagrams of transition metals of VI group (Cr, Mo, W). There are several phase diagrams available for the Cr–B system, but not all of them correspond to chromium boride data. In general, we know about the existence of the following phases: Cr_2B, Cr_5B_3, CrB, $Cr_{1-x}B$, Cr_3B_4, Cr_2B_3, $CrB_{2,0-2,6}$, CrB_4.

The most prominent among this group of transition metals is the Mo–B state diagram, although there are some inaccuracies. Thus, the Mo_3B_2 phase is not definitively determined, and the composition of the higher boride is not precisely determined. The phases such as Mo_2B, α-MoB, β-MoB, MoB_2, $MoB_{2,3-2,5}$, $Mo_{1-x}B_3$ are likely to exist in this system.

The phase diagram of the W–B system is based on many different sources, which investigated the existence of different tungsten boride phases. The most probable is the existence of the following phases: W_2B, α-WB, β-WB, β-$WB_{2,00-2,27}$, α-W_2B_5, $W_{1-x}B_3$.

4.2. Features of electronic structure of borides

The IV–VI transition metal compounds of boron have a number of peculiarities related to the presence of unfilled internal electronic levels of transition group elements. The electronic collective in borides mainly belongs to transition metal atoms.

The Hägg's rule can only be applied to transition metal compounds with boron within certain limits. For metals of IV and V groups of the periodic table of elements, the ratio r_x/r_{Me} is close to the critical one (0,59), except for vanadium, and metals of VI, VII, and VIII groups have a much larger deviation. This, of course, can be explained by the fact that MB_2-type compounds, which are crystallized into fairly simple hexagonal lattices, are the most stable in IV and V boron systems. In contrast, compounds of MB_2 type of VI group metals are much less stable, and the existence of WB_2 boride is generally problematic. However, even in IV and V metal boron systems there are compounds of a more complex type, although less stable than diborides.

The isolated boron atom has a $2s^2 2p$ valence electron configuration. This energy-unstable configuration is able to transform into more energy-resistant $2s2p^2$ through the $s \rightarrow p$ transition in the process of formation of both elemental boron. The $2s2p^2$ configuration inclined to the completion of the most boron-resistant $2s2p^3$ configuration. Boron in compounds with metals that are commonly used to demonstrate donor properties is a highly expressed electron acceptor, which determines both the crystalline and the electronic structure of borides and their properties. The high acceptor properties of boron primarily cause the formation of covalent bonds between its atoms not only in elemental boron, but also in borides, where not only the valence electrons of boron, but also the partner-metals compounds in the formation of boron are involved in their formation. This leads to the formation of structural elements of boron atoms, the more complex the smaller number of electrons of the partner metal atoms can participate in the formation of B–B bonds, which means that the more direct exchanges of valence electrons between

the boron atoms are more defined. Therefore, the formation of boride phases with structural frame elements of boron atoms (MB_6 hexaborides, MB_{12} dodecaborides) is characteristic of alkaline, alkaline earth metals, rare earths. At the same time, *d*-metals are strong electron donors, suitable to the formation of boride phases with simpler structural elements from boron atoms – linear and flat. The ability of transition metals with unfinished *d*-shell to half-valence and the formation of *M–M* covalent bonds determine the diversity of boride phases, crystalline structures and properties.

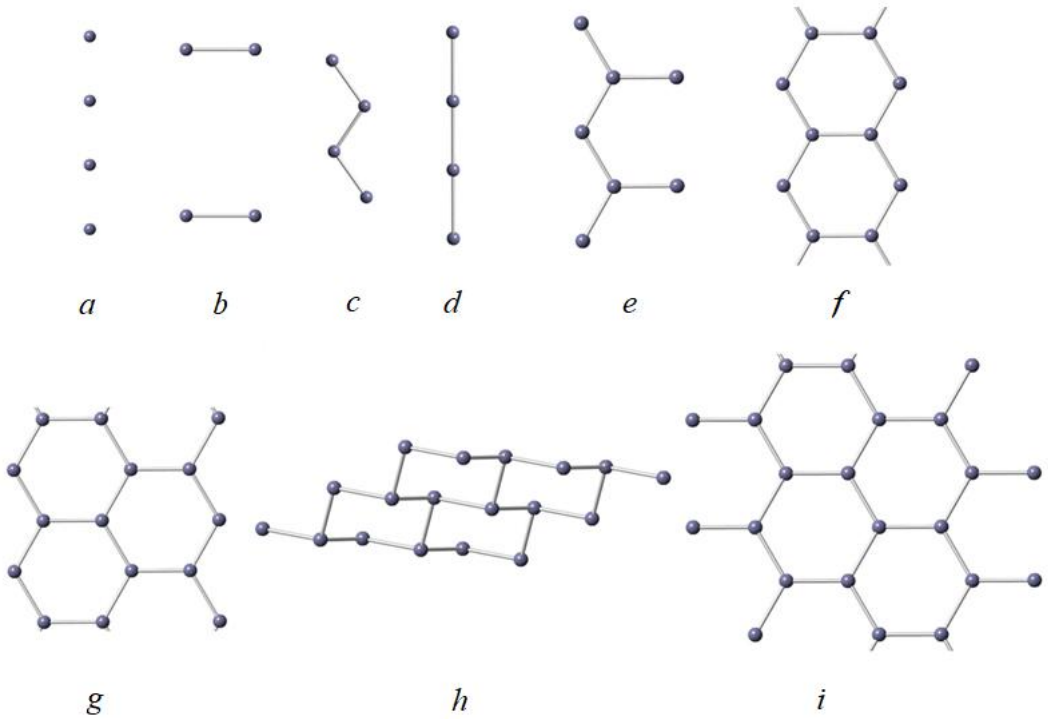
The approach for the formation of boron atoms in borides of sp^3-hybrid configurations, which are carriers of hardness and brittleness, largely determines the hardness and brittleness of most borides. However, their hardness and brittleness are less than those of the corresponding carbides, since the structural elements of boron atoms usually combine sp^3- and other configurations (sp^2-, s^2p-, *sp*-), while the carbon atoms in carbides are most characteristic of sp^3-hybridization [9].

4.3. Crystal chemistry and borides structural features

Questions about the relationship between the composition, structure and type of chemical bond in borides are very complex. It is known that the type of crystalline structure of a compound is determined by its composition and type of chemical bond. And the composition of the compound is determined by the valence, the electron concentration, the size of the atoms, and the structural features.

Important factors that determine the composition of all boron compounds are: size factor, electrochemical factor associated with electronic transitions, electronic concentration, which is determined by the degree of localization and delocalization of electrons. All the factors are interrelated and depend in some extend on the location of the elements in the periodic system of elements. The formation of various structural elements from boron atoms in borides is explained by the specificity of the electronic structure of boron, the energy instability of the external electronic states $2s^2 2p$.

It is revealed that with the increase of boron content in borides, the evolution of bonds occurs – the transition from 1) isolated boron atoms (Fig. 4.2 *a*), or pairs formed by boron atoms (Fig. 4.2 *b*) to 2) chains of different complexity (straight, zigzag, zigzag with lateral branches) directly connected to each other boron atoms (Fig. 4.2 *c*, *d*), then to 3) twin (Fig. 4.2 *e*), triple chains (strips) (Fig. 4.2 *f*), and , at the very end, up to 4) corrugated (Fig. 4.2 *i*), close-packed (Fig. 4.2 *k*) grids and 5) two- and three-dimensional frames, when two structures can be distinguished in the structure side lattices (boron atoms and metal atoms) that penetrate into each other. In all these structures, metal-to-metal bonding is retained and an important feature of borides is the substantially metallic nature of their properties, as well as high hardness and high melting points [10].

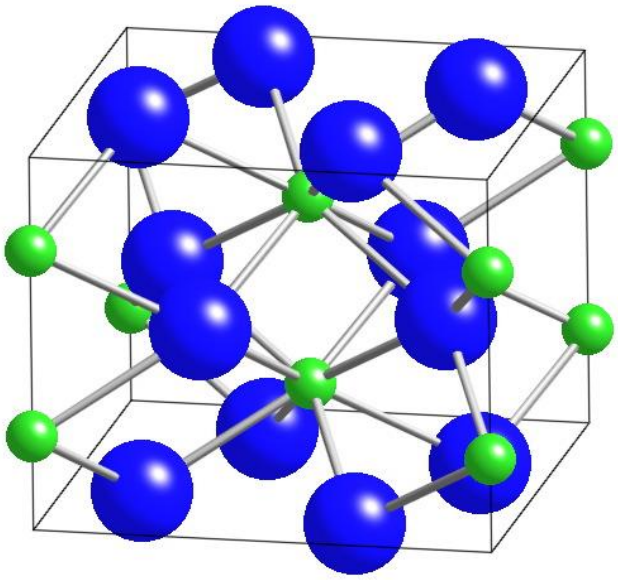


a – isolated boron atoms; *b* – couples of boron atoms; *c* – zigzag chains; *d* – straight chains; *e* – branched chains; *f* – double chains; *g* – triple chains; *h* – corrugated flat grids; *i* – close-packed grids

Fig. 4.2. Structural elements of boron atoms in borides [11]

The evolution of the configurations of boron atoms from the isolated to the continuous three-dimensional framework described above corresponds to the stoichiometric series $M_2B \rightarrow MB \rightarrow M_3B_4 \rightarrow MB_2 \rightarrow MB_6 \rightarrow MB_{12}$.

Borides with isolated boron atoms (Fig. 4.2 *a*). This group includes M_4B and M_2B (hemiborides) borides with a $CuAl_2$ (C16) structure consisting of metal tetrahedron layers and boron atoms in the pores between these layers, which form rows inside a metal lattice, the distance B–B in which is twice larger for the diameter of the boron atom (Fig. 4.3). Although the formation of B–B bonds in such rows has not yet taken place, the presence of such rows can already be considered as the first step towards their formation. These include a large number of phases: Ta_2B, Mo_2B, W_2B, Mn_2B. All hemiborides are compounds of metals of VI–VIII groups, hence metals of small size atoms.



large spheres – *M*, small spheres – B

Fig. 4.3. Unit cell of M_2B hemiborides [12]

Borides with chains of boron atoms (Fig. 4.2 *b*–*e*). Several types of structures are formed from boron atoms forming chains. In borides of *M*B composition crystallizing into structural types of TaB (VB, NbB, TaB, CrB, β-MoB, β-WB), FeB (TiB, δ-MnB), α-MoB (α-WB), boron atoms form zigzag chains [9]. All three types

are distinguished by the mutual arrangement of prisms that form metal atoms. FeB and TaB structures are characteristic of *M*B compounds of permanent composition. MoB-type structures are typically formed in compounds that have a small range of homogeneity, the boundaries of which lie on different sides of the stoichiometric composition. Changing the composition within the boundaries of the homogeneity range is accompanied by a change in the unit cell parameters. The possibility of occurrence of vacancy boron atoms in the chains or the appearance of excess boron atoms in them is facilitated by the large sizes of Mo and W atoms.

In TaB or CrB structures (a rhombic cell with four formula units), metal atoms form triangular prisms in the centers of half of which are metal atoms, zigzag chains of boron atoms pass through other prisms parallel to the *OZ* axis (Fig. 4.4).

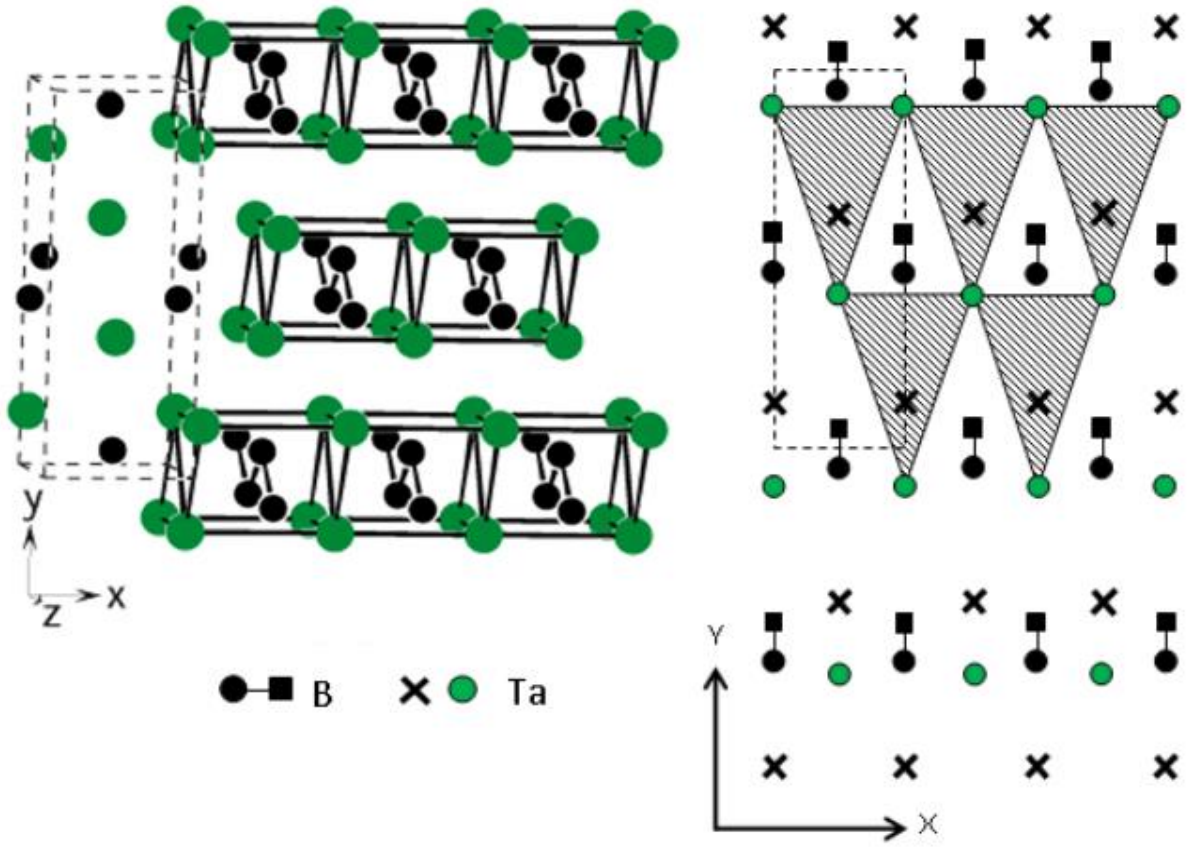


Fig. 4.4. TaB (CrB) structural type [12]

The structure of FeB type borides differs from TaB by the size of the prisms and their arrangement (Fig. 4.5).

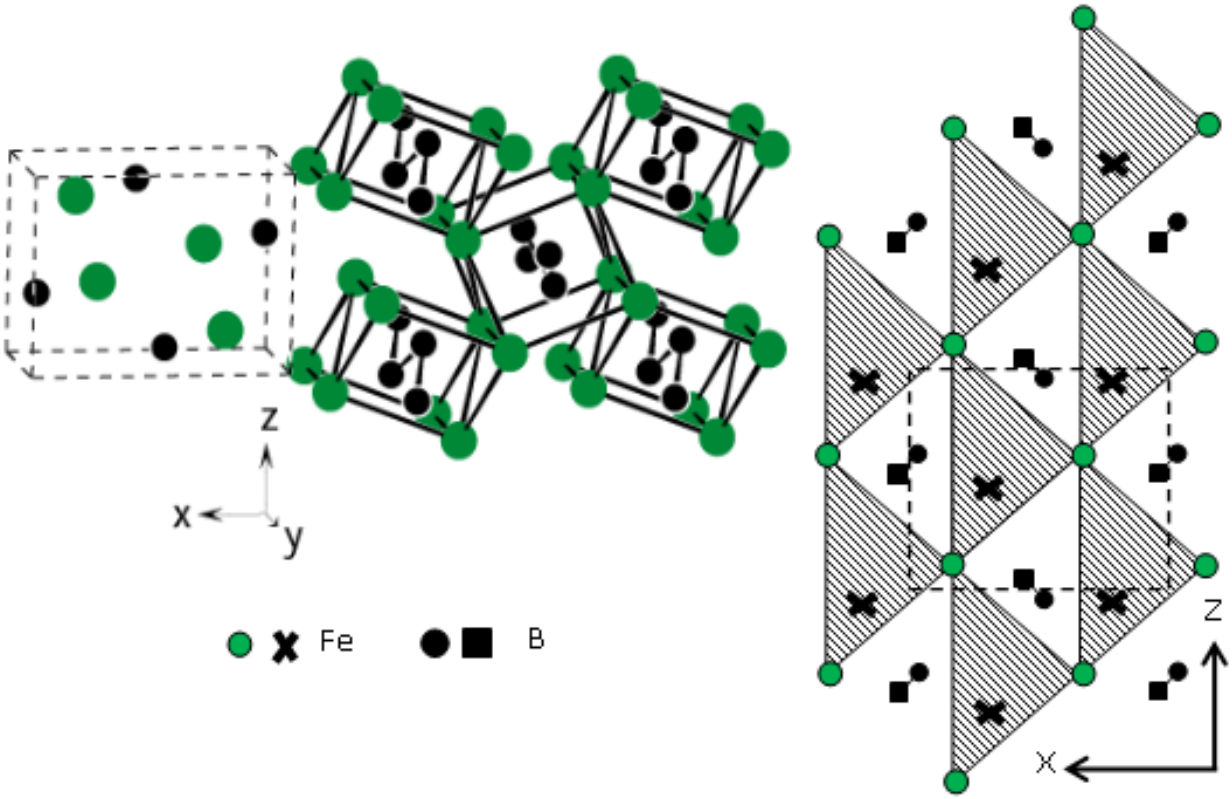


Fig. 4.5. FeB structural type [12]

The MoB structure is shown in Fig. 4.6 (a tetragonal cell with eight formula units) differs from the TaB and FeB structures in that the prisms of the metal atoms are arranged in layers with alternation of the direction of their lateral faces (one parallel to the *OX* axis, the other to the *OY* axis).

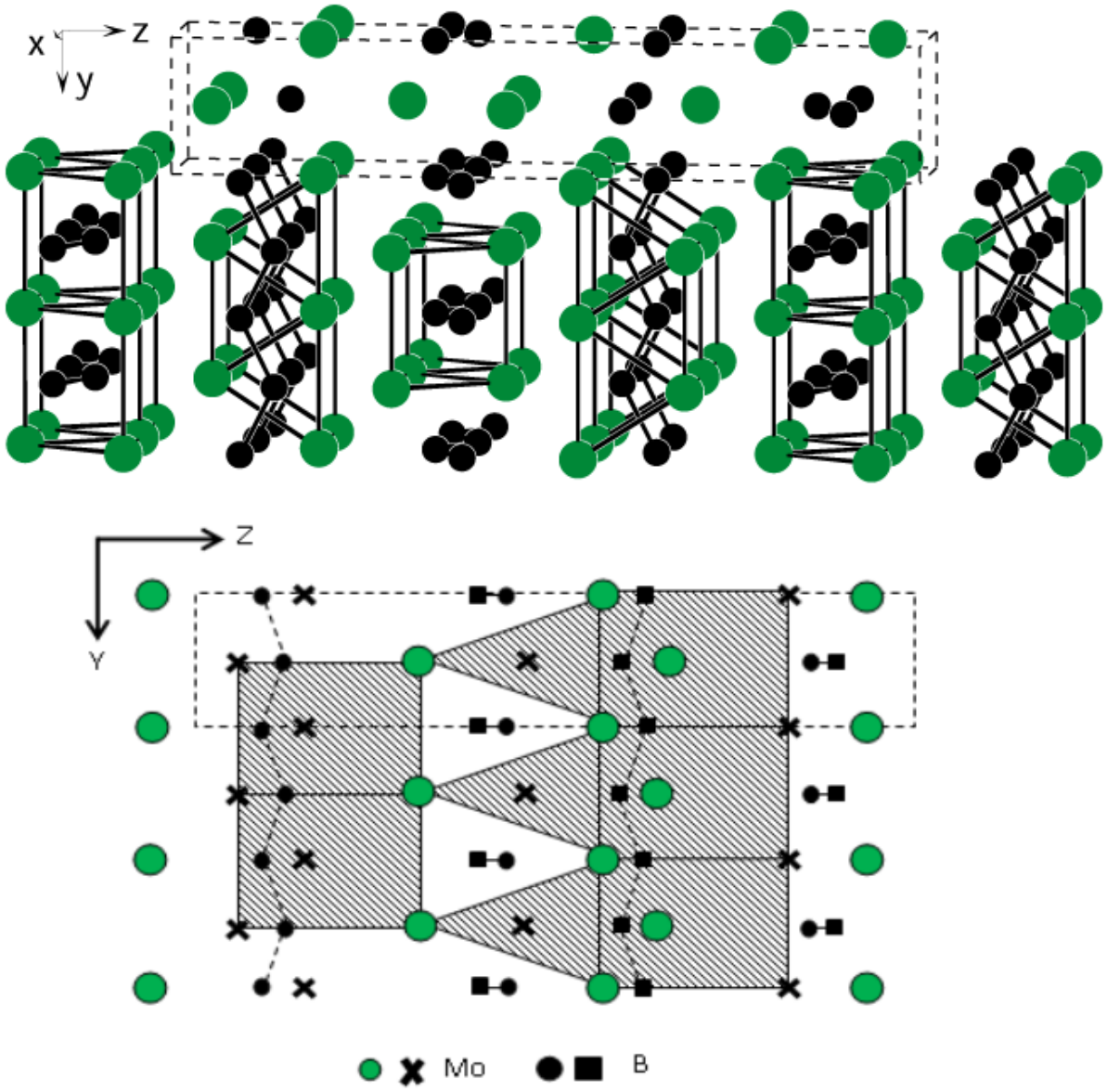


Fig. 4.6. MoB structural type [13]

Structural types with double chains of boron atoms. This type includes borides with the formula M_3B_4. A typical structure is Ta_3B_4 with a rhombic elementary cell with two formula units (Fig. 4.7). The structure consists of double rows of triangular prisms of two types. The δ-Nb_3B_4, η-Cr_3B_4 phases are also constructed according to this type. Such double chains can be considered as an intermediate stage on the way to the formation of two-dimensional grids, which are implemented in MB_2 type borides.

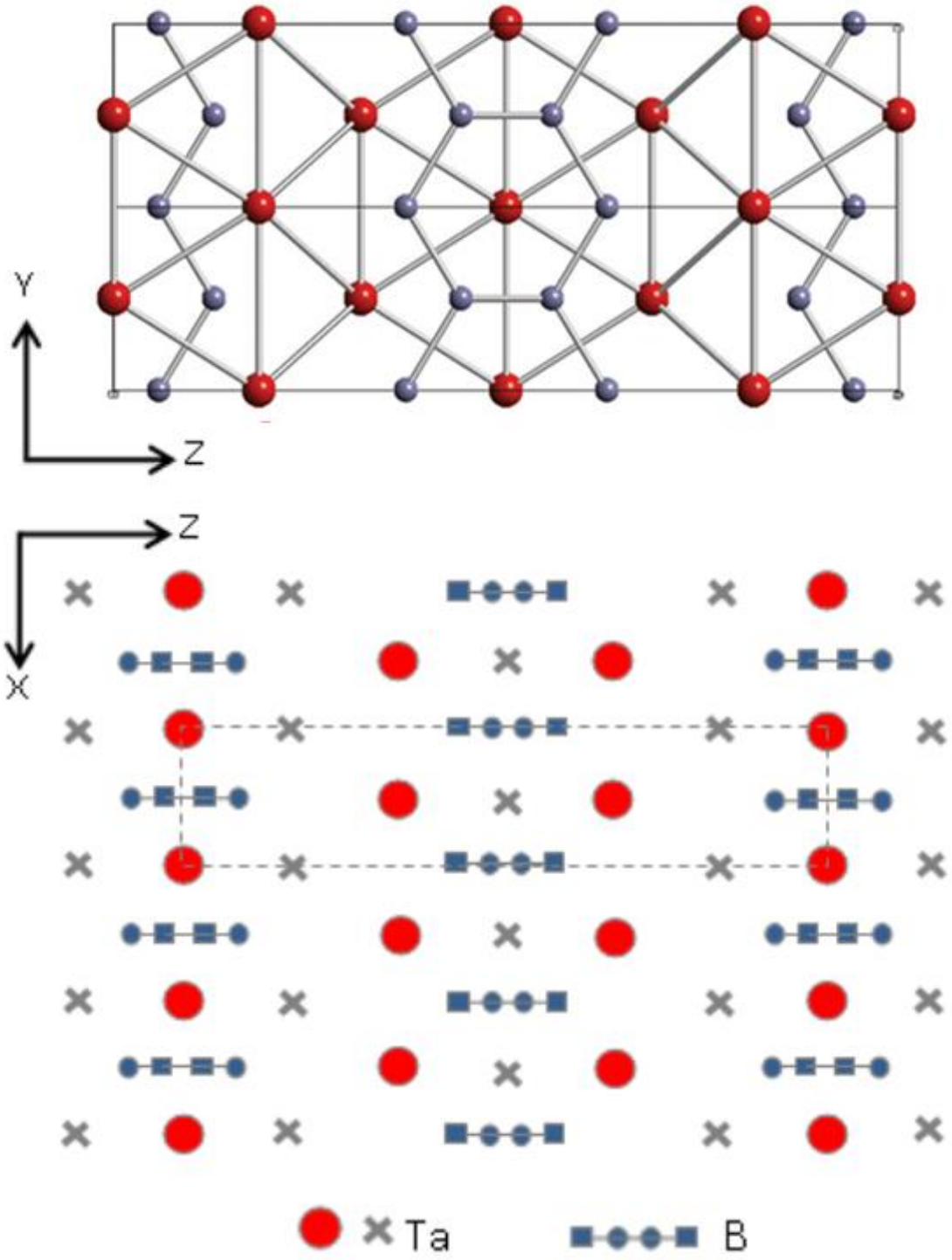


Fig. 4.7. Ta_3B_4 structural type [14]

Borides with mixed elements from boron atoms. Among borides, there are structures with different combinations of structural elements from boron atoms. For example, atoms of V_3B_2 and Cr_5B_3 have isolated atoms and pairs of boron atoms.

Borides with grids of boron atoms. In a number of borides containing boron with more than 50 atomic particles, its atoms are bonded to a framework consisting

of corrugated grids (structural type α-$ThSi_2$, CrB_4, MnB_4) or octahedron B_6 (ThB_6, CaB_6).

For transition metal diborides, the characteristic structure is AlB_2 (hexagonal cell with two formula units) (Fig. 4.8). The structure of this type is made of triangular prisms, at the vertices of which metal atoms are located, and at the centers of the prisms are boron atoms, which form graphite-like flat grids. The layers of boron atoms alternate with the layers of metal atoms. Boron atoms are surrounded by six metal atoms and three boron atoms, and metal atoms are six metal atoms and twelve boron atoms. All structural transition metals of TiB_2, ZrB_2, HfB_2, VB_2, NbB_2, TaB_2, CrB_2, MoB_2, WB_2 transition metals have this structural type.

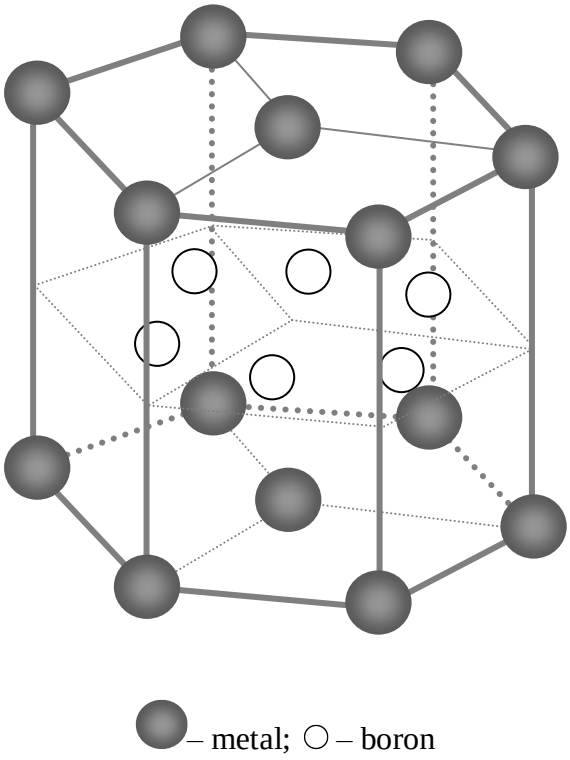


Fig. 4.8. AlB_2 type structure

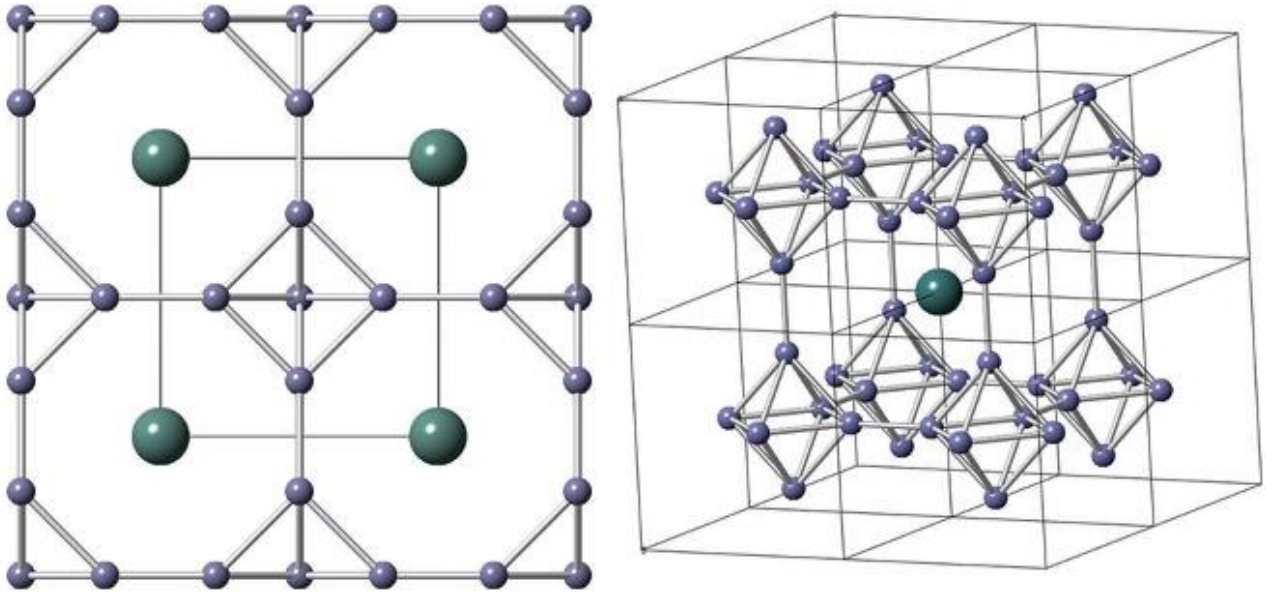
The Mo–B and W–B systems have M_2B_5 phases, which are a more complex version of MB_2 phases. The main difference between them is the different sequence of packing, namely in MB_2 borides the layers of metal atoms are packed in order …*AAAA*… (simple hexagonal structure, as in tungsten WC carbide (Fig. 3.6)), whereas in W_2B_5 the packing …*AABBAABBAABB*… is realized, and in Mo_2B_5 –

…*AABBCCAABBCC*…. The grids of boron atoms in these structures are implemented in nodes of the metal lattice in different ways.

Borides with frames of boron atoms. In structures of borides containing boron of 85 atomic particles, a framework of boron atoms is formed – cubooctahedron (VB_{12}) or icosahedrons (B_4C, NaB_{15}, AlB_{10}).

Among the borides having three-dimensional formations of boron atoms, the following basic structural types are distinguished: UB_4, CaB_6, UB_{12}.

The particular interest is the structure of the CaB_6 type, which has a cubic lattice of the CsCl type centered by a complex of six boron atoms (Fig. 4.9). The metal atoms are located in nodes of the prime cube in positions (000), and the boron atoms form octahedron. Rare earth metal borides Y, La, Ce, Pr, Nd and elements of II–IV groups (except for beryllium and magnesium) have this structural type.



a *b*

a – projection of MB_6 structure on the plane (001); *b* – MB_6 lattice
Fig. 4.9. CaB_6 type structure [15]

It is interesting to consider the structure of CaB_6 as a cubic one, with octahedron of boron atoms at the nodes and metal atoms in the cavities, since boron atoms have a decisive influence on the overall structure and size of the electronic

cell (Fig. 4.10). Metal atoms occupy cavities of sufficient size to prevent their deformation.

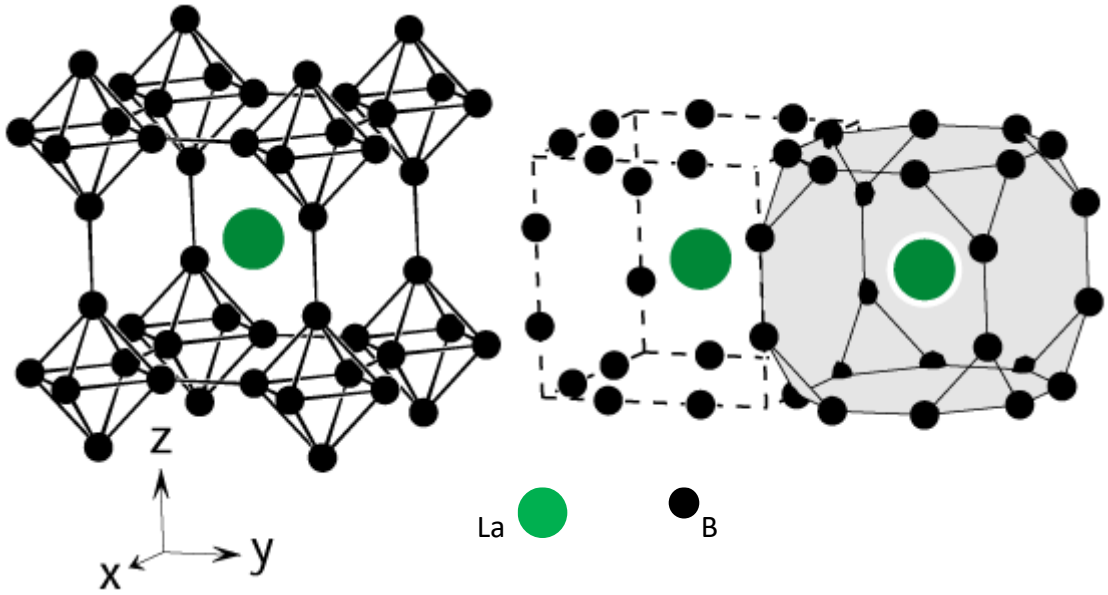


Fig. 4.10. CaB_6 type structure [16]

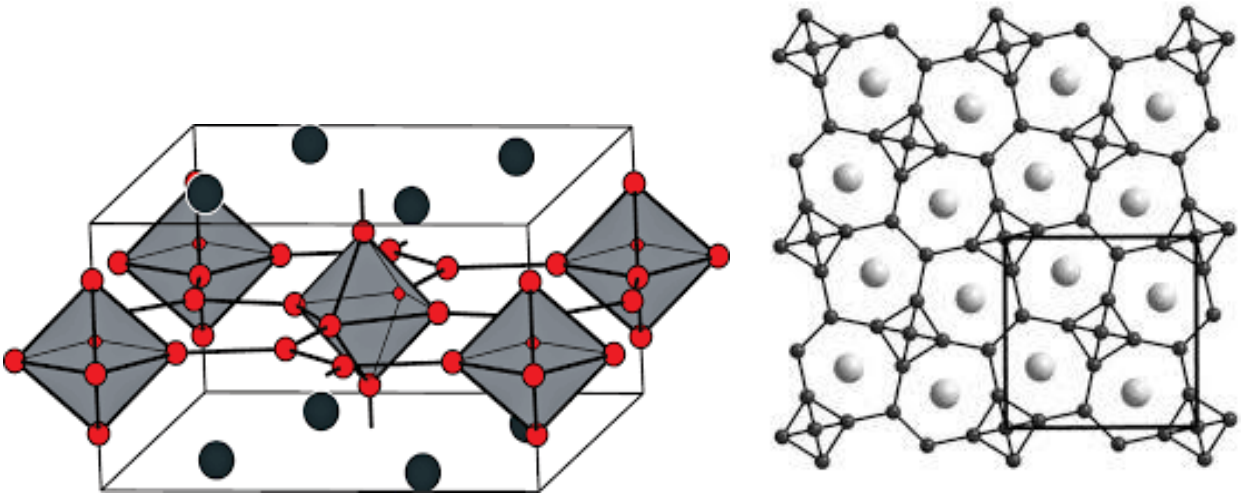
Precise measurements of the lattice of hexaborides of rare earth elements have shown that the change in their magnitudes corresponds to the general concept of lanthanide compression in a number of rare earth elements. One of the prerequisites for the formation of compounds with CaB_6 structure is to exceed the energy of the *d*-states over the energy of the *s*-states by no more than 2,76 *eV*.

It follows that the absence of Li, Na, K, Be hexaborides with CaB_6 structure can be explained by the relatively high position of the *d*-level in the atoms of these metals.

It is interesting to note that the melting temperatures of all hexaborides are sufficiently close (2210 ºC in LaB_6, 2190 ºC in CeB_6, 2235 ºC – CaB_6 and SrB_6, 2270 ºC – BaB_6 and 2195 ºC in ThB_6), unlike the melting temperatures of other isomorphic boron families metal, such as diborides. This feature is related to the dominant role of the spaceframework of boron atoms; metal atoms are located in its cavities and have almost no effect on bond strength. This feature is also reflected in the proximity of the lattice parameters: 4,156 Å in LaB_6, 4,141 Å in CeB_6, 4,145 Å – CaB_6 and 4,19 in SrB_6, 4,268 Å – BaB_6.

A characteristic feature of rare earth hexaborides (cubic CsCl type structure) is the defined metallic nature of their properties: they have high electrical conductivity and thermal conductivity (for example, the specific electrical resistance of lanthanum hexaboride is equal to $27 \cdot 10^{-6}$ *Ohms·cm*, i. e. less than metal lanthanum: $59 \cdot 10^{-6}$ *Ohm·cm*), they are solid, quite strong and, although brittle, subject to (with some caution) machining.

The tetraboride structure (UB_4 type) can be represented as a combination of two structures AlB_2 (Fig. 4.8) and CaB_6 (Fig. 4.9 *b*); it has an AlB_2 type triangular prism and four-sided prisms similar to the slightly curved CaB_6 cube (Fig. 4.11). Boron atoms are located in the centers of the triangular prisms, and octahedron of boron atoms are placed in the centers of the channels penetrating the quadrangular prisms. These octahedrons have no common vertices and are connected to each other only by a pair of boron atoms along the tetragonal axis. That is, boron atoms from square sections and boron atoms in triangular prisms form flat grids of four- and seven-membered rings.



a *b*

a – MB_4 lattice [17]; *b* – projection of MB_4 structure on the plane (001)
Fig. 4.11. UB_4 type structure

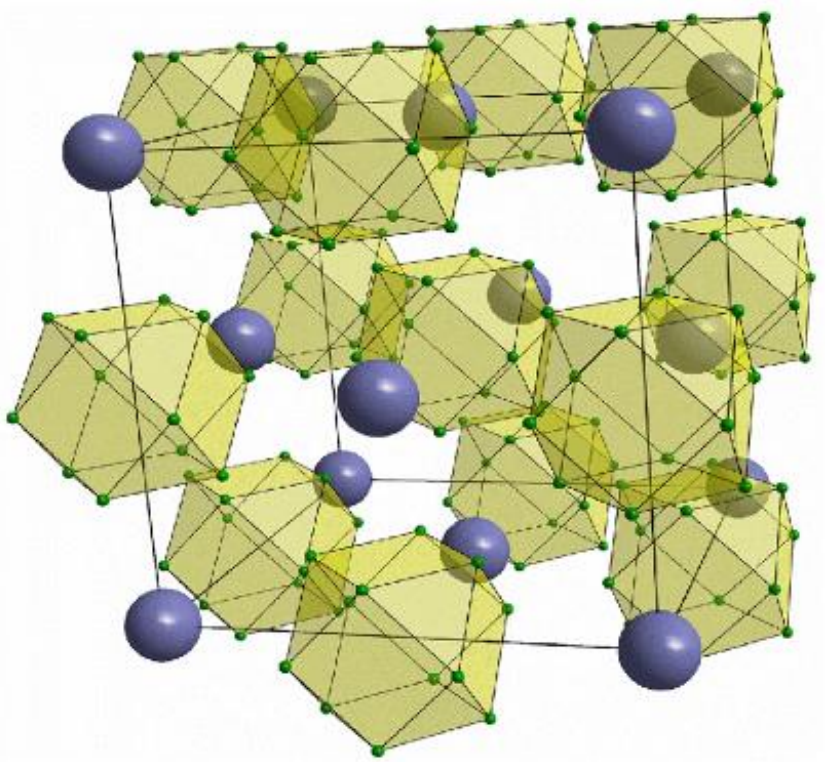
The metallic properties of tetragonal tetraborides are expressed much less than that of hexaborides. This is due to the substantially ionic nature of the chemical bond in these compounds, which is also reflected in the interatomic distance.

The UB_{12} structural type brings together a large group of transition metal dodecoborides, including lanthanides and actinides. This structure, unlike CaB_6, is constructed of regular cuboctahedra of boron atoms, in cavities between which metal atoms are placed. Boron atoms form a spacecoordination around metal atoms; each boron atom has five adjacent boron and two metal atoms.

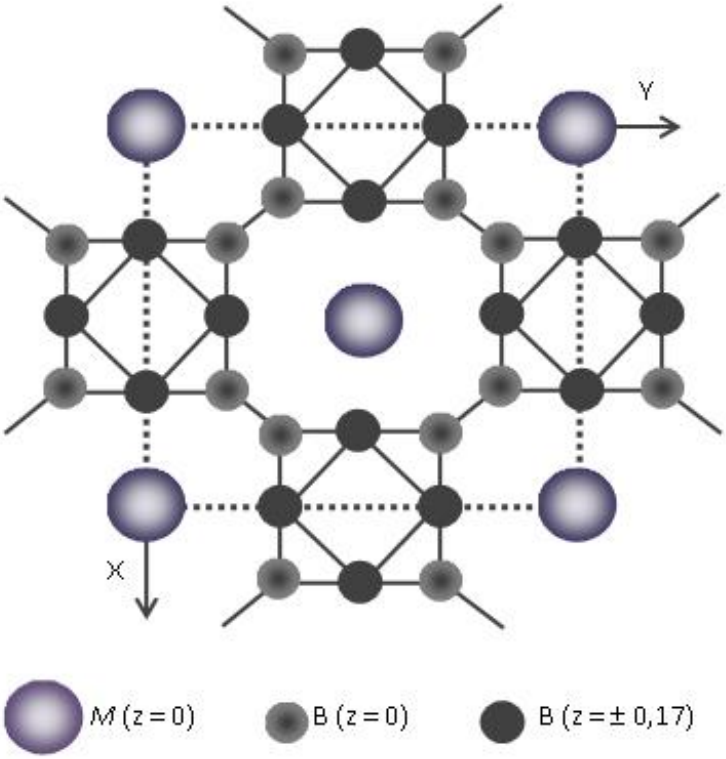
The UB_{12} structural type can be deduced from the structure of the NaCl type if sodium atoms are replaced by uranium atoms and chlorine atoms by Archimedean cubo-octahedron B_{12} (Fig. 4.12). The cubo-octahedron is formed by squares [100] and triangles [111]. The distance between boron atoms in the cubo-octahedron is much shorter than the distance in octahedron from boron atoms in structures of the CaB_6 type.

The question whether the borides with high boron content the interstitial phases is remains controversial. Indeed, some of the transition metal borides are already beyond the scope of the concept of interstitial phases. And it is the stronger – the greater the boron content. Three-dimensional frame structures of the MB_{12} type can almost be considered as reversed phases of interstitial, since in them metal atoms occupy large cavities inside the frame of boron atoms (Fig. 4.13). This also explains the increase in the range of homogeneity in higher borides – due to the relative freedom of substitution of boron and metal atoms.

Therefore, the main feature of borides, new in comparison with carbides and nitrides, is the existence of B–B bonds. While boron atoms remain isolated in the lattice, as in M_2B, the borides belong to Hague phases and are similar in structure to phases such as carbides and nitrides. However, the criterion for the ratio of radii becomes a less important factor with the emergence of B–B bonds and their increase in strength. The evolution of independent bonds between boron atoms (chains of boron atoms → annular chains → hexagonal grids → three-dimensional frameworks) is at the forefront. Initially, the lattice of boron atoms is simply introduced into a hexagonal lattice of metal atoms, which results in different sequences of atomic layer packing; later, the presence of a lattice of boron atoms causes more serious changes in structure.



a



b

Fig. 4.12. UB_{12} type dodecaboride structure (*a*) [18] and projection on the *XOY* plane (*b*)

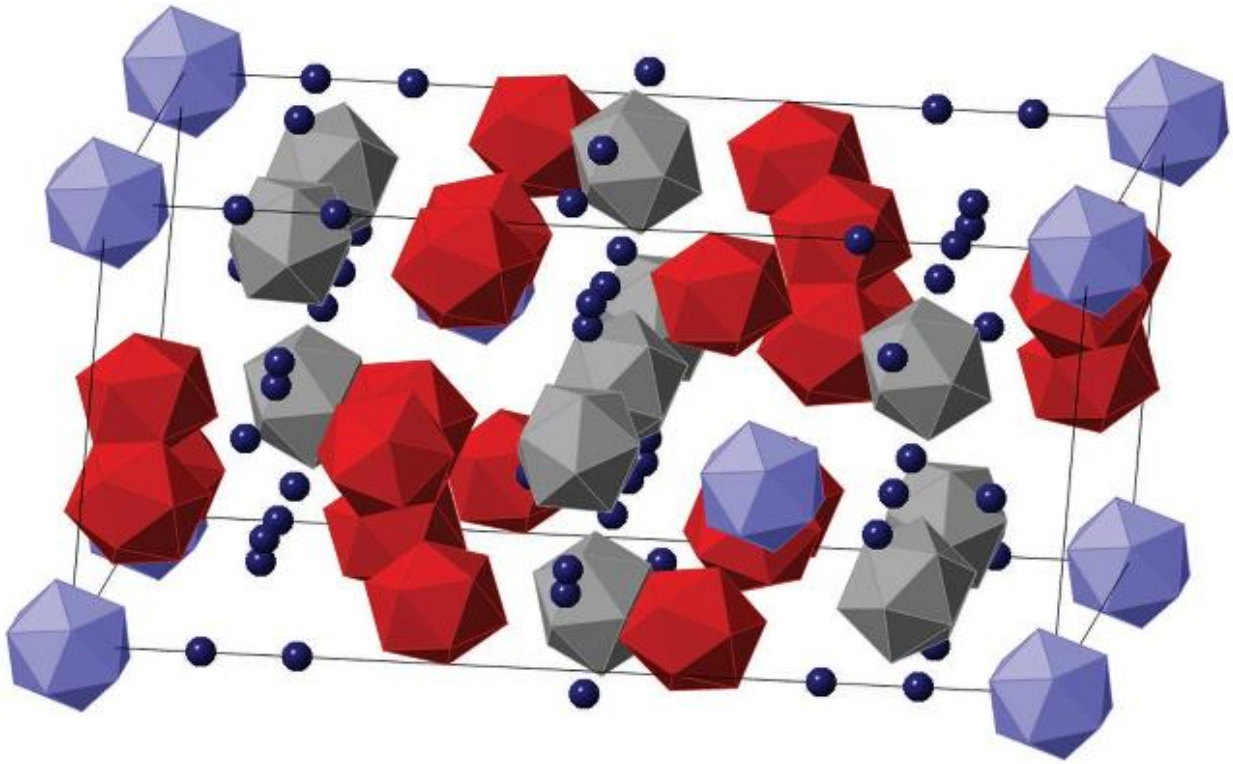


Fig. 4.13. Solid solution of transition metals in β-rhombohedral boron: crystal structure of HfB_{50} [19]

The formation of B–B bonds, which are organized into covalent chains or grids, means that electrons are released which can pass from boron to metal atoms. And this determines the metallic properties of borides (high values of hardness, refractoriness, electrical conductivity, etc.). In this sense, borides behave as typical "carbide-like" compounds.

According to quantum mechanical calculations, the boron atom can form *s*-, *p*- and *d*-bonding functions. It is likely that the *s*- and *p*-functions, forming hybrid orbits, are used in the bonds between the boron atoms themselves in the structural complexes, while the *d*-functions together with the remaining *p*-functions are used to organize the *M*–B bonds.

With the increase of boron content in borides, the number of boron atoms bonded to each other increases, which corresponds to an increase in the proportion of covalent bond in the structures of borides.

The peculiarities of the crystalline structure of borides, the nature and energy of the interconnections, the electronic structure of the metal atoms that form the

boride significantly determine the structure and chemical properties of the boride phases.

The calculation of the bonding energy in borides shows that the maximum value is Ti in the first long period and for Nb and Ta in the second and third long periods. This decrease in the boinding energy of the transition metals from IV group compounds to V and VI group compounds of the periodic table of elements occurs in the case of all interstitial compounds, but is weaker in the nitride – carbides – borides – silicides sequence.

4.4. An overview of the basic properties of borides

Complications of structural elements from boron atoms are observed in the case of transition from lower borides to higher ones. This leads to an increase in the hardness of the crystal lattice in the $M_4B \rightarrow M_3B_2 \rightarrow MB \rightarrow M_3B_4 \rightarrow MB_2$ series. In the same direction, the formation temperature decreases, the melting temperature increases, the hardness, oxidation resistance, mechanical strength increase, the ability to hydrolysis decreases.

The main attractive features of borides are their high hardness (and, unfortunately, respectively high brittleness) and high refractory properties. The latter can be compared to refractory carbides and nitrides. High hardness allows transition metal borides to be used as abrasives, which provide higher surface cleanliness than plastic synthetic diamonds when machining plastic metals and alloys. In addition, borides, like silicides, have extreme chemical resistance and inertness, and often high resistance to oxidation at high temperatures. This causes them to be used as components of refractory and protective coatings.

Another attractive feature of borides is the relatively high creep resistance. Due to this, as well as high resistance to oxidation of boride they are widely used as components of nuclear reactors, where both thermal and chemical resistance plays an important role.

With the formation of transition metal compounds with boron, there is a narrowing of the electron groups both due to the *s*- and *d*-electrons of the metal and due to the valence electrons of boron. This leads to a reduction in the sputtering of the current carriers by lattice and to the high electrical conductivity of borides, sometimes even higher than that of the corresponding metal.

The conductivity of transition metal borides is mainly determined by the degree of incompleteness and the energy level of the *d*-band of the crystals of the corresponding metals.

Due to the lower ionization potential of boron, the carbon resistance of borides is generally lower than that of carbides compared to carbon.

The presence of structural elements of the boron atoms that strengthen the lattice causes relatively moderate values of the coefficient of thermal expansion, high refractory and chemical inertness.

The high heat resistance of some borides makes them promising components of heat-resistant alloys, especially composite materials reinforced with boride fibers or dispersed-hardened borides.

The refractory properties of some borides, especially zirconium diboride, are widely known and are highly resistant to molten steels, cast iron and other metals and alloys. This allows producing thermocouple cases and thermocouples, as well as various refractory lining, electrode and other similar materials and details of metallurgical furnaces, from borides.

Another application area of diborides is related to their application in combination with silicides and other compounds. For example, a refractory material, boride-Z, consisting of ZrB_2+$MoSi_2$, was developed. This material resists oxidation in air to almost 1100 °C and has high electrical conductivity and high resistance to thermal shocks.

It is interesting to use borides in those areas where their role as couplant to other compounds, such as in heterogeneous materials, e. g. special ceramics, metal ceramics, in various types of transition (mechanical) compounds or coatings for high-temperature ones, comes to the fore alloys. This applies, for example, to borides in

combination with already known silicides, where they enhance their properties such as the ability to bind particles and give the material some fluidity (ability to glass). An important feature of such systems is the existence of similarities of structures of borides and silicides of transition metals, which allows, by selecting a metal with the appropriate atomic size and valence, to obtain solid solutions between different phases in the adjacent parts of the matrix.

Also of interest are the thermal emission properties of transition metal borides, and especially lanthanide borides. These compounds have low work of electron output, high AC densities and high resistance to ion bombardment.

A number of borides are widely and successfully used as catalysts in organic synthesis reactions.

Important role is played by borides in the creation of surface coatings on iron, steels, refractory metals; these coatings are characterized by high durability, corrosion resistance, and adhesion strength on the base metal.

From all the interstitial compounds, borides are likely to have the most versatile application (mainly due to the critical size and specific structure of the boron atoms), and not only in themselves but also in the composition of various complex materials and alloys [20].

Control questions

1. Describe the features of the electronic structure of borides.
2. What structural elements form boron atoms in compounds?
3. What borides form structures with isolated atoms?
4. What are the structural types of borides with chains of boron atoms?
5. What structural types have a structure with boron atoms grids?
6. Describe the structural elements of boron atoms occurring in refractory compounds by the example of structural CaB_6 type.
7. Describe the structural elements of boron atoms occurring in refractory compounds by the example of structural type UB_4.

8. Describe the structural elements of boron atoms occurring in refractory compounds by the example of structural type UB_{12}.

9. What influences the difference in the properties of borides, carbides and nitrides?

5. SILICIDES

No element of the periodic table of elements has as many compounds as silicon. There are now more than 270 double compounds known and the number of triple compounds are difficult to calculate. From the 270 known binary compounds 255 are compounds of silicon with metals. From the 103 elements of the periodic system, only 15 do not form compounds, and 28 have not yet been studied for interactions. These are inert gases which interaction with silicon is unlikely. It should be noted that with increasing atomic number, there is an increase in the number of phases in the system; the maximum of compounds is found in elements IV (for metals) and VII groups [21].

5.1. Phase diagrams of the transition metal-silicon systems

The silicon binary compounds with the elements are characterized by a variety of formulaic compositions and crystalline types of structures. Fig. 5.1 shows the phase diagrams of the binary systems of transition metal of IV–VI groups–silicon. There are now more than 60 structural types in which silicides are crystallized.

5.2. Features of the silicides electronic structure

Silicon atoms have a relatively large radius r_{Si} = 1,17 Å and most silicides cannot be attributed to the interstitial phases, since for most silicides, r_{Si}/r_{Me} approaches one, i. e. much more than 0,59. Rather, silicides occupy a position intermediate between the interstitial compounds and the intermetallic compounds.

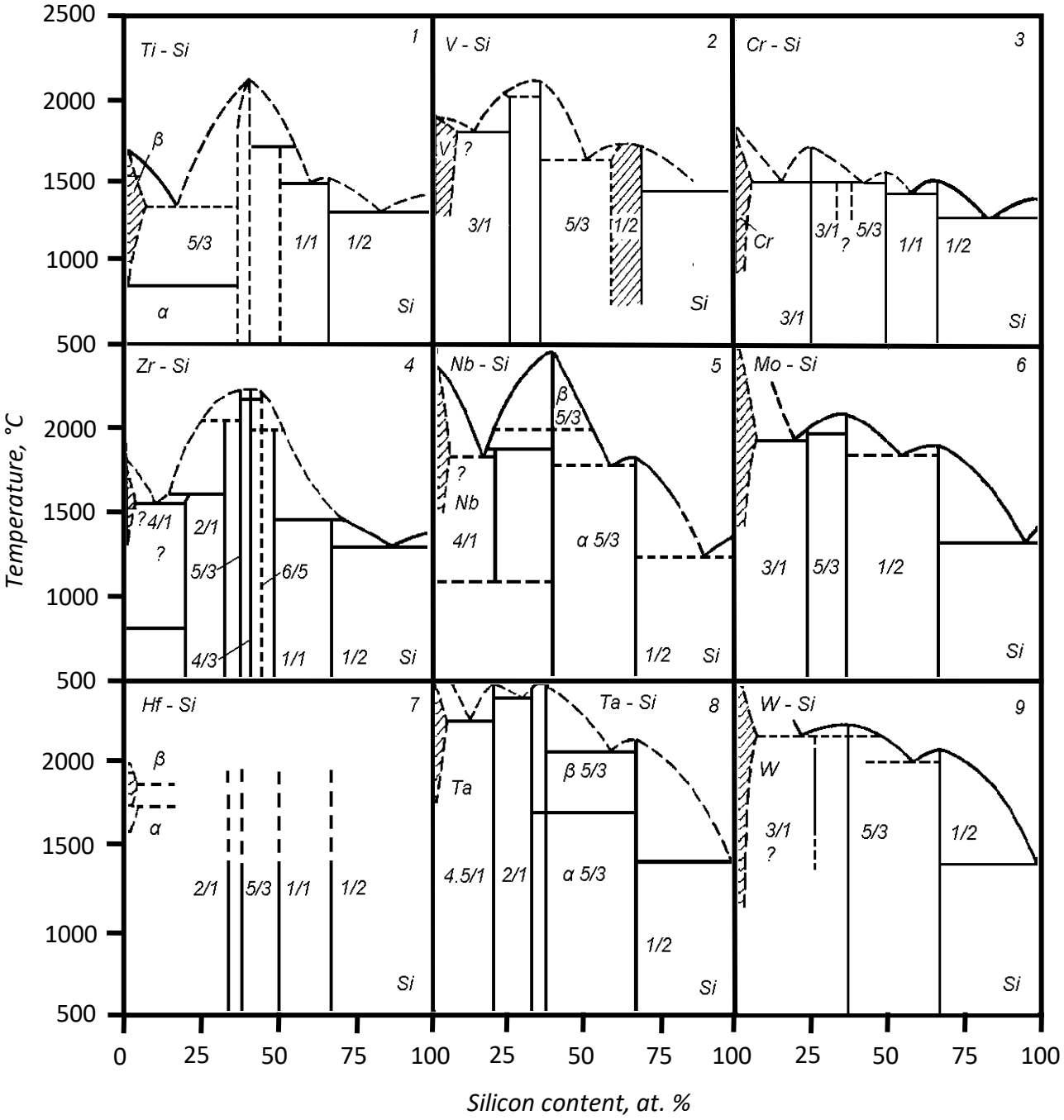


Fig. 5.1. Phase diagrams of the metal–silicon binary systems [21]

The structure and properties of silicides substantially determine the position of silicon in the periodic system of elements, where it is located near boron, aluminum, carbon, phosphorus and germanium, but above all has similar characteristics with boron, carbon and nitrogen. Both in carbon and in nitrogen, the electronic stable configuration of sp^3 is formed, which is formed in carbon by the one-electron $s \rightarrow p$-junction ($s^2p^2 \rightarrow sp^3$), and in the nitrogen by the transition in the scheme $s^2p^3 \rightarrow$

$sp^4 \rightarrow sp^3+p$. The same configuration is typical of silicon atoms, however, the higher principal quantum numbers of *s*-, *p*-electrons located on the valence subshells lead to less energy stability of the sp^3 hybrids than in the case of carbon and nitrogen. In silicon carbon, it borrows sp^3 hybridization, and in nitrogen, this hybridization is significantly weakened and, as a consequence, the donor properties are weakened. In general, the level of properties of silicides (melting point, hardness) is lower than that of borides, carbides and nitrides due to the lower position in the periodic table of the elements.

By structure, some properties, and application, silicides are, first of all, similar to borides. In silicides, as in borides, the role of direct Si–Si bonds is increasing. This causes the transition from a metal bond in lower silicides to a gradual increase in the proportion of covalent bonds between silicon atoms with an increase in their content in higher silicides. So the M_3Si silicides (structural type β-W) are still similar in structure to the corresponding metals. However, with increasing silicon content, the crystalline structure of the compounds is complicated, and the properties become similar to semiconductors (MSi_2), as in silicon. Like boron, silicon forms structural compounds in compounds that are complicated by the increase in silicon content:

– isolated Si atoms bound only to metal atoms (for example, in a U_3Si structure);

– pairs of Si atoms isolated in U_3Si_2;

– one-dimensional (zigzag) chains of Si atoms (Mo_5Si_3);

– two-dimensional close-packed layers of atoms, both Si and metal ($MoSi_2$, $NbSi_2$, $TiSi_2$);

– three-dimensional frameworks of Si atoms in $ThSi_2$ and disilicides of rare earth's elements [21].

In some cases, the silicides behave like intermetallic compounds, in other cases exhibit features of both intermetallic compounds and carbide-like compounds.

Permanent compounds with silicon form metals of the same groups of the periodic system as in the case of borides. On the other hand, aluminum does not form silicides, such as, for example, AlB_2 boride. However, the structure of type AlB_2 is

found among silicides of other metals. It is necessary to note the following feature: in the periodic system the area of elements for which there are stable hydrides, nitrides, carbides, borides and silicides gradually expands in the order of the listed compounds, that is, with increasing size of the non-metal atom.

Structurally, silicides are more complex than carbides, nitrides and borides. This feature is related to the formation of direct Si–Si bonds (with the exception of the lower compounds), except *M*–*M* and *M*–Si. Lattices of metal atoms in silicides, unlike carbides and nitrides, differ significantly from typical metal structures – a feature that can be observed already in the case of borides.

All silicides except VSi_2 are characterized by the absence of homogeneity ranges unlike borides. The reasons for this have not yet been clarified.

Another important feature of silicides is their tendency to polymorphism.

5.3. Crystal chemistry of metal silicides

By chemical bonding, silicides can be divided into three groups [22]:

- ion-covalent;
- covalent;
- metallic.

Ion-covalent silicides are formed by highly positive metals which atoms have valence *s*-electrons. They include the alkaline and alkaline earth metal silicides and the copper and zinc sub-group metal silicides, that is, metal silicides, which are strong donors of valence electrons.

This group of compounds is characterized by the combination of an ionic bond forming metal atoms and silicon with a covalent bond forming silicon atoms.

Alkaline earth metals form silicides, characterized by the formation of structural elements from silicon atoms, which are complicated by the increase in the number of silicon atoms. In these compounds, a covalent bond plays a significant role, the ionic component being negligible. Increasing the covalent component leads

to an increase in melting temperatures, chemical and thermal stability, resistance to oxidation of alkaline earth metal silicides.

Covalent silicides are formed by *s*-, *p*-elements and characterized mainly by covalent bonding between atoms. The possibility of formation and stability of compounds is determined by the mutual redistribution of the *s*-, *p*-states of non-metal atoms and the ability to create the most stable states of the type sp^3 and s^2p^6. The name "silicides" in this case is conditional, since the composition of covalent silicides includes elements more electronegative than silicon (having Pauline electronegativity of 1,8), such as boron (2,0), carbon (2, 5), nitrogen (3,0), oxygen (3,5), phosphorus (2,1), sulfur (2,5). Therefore, it is correct to refer to them as derivatives of the more electronegative element – borides, nitrides, silicon carbides.

Most covalent silicides are dielectrics, have a low coefficient of thermal expansion (which determines their technically important properties of high resistance to heat shock), melt incongruously, have exceptionally high chemical resistance, high scale resistance and heat resistance. This group includes a large number of super hard substances such as silicon carbide and silicon boride.

Metallic silicides form mainly transition metals. They are characterized by the combination of a metal bond between the metal and silicon atoms with a covalent bond between the silicon atoms, and a small fraction of the covalent bond between the metal atoms, which increases with decreasing donor capacity of the metals. Some of the valence electrons of transition metals are localized to stable d^5- and d^{10}-configurations, and some are non-localized and therefore able to pass into p-states, stabilizing stable s^xp^y configurations. With increasing degree of localization of valence electrons in transition metal atoms, the bond *M–M* is strengthened, which has a covalent nature, the proportion of electrons capable of transitioning to *p*-states decreases, and accordingly the bonding energy *M*–Si decreases and, consequently, the probability of formation and thermodynamic stability of silicide phases is reduced. The proportions of the various types of bonding between metal and silicon atoms vary widely depending on the degree of unfinished *d*- and *f*-electron shells of the transition metals and on the relative content of the metal and silicon atoms in the

silicides. The increase of silicon content in silicides of this type complicates their structure accordingly. Silicon-transition metal systems are characterized by the formation of a large number of silicide phases, as well as the structural types in which they are crystallized [23].

Increasing the content of silicon in silicides complicates their crystalline and electronic structure, leading to the formation of strong covalent bonds between atoms of metal and silicon.

The structure of silicon-poor compounds, for example, V_3Si, Mo_3Si (type β-W), can still be considered as a deviation from the *BCC* structure of the corresponding metal (Fig. 5.2).

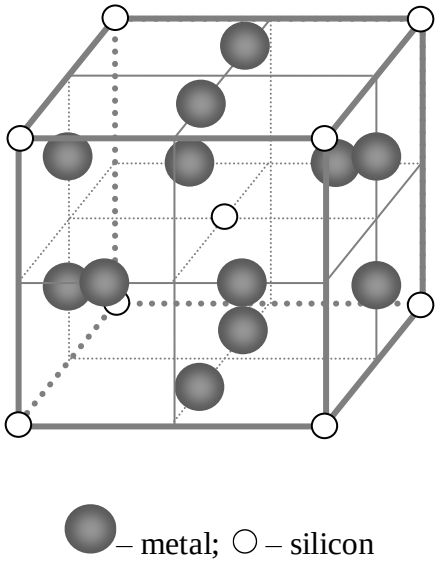
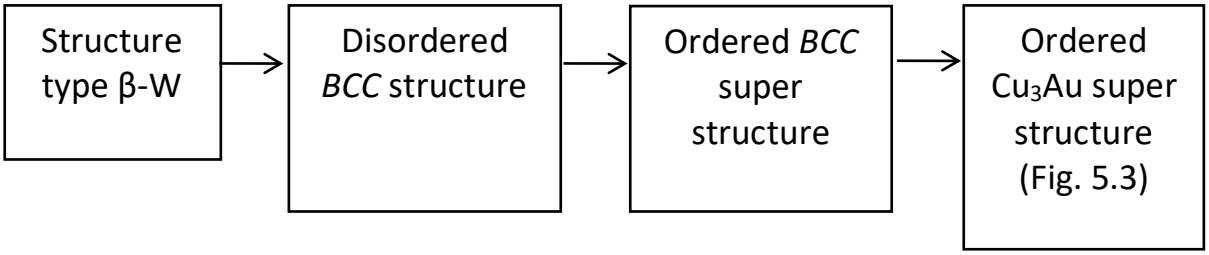
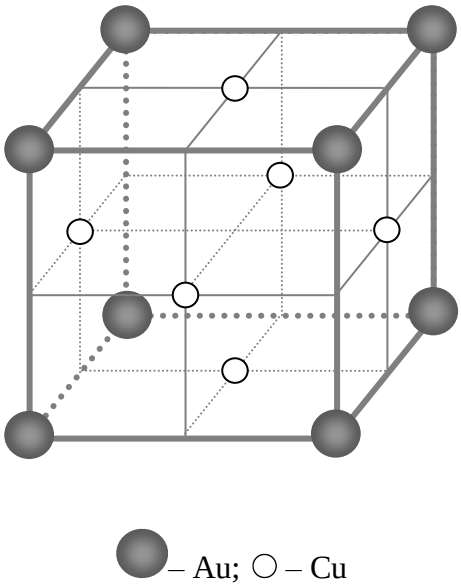


Fig. 5.2. β-W type of structure

As the atomic number changes, the following evolution of M_3Si structures can be observed [21]:



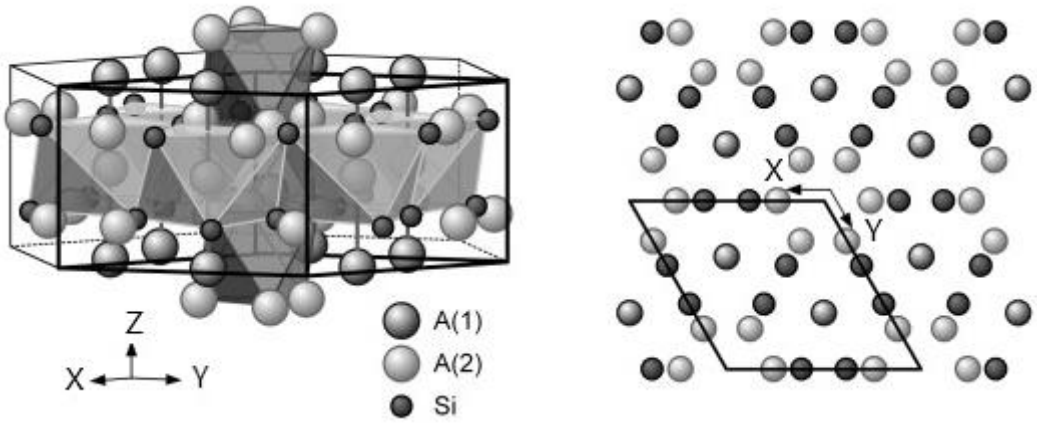
The tendency to form polymorphic modifications is another important feature of silicon-poor structures (for example, in silicides of the M_5Si_3 – α family and β-Nb_5Si_3).



– Au; ○ – Cu

Fig. 5.3. Structure of type-Cu_3Au

All M_5Si_3 (or M_3Si_2) phases have a tetragonal lattice, either isomorphic or very similar in structure. A characteristic feature of these phases is the tendency to form in the structure of separated pairs of silicon atoms, for example in the structure of U_3Si_2. Another feature of these phases is the very high sensitivity to the presence of impurities. Adding a very small amount of carbon or other interstitial impurities (B, N, O) to M_5Si_3 compounds (e. g., Nb_5Si_3) can lead to the transformation of the structure into a $D8_8$ type structure, the so-called Nowotny phase. They are formed by the fact that small carbon atoms enter the lattice interlayer and displace silicon atoms, forcing them to occupy places in the lattice sites. In the case of pure simple silicides (double phases), this structure is characteristic only of IV group metal compounds, for example, Ti_5Si_3 (Fig. 5.4), but not of V and VI groups. Because the silicides of the latter two groups are in fact triple phases, they are stable only in the presence of the second interstitial element.



a *b*

Fig. 5.4. Ti_5Si_3 with the hexagonal *D8₈* structure (*a*) and (0001) projection (*b*) [24]

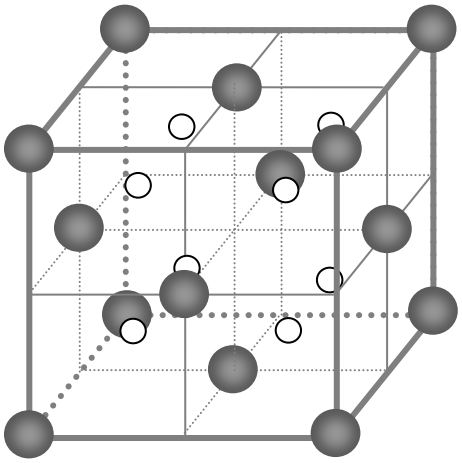
In the composition range from M_2Si to MSi_2, silicides have the greatest similarity to borides. In M_2Si structures, only metal atoms form layers and silicon atoms fill the gaps between them. Whereas in M_5Si_3 structures, such as α- and β-Nb_5Si_3, silicon atoms begin to appear in layers of metal atoms, but are placed in substitution. Thus, these silicides are a fundamentally new case of a mixed solid solution of silicon – both substitution and interstitial.

If the silicon content in the silicide exceeds 33%, the following structural types are observed: CrB (Fig. 4.4), FeB (Fig. 4.5), FeSi, MnP. Atoms of 3*d*-transition metals in mono-silicides, unlike silicides with lower silicon content, are not located at close distance from each other but incline to surround themselves with silicon atoms that do not form pairs, chains, and grids, and are surrounded by metal atoms. This is probably due to the fact that the *M*–Si atomic interaction energy exceeds the *M*–*M* and Si–Si interaction energy.

It is also worth noting the isomorphism of many silicides with germanium. Because the valences of silicon and germanium are the same, it is quite natural. However, since the germanium atoms are larger, isomorphism is observed only when the metalloid atoms enter the lattice not by the interstitial principle but by the substitution principle.

Among the silicides, MSi_2 disilicides are the most important in application, although they are not the most stable phases. They are represented by five structural

types: $TiSi_2$, $ZnSi_2$, $ThSi_2$, $CrSi_2$, $MoSi_2$. As one approaches to VIII group, there is a gradual transition to simpler structures. Thus, in the case of $CoSi_2$ and $NiSi_2$, the structure is of the cubic type CaF_2 (Fig. 5.5), while $MnSi_2$ and $FeSi_2$ have similar tetragonal curved lattices.



– metal; ○ – silicium

Fig. 5.5. Structure of CaF_2 type

The related structures of $MoSi_2$, $CrSi_2$, $TiSi_2$ presented in Fig. 5.6 can be described simply by changing the packing sequence of hexagonal layers of metal atoms and silicon with a reiteration 2, 3 and 4 periods, respectively.

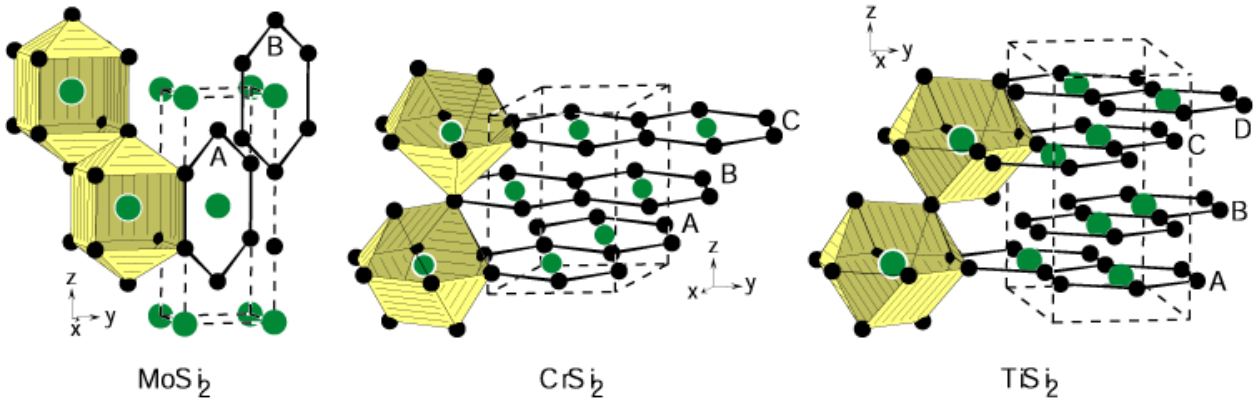


Fig. 5.6. $MoSi_2$, $CrSi_2$, $TiSi_2$ structural types [25]

The structure of disilicides can be imagined otherwise, as consisting of "graphite-like" two-dimensional grids of silicon atoms, in the holes of which metal atoms are located (Fig. 5.7).

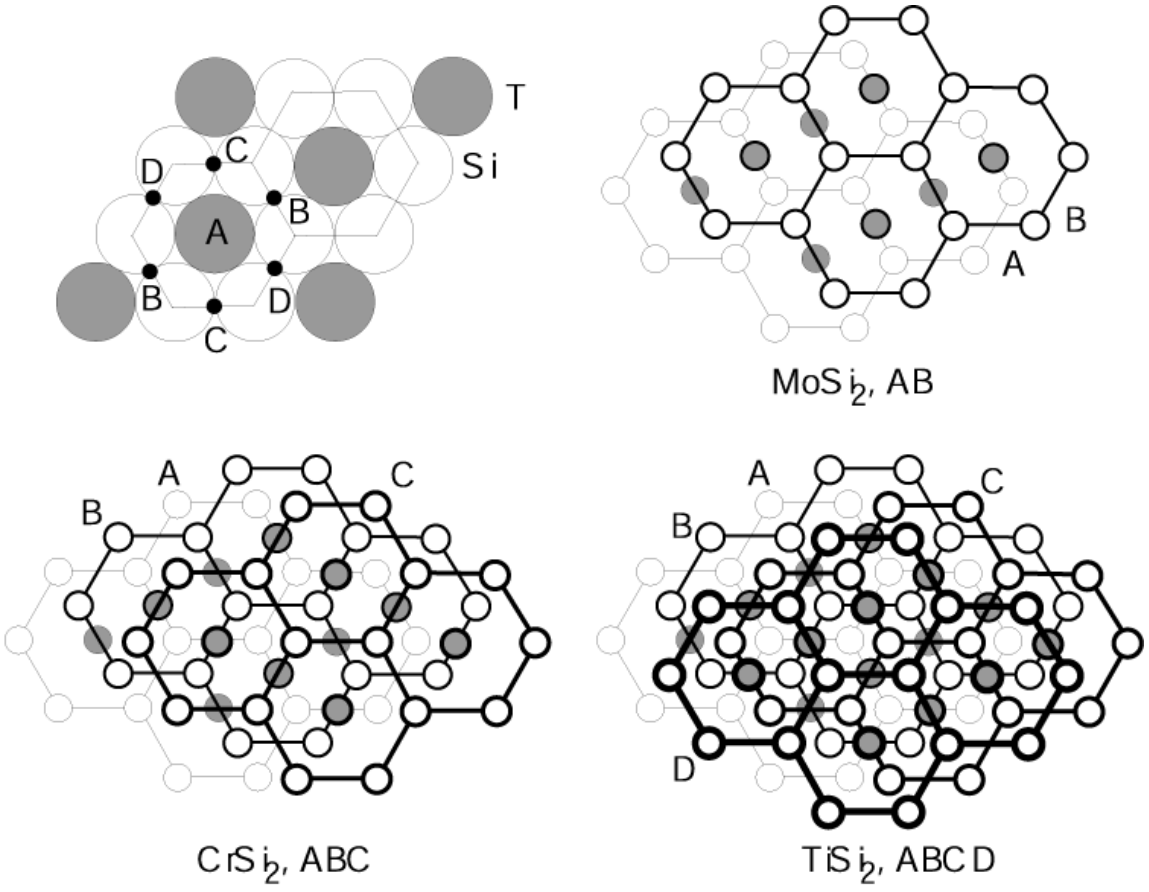


Fig. 5.7. Graphite-like silicon grids in disilicide structures [26]

As opposed to borides, silicides with a Si: *M* ratio greater than 3:1, similar to MB_4, MB_6, MB_{12}, do not exist. Free silicon is in direct equilibrium with disilicide; its diamond-like structure can be found in some silicides.

Silicides with the highest content of silicon form metals of VIII group (trisilicyls MSi_3). There is one interesting feature of such silicides: with the increase in the group number of metal the distance metal–silicon tends to decrease.

In this way, the *M*–Si bond can vary widely. Although, there is a tendency to reduce the distance Si–Si in silicides. In some cases this distance is shorter than the elemental silicon distance. So, the silicides are significantly different from carbides and nitrides, in which, on the contrary, C–C and N–N distances increase.

The ability of the lattice of silicides to produce defects is lower than borides – a circumstance that strongly influences their properties and determines the nature of their application, for example for protective coatings.

Although for platinum group metals silicides still exist (unlike carbides), but for the elements at the end of each transition period, they are not formed: Ag and Au with silicon form only simple eutectics. However, copper forms a lower silicide ~ Cu_5Si with silicon; it has three modifications, which are variants of a hexagonal close-packed structure.

5.4. Overview of silicides basic properties

Transition metal silicides have some physical and chemical properties similar to carbides, nitrides, and especially borides. They are metal compounds of high electrical conductivity and go into superconducting state at low temperatures [20], [21], [23].

Most transition metal disilicides have a metallic conductivity type.

The electrical resistance of silicides is 1,8–4,0 times higher than that of the corresponding metals; the $NbSi_2$ electrical resistance, for example, is 1,8 times higher than the niobium electrical resistance, for $ZnSi_2$ and Zn this ratio is 3,94. VSi_2 electrical resistance alone is 0,52 of vanadium electrical resistance.

The higher electrical resistance of the silicides compared to the electrical resistance of the corresponding metals can be explained by the formation of covalent bonds between the silicon atoms. The metallic nature of the silicides is weakened by the decrease in the defectivity of the *d*-levels of the transition metal atoms, that is, by the increase in the atomic numbers of the metals in the transition groups and periods.

The ideal electrical resistance of $TiSi_2$, $ZnSi_2$, VSi_2, $NbSi_2$, $MoSi_2$ increases with increasing temperature, which is characteristic of metal semiconductors with degenerate carriers.

The melting point of silicides is much lower than the melting point of other refractory compounds.

The micro-hardness of silicides is also less than that of other refractory compounds.

Silicides have a high creep resistance. This power of silicides can be improved by the introduction of small additives of carbon (0,1–0,3 %) and boron (up to 0,12 %).

Chemically, the silicides of this group are quite resistant to oxidation among all oxygen-free compounds (e. g. $MoSi_2$).

The chemical stability of transition metal silicides increases from lower to higher: $M_3Si \rightarrow M_5Si_3 \rightarrow MSi \rightarrow MSi_2$, which suggests that the weakest bond in transition metal silicides is the *M*–*M* bonds that prevail over the *M*–Si and Si bonds (M_3Si and M_2Si silicides are mostly absent). Strong *M*–Si and Si–Si bonds are responsible for the chemical resistance of the silicides. The decrease in the number of silicides with increasing order number of the transition metal indicates a decrease in the electron interaction between the atoms of the metal and silicon, and the weakening of the sp^3-hybridization.

An analysis of the nature of the interaction between silicon and the elements of the periodic system shows that the highest characteristics are found in silicon compounds with metals and non-metals, which are located to the left of silicon or in one group.

The properties of silicides also differ depending on the position of the metal in the periodic system.

Silicides are used for the manufacture of heaters of high-temperature furnaces. Silicide coatings are used to protect against oxidation of refractory metals. WSi_2, $MoSi_2$ compounds can be used to make blades and other gas turbine parts.

In the chemical industry, silicide products are used as a resistant to the action of chemical reagents – acids, melts, and salt solutions. A mixture of molybdenum and silicon is used for high-temperature soldering of ceramics with metals or metals with each other.

Control questions

1. Describe the structure of transition metal silicides.

2. Explain the nature of the silicides classification.

3. What elements of the periodic table form ionic covalent silicides with silicon?

4. What elements of the periodic table form metallic silicides with silicon?

5. What elements of the periodic table form covalent silicides with silicon?

6. What structural elements form silicon atoms in transition metal compounds?

7. In the example of compounds poor on silicon V_3Si, Mo_3Si tell about their structural types.

8. What structural types are characteristic of transition metal mono-silicides?

9. What are the structural types characteristic of transition metal disilicides?

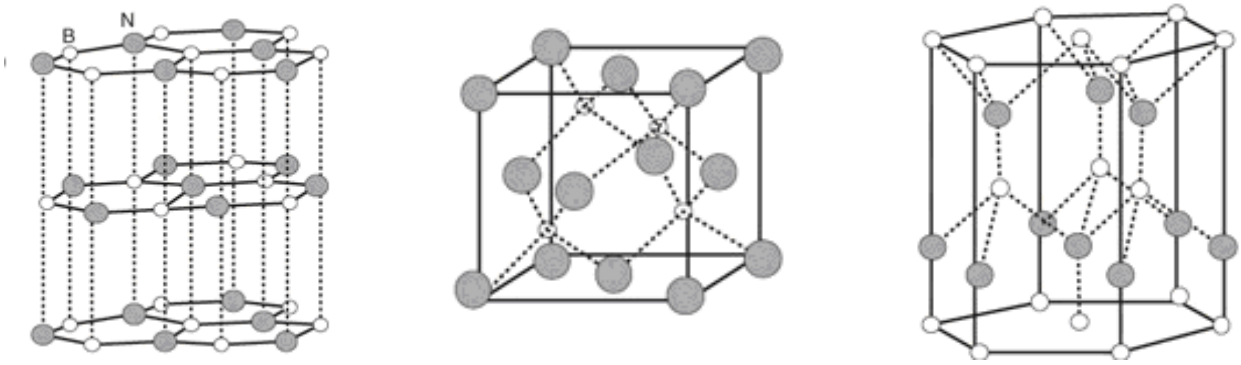
10. Discover the basic properties of metal silicides.

6. NON-METALLIC REFRACTORY COMPOUNDS

Non-metallic refractory compounds include carbides and boron nitrides, silicon, aluminum, boron silicide. These compounds melt incongruously at temperatures of 3000–3500 °C, are dielectrics or semiconductors with a wide band gap, their hardness ranges from low values for hexagonal boron nitride to values exceeding the hardness of all known materials (for boron carbide 50 *GPa*) .

6.1. Boron nitride

Boron nitride was discovered more than a hundred years ago by Balman. Three modifications of boron nitride are now known (Fig. 6.1) – α-BN (hexagonal), β-BN (cubic) and γ-BN (hexagonal close-packed) [27].



α-BN β-BN γ-BN

Fig. 6.1. Crystal structures of boron nitride modifications

α-BN has a hexagonal crystalline structure similar to that of graphite. It consists of graphite grids, unlike the graphite structure exactly below each other with alternation of boron and nitrogen atoms along the *Z* axis. Space group – *C*6*m2*. Due to the similarity of the structure and some of the physical properties of graphite and boron nitride, the latter is often called “white carbon-black” or “white graphite”.

β-BN has a cubic crystalline lattice similar to the diamond lattice, i. e. crystallized into structure of zinc blende – ZnS sphalerite.

The γ-BN has a hexagonal, close-packed lattice of wurtzite type.

α-BN hexagonal boron nitride. If we consider boron nitride from the point of aspiration of atoms in the formation of compounds to the most stable electronic configurations, we can assume that during the formation of hexagonal boron nitride boron atoms predominantly transmit valence *p*-electrons to the atoms of nitrogen, resulting in stiffening atoms of s^2, and the nitrogen atoms are s^2p^6. The presence of a certain (and high) statistical weight of the s^2p^6 configurations of the nitrogen atoms usually causes the ionic bond, and the energy separation of these configurations results in the presence of a wide energy gap and, as a consequence, the dielectric properties of boron nitride.

The distribution of electron density in α-BN is similar to that in graphite. Between the layers (grids), 15–16 % of all electrons are placed in the α-BN, which corresponds to two electrons from each pair of B–N atoms in the nitride (in graphite, one electron from each atom). This leads to the conclusion that there is an ionic bond between boron and nitrogen atoms in the grids and no metal bonding between the grids, unlike graphite.

The distance between the grids in the boron nitride lattice is 3,34 Å, which is less than in the graphite (3,40 Å). This indicates stronger bonding between the grids in the structure of boron nitride than graphite [27].

Hexagonal boron nitride is a typical semiconductor.

The relatively high thermal conductivity and features of the structure cause the high resistance of BN products to heat shock.

The exceptional fineness of the particles of boron nitride powder, along with its crystalline structure and low hardness (about 2 Mohs), determines its better lubricating properties than graphite and molybdenum sulfide.

An important property of boron nitride is its ability to luminescence.

Cubic boron nitride β-BN. Under the influence of high pressure, hexagonal boron nitride goes into cubic modification ("*borazon*") similar to the transition of hexagonal graphite into cubic diamond. Crystals of cubic boron nitride were obtained at high pressures (4,5–7,5 *GPa*) and temperatures (1200–2000 ºC) from a mixture of

hexagonal boron nitride and lithium or magnesium nitride (as catalysts) with the addition of some impurities. Impurities of 0,1–1 % Be in the form of metal or salt cause the formation of crystals of blue *p*-type cubic boron nitride. The conductivity type was set by thermo-electric power. Beryllium is thought to replace boron or nitrogen atoms in the cubic BN lattice. Elemental sulfur impurities lead to the formation of *n*-type borazon in a pale yellow color. Sulfur replaces nitrogen in borazon, as indicated by the existence of a BS compound with a cubic lattice formed at high temperatures and pressures.

The electronic scheme for the formation of borazon can be represented as follows: boron atoms having the isolated configuration of valence electrons s^2p, as a result of the $s \rightarrow p$ transition, acquire the sp^2 configuration, then due to the involvement of the easily moving electron of the nitrogen atom – the sp^3-configuration. The valence electrons of the nitrogen atom, respectively, undergo the following transformation: $s^2p^3 \rightarrow sp^4 \rightarrow sp^3 + p$ and, by transmitting one *p*-electron to boron, acquire the sp^3 configuration. Thus, a high statistical weight of atoms having a sp^3-configuration of localized valence electrons is created in borazon, which provides the cubic diamond-like structure of this compound. However, the statistical mobility of the electron of the nitrogen atom causes a slight decrease in the statistical weight of the sp^3 configurations of boron and nitrogen atoms, which in turn leads to less bonding energy, lower electrical resistance, a narrower band gap and less hardness of borazon compared to diamond. On the other hand, the smaller proportion of rigid, directional bonds in the borazon lattice causes a somewhat higher degree of freedom in the case of thermal excitation, a higher temperature of polymorphic conversion into hexagonal boron nitride. According to some estimates, it is 2000 °C, while for diamond it is approximately 900 °C. For the same reason, borazon has a higher heat resistance than diamond and a greater impact resistance due to the acquisition of a certain “plasticity” caused by the appearance of some statistical fraction of non-localized electrons [27].

The density of borazon is 3,45 g/cm^3, the lattice period a = 3,615 Å, the hardness is 70 *GPa*.

6.2. Silicon nitride

A study of the production conditions and properties of a compound of silicon with nitrogen, begun as early as 1844, revealed the presence of several chemical compounds in this system, which were attributed to the compositions SiN, Si_2N_3, Si_3N_4. Now, the existence of only one chemical compound, the silicon nitride Si_3N_4, has been clearly demonstrated in the silicon system [27].

Silicon nitride has three modifications – α-, β- and γ-Si_3N_4.

Alfa and β-Si_3N_4 modifications are hexagonal.

Both structures are constructed on Si_3N_4 tetrahedron (Fig. 6.2) and differ in the way of coupling of this tetrahedron (SiN_4 tetrahedron are almost correct).

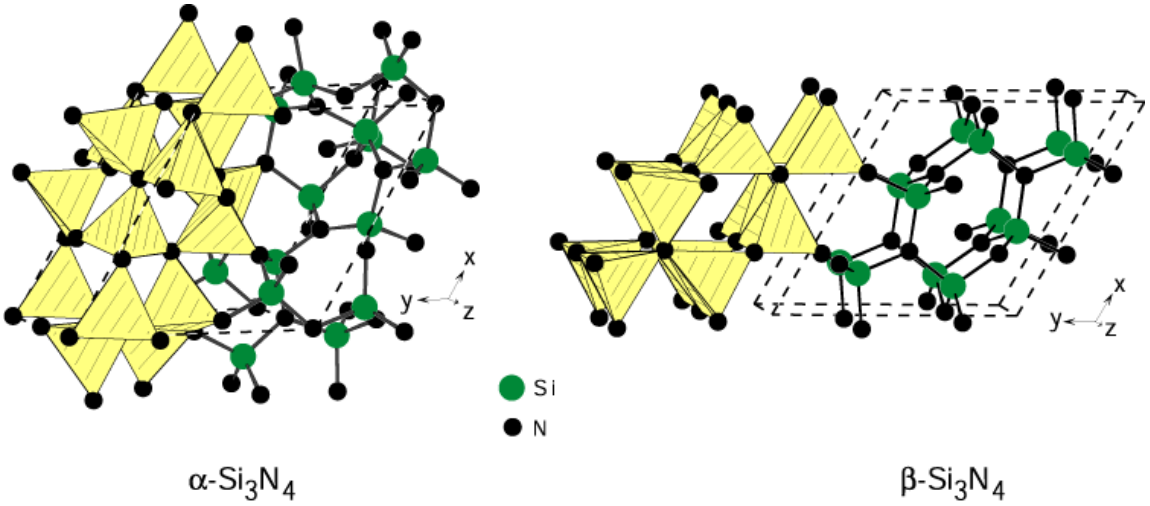


Fig. 6.2. α-Si_3N_4 and β-Si_3N_4 structures [28]

The structure of β-Si_3N_4 (space group $P6_3/m$) can be deduced from the structure of Be_2SiO_4 by the substitution of oxygen atoms and beryllium by nitrogen and silicon, respectively. Each silicon atom is located in the center of a slightly irregular tetrahedron of nitrogen atoms. The Si_3N_4 cell is joined by common angles such as each nitrogen atom is common to all tetrahedrons. Otherwise, the structure can be represented in the form of eight-membered Si_3N_4 rings, interconnected accordingly [27].

The structure of α-Si_3N_4 (space group *P31c*) is different from β-Si_3N_4: in the last plane they are connected along the (001) direction in the sequence ...*ABABAB*..., while in the α-Si_3N_4 lattice – in the sequence ...*ABCDABCD*….

The number of formula units in the unit cell of α-modification is four; and in β-modification – 2.

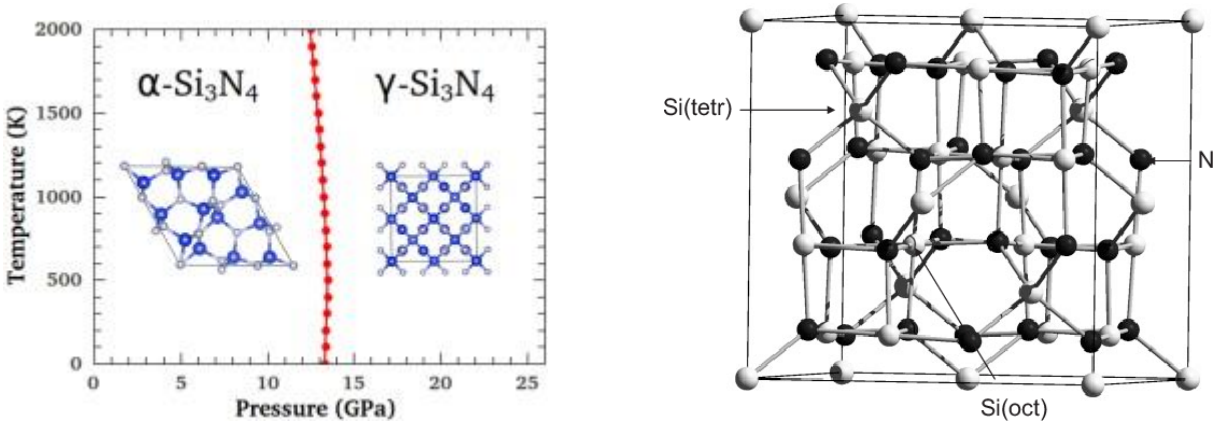
Nitrogen solubility in solid silicon is not well established, solubility in liquid silicon is 10^{19} *atoms*/*cm*^{3}.

γ-Si_3N_4 was first synthesized in *LH-DAC* (laser-heated diamond anvil cell) by the chemical reaction of elemental silicon with nitrogen at high pressures of around 15 *GPa* at temperatures around 2200 *K* [29]. The phase diagram (Fig. 6.3*a*) involving the alpha and *γ* polymorphic structures of Si_3N_4 is predicted within the approach of the quasiharmonic theory [30].

The γ-phase has spinel structure (cubic, space group $Fd\bar{3}m$, № 227, *a* = 7,80(8) Å), which is often designated as c-modification in the literature in analogy with the cubic modification of boron nitride (c-BN) [29]. It has a spinel-type structure in which two Si-atoms each coordinate six nitrogen atoms octahedrally, and one Si atom coordinates four nitrogen atoms tetrahedrally (Fig. 6.3*b*). The cubic-phase comprises of alternating SiN_4 tetrahedrons and SiN_6 octahedrons in 1:2 ratio, which are sequentially connected to one another at the N−corners in 3*D* extension. The sixfold coordination of Si with N results in a significantly closer atomic packing, associated with a density almost 26 % higher than that of the hexagonal phases [31].

The nitrogen atom and silicon in Si_3N_4 are coupled by covalent unsaturated bonds, the presence of which results from the fact that every fourth hybrid sp^3 orbit of the silicon atom is overlapped with the hybrid sp^2 orbit of the nitrogen atom. The covalent bond is evidenced by the high electrical resistance of the nitride – more than 10^{12} *Ohm·cm*.

Due to the strong covalent bonds between the atoms, the silicon nitride has a high hardness, a small value of the thermal expansion coefficient. The energy separation of the groups of atoms that make up it causes it to dissociate even before melting, like all other covalent nitrides that have non-metallic properties.



a *b*

Fig. 6.3. The phase diagram (*a*) involving the alpha and *γ* polymorphic structures of Si_3N_4 [30] and unit cell of γ-Si_3N_4 (*b*) [32]

One of the most important chemical properties is its exceptionally high chemical resistance. It is resistant to oxygen and oxidation by air. Silicon nitride is weakly reacts with chlorine.

Silion nitride has a fairly high resistance to molten metals [27].

6.3. Aluminum nitride

In 1862, the first paper on aluminum compounds with nitrogen was published. In fact, in all the works, only one compound was found, AlN, to which the formula Al_2N_2 was sometimes attributed.

Aluminum nitride crystallizes into a hexagonal lattice of the Wurtzite type (Fig. 6.4). Depending on the purity of the material, the lattice parameters have the values a = 3,10–3,13 Å, c = 4,93–4,98 Å [27].

Nitrogen is almost insoluble in aluminum.

Powdered aluminum nitride is usually white, single crystals watery white (transparent). The melting point is determined in the range of 2000–2500 °C. But aluminum nitride decomposes into components, not reaching the melting temperature; the temperature of the beginning of the decomposition depends on the conditions of determining the “melting temperature”.

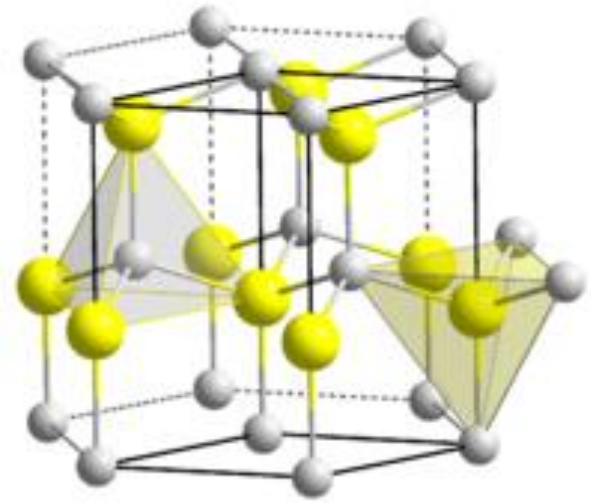


Fig. 6.4. AlN unit cell

Aluminum nitride is a typical dielectric with a large band gap and high electrical resistance (about 1020 *Ohm·cm*). The calculation of the electronic component of thermal conductivity shows that thermal conductivity occurs only due to the lattice oscillation. The mechanism of formation of a bond in aluminum nitride is as follows: one of the electrons of the nitrogen enters the aluminum atom with the formation of such electronic configurations – $Al^{-}\ 3s^2 3p^2$; $N^{+}\ 2s^2 2p^2$. In wurtzite-type compounds, each metal atom is surrounded by four non-metal atoms at equal distances from it along the vertices of the correct tetrahedron (in AlN the tetrahedron is slightly curved). Thus, each atom has four equal bonds, each of which is made by *s*- and *p*-electrons coming from one of each atom. Such covalent bonds, which are strengthened by the ionic bonds superimposed on them, cause a high rigidity of the lattice. This determines the low value of the coefficient of thermal expansion, the high values of the modulus of normal elasticity, the characteristic temperature and the photonic component of thermal conductivity.

This scheme seems to be generally correct, but given the *s*–*p* junctions, it must be taken into account that the configuration of part of the aluminum and nitrogen atoms is of the form sp^3. In addition, along with the electron transition from the nitrogen atom to the aluminum atom, the valence electrons transition from part of the

aluminum atoms to the nitrogen atoms, with the formation of Al $2s^2 2p^6$ and N $2s^2 2p^6$ configurations, this causes the presence of an ionic bond in aluminum nitride [27].

The structure of AlN differs from the ideal structure of wurtzite, since the ratio of *c*/*a* is equal to 1,600 instead of 1,633. Compression of the tetrahedron along the *OZ* axis in the AlN structure leads to some distortion of the correct tetrahedral arrangement of the Al–N bonds.

Unlike isostructural SiC and ZnS, poly-type structures were not established for aluminum nitride by *X*-ray diffraction analysis.

The strength of aluminum nitride at high temperatures (about 1400 °C) can be compared with the strength of oxide ceramics at ordinary temperature.

6.4. Boron carbide

For the first time, boron-carbon compound was obtained by Moissan in 1899 by fusion in an electric arc furnace of boron anhydride with sugar coke.

Initially, boron carbide was attributed to various compounds: BC, B_2C_2, B_3C, B_4C, B_6C. In 1939, it was found that there was only boron carbide of formula B_4C, which melts with decomposition and is formed at temperatures of 2250 ºC, by the peritectic reaction between boron and carbon-rich liquid phase. The structure of B_4C boron carbide has a rhombohedra crystalline lattice with a period a = 5,60 Å, c =12,1 Å (Fig. 6.5). It is a dark gray (almost black) crystalline powder. A hardness of 50 *GPa*, boron carbide is second only to diamond [33].

For boron carbide, part of the carbon atoms of boron may be substituted with boron atoms, with the structure $B_{12}C_3$ (=B_4C) converted to $B_{13}C_2$ (=$B_{6,5}C$). This carbide is formed by diffusion substitution and is prone to decay into boron and B_4C:

$$3B_{13}C_2 = 2B_{12}C_3 + 15B,$$

and more solid and resistant to chemical agents than B_4C.

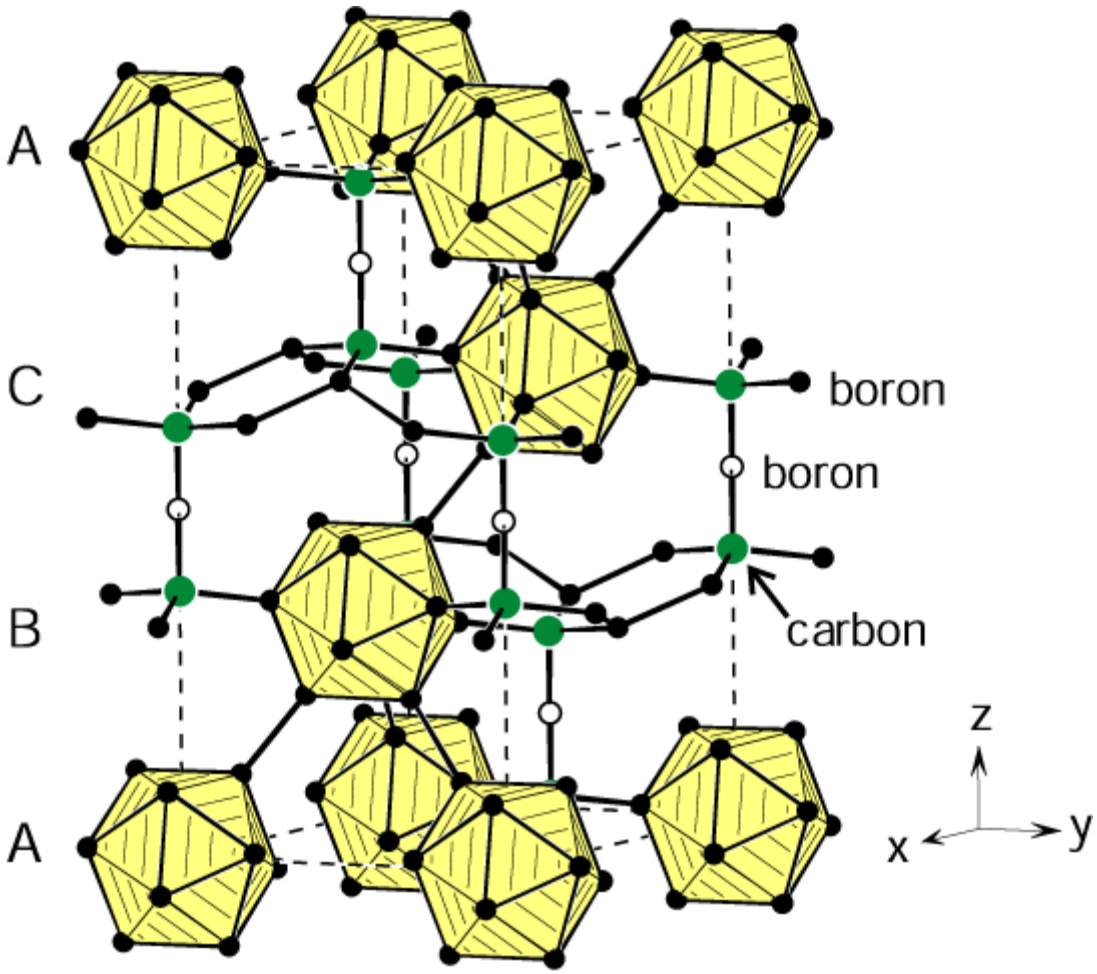


Fig. 6.5. Boron carbide structure [34]

Boron carbide is a semiconductor with a band gap from 2,5 *eV* to 1 *eV*. Its electrical resistance is higher than that of silicon carbide and silicon nitride. The nature of the change in electrical resistance with increasing carbon content in the alloys has suggested such a crystal-chemical picture. The electrical resistance of pure boron is very large, which is explained by the complete compensation of the bonds of atoms in the crystalline boron lattice. Addition to the boron of carbon in an amount exceeding the limit of its solubility in the boron leads to the rearrangement of the lattice of the latter in the lattice of boron carbide. However, not all the vacancies of the carbohydrate atoms in the –C–C–C– chain are filled, i. e. bond decompensation occur and perforated-conductivity occurs. Further increasing the carbon content of the alloys will fill the vacancies in the chain –C–C–C– and establish the covalent bonds inherent in the boron carbide lattice. This causes a decrease in electrical conductivity. Its smallest value is the completion of the B_4C direct bonding process.

Adding carbon to boron in the amount of 2–3 % leads to the formation of eutectic boron or a solid solution in it carbon with boron carbide $B_{13}C_2$, this has a defective lattice, i. e. vacancies on the line –C–C–C– boron carbide $B_{13}C_2$.

With increasing carbon content, these vacancies are further filled up to the boron content corresponding to carbide $B_{13}C_2$. The latter is capable of forming solid carbon substitution solutions and thus converting to carbide $B_{13}C_2$, i. e. instead of the line –C–B–C– the line –C–C–C– appears. The transition from composition $B_{13}C_2$ to $B_{12}C_3$ is continuous, as evidenced by the wide homogeneity range from 5 parts by weight to 24 parts by weight of the carbide phase carbon.

The $B_{13}C_2$ phase, which structure is characterized by a linear chain –C–B–C–, has electronic conductivity, and the B_4C phase with the chain –C–C–C– is a hole-semiconductor [33].

Boron carbide is used as an abrasive material for grinding, sharpening and finishing.

High thermal-electric power of boron-carbon alloys in combination with their relatively high melting points, heat resistance and chemical resistance is of technical use in high-temperature semiconductor devices, including semiconductor thermocouples, neutron absorbers.

6.5. Silicon carbide

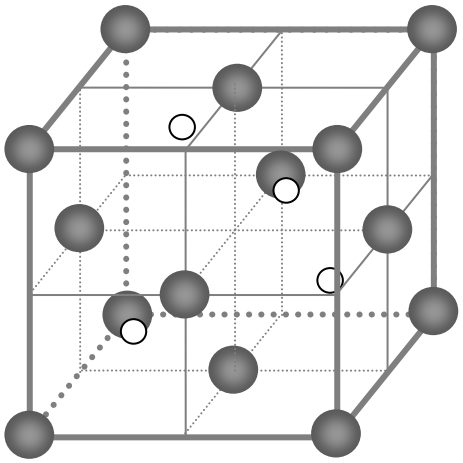
So far, the crystalline structure of SiC has been thoroughly investigated due to the fact that this compound has modifications which, under certain conditions, pass into each other. Chemically pure silicon carbide is colorless and technical – greenish or blue-black.

Silicon carbide has two polymorphic modifications – β-SiC and α-SiC.

β-SiC is a cubic modification of the sphalerite type (Fig. 6.6), α-SiC is hexagonal. Modifications of silicon carbide differ in thermodynamic stability. The formation of a certain modification is due to the presence of a certain degree of tension in the system. This tension arises from the presence of impurities adsorbed by

the surface of the growing crystals; the degree of super-saturation of the medium during crystallization; thermal stresses during crystal growth at high temperatures.

The cubic form of silicon carbide is more stable up to a temperature of 2100 °C. At temperatures above 2093 °C, the cubic β-SiC transforms into α-SiC with a hexagonal structure. Initially, this process is slow, but at a temperature of 2400 °C it quickly passes through. Impurities of 0,2 % Al stabilize high temperature modifications of silicon carbide [33].



– silicon; ○ – carbon

Fig. 6.6. β-SiC unit cell

Hexagonal silicon carbide with the $P6_3/mc$ space group has a large number of poly-types. Poly-types are structures that are constructed of identical layers with different sequences of alternation. The lattice parameters in the poly-types in the plane of the layer are unchanged, and in the direction perpendicular to the layers differ, but always multiple of the distances between the nearest layers.

The most common is a six-layer silicon carbide package …*B ABCACB ABCACB ABCACB A*… (Fig. 6.7). The lattice parameters are: $a = b$ = 3,078 Å, $c = 6 \cdot 2{,}518$ Å. In addition to the six-layer packaging, there are poly-type modifications in which the same layers have different packing, leaving cell a and b unchanged, and parameter c acquiring *nc* values, where n is the period of identity of the alternation of layers in the structure. Known poly-types, in which n = 2, 4, 6, 15,

21, 33, 51 and further up to n = 192, 270, 400, 594 and even 1200, that is, with various alternation of layers and with giant elementary cells, where c = 1500 Å for the 594*R* poly-type [35].

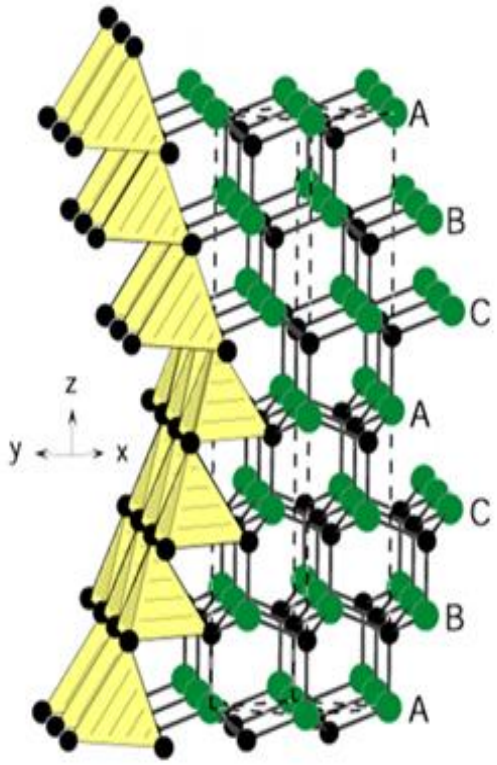


Fig. 6.7. Crystal structure of poly-type 6*H* α-SiC [36]

Poly-types are characterized by a number indicating the number of layers in a unit cell and a letter defining the type of lattice: *nH* means a structure with a period of recurrence of layers *n* along the *OZ* axis and a primitive hexagonal cell; *nR* is a structure with a period of recurrence of layers *n* along the *OZ* axis and a primitive rhombohedra cell.

The most common silicon carbide poly-types are 6*H*, 4*H*, and 15*H* (…*B ABCBACABABACBCACB ABCBACABABACBCACB A*…). Altogether, more than 50 poly-type modifications have been found for silicon carbide.

Silicon carbide is a semiconductor with electrical resistance that occupies an intermediate position between the electrical resistances of metal conductors and insulators.

The formation of ion film of SiO oxide on the surface of the silicon carbide determines its rectifying effect, as well as a negative temperature coefficient of resistance and photocurrent.

The chemical resistance of silicon carbide is very high. It decomposes only with a mixture of nitric and hydrofluoric acids, as well as phosphoric acid. However, silicon carbide is easily decomposed by molten alkalis to form silicates.

Silicon carbide is widely used as a heat-resistant material. It is made of bricks and plates for lining, heaters of electric resistance for high-temperature furnaces. Silicon carbide powder is used as an abrasive material, and single crystals are used to produce detectors.

Silicon carbide is made of small-sized non-linear supports, as well as magnetron igniters with high mechanical strength.

Silicon carbide is used as acid-resistant material in the chemical industry and in laboratory practice.

6.6. Boron silicide

For the first time to obtain the SiB_3 and SiB_6 phases, Moissan and Stock were able to melt silicon and boron in 1900. Compounds such as Si_2B (β), SiB_3, SiB_4, SiB_6 та SiB_n (n =10–14) were found in the boron–silicon system. The SiB_4 and SiB_6 phases are now considered to be well established.

SiB_4 has a rhombohedra lattice with increasing boron content in which the parameters increase – a = 7,132–7,203 Å, c = 4,026–4,089 Å [33].

SiB_6 has a cubic lattice with the space group $Pm3m$, as in hexaborides of alkali and rare earth metals (Fig. 4.9). The lattice parameter with boron content in this compound decreases – a = 4,1333–4,1292 Å. The density of this compound is less than the density of silicon and boron ($\gamma_{X\text{-ray}}$= 2,18 kg/cm^3, γ_{pix} = 2,15 kg/cm^3).

The density of the formed Si–B solid solution increases and the lattice period decreases with increasing boron concentration, i. e. dissolution of boron in silicon causes lattice compression. If a solid solution of boron substitution in silicon were

formed, then the density of the solution, which is not observed, would have to decrease. Obviously, boron dissolution is not due to the substitution of silicon atoms, but to the filling of the lattice defects.

Addition from 0,01 % to 1,0 % boron to silicon causes a perforated-conductivity. The maximum mobility of current carriers is achieved at concentrations of boron in silicon from 0,0005 % to 0,001 %, which is explained by the "correction" of the silicon lattice by small impurities of boron. Each boron atom in the solid solution gives one electron to the conduction band, leaving behind one hole.

The semiconductor properties of a solid boron solution in silicon have been used in the creation of solar cells, the photocells used to convert solar energy into electrical energy. The solar battery consists of a series of thin plates of pure silicon, each slightly longer and narrower than the razor blade. A thin layer of boron (1–10 *microns*) is applied to the plates. The layer that occurs at the point of contact has one-way conductivity (*p–n* transformation). In the case of irradiation of such an element by photons (sunlight, *X*-rays, light of an electric lamp), an electron transition occurs at the point of contact, and a current can be obtained in the external circuit of the photocell.

Chemically, boron silicides are quite stable. Oxidation of air with oxygen is difficult and only at relatively high temperatures. Therefore, boron silicides are used in the composition of heat-resistant and refractory metal–ceramic alloys – cermets. Boron silica-based refractories can be used up to 1550 °C [33].

The high boron content of SiB_4 and SiB_6 compounds allows them to be used as nuclear materials for the manufacture of control rods and protective means in nuclear reactors.

Control questions

1. Describe the structural types and basic properties of boron nitride.
2. Describe the structural types and basic properties of aluminum nitride.
3. Describe the structural types and basic properties of boron carbide.

4. Describe the structural types and basic properties of silicon nitride.
5. Describe the structural types and basic properties of silicon carbide.
6. Describe the structural types and basic properties of silicon boride.

7. ANALYTICAL DESCRIPTION OF CRYSTAL STRUCTURES

Practical work № 1. Unit cells of crystal structure description

The aim of the work – distinguish the unit cell in the crystal structure, to identify its type, coordinate numbers and coordinate polyhedron and the numbers of structural and formulaic units.

Theoretical information

The whole variety of crystalline structures is described by 14 Bravais cells (lattices), differing by shape and symmetry.

To identify the Bravais unit cell, it is necessary to find the 3 shortest and non-coplanar translations *a*, *b*, *c*, started and ended at the same node type (atoms, ions, etc.). Then check whether it is possible to build a Bravais cell on them, fulfilling 3 basic conditions:

a) the symmetry of the cell corresponds to the symmetry of the crystal;

b) the unit cell must have the maximum number of right angles;

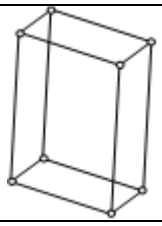
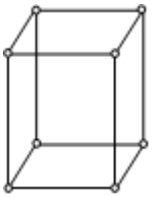
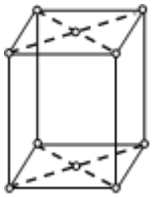
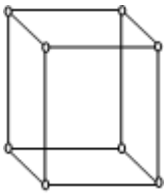
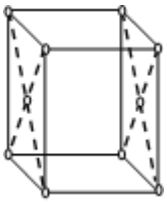
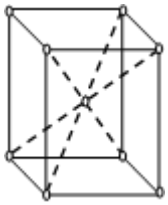
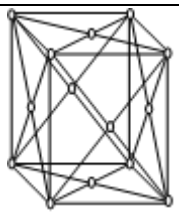
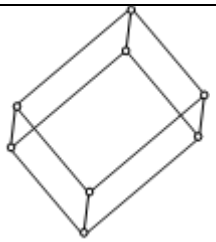
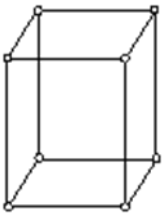
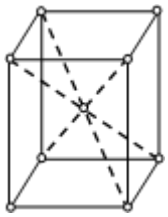
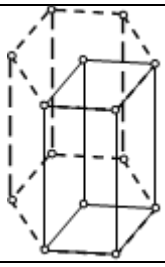
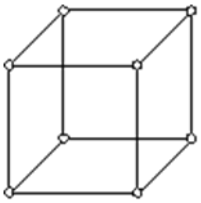
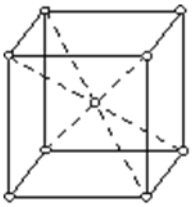
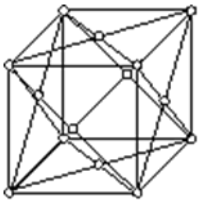
c) the unit cell must have the smallest volume.

According to the nature of the mutual arrangement of the main transmissions or the location of the nodes, all crystal lattices are divided, according to Bravais, into four main types:

- primitive (*P*);
- base-centered (*A*, *B*, *C*);
- body-centered (*I*);
- face-centered (*F*) [35].

Primitive cells, which have nodes only at the vertices of the cell, are characteristic of all syngonies and give a coordinate system, most convenient for describing the structure and properties of the crystal. However, in some cases it is more convenient to choose a cell that is not primitive. Additional translations must be detected to determine the type of Bravais cell. The list of all Bravais cells and their distribution by syngonies is given in Table 7.1.

Table 7.1. Distribution of Bravais cells by syngonies [37]

Syngony, axes units	Bravais cell types			
	Primitive *P*	Base-centered *A, B, C*	Body-centered *I*	Face-centered *F*
1	*2*	*3*	*4*	*5*
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$				
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$				
Rhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$				
Trigonal (rhombohedral) $a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$				
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$				
Hexagonal $a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$				
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90°$				

All four basic types of Bravais cells are found only in rhombic structures. The absence of some types in other syngonies is due to the feature of symmetry allowed to choose another type of Bravais cell that best meets the three basic conditions.

An important characteristic of the unit cell of matter is *the number of structural units* (*n. s. u.*), i. e. the number of atoms per cell [35].

Determining the number of structural units, it is necessary to take into account that the unit cell geometrically represents a parallelepiped, and atoms or ions – spheres. Therefore, the position of the atom in the unit cell determines which part of the sphere belongs to the selected cell. Considering, for example, the chlorine ion in the NaCl structure (Fig. 7.1) located at the top of the unit cell, which belongs to the cubic syngony, where 8 cells converge simultaneously, then one cell will belong to only 1/8 of this ion. If the sodium ion is on the rib, then it belongs to four cells at the same time and the fraction of its contribution is 1/4. The chlorine ion located on the face of the unit cell belongs to two cells and therefore each of them has 1/2 atom. Only the atoms in the middle of the cell belong to it completely.

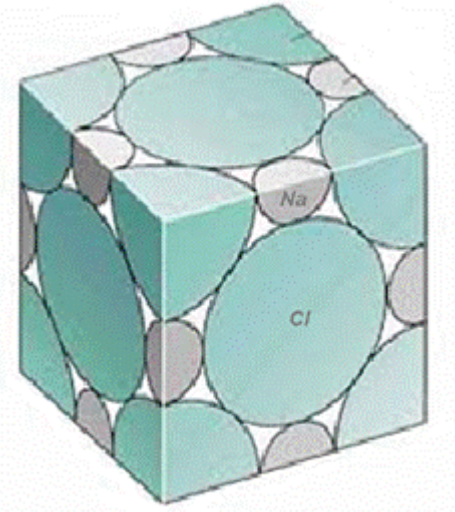


Fig. 7.1. NaCl unit cell

Thus, determining the number of structural units, it is necessary to multiply part of the contribution of each atom by their number and add the results. The number of structural units is usually expressed as an integer.

The number of formula units (*n. f. u.*) is the number of formulas (molecules) of a given compound per unit cell, which is determined by the number of structural units in the unit cell of heterogeneous atoms that form the compound [35].

The coordination number determines the number of adjacent atoms or ions of the crystal structure closest to the atom or ion. If the centers of these nearest atoms or ions are connected by straight lines, a *coordination polyhedron* is formed. The atom for which the coordination polyhedron is built is in its center. To determine the coordination numbers and coordination polyhedrons the elementary cellis not enough, we must consider the structure as a whole. Coordination numbers in most crystal structures correspond to specific coordination polyhedrons: 2 – dumbbell; 3 – triangle; 4 – tetrahedron or trigonal pyramid; 6 – octahedron, tetragonal dipyramid or trigonal prism; 8 – cube or tetragonal prism; 12 –cuboctahedron or hexagonal prism [35].

The shape of the coordination polyhedron has nothing in common with and does not correspond to the external shape of the crystal.

Determining the coordination numbers of layered structures, it is necessary to take into account the nearest neighbors in the layer and in the adjacent layers. Thus, in the structure of graphite, each atom in a layer is surrounded by three atoms, but their environment is surrounded by atoms from adjacent layers. In one case, there are 2 atoms at the closest distance, and therefore the coordination numbers are 3 and 2, respectively; in the second – 12, then the coordination numbers 3 and 12.

Consideration of structures consisting of two or more types of atoms requires the determination of coordination numbers and coordination polyhedrons, both for the same atoms and for atoms of different types.

Work performance

1. Using computer or visual models of the main types of crystal structures select and represent a unit cell.

2. Identify and record the syngony and the type of Bravais cell.

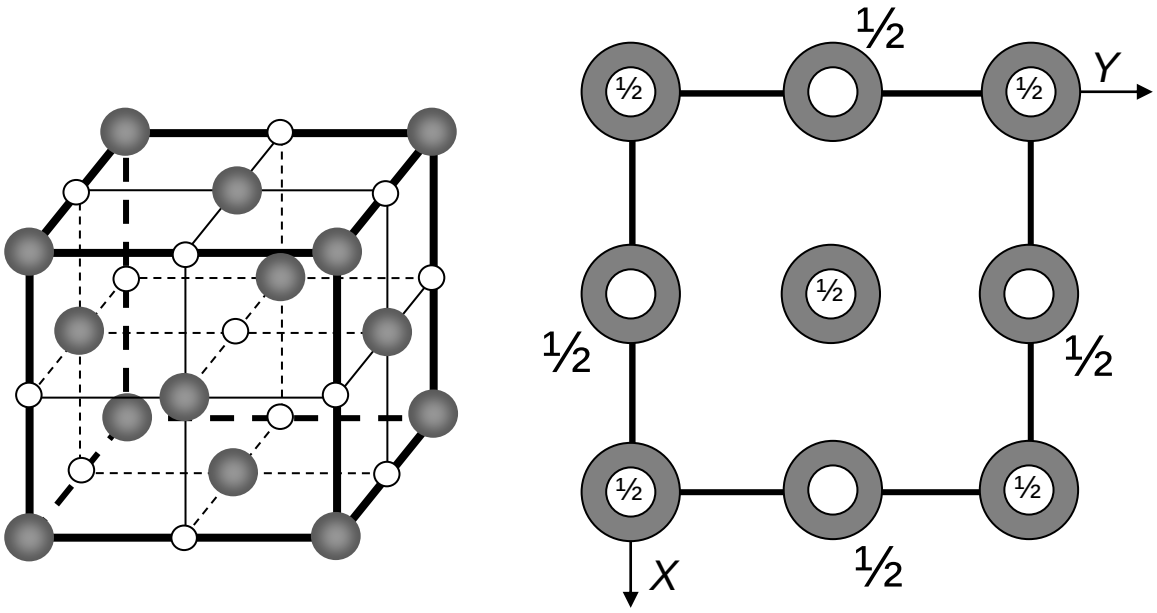
3. Design a unit cell on the plane (001).

4. Determine and record the number of structural units, and for chemical compounds − the numbers of structural units for each element of the compound and the number of formula units.

5. Define and write coordination numbers and coordination polyhedrons.

Example of task performance

Lead sulfide PbS is an ionic compound in which sulfur anions are structure-forming and lead cations occupy the cavities between them. The PbS structure belongs to the cubic syngony, as $a = b = c$, $\alpha = \beta = \gamma = 90°$, the unit cell is face-centered, because sulfur anions are located at the vertices of the cell and in the center of each face. The ions of lead occupy positions in the middle of the cell edges and in its center. The unit cell is shown in Fig. 7.2*a*, the projection of the unit cell on the plane (001) is shown in Fig. 7.2*b*.



a *b*

a –unit cells of the PbS structure;

b – projection on the plane (001) of the unit cell of the PbS structure

Fig. 7.2. Example of task performance

Hence

$$n.\ s.\ u.^{S} = 1/8 \cdot 8 + 1/2 \cdot 6 = 4;$$

$$n.\ s.\ u.^{Pb} = 1/4 \cdot 12 + 1 = 4;$$

$$n.\ f.\ u.^{PbS} = \quad 4S + 4Pb = 4PbS.$$

Since the compound PbS includes two elements, it is necessary to determine four coordination numbers and, accordingly, four coordination polyhedrons:

$$c.\ n.^{Pb–Pb} = 12 – \text{cubic octahedron};$$

$$c.\ n.^{Pb–S} = 6 – \text{octahedron};$$

$$c.\ n.^{S–Pb} = 6 – \text{octahedron};$$

$$c.\ n^{\cdot\ S–S} = 12 – \text{cubic octahedron}.$$

Control questions

1. What requirements must be met choosing a Bravais unit cell?
2. Which of Bravais's requirements for choosing a unit cell is the most important?
3. Why is there only a primitive cell in a triclinic syngony?
4. What is the number of structural units?
5. What should be considered determining the number of structural units?
6. What is the number of formula units?
7. How is the number of formula units determined?
8. What is a coordination number?
9. How many coordination numbers need to be determined for a compound of three elements?
10. What are coordination polyhedrons?
11. How is the shape of the coordination polyhedron related to the external shape of the crystal?

Practical work № 2. Symmetry elements of crystal structures

The aim of the work is to learn to determine the location of simple and complex elements of symmetry in the unit cell of the crystal structure.

Theoretical information

The main property of the construction of the crystal structure is the periodic and regular arrangement of elementary particles in space. The space lattice allows us to reproduce this pattern in the form of a geometric scheme built on three non-coplanar vectors – elementary translations. But the translation is not only the shortest of the possible distances between the same points in the structure, but also an element of symmetry, which corresponds to the symmetric transformation (operation) *transfer by the value of the translation* [35]. The interaction of the translation operation with a mirror image or with a rotation at a certain angle leads to the formation of complex elements of symmetry (of the second kind): the planes of sliding reflection and helical axes, which are unique to crystalline structures.

Thus, in crystal structures the number of symmetry elements increases significantly in comparison with crystalline polyhedrons, because in addition to the planes of mirror reflection, rotary and inversion axes of symmetry, they have sliding reflection planes and helical axes of symmetry.

The planes of sliding reflection, as mentioned above, are formed as a result of successive operations of symmetry – mirror reflection and translational transfer along the plane. Depending on the part of the translation period, the value of which is transferred, the planes of sliding reflection are divided into the following types:

- *a, b, c* type;
- *n* type (wedge plane);
- *d* type (diamond) [35].

Sliding mapping planes of *a, b, c* type are included in the first group of planes for which sliding occurs on 1/2 of the translation. Depending on which coordinate axis *OX*, *OY* or *OZ* slides, i. e. on *a*/2, *b*/2 or *c*/2, the planes are marked as *a, b* or *c*,

respectively. The symbols of the sliding mapping planes of *a* and *b* type are a dashed line, and the planes of *c* type – a dotted line (Table 7.2).

Table 7.2. Symbols of sliding reflection planes [37]

№	Plane name	The sliding component in fractions of main translations						Plane symbols perpendicular to the plane of projection
		a/2	*b*/2	*c*/2	*a*/4	*b*/4	*c*/4	
1	*a*	+						
2	*b*		+					
3	*c*			+				
4	*n*	+	+					
5	*n*	+		+				
6	*n*		+	+				
7	*n*	+	+	+				
8	*d*				+	+		
9	*d*				+		+	
10	*d*					+	+	
11	*d*				+	+	+	

This type of plane can be found in structures having face-centered unit cells, for example, the structure of γ-iron, the projection of which on the plane (001) is shown in Fig. 7.3.

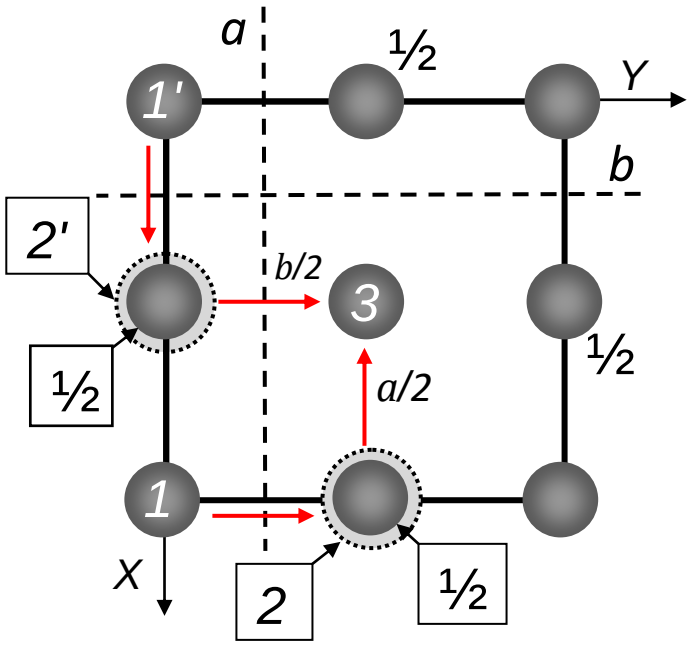


Fig. 7.3. The move of sliding mapping planes of type *a* and *b*

An iron atom *1* will align with another iron atom *3* if it is mapped in the *a* plane and moved atom *2* along this plane by half of the translation *a*/2 along the *OX* axis. The plane *b* acts similarly (Fig. 7.3).

Another plane of the sliding reflection of *c* type is perpendicular to the plane of the drawing, and sliding in it occurs along the axis *OZ* (Fig. 7.4).

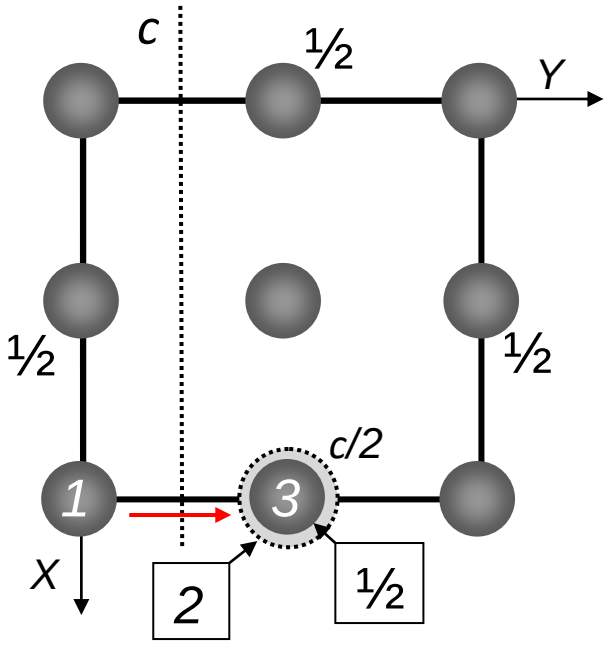


Fig. 7.4. The action of the plane of the *c* type sliding reflection

The second group includes planes of sliding reflection of *n* and *d* type, which have two or three components of sliding.

The sliding reflection planes of *n* type have a sliding component directed along the diagonal of the parallelogram, built on elementary translations lying in this plane, and is equal to 1/2 the length of the diagonal (Fig. 7.5).

The diagonal forms an oblique angle with coordinate axes. Here the name of such planes of sliding reflection – *wedge planes*. The symbol for planes of *n* type is a dashed line (Table 7.2).

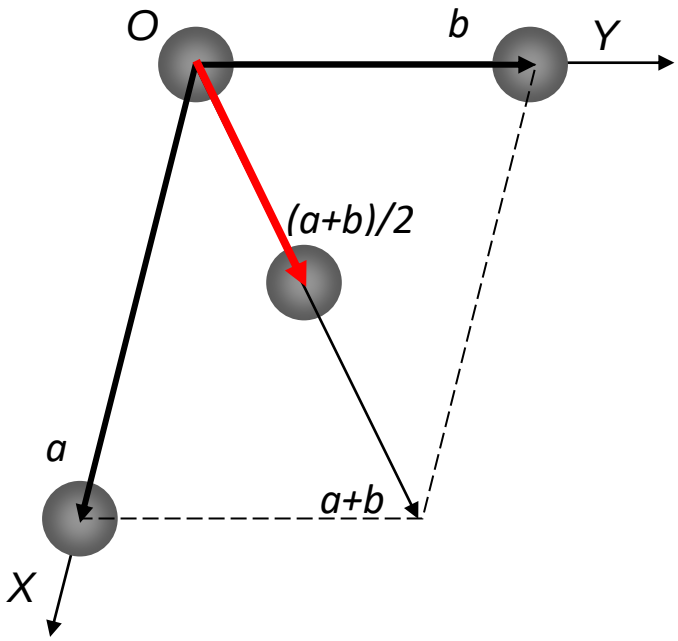


Fig. 7.5. Sliding component of the sliding reflection plane of *n* type

The *n* type planes are found in a body-centered cubic lattice, such as an α-iron cell. Its projection on the plane (001) is shown in Fig. 7.6.

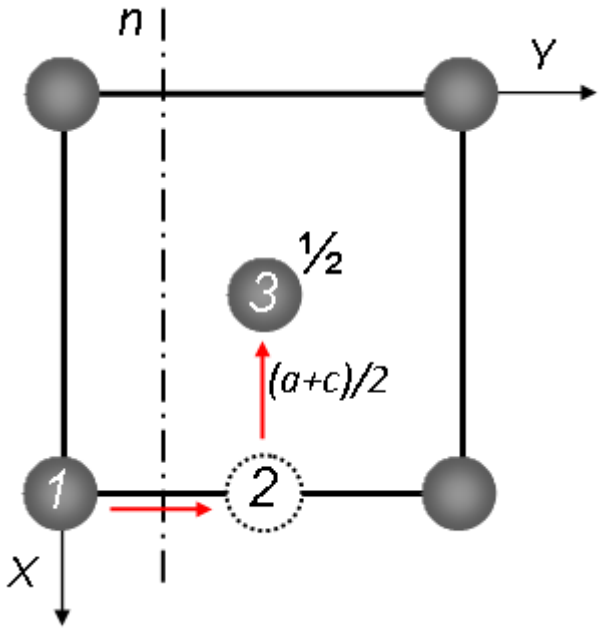


Fig. 7.6. The action of the *n* type sliding plane

The atoms at the vertices of the cell will be in the projection plane, and the atom in the center of the cell will be above the projection plane at a distance of *c*/2.

The *1* atom can be combined with *3* atom if the *1* atom is reflected in the *n* plane, which is in a quarter of the translation (*a*/4) and then 2 moves along this plane by the amount of slip equal to (*a* + *c*)/2 or (*b* + *c*)/2.

Lanes of sliding reflection of *d* type are called "*diamond*" (Fig. 7.7). They are characteristic of face-centered lattices and located parallel to the faces of the unit cell in the middle between adjacent vertical atomic planes. The sliding components for this type of plane are (*a* + *c*)/4, (*b* + *c*)/4 and (*a* + *b*)/4. The symbol for planes of *d* type is a dashed line with an arrow indicating the direction of movement (Table 7.2).

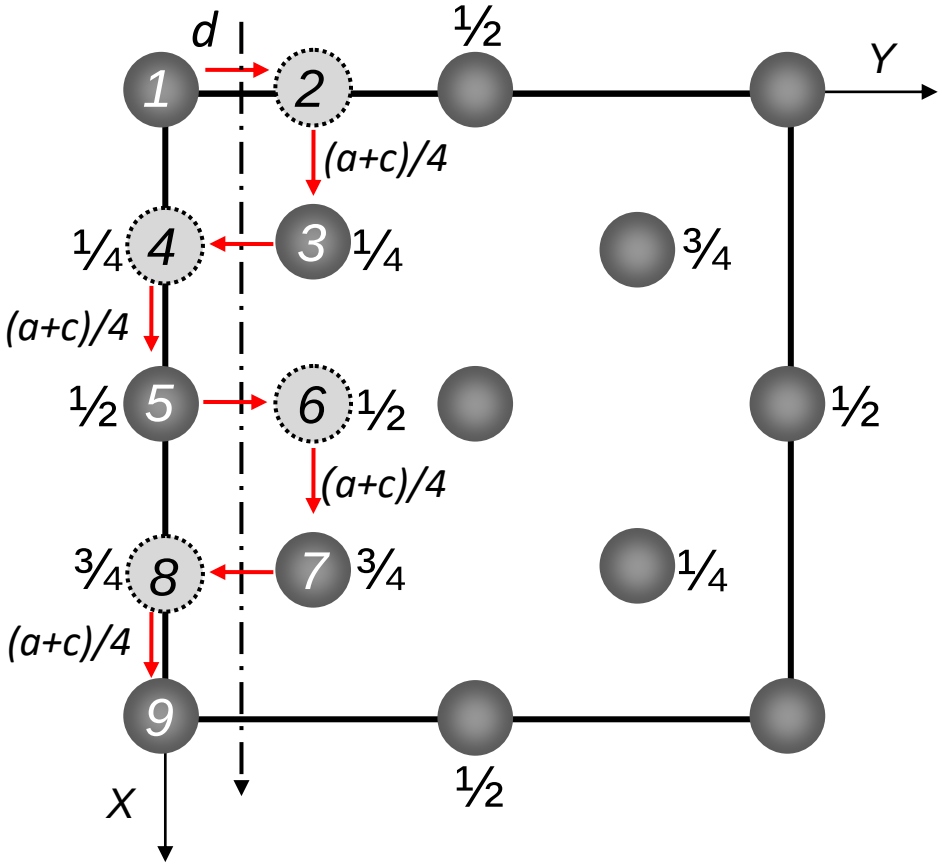


Fig. 7.7. The action of the sliding plane of *d* type

The *helical axes of symmetry* are formed as a result of successive operations of symmetry – rotation by a certain elementary angle α and translational transfer along the axis [35]. Depending on the part of the translation period to which the transfer takes place, the helical axes of symmetry are of the second, third, fourth and sixth orders.

There are *right* and *left helical axes*. In the case of the *right helical axis*, the movement along the axis is rotated clockwise, and in the case of the *left* – counter clockwise.

The helical axes of symmetry are indicated by an international symbol consisting of two digits, for example 4_1. A large digit indicates the order of the axis. The fraction of the division of the figure in the index (*1*) by the major (*4*), i. e. 1/4, gives the amount of transfer along the axis, expressed through the elementary translation on this axis. The transfer vector is also called the move of the helical axis. Some helical axes are equivalent. For example, the fourth-order helical axes, which are placed in the face-centered diamond, cell (Fig. 7.8). The right axis 4_3 is equivalent to the left axis 4_1, just as the left 4_3 to the right axis 4_1.

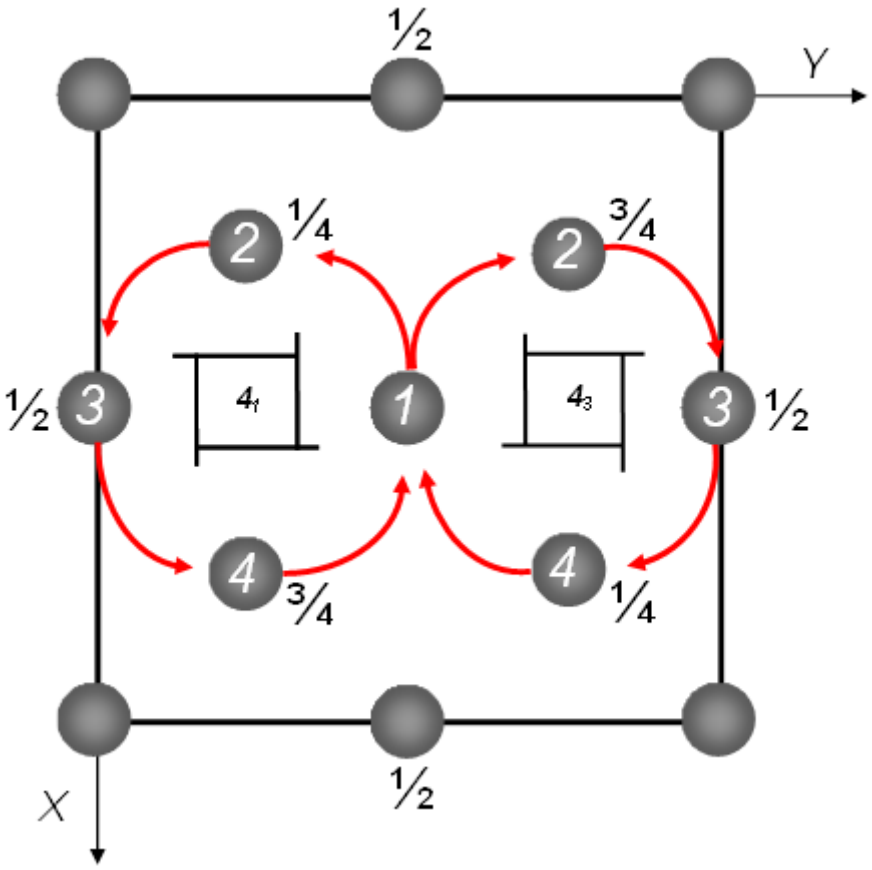


Fig. 7.8. Action of equivalent fourth-order helical axes

In structures with close-packed hexagonal lattices (magnesium, wurtzite) there are 6_3 helical axes with a pitch of 3/6=1/2*t*, which are neutral: turning clockwise or counterclockwise leads to the same result (Fig. 7.9). At the same time, axis 6_3 is a rotary axis *3* (*but not vice versa!*).

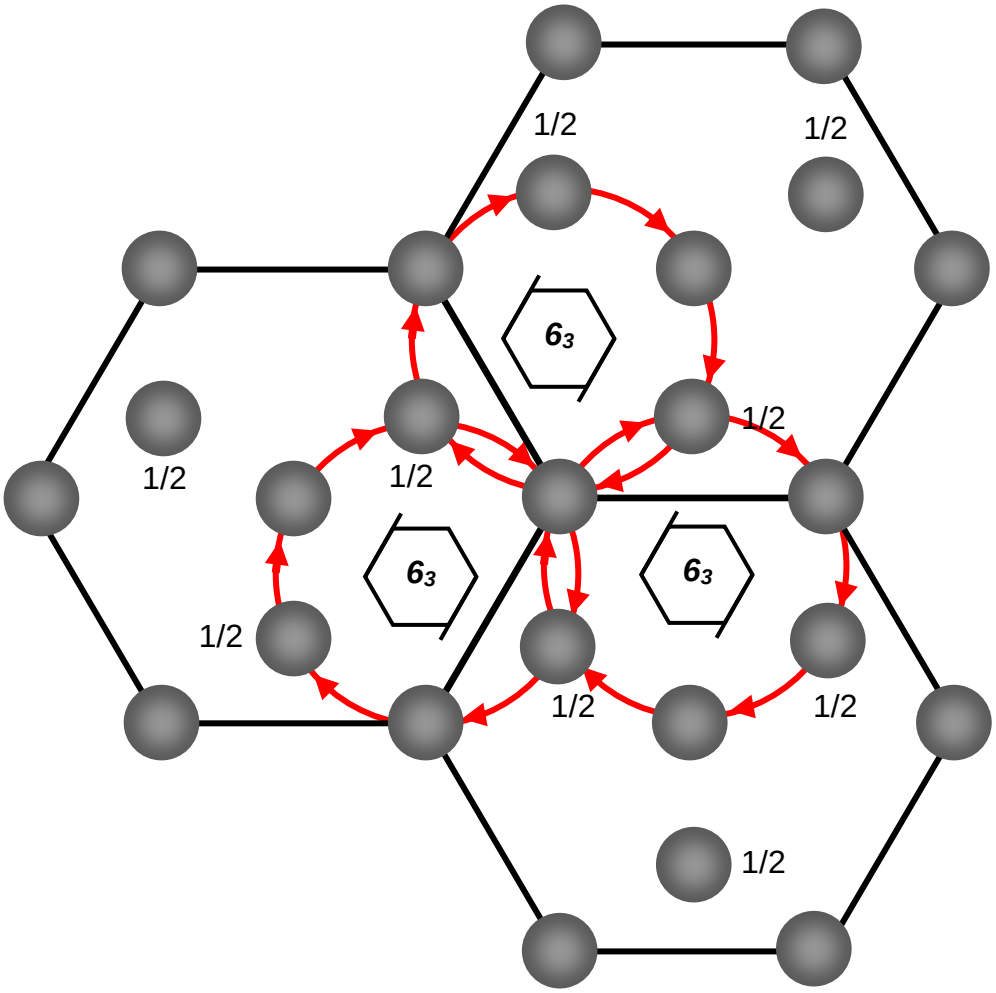
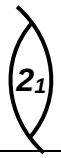
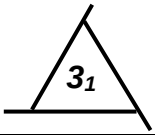
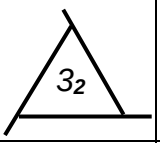
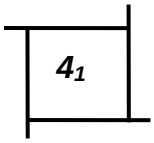
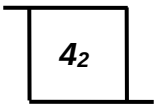
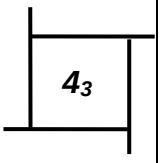
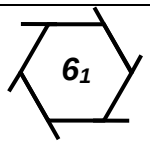
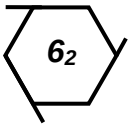
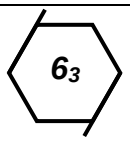
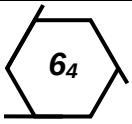
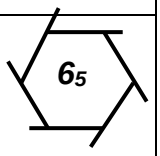


Fig. 7.9. The action of the helical axis of the sixth order 6_3

The symbols of the helical axes are given in Table 7.3, having showed some axes may have the same sliding components, but differ in elementary angles of rotation.

Nota bene! The existing elements of symmetry must be valid for all types of atoms that included to the compound.

Table 7.3. Symbols and values of the screw axes of symmetry [37]

Axis order	Sliding component in translation fractions						
	1/6	1/4	1/3	1/2	2/3	3/4	5/6
second							
third							
fourth							
sixth							

Work performance

1. Using computer or visual models of the main types of crystal structures select and make a unit cell.

2. Identify and record the syngony and the type of Bravais cell.

3. Design a unit cell on the plane (001).

4. After analyzing the location of atoms of a simple substance or atoms (ions) of the elements of the compound to determine and make the position of the existing elements of symmetry perpendicular to the plane of projection in the following sequence:

– planes of mirror reflection;

– planes of sliding reflection;

– rotary axes of symmetry;

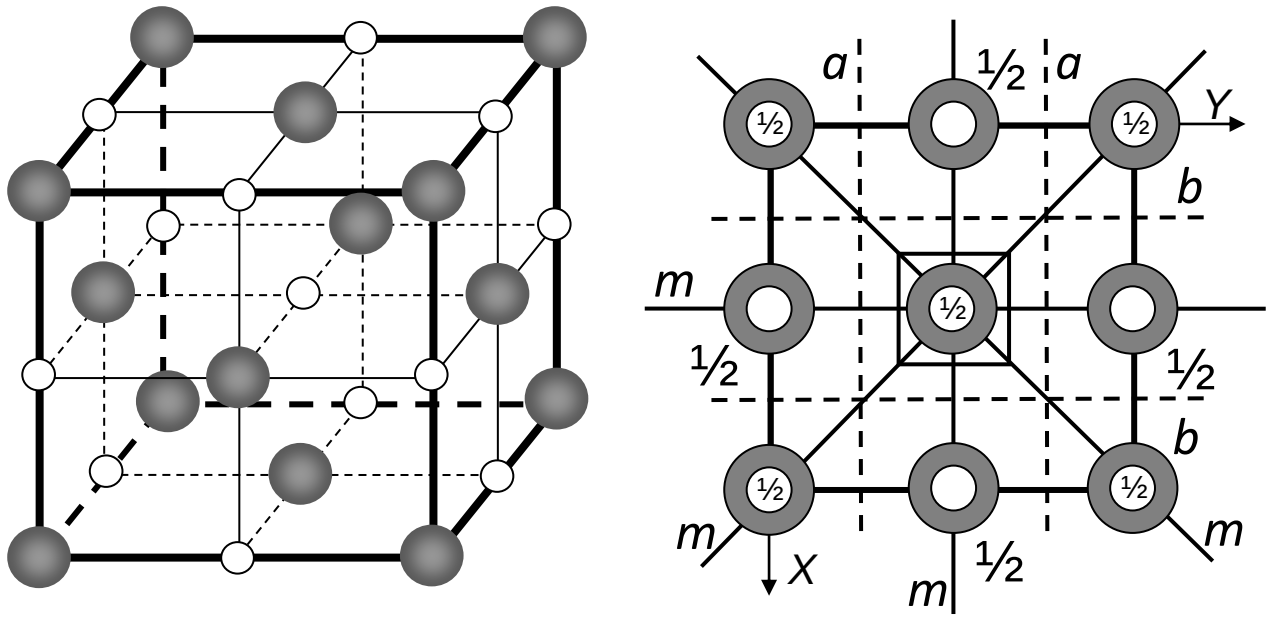
– inversion axes of symmetry;

– helical axes of symmetry.

5. Make a conclusion, atoms (ions) of which variety make up the unit cell and are included in it, what positions occupy and how it affects the elements of symmetry inherent in this crystal structure.

Example of task performance

PbS lead sulfide is an ionic compound in which sulfur anion sare structure-forming and lead cations occupy the cavities between them. The PbS structure belongs to the cubic syngony, as $a = b = c$, $\alpha = \beta = \gamma = 90°$, the unit cell is face-centered, because sulfur anions are located at the vertices of the cell and in the center of each face. The unit cell is shown in Fig. 7.10*a*, the projection of the unit cell on the plane (001) and the symmetry elements are shown in Fig. 7.10*b*.



a *b*

a – unit cells of the PbS structure; *b* – projection on the plane (001) of the unit cell of the PbS structure and elements of symmetry

Fig. 7.10. Example of task performance

Control questions

1. What elements of symmetry are inherent in crystalline structures?
2. What types of planes of sliding reflection are inherent in face-centered cells?
3. What types of sliding reflection planes are characteristic of body-centered cells?
4. Which types of unit cells are characterized by sliding reflection planes of *d* type?
5. How determine the motion of the helical axis of symmetry?
6. What does “neutral helical axis of symmetry” mean?
7. In what order is the helical axes equivalent?

Practical work № 3. Symmetry space groups of crystal structures

The aim of the work – learn to write the international symbol of the space group of symmetry of crystal structures.

Theoretical information

A space group of symmetry is a set of all possible elements of symmetry of the crystal structure. All possible combinations of elements of symmetry of crystal structures were mathematically derived simultaneously and independently of each other by E. S. Fedorov and A. Shenflis in 1890–1894. A total of 230 space discontinuous groups of symmetry of crystal structures, also called Fedorov groups, were derived [35]. However, most of these groups have no representatives among the studied crystal structures.

Each point group (class symmetries of crystalline polyhedrons) corresponds to several space groups. Space symmetry groups, as well as point ones, are divided into syngonies; there is a set order of writing the symbol for them.

International symbols or Schoenflies symbols are used to denote a space group. The international symbol of a space group is composed in such a way that the whole set of symmetry operations of this group can be clearly represented by the form of the symbol and by means of theorems on the combination of symmetry elements of crystal structures (Table 7.4). In the symbol of the space group only the generating elements of symmetry are written.

Table 7.4. Rules for writing the symbol of the space group [37]

<table>
<tr><td rowspan="2">Syngony</td><td colspan="4">Position in symbol</td></tr>
<tr><td>1st</td><td>2nd</td><td>3rd</td><td>4th</td></tr>
<tr><td>Triclinic</td><td rowspan="7">Bravais lattice type</td><td>Available symmetry element</td><td>–</td><td>–</td></tr>
<tr><td>Monoclinic</td><td>2 or 2_1 axis and perpendicular plane</td><td>–</td><td>–</td></tr>
<tr><td rowspan="2">Rhombic</td><td colspan="3">Perpendicular planeorparallel axis</td></tr>
<tr><td>to OX axis</td><td>to OY axis</td><td>to OZ axis</td></tr>
<tr><td>Trigonaland hexagonal</td><td rowspan="2">Axis of higher order and perpendicular plane</td><td rowspan="2">Coordinate plane or axis</td><td rowspan="2">Diagonal plane or axis</td></tr>
<tr><td>Tetragonal</td></tr>
<tr><td>Cubic</td><td>Coordinate plane or axis</td><td>3</td><td>Diagonal plane or axis</td></tr>
</table>

In the first place in the international symbol of the space group the type of Bravais cell is always indicated. The Bravais cell type indicates a set of translations, both main and auxiliary ones.

The generating elements are written in a certain sequence, taking into account the main directions characteristic of each syngony (Table 7.5). The writing order infringement changes the essence of the symbol.

In the symbol notation, “simple” elements of symmetry are preferred – the planes of the *m* mirror reflection and the rotary axes of symmetry *1, 2, 3, 4, 6*. If

there are planes and axes in one direction, then the plane is written in the symbol. If there is no mirror plane of symmetry, the symbol of the plane of sliding reflection (*a, b, c, n* or *d*) is specified. If at some position there is no element of symmetry, then write the number *1* (for example, *P312*, $P3_112$), so as not to change the order of writing.

Table 7.5. Main directions in crystals of different syngonies [37]

Syngony	Position in the symbol of the spacegroup			
	1	2	3	4
Cubic	*P, I, F*	[001]	[111]	[110]
Tetragonal	*P, I*	[001]*	[100]	[110]
Hexagonal	*P*	[0001]*	$[11\bar{2}0]$	[1100]
Trigonal	*P*	[0001]*	$[11\bar{2}0]$	[1100]
Rhombic	*P, C(A, B), I, F*	[100]	[010]	[001]
Monoclinic	*P, C*	[010]	–	–
Triclinic**	*P*	–	–	–

* In the crystals of the middle category after the symbol of the axis of the higher order (2^{nd}position) under the dash, the existing plane of symmetry isindicated, perpendicular to the axis of the higher order.

** The symbol, except for the Bravais cell type, indicates only the presence (or absence) of a symmetry center.

If the crystal structure has not one but several axes of symmetry of higher order of different types, preference is given to the rotary axis (except for crystals of trigonal syngony, where the simultaneous presence of *3* and $\bar{3}$ in the symbol of the space group indicates the inversion axis). In the simultaneous presence of helical and inversion axes of symmetry of the same order, the helical axis is preferred (except for trigonal syngony).

In crystals of the middle category, the second position of the symbol of the space group of symmetry, except for the axis of the higher order, the presence of a perpendicular plane of symmetry is indicated.

For structures of cubic syngony at the third position of the symbol of the space group *3* is always written, this means the presence of four rotary axes of the third order.

Work performance

1. Using computer or visual models of the main types of crystal structures select and represent a unit cell.

2. Identify and record the syngony and the Bravais cell type.

3. Design a unit cell on the plane (001).

4. Having analysed the location of atoms of a simple substance or atoms (ions) of the elements of the compound, determine and show the position of the existing elements of symmetry perpendicular to the plane of projection in the following sequence:

– mirror reflection planes;

– sliding reflection planes;

– rotary axes of symmetry;

– inversion axes of symmetry;

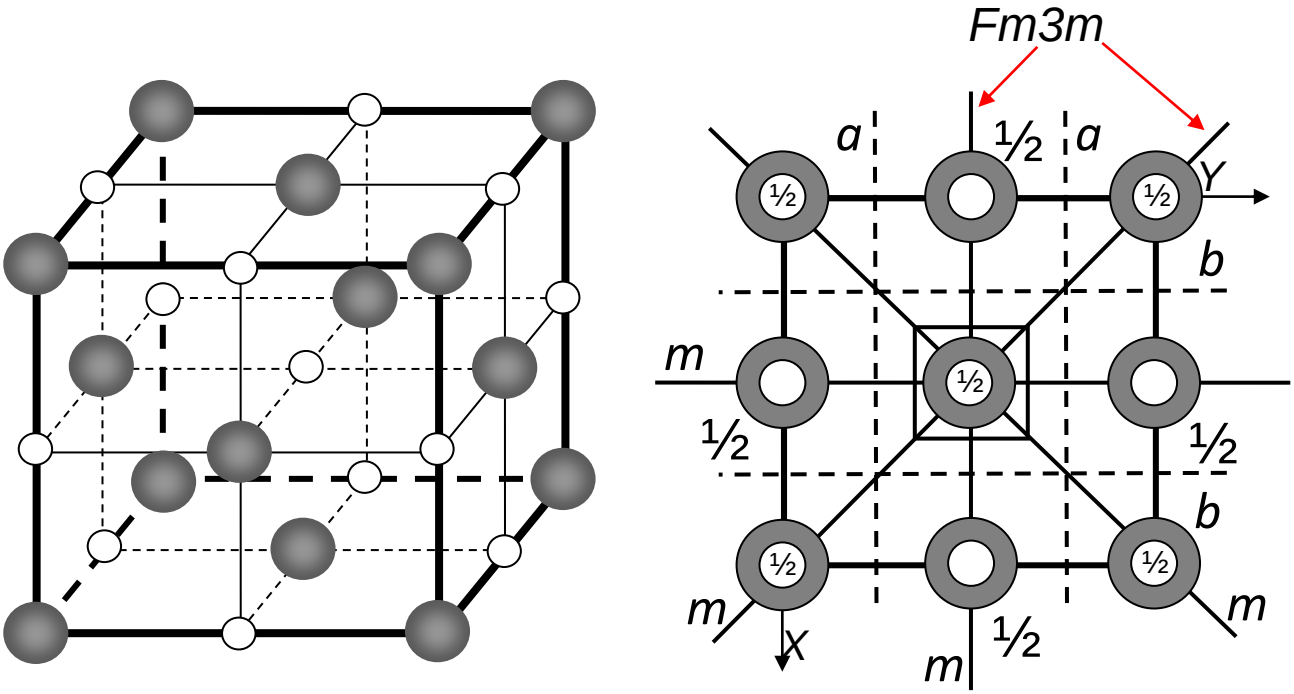
– helical axes of symmetry.

Nota bene! Defining the characteristic elements of symmetry should not be limited to one unit cell.

5. Write next to the projection the international symbol of the space group, preferring the “simple” elements of symmetry and indicate their location on the projection by the arrows.

Example of task performance

The model of the PbS structure refers to cubic syngony, since a = b = c, α = = β = γ = 90°, the unit cell is face-centered, because atoms of the same type are located at the vertices of the cell and in the center of each face. The unit cell is shown in Figure 7.11*a*, the projection of the unit cell on the plane (001) and the symmetry elements are shown in Figure 7.11*b*.



a *б*

a – the unit cell of the PbS structure;

b – projection on the plane (001) of the unit cell of the PbS structure and elements of symmetry

Fig. 7.11. Example of task performance

Control questions

1. What is a space symmetry group?

2. How are space and point symmetry groups related?

3. What rules of writing the symbol of the space group of cubic syngony crystals should be followed?

4. What rules of writing the symbol of the space group of crystals of the middle category should be followed?

5. What elements of symmetry are preferred in the international symbol of a space group?

Practical work № 4. X-ray density and reticular density of crystal structures

The aim of the work – learn to determine the *X*-ray density and reticular density of crystal structures.

Theoretical information

X-ray density is the theoretical density of an ideal crystal that has no structural defects [38]. It is calculated as the ratio of the mass of all structural units included in the unit cell to its volume, calculated according to *X*-ray diffraction analysis. Therefore, the units of *X*-ray density are $\left[{}^{g}/_{cm^3}\right]$.

Calculate the *X*-ray density γ_ρ by the formula

$$\gamma_\rho = \frac{n \cdot M}{N_A \cdot V}, \tag{7.1}$$

where n – the number of structural units for simple substances or formula units for the compound;

M – the atomic or molecular weight of the substance or compound, *g/mol*;

N_A – Avogadro's constant, $6{,}02 \cdot 10^{+23}$ mol^{-1};

V – the volume of the unit cell, cm^3 (taking into account that $1Å^3 = 10^{-30} m^3$).

Formulas for calculating cell volumes are given in Table 7.6.

Since the *X*-ray density does not depend on interruption of the crystal structure of real matter (pores, vacancies, dislocations, etc.), it can be used as a standard. Thus, if, for example, the pycnometric density (experimental) is higher than the calculated *X*-ray density, it indicates that there are internodal defects in the crystal or defects of light atom replacement by heavy. An increase in density with increasing deviation

from stoichiometry indicates the presence of interstitial atoms or the replacement of light atoms by heavy ones.

Table 7.6. Formulas for calculating the volumes of unit cells [37]

Syngony	Formula
Cubic	a^3
Tetragonal	$a^2 \cdot c$
Trigonal	$a \cdot \sqrt{1 - 3cos^2\alpha + 2\,cos^2\alpha}$
Hexagonal	$0{,}86 \cdot a^2 \cdot c$, where $0{,}86 = sin\ 60°$

On the contrary – pycnometric density is less than *X*-ray – there is the presence of vacancies or replacement of heavy atoms by light ones. The presence of cavities and cracks will be evidenced by an abnormally small value of pycnometric density [38].

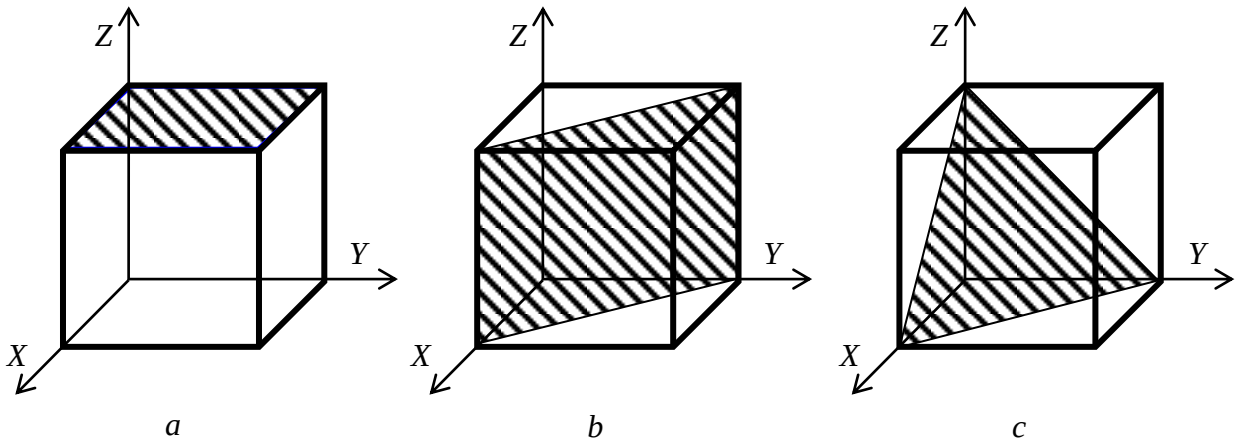
The reticular density of the atomic plane is defined as the number of structural units per unit area of the plane (*hkl*) of the crystal structure [35].

In a real crystal, the formation of a face depends on the growth conditions, on its reticular density. On the surface of the crystal mainly faces with the highest values of reticular density are formed and grow, which according to Bravais law, have simple symbols and the lowest growth rate [38]. Therefore, the reticular density in the crystals is determined for certain crystallographic planes. Thus, for cubic syngony crystals are for planes (001), (110) and (111) (Fig. 7.12), for hexagonal – (0001), ($\bar{1}$100), (11$\bar{2}$0) (Fig. 7.13).

To calculate the reticular density of the face, it is necessary to select this face in the crystal structure, determine the *S* area of its surface and the *n* number of atoms (structural units) of this plane (Table 7.7). Dividing the number of atoms by the surface area *n/S*, we obtain the reticular density in $Å^{-2}$.

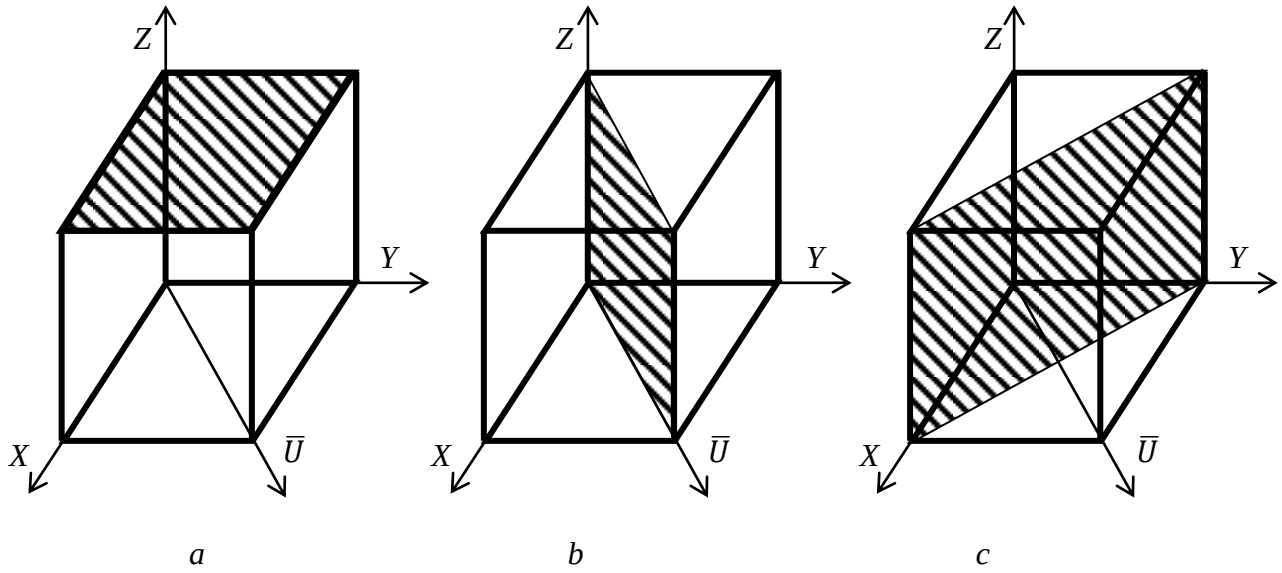
Work performance

1. Using three-dimensional computer or visual models of the main types of crystal structures select and represent a unit cell (Fig. 7.14).



a – (001); *b* – (110); *c* – (111)

Fig. 7.12. Crystallographic planes in cubic syngony crystals
for reticular density determination



a – (0001); *b* – ($\bar{1}$100); *c* – (11$\bar{2}$0)

Fig. 7.13. Crystallographic planes in crystals of hexagonal syngony
for reticular density determination

2. Identify and record the syngony and the Bravais cell type.

3. Using the value of *n. s. u.* or *n. f. u.* defined in practical work № 1 and cell parameters from Table 7.7, calculate the *X*-ray density according to formula (1) for a simple substance or compound determined by the teacher.

Table 7.7. Parameters of unit cells

№	Name	Parameters of unit cell, Å		Literature
		a	*c*	
1	α-iron	2,87	–	[39]
2	γ- iron	3,65	–	[39]
3	Tungsten	3,165	–	[39]
4	Copper	3,615	–	[39]
5	Diamond	3,5667	–	[39]
6	Germanium	5,657	–	[39]
7	Magnesium	3,21	5,21	[39]
8	Zinc	2,66	4,55	[39]
9	CsCl	4,115	–	[40]
10	NaCl	4,32	–	[40]
11	Cu_2O	4,27	–	[40]
12	CaF_2	5,4625	–	[40]
13	ZnS sphalerite	5,43	–	[40]
14	ZnS wurtzite	3,823	6,261	[40]
15	$CaTiO_3$	3,905	–	[40]

4. Select in the unit cell and display the corresponding crystallographic planes.

5. Calculate the value of reticular density on each crystallographic plane for each element, for which firstly determine:

– the number of structural units of each element per plane;

– area of the plane.

6. Make a conclusion about the element on which crystallographic plane corresponds to the highest reticular density.

Example of task performance

PbS lead sulfide is an ionic compound in which sulfur anions are structure-forming and lead cations occupy the cavities between them. The PbS structure belongs to the cubic syngony, as $a = b = c = 5{,}936$ Å, $\alpha = \beta = \gamma = 90°$, the unit cell is face-centered, because sulfur anions are located at the vertices of the cell and in the center of each face. The unit cell is shown in Fig. 7.14.

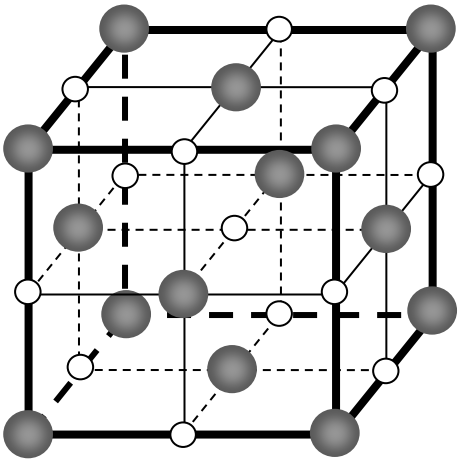


Fig. 7.14. PbS unit cell

The *X*-ray density of PbS is calculated by formula (7.1), for which we find:

– the number of formula units $n = 4$;

– molecular weight $M = 207{,}2 + 32{,}1 = 239{,}3$ *g/mol*;

– Avogadro constant $N_A = 6{,}02 \cdot 10^{23} mol^{-1}$;

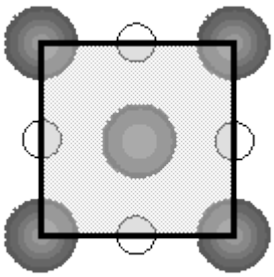
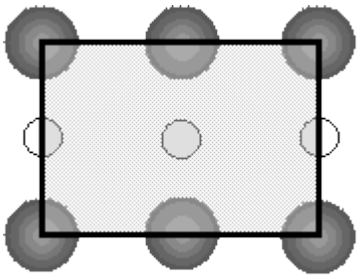
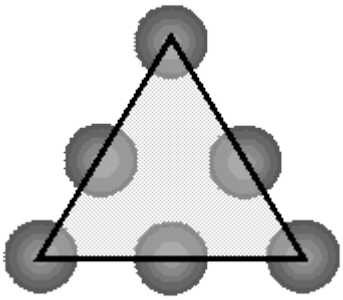
– volume of a cubic elementary cell $V = a^3 = 209{,}16 \cdot 10^{-24}\ cm^3$.

Then

$$\gamma_\rho = \frac{4 \cdot 239{,}3}{6{,}02 \cdot 10^{23} \cdot 209{,}16 \cdot 10^{-24}} = 7{,}6 \left[{}^{g}/_{cm^3}\right].$$

The reticular density for cubic syngony is determined for the crystallographic planes (001), (110) and (111), the shape and location of the structural units for PbS are presented in Table 7.8.

Table 7.8. Example of task performance

Plane symbol	(001)		(110)		(111)	
Plane type						
Element	Pb	S	Pb	S	Pb	S
n	1/2·4=2	1/4·4+1=2	1/2·2+1=2	1/4·4+1/2·2=2	–	1/6·3+1/2·3=2
S	a^2		$a^2\sqrt{2}$		$a^2\frac{\sqrt{3}}{2}$	
Formula γ_{ret}	$2/a^2$	$2/a^2$	$\sqrt{2}/a^2$	$\sqrt{2}/a^2$	–	$4/a^2\sqrt{3}$
γ_{ret}, Å^{-2}	0,057	0,057	0,0401	0,0401	–	0,0655

Conclusion: The densest packing of sulfur atoms is observed for the crystallographic plane (111), lead atoms – (100).

Control questions

1. Why is *X*-ray density used as a standard?
2. How are the number of structural and the number of formula units determined?
3. What is called reticular density?
4. What is the need for knowledge of reticular density?

5. For which crystallographic planes of cubic syngony is the reticular density determined?

6. For which crystallographic planes of hexagonal syngony is the reticular density determined?

7. What are the units of *X*-ray density and reticular density?

Practical work № 5. Description of crystalline structures of refractory compounds

The aim of the work – learn to represent the structures of refractory compounds according to the available literature data on the space group, structural type and geometric parameters of the unit cell.

Theoretical information

Compounds of transition metals with nonmetals, such as borides, carbides, nitrides, etc., are classified as refractory. But the modern view of these compounds takes into account not so much the presence of high melting point, as – a set of properties that are mainly due to the composition of the compound and the nature of the chemical bond between its components.

The composition of the compound is influenced by valence, electron concentration, atomic size, etc. Depending on the position of metals in the periodic table, there is a continuous and systematic change in the structure and properties of both the transition metals themselves and their compounds.

The formation of a chemical bond is accompanied by a change in the states of all electrons, especially valence ones. Thus, a sign of the realization of a covalent bond during the formation of a crystal is the strong localization of valence electrons, i. e. the high statistical weight of half-filled electronic states. The greater the energy stability of the configurations, the stronger the covalent bond. The metallic type of bond is due to collectivized electrons, and the ionic type is due to the maximum

statistical weight of the most stable s^2p^6 configurations of the compound components. The nature of the bond imposes certain requirements on the geometry of the structure – the type of symmetry of the crystal lattice, which is one of the most important characteristics of a solid, associated with a set of physical-chemical properties. The change in symmetry is attended by a change in such physical properties of a solid as density, specific heat, conductivity, magnetism, hardness, tensile strength, ductility [2].

Refractory compounds of transition metals with nonmetals have very different compositions and structural types. Most refractory compounds belong to the interstitial phases for which the Hägg's rule holds.

Thus, transition metals of IV–VI groups with carbon and nitrogen form typical interstitial phases with simple structures that are not distinguished by a variety of structural types. Monocarbides and mononitrides are characterized by structures with fcc unit cell, in which the packing of particles is the densest. Subcarbides and subnitrides are characterized by either simple or close-packed hexagonal structures.

But with boron and silicon, the transition metals of IV–VI groups form phases that, in terms of size factor, are not interstitial phases and the formed structures, in most cases, are either layered or complex with low symmetry. Borides and silicides are distinguished by the formation of direct strong covalent bonds between non-metal atoms, which lead to the formation of structural elements from boron and silicon atoms, the more complex the higher the nonmetal content in the compound and the worse the donor is metal-partner. The consequence of the complication of structural elements is an increase in the proportion of covalent bonds and, consequently, an increase in the level of properties associated with it [41].

Therefore, knowledge of the crystallographic and crystal chemical features of refractory compounds allows, in many respects, to understand their nature and explain their unique properties – high melting point, hardness, heat resistance.

Work performance

1. Using the data in Table 7.9, represent the unit cell of the crystalline structure of the refractory compound.

2. Write down the syngony and the type of Bravais cell.

3. Determine the number of formula units of the compound.

4. Calculate the *X*-ray density by the formula (7.1).

5. Select in the unit cell and represent the corresponding crystallographic planes.

6. On each crystallographic plane for each element calculate the value of reticular density, firstly determine:

– the number of structural units of each element per plane;

– area of the plane.

7. To make a conclusion whether this structure belongs to the most close-packed.

Control questions

1. What compound features correspond them to the “interstitial phase”?

2. Explain the essence of the Hägg’s rule.

3. Explain the differences between the notions of “interstitial phase” and “solid solution interstitial”.

4. What elements of the periodic table form refractory compounds?

5. What types of bonds occur in refractory compounds?

6. What are the crystallographic features of the borides and silicides structures?

7. What parameter of the crystal structure characterizes its densest packing?

Table 7.9. Crystal structure of refractory compounds [41]

№	Phase	Syngony	Number, space group formula [42]	Structural type	Cell parameters, Å	
					a	*c*
1	*2*	*3*	*4*	*5*	*6*	*7*
1	TiC	Cubic	225,$Fm\bar{3}m$	NaCl	4,317	
2	ZrC	Cubic	225,$Fm\bar{3}m$	NaCl	4,682	
3	HfC	Cubic	225,$Fm\bar{3}m$	NaCl	4,639	
4	V_2C	Hexagonal	194,$P6_3/mmc$	Mo_2C	2,884	4,587
5	VC	Cubic	225,$Fm\bar{3}m$	NaCl	4,118	
6	Nb_2C	Hexagonal	194,$P6_3/mmc$	Mo_2C	3,126	4,965
7	NbC	Cubic	225,$Fm\bar{3}m$	NaCl	4,433	
8	Ta_2C	Hexagonal	194,$P6_3/mmc$	Mo_2C	3,101	4,933
9	TaC	Cubic	225,$Fm\bar{3}m$	NaCl	4,41	
10	γ-MoC	Hexagonal	187,$P\bar{6}m2$	WC	2,898	2,809
11	Mo_2C	Hexagonal	194,$P6_3/mmc$	Mo_2C	2,997	4,727
12	β-WC_{1-x}	Cubic	225,$Fm\bar{3}m$	NaCl	4,222	
13	WC	Hexagonal	187,$P\bar{6}m2$	WC	2,906	2,837
14	α-W_2C	Hexagonal	194,$P6_3/mmc$	Mo_2C	3,001	4,736
15	LaN	Cubic	225,$Fm\bar{3}m$	NaCl	5,3	
16	β-Ti_2N	Tetragonal	136,$P4_2/mnm$	TiO_2	4,946	3,03
17	TiN	Cubic	225,$Fm\bar{3}m$	NaCl	4,249	
18	ZrN	Cubic	225,$Fm\bar{3}m$	NaCl	4,537	
19	HfN	Cubic	225,$Fm\bar{3}m$	NaCl	4,5	
20	VN	Cubic	225,$Fm\bar{3}m$	NaCl	4,136	
21	Nb_2N	Hexagonal	186,$P6_3mc$	ZnS	3,056	4,995
22	NbN	Cubic	225,$Fm\bar{3}m$	NaCl	4,392	
23	Ta_2N	Hexagonal	186,$P6_3mc$	ZnS	3,042	4,909

Table 7.9 continuation

1	*2*	*3*	*4*	*5*	*6*	*7*
24	TaN	Cubic	225,$Fm\bar{3}m$	NaCl	4,4344	
25	CrN	Cubic	225,$Fm\bar{3}m$	NaCl	4,148	
26	Mo_2N	Cubic	225,$Fm\bar{3}m$	NaCl	4,168	
27	MoN	Hexagonal	187,$P\bar{6}m2$	WC	5,725	5,608
28	W_2N	Cubic	225,$Fm\bar{3}m$	NaCl	4,128	
29	WN	Hexagonal	187,$P\bar{6}m2$	WC	2,893	2,826
30	ScB_2	Hexagonal	191,*P6/mmm*	AlB_2	3,146	3,517
31	ScB_4	Tetragonal	127,*P4/mbm*	UB_4	7,7	3,64
32	ScB_6	Cubic	221,$Pm\bar{3}m$	CaB_6	4,435	
33	LaB_6	Cubic	221,$Pm\bar{3}m$	CaB_6	4,156	
34	TbB_{12}	Cubic	225,$Fm\bar{3}m$	UB_{12}	7,501	
35	TiB	Rhombic	62,*Pnma*	FeB	a = 6,12 b = 3,06	4,56
36	TiB_2	Hexagonal	191,*P6/mmm*	AlB_2	3,026	3,213
37	ZrB_2	Hexagonal	191,*P6/mmm*	AlB_2	3,168	3,528
38	ZrB_{12}	Cubic	225,$Fm\bar{3}m$	UB_{12}	7,408	
39	HfB_2	Hexagonal	191,*P6/mmm*	AlB_2	3,141	3,47
40	VB_2	Hexagonal	191,*P6/mmm*	AlB_2	3,001	3,061
41	Ta_2B	Tetragonal	140,*I4/mcm*	$CuAl_2$	5,778	4,864
42	NbB_2	Hexagonal	191,*P6/mmm*	AlB_2	3,089	3,303
43	TaB_2	Hexagonal	191,*P6/mmm*	AlB_2	3,078	3,265
44	CrB_2	Hexagonal	191,*P6/mmm*	AlB_2	2,97	3,074
45	Mo_2B	Tetragonal	140,*I4/mcm*	$CuAl_2$	5,544	4,735
46	α-MoB	Tetragonal	141,$P4_1/amd$	MoB	3,11	16,97
47	Mo_2B_5	Trigonal	166,$R\bar{3}m$	Mo_2B_5	3,011	20,93
48	MoB_4	Tetragonal	127,*P4/mbm*	UB_4	6,34	4,5

Table 7.9 continuation

1	*2*	*3*	*4*	*5*	*6*	*7*
49	α-WB	Tetragonal	161,$P4_1/amd$	MoB	3,115	16,93
50	β-WB	Rhombic	63,*Cmcm*	CrB	a = 3,19 b = 8,46	3,07
51	WB_2	Hexagonal	184,$P6_3/mmc$	W_2B_5	2,983	13,879
52	W_2B_5	Hexagonal	184,$P6_3/mmc$	W_2B_5	2,982	13,87
53	FeB	Rhombic	62,*Pnma*	FeB	a = 2,952 b = 4,061	5,506
54	TiSi	Rhombic	62,*Pnma*	FeB	a = 3,638 b = 4,997	6,544
55	$TiSi_2$	Rhombic	70:1,*Fddd*	$TiSi_2$	a = 8,279 b = 4,819	8,568
56	$ZrSi_2$	Rhombic	63,*Cmcm*	$ZrSi_2$	a = 3,72 b = 14,76	3,67
57	Hf_2Si_2	Tetragonal	140,*I4/mcm*	$CuAl_2$	a = 6,48 b = 5,21	0,804
58	$HfSi_2$	Rhombic	63,*Cmcm*	$ZrSi_2$	a = 3,69 b = 14,46	3,64
59	VSi_2	Hexagonal	180,$P6_222$	$CrSi_2$	a = 6,374 b = 4,572	0,718
60	$NbSi_2$	Hexagonal	180,$P6_222$	$CrSi_2$	a = 4,803 b = 6,604	0,718

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